

***Direct methane to methanol transformation
over zeolites – kinetic evaluation and
process simulation***

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Abstract

The direct methane to methanol transformation has been a topic of intensive research for many decades. The challenging activation of methane along with the potent overoxidation of methanol at high temperatures renders the development of an efficient catalyst and an industrial process particularly challenging. This thesis aims to extend the understanding of the direct methane to methanol (DMTM) transformation over copper-exchanged mordenite and to suggest an industrially viable process inspired by the findings.

A series of experiments led to the development of a laboratorial process over a 3% wt. copper Mordenite catalyst (CuMOR), which maximises the methanol (CH_3OH) yield. The suggested step-wise process involves three subsequent steps, specifically a catalyst activation step, a CH_4 pre-adsorption step and a reaction and CH_3OH desorption at 200°C .

A kinetic study of the reaction was carried out. Kinetic equations were derived based on experimental and literature data about the reaction. A model with an added associative CH_4 desorption term provided the best fit to the experimental data, while having direct physical meaning. The apparent activation energy of the process was calculated with help of an Arrhenius plot.

An industrial application of the process was conceptualised and modelled. A technoeconomic evaluation of the project revealed that under current catalyst performance, the process could never achieve profitability. A comparison of different case scenarios for the performance of the catalyst led to the conclusion that a 40-fold more efficient catalyst is the ideal target for future research with 2.5 years of payback time.

Finally, the role of the eight membered rings (8MR) of zeolites in the DMTM was investigated. 4 zeolitic frameworks (Gismondine, Phillipsite, Merlinoite and Edingtonite) containing 4MR and 8MR were synthesised and tested in the reaction. Only the Edingtonite (EDI) framework was able to produce $4.6\mu\text{mol}$ of CH_3OH per gram of catalyst throughout the duration of the experiment, while conclusions were reached regarding the effect of the Si/Al ratio and the zeolite topology on the DMTM.

Declaration of originality

Herewith I declare that the present thesis is primarily the product of my own work. The contribution of Nan Hu, Seong Baek and Zhiyan Qiu is acknowledged as part of collaborative projects designed and supervised by myself and is appropriately referenced in text when necessary. All work comprising the present thesis was designed and carried out by the author, including the compilation of the manuscript as part of a degree of Doctor of Philosophy at Imperial College London supervised by Prof. Klaus Hellgardt. This work is wholly original and any work belonging to others is properly acknowledged.

Ioannis-Dionysios Tzouganatos, March 2022

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Nomenclature (in order of appearance in text)

DMTM	Direct methane to methanol
MOR	Mordenite
CuMOR	Copper-exchanged mordenite
GIS	Gismondine
MER	Merlinoite
PHI	Phillipsite
EDI	Edingtonite
4MR	4-membered ring
8MR	8-membered ring
Syngas	Synthesis gas
R/P	Reserves to production ratio
ΔH_{298K}	Reaction enthalpy at 298K (kJ/mol)
MFI	ZSM-5
FAU	Faujasite
BEA	Zeolite beta
pMMO	Methane monooxygenase (particulate form)
sMMO	Methane monooxygenase (soluble form)
wt%	Weight percentage
EXAFS	Extended X-ray absorption fine structure
TEM	Transmission electron microscopy
EPR	Electron paramagnetic resonance
DFT	Density functional theory
PTFE	Polytetrafluoroethylene
MS	Mass spectrometer
XRD	X-ray diffraction
XRF	X-ray fluorescence
SEM	Scanning electron microscopy
BET	Brunauer-Emmett-Teller
GC	Gas chromatography
m/z	Mass to charge ratio (-)
u	Unified atomic mass unit
TPR	Temperature programmed reaction
Ca	Carberry number (-)

R_{v, H_2O}^{obs}	Apparent reaction rate per catalyst volume ($\text{mol}/\text{m}^3_{\text{cat}} \cdot \text{s}$)
k_G	External mass transfer coefficient (mol/m^3)
a_v	Specific external surface area of catalyst pellet ($\text{m}^2/\text{m}^3_{\text{pellet}}$)
d_p	Diameter of pellet (m)
$C_{H_2O,b}$	Concentration of H_2O in the bulk (mol/m^3)
$C_{H_2O,s}$	Concentration of H_2O on the surface (mol/m^3)
n	Order of reaction, number of reactors (depending on context)
Φ	Weisz modulus
$D_{H_2O,eff}$	Effective diffusivity of H_2O inside the catalyst pellet (m^2/s)
ΔT_{film}	Temperature difference over the film of pellet (K)
$\Delta_r H$	Reaction enthalpy (J/mol)
α_p	Particle heat transfer coefficient ($\text{W}/\text{m}^2 \cdot \text{K}$)
R	Ideal gas constant (J/mol·K)
E_a	Apparent activation energy (J/mol)
ΔT_{rad}	Temperature difference between the average bed temperature and temperature of catalyst near reactor wall (K)
b	Fraction of inerts in catalyst bed ($\text{m}^3_{\text{inert}}/\text{m}^3_{\text{inert+cat}}$)
ε_b	Bed void fraction
λ_{er}	Effective radial thermal conductivity in bed ($\text{W}/\text{m} \cdot \text{K}$)
ΔT_{int}	Temperature difference between the edge and the core of a catalyst pellet (K)
λ_p	Thermal conductivity of pellet ($\text{W}/\text{m} \cdot \text{K}$)
PFR	Plug flow reactor
CSTR	Continuously stirred tank reactor
RMSE	Root mean square error
C_A	Concentration of species A (mol/ml)
r_A	Rate of reaction in respect to A ($\text{mol}/\text{ml} \cdot \text{s}$)
k	Rate constant

XAS	X-Ray absorption spectroscopy
FTIR	Fourier transform infrared spectroscopy
$S_{(S)}$	Cu-O-Cu active sites on the catalyst surface
$F_{(S)}$	Framework sites on the catalyst surface
k_i, k_{-i}	Rate constants of the forwards and backwards process respectively
K	Equilibrium constant
C_S	Total concentration of active sites (mol/ml)
$S^o_{(S)}, S_{(S)}$	Two copper atoms bridged by oxygen, two copper atoms in absence of oxygen
$[CH_3^*]$	Concentration of pre-adsorbed methoxy species on the catalyst (mol/ml)
k_0	Pre-exponential factor (ml/mol·s)
C_i, Q_i	Cost, capacity of equipment (\$, m ³)
m	Cost exponent
I	Chemical engineering plant index cost
FC	Fixed capital (\$)
WC	Working capital (\$)
TCI	Total capital investment (\$)
PCE	Purchased cost of equipment (\$)
S	Total annual revenue (\$)
TOC	Total operating costs (\$)
OL	Operating labor (\$)
ROI	Return of investment
D	Depreciation (\$)
AE	All expenses (\$)
NP_b, NP_a	Net profit before, after tax (\$)
CF	Cash flow (\$)
PV_n	Present value in year n (\$)
NPV	Net present value (\$)
T_s, T_T	Source and target temperature (°C)
ΔT_{min}	Min. allowed temperature difference (°C)
$\dot{m}$	Mass flowrate (kg/h)
$Q/\Delta H$	Enthalpy change (kW)
CP	Heat capacity (kW/°C)

$Q_{\text{cold}}, Q_{\text{hot}}$

T_{pinch}

CHA

FER

Si/Al

θ_{bending}

θ

Cold and hot energy needs of process (kW)

Pinch temperature ($^{\circ}\text{C}$)

Chabazite

Ferrierite

Silicon/Aluminum ratio

Bending angle ($^{\circ}$)

Cu-O-Cu angle ($^{\circ}$)

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1. Introduction

Natural gas represents one of the main fuels of the global energy landscape, with uses in several sectors ranging from industrial use, to the transportation sector and domestic applications. In the transition from fossil fuels to a greener energy mix, natural gas is thought to play a pivotal role. The proven reserves of natural gas are very large around the globe, however, many of them exist in unconventional forms and many of the natural gas reservoirs are located in remote areas. (Zichittella & Pérez-Ramírez, 2021)

The extraction of natural gas with subsequent liquification and transport is often not economically favorable since it involves the cooling to temperatures below -162°C at atmospheric pressure, thus leading to large unutilised amounts of natural gas. A method to transform the extracted natural gas at the extraction site to liquid derivatives would render the exploitation of reserves in remote areas more economically attractive. (Shell, 2022)

1.1 Methane to methanol

Natural gas, which mostly consists of methane, is not only an effective fuel but can also act as a feedstock for the production of chemicals. In fact, one of the main routes of transformation of methane to derivatives involves the formation of synthesis gas as a first step. Depending on the specifications of the produced synthesis gas, it is further used to produce different fuels and chemicals, including methanol. However, the synthesis gas route involves intense conditions of temperature and pressure, thus being a particularly costly option. (Srivastava et al., 2021)

Identifying the economical bottleneck of the indirect transformation, researchers have been investigating the potential of a direct methane to methanol transformation for several decades. Although extensive efforts have been dedicated to achieving any methanol yields that would be industrially relevant, a profitable industrial concept of the direct methane to methanol transformation (DMTM) is yet to be proposed. In fact, the DMTM is considered to be the “holy grail” of catalysis, as a major breakthrough that would lead to industrial viability would potentially revolutionise the global chemical landscape. (Song et al., 2022)

A number of different routes have been explored for the direct methane to methanol transformation, including homogeneous and heterogeneous catalysis in the liquid and gas phase, plasma catalysis and photocatalysis. To date, heterogeneous catalysis is considered to be the most

promising avenue due to the shortcomings of other methods in terms of complexity of the process, selectivity to methanol and methanol yields. Several catalysts have been explored over the years with limited success. However, a breakthrough has been made with the use of copper exchanged-zeolites in the gas-phase, which yielded significantly improved amounts in comparison to their precedents. (Li et al., 2021a)

Although major progress has been made with the use of zeolites, many questions remain unanswered regarding the exact reasons behind their good performance in the reaction. Moreover, the catalytic yields achieved, although improved compared to the past, still remain relatively low and an industrial process concept has not yet been suggested.

1.2 Thesis overview

In an effort to better understand the reaction over one of the best performing catalysts to date, copper-exchanged mordenite, the present thesis will aim to identify the most favorable conditions for the reaction over the catalyst. The kinetics of the reaction will then be investigated. This will aid in identifying potential improvements and suggestions over the reaction method and will provide a kinetic basis which can be expanded and used in process models.

Keeping an engineering perspective on the problem, it has been attempted to develop an industrial concept of the laboratorial process. Once developed, the suggested process has been optimised and a full technoeconomic analysis will be performed to identify profitability and economic potential, as well as bottlenecks which can lead to improvements of the process. The technoeconomic analysis was also used to pinpoint the required performance of the catalyst for the development of a profitable industrial project and will help understand how far from the target current advances are.

Finally, the thesis touched on the aspects of zeolites which make them particularly good hosts of active sites which have a good performance in the DMTM. Targeted synthesis of zeolitic frameworks will attempt to reach conclusions on factors which affect the number and nature of active sites formed on zeolitic frameworks and to find common characteristics between zeolitic frameworks which have the best results to date.

2. Literature review

2.1 Energy and methane

2.1.1 Modern energy landscape and natural gas

As human civilisation has been developing over the centuries, it has been increasingly dependent on various energy sources. Global energy demand has been on a constant rise through time (Keay, 2007)(BP, 2021). However, the industrial revolution brought upon a vast increase in per capita consumption of energy, which has been steadily rising ever since (Fouquet & Pearson, 2012). The global energy demand is currently covered by primary energy sources, such as fossil fuels, renewable sources and nuclear energy as well as secondary sources like electricity (EIA, 2021a).

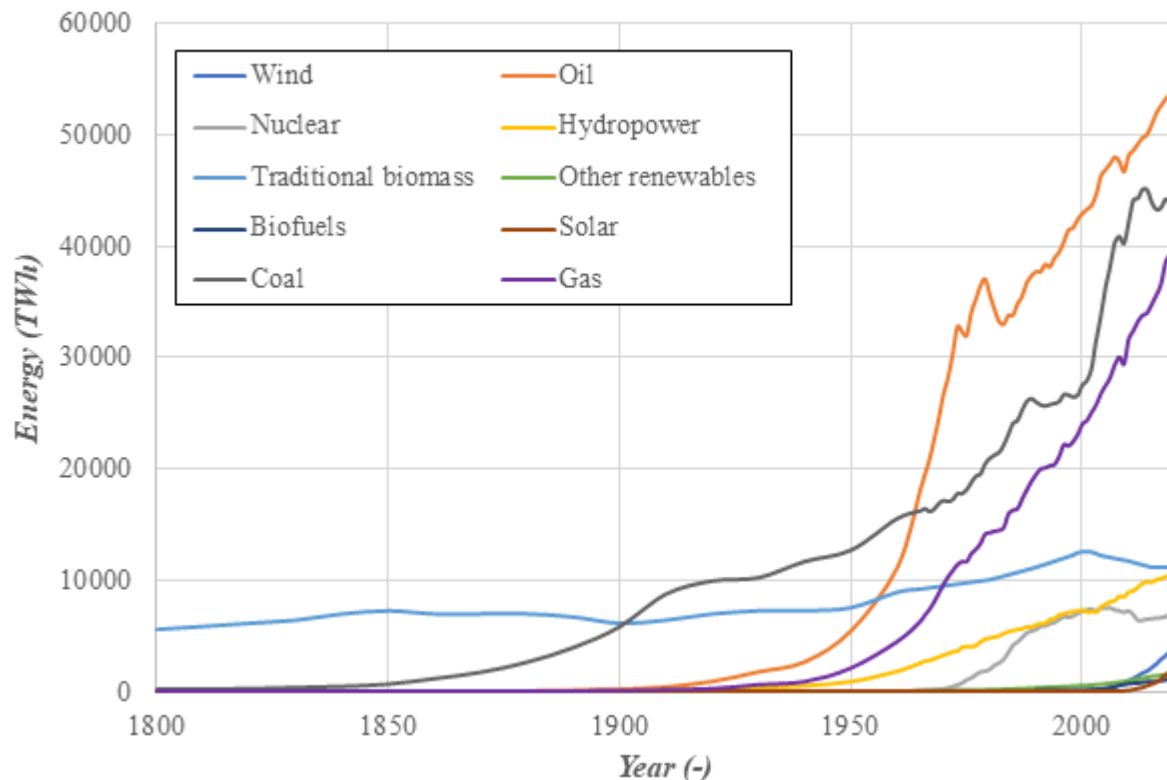


Figure 1: World energy consumption by source from 1800 to present (adapted from Ritchie and Roser 2020).

The global energy mix has shown some interesting changes from earlier years to the present. As seen in **Figure 1**, the only energy source that has seen little increase in usage over the past two centuries is traditional biomass like wood. Oil, coal and gas present the largest increases in usage especially over the past century, with percentages of 31%, 25% and 23% respectively of the total

global energy demand in 2019. Hydropower has also shown a substantially steady increase over the past decades, reaching a percentage of 6% in 2019, while other sources like nuclear, wind and renewables also present a rise in usage but still cover only a small fraction of the global demand. This increase in global energy demand is not only attributed to the industrialisation of the modern world but also in a steadily rising global per capita consumption of electricity, which is closely related with the modern lifestyle. Specifically, the global electricity usage per capita has risen from 2.1MWh in 1990 to 3.3MWh in 2018, an impressive rise of more than 50% (IEA, 2021b).

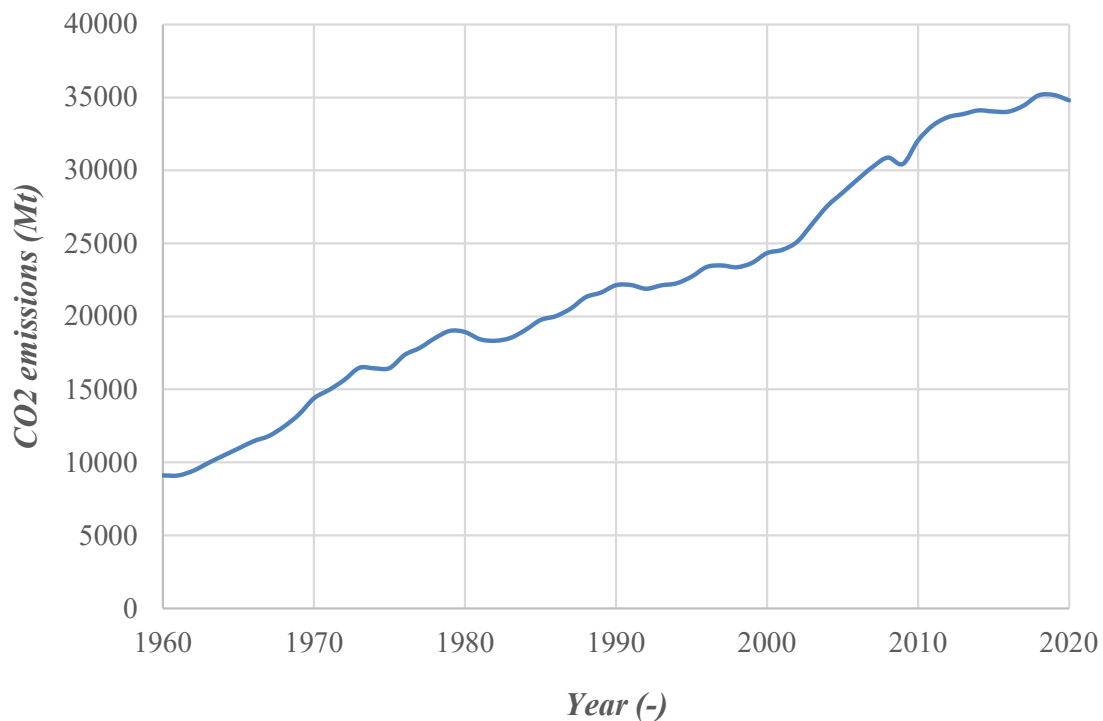


Figure 2: Global CO₂ emissions from 1960 to 2019 (adapted from Global Carbon Atlas 2021).

Naturally, this rise in global energy consumption is closely related to an increase in anthropogenic CO₂ emissions. As seen in **Figure 2**, global CO₂ emissions have been on a steady rise for the past century, with only small declines around 2009 with the global economic crisis and 2020 with the coronavirus pandemic. Despite the historically largest decline of CO₂ emissions in 2020, the emissions are expected to not just rebound but also to rise further in 2021 (IEA, 2021a). The large amounts of CO₂ which are released into the atmosphere contribute largely to global warming, as they are the main contributor in the greenhouse effect (NASA, 2021). As seen in **Figure 3**, the global surface temperature has risen more than 1°C in comparison to the pre-industrial times and it is expected to rise further in the years to come (Tollefson, 2020).

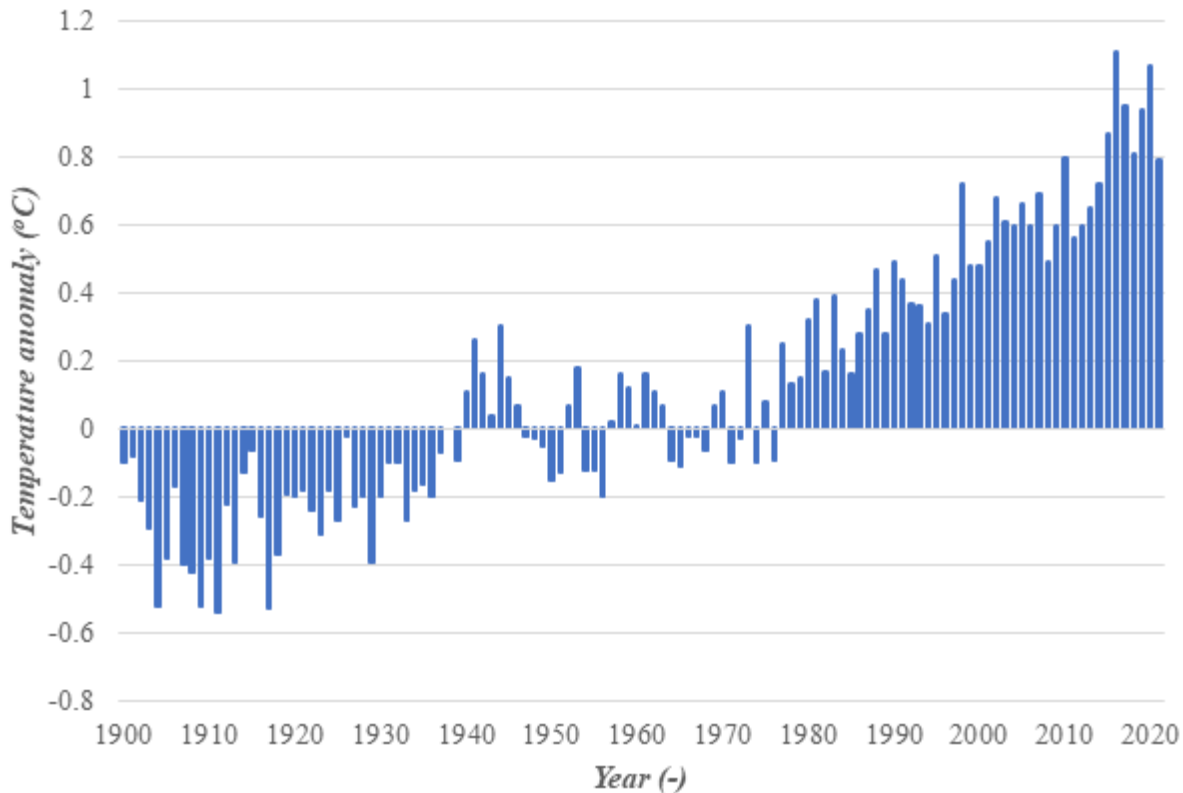


Figure 3: Global temperature anomaly on land and ocean from 1900 to 2021 (adapted from National Oceanic and Atmospheric Administration 2021).

Observing the alarming rise in anthropogenic CO₂ emissions and global warming, the Paris Agreement was signed by world leaders in 2015 which legally binds countries to mitigate their emissions with the ultimate target of keeping the global temperature rise to below 2°C or ideally 1.5°C by 2100 (Liu & Raftery, 2021)(UNFCCC, 2021). Consequently, in order to comply with the limitations in annual carbon dioxide emissions that the Paris Agreement imposes, nations across the globe have to seek greener energy sources for a “cleaner” energy future (UNFCCC, 2015).

Naturally, a well-orchestrated effort is required to mitigate emissions on a global scale. This involves both an optimisation of the industrial and transport sectors, as well as a more diverse energy mix that does not rely as heavily on fossil fuels. Fossil fuels are, of course, expected to continue to be used for decades to come. However, the target is that renewable sources slowly take over and eventually replace them (Cohen, 2021). Interestingly, **Figure 1** displays not just a dominant usage of fossil fuels compared to other energy sources, but also a rise in the net usage of oil over the years. At a closer look it can be observed that although oil and coal represent the largest

shares of the energy mix in 2010 with 27.6% and 31.6% for coal and oil respectively, their shares in 2019 are 25.3% for coal and 30.9% for oil, indicating a downwards trend. This drop in the percentages of oil and coal are caused by the steady rise of renewables and other secondary energy sources, as well as the rise in use of natural gas. Natural gas in 2010 represented the 20.8% of the energy mix, steadily rising to reach 22.6% by 2019.

The question arises why natural gas, being a fossil fuel, is not declining but rising in usage in an era where diversification from fossil fuels is of paramount importance. Although it is a fossil fuel, its role is believed to be pivotal to a greener energy mix (Weissman, 2016). Natural gas mostly consists of methane (up to more than 90% (NatGas, 2013)) which has the highest higher heating value (HHV) among all other hydrocarbons as seen in **Table 1**, with combustion emissions limited to just CO₂ and H₂O.

Table 1: Higher heating value of common hydrocarbons (NIST, 2016).

Fuel	HHV (MJ/kg)
Methane	55.53
Benzene	41.83
Diesel	44.80
Coal (anthracite)	32.50
Coal (lignite)	15.00
Methanol	22.32
Ethane	51.90
Propane	50.35
Butane	49.50
Gasoline	47.00

A comparison of CO₂ emissions per kJ of energy for various fuels is given in **Table 2**. As seen in **Table 2**, when used as a fuel, methane has a larger energy output during combustion per unit mass compared to other fuels, hence why it is considered “cleaner”. Additionally, it possesses one of the lowest values of CO₂ emissions among fuels when burned, at 55.8 kgCO₂/GJ, with gasoline, coal and diesel fuel at 69.3, 94.6 and 74.1 kgCO₂/GJ respectively (Quaschnig, 2019). This explains its widespread use in the industrial, transport and domestic sectors. Natural gas uses are still

growing and its demand is expected to rise further in the coming years, serving as the bridge fuel to a decarbonised future (Shell Global, 2021).

Table 2: CO₂ emissions per kJ of energy for common fuels. (adapted from U.S. Energy Information Administration (EIA) 2021)

Fuel	CO ₂ emissions (kg/kJ)
Natural Gas	50.3
Diesel	69.4
Coal (anthracite)	98.3
Coal (lignite)	92.6
Propane	59.8
Gasoline	67.7

2.1.2 Need for methane transformation and transformation options

What makes natural gas particularly valuable is that it is not only a pillar fuel in the global energy mix, but also a very important feedstock in the production of chemicals through the route of synthesis gas. Synthesis gas (or Syngas) is a mixture of H₂ and CO, in fractions that vary depending on the method of production. It can be produced via coal gasification or via the reforming of methane (Bell & Towler, 2011). Different types of reforming lead to different ratios of H₂/CO. This is displayed in Equations (2.1), (2.2), (2.3) (Roseno et al., 2018). These equations describe the steam reforming of methane, the dry reforming with CO₂ and the partial methane oxidation reactions respectively.



Syngas is incredibly versatile and there are numerous pathways for its further transformation to derivatives based on the H_2/CO ratio. A few of the possible routes are displayed in **Figure 4**.

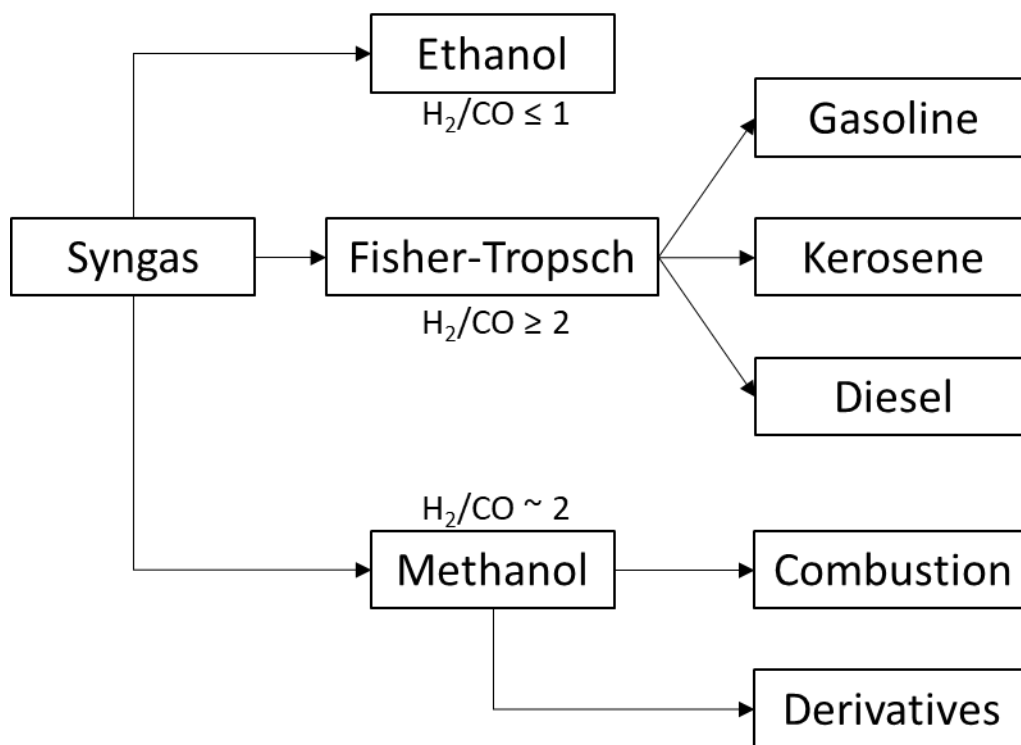


Figure 4: Indicative potential routes for Syngas transformation (adapted from Chae et al. 2020).

The wet and dry reforming of methane, both for the production of H_2 as well as for the production of other derivatives via the aforementioned routes, are some of the most widely used processes in the modern industry (Simpson & Lutz, 2007) (Luyben, 2014). However, there is a major drawback of these processes that can be seen in Equations (2.1), (2.2), (2.3). Both the wet and the dry methane reforming reactions are strongly endothermic, with the reaction enthalpies being 206kJ/mol and 247kJ/mol respectively. As a result, considerably high temperatures are required for the formation of products. Notably, dry reforming reactions are typically carried out at temperatures above 800°C and low pressure, wet reforming at 800-950°C and 15-40 bar and although the partial oxidation of methane is a slightly exothermic reaction, the industrial conditions employed are typically 900-1000°C in the presence of a catalyst. (Wittich et al., 2020)

Considering the versatility of natural gas as a feedstock for chemicals production it becomes clear why it holds such a strong position in the global energy mix and why it is expected to stay dominant for the years to come. Luckily natural gas exists in large abundance, with new reserves being

constantly discovered. The proven reserves for the past 20 years in each continent are displayed in **Figure 5**. It is interesting to note that the R/P (reserves to production ratio) of natural gas is 48.8, meaning that based on the rate of consumption in 2020, the current natural gas reserves would last for approximately another 50 years. (BP, 2021)

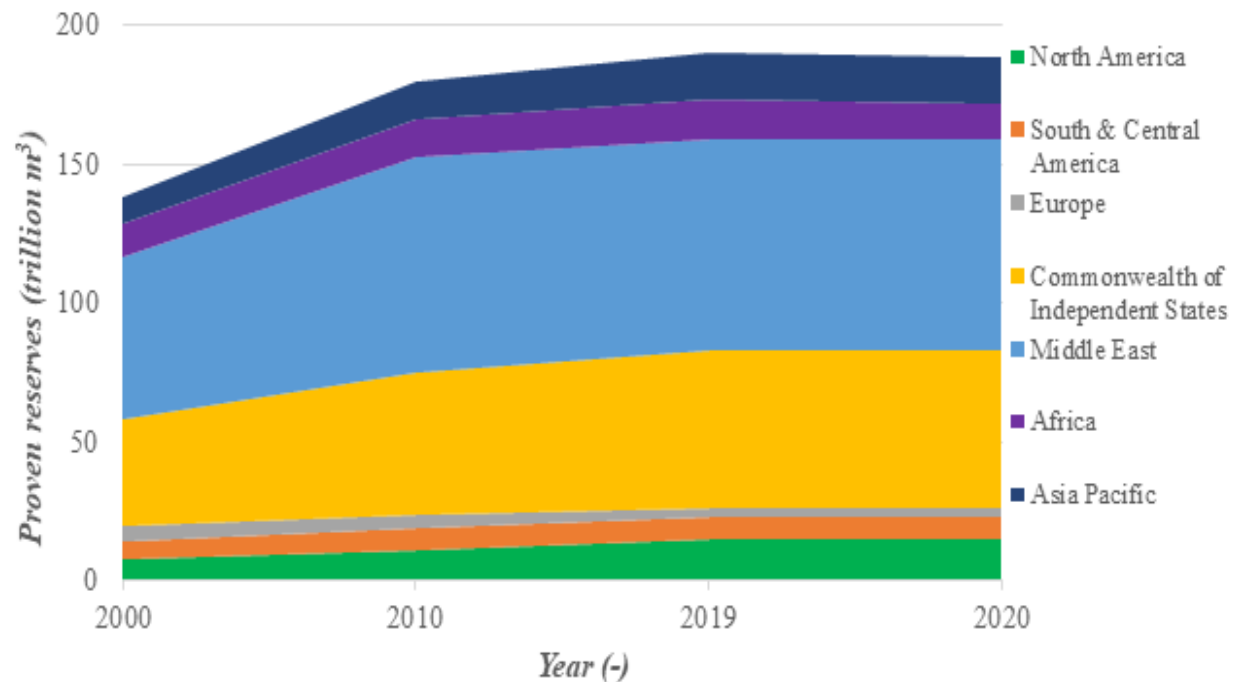


Figure 5: Global proven reserves in the past 20 years. (adapted from BP 2021)

The reserves of natural gas exist in various different forms. The two main categories of reserves are conventional and unconventional. Conventional sources are non-complex formations that are easily extractable with minimal cost. Unconventional sources enclose natural gas in much more difficult to extract forms or formations (Energy Education, 2019). The main unconventional gas reserves include Coal bed methane, shale gas, tight gas and methane hydrates. (McGlade, Speirs & Sorrell, 2013)(Qin et al., 2018)(Chong et al., 2016)

Although the proven reserves, both conventional and unconventional, are large, their location plays a big role in how economically favorable they are to extract. At the moment, natural gas is transported either by pipelines, which is a cost-effective transportation method or by liquification. Although transportation by pipeline is an economically attractive option, the exploration of natural gas at remote regions and offshore sites located hundreds of kilometers away from shore can render it unfavorable (Interlenghi, de Medeiros & Araújo, 2021). In many cases the reserves are in remote

regions, off-shore, or in areas which are not easily accessible. Consequently, once extracted the natural gas would have to be liquified under high pressure at the extraction site and transported to industrial facilities to be further utilised. This would require appropriate equipment and infrastructure at the extraction site (Hall, 2005). To liquify natural gas, it has to be cooled to approximately -162°C . Liquified natural gas (LNG) occupies 600 times less volume than the gaseous form and can be transported by tanker ships (LNG carriers) in special supercooled cryogenic tanks over sea when transportation by pipeline is not a viable option (Shell, 2022). Once LNG reaches its destination it is returned to the gaseous phase by a process called regasification. All of the aforementioned steps of liquification, appropriate cryogenic storage, transportation and regasification of natural gas, as well as importation to the country of destination have a direct impact on the final cost of LNG (EIA, 2022). Nevertheless, in the existing natural gas extraction sites gas is being re-injected or even flared due to fluctuations in demand or difficulties in liquification and transportation. As a result, numerous current reserves remain unexploited as they would be economically unfavorable to extract. (Lunsford, 2000)

Considering the large abundance of natural gas in remote regions, the need for a liquification process and the very energy intensive and expensive indirect route of methane to syngas, the need for a direct transformation of methane to liquid derivatives becomes apparent. Naturally, an industrially viable, on-site applicable, facile process of transforming methane to liquid derivatives which would be easier to transport, would revolutionise the global energy landscape. Such a process would open the way to extracting numerous unexploited reserves in remote regions, so it comes as no surprise that heavy research has been carried out on the topic for the past decades.

2.1.3 Direct transformation options to different derivatives

Historically, there have been extensive efforts to establish an industrially viable method of direct methane conversion to derivatives like methanol, ethylene and aromatics. Some of the main methods of direct methane conversion are displayed below.

Coupling to ethylene

One of the methane derivatives that have been explored is ethylene. Ethylene is the simplest alkene and has a global market of approximately 200 million tones, which are expected to rise by an

additional 50% by 2025. It is commonly used in the production of polyethylene and a wide array of other chemicals. (Fernandez, 2021)

The coupling of methane to ethylene has been widely explored as a potential direct methane conversion method. Depending on the presence or absence of oxygen in the process, the coupling can happen in an oxidative or in a dehydrogenative fashion. The reactions that describe this process are given below. (Tang et al., 2014)

Dehydrogenative coupling



Oxidative coupling



As displayed in Equations (2.4) and (2.5), the dehydrogenative coupling happens in two steps, with both steps being endothermic. This means that high temperatures are necessary and a very energy intensive multi-step process is unavoidable. A typical dehydrogenative process would employ temperatures as high as 800°C (Ogihara et al., 2020). As a result, this is a far less explored route compared to oxidative coupling.

Similarly to dehydrogenative coupling, the oxidative coupling of methane to ethylene is a two-step process. In the first step, methane is catalytically activated and the free radicals which form couple towards ethane. Then, ethane is dehydrogenated in the presence of oxygen and ethylene is formed. Contrary to the dehydrogenative coupling of methane, the oxidative coupling reactions are thermodynamically favorable. However, there are two main limitations to the process. In the first step of the process, the mechanism progresses through the formation of radicals which are very hard to control and prone to react in side reactions. Additionally, methane and ethane are both very susceptible to overoxidation to CO₂ in the presence of a strong oxidant like oxygen. (Liu et al., 2021)

Although the route of methane coupling to ethylene has been sporadically revisited over the years, it has yet to produce any promising results with potential for a scale-up to an industrial process, while the upper yield bounds for a continuous operation were early established and showed that only catalysts of very specific design could ever achieve such a target. (Su, Ying & Green, 2003)

Dehydroaromatisation to aromatics

A main route for exploration was opened in 1993 when the dehydroaromatisation of methane under non-oxidative conditions was reported for the first time (Wang et al., 1993). An array of zeolitic catalysts was investigated at high temperatures (973K) with methane being the sole reactant. Researchers reported a 100% selectivity towards benzene, but with low CH₄ conversion. The dehydroaromatisation reaction of methane is shown below.



As seen in Equation (2.8), the reaction is strongly endothermic. This means that in order to achieve any considerable benzene yields, very high temperature (as high as 1200°C) would have to be employed. However, in the 300-1100°C range, the formation of coke is thermodynamically preferable. As a result, such a process would strictly need efficient catalysts to maximise the benzene yields and minimise coke formation. Despite these limitations, the process is still attractive because of the good atom economy of the reaction, as it also produces hydrogen which is a valuable chemical. (Kosinov & Hensen, 2020).

Numerous studies have been carried out in the field of dehydroaromatisation of methane and strategies have been proposed to improve the catalyst performance of potential catalysts, with zeolites still playing a big role at the front of recent advances and with new technologies for industrialising the process being suggested. However, an economically viable industrial process, or a benzene yield that would spike the interest towards a scale-up is yet to be achieved. (Ma et al., 2013)(Brady et al., 2021)

Partial oxidation to methanol

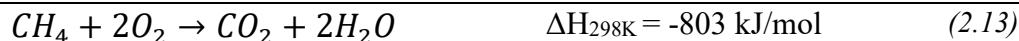
One of the most desirable derivatives of methane is methanol. Methanol, which is the simplest of alcohols, is biodegradable, clean-burning and finds great use both as a fuel as well as a chemical in numerous products like paints and plastics.

Presently, most of the methanol produced worldwide (> 90%) is produced via the synthesis gas route and specifically via the steam reforming of natural gas with a subsequent catalytic conversion of syngas to methanol. Moreover, approximately half of the syngas produced annually worldwide, which amounted to 598 million tons in 2018, is produced by the reforming of natural gas (Schreiber et al., 2020). Around 11% of the global syngas production is used for the synthesis of methanol. With a global market size of 83.8 million tons and a worth of \$28 billion in 2020, the methanol market is constantly on the rise, with both its demand and its price steadily rising over the years (Methanol Institute, 2021) (Mordor Intelligence, 2021) (Fortune Business Insights, 2021). (Frazão & Walther, 2020)

The rise in global methanol demand is easily explained by the fact that methanol is a very attractive chemical due to its versatility and various applications. In one of the several uses of methanol, it can serve as a fuel or a fuel additive in internal combustion engines or in specifically designed methanol fuel cells. Methanol both as a standalone fuel or as an additive can lead to improved horsepower, better anti-freeze properties of the fuel and to a higher flashpoint, while it is generally more environmentally friendly in comparison to gasoline. (Verhelst et al., 2019)

Although the uses of methanol as a fuel or fuel additive have attracted more interest in recent years, they only currently represent an 8% of the annual global use of methanol. Most importantly, methanol is used as a feedstock for the production of various other chemicals. In fact, approximately 35% of global methanol is used for the production of formaldehyde, 19% is used for the production of methyl tert-butyl ether (MTBE) which is an important gasoline additive and 10% is used for the production of acetic acid (Dalena et al., 2018). The remaining percentage of annually produced methanol is used for the production of an array of chemicals including ethylene (methanol-to-olefins or MTO), propylene (MTP), liquified petroleum gas and dimethyl ether, which itself can find various applications and has drawn increasing attention lately as a clean and environmentally friendlier alternative to diesel as a fuel (Brunetti et al., 2020). With such a wide array of potential applications, the global methanol demand is expectedly on the rise and the methanol market is far from saturation, thus making the choice of methanol as a liquid derivative from natural gas particularly attractive (Polaris, 2019). (Calise et al., 2021) (Petrakopoulou & de la Rocha Camba, 2022)

In presence of an oxidant, methane can be partially oxidised to form methanol (CH₃OH) or completely oxidised to CO₂. The oxidation reactions of methane with oxygen are displayed below.



As displayed in Equations (2.9), (2.10), (2.11), (2.12), (2.13) the oxidation of methane can lead to the direct formation of CO₂ or to the formation of methanol (CH₃OH), which can be further oxidised to formaldehyde (HCHO), carbon monoxide (CO), and carbon dioxide (CO₂) subsequently. The reaction enthalpies seen above reveal that all of the reactions involved are thermodynamically favourable. However, they also reveal the main challenge of the partial oxidation to methanol, which is the susceptibility for overoxidation. This is also apparent when examining the energy required to cleave a C-H bond in methane (438.9kJ/mol) versus methanol (389 kJ/mol). These energies indicate that it is more thermodynamically favourable for CH₃OH to be further oxidised than for CH₄ to be partially oxidised. (Horn & Schlögl, 2014)(da Silva, 2016)(Schwarz, 2011)(Ruscic, 2015)

The aforementioned thermodynamic limitations make the direct partial oxidation of methane to methanol a great challenge to successfully implement. Because of the immense profit potential attached to a successful industrial direct methane to methanol (DMTM) process, as well as how difficult it is to achieve, DMTM has been named the “holy grail” of catalysis and the energy industry. The challenges and progresses in this field will be discussed in more detail in the next sections. (Yuan et al., 2020)

2.2 Direct methane to methanol

The direct transformation of methane to methanol has been approached in several different ways. This subchapter will give an overview of the different routes for DMTM and discuss their potential and shortcomings in the pursuit of an industrially viable process.

2.2.1 Possible routes in the DMTM

Homogeneous radical gas phase reaction

Over several decades, numerous different methods have been employed for the direct partial oxidation of methane to methanol. The simplest method that has been employed is that of the homogeneous gas phase reaction. In this process, high temperatures and pressures are employed to activate methane and form free radicals, which then react with oxidants like oxygen or N_2O in the absence of a catalyst towards oxygenates like methanol and formaldehyde. Typically, the conditions employed in this method are temperatures in the range of 350-650°C and pressures as high as 60 bar (Foulds & Gray, 1995) (Zakaria & Kamarudin, 2016). Holmen in 2009 reviewed several works on the topic and claimed that according to findings the best pressure range is 30-60 bars in the temperature range of 430-470°C. However, he also reported that most studies had achieved conversions of 5-10% under optimal conditions, with a selectivity towards oxygenates of 30-40%.

Although this is a simple method that initially showed some promise, there are several challenges with its implementation. Since the reaction is governed by the formation and reaction of free radicals, it is extremely hard to control towards the formation of desired products while avoiding complete oxidation of methane to CO_2 . Additionally, the use of alternative oxidants like N_2O would render the process economically unfavorable due to their high cost. Moreover, since the reaction is exothermic, the use of high temperatures needed for the formation of free radicals is counter-intuitive for maximising the yield. It has also been reported that unless high pressures are employed, the material of the reactor wall could have a considerable effect on the reaction which poses another challenge to controlling the reaction. Nevertheless, due to all these limitations, the homogeneous radical gas phase reaction has been unable to provide even remotely satisfactory results and has been long abandoned. The shortcomings of this method, however, are a clear indication that in order for a route to be successful, it would have to be able to provide good control over the selective formation of desired products. Such requirements typically call for the design of suitable catalysts and catalytic processes. (Hunter et al., 1990)

Liquid phase homogeneous catalysis

As previously discussed, a successful DMTM process would ideally involve mild conditions (low temperature and pressure) for both economic and thermodynamic reasons, as well as a high selectivity towards the desired product, methanol. To meet these requirements, researchers turned to the design of efficient catalysts to catalyse the selective partial oxidation to CH_3OH and several homogeneous catalysts in the liquid phase were investigated. In this route, methane is usually oxidised with acids in the liquid phase. The first remarkable results in this front were achieved by (Periana et al., 1993), who designed a process that went through the intermediate methyl bisulfate. The group reported a 50% conversion of methane with a 85% selectivity to methyl bisulfate, with CO_2 being the main side product. In the first step of the proposed scheme, they employed mercuric ions Hg(II) in a pure sulfuric acid environment to readily activate the carbon hydrogen bond under mild conditions, to produce sulfuric bisulfate and sulfur dioxide. In the second and third step of the reaction, the produced sulfuric bisulfate was hydrolysed to produce methanol, while sulfur dioxide was hydrolysed to sulfuric acid to close the cycle of the reaction. The same group later further improved their method with the use of platinum and mercuric based catalysts, achieving a 72% one-pass yield and 81% selectivity in regards to methane (Periana et al., 1998). Although these results were ground-breaking and more studies have been carried out by researchers in the field, the main challenge in the liquid phase homogeneous catalysis is that it has very limited potential for industrial use. With the reaction taking place in the liquid phase, the process would unavoidably need one or several separation steps to isolate the product in an acceptable purity. Furthermore, the acidic environment under which the reaction takes place would impose high capital and maintenance costs to facilitate the materials flowing through the process, which would limit profitability of the respective industrial process.

Plasma technologies

Plasma technologies have been explored in the field of DMTM. Plasma, essentially being an ionised gas, is a mixture of electrons, atoms, molecules and radicals. Depending on the state and temperature of these constituents it can be classified as thermal or non-thermal plasma. Thermal plasma, as the name indicates, can be as hot as several thousands of degrees, while non-thermal plasma exists at relatively low temperatures. In the case of non-thermal plasma, the provided

energy to the system is mostly spent for the emission of energetic electrons. (Matsumoto et al., 2012)

Non-thermal plasma technologies have been used in a variety of applications including the direct methane to methanol transformation. Since lower temperatures favor the reaction, non-thermal plasma is more suitable in this case. In one of the first attempts, Zhou et al. in 1998 achieved the partial oxidation of methane and reported a methanol yield of 3% with a selectivity of up to 30%, results which were far from competitive with other methods. Nozaki et al. in 2011 employed a non-thermal plasma process in a microreactor to produce oxygenates including methanol and formaldehyde in the absence of a catalyst. They reported one pass yields ranging from 5-20% with 70-30% selectivity, while they also reported the side production of syngas, numbers which the researchers themselves deemed inadequate. Even hybrid methods have been recently investigated with the combined use of non-thermal plasma along with a catalyst, but results were still far from satisfactory regarding methanol yield. (Lee & Kim, 2018)(Chawdhury, Ray & Subrahmanyam, 2018)

Unfortunately, this technology is thermodynamically limited at lower temperatures by the low solubility of methane in water, which has a direct impact on the methanol yields achievable. As a result, all attempts so far have given results which are far from industrially viable, both in regard to conversion as well as product selectivity. (Pruteanu et al., 2017)

Photo-catalysis and supercritical water technologies

Photocatalysis is another explored route in the chase of direct methanol production from methane. As photocatalytic systems in this reaction typically operate under mild conditions (22 – 94°C), photocatalysis shows good potential. In fact, research has shown that the conversion of methane to methanol is possible under UV light without the need for a catalyst. However, the factors affecting methanol yields in this route are several and not yet fully understood. (Hameed et al., 2014)(Tian, Piao & Chen, 2021)

Supercritical water technologies were also explored, especially in the past, with researchers reporting conversions up to 6% and yields up to 0.7% (Savage, Li & Santini, 1994). The topic has been recently revisited, but with the researchers reporting only the complete overoxidation of methane to CO and CO₂. (Vostrikov et al., 2016)

Unfortunately, both of the aforementioned technologies have produced underwhelming results and have little progress over the past decades.

2.2.2 Heterogeneous catalysis as the most promising option

As previously discussed, the ideal DMTM process would be continuous, highly selective towards methanol, would require low temperature and pressure and would not require several and complicated separation steps to isolate the product and regenerate the catalyst, so that it would have an industrial scale-up potential. These requirements clearly point towards heterogeneous catalysis in the gas phase. As expected, the route of heterogeneous catalysis in the gas phase has been widely explored with exciting findings and progress over the past decades. Several different types of catalysts have been investigated. Some of the investigated catalysts have not shown great potential, while others have given promising results which could lead to an industrially scalable process.

With the field of heterogeneous catalysis in the DMTM having a large history, older and recent progressions will be outlined in more detail in the following sections. The discussion will cover the different catalysts investigated, as well as their performance and conditions used. For certain catalysts the discussion will be extended to the analysis of the support and active sites, which are relevant to the present thesis.

2.3 Catalysis in the DMTM

2.3.1 Catalysis and the benefits

Catalysts are substances that are widely used in the facilitation of reactions. When present in a reaction they can shift it faster towards thermodynamic equilibrium. While they play an important role by lowering the activation energy barrier usually by introducing a different reaction pathway, at the end of the reaction their chemistry remains unchanged. They serve as incredibly powerful tools in facilitating reactions at milder temperatures and pressures, while also increasing the conversion of reactants and the selectivity towards the desired products. As a result, catalysts are an integral part of reactions both in research as well as in the industry. (Thomas & Thomas, 2015)

Different catalysts are suitable for different reactions, depending on several factors like the reaction conditions, the desired products and the chemistry of the catalyst itself. The catalyst is comprised by two main components, the *active component* and the *support*. The active sites play

the main role in catalysing a reaction, as this is where the interaction with the reactants takes place. Some of the most frequently encountered active components are metals, oxides and sulfides. Understandably, the most important step in manufacturing a successful catalyst is identifying an active component that is suitable for the reaction. Active sites, however, typically lack the mechanical properties necessary to withstand reaction conditions and to efficiently interact with reactants. As several reactions need to be carried out under conditions of high temperature and pressure, a catalyst needs to be thermally and mechanically durable, to avoid melting, sintering etc.. The materials of choice here are materials with good mechanical and thermal stability as well as high surface area, so that the active components can be adequately dispersed on them and reactants can easily reach them. Typically, metal oxides and zeolites, which have highly porous structures and large surface areas, are successfully used as catalytic supports. (Ross, 2012)

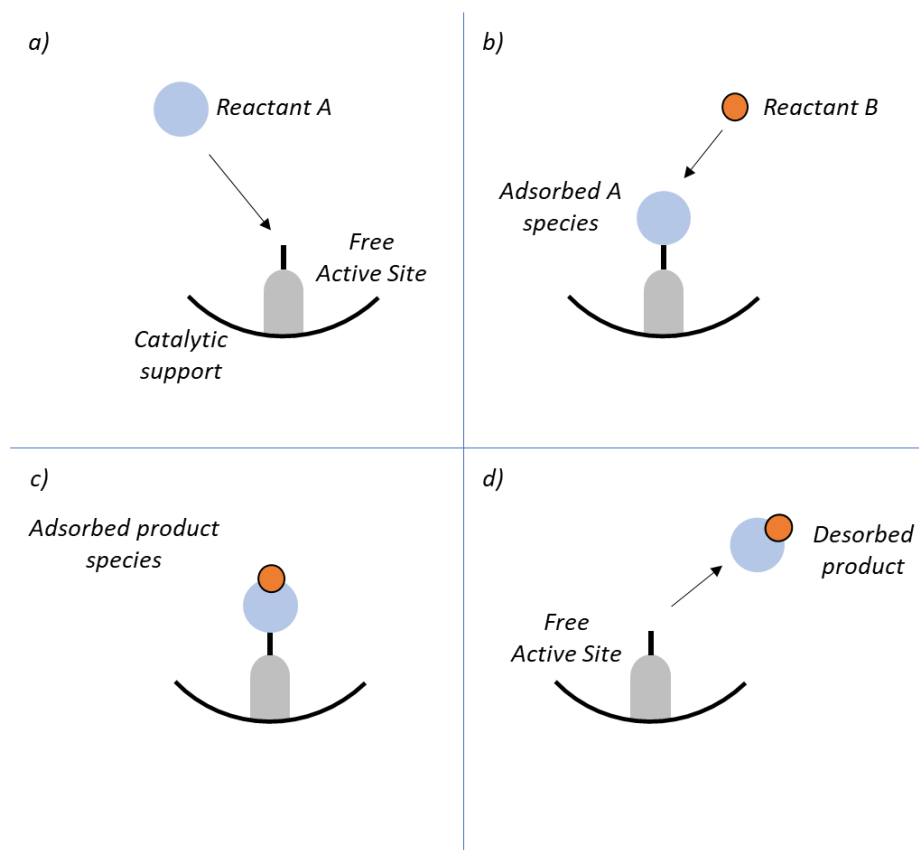


Figure 6: Schematic representation of reaction catalysis steps.

The catalysis of a reaction takes place in subsequent steps. First the reactants approach the catalyst via external diffusion in the bulk and then diffuse inside of the porous structure of the support to reach the active sites. The reactants then adsorb onto the active sites and then react on the catalyst

surface towards the formation of products. The product which is formed in an adsorbed state is then desorbed and diffuses first through the pores of the catalyst and then in the bulk. A simplified visualisation of this process is displayed in **Figure 6**.

Depending on the phase of the reactants and the catalyst itself, catalysts are classified as homogeneous or heterogeneous. Homogeneous catalysts exist in the same phase as the rest of the participants, while heterogeneous catalysts exist in a different phase. Usually, heterogeneous catalysts are in the solid state, while reactants are either gaseous or liquid. In the case of DMTM, heterogeneous catalysts have been employed in both liquid and gaseous systems. These cases will be discussed in more detail in the following sections.

2.3.2 Need for heterogeneous catalysts in DMTM

As discussed in previous sections, there is a number of reasons why other routes have fallen short and heterogeneous catalysis has emerged as the most promising route in the DMTM. This section will serve as a brief and concise summary of the requirements of this reaction and of a prospective industrial process to be economically viable, which led to researching heterogeneous catalysts in the DMTM.

- Methane (CH_4) is a small, stable, tetrahedral molecule with high symmetry (Li et al., 2021b). It is non-polar and has no dipole moment. Due to these properties, it has a first hydrogen bond activation energy of 438.9kJ/mol at 298K (Ruscic, 2015). This makes it particularly hard to activate, especially at mild conditions.
- For a DMTM process to be industrially viable and economically competitive to alternatives like the Syngas route, it requires mild conditions (relatively low temperature and pressure) and no complex steps for the separation of products and for the regeneration of the catalyst.
- Methane has a C-H bond activation energy of 438.9kJ/mol while the equivalent energy for methanol is 389 kJ/mol. This means that the system is thermodynamically more keen to overoxidise the desired product, methanol, than to cleave a bond from methane to further partially oxidise it. However, Equations (2.9), (2.10), (2.11), show energy gaps between the formation of methanol. Thus it is theoretically possible to halt the reaction before the complete overoxidation of oxygenates.

- The facts that CH₄ has a high activation energy barrier especially at mild conditions and that methanol is prone to overoxidation create a great challenge for researchers. High conversion of methane and selectivity towards methanol under the desired conditions are key to the success of the process. However, they are particularly difficult to achieve in satisfactory levels.
- Homogeneous gas phase reactions are unable to yield the desired results as the reaction is particularly hard to control under a free radicals regime.
- O₂ has a high bond dissociation energy (498kJ/mol) and is thus hard to activate for the donation of an oxygen atom at mild conditions, making it even harder to combine mild conditions and good activity/selectivity. (Luo, 2009)
- Nature indicates that the methane to methanol transformation is possible even at ambient conditions, with the existence of certain methanotrophic bacteria which produce methanol. This will be discussed in detail in a later section. However, thermodynamics also indicate that obtaining methanol selectively at milder conditions is challenging, as CO and CO₂ are by far the more thermodynamically favorable outcomes of the reaction with oxygen. (Khirsariya & Mewada, 2013) (Li et al., 2021) (Ross & Rosenzweig, 2017)

Although thermodynamically possible, an important piece of information is the equilibrium conversion of CH₄ when partially oxidised by water, which is the oxidant of choice in latest research in the DMTM. The calculated equilibrium conversion (detailed in the Appendix of the present work) exhibits a low value of $3.2 \cdot 10^{-7}$ at 200°C, which is the temperature typically employed in recent DMTM studies. The low value of CH₄ conversion is in alignment with early research in the field, in which the reactants were continuously co-fed over catalyst and which reported very low conversion values as well as low CH₃OH yields (Lunsford, 2000). However, it is important to note that the calculated equilibrium conversion refers to the partial oxidation of CH₄ with H₂O when co-existing and reacting in the gas phase. State-of-the-art research in the DMTM typically employs a step-wise process, which will be discussed in detail later, in which a pre-adsorption of methane takes place on the catalytic active sites before the introduction of water to the system. As a result, the calculated equilibrium conversion is not directly applicable to the reaction described in the present work, as proven also by the significantly improved results of modern DMTM works in comparison to earlier years. (Sushkevich et al., 2017) (Tomkins, Ranocchiari & Van Bokhoven, 2017)

All of the above highlight the need for an active catalyst that can drive the reaction through a selective pathway towards methanol under mild conditions. Several attempts to design such a heterogeneous catalyst have been made in the past decades. A historic review of some of the most impactful attempts follows in the next section leading to the present state-of-the-art research and findings.

2.3.3 Heterogeneous catalysis in the DMTM

Heterogeneous catalysis implies the existence of a catalyst in a different phase than the reactants. In the case of a solid heterogeneous catalyst, the reaction takes place either in the gas, or in the liquid phase. Indeed, in the field of DMTM, the route of liquid phase heterogeneous catalysis has been explored. The driving force, and the common characteristic of most of those studies, has been the use of H_2O_2 as an oxidant. As mentioned earlier, O_2 is a strong oxidant with a high energy barrier to donate oxygen atoms to the reaction. On the contrary, hydrogen peroxide, as well as N_2O which will be mentioned in more detail later, are milder oxidants, keen to donate oxygen atoms to the reaction. By using milder oxidants, researchers hoped to achieve better control of the reaction, leading to better conversion and selectivity. (Li et al., 2021)

The DMTM with H_2O_2 as an oxidant was investigated by Ab Rahim et al. in 2013 using supported Au/Pd nanoparticles in the liquid phase. The group achieved a selectivity to methanol of up to 60%, although with relatively poor methanol yields (highest total productivity of $1.86 \text{ mol CH}_3\text{OH/kg}_{\text{cat}}\cdot\text{h}$) in all of the cases of different catalysts and conditions investigated. In another study, Fe- Cu- and Fe/Cu- zeolites were investigated by Kalamaras et al. in 2016 for the oxidation of methane in the liquid phase via H_2O_2 . The group investigated the effect of the different Si/Al ratio of the zeolite in the formation of Bronsted acid sites on the catalyst. They also reported that the presence of Fe usually led to production of formaldehyde or complete overoxidation, while the presence of Cu benefitted the milder oxidation of CH_4 to methanol, achieving a considerably larger selectivity. Another approach which involved zeolites and the use of hydrogen peroxide attempted to produce the peroxide in situ in the liquid phase. The group modified zeolites for hydrophobicity and carried out the reaction at 70°C on Au/Pd active sites, but finally reported that their results were still far from satisfactory for industrial application. They also commented that the batch-like nature of their recommended process would be another big hurdle to overcome. (Jin et al., 2020)

Although there is a plethora of attempts to make a breakthrough in the field of heterogeneous catalysis in the DMTM in the liquid phase, no significant yields have been reported yet. Additionally, the fact that the liquid phase poses additional separation challenges and increased capital, operational and maintenance costs for a prospective industrial application is the reason behind more effort being put into the heterogeneous catalysis of DMTM in the gas phase.

The heterogeneous catalysis of the DMTM in the gas phase has been the subject of study for almost a century. As Molybdenum is an active component that has been widely used for hydrocarbon production, it was one of the first to be investigated in the DMTM. Similarly to the use of H_2O_2 in the liquid phase, N_2O has been used for the partial oxidation of methane in the gas phase as a milder oxidant compared to O_2 which could allow for lower temperature and pressure.

Some of the first studies involved the partial oxidation of methane with N_2O over silica supported Molybdenum oxide and Molybdenum. The researchers reported methanol and formaldehyde as products of the reaction with a relatively low conversion level (16% for Molybdenum oxide and 3% for the Molybdenum), although they reported a promising 78% selectivity to oxygenates for the case of Mo oxide. Interestingly, they also reported the presence of water vapour in their reaction which they claimed to play a role in the formation of desired products. As the group reported, spectroscopy revealed the initiation of the reaction by an oxygen atom abstraction which then coordinated to surface Mo^{VI} . This surface oxygen then cleaved a hydrogen bond from CH_4 and the methyl radicals formed methoxide species on the catalytic active sites. These methoxy species either decomposed to form HCHO or were hydrolysed to form and desorb CH_3OH , leaving the active site in its original state. **This was maybe the first time to be reported that the presence of water plays a significant role in the selective formation of CH_3OH .** It is truly intriguing to realise that this finding of almost half a century ago will be extremely relevant to the present study. (Liu, Iwamoto & Lunsford, 1982)(Liu et al., 1984)

In 1993, a group investigated the influence of both the oxidant (O_2 vs N_2O) as well as the Mo content of catalysts. They reported relatively low yields of formaldehyde and methanol and claimed that under the conditions they used (863K) formaldehyde was formed more selectively. Of course, this was an expected outcome as higher temperatures favour the overoxidation of methanol (Bañares, Fierro & Moffat, 1993). Kennedy et al. in 1992 also reported the production

of formaldehyde over Vanadium and Molybdenum silica systems using N_2O at higher temperatures (500-600°C) with low yields.

Molybdenum- as well as Tungsten-based catalysts were studied for selectivity towards methanol in the DMTM by Taylor et al. in 1998. Although they reported their Cu/MoO_3 catalyst to be more selective towards methanol than the homogeneous gas phase radical reaction, they concluded that the $\text{Ga}_2\text{O}_3/\text{MoO}_3$ catalyst they used was superior in terms of final CH_3OH productivity. They attributed this to the synergistic effect between Mo and Ga.

N_2O was also employed over a $\text{V}_2\text{O}_5/\text{SiO}_2$ catalyst, with the group reporting good selectivity to oxygenates but very low conversions that did not exceed 0.2% (Zhen et al., 1985). It is important to note that N_2O might be a milder oxidant compared to oxygen or atmospheric air, which can help with selectively oxidising methane to methanol. However, the use of N_2O introduces another challenge as it is considerably more expensive than the aforementioned oxidants and would immediately make a potential industrial process considerably less economically favourable. Although the N_2O studies diminished over time, studies that use it as an oxidant are still emerging to the present day. One research group recently reported that the achieved methanol yields with oxidation via N_2O at higher temperatures (600°C) were considerably higher in comparison to these achieved by O_2 under milder conditions (200°C) (Starokon et al., 2013). However, from a logical perspective, these findings are not truly more competitive as they have a much lower potential of being economically viable in the industrial scale due to prohibitively high cost of oxidants like N_2O . (Bols et al., 2018)

Along with the molybdenum based catalysts, vanadium had also been a popular active component in early studies of the partial oxidation of methane. Some of the first results were reported as early as 1989 with Spencer and Pereira achieving a formaldehyde selectivity of 70% at low conversions in a temperature range of 500-600°C and atmospheric pressure. Chen and Willcox in 1993 investigated the effect of V_2O_5 loading on a silica support used in the partial oxidation of methane. They employed both oxygen and nitrous oxide as oxidants and concluded that nitrous oxide was considerably more active. In later years, more research went into the Vanadium based catalysts with researchers investigating the selectivity of active sites on $\text{V}_2\text{O}_5/\text{SiO}_2$ catalysts for the conversion of CH_4 to oxygenates (Sexton et al., 1998).

Parmaliana et al. in 1993 also reported on the activity of V-based catalysts for the partial oxidation of methane to oxygenates and especially formaldehyde at 600-650°C with molecular oxygen. Following the research that had been carried out in previous years on both Mo- and V- based catalysts, Faraldos et al. published their work in 1996, which compared catalysts with the two active components. They concluded that generally Vanadium catalysts displayed better activity but led to the production of formaldehyde.

As previously mentioned, the choice of oxidant seems to play an important role in the DMTM. The choice of oxidant has a direct impact on the conditions of the reaction as well as on the final methanol yield achieved. Typically, strong oxidants can easily activate the CH₄ bond but will also tend to overoxidise the produced methanol to CO and CO₂. Additionally, strong oxidants like N₂O will typically have higher costs which directly affect the process economics.

The most widely used and reported oxidants in the DMTM have been N₂O, H₂O₂, O₂ and H₂O. These oxidants are ranked below in **Table 3** according to the energy required to activate their oxygen bond.

Table 3: Oxidants used in the DMTM and their respective oxygen bond activation energies. (Cox & Nelson, 2008) (NIST, 2022)

Oxidant	Oxygen bond dissociation energy (kJ/mol)
O ₂	498.4
N ₂ O	480.7
H ₂ O	497.1
H ₂ O ₂	213.8

As seen in **Table 3**, the required energy to activate the oxygen bond in O₂, N₂O and H₂O is rather large, while the respective energy for H₂O₂ is considerably lower. To overcome the hurdle of the high bond activation energy of the oxidant, early research typically employed high temperatures and pressures. The oxide catalysts including the aforementioned MoO₃, V₂O₅, Ga₂O₃, SiO₂ and CeO₂ employed oxygen as an oxidant at temperatures between 350-520°C at low conversions of <1%. Additionally, oxide catalysts using oxygen resulted in limited selectivity to CH₃OH as in the presence of a strong oxidant like O₂, and at the elevated temperatures and pressures required for the activation its activation, the produced methanol is prone to overoxidation (Zhang et al.,

2005)(Chen & Willcox, 1993) (Zhang et al., 2018).The partial oxidation of methane to methanol using oxygen is presented below.



Due to the poor conversion and selectivity achieved due to overoxidation when using molecular oxygen, N₂O was employed as a milder oxidant. Although N₂O has a high energy to activate the oxygen bond, literature suggests that it can be effectively decomposed on various catalysts and especially on iron-based catalysts (typically zeolites), to produce a highly efficient active site which has been named α -Fe, which can facilitate the DMTM at relatively low temperatures (300°C) with good selectivity to CH₃OH (>90%). It has been reported that the α -Fe site can react with CH₄ upon oxygenation from N₂O decomposition to form methoxy groups. Subsequently, hydrogen atoms produced by further activation of CH₄ can react with the methoxy groups to form and desorb CH₃OH. The overall reaction of CH₄ with N₂O is presented below. (Panov et al., 1997)



As previously mentioned, studies which employed N₂O as an oxidant, both at higher and lower temperatures in comparison to O₂ (160-300°C) achieved generally higher methanol productivities (Starokon et al., 2013). However, the low availability of N₂O and its consequent high price are counter-intuitive to the development of an economically competitive direct methane-to-methanol industrial process and research using it as an oxidant has been abandoned in present research. (Li et al., 2021)

Aiming for very mild oxidation conditions, researchers took advantage of the relatively low activation energy of the oxygen bond in H₂O₂. Another advantage of hydrogen peroxide as an oxidant is that it has a clean decomposition to water. H₂O₂ has been a popular oxidant of choice in the DMTM, typically employed in the liquid phase and on noble metal based catalysts (Pd, Au, Rh) as well as zeolites in latest research. The DMTM using H₂O₂ as oxidant is shown below. (Periana et al., 1993)



The use of H₂O₂ produced some of the first ground-breaking results in the DMTM over platinum based catalysts in the liquid phase, which sparked the interest for further research in the field after the underwhelming results of early research using molecular oxygen (Periana et al., 1998). Studies employing H₂O₂ as oxidant have been typically able to produce methanol at very mild conditions of 50-70°C, with good selectivity to CH₃OH (up to 92%) but with relatively poor overall methanol productivity due to low conversion values (Ab Rahim et al., 2013)(Jin et al., 2020)(Kalamaras et al., 2016)(Hammond et al., 2012). Although the O-O bond in H₂O₂ can be easily activated to supply oxygen to the catalytic surface, enabling the activation of methane at lower temperatures, the mechanism for methane activation using hydrogen peroxide as oxidant is radical-like. This means that just like in high temperature, homogeneous DMTM, CH₃OH is more prone to overoxidation than the further partial oxidation of methane, leading to an inevitable trade-off between conversion and selectivity when reactants are continuously co-fed on the catalyst. (Li et al., 2021)

Finally, the most promising results in the DMTM have been produced by another oxidant with a seemingly high bond activation energy, H₂O. However, the facile adsorption of water on zeolites has enabled the use of water in the DMTM as a mild oxidant with a low activation barrier of adsorption (Resasco et al., 2021). In fact, it was suggested in early research that water might play an important role in the selective production of CH₃OH over zeolites (Liu, Iwamoto & Lunsford, 1982). The partial oxidation of methane to methanol using water as an oxidant is displayed below.



The use of water as an oxidant on zeolitic catalysts for the DMTM opened a new avenue which has produced the best methanol productivity results to date. The roles of water in the DMTM is two-fold, as it acts both as a mild oxidant due to the affinity of zeolites towards water adsorption which allows for the employment of milder conditions (150-200°C), as well as a displacing medium for CH₃OH which shields it from overoxidation (Zhang et al., 2022)(Sushkevich & Van Bokhoven, 2019)(Newton et al., 2020). The use of water as an oxidant on zeolitic catalysts will be discussed in detail in later sections of the present thesis.

Metal oxide catalysts showed some relatively good performance and were being investigated heavily until the end of the previous century. However, great breakthrough was achieved with the

use of zeolites as catalytic supports, with different metals being used as active components. Because zeolites are to the present day the most promising catalysts in the direct partial oxidation of methane to methanol, the next section is specifically dedicated to discussing their characteristics, the inspiration that led to their employment, their history in the DMTM and a deeper analysis of the most successful active sites to date.

2.4 Zeolites

2.4.1 Theory of zeolites

Zeolites are a class of materials that display a very unique structure and properties, which are a result of their interesting chemical composition. They consist mainly of silica $[\text{SiO}_4]^{4-}$ and alumina $[\text{AlO}_4]^{5-}$ tetrahedra, which are interlinked in a very specific orientation via the oxygen atoms in the corners of each tetrahedron which form a three-dimensional framework. It is also known, that according to Lowenstein's rule there cannot be any Al-O-Al bridges in the framework, which is an additional constraint to the structure (Lowenstein, 1954). This means, of course, that the minimum Si/Al ratio of a zeolite is 1 (Blay, Bobadilla & Cabrera-García, 2018).

The three-dimensional framework is characteristic to each zeolite type. Different types of zeolites occur via the ratio of Si/Al in the framework as well as the presence of other ions and water. Due to the negative charge of the tetrahedra and the charge difference between silica and alumina, there are overall charges in the framework, which are balanced out by the presence of other cations like Na^+ , K^+ , Ca^{2+} , Mg^{2+} . The overall charge of the framework and consequently the number of cations required to balance it out depend on the ratio of silica and alumina, with alumina tetrahedra having a larger negative charge (Mccusker & Baerlocher, 2019). The presence of these negative charges leads to the formation of both Bronsted as well as Lewis acid sites in framework or extra-framework positions. The number of Bronsted sites is influenced by the Si/Al ratio of the zeolite. (Manoj Ravi, L. Sushkevich & Bokhoven, 2021). This can be seen schematically in **Figure 7**.

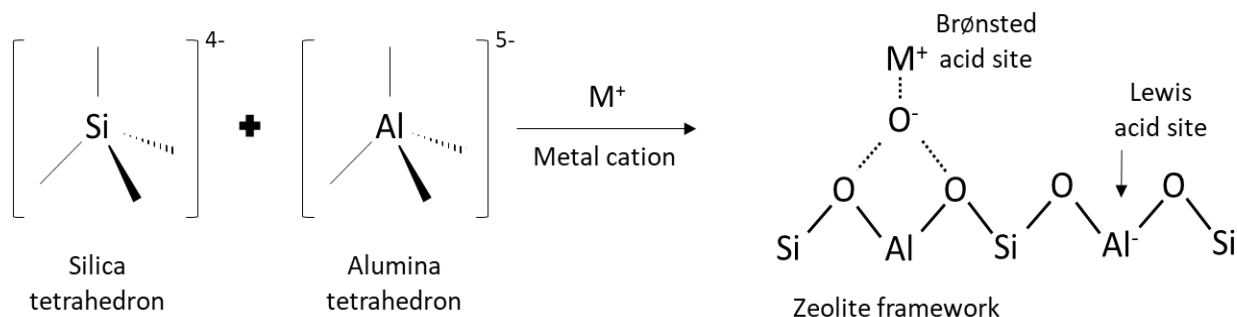


Figure 7: Brønsted and Lewis active sites on a zeolitic framework.

The zeolitic three-dimensional frameworks consist of large channels and pores, which contain the aforementioned cations and water molecules. These cations can be relatively easily exchanged with other cations and the water can be removed usually via heating in a process called reversible dehydration. Each zeolitic type has a very specific framework with pores and channels of certain dimensions which can allow the passage of molecules of equivalent sizes. This makes zeolites excellent molecular sieves, as they can allow for small molecules to pass through them, while larger molecules are blocked. **Figure 8** displays some common zeolitic frameworks, with the geometric arrangement of the silica tetrahedra, as well as their pore and channel structure (Zimmermann & Haranczyk, 2016). The mordenite framework which is particularly relevant to this work is also displayed in closer detail, including the cation positions. (Jacobs et al., 2001)

Nevertheless, zeolites also perform as incredibly efficient dessicants, as they can very potently hold water passed over them even at very low partial pressures. The adsorbed water can be easily desorbed via simply exposing the zeolite to relatively high temperature, so that they can be reused for water adsorption (Jha & Singh, 2016). However, the hydrothermal stability of certain types of zeolites can be a challenge as their frameworks tend to partly or completely collapse in the presence of gaseous or liquid water at higher temperatures, leading to the loss of their crystallinity and characteristic geometrical structure. However, some zeolitic frameworks like MFI (ZSM-5), can withstand temperatures as high as 500°C or more even in the presence of superheated steam, thus

being suitable catalytic supports in energy-intensive catalytic processes. (Xiong, Pham & Datye, 2014).

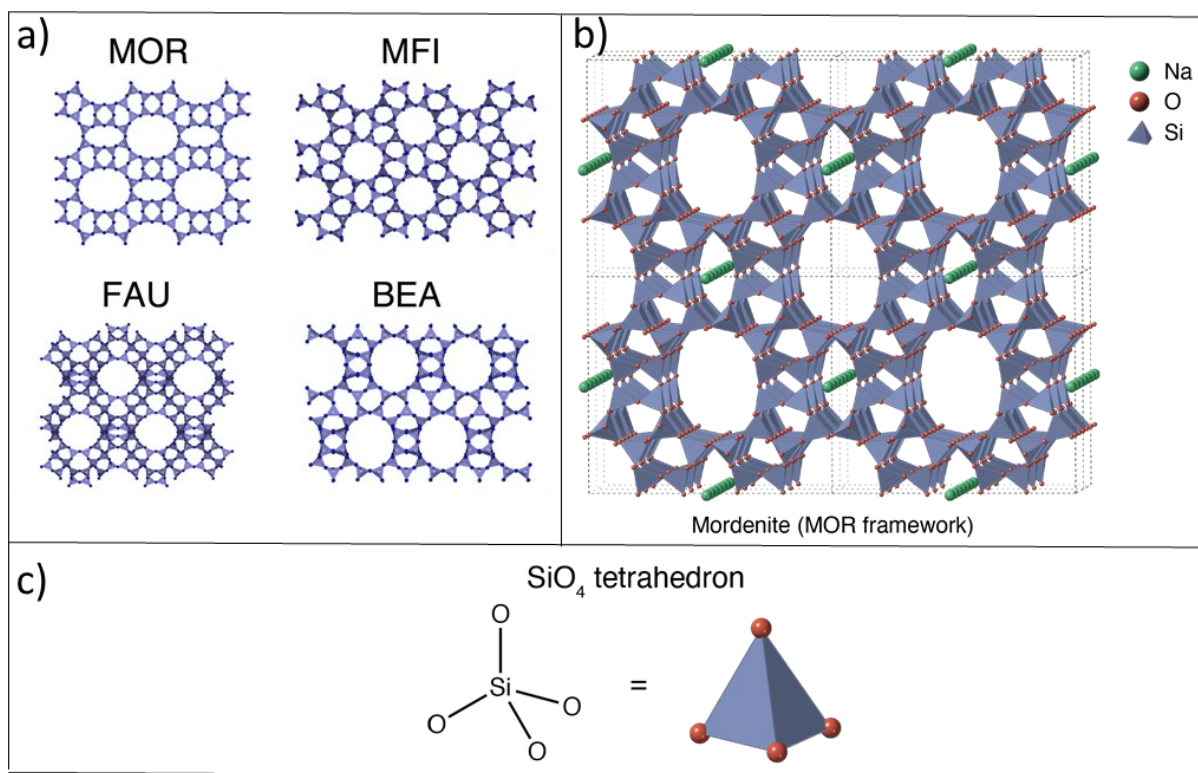


Figure 8: Graphical depiction of a) some common zeolitic frameworks (adapted from (Zimmermann & Haranczyk, 2016)), b) the mordenite (MOR) framework in more detail (image courtesy of Francois-Xavier Coudert) and c) the SiO₄ tetrahedron.

Due to their properties, zeolites have been researched on extensively and are used in a variety of applications in the industry including catalysis, adsorption and ion exchange (Li, Li & Yu, 2017). Their porous framework, large surface areas and the ability to easily exchange ions in their lattice or in extra-framework positions to substitute them with desired cations, makes zeolites exceptional catalytic supports. Although they occur naturally, zeolites have been successfully synthesised artificially, with scientists engineering zeolites with desired properties like pore geometry, size, polarity etc.. Over two hundred known zeolitic frameworks exist to the present day (Sadeghbeigi, 2020). Today, zeolites catalyse thousands of reactions and one of their successful applications has been the DMTM. (Li & Yu, 2021)

The following sections will discuss the inspiration which led to zeolites in the DMTM, the progress in their use and the active sites of the most successful zeolites in the DMTM to date.

2.4.2 Inspiration from particulate monooxygenase (pMMO)

Oftentimes, when scientists research on a potential new technology or invention, or when they are simply looking for a solution to an existing problem, inspiration is derived from the observation of nature. As discussed in previous sections, thermodynamics indicate that the DMTM under mild conditions is possible.

Decades ago, it was discovered by scientists that certain bacteria can activate methane at ambient conditions to partially oxidise it to methanol (Patel, Hou & Felix, 1978). These bacteria are *methanotrophs*, which means that they “feed” on methane. As a result, they exist in environments with an abundance of CH₄, like wetlands, sewage sludge etc. (Sharma et al., 2020). It was slightly later identified that *methane monooxygenase (MMO)* was an enzyme in these methanotrophic bacteria that was responsible for the partial oxidation of methane (Dalton, 1980). A model of the pMMO as well as the location of active sites, which will be discussed in more detail are displayed in **Figure 9**.

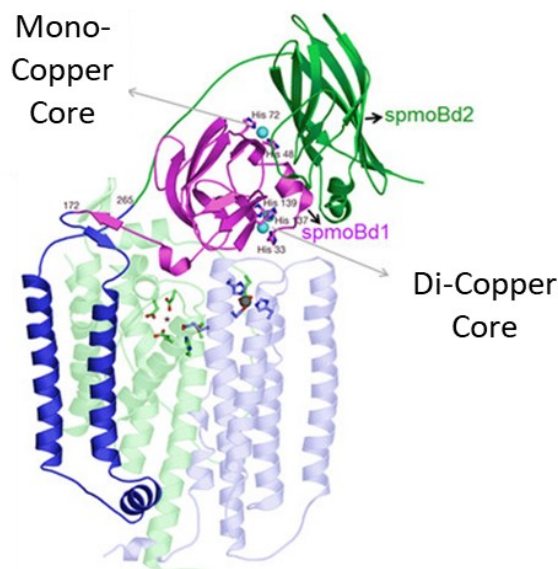


Figure 9: Visual presentation of the structure and location of active sites of particulate methane monooxygenase. (adapted from (Chidambarampadmavathy, Obulisamy P. & Heimann, 2015))

Further research into these bacteria that could naturally achieve the DMTM at ambient conditions revealed the existence of two distinct MMOs, particulate MMO (pMMO) and soluble MMO (sMMO). As the name suggests, the latter is a soluble form of MMO, while the former exists in a particulate, membrane-bound form. They are both capable of activating and oxidising methane

through different pathways (Hanson & Hanson, 1996). The catalytic active sites on sMMO are di-iron oxygen-bridged cores, while the active sites on pMMO are copper based (Ross & Rosenzweig, 2017). The proposed active sites on sMMO can be seen in **Figure 10**.

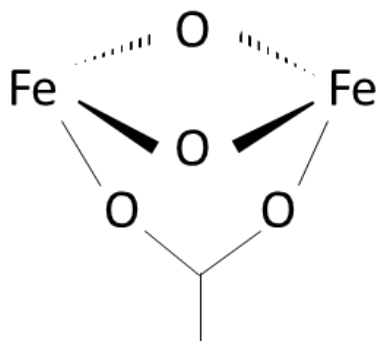


Figure 10: The proposed di-iron active site on sMMO. (adapted from (Hwang et al., 2014))

Although it was thought that both a di-copper core as well as a mono-copper core are the active sites responsible for the DMTM on pMMO, it was recently reported that the active sites on pMMO are in fact mononuclear copper centers, which are, however, assisted by other sites in the whole mechanism of the reaction (Ross et al., 2019). The initially proposed di-copper oxygen-bridged cores are displayed in **Figure 11**.

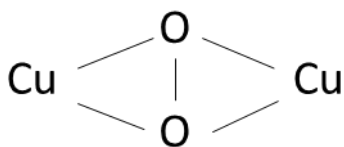


Figure 11: Di-copper cores of pMMO, initially suggested as the active sites for the partial oxidation of methane to methanol. (adapted from (Dinh et al., 2021))

Having proof that methane can be activated and partially oxidised successfully at ambient conditions with reasonable yields, researchers in the field of DMTM came up with the concept of mimicking the active sites of sMMO and pMMO and replicating them onto suitable catalytic supports. The nature of zeolites, with their consistent and customisable structure and composition which can be tailored to need, the ability to exchange extra-framework cations to form active sites of desired metals, as well as the confined spaces within their channels and pores that due to their cylindrical shape can bring extra-framework cations closer to each other to potentially form

oxygen bridges between them, made zeolites a dream catalytic support for the replication of the pMMO and sMMO active sites. Indeed, zeolites have been perhaps the largest and most successful chapter of heterogeneous catalysis in the DMTM history to date. An overview of progress in the field will follow.

2.4.3 History of zeolites in DMTM

The first reports of attempts to replicate the methane monooxygenase active sites on zeolites emerged at the end of the previous century. Although MMO was at the time clearly understood, early attempts failed to successfully replicate the cores and produce successful results (Shteinman, 1995). Anderson and Tsai in 1987 reported the production of methanol over a FeZSM-5 catalyst, but both their conversion and selectivity were low. However, the first breakthrough happened in 1997, with Panov et al. reporting the successful installation of iron complexes on a ZSM-5 as a novel artificial model of MMO. The group employed a FeZSM-5 catalyst with a 0.56% wt. Fe content and after calcining it, they exposed it to N_2O for oxygen loading. Subsequently they passed methane over the catalyst surface at room temperature and then extracted the product. The researchers conducted additional analysis to confirm that the formed active sites were indeed oxygen-bridged binuclear Fe complexes. CH_3OH was identified as the only product of the reaction.

Several attempts to better understand and improve the performance of ZSM-5 and other zeolites in the DMTM followed over the next decades. The DMTM as well as the benzene transformation to phenol via N_2O was investigated in a study by Yoshizawa et al. in 2000, which suggested that the pathways for the two transformations were similar at 300-400°C with 100% selectivity to desired products at relatively low conversions. To get a better understanding of the active sites on FeZSM-5, Battiston, Bitter, and Koningsberger applied in-situ XAFS spectroscopy. The group suggested that on their FeZSM-5 catalyst, the active sites were extra-framework Fe-oxo/hydroxo complexes located at the Bronsted aluminum sites. They further suggested that these Fe-O-Fe active sites were reduced when thermally treated in an inert atmosphere at 350°C to produce Fe-X-Fe vacancies. These vacancies could be filled via oxidation in the presence of an oxidant. A similar study which used nitrous oxide as the oxidant concluded that active sites were indeed extra-framework sites of exchanged cations on the zeolite. The group suggested that in the presence of CH_4 and N_2O , methoxy species could be formed on the FeZSM-5. However, raising the temperature of the reaction above 250°C led to the decomposition of these species. On the contrary,

when these species were exposed to H₂O, they were promptly hydrolysed and desorbed as methanol (Wood et al., 2004).

One of the first works of DMTM on FeZSM-5 that used molecular oxygen as the oxidant was that of Michalkiewicz in 2004. Michalkiewicz investigated the DMTM in a temperature range of 350-650°C and concluded that large contact times with the catalyst, as well as higher temperatures had negative impact on the selectivity towards methanol due to overoxidation. Xia et al. in 2010 with their extensive study of the NO and N₂O decomposition over FeZSM-5 using in situ IR and Raman spectroscopy, confirmed that the active sites on FeZSM-5 were indeed binuclear Fe sites. They also reported on the hindering effect that even trace amounts of water can have on the active sites, as it oxidised the Fe²⁺ sites during N₂O decomposition. As the topic was further investigated over the years, researchers exchanged different metals on the zeolitic extra-framework positions, like Co, but with relatively limited success compared to Fe (Krisyuningsih Krisnandi et al., 2015).

On the contrary, researchers had great success with the use of copper, which is the metal on the pMMO active sites. A recent study that employed DFT calculations to compare different metal-exchanged (Fe, Co, Ni, Cu) ZSM-5 catalysts revealed that CuZSM-5 not only outperformed other metals in terms of activity but also in potential CH₃OH selectivity (Mahyuddin et al., 2016). Early studies showed that the partial oxidation of methane to methanol can happen on CuZSM-5 and CuMOR catalysts (Groothaert et al., 2003) (Groothaert et al., 2005). In fact, in comparative studies CuMOR has been proven to perform better in final methanol production for the DMTM than CuZSM-5, while Cu-MAZ outperformed both aforementioned catalysts (Park et al., 2017). This will be further discussed in a later section.

Nevertheless, the synergistic effect of Fe and Cu has been investigated on ZSM-5, although such studies have been more frequent in the case of heterogeneous catalysis in the liquid phase. Xu et al. in 2016 reported on the co-impregnation of the zeolite with Fe and Cu that resulted in a 92% selectivity at 0.5% conversion, which the group attributed to the synergistic effect of the metals.

To date, one of the most competitive overall performances of a zeolite in the field of DMTM is that of CuMOR. CuMOR has been extensively studied and although there have been extensive debates in the scientific community over the nature of active sites responsible for its performance on the DMTM, recent studies attempt to shed more conclusive light on the matter. Ground-breaking results were achieved using a copper mordenite by Tomkins, Ranocchiari, and Van Bokhoven in

2017, who published their work on a step-wise process of DMTM over a CuMOR. The group reported a process in which they activated the catalyst at 450°C under oxygen, then exposed the catalyst to methane of different pressures and subsequently reacted the formed methoxy species on the catalyst with steam to desorb methanol. They achieved better methanol yields (as high as 103.3 μmol/g catalyst) by increasing the methane pressure of the second step up to 36 bar. This result was the highest single-pass methanol production achieved by that time via heterogeneous catalysis in the gas phase without the use of an expensive oxidant like N₂O.

With further studies on the matter, the group further improved their process by carrying out their activation under helium instead of oxygen and employed spectroscopy to investigate and conclude on the nature of active sites and mechanism of reaction (Sushkevich et al., 2017a). Even more extensive studies from the same group led to conclusions about the different species formed on the catalyst during the reaction, the effect of pressure during the methane adsorption step and the hindering character of water on the active sites (Sushkevich & Van Bokhoven, 2020). It is noteworthy that the role of water over the CuMOR is two-fold, as both a soft oxidant which aids in the formation of methoxy species, as well as a strong medium to displace and desorb the formed methanol, protecting it so from overoxidation. Several of the same conclusions, as well as the nature of the step-wise process that this group suggested, were reached during the present thesis. This will be discussed in more detail in a later chapter. In the following section, the catalytic active sites of the most relevant catalyst to date will be discussed in more detail.

As mentioned in the present chapter, several different catalysts have been investigated in the DMTM throughout the years. Although the results of the DMTM over a large number of catalysts is reported in the literature, it is challenging to draw a direct comparison of catalysts between different studies. This is due to the fact that different catalytic systems have been tested over a range of different conditions and experimental procedures, as well as because in several cases the selectivity or the conversion of reactants was not explicitly reported. Early studies were typically investigating the DMTM under isothermal conditions, with a continuous flow of reactants over the catalysts. However, latest research and particularly on zeolites has been employing a step-wise, batch-like reaction sequence which requires the reactivation of the catalyst between cycles of reaction. Due to the pre-adsorption of methane and formation of methoxy species on the catalytic active sites, conversion is generally not mentioned by researchers, but instead, the selectivity

towards products and specifically CH₃OH is most commonly mentioned and compared for different catalysts. Additionally, the most commonly used key performance indicator for different catalysts employing this experimental method is the total moles of methanol formed during reaction per gram of catalyst for one cycle of reaction. Given the step-wise nature of the reaction sequence, new catalysts aim towards a high selectivity to CH₃OH to avoid overoxidation to CO₂, thus leading to a higher methanol production per cycle, as well as conditions which are as mild as possible, since conditions of higher temperature and pressure favor overoxidation. (Sushkevich et al., 2017) (Li et al., 2021)

2.4.4 Active sites in ZSM-5 and MOR

Groothaert et al. in 2005 conducted a joint characterisation via EXAFS, TEM and EPR to identify the active sites on CuZSM-5, responsible for the DMTM via N₂O and O₂. Identifying a UV-vis band at 22700cm⁻¹, they concluded that it could only be proof of the presence of bis(μ-oxo) di-copper cores [Cu₂(μ-O)₂]²⁺, on which oxygen was formed and released. The same group later investigated the active sites more extensively and via spectroscopy and DFT analysis reached the conclusion that the active site is in fact a bent mono(μ-oxo) di-copper core [Cu₂(μ-O)]²⁺ (Woertink et al., 2009). This work was complemented by another study which claimed that along with the dispersed Cu-oxo species within the pores of the zeolite, there was a large number of copper monomers (Cu-O) in the outer surface of the zeolite, which the group confirmed to not play a role in the reaction (Beznis, Weckhuysen & Bitter, 2010). The existence of even trinuclear copper clusters on ZSM-5 that can also be active for the reaction with even higher selectivity to methanol has been reported, according to another group (Li et al., 2016). Another study which investigated the formation of iron active sites on ZSM-5 reached the conclusion that it was possible to form both framework and extra-framework Fe on the zeolite. The FeZSM-5 prepared by the group contained Fe³⁺ in framework positions and Fe²⁺ in extra-framework positions and was active for the decomposition of N₂O. (Lazar et al., 2006)

Since mordenite and especially CuMOR catalysts were found to perform exceptionally well in the reaction, the nature of their active sites has also been the subject of extensive study. The aforementioned first study by Groothaert et al. had revealed the existence of bis(μ-oxo) di-copper cores [Cu₂(μ-O)₂]²⁺ on mordenite, just like in ZSM-5, which were the first active sites on mordenite identified to be active for the DMTM. More recent studies revealed that in mordenite, single site

tri-nuclear Cu clusters $[\text{Cu}_3\text{O}_3]^{2+}$ were capable of catalysing the DMTM and in fact could be the reason of the improved performance of MOR over ZSM-5 (Grundner et al., 2015)(Grundner et al., 2016). The existence of clusters of even more copper atoms has been speculated by Palagin et al. in 2017, while mono-copper $[\text{CuOH}]^+$ active sites have also been identified, although the reports on their existence and activity for the DMTM is rather limited (Kulkarni et al., 2016). To date, the di- and tri-copper cores are those which are believed to host the partial oxidation of methane to methanol at mild conditions.

Among the several different copper active sites which can form on zeolitic frameworks, the di-copper core (Cu-O-Cu) has been the most widely reported active site, also responsible for the transformation of methane to methanol at ambient conditions in nature (Pappas et al., 2018) (Balasubramanian et al., 2010). In literature, large effort has been dedicated to understanding the mechanism of the reaction over the di-copper site, often accompanied by different in-situ characterisation techniques, as well as density functional theory (DFT) calculations. However, no conclusive results have yet been reported and although progress has been made towards the understanding of the mechanism of the DMTM over copper-exchanged zeolitic frameworks, it still remains a widely debatable topic. The work of Sushkevich, Palagin, Ranocchiari, and Bokhoven which involved in-situ x-ray absorption spectroscopy (XAS) and Fourier transform infrared spectroscopy (FTIR) at reaction conditions proved that the reaction begins with the dissociative adsorption of CH_4 on the copper active sites. The researchers observed that the adsorption of methane onto the active sites was accompanied by the formation of Bronsted sites on the zeolitic framework, which linearly increased with an increase of adsorbed methoxy species on the di-copper cores. This led to the conclusion that the dissociation of CH_4 takes place on two sites different in nature. The dissociation of CH_4 leads to the formation of a methoxy species on the Cu-O-Cu bridge, while the abstracted hydrogen atom is adsorbed on a nearby framework site to form the aforementioned Bronsted site. The Bronsted sites do not directly play a role in the reaction but rather act as spectator sites, temporarily holding a hydrogen atom before it later reacts towards the formation and desorption of H_2 . Additionally, it is widely accepted that in the subsequent step of the introduction of water into the system, water is adsorbed on the same di-copper site which had previously adsorbed the methyl radical. Although the H_2O adsorption is thought to also be dissociative, the exact nature of the H_2O dissociative adsorption is still a matter of debate among researchers. (Palagin, Sushkevich & Van Bokhoven, 2019)

2.4.5 8-MR theory

As discussed earlier, zeolites are, due to their topology and characteristics, perfect hosts for active sites that could mimic those of sMMO and pMMO. Indeed, along with the identification of the active sites on CuZSM-5 and CuMOR, it was important for the exact location of these active sites within the zeolitic framework to be pinpointed. The location where the active sites formed could provide information related to the requirements for a suitable active site for the DMTM, as well as information about the exact reaction mechanism.

The identification and analysis of active sites, their location and the reaction mechanism on them, as well as the difference in performance of different copper-containing zeolitic frameworks, sparked interest into the investigation of the effect of zeolite geometry in the DMTM. Indeed, studies have emerged which compared several zeolitic frameworks against each other in the DMTM (Park et al., 2017). The reason why specific active sites form more preferably on some frameworks than others has been attributed to their different pore size and the number of Si atoms that constitute a pore ring in each framework. This leads to new studies reporting that other frameworks with pores and channels of larger diameter seem to be outperforming small-pore zeolites (Wulfers et al., 2015). As a result, a scientific discussion has started over the past years over the importance of pore size in the DMTM, with the existence of 8-MR pores appearing to play a significant role in the formation of desired active sites. This will be discussed in more detail in the last chapter of this thesis, which is dedicated to the effect of the 8-MR on the DMTM.

To give the reader a better understanding of the connection between the active sites mentioned earlier and the 8-MR membered rings within the zeolite, **Figure 12** is presented. **Figure 12** provides a three dimensional visualisation of the tri-copper active nucleus, which is located at the 8-MR pore opening of the side pocket (Grundner et al., 2015).

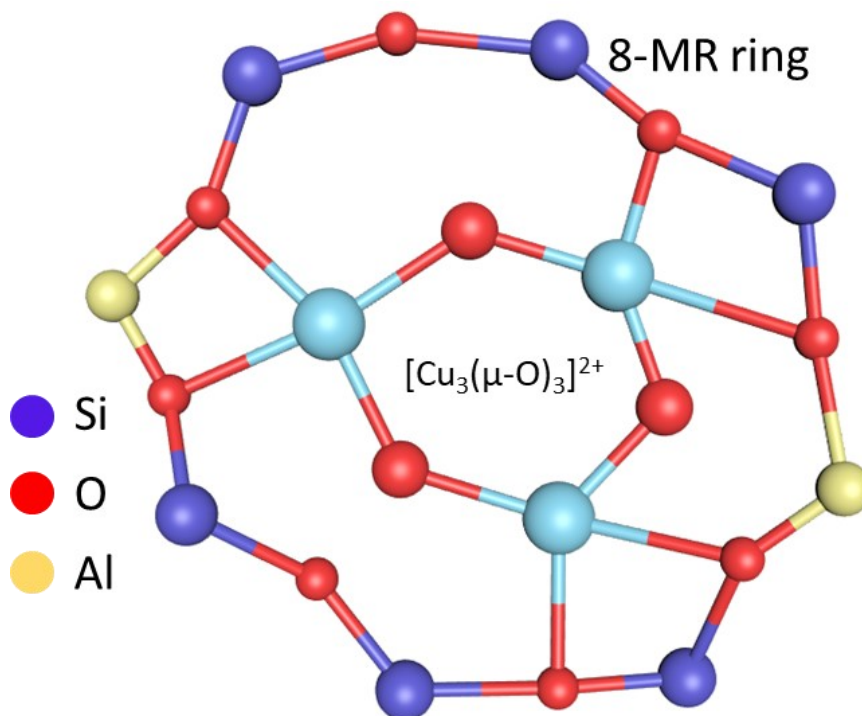


Figure 12: Three dimensional depiction of the structure and position of the tri-copper active site at the entrance of an 8-MR pore on the mordenite framework (structure drawn with the ChemDoodle software).

2.5 Thesis outline

The main content of the present thesis is laid out in four chapters. Before these chapters, the experimental setup, the experimental protocols, the quantification of product and characterisation protocols are presented. The aim and the objectives of the present work will be discussed in the next chapter.

Chapter 5 focuses on early experiments which led to the establishment of the experimental procedure and methodology. The qualitative and quantitative experiments are discussed, which led to conclusions regarding the needs of the CuMOR catalyst, the limitations in conditions, the parameter evaluation of the catalyst itself as well as the development and refinement of the laboratorial method. Important experimental observations are discussed to reach conclusions regarding the progression of the reaction. Finally, the refined experimental process is presented and discussed.

Chapter 6 focuses on experiments carried out on the best performing catalyst (3% CuMOR) and the most favorable experimental method in terms of CH₃OH yields. The experimental results are

used for the quantification of product and the comparison with the current state-of-the-art research results. The results are then be used for a kinetic analysis of the reaction, in an attempt to develop a kinetic model which can describe the evolution of different species in the reaction. This can help to further target bottlenecks of the DMTM process and to potentially increase methanol yields, since such a model can be also used in the simulation of the process in a larger scale.

Chapter 7 aims to establish the concept of an industrial-scale process based on the findings of Chapter 5 and 6. The exact lab-scale process with all its limitations serve as the baseline for the concept. Once established, the industrial scale process is then be laid out in detail including all the steps from the raw materials to the delivery of a product with the highest market specifications. An optimisation of process is be carried out as well as a thorough technoeconomic evaluation including heat integration to conclude on the profitability of the process with the current performance of the catalyst. Additionally, a target is set for the catalyst performance, which serves as a guide for future research. Furthermore, the discussion includes bottlenecks of the process and how they can be improved in the future. This work is considered to be necessary for perspective on where the DMTM over Cu-zeolites stands industrially. It is important to note that extensive research is being carried out in the direction of catalyst improvement, but no detailed study has been carried out on the profitability of the suggested processes in the literature.

To complement the outlook given in the previous chapters regarding improvement of the process Chapter 8 investigates the speculation that 8-MR-containing zeolites exhibit a better performance in the DMTM compared to other catalysts. This chapter includes the synthesis of some 8-MR-containing frameworks and the investigation of their performance in the DMTM, trying to isolate the effect of the 8MR. A discussion based on the findings as well as the relevant literature attempts to shed light into the potential of improving zeolitic catalysts in the future to maximise the methanol yields and make the industrial process suggested in Chapter 7 more economically attractive.

Finally, Chapter 9 summarises the most important findings, results and conclusions of the present work. With a well-rounded understanding of both the lab-scale and the industrial-scale process and its weaknesses, suggestions are made on where research needs to be directed in the future.

3. Aim and objectives

It is considered essential for any research work to set a clear aim and objectives. These are laid out below for the present work.

3.1 Aim

The aim of the present thesis is to set a clear understanding of the DMTM process over a heterogeneous copper-mordenite catalyst. It is necessary to obtain essential information about the reaction regarding conditions and its bottlenecks, to understand how the process can be improved and to utilise this knowledge in order to visualise the reaction and lab-scale process at the larger scale. Although the understanding and development of the lab-scale process is essential, it is also of great importance to set a perspective of economic relevance of this study to the current market. In order to achieve this aim, certain objectives are set. These objectives are explained below.

3.2 Objectives

The objectives set for this work are the stepping stones which will lead to achieving the final aim explained previously. The objectives set are the following.

- a) The first objective of the present work is to qualitatively and quantitatively approach the reaction in the lab scale in order to reach conclusions on how the experimental method can be improved/perfected for maximising CH₃OH yields. This objective is to be achieved through a set of targeted experiments, which will give information about the most favorable conditions, the intermediates of the reaction and the importance of different reactants. By achieving this objective, the lab-scale process will be refined to a point that can be further studied. Information regarding the mechanism of reaction will also be extracted from experimental findings, when possible.
- b) Developing a kinetic model based on experimental findings and literature information, which can describe the evolution of species throughout the reaction, is particularly beneficial as it can be used for process refinement and economic optimisation in the industrial scale. Successfully developing a kinetic model for the DMTM over CuMOR is another important objective of this study.
- c) When researching a topic from an engineering perspective, it is always important to investigate the relevance of micro-scale results in the industrial scale. Parallel to gathering information about

the reaction through experimental and kinetic analysis, it will be attempted to utilise experimental results to conceptualise an industrial process of the DMTM over a copper-mordenite catalyst. A key objective of this work will be to develop the industrial concept of the process as well as to carry out a technoeconomic analysis that will set a target for the catalytic performance necessary for economic viability and profitability.

e) The final objective of this work will be to sufficiently interpret the experimental data, including the synthesis and investigation of 8-MR zeolites, the kinetic analysis as well as the knowledge gained about the process both in the lab- and the industrial scale and suggest improvements and a future research outlook for research to follow.

4. Experimental setup, methodology and characterisation

4.1 Experimental setup

The experimental setup used in this work was custom made by Dr. Fessehaye Zemichael. A simple design was employed which allows for precise temperature control of the process as well as live monitoring of the composition of the gases leaving the reactor. The experimental setup can be seen in **Figure 13**.

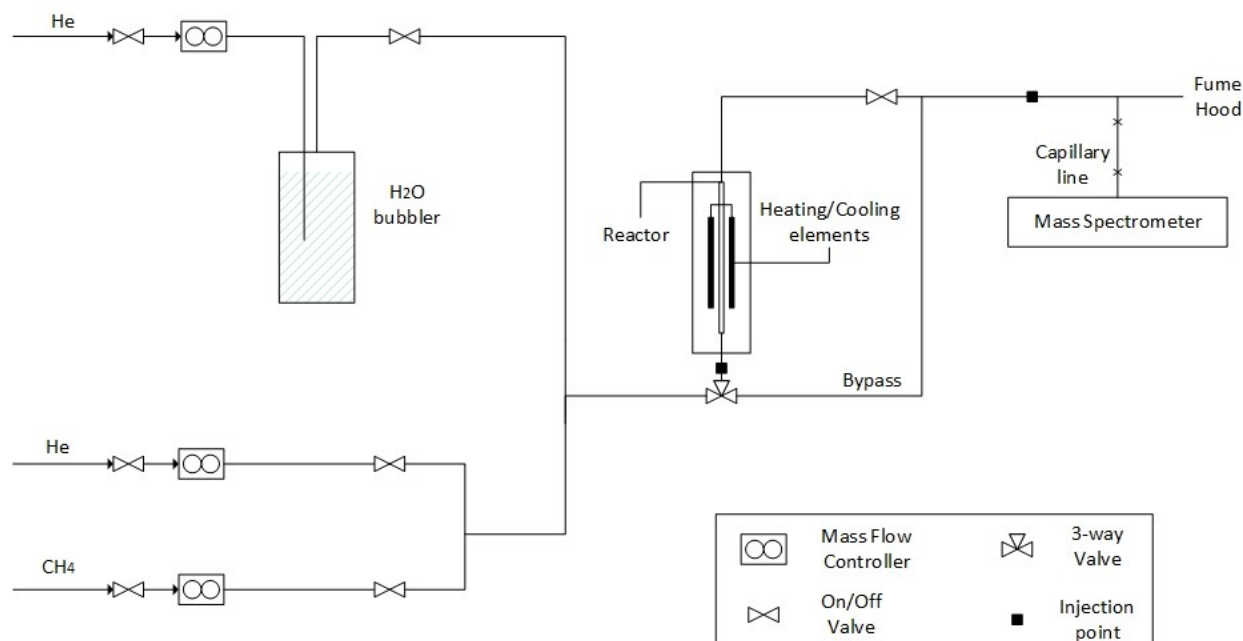


Figure 13: Experimental setup used for DMTM experiments and characterisation.

The gases used in experiments (N6.0 grade >99.9999% purity He, CP grade CH₄, supplied by BOC) were passed into mass flow controllers which regulated their flow. AALBORG GFC17 and BROOKS Smart Mass Flow Controllers 5850S were used. The flow could be controlled either via manual controllers or via a Brooks Instrument Read Out & Control Electronics 0152 control box. Typically, the total flow of gases in the system was 25ml/min. All lines used were Swagelok Stainless Steel 316 lines of different diameters (1/16in, 1/8in and 1/4in O.D.). All valves and fittings used were supplied by Swagelok.

Each gas was passed into the system through a separate tubing line. One line was assigned to dry helium, fed into the system right from the cylinder, one line was assigned to CH₄ fed into the system right from the cylinder and one line was assigned to wet helium. For the wet He line, helium

from the cylinder was passed into the system and fed into a custom-made water bubbler. The water bubbler which is shown schematically in **Figure 13**, is a stainless steel vessel almost fully filled with deionised water, with an immersed inlet tubing which allowed helium to enter the body of water and an outlet on the top of the vessel which allowed helium that passed through the water body and was saturated in H₂O to leave the vessel and continue into the lines. It is assumed that through the direct contact with liquid H₂O, the helium stream was saturated in moisture under the given conditions. All individual gases met at a mixing point and continued towards the reactor. A three-way valve before the reactor allowed the stream to either bypass the reactor entirely and continue to the system outlet, or to enter the reactor and then continue further to the outlet.

The reactor used was a 30cm in length, 1/4in O.D. 316 SS tube. To ensure even heat distribution along the reactor, the reactor tube was encased in a solid stainless steel block. To prevent heat losses, the metal block was further encased inside a PTFE block, with a layer of quartz wool between the PTFE and the stainless steel block. Quartz wool was supplied by Sigma Aldrich and Agilent Technologies. A thick layer of quartz wool held in place by a tight layer of aluminum foil surrounded the PTFE block when the system was in operation. A schematic representation of the reactor block can be seen in **Figure 14**.

To allow for strict temperature control of the reactor, two heating/cooling elements were located inside the PTFE and metal casings to the left and right of the reactor, as seen in **Figure 14**. These elements could heat up or release liquid nitrogen (LN₂) inside the metal casing to heat or cool down the reactor when needed. Liquid nitrogen was stored in a 60L STATEBOURNE Cryostor 60 stainless steel tank. The heating elements were controlled via a NEWTRONIC MICRO 96 TP10+ temperature controller. The input to the controller was received via a stainless steel shielded 1/16in diameter K-Type thermocouple, which was inserted through an airtight custom-made fitting at the top of the reactor and sat on the catalyst bed when the reactor was in operation to give a live temperature reading of the reactor and catalyst bed. When a specific temperature setpoint or temperature programme was inserted in the NEWTRONIC temperature control box, the thermocouple reading was used by the control box to appropriately raise or lower the temperature via the heating/cooling elements. When cooling of the reactor was needed, the NEWTRONIC box opened a solenoid valve appropriately, to allow for the flow of LN₂. The box allowed for the

creation of custom temperature programs, which will be more specifically explained in a later section.

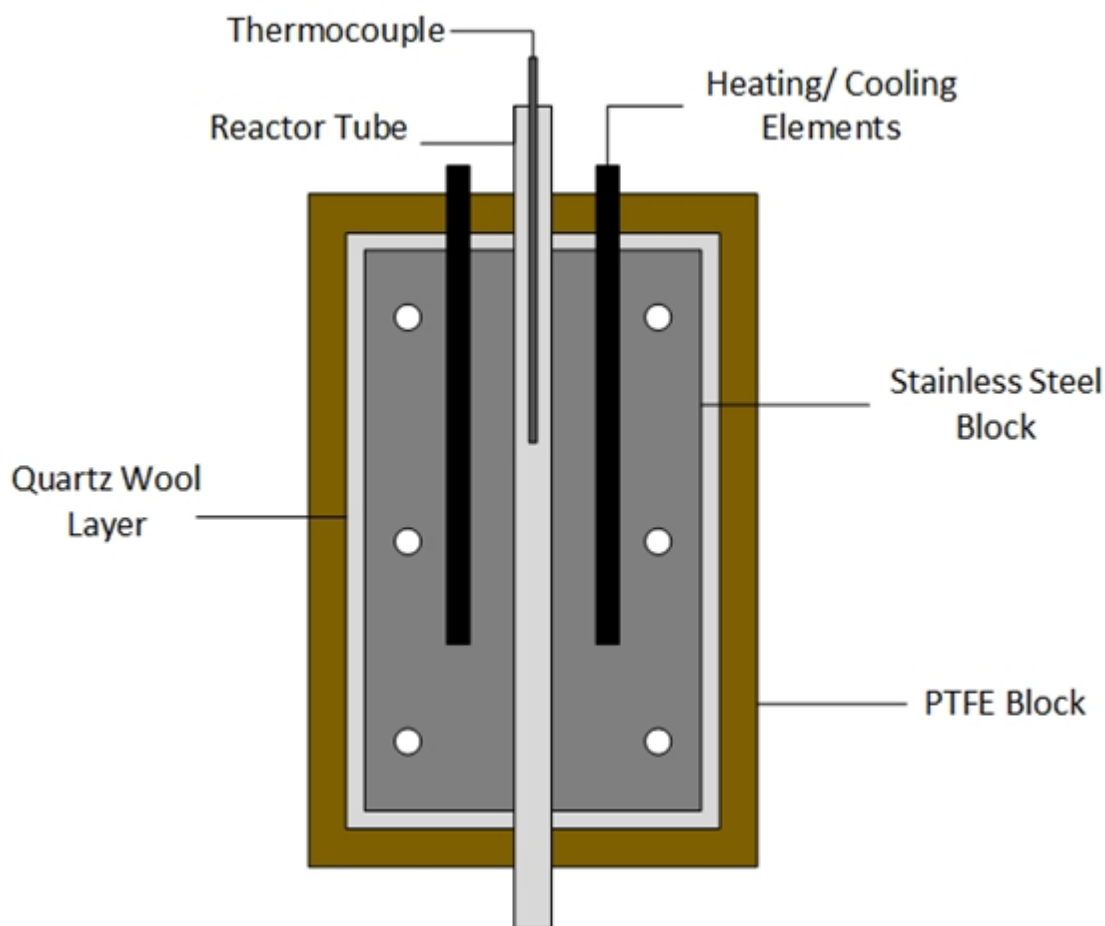


Figure 14: Reactor tube and surrounding blocks.

All gases that passed through the system, either in bypass or through the reactor, were finally led to a fume hood. Before leaving the system to the fume hood, the gas mix that left the reactor was sampled through a capillary line by a ThermoStar Gensys-Pfeiffer Vacuum Quadstar GSD 320T Mass Spectrometer. The Mass Spectrometer (MS) allowed for live monitoring of up to 63 masses in the range of 1-300 atomic mass units (a.m.u.).

To ensure that there was no water condensation inside the stainless steel lines, all lines were surrounded by heating tape and were kept to temperatures above 100°C (typically 110-120°C). The temperature of the heating tapes was controlled via a TENMA 72-10480 Digital-Control DC Power Supply, and two custom-made Eurotherm 94C 450W Temperature controllers. To prevent

heat losses, all lines were encased in a layer of quartz wool and wrapped with aluminum foil. Two injection points were installed for specific injection experiments at the entrance of the reactor and before the sampling point of the mass spectrometer. The injection points were made using a T-type fitting in which the top end was blocked by an airtight, penetrable silicon piece. The temperature of the room was kept constant via an air conditioning system at 21°C.

Appropriate calibrations displayed in the Appendix section took place for all of the instruments used, as well as frequent checks of these calibrations to ensure that the operation of equipment and respective readings were not erroneous. Frequent checks for leaks were carried out along the whole steel tubing of the system using a soap-water solution.

4.2 Materials and catalyst preparation

NH₄-Mordenite with a SiO₂/Al₂O₃=20 was used as a catalytic support, as purchased by ZEOLYST INTERNATIONAL. In order to produce the desired CuMOR, the copper precursor used was a copper(II) nitrate trihydrate Cu(NO₃)₂·3H₂O, which was purchased by Sigma Aldrich. First, according to the desired amount (%wt) of copper in the final catalyst, the required amount of copper nitrate trihydrate precursor was calculated. The precursor was then added to a beaker containing 30ml of deionised water and stirred continuously until fully dissolved (30min). Then, the appropriate amount of mordenite was added and stirred continuously with the precursor solution for 1h. The mixture which had a thin slurry-like consistency was then added to a petri-dish and left in the oven at 80°C to dry completely overnight.

The dry catalyst was then collected from the petri dish, placed into a suitable ceramic container and moved to a furnace for calcination. The furnace was programmed to ramp up the temperature at a rate of 3°C/h up to 500°C, where the temperature was held for 5h. The calcined catalyst was then left to cool down at a natural heat loss rate from the furnace. The calcination procedure was performed overnight and was followed for all prepared catalysts. The calcined CuMOR was sieved to obtain a particle size of 250>d_p>106µm. This was the final form of the catalyst, of which an amount of 0.4g of CuMOR was used in experiments.

The materials used for catalyst synthesis were aluminum sulfate hydrate of purity higher than 97%, sodium aluminate (technical) supplied by Alfa Aesar, potassium hydroxide pellets of purity higher than 85%, sodium hydroxide pellets higher in purity than 98% from VWR, LUDOX AS-40

colloidal silica (40%) supplied by Sigma Aldrich, amorphous fumed silica (Cab-O-Sil® M5) from INOXIA, potassium hydroxide pellets in purity higher than 85% from VWR and aluminum wire of purity higher than 99.999% from Sigma Aldrich. Copper nitrate trihydrate of purity greater than 99% by Sigma Aldrich was used in all copper solutions produced for ion exchange.

All zeolitic frameworks synthesised in the present work, were synthesised following recipes found in literature (Oleksiak et al., 2016) (Robson & Lillerud, 2001). The synthesis took place hydrothermally, without the use of any organic structure directing agents.

4.3 Temperature programmed runs and Mass Spectrometer

The experimental rig that was previously described allowed for carrying out experiments in a temperature programmed fashion. The NEWTRONIC MICRO 96 TP10+ temperature controller allows the user to set up custom temperature profiles, with several temperature setpoints and adjustable heating/cooling rates between them. Temperature programmed reactions can give information about the reaction mechanism and most favorable conditions of the reaction, as well as potentially give insight on how the process can be adjusted for better product yields. With help of the experimental setup and temperature programmed runs, the oxidation/reduction of the catalyst, the adsorption of desired species on the catalytic surface, as well as the reaction and desorption of products are possible (Fadoni & Lucarelli, 1999). In fact, temperature programmed reactions have been used for decades in the field of DMTM (Arena et al., 1995). Coupled with the Pfeiffer GSD 320T mass spectrometer, the gases leaving the reactor were sampled and monitored live during the temperature programmed reactions. Different temperature programmed reactions were carried out in the present work on the CuMOR, as will be explained in more detail in the next chapter.

4.4 Experimental protocol

During a typical experimental run, after preparation, calcination and sieving of the catalyst to the right particle size, the reactor was disassembled and 0.4g of the catalyst were loaded inside, fixed in the middle of the reactor tube. The catalytic bed was held in place by quartz wool plugs placed at the bottom and top of the catalyst bed. The reactor tube was then put back in place and sealed with appropriate fittings on both ends, while the K-type thermocouple that sent input to the

temperature control box was placed on the catalytic bed, to accurately monitor the temperature of the catalyst during reaction as seen in

Figure 14. The space velocity of the reactions was calculated based on Equation (4.1), where τ is the space velocity (min^{-1}), q is the total volumetric flowrate of gases in the reactor (ml/min) and V_{packing} is the volume of packing inside the reactor (ml). The space velocity of reactions was calculated to be 23.5min^{-1} .

$$\tau = \frac{q}{V_{\text{packing}}} \quad (4.1)$$

Subsequently, the system was purged with helium for enough time to remove the air and moisture that entered the system while loading the catalyst. Meanwhile, a setpoint temperature of 25°C was typically set at the temperature control box to prepare the catalyst for a temperature programmed run. Then an appropriate programme was set in the control box and it was subsequently initiated. A purge of the system with helium was performed before a different gas was introduced into the system during the reaction sequences. For example, if methane was flown on the catalyst for adsorption, the system was purged after with helium for an appropriate amount of time until the mass spectrometer signal of CH_4 in the system was back at baseline value, and then the next reaction step was carried out. Frequent checks of the mass spectrometer signals were performed on different days before experiments to ensure that there were no irregularities.

4.5 Quantification of molecules via the Mass Spectrometer

The quantification of methanol, which was the desired product of the reaction, happened through the Mass Spectrometer. The signal intensities that appear in the Mass Spectrometer are an indication of the relative concentrations of molecules in the system. Although the signal intensities are given in arbitrary units and do not have a direct quantitative meaning, they can give a good qualitative picture of concentrations and their changes over time inside the system. Furthermore, the use of an inert background gas can allow for the quantification of other gases in the system. The background gas used in the present study was helium.

The role of helium in the system is two-fold. As signal intensities are relative, a change in concentration of a gas would cause a rise in its signal, but also a decline of other signals tracked. Having a background gas flowing in excess, the relative changes in signal intensities cause less

“disturbance” to other signals and render it easier to track signal changes. Furthermore, the presence of a background inert gas makes it possible to quantify the rest of molecules tracked through their respective signals.

The quantification of gases happened through normalising signals against the helium signal. The quantification protocol followed for being able to quantify gases using the Mass Spectrometer was simple. Since helium flows inside the system at a known flowrate, mixtures of different compositions can be created by ranging the flow of the gas in interest. Each composition is run inside the system and tracked for a specific amount of time. Knowing the flowrate of the gas in interest and the time for which it flowed through the system, the number of moles that correspond to that timeframe can be easily calculated by simple multiplication of the molar flow with the investigated timeframe. The signal of the aforementioned gas was then normalised against the signal of helium to get the normalised signal of the gas for the timeframe. The area underneath the normalised signal can then be calculated by a simple integration of the normalised signal curve over the flow time. Finally, the calculated area corresponds to the calculated number of moles. This protocol is repeated for all investigated compositions and the results are plotted in an Area vs Moles graph, where each composition represents a point in the graph.

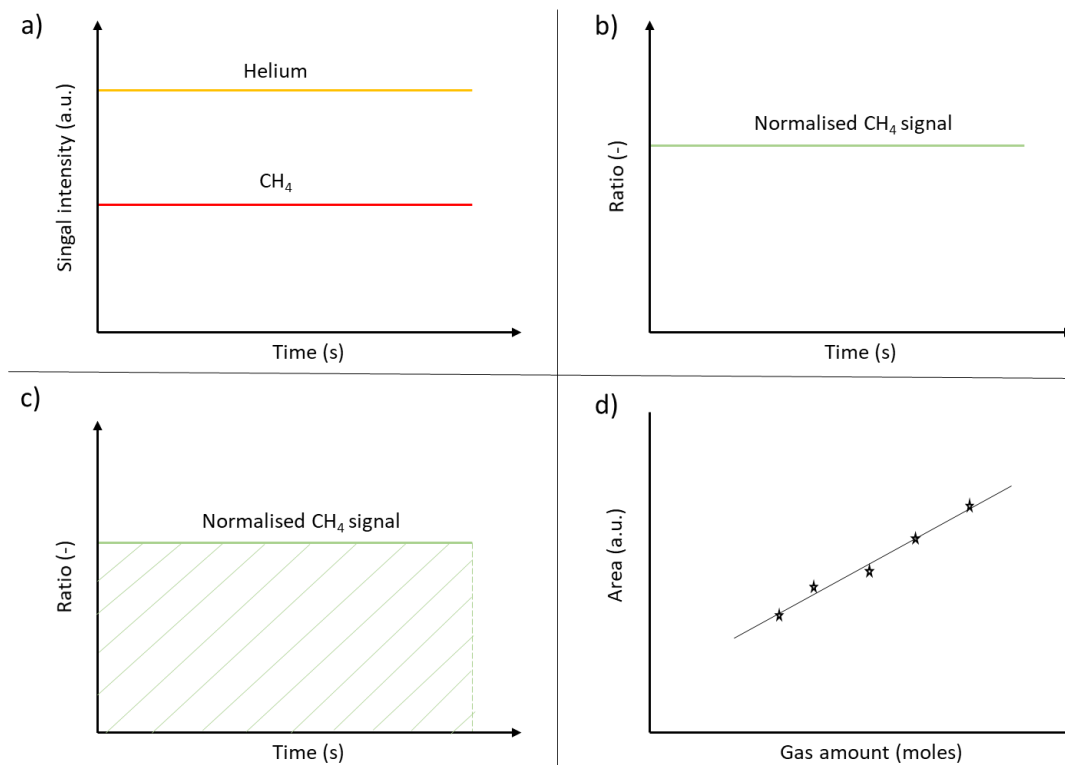


Figure 15: Graphical explanation of gas quantification via the Mass Spectrometer. a) Gas in interest and He flowing at a constant flowrate b) Normalised signal of gas in interest c) Integration of normalised signal to obtain area d) Area vs Gas amount plot to obtain quantification correlation.

The calculation of a trendline between points allows for obtaining a typically linear correlation between a number of moles and the area they represent for a given gas. This correlation can be used in a reverse manner to calculate how many moles of a gas tracked during an experiment correspond to its respective signal. For example, the desorption or production of a gas during an experiment would typically give a rise in the respective gas signal in the shape of a curve. The normalised signal of the gas can be integrated to obtain the area underneath the curve. Then, the aforementioned correlation would be used to calculate the number of moles desorbed/produced during the experiment. A graphical representation of the protocol follows in **Figure 15**.

The aforementioned protocol can be easily followed for the quantification of molecules that exist in the gas phase at room temperature. However, the quantification of methanol which is liquid at standard conditions was necessary for this study. Although the previously explained protocol cannot be used in the case of methanol, a similar protocol was followed. Several known quantities of methanol were injected via appropriate micro-syringes in the injection point installed before the Mass Spectrometer sampling point, while a known amount of helium was flowing in the

background. Since the stainless steel line was heated at a temperature of 110-120°C, the injected methanol instantly vaporised and was carried along with helium flowing through the system to the Mass Spectrometer. This caused a rise in the methanol signal in the shape of a curve. Similarly to the previously explained protocol, the signal of methanol was normalised against the helium signal. The area underneath the normalised methanol signal would then be calculated by integration, as well as the number of moles in the known volume of methanol injected. This procedure was performed for each different methanol volume injected to obtain an Area vs Moles graph. The trendline correlation was then calculated and used for the quantification of methanol moles for given methanol signals tracked during experiments. This is shown schematically in **Figure 16**.

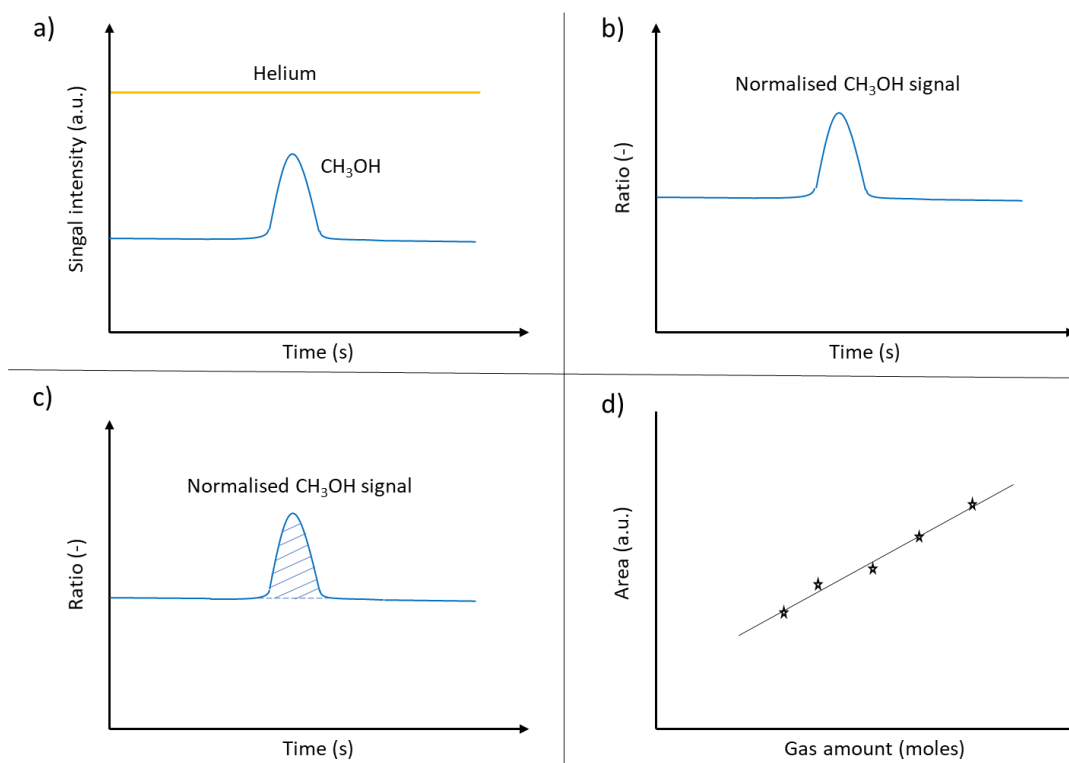


Figure 16: Graphical explanation of methanol quantification via the Mass Spectrometer. a) Methanol injection of known volume in a flow of helium b) Normalised signal of methanol c) Integration of normalised signal to obtain the area underneath the curve d) Area vs Methanol amount plot to obtain quantification correlation.

More details on the masses tracked in the present study as well as the principle of operation of the Mass Spectrometer will be given in the following chapter.

4.6 Characterisation

Different techniques were employed to characterise the commercial and synthesised zeolites in the present thesis. To assess the crystallinity of zeolitic structures, X-Ray Diffraction was employed. X-Ray Diffraction (XRD) was carried out on a X-Ray Diffractometer PANalytical X'Pert Pro powder, (Cu K α radiation, 40kV, 20mA, 1.54Å) to assess the crystallinity of synthesised zeolites. The range used was 5-50° 2 θ and the step of the scan was 0.106°/min.

The elemental composition of as synthesised and ion-exchanged zeolites was characterised via X-Ray fluorescence. X-Ray Fluorescence (XRF) was performed on a PANalytical Epsilon 3 XLE X-ray Fluorescence Spectroscopy machine to identify the molecular composition of the approximately 1g of zeolite loaded on it.

The structures of zeolites were also assessed and depicted via Scanning Electron Microscopy (SEM). A JSM-6010LA InTouchScope Multiple touch panel scanning electron microscope was employed. Finally, the information regarding the pore volume and catalyst surface area was obtained via Brunauer-Emmett-Teller (BET) analysis. 100mg of the zeolite sample were degassed overnight in a N₂ environment at 200°C using a Flow prep 060 by Micromeritics. A Tristar 3000 by Micromeritics was used for a N₂ adsorption at 77K at increasing pressures.

5. Development of the laboratorial DMTM reaction sequence over CuMOR

This chapter explains how selected experiments led to the suggestion and refinement of a stepwise process for the DMTM over a CuMOR catalyst as well as further information about the reaction.

5.1 Mass spectrometer and molecules of interest

The main analytical tool used in the present study is mass spectrometry. Mass spectrometry was developed several decades ago and is still to the present day one of the most powerful techniques which can be used either as standalone or coupled with other techniques like Gas Chromatography (GC-MS) for identification and/or quantification of molecular species in a system.

Mass spectrometry relies on a simple but ingenious principle of operation. The sample of interest, or the *analyte*, enters the mass spectrometer through a capillary tube and is heated and vaporised, if not already in the gas phase. The analyte is then bombarded with electrons emitted by a hot filament (*ion source*) and becomes ionised. During the ionisation process, the analyte molecules can become simply positively charged by losing usually one or sometimes two electrons but can also be fragmented by the cleavage of interatomic bonds into smaller, positively charged ions. The ions are then led to an electric field which accelerates them to different speeds depending on their mass to charge ratio (m/z). The accelerated particles are separated via a magnetic field which bends their trajectories to different extents depending again on their m/z ratio. The electric and magnetic fields comprise the *mass analyser* of the mass spectrometer. Finally, the deflected ions end up on an electron multiplier (*detector*) which detects them and can give a spectrum of the m/z ratios that reach it. Typically, a mass spectrometer operates under a high vacuum. (Deutsche Gesellschaft für Massenspektrometrie, 2021)(Gross, 2017)

By analysing the m/z spectra, it is possible to identify the molecular species present in a system. As the most frequent occurrence is the removal of just one electron from the analyte molecules, typically the charge (z) of ions picked up by the detector would be equal to 1. As a result, ions analysed in the MS would give their highest signals at a m/z equal to their atomic/molecular mass. However, it should be kept in mind that a cleavage of molecular bonds and fragmentation of ions is also possible. Consequently, molecules under analysis could give signal peaks at several m/z ratios. For example, when analysing CH_4 molecules in a Mass Spectrometer, signal peaks are to

be expected at $m/z = 16$ (ionisation without fragmentation), as well as at $m/z = 15$ (ionisation with abstraction of a H atom) and $m/z = 14$ (ionisation with abstraction of two H atoms), although at different intensities. The intensity of peaks in this case would depend on the frequency of occurrence for each fragmentation incident.

When employing mass spectrometry for sample analysis, two things have to be kept in mind: a) Two molecules, or a molecule and a large atom can have the same atomic/molecular mass and as a result can be detected at the same m/z signal and b) A single molecule can be detected at several m/z ratios once ionised. For example, N_2 , CO and CH_4 molecules could all be detected at a signal of $m/z = 14$ when analysed in a MS (N_2 ionisation with cleavage of the interatomic bond, CO ionisation without fragmentation, CH_4 ionisation with abstraction of two H atoms). This means that there can be an overlap of ions detected in a single m/z ratio, leading to artifact observations. Understandably, it is essential to carefully identify the m/z used for the detection of each molecule. Specific m/z ratios should be selected and tracked for each molecule in interest, which cannot have any potential considerable overlap with other ions present in the system.

Table 4: Molecules of interest and their respective tracked m/z and fragments in the Mass Spectrometer. (Spectral Database for Organic Compounds, 2022)(NIST, 2021)

Molecule	Atomic/Mol. weight (u)	Chosen m/z of detection (u)	Main fragment ion m/z (u)
H_2	2	2	1, 2
He	4	4	4
N	14	14	14 , 15
CH_4	16	15	12, 13, 14, 15, 16
CH_4/O	16	16	-
H_2O	18	17, 18	17, 18
N_2/CO	28	28	14, 28 , 29
HCHO	30	29	28, 29 , 30
CH_3OH	32	31	15, 28, 29, 30, 31 , 32
O_2	32	32	16, 32
CO_2	44	44	12, 16, 28, 44

Because of the aforementioned limitations, typically a mass spectrometer is not used to reliably track and quantify certain molecules, especially with very low m/z ratios (like H_2) without pairing with a supplementary analysis technique. **Table 4** presents the molecules of interest and the m/z chosen to track them for the present study.

As displayed in **Table 4**, several molecules are tracked for each experiment. However, several points are noteworthy. Although H_2 is among the tracked masses, its quantification via the m/z signal is not considered to be reliable with the mass spectrometer being the sole analysis tool. Because CH_4 has a molecular mass of 16u, which matches the weight of atomic oxygen, it is tracked at $m/z=15$, which corresponds to CH_4 with an abstracted H atom and does not overlap with other tracked masses. Similarly, CH_3OH has a molecular weight of 32u which matches that of molecular oxygen and is thus tracked at $m/z=31$ which corresponds to CH_3OH with an abstracted H atom. $HCHO$ has a molecular weight of 30u and is tracked at $m/z=29$. However, this m/z ratio could also correspond to a CH_3OH molecule with three H atom abstractions, although this is a low frequency incident. Finally, CO shares its molecular mass with N_2 at 28u and could not be reliably quantified. Nevertheless, the $m/z=28$ is still tracked as if the signal remains at its baseline level during experiments, this still gives reliable information regarding the non-presence of CO in the system.

Through a combination of quantitative and qualitative analysis of selected experiments, which will follow in next sections, as well as a smart interpretation of the data obtained by the mass spectrometer, the development of the laboratorial DMTM process over CuMOR has been made possible.

5.2 Parameter evaluation of Cu content on Mordenite

Early experiments were carried out to identify the best performing Cu content on the mordenite support. Using the same catalyst preparation method, several batches of catalyst were prepared with Cu contents ranging from 0.5-6.0% Cu wt.. All of these were tested for the reaction using the same experimental procedure and evaluated for CH_3OH productivity. The experimental sequence used was as follows:

- A temperature ramp-up under a flow of 25ml/min of pure dry helium from 25-400°C at a ramp rate of 10°C/min, a temperature hold at 400°C for 12 min, and a temperature ramp

down at 12°C/min to 200°C. This step serves as a catalyst preparation step, to desorb any moisture and impurities on the catalytic surface that occurred from the exposure of the catalyst to air between the calcination and the experiment.

- An exposure of the catalyst to a 25ml/min flow of pure methane for 30min to adsorb CH₄ species on the catalytic surface.
- A reaction step, where wet He (He saturated in water (2.34% v/v) by passing through a H₂O bubbler) flows at 25ml/min over the catalyst, carried out in a temperature programmed fashion. The reaction step was initiated at 200°C with a ramp up rate of 10°C/min to 400°C. It was earlier discussed that a mild oxidant is necessary for the selective partial oxidation of CH₄ to CH₃OH. Additionally, some reports had been made in early research about the beneficial presence of H₂O in the DMTM. As a result, a wet He stream was chosen, hypothesising that H₂O can act as a mild oxidant in the DMTM over the CuMOR. (Liu et al., 1984)

It should be noted that preliminary experiments carried out during the early stages of the present work involved very slow ramp rates of 1-2°C/min in each step, resulting in very long experimental times, where a full experimental cycle would last several days. Following the series of experiments detailed later in the present section, the CH₄ adsorption step as well as the step of exposure to H₂O following CH₄ adsorption finally took place isothermally to maximise CH₃OH production. A temperature ramping is only used for the first step of the sequence, which serves to prepare the catalyst for CH₄ adsorption by desorbing any moisture and impurities. The finally used ramp rate of 10°C/min was chosen to reduce the total time of an experimental cycle and since it was only applied to the catalyst preparation step, while the CH₄ adsorption and exposure of catalyst to H₂O for CH₃OH production took place isothermally, it had no effect on the final experimental results. Additionally, the ramp rate was chosen to be such to not compromise catalyst stability by collapsing the aluminosilicate framework.

A quantification of CH₃OH desorbed during the reaction step was carried out for each of the CuMOR tested and the results are presented in **Figure 17**. A blank experiment using mordenite without any Cu treatment was also carried out as a control, with no CH₃OH production being observed throughout the duration of the experiment.

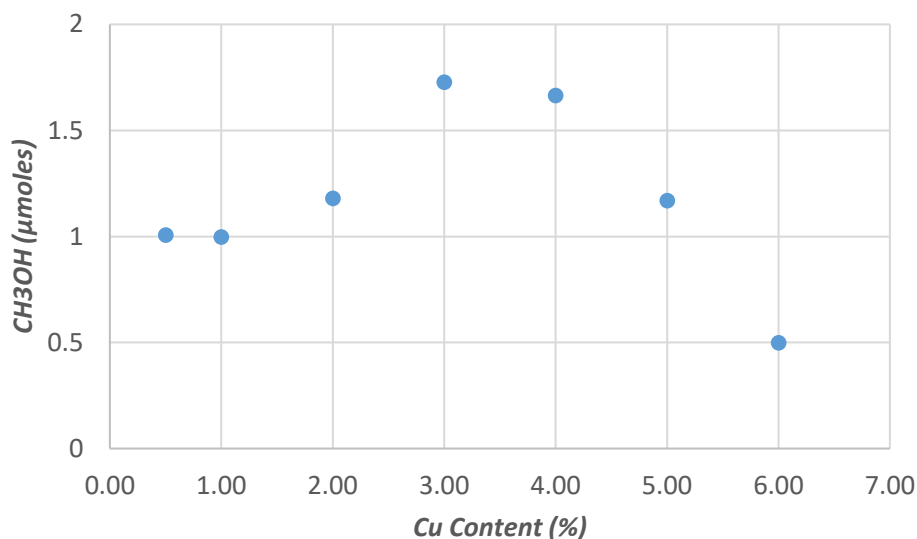


Figure 17: Production and desorption of methanol during a temperature ramp-up from 200–400°C for the Cu% wt. content parameter evaluation on CuMOR.

Figure 17 displays the copper content on mordenite following a bell-like trend, with a peak of CH₃OH production at 3% wt. Cu. A very similar CH₃OH production (although slightly lower) was observed for the 4% wt. CuMOR. However, for a similar production, a smaller active metal content it is naturally preferable. The CO₂ desorbed during each run was also monitored and quantified. The CO₂ production results for each catalyst are presented in **Figure 18**. It is worth noting that the CO₂ production for different Cu contents followed a linear trend.

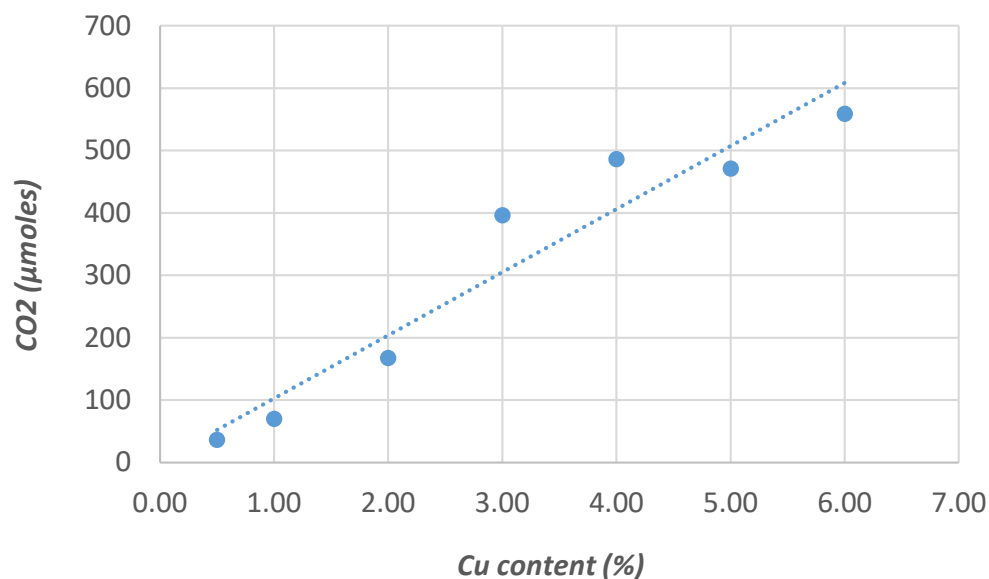


Figure 18: Production and desorption of carbon dioxide during a temperature ramp-up from 200–400°C for the CO₂ desorbed for CuMOR of different Cu% wt. contents.

For a better overview of the desorbed products during the temperature ramp-up from 200-400°C, the CH₃OH selectivity is also presented in **Figure 19**. As **Figure 19** shows, as the copper content of the catalyst increases, the selectivity to CH₃OH decreases, especially at copper contents above 4% wt. since CO₂ production increases linearly, while CH₃OH production decreases.

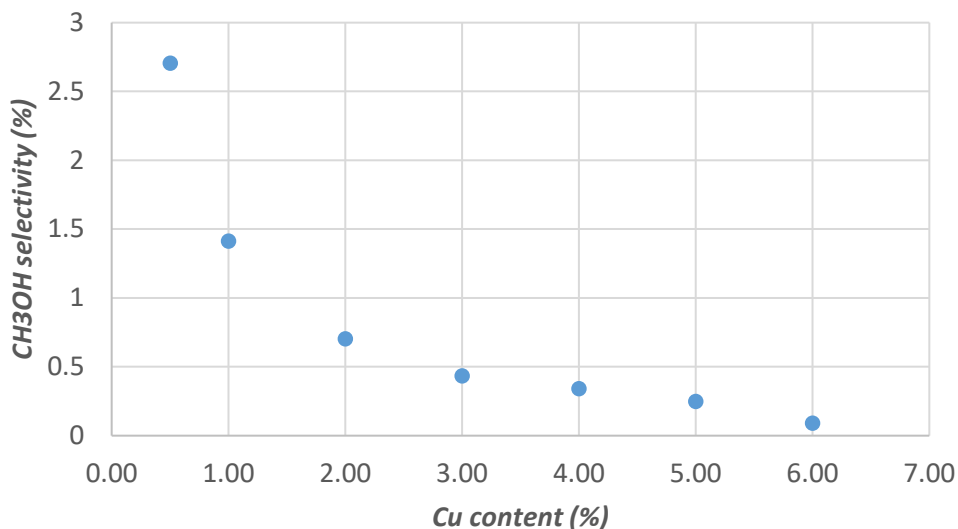


Figure 19: CH₃OH selectivity during the desorption of methanol and carbon dioxide during a temperature ramp-up from 200-400°C at different Cu% wt. contents.

Based on the results of **Figure 19**, a logical approach for the selection of catalyst could be the relatively higher CH₃OH selectivity at lower copper contents. However, more aspects need to be considered in the selection of the catalyst for the present study. As previously mentioned, the copper content evaluation experiments were carried out in a temperature programmed fashion, where the temperature ranged from 200-400°C, where side reactions lead to the overoxidation of methanol and as a result the production of considerable amounts of CO₂. However, latest research carries out the DMTM over copper-exchanged zeolites isothermally (typically at 200°C) and in a batch-like reaction cycle, as will be discussed in detail later in the present chapter, where there is a minimal or no production of CO₂. As a result, all performance comparisons of catalysts in the literature are carried out on a basis of total CH₃OH productivity at the end of one reaction cycle, since methanol selectivity under the aforementioned conditions is close to 100% (Sushkevich & Van Bokhoven, 2019). Additionally, another factor which needs to be considered is the very slow rate of the reaction leading to small methanol productivities during experimental cycles. Selecting a low active metal content would lead to minimal increase in methanol selectivity, while it would

significantly decrease the overall methanol productivity. Consequently, considering these aspects of the reaction and following the results of **Figure 17**, it is concluded that **3% wt. CuMOR** displays the best performance regarding methanol productivity and is the catalyst used throughout the present study.

The Cu content parameter evaluation experiments led to some further noteworthy observations. **Figure 20** presents the experiment over the 3% wt. CuMOR catalyst, where the signals of CO₂, H₂O and CH₃OH, normalised against the signal of helium, are plotted against temperature. The first observation made in **Figure 20** is the hygroscopic character of the zeolite which causes a large decrease in the water signal, which then later rises back up. This is believed to be caused by the absorption of water onto the zeolite, which acts as a strong desiccant until saturation with water. Upon saturation, the concentration of water in the carrier gas returns to the moisture level at which it leaves the water bubbler. In the small timeframe where the experiment is started, wet helium is introduced into the reactor and before the zeolite starts adsorbing moisture, small spikes in the production of CO₂ and CH₃OH are observed. Interestingly, this starts to happen at a temperature as low as ~200°C, indicating that the reaction at that temperature is indeed feasible.

Another important observation is the behavior of the methanol signal relative to the H₂O signal. It is clear in **Figure 20** that CH₃OH follows the behavior of H₂O closely, i.e. methanol starts being desorbed from the catalyst as soon as the H₂O signal rises back up to the baseline level. Moreover, while CuMOR still acts as a desiccant and no gaseous H₂O is present in the system, no production of methanol is observed.

On the contrary, the CO₂ signal exhibits a relatively large rise throughout the whole experiment, peaking at ~330°C. Interestingly, the CO₂ signal rises even in the absence of moisture in the system, when no CH₃OH is observed. This could be explained by the fact that as discussed in earlier sections, the methoxy species adsorbed onto the catalyst during the CH₄ adsorption step are very prone to overoxidation, especially at higher temperature conditions. However, the presence of water seems to shift the selectivity of the reaction towards CH₃OH and to be shielding the methoxy species from overoxidation.

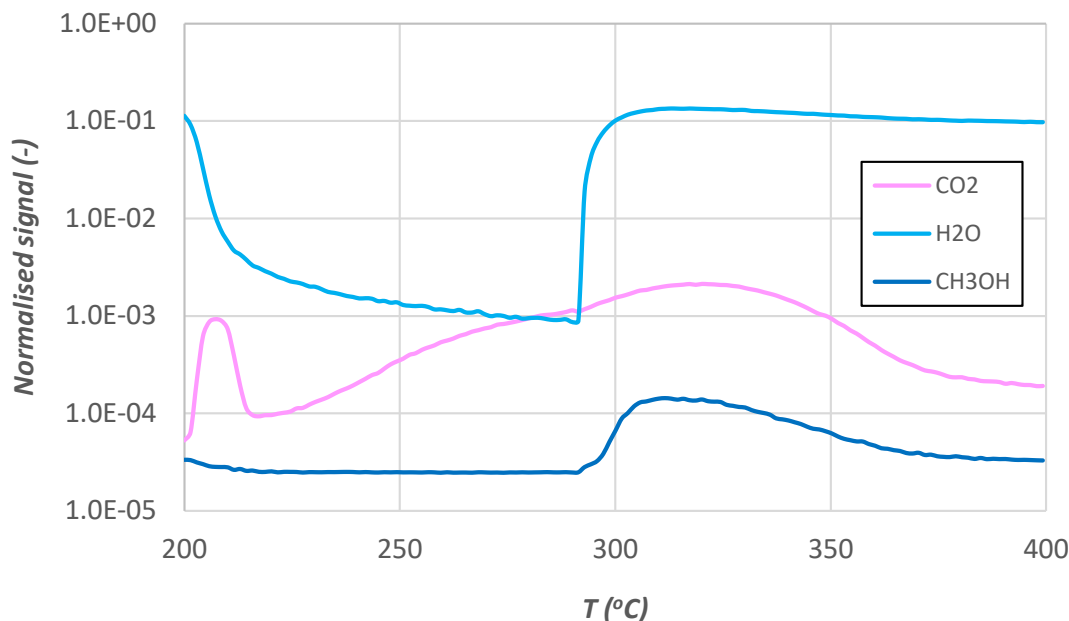


Figure 20: DMTM performed in a TPR fashion in the range of 200-400°C over 3% wt. CuMOR.

Important hints about the reaction and the identification of most favorable conditions arise by combining the coincidence of H₂O and CH₃OH signal rises, the presence of CH₃OH in the system at a low temperature (less than 300°C) and the fact that higher temperatures favor the overoxidation of the methoxy species on the catalyst. There are clear indications that a lower temperature (even as low as 200°C) could facilitate the DMTM reaction selectively towards methanol over the 3% CuMOR catalyst, while the presence of water in the system seems to be playing a key role in the selective production of methanol.

The next sections aim to further investigate these points, as well as other interesting aspects of the DMTM reaction over the 3% CuMOR.

5.3 DMTM over CuMOR insights

In the course of developing a DMTM reaction process over the 3% CuMOR several points need to be addressed involving the effect of temperature, as well as obtaining information about the reaction, its bottlenecks and ways to improve it to maximise selectivity and yield. This section presents a selection of several experiments designed to cover these points and finally suggest a reaction protocol for the DMTM over a copper-mordenite catalyst. It should be noted that fresh catalyst was used for each of the experiments listed below.

5.3.1 Catalyst pre-treatment

Before the interaction of the catalyst with any of the reactants, it is necessary to prepare the catalyst by desorbing any moisture and impurities present. It is reminded that zeolites are potent hygroscopic materials, which are expected to hold a considerable amount of water within their framework, which may interfere with the DMTM reaction. The pre-treatment step would need to involve a rise of temperature high enough for a complete desorption of H₂O. In order to assess the temperature needed for a complete desorption of H₂O, a temperature programmed rise of the temperature up to 400°C was carried out on a 3% CuMOR at a rate of 10°C/min. The results of the normalised H₂O signal are presented below in **Figure 21**.

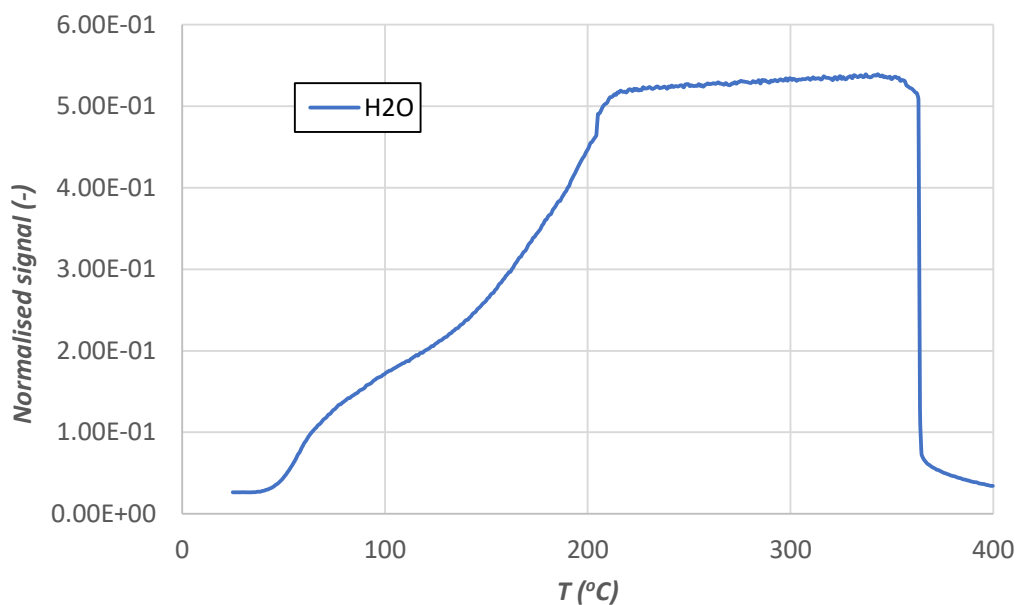


Figure 21: Temperature programmed desorption of H₂O from the 3% CuMOR at a ramp rate of 10°C/min to 400°C.

As observed in **Figure 21**, the desorption of H₂O starts almost immediately with the initiation of the temperature rise, peaking in the range of ~200-360°C. The desorption of H₂O then presents a sharp drop to the base line, indicating that the entirety of the water content of the zeolite has been removed.

The temperature programmed treatment step of the catalyst revealed that a temperature of ~360°C would be sufficient for a complete desorption of H₂O prior to subsequent steps. This is also in excellent agreement with the findings of Hunger et al. who investigated the adsorption of water on

different zeolites and found that a complete desorption of H₂O occurred in the case of mordenite up to the temperature of 327°C. Thus, a dry helium treatment step at a ramp rate of 10°C/min up to 400°C is employed as the first step before each experimental run on the 3% CuMOR catalyst.

5.3.2 CH₄ adsorption insights

The adsorption of CH₄ onto the 3% CuMOR is an important aspect in the development of a DMTM process. It is important to gather information on the temperature range where the CH₄ adsorption is possible as well as what the most favorable conditions would be. To assess this, a couple of experiments were performed, where CH₄ was adsorbed onto the catalyst at 25°C and 200°C respectively.

In each case, the catalyst was first prepared via a dry He preparation step, which involved raising the temperature of the catalyst from 25-400°C at a rate of 10°C/min to desorb any impurities from the catalytic surface and prepare the active sites for the CH₄ adsorption step. Subsequently, 25ml/min of CH₄ were flown over the catalyst for 1hr at 25°C and 200°C in each case respectively. The selection of a 1hr exposure of the catalyst to CH₄ is supported by the study of Zheng et al. who investigated the effect of the duration of the CH₄ adsorption step on the final methanol yield and concluded that for atmospheric pressure the increase of duration of CH₄ adsorption only had a minimal effect on the final methanol yield.

Following the CH₄ adsorption step the system was flushed with He until the CH₄ signal returned to the baseline level. Finally, the catalyst in both cases underwent a temperature programmed desorption step under the flow of 25ml/min He, raising the temperature from 25-600°C at 1°C/min, to desorb any pre-adsorbed species. The temperature programmed desorption steps for the case of CH₄ adsorption at 25°C and 200°C can be seen in **Figure 22** and **Figure 23** respectively. **Figure 22** and **Figure 23** present the CH₄ signal normalised by the He signal over the range of 25-600°C and 25-400°C respectively. The 400-600°C range in **Figure 23** is not presented as the signal presents no change. In both cases, a desorption of CH₄ is observed in a temperature range similar to the temperature of previous CH₄ adsorption. It is interesting to note that in the case of 25°C adsorption, a desorption of methane occurs at a temperature range of 25-100°C, while in the case of 200°C adsorption, methane is desorbed from the catalyst at a range of 200-250°C. This indicates that the adsorption of methane is possible even at temperatures as low as 25°C. It should also be noted that a very slight increase of the methane signal is observable for the adsorption at 25°C at

a temperature slightly above 200°C. The desorption of CH₄ at different temperature ranges in the case of adsorption at different temperatures can also indicate the existence of different active sites, but most importantly a different type of adsorption. At lower adsorption temperatures, the physisorption of CH₄ is more likely, which is also indicated by a small activation energy for desorption leading to the CH₄ desorption at low temperature as observed in **Figure 22**, in the case of 25°C adsorption, since it is loosely bound to the active sites. Higher temperature adsorption is needed for CH₄ to chemically bind to the active sites to form methoxy species, which, respectively, require higher temperatures to associatively desorb as seen in **Figure 23**.

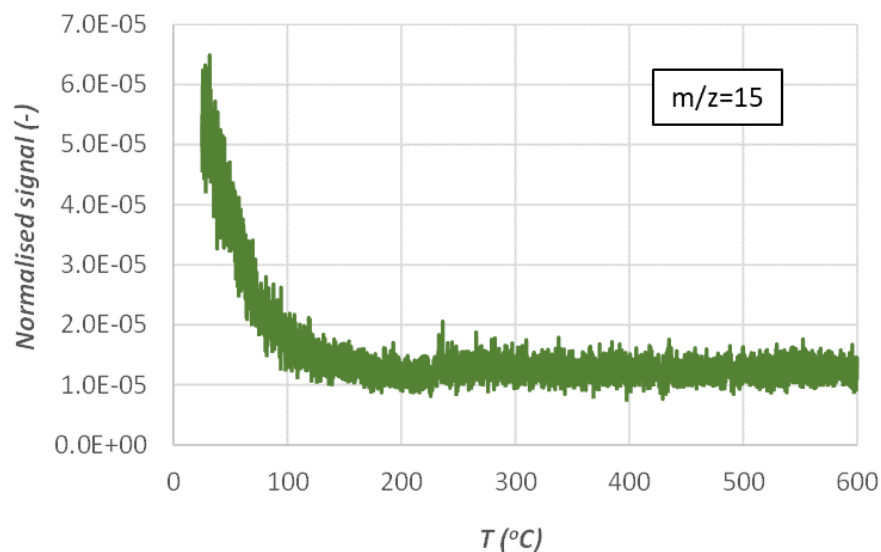


Figure 22: Temperature programmed desorption (1°C/min) of CH₄, following CH₄ adsorption at 25°C.

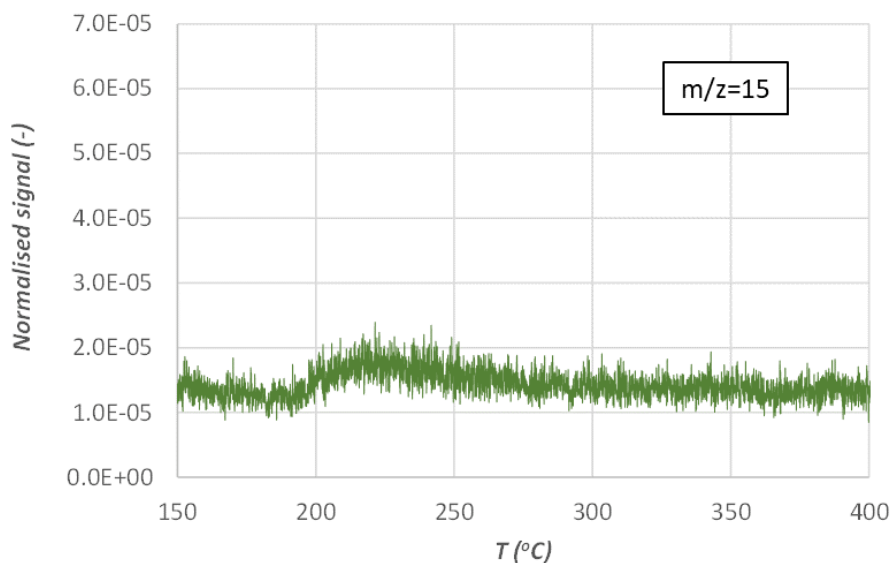


Figure 23: Temperature programmed desorption (1°C/min) of CH₄, following CH₄ adsorption at 200°C.

The hypothesis of existence of different active sites is supported by the literature, which suggests the existence of a plethora of different copper active sites on zeolites responsible for the DMTM (Li et al., 2021). The CH₃OH desorption step in both cases holds further information when all tracked signals are taken into consideration. The normalised signals of all species during TPD are presented in **Figure 24** and **Figure 25** for the cases of CH₄ adsorption at 25°C and 200°C respectively.

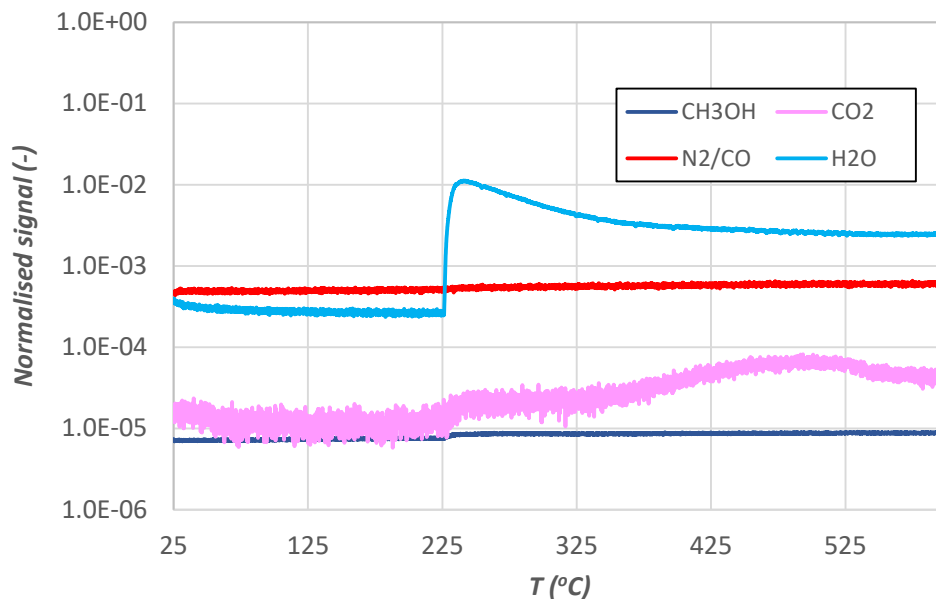


Figure 24: Signals of all species desorbed during TPD following CH₄ adsorption at 25°C.

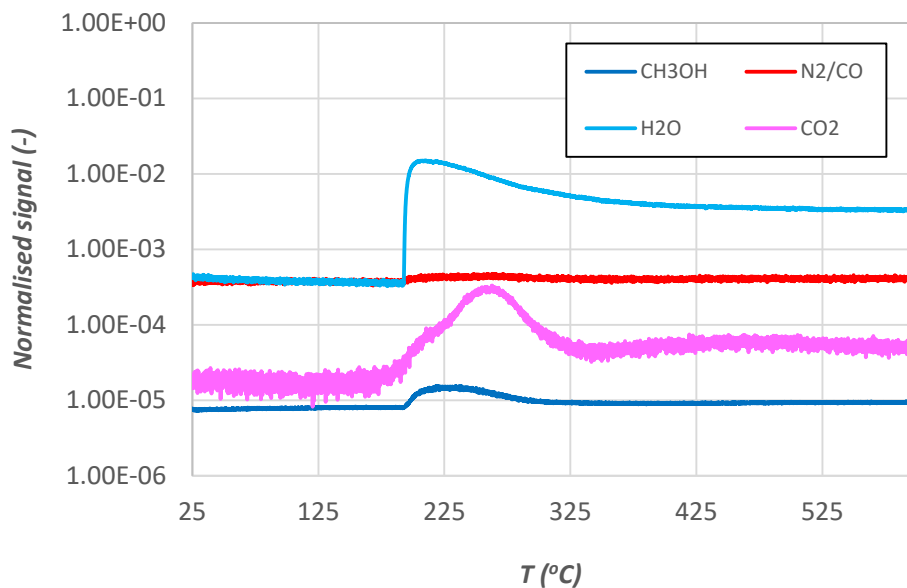


Figure 25: Signals of all species desorbed during TPD following CH₄ adsorption at 200°C.

In both cases, no formation and desorption of CO is observed throughout the whole desorption step. As expected, the water signal presents a rise after the zeolite is saturated with moisture adsorbed from the moisture traces present in the carrier gas. In both cases, a desorption of CO₂ is observed after ~200°C, which continues throughout the course of the experiment to 600°C. This confirms the reports in literature claiming that higher temperatures favor the overoxidation of methoxy species on the catalyst towards the formation of CO₂ (Xi & Heyden, 2019). However, in the case of CH₄ adsorption at 200°C, the CO₂ signal presents a more regular, sharp rise in the range of 200-300°C, possibly indicating that the reaction towards methanol is favored at this temperature range, as well as that the adsorption of CH₄ at the temperature of 200°C could be beneficial for CH₃OH formation.

This speculation is further reinforced by the fact that in the case of CH₄ adsorption at 25°C no rise in the CH₃OH signal is observed, while in the case of CH₄ adsorption at 200°C, there is a small rise in the CH₃OH signal in the temperature range of 200-250°C. Interestingly, the rise of the methanol signal coincides with the rise in the H₂O signal, which as discussed earlier is thought to play a role in the formation and desorption of methanol over the CuMOR. As a result, a temperature of 200°C was chosen as the most favorable CH₄ adsorption temperature.

5.3.3 The role of H₂O

Following the identification of the CH₄ adsorption temperature, the role of water was to be further investigated. A similar experiment was carried out, in which the first two steps of catalyst preparation (ramping up of temperature under dry helium to desorb moisture and impurities) and CH₄ adsorption at 200°C were carried out as previously described. The final step in this case was a steady temperature desorption under a dry helium flow of 25ml/min at 200°C for 3hr. The normalised signals of desorbed species are presented in **Figure 26**.

In the case of a steady temperature desorption under dry conditions, the water signal as expected rose after the catalyst was saturated with H₂O. No CO was formed and desorbed, while there were only negligible trace amounts of CH₃OH observed, which once gain started being desorbed once the concentration of H₂O in the system rose. The results of this experiment strongly indicate that the selective formation of CH₃OH is not possible over the CuMOR under mild conditions in the absence of H₂O. This is in agreement with the literature indicating that significant rises in CH₃OH

yields were observed when water was introduced to catalytic DMTM systems to extract methanol (Ravi, Ranocchiari & van Bokhoven, 2017).

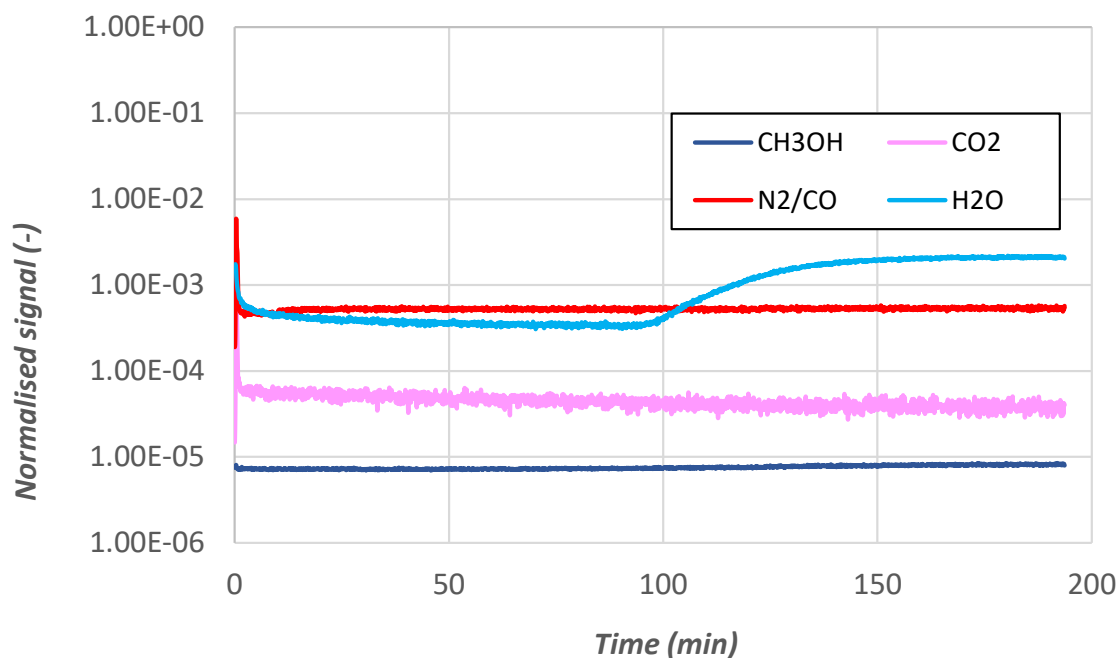


Figure 26: Desorption of species from 3% CuMOR under a flow of 25ml/min dry He at 200°C following CH₄ adsorption.

Following the conclusion that dry conditions do not allow for the formation of CH₃OH over the CuMOR, as well as the indication of the role of water in the DMTM, a qualitative experiment was carried out to assess the role of water. In order to confirm the hypothesis that the presence of water holds critical importance in the formation and desorption of CH₃OH, an experiment involving water injections into the system was designed.

In this case, the catalyst was prepared via a dry He desorption step and subsequently a CH₄ adsorption step at 200°C for 1hr. After CH₄ adsorption, the system was flushed with dry He until the CH₄ signal returned to the baseline level. Subsequently, three deionised H₂O injections of 10µl were performed at the entrance of the reactor into a 25ml/min dry helium flow. The line into which the water injections were performed was held at a temperature greater than 120°C, so it is assumed that the small quantity injected was instantly evaporated. The results of water injections at the entrance of the reactor are presented in **Figure 27**.

Figure 27 clearly highlights the close relationship between CH_3OH formation and H_2O presence in the DMTM over a CuMOR catalyst. The patterns of the CH_3OH and H_2O signals follow an identical trend, with CH_3OH production and desorption occurring simultaneously with the water concentration rise caused by the injections. Additionally, the production of CH_3OH ceases once the concentration level of water returns to the baseline before and between water injections. This experiment proves the crucial role that H_2O plays in the formation of CH_3OH and the necessity of its presence throughout the reaction. It should be noted that the pre-adsorbed CH_4 on the catalyst exists in abundance on the catalytic active sites in comparison to the amount of water injected during the experiment, and is thus not depleted between injections.

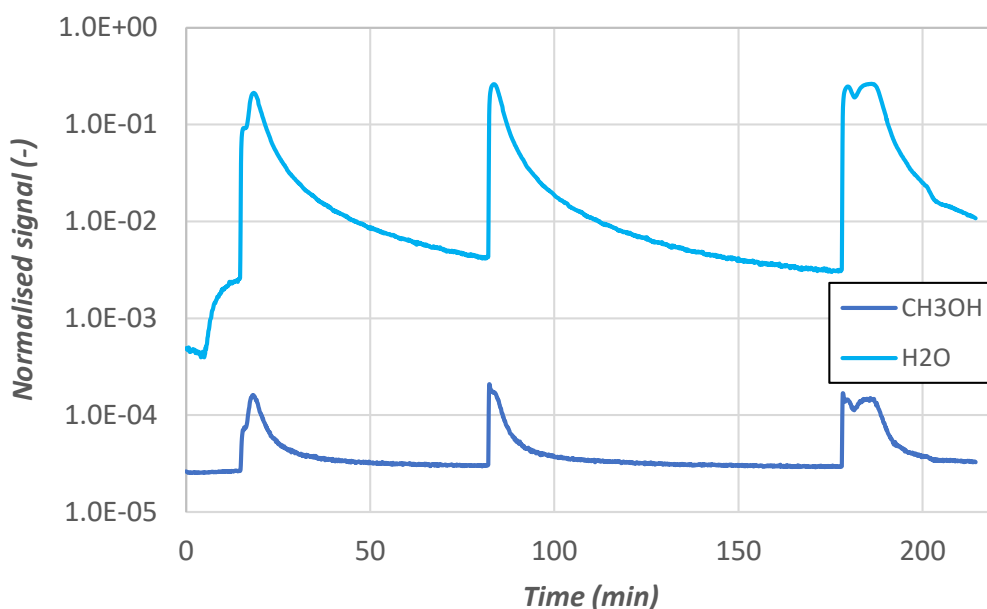


Figure 27: 10 μl deionised H_2O injections at the reactor inlet (at 200°C) following CH_4 adsorption on 3% CuMOR.

Although the presence of water was proven to be necessary for the maximisation of CH_3OH production, further information was required regarding interaction of H_2O and CH_4 if co-fed into the system (Ravi, Ranocchiari & van Bokhoven, 2017). An experiment was carried out in which after a dry He catalyst preparation step, a 12.5ml/min CH_4 stream and a 12.5ml/min wet (passed through a H_2O bubbler to reach moisture saturation at 21°C) helium stream were mixed and co-fed into the reactor at 200°C for 3hr. The normalised signals of desorbed species during this experiment are displayed in **Figure 28**.

Figure 28 shows no production of CO throughout the experiment, while trace amounts of CH₃OH and CO₂ are desorbed from the catalyst once the H₂O signal stabilises after saturating the zeolite. The low productivity of CH₃OH as well as the production of CO₂ along with methanol indicate that the co-feeding of reactants is not beneficial for a selective production of CH₃OH. Potentially, a “pre-loading” of the catalyst with adsorbed CH₄ species and subsequent reaction with H₂O could boost the selectivity towards methanol and the methanol yield. The low productivity of methanol is attributed to CH₄ and H₂O competing for the same active sites, with H₂O potentially hydrolysing them and thus rendering them inactive for subsequent CH₄ adsorption and reaction.

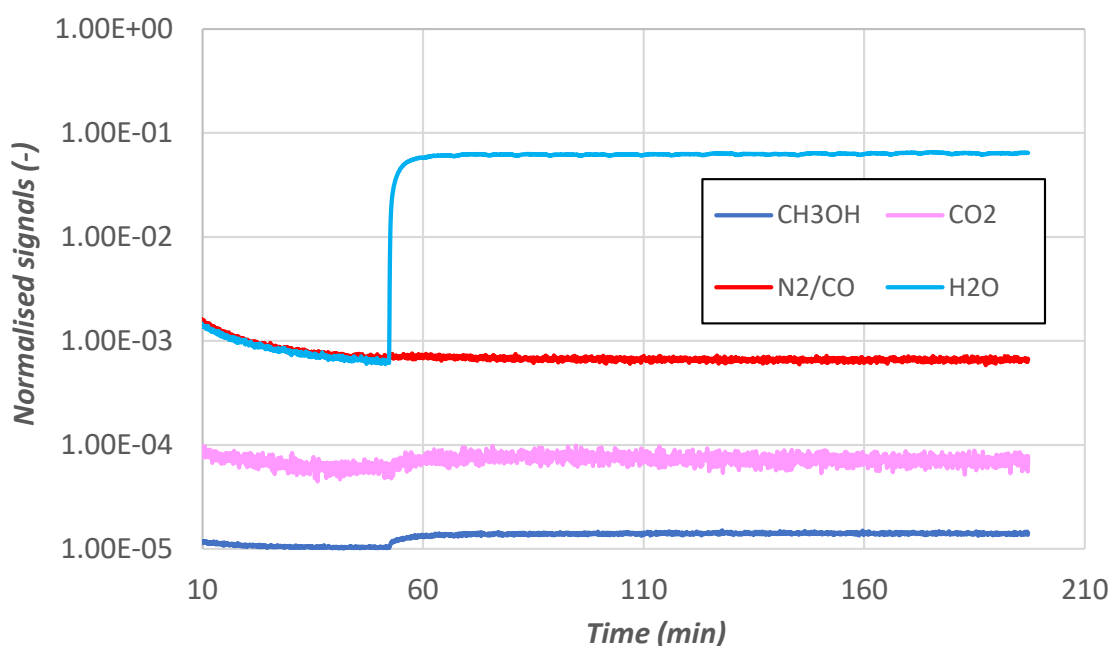


Figure 28: Normalised signals of desorbed species during co-feeding CH₄ and wet He at 200°C over a 3% CuMOR.

To further assess this speculation that H₂O and CH₄ compete for the occupation of active sites and H₂O can more potently adsorb on the sites before CH₄, one more experiment was carried out in which after the dry He preparation step of the catalyst, a wet helium stream was flown over the catalyst for 1hr at 200°C before the CH₄ adsorption step at 200°C for 1hr. Following the CH₄ adsorption step, a wet helium stream was flown again over the catalyst at 200°C for 3hrs. The species desorbed under the wet helium stream after subjecting the catalyst to a wet He and subsequent CH₄ adsorption step is presented in **Figure 29**. As seen in **Figure 29**, no CO is

produced throughout, while only trace amounts of CH_3OH and CO_2 are present in the system throughout the duration of the experiment.

These results confirm the speculation that water can indeed pre-occupy the catalytic active sites, thus preventing the adsorption of CH_4 . In this case, the catalyst was subjected to a wet helium stream before the CH_4 adsorption which led to the hydrolysis of active sites and consequently to the inability of CH_4 to adsorb onto the catalyst in order to further react to CH_3OH . This also serves as an indication that the first step of preparing the catalyst via a dry He desorption steps to desorb any moisture and impurities before CH_4 adsorption is essential.

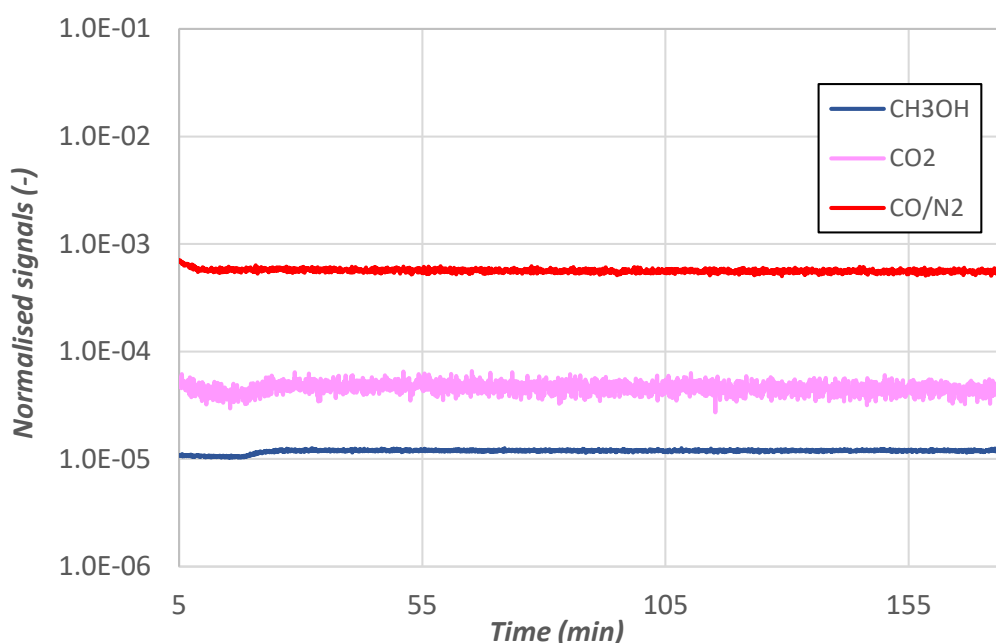


Figure 29: Desorption of species from 3% CuMOR under wet He at 200°C after previous wet He and CH_4 adsorption steps.

5.3.4 Additional reaction insights

Along with experiments targeting the identification of the most favorable adsorption conditions and the identification of the role of water in the reaction, some extra experiments were carried to obtain a more well-rounded understanding about the DMTM over the CuMOR.

Aiming to further confirm the nature of active sites, an experiment was carried out in which a H_2 step was included before the CH_4 pre-adsorption step. More specifically, a dry He preparation step was performed on the catalyst, then a 25ml/min H_2 stream was flown over the catalyst at 200°C

for 1hr, followed by a dry He purge of the system and a CH₄ adsorption step at 200°C for 1hr. Finally, a wet He desorption step was performed on the catalyst at 200°C. The desorbed species are presented in **Figure 30**. Similarly to the pervious experiment where H₂O was introduced to the catalyst before the adsorption of CH₄, the sites were reduced during exposure to H₂, leading to a poor adsorption of CH₄ in the adsorption step that followed. As a result only trace amounts of CH₃OH and CO₂ are observed in **Figure 30**. As mentioned previously, this highlights the importance of desorbing any pre-adsorbed species from the catalyst before the CH₄ adsorption step to maximise methanol yields. Furthermore, these findings are in agreement with the literature speculating the Cu-O-Cu bridge to be the active site in the DMTM reaction over CuMOR, with the Cu-O-Cu bridge being reduced to Cu-OH-Cu, or Cu-OH₂-Cu species during the wet He or H₂, which are then unable to further adsorb CH₄ to form methoxy species (Mahyuddin et al., 2018).

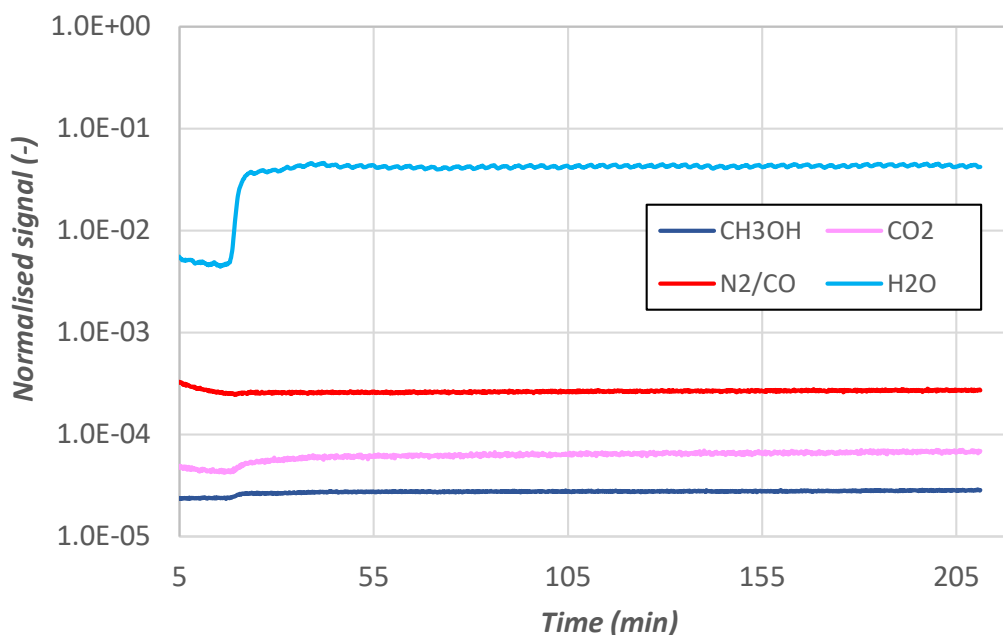


Figure 30: Desorption of species from 3% CuMOR under wet He at 200°C after previous H₂ and CH₄ adsorption steps.

Finally, the reaction temperature was investigated. A dry He preparation step and subsequent CH₄ pre-adsorption at 200°C for 1hr took place on the catalyst, which was then exposed to a 25ml/min wet He stream at the same temperature until the formation of methanol. The reaction was then stopped by switching the wet He to a 25ml/min dry He stream and the temperature of the reactor was reduced to 25°C. The catalyst then underwent a temperature programmed desorption step from 25-600°C at 1°C/min under a flow of 25ml/min dry He. The normalised CH₃OH signal monitored

during the dry He desorption step is presented in **Figure 31**. The normalised signals of other species desorbed during the ramping of temperature are also presented in **Figure 32**.

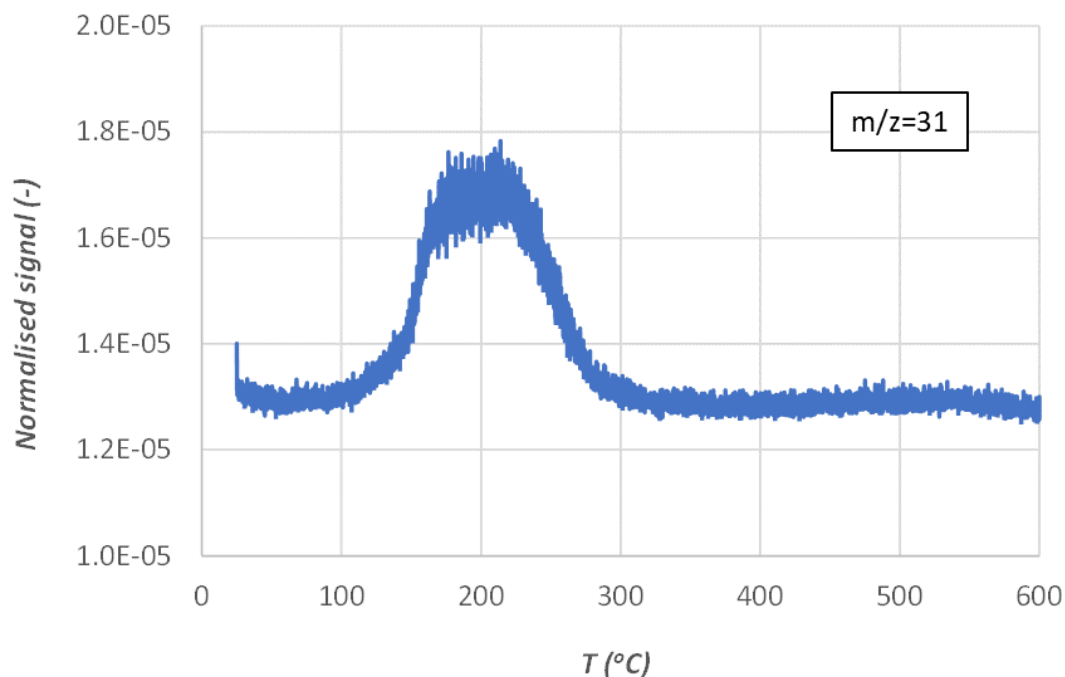


Figure 31: Temperature programmed desorption of CH₃OH (following initiation of the DMTM at 200°C) from 25-600°C at 1°C/min.

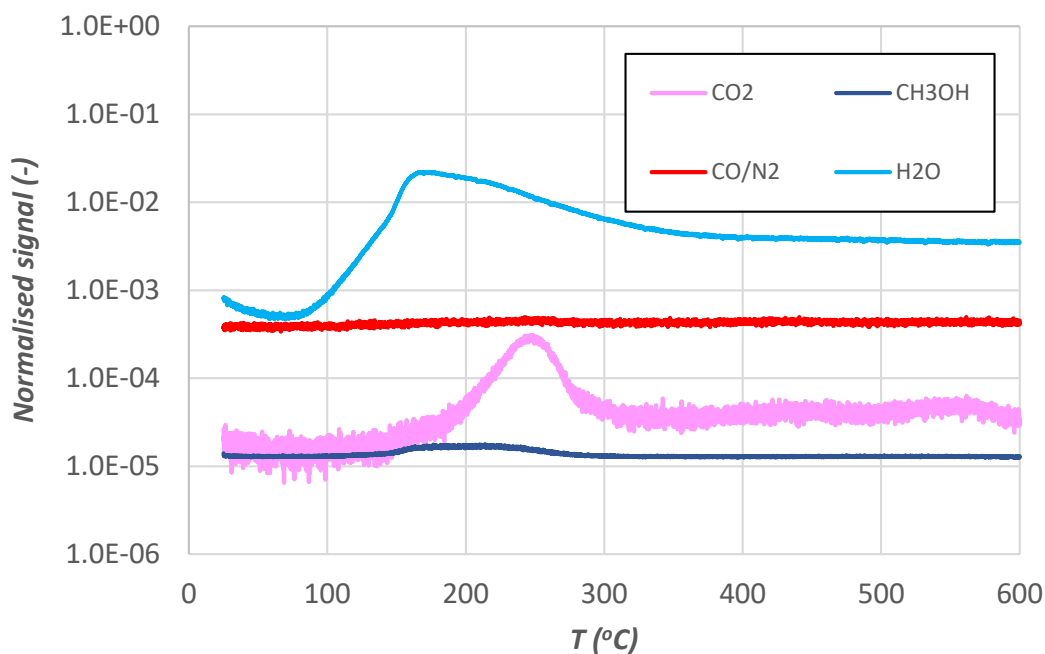


Figure 32: Normalised signals of species desorbed from 25-600°C at 1°C/min (following initiation of the DMTM at 200°C).

The normalised CH₃OH signal in **Figure 31** reveals that methanol is desorbed from the catalyst in the temperature range of 150-250°C, with desorption peaking at 200°C. Additionally, **Figure 32** reveals that CO₂ starts being desorbed at 200°C up to 600°C and peaking at ~300°C. The maximum rate of methanol production coincides with the initiation of CO₂ production, which leads to the conclusion that 200°C is the ideal temperature to selectively produce CH₃OH over a 3% CuMOR, avoiding its overoxidation to CO₂.

5.4 Experimental conclusions

The first indications about the importance of water presence and the potentially most favorable temperature of reaction were observed already at the stage of Cu content parameter evaluation on the CuMOR. During the experiments carried out, any rise in the methanol signal coincided with a rise in the concentration of water and oxygenated products were being desorbed from the catalyst at a temperature as low as 200°C.

The investigation of the most favorable CH₄ adsorption temperature showed that CH₄ species could be adsorbed onto the catalytic surface even at room temperature conditions. However, the adsorption of CH₄ at a temperature of 200°C resulted in the desorption of pre-adsorbed species in a narrower temperature range, accompanied with a production and desorption of methanol. The desorption of methanol peaked at a temperature of ~200°C, with CO₂ being desorbed in the range of 200-300°C, findings which were in agreement with these from the Cu content parameter evaluation. Indeed, there are well-known reactions which can lead to the overoxidation of methanol at higher temperatures. In the range of 200-300°C the steam reforming of gaseous methanol towards CO₂ and H₂ can take place, which is typically catalysed by Cu-base catalysts (Iulianelli et al., 2014). Cu-based materials are also the catalysts of choice in the case of methanol autothermal reforming. The autothermal reforming takes place in the temperature range of 250-330°C and leads to the production of CO₂ and H₂ with a slightly different ratio than steam reforming (Geissler et al., 2001). Finally, the partial oxidation of methanol to CO₂ in the presence of oxygen can take place at temperatures above 325°C, a reaction which is typically catalysed by transition metals supported on ceria and zirconia (Zaman, Al-Zahrani & Bake, 2021).

The role of water in the DMTM over a CuMOR catalyst was proven through a series of experiments. A steady temperature desorption of pre-adsorbed CH₄ species under dry conditions resulted in no production of methanol, thus excluding the possibility of CH₃OH production over

CuMOR at mild conditions without the presence of H₂O. Moreover, the sharp rise in water concentration caused by water injections at the entrance of the reactor caused rises in the signal of methanol, on a CuMOR catalyst pre-loaded with CH₄ species. The pattern of the CH₃OH followed any changes in the H₂O identically, thus providing evidence that the production of CH₃OH over the CuMOR is very closely related to the presence of water in the system during the reaction. These findings about the role of water are in good agreement with several reports in the literature mentioning the potentially beneficial role of water in the DMTM over heterogeneous catalysts. (Liu et al., 1984) (Okolie et al., 2017) (Liu et al., 2020)

Having identified the necessity of water presence for the reaction, more light needed to be shed onto its role and how the CH₃OH yield could be maximised. The co-feeding of the two reactants (CH₄ and H₂O through a wet He stream) was investigated, as from a process perspective a continuous production of methanol through co-feeding the reactants onto the catalyst would be ideal. However, it was found that co-feeding the reactants led to only minimal production of CH₃OH while also CO₂ was produced along with the desired product, methanol. The minimal production of methanol during co-feeding leads to the conclusion that H₂O acts as a competitor to CH₄ for the adsorption on active sites and as a result occupies the sites if it accesses them before the adsorption of CH₄ takes place, by hydrolysing the Cu-O-Cu bridge.

This speculation was further confirmed by two additional experiments where a wet helium step and a H₂ step was included before the adsorption of CH₄ onto the catalyst in each case respectively. In both cases only trace amounts of CH₃OH were observed during the steady temperature desorption under wet He at 200°C, confirming that the active sites are rendered inactive for the adsorption of methoxy species once reduced by hydrogen. Furthermore, the results of these experiments highlighted the necessity for a catalyst preparation step before the adsorption CH₄, in order to desorb any potential impurities or moisture from the catalyst and to re-oxidise the active sites to facilitate CH₄ adsorption.

Finally, in an experiment which served the identification of the ideal reaction conditions, the CuMOR that had pre-adsorbed CH₄ species was exposed to wet He at 200°C until the production of methanol. The reaction was the stopped and a temperature programmed desorption was performed from 25-600°C. This TPD revealed the desorption of methanol from the catalyst in the range of 150-250°C, with a highest rate of desorption at 200°C. Interestingly, just above 200°C

was the temperature at which the production of CO_2 was initiated. These findings pinpoint the ideal reaction temperature at 200°C where CH_3OH is produced selectively without the overoxidation to CO or CO_2 .

5.5 Refinement of experimental process

The experiments carried out provide important insights into the DMTM over a 3% CuMOR. The most important points are summarised below:

- A pre-treatment of the catalyst up to 400°C is necessary to desorb water and impurities from the catalyst.
- The adsorption of CH_4 happens most efficiently for the production of methanol at 200°C .
- No CH_3OH can be produced in the absence of H_2O .
- The presence of H_2O plays an important role in the formation and desorption of CH_3OH .
- H_2O hydrates pre-adsorbed methoxy species.
- Since H_2O is potently adsorbed onto the active sites, it can also cause the displacement of methanol species that form.
- CH_3OH is produced in the range of $150\text{--}250^\circ\text{C}$.
- CH_3OH production peaks at 200°C .
- CO_2 production starts at 200°C and continues at any temperature above.
- H_2O and CH_4 compete for the same active sites.
- Reduced/hydrated active sites are unable to adsorb CH_4 .
- Co-feeding of reactants should be avoided as it leads to low CH_3OH production, while also to the production of CO_2 .

The aforementioned points need to be taken into consideration when designing a DMTM process over the CuMOR, in order to achieve a selective production of CH_3OH at maximum yield. More specifically, the ideal process would need to first include a catalyst preparation step, in which the temperature of the catalyst is raised to a relatively high temperature (400°C), considerably higher than the temperature at which the reaction takes place. This step would serve to bring the active sites to an oxidised state and to rid the catalyst of impurities and moisture.

The presence of water in the system is necessary for the production of methanol. However, the adsorption of CH_4 needs to happen separately to the exposure of the catalyst to H_2O and more

specifically, it should precede any exposure of the catalyst to water. As a result, the preparation of the catalyst under dry conditions up to a high temperature and the pre-adsorption of CH₄ prior to reaction with H₂O would have to happen as two separate, subsequent steps. The pre-adsorption of CH₄ is ideally carried out at 200°C.

Upon saturation of the catalyst with adsorbed methoxy species, the possibility of any interaction of remaining CH₄ in the gas phase with either the catalyst or the gas-phase H₂O introduced to the reactor after the CH₄ adsorption step needs to be eliminated. To achieve this, a flushing of the system with dry He would be necessary for sufficient time until no gaseous CH₄ remains in the reactor.

Finally, a step in which gaseous water is introduced in sufficient quantities into the reactor needs to be included. This could happen via a He stream that passes through a H₂O bubbler to reach its moisture saturation level and carry H₂O along into the reactor. The chosen reaction temperature based on experimental findings is 200°C. The water vapor can then interact with the methoxy species to form methanol and desorb it into the gas phase, leaving the active sites hydrated and inactive for further reaction. However, the suggested step-wise process could be restarted from the first step in a cyclic operation, which would regenerate the sites and prepare the catalyst for a fresh round of methane adsorption and methanol production. This would essentially lead to a chemical looping process, which can be run over numerous cycles.

The suggested stepwise process of DMTM over a 3% CuMOR designed within the framework of the present study is presented schematically in **Figure 33**.

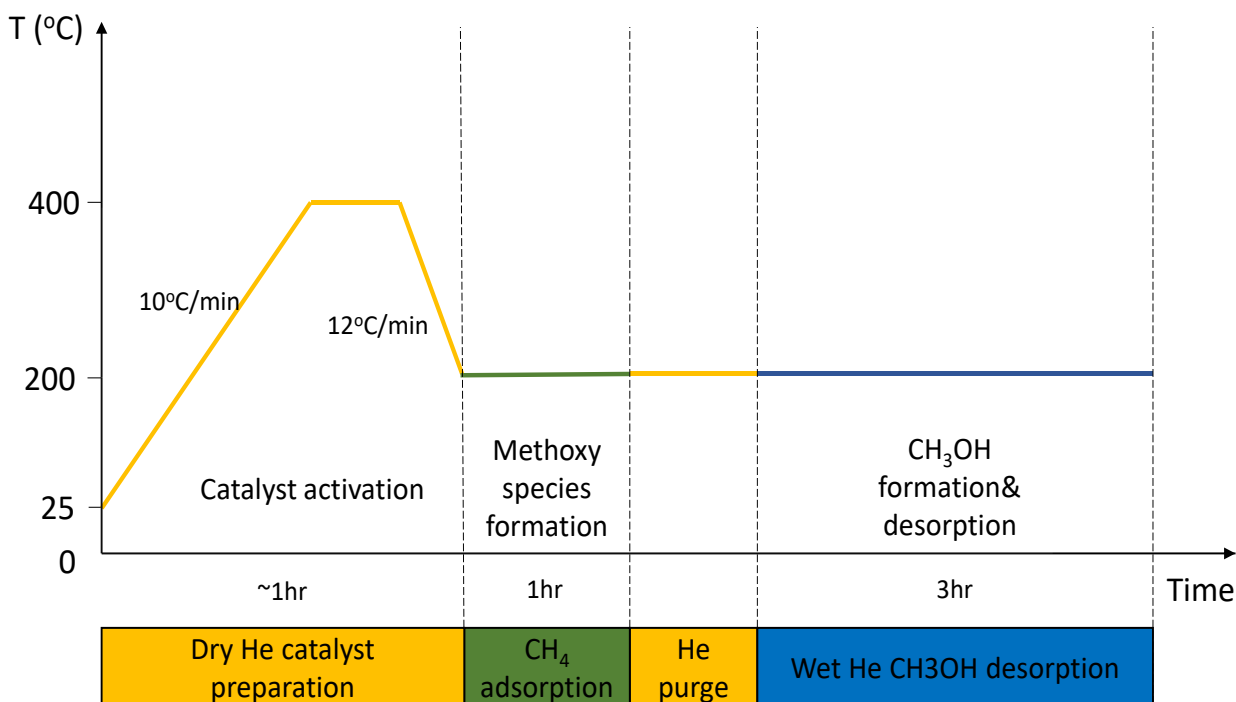


Figure 33: The designed laboratorial reaction process for the DMTM over a 3% CuMOR.

Figure 33 displays the final refined DMTM method used in the present study. As previously discussed, the suggested method consists of three main steps:

- **A catalyst preparation step** – A temperature programmed desorption under a 25ml/min flow of dry He from 25-400°C at 10°C/min. At 400°C the temperature is held for 12min and then taken down to 200°C at a rate of 12°C/min.
- **A methane pre-adsorption step** – An isothermal adsorption (200°C) of CH₄ on the catalytic active sites, which happens under a flow of 25ml/min of CH₄ for 1hr. A purge of the system with a 25ml/min flow of dry Helium follows this step until no gaseous CH₄ remains in the system.
- **A reaction step** – An isothermal reaction of gaseous water with the pre-adsorbed methoxy species located on the active sites. A dry He stream at 25ml/min is passed through a H₂O bubbler at 21°C to saturate in moisture (2.34% v/v) and is then introduced as a wet helium stream to the reactor. The gaseous water molecules carried by the helium stream react with the methoxy species on the active sites to form methanol, which is then displaced by H₂O and desorbed from the catalyst into the gas phase.

After conceptual development, the suggested step-wise method was implemented using a 3% CuMOR catalyst. The desorption of species of interest during the reaction step of the step-wise DMTM process is presented in **Figure 34**.

Figure 34 reveals that expectedly, under a wet He stream the moisture saturation of the catalyst is quickly achieved and the H₂O signal reaches a steady concentration level after a few minutes. As hypothesised, the methanol signal exhibits a considerable rise in agreement with the rise in the H₂O concentration, which appears to have only a minor decrease after 3hr on stream. The decrease in the CH₃OH signal over time is expected as the catalyst acts as a “reservoir” of CH₄ species that are available to react with H₂O towards the formation of CH₃OH.

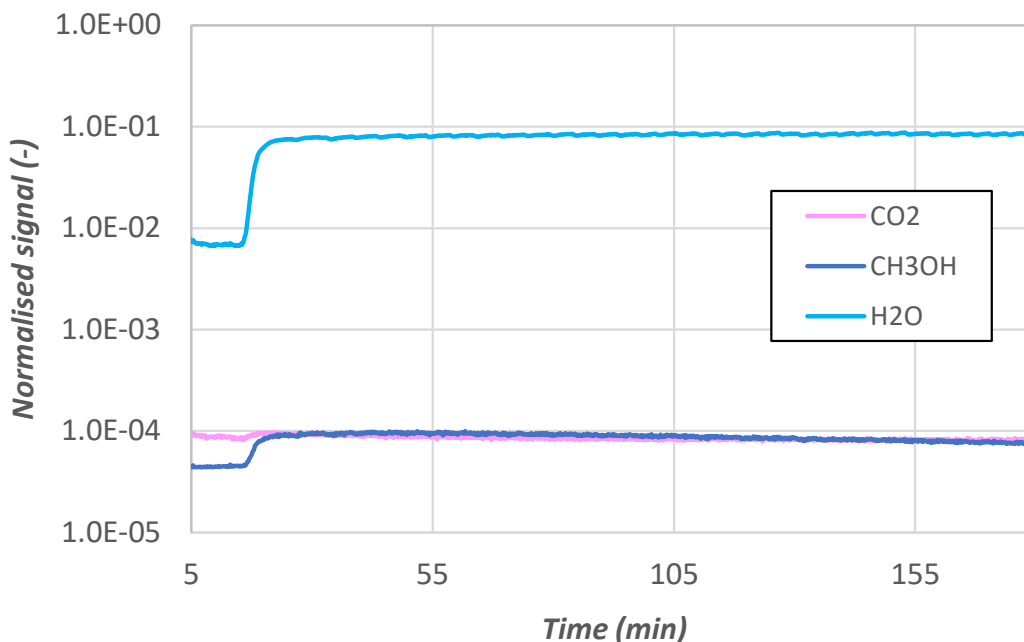


Figure 34: Desorption of species during the reaction step of the suggested step-wise DMTM process over a 3% CuMOR catalyst at 200°C.

The selection of a 200°C reaction temperature was made with an aim to maximise the CH₃OH production while avoiding any overoxidation of the desired product to CO₂. Significantly, no CO₂ production is observed in **Figure 34**. This is perfectly in accordance with the findings of the method refinement experiments, which showed no CO₂ production in temperatures equal or lower to 200°C. Thus, the direct methane transformation can be carried out selectively to CH₃OH using the suggested step-wise process over a 3% CuMOR catalyst. It should be noted that the spread-out

methanol signal in **Figure 34** is observed due to the isothermal operation of the reactor which leads to a continuous production of CH₃OH at a low rate, until all pre-adsorbed CH₄ is depleted.

An additional important aspect of the catalytic process suggested in the present work is the effect of subsequent reaction cycles of the step-wise process on the methanol productivity. To assess this, two subsequent cycles of the reaction were carried out and the results for the methanol desorption step were compared qualitatively as well as quantitatively, based on the final methanol produced throughout the duration of the experiment. After a full reaction cycle involving all of the three steps described previously, a new reaction cycle was initiated by purging the system with dry helium and starting over from the first step of the sequence. The results of the methanol production and desorption step of the two cycles over a 3% CuMOR catalyst are presented in **Figure 35 a)** and **b)**.

As seen in **Figure 35 a)** and **b)**, running a second cycle over the same catalyst appears to have no effect on the methanol production step, with both reaction cycles displaying an almost identical behavior during the methanol desorption step. This was further confirmed by the quantification of methanol desorbed during the duration of each experimental cycle, with the methanol desorbed during the first cycle being 17.6 μmol, while 18.5 μmol of CH₃OH desorbed during the second reaction cycle. The negligible difference between the two reaction cycles suggests that the catalyst can be used in the suggested DMTM process over several cycles without any significant performance loss. This is also in good agreement with literature suggesting that several cycles of the reaction exhibit no significant alteration in the performance of the catalyst towards CH₃OH productivity, even after 19 cycles of reaction, while in fact subsequent cycles after the first might even display a small increase in methanol productivity, as also observed in the present study (Zheng et al., 2020)(Álvarez, Marín & Ordóñez, 2020)(Sushkevich et al., 2017).

Unfortunately, at the time of these findings and the development of the method, a very similar step-wise method was suggested by another research group. In fact, Tomkins et al. in 2017 reported on a stepwise process which included an activation step, a methane adsorption step and a reaction step using water vapor. However, the reported method of this group performed the activation step of the catalyst under a flow of pure oxygen as opposed to the He activation step in the present study. Additionally, the activation step was in that case performed up to a temperature of 450°C

with a subsequent lowering to 200°C or alternatively with only a rise of temperature to 200°C with no further alterations.

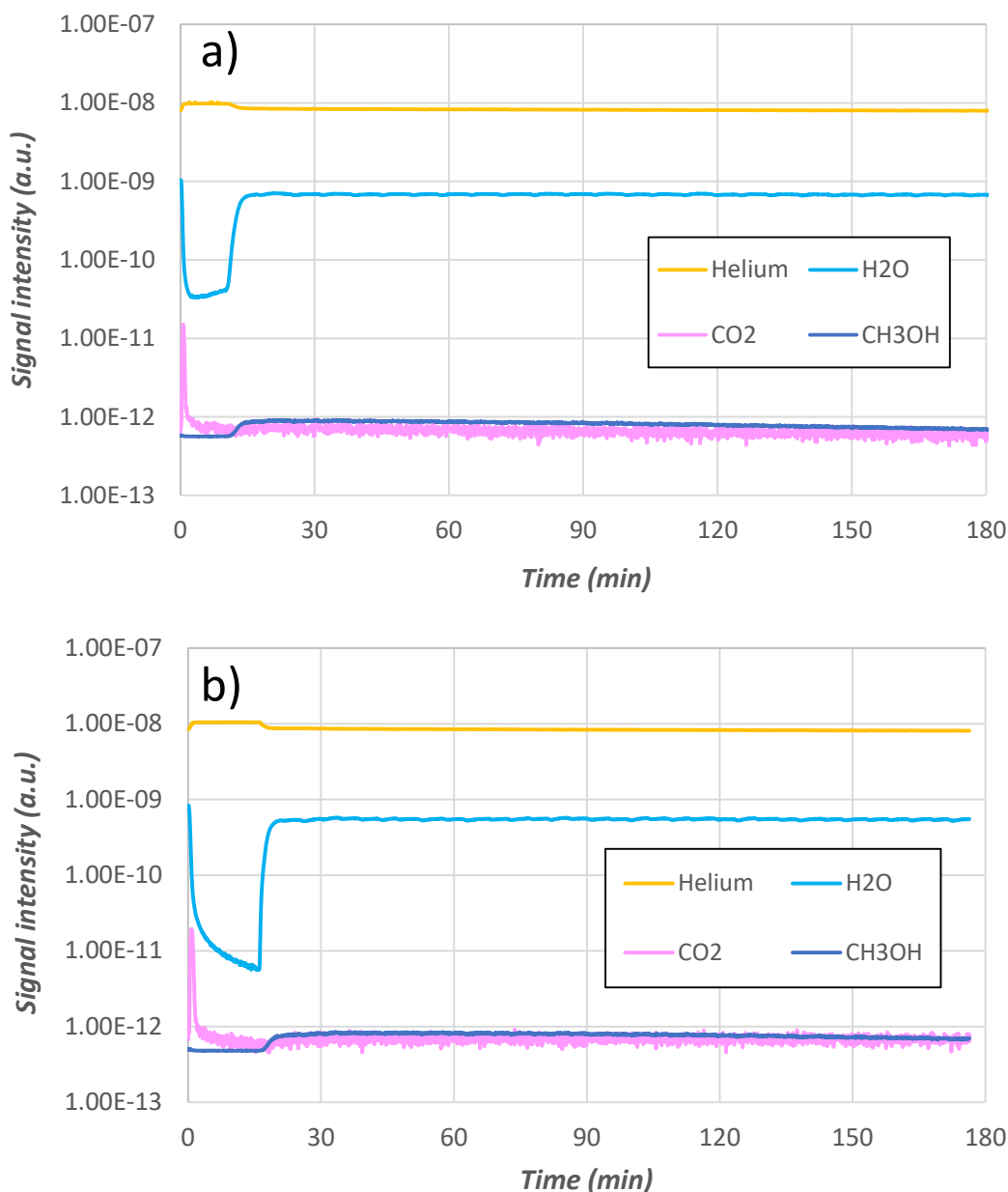


Figure 35: Desorption of species during the methanol production step of the a) first reaction cycle of the suggested step-wise process over a fresh 3% CuMOR catalyst at 200°C and b) second reaction cycle on the same catalyst.

Similarly to the present study, the methane adsorption step as well as the isothermal reaction were both carried out at 200°C. However, the group also investigated the effect of pressure of methane

during the adsorption step to the final CH₃OH yield. The group investigated pressures as high as 36bar. In a later study, researchers of the same group (Sushkevich et al., 2017a) reported again on the stepwise DMTM over a CuMOR, having modified the method to practically a method which perfectly matches the one suggested in the present study. Namely, the group had changed their activation step to reach a temperature of now 400°C and was performed under a flow of helium, while they used a wet He stream for the reaction step. The main difference of the two methods is the methane adsorption step, which in the present study is carried out under a flow of pure CH₄ as opposed to the diluted CH₄ stream used by Sushkevich et al.. Additionally, the CH₄ adsorption step was performed under atmospheric pressure in the present study as opposed to the 7bar pressure used by the other group.

Nevertheless, the fact that a very similar reaction method was reported by other researchers marginally before the findings of the present study could be published can be considered unfortunate. However, the fact that an unrelated research group came to practically the same conclusions is very encouraging for the credibility of the findings and boosts confidence that the developed method is the way to go regarding the DMTM over a CuMOR catalyst.

5.6 Discussion

A custom-made experimental setup capable of carrying out temperature programmed experiments was used in the present study. Upon carrying out DMTM experiments on a CuMOR catalyst of different Cu contents, it was observed that the highest CH₃OH yields were obtained from a 3% CuMOR (% w.t.), which was used in further experiments. Temperature-programmed adsorption and desorption experiments at different temperatures revealed that although the 3% CuMOR could adsorb CH₄ even at ambient conditions, the adsorption happened most efficiently for the production of CH₃OH on the catalyst at 200°C.

Indications of the important role of H₂O in the production of methanol over the CuMOR were observed throughout several experiments. A series of more targeted experiments including H₂O injections at the reaction entrance of a fixed bed reactor loaded with a 3% CuMOR that had pre-adsorbed CH₄ species showed that the CH₃OH desorption trend always followed closely the trend of H₂O concentration increase, clearly indicating that there is a direct correlation between the presence of water and the production of methanol. Additionally, it was observed that no methanol was being produced using the same reaction sequence in the absence of water. The role of H₂O

appears two-fold in the DMTM over a CuMOR, as it hydrates the pre-absorbed methoxy species, forming CH_3OH , and as zeolites are strong desiccants, H_2O tends to promptly adsorb onto the zeolite, displacing the formed CH_3OH in the process.

Temperature programmed experiments revealed that there is only a narrow window for CH_3OH desorption, in the temperature range of 150-250°C, while CO_2 starts being produced and desorbed at 200°C and continues being desorbed at any temperature above 200°C possibly via the overoxidation of CH_3OH by steam reforming and autothermal reforming and potentially via a different reaction mechanism which involves the overoxidation of adsorbed methoxy species on the active sites. With CH_3OH desorption peaking at 200°C, this is thought to be the most favorable temperature to carry out the reaction isothermally for maximum CH_3OH production, while also avoiding the production of CO_2 .

Finally, exposure of the active sites to H_2 and H_2O prior to methane adsorption revealed that the reduced or hydrated active sites were unable to yield any CH_3OH when tested in reaction, leading to the conclusion that the active sites were pre-occupied before their exposure to CH_4 , resulting in no CH_4 adsorption. The apparent competition between H_2O and CH_4 for the same active sites led to the investigation of the case where the reactants (CH_4 and H_2O) were co-fed onto the catalyst at a temperature of 200°C. The co-feeding of reactants yielded only a negligible amount of CH_3OH , while also a small amount of CO_2 was observed. It is, thus, concluded, that the co-feeding of reactants should be avoided as H_2O and CH_4 seem to compete for the active sites, with H_2O adsorbing on them more potently.

Based on the aforementioned conclusions, a step-wise, three-step experimental process was suggested for the DMTM over a 3% CuMOR. The first step aims to prepare the catalyst, by desorbing any pre-adsorbed species and ridding of impurities. The second step involves the pre-adsorption of CH_4 onto the active sites. Finally, the reaction step involves the exposure of the catalyst to water for an isothermal reaction towards methanol at 200°C. The suggested method considers all the aforementioned conclusions to maximise CH_3OH yield.

6. *Kinetic model development*

The present chapter aims to investigate the kinetics of the DMTM reaction over a 3% CuMOR catalyst. The lab-scale method described in the previous chapter was used, along with experimental findings and data from the literature to derive kinetic equations which describe the evolution of different species during the reaction. Different variations of the kinetic model are evaluated against experimental data and a conclusion is made on the best-fitting model which could potentially be used in a larger scale modelling of the reaction.

6.1 Methodology

6.1.1 Data validation

To further assess the validity of the experimental method and results, the experimental results of the DMTM over a CuMOR catalyst were compared to similar data from the literature. As previously mentioned, a similar experimental method and catalyst were used by Tomkins, Ranocchiari & Van Bokhoven in 2017. While the present study employed atmospheric pressure for the DMTM reaction, the aforementioned group investigated the effect of the CH_4 pressure during the adsorption step on the final yield of CH_3OH from 0.05bar to 36bar. Nevertheless, the CH_3OH yield results for a CH_4 adsorption step at 1bar can be directly compared to the results of the present study.

The methods used in the two studies involved a stepwise process of catalyst preparation, CH_4 adsorption and reaction to CH_3OH under a wet He stream taking place under similar conditions. In both cases the CH_4 pre-adsorption step as well as the reaction to CH_3OH were carried out at 200°C. In the experiment used for comparison with the work of Tomkins, Ranocchiari & Van Bokhoven in 2017, the water bubbler saturating the helium stream in H_2O vapor was kept at 40°C. The elevated temperature employed leads to a higher level of H_2O concentration in the He stream flowing into the reactor compared to the bubbler kept at 21°C in other experiments, which in turn leads to a higher reaction rate and a faster completion of the experiment due to a higher depletion of the CH_4 species on the catalyst. However, since the comparison of the two studies is based on the final yield, this does not impact the final results, since in both cases the reaction was carried out until completion.

Comparing the results of the two experimental works, the methanol yield achieved in the present study reached $42.5\mu\text{mol}\cdot\text{g}^{-1}$ catalyst in a single-pass experiment, while the CH_3OH yield reported by Tomkins, Ranocchiari & Van Bokhoven in 2017 was $45.3\mu\text{mol}\cdot\text{g}^{-1}$ catalyst for a CH_4 pre-adsorption step carried out at atmospheric pressure. The fact that the CH_3OH yield achieved in the present work is in excellent agreement with the yield reported for a similar experiment carried out in literature strengthens the validity of the experimental method and results.

6.1.2 Mass & heat transfer limitations investigation

To guarantee the accuracy of any kinetic analysis carried out on the experimental results of the reaction, it must first be ensured that the reaction is carried out under an intrinsic kinetics regime. More specifically, mass and heat transfer limitations can potentially severely affect the observed reaction rates in a heterogeneously catalysed reaction. It is thus essential to quantify the influence of diffusion limitations and heat transfer phenomena inside the catalytic bed and the catalytic particle itself.

Mass and heat transfer limitation studies were carried out in the present study with the aid of a tool developed by the Eurokin Consortium specifically for the investigation of the intrinsic kinetics regime in catalytic fixed bed reactors (Eurokin, 2012b)(Eurokin, 2012a). More details on the calculations carried out by the online tool are given below. The activation energy of the DMTM reaction over a CuMOR used in the tool was taken from Sushkevich et al. (2017b), while all information regarding catalyst surface area and pore area and volume was derived from a BET analysis of the 3% CuMOR. The density of the catalyst was taken to be $2.1\text{g}/\text{cm}^3$ (Mindat.org, 2020). The catalytic bed was not diluted, and the observed reaction rate was calculated from the experiment carried out over a 3% CuMOR under most favorable conditions. The thermal conductivity value of mordenite was taken from the literature (Shimonosono et al., 2018). Diffusion volumes of different molecules were calculated following the protocol and data detailed in the work of Asman, Jørgensen & Jensen in 2003.

External mass transport limitations

External mass transport limitations were investigated using the Carberry number. More specifically, if the following criterion holds true, the resistance due to external mass transport phenomena is less than 5% in comparison to the reaction limitation (Mears, 1971):

$$Ca = \frac{R_{v,H_2O}^{obs}}{k_G \cdot a_v \cdot C_{H_2O,b}} = \frac{C_{H_2O,b} - C_{H_2O,s}}{C_{H_2O,b}} < \frac{0.05}{n} \quad (6.1)$$

where Ca is the Carberry number (-), R_{v,H_2O}^{obs} is the apparent reaction rate per catalyst volume ($\text{mol}/\text{m}^3_{\text{cat}} \cdot \text{s}$), k_G is the external mass transfer coefficient, a_v is the specific external surface area of a catalyst pellet ($\text{m}^2/\text{m}^3_{\text{pellet}}$) which for a spherical particle is equal to $6/d_p$, $C_{H_2O,b}$ is the concentration of H_2O in the bulk, $C_{H_2O,s}$ is the concentration of H_2O at the catalyst surface (mol/m^3) and n the order of reaction.

Internal diffusion limitations

The effect of internal diffusion phenomena was investigated via the Weisz-Prater criterion and the calculation of the Weisz modulus Φ . Specifically, for first order kinetics (the reaction is pseudo-first order in the present case due to the negligible change in H_2O concentration in the gas phase), the Weisz modulus is calculated as follows (Froment, De Wilde & Bischoff, 2010):

$$\Phi = \left(\frac{n+1}{2} \right) \frac{R_{v,H_2O}^{obs} \cdot \left(\frac{d_p}{6} \right)^2}{D_{H_2O,eff} \cdot C_{H_2O,s}} \quad (6.2)$$

where Φ is the Weisz modulus, d_p is the catalyst pellet diameter and $D_{H_2O,eff}$ is the effective diffusivity of H_2O inside the catalyst pellet (m^2/s). The deviation due to diffusion limitation inside the catalyst pores is smaller than 5% if the Weisz modulus is smaller than 0.08. (Anderson & Pratt, 1985)

External heat transfer limitations

The external heat transfer limitation can be considered negligible if the following criterion is fulfilled. More specifically, the temperature of the film surrounding the catalyst pellet would have a less than 5% difference to the bulk gas temperature if (Mears, 1971):

$$\Delta T_{film} = \frac{R_{v,H_2O}^{obs} \cdot |\Delta_r H| \cdot d_p}{6a_p} < \frac{0.05 \cdot R \cdot T_G^2}{E_a} \quad (6.3)$$

where ΔT_{film} is the temperature difference over the film on catalyst pellets (K), $\Delta_r H$ is the reaction enthalpy (J/mol), α_p is the particle heat transfer coefficient, R is the ideal gas constant (J/mol·K), T_G is the temperature of the gas in the bulk (K) and E_a is the apparent activation energy of the reaction (J/mol).

Radial heat transfer limitations

The following criterion can be used for the investigation of the radial heat transfer limitations in the catalytic bed (Mears, 1971):

$$\Delta T_{\text{rad}} = \frac{R_{v,H_2O}^{obs} \cdot |\Delta_r H| \cdot (1 - \varepsilon_b) \cdot (1 - b) \cdot d_t^2}{32\lambda_{er}} < \frac{0.05 \cdot R \cdot T_w^2}{E_a} \quad (6.4)$$

where ΔT_{rad} is the temperature difference between the average bed temperature and the temperature of the catalyst near the reactor wall (K), b is the fraction of inerts in the catalytic bed ($\text{m}^3_{\text{inert}}/\text{m}^3_{\text{inert}+\text{cat}}$), ε_b is the bed void fraction and λ_{er} is the effective radial thermal conductivity in the bed (W/m·K).

Internal heat transfer limitations

The internal heat transfer limitations were evaluated with the following criterion (Mears, 1971):

$$\Delta T_{\text{int}} = \frac{R_{v,H_2O}^{obs} \cdot |\Delta_r H| \cdot d_p^2}{60\lambda_p} < \frac{0.05 \cdot R \cdot T^2}{E_a} \quad (6.5)$$

where ΔT_{int} is the temperature difference between the edge and the core of a catalyst pellet (K), λ_p is the thermal conductivity of the pellet (W/m·K). The effect of the intraparticle temperature gradient on the methanol production rate is negligible (less than 5%) if the above criterion is held.

The aforementioned criteria were calculated employing the Eurokin tool and compared to the limit values in each case. The results are presented in **Table 5**.

Table 5: Summary of mass and heat transfer limitation criteria results.

	Calculated value	Criterion limit	Phenomenon	Criterion status
Ca	$2.70 \cdot 10^{-8}$	0.05	External mass transport	OK
Φ	$4.30 \cdot 10^{-4}$	0.08	Internal diffusion	OK
ΔT_{film}	$1.66 \cdot 10^{-6}$	0.91	External heat transfer	OK
ΔT_{rad}	$2.70 \cdot 10^{-4}$	0.91	Radial heat transfer	OK
ΔT_{int}	$2.08 \cdot 10^{-8}$	0.91	Intraparticle heat transfer	OK

As seen in **Table 5**, the calculated values in all cases are several orders of magnitude smaller than the criteria limit values. As a result, it is safe to conclude that the reactor operates in the intrinsic kinetics regime for the reaction of methane to methanol over a CuMOR catalyst at 1 bar and 200°C. Both mass and heat transport phenomena pose negligible hinderance to the progression of the reaction and as a result, experimental data can be directly utilised for kinetic analysis.

6.1.3 Data preparation for input in Python code

The kinetic analysis and optimisations carried out in the present study were performed on Python programming language routines which were either pre-existing (developed by Ilia Dorokhov, as acknowledged later in the present thesis) or developed specifically for this work. A specific protocol was followed to prepare the signal data obtained from the mass spectrometer for input into the Python models.

As explained in previous sections, data regarding the concentration of different species in the system is obtained as a signal intensity with arbitrary units from the mass spectrometer. Following the protocol explained in a previous section, the signal intensity of each tracked mass was first normalised against the signal of background helium. Appropriate calibrations for each species provided a “calibration factor”, which related the area underneath a signal curve with the molar quantity of the species. The molar flow of a molecule was calculated by dividing the normalised signal of the molecule with the aforementioned “calibration factor”. The molar flow was then further converted to a concentration of each species by division with the total volumetric flow inside the system. Finally, the calculated concentration was used as input into the Python models.

It should be noted that the relevant part of the CH_3OH desorption experiment for kinetic modelling was after the initiation of CH_3OH production and desorption. As a result, the initial part of the experiments was discarded, so that the desorption of CH_3OH would start at $t=0\text{s}$. Additionally, the lowest value of CH_3OH was subtracted from all experimental data input into the model, so that the concentration data would start at zero. This is thought to have no effect on the concentration data, as the lowest value was orders of magnitude smaller than the CH_3OH concentration values during CH_3OH production and desorption.

6.2 Non-ideality and CSTRs in series model

In the lab-scale process developed, the DMTM reaction was carried out in a tubular stainless steel reactor over a catalytic fixed bed. Typically, in theory tubular reactors are approached with the Plug Flow Reactor (PFR) model, which assumes no mixing in the axial direction as the fluid travels within the reactor. In the PFR model, an infinite number of individual “plugs” of fluid of infinitesimal length are assumed to be advancing in the axial direction, each with a unique composition, as displayed in **Figure 36**. (Schmidt, 2005)

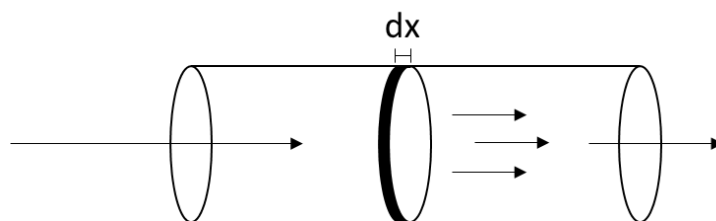


Figure 36: Fluid flow inside a plug flow reactor.

The plug flow reactor model is an ideal case model, based on the assumption of no intermixing of the fluid. However, it would be unrealistic to make this assumption for a lab-scale reactor system. Potential dead volumes, bypassing and micromixing spots can cause deviations from the PFR behavior, which would consequently introduce errors in the development of a kinetic model to describe the system. There are several ways to account for this non-ideality of the system, among which the tanks in series or continuously stirred tank reactors (CSTRs) in series model is chosen for the present study. This section aims to give a brief theoretical background to the CSTRs in series model and how it was employed in this case.

6.2.1 CSTRs in series concept

As opposed to the PFR, the operation of the Continuously Stirred Tank Reactor (CSTR) is based on the assumption of perfect mixing inside the tank, resulting in a steady state operation under outlet concentration.

Applying the basic concept of:

$$\textbf{Input} - \textbf{Output} - \textbf{Generation} = \textbf{Accumulation}$$

for each of the two reactor model cases of a CSTR and a PFR, the following design equations can be obtained respectively (Levenspiel, 1999):

$$V = F_{Ao} \left(\frac{1}{-r_A} \right) X \quad (6.6)$$

$$V = F_{Ao} \int_0^X \frac{1}{-r_A} dX \quad (6.7)$$

where V is the reactor volume, F_{Ao} is the molecular flow of reactant A, X is the conversion of A and $-r_A$ is the rate of disappearance of reactant A due to the reaction.

Plotting the inverse of the rate of disappearance of A versus the conversion of A, known as a Levenspiel plot, can lead to some interesting observations regarding the operation and design of a CSTR and a PFR. A typical Levenspiel plot describing the operation of a CSTR and a PFR is displayed in **Figure 37**.

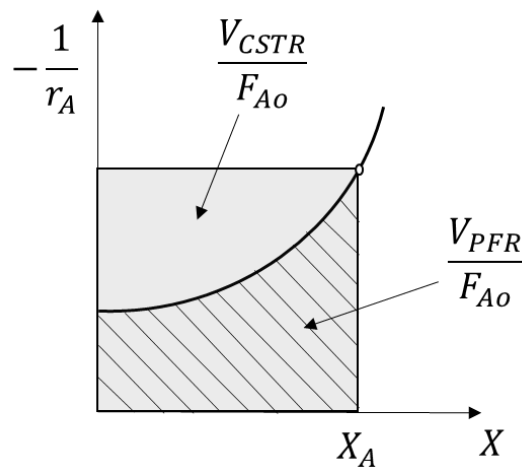


Figure 37: Levenspiel plot for a PFR and a CSTR.

When comparing the operation of the two reactors, it is easily understood from **Figure 37** that for the same conversion of a reactant, a considerably larger volume is needed when using a CSTR. As the graph reveals, the volume needed in a CSTR for a specific conversion is proportional to the rectangle drawn by following the outlet conditions of a CSTR towards the x- and y-axis. In the case of a PFR, the reactor volume needed for the same conversion corresponds to just the area underneath the conversion curve, which is considerably smaller in comparison to a CSTR. The ideal operating case of a PFR could indeed be theoretically approximated by using an infinite number of infinitesimal CSTRs in series of the same total volume as a PFR. A graphical representation of this case follows in **Figure 38**.

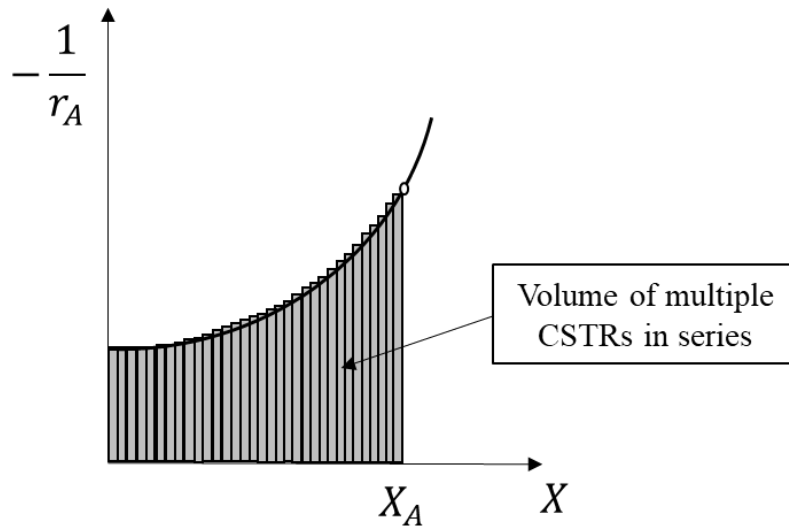


Figure 38: Approximation of a PFR by infinite CSTRs in series.

As **Figure 38** displays, each of the CSTRs operates at outlet conditions which follow the conversion curve. This leads to a small excess volume for each of the reactors in comparison to a PFR of the same performance, which decreases as the volume of each CSTR decreases. In the case of infinitesimal reactors, the excess volume of a CSTR in comparison to a PFR of the same conversion is eliminated. Consequently, a series of infinitesimal CSTRs would theoretically perform identically to a PFR of the same volume.

Levenspiel plots were employed to prove how the ideal reactor behavior of a PFR can be approximated by the infinitesimal CSTRs in series concept. Nevertheless, it was previously discussed that no reactor system is perfect in reality and the non-ideality of each system needs to be taken into consideration. Employing the same concept in reverse, the CSTRs in series model

can be used to approximate and model the non-ideality of a system. It was shown by **Figure 38** that the ideal system behavior is achieved by minimising the excess volume of each CSTR. Respectively, to model a non-ideal system of a known total volume, a CSTRs in series model is employed in which the number of CSTRs in series of total volume equal to the system volume, is manipulated to achieve the same degree of deviation from the ideal behavior as experimentally observed. The benefit of the CSTRs in series model is that it is easily applied to model most systems and can be used with any kinetics. (Levenspiel, 1999)

6.2.2 CSTRs in series model and CO₂ injections

The most commonly used method to develop a tanks-in-series model is through a pulse input. A pulse of an inert tracer of known quantity is injected at the entrance of the system. The concentration of the tracer is then tracked over time at the exit of the system, to obtain the outlet pulse curve in the effluent. A tanks-in-series model is then developed, in which the total volume of the system is equal to the sum of the volumes of the tanks. Feeding the initial tracer injection as an input to the model, the number of tanks in series is manipulated to achieve a good fit between experimental data and the model outlet data from the last reactor of the series. The pulse method is shown schematically in **Figure 39**. (Conesa, 2020)

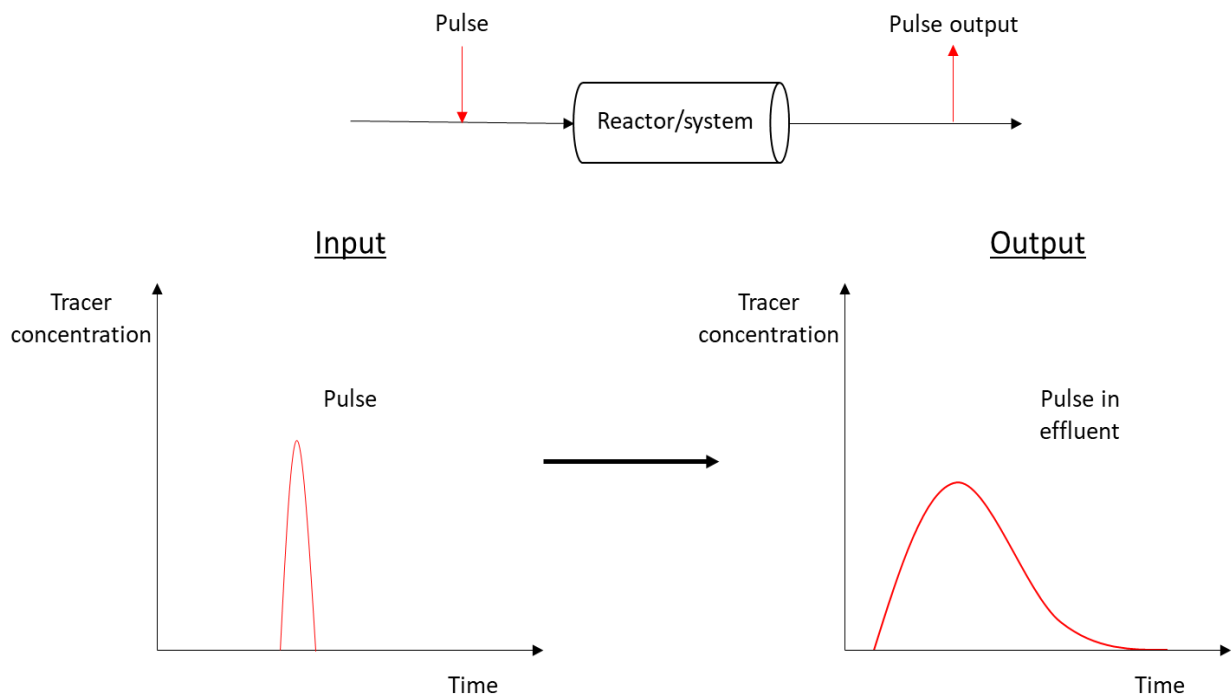


Figure 39: Tanks-in-series pulse calibration method.

In the present study, the system volume was calculated by considering all empty volume from the reactor entrance to the mass spectrometer inlet. The volumes were calculated by measuring the length of each piece of tubing and employing $V=\pi r^2 L$, where V is the volume, r is the internal radius and L is the length of the tube, for the respective internal diameters of each tube. To account for the volume occupied by the solid, the length of the catalytic bed was measured to be $L=65\text{mm}$. The volume of the bed was calculated and multiplied with the bed porosity $\varepsilon=0.4$ to obtain the empty volume inside the catalytic bed. The bed porosity was measured experimentally via introducing water to bed of catalyst of known volume until the liquid started layering on top of the bed. The bed porosity of $\varepsilon=0.4$ is typical of zeolites and in good agreement with literature (Triebe & Tezel, 1995)(Erdős et al., 2021). The volume corresponding to the bed voidage was then added to the empty tubing volume sum to obtain the total volume of the system used in the model.

The total volume of the system used in the tanks in series model was $V_t = 4.28\text{ml}$. The tracer used was CO_2 and 0.1ml injections were performed at an injection point at the entrance of the reactor. The injections took place under reaction conditions, i.e. at 200°C under a flow of 25ml/min of helium, while the reactor was loaded with a bed of 0.4g of mordenite to replicate the catalytic bed under reaction conditions. The CO_2 signal in the effluent was monitored and analysed using the mass spectrometer, while the quantification of CO_2 and the conversion of the MS signal to concentration took place as explained in previous sections.

To model the pulse, a Gaussian function model was used. The Gaussian function was used as input into a Python model which will be discussed in more detail in the next section. The Python Gaussian function routine used three parameters as input, i.e. the position of the center of the peak, the total area underneath the curve and the standard deviation σ . The area used in the Gaussian function model was equal to the total area calculated underneath the curve of experimental data for the pulse injection, the position of the center of the peak value was selected so that the peak exiting the last reactor in series would match that of the experimental data, while the variance was calculated based on the area underneath the curve and the assumption that the injection takes place over the time of one second.

6.2.3 CSTRs in series Python model

To optimise the number of tanks in series needed to describe the non-ideality of the system, a Python code was developed. Pre-coded routines for CSTR reactors were used, in which the required inputs were defined. Ilia Dorokhov is kindly acknowledged for the development of routines for CSTRs, which can also operate in series. The cases of 3, 4, 5 and 6 CSTRs in series were investigated, where the volume of each reactor was equal to the total calculated real volume of the system divided by the number of reactors used in each scenario ($V_n = V_{\text{system}}/n$, where n is the number of reactors). The total flow inside the system was defined to be $q = 25\text{ml/min} = 0.4167\text{ml/s}$. The Gaussian function representing the pulse injection was set as input in the first reactor. The experimental data was imported to the model and the model data of the last reactor in series in each case was plotted against the experimental data.

The pre-coded Python CSTR routines operate by solving the equations corresponding to a CSTR. The CSTRs are interconnected, with the first reactor using the tracer concentration input set by the user (the Gaussian function in this case), while the rest of the reactors use the outlet concentration from the previous reactor in the series as input. Specifically in the case of the pulse injection, the following equations describe the model solved in Python. For the first reactor, Equation (6.8) describes the rate of disappearance of the pulse.

Input – Output + Generation = Rate of disappearance of pulse

$$F_{A0} - F_{A1} + 0 = \frac{dN_A}{dt} \quad (6.8)$$

where F_{A0} and F_{A1} are the molecular inflow and outflow of the reactor respectively and N_A is the number of moles of the tracer. For the case of reactors in series where the volume of each reactor corresponds to the total volume divided by the number of reactors, the previous equation can be modified as:

$$C_{A0} - C_{A1} = \frac{\left(\frac{V_{\text{system}}}{n}\right)}{q} \frac{dC_A}{dt} \quad (6.9)$$

Where q is the volumetric flow inside the reactor, C_{A0} and C_{A1} are the concentrations of the tracer in the inlet and outlet of the reactor and n is the number of reactors in series. A schematic representation of the reactors in series model follows in **Figure 40**.

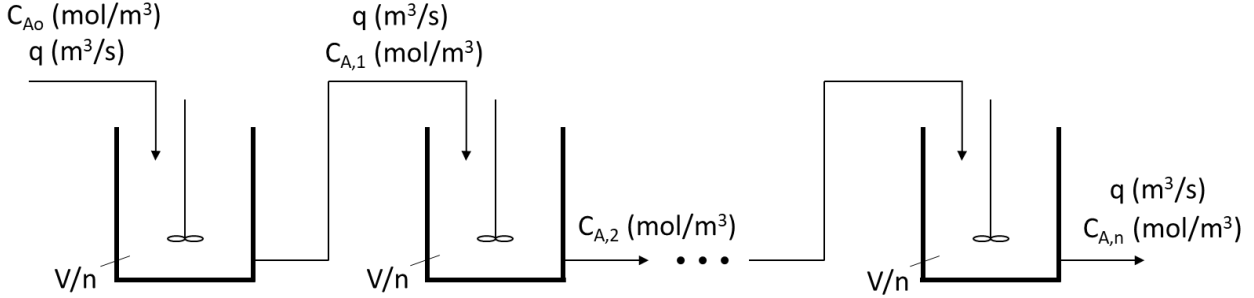


Figure 40: CSTRs in series model.

Generalising Equation (6.9), Equation (6.10) can be used to describe the disappearance of the pulse inside the CSTRs in series system.

$$C_{A(i-1)} - C_{Ai} = \frac{V_{system}}{nq} \frac{dC_A}{dt} \quad (6.10)$$

where i denotes the number of reactor in series and C_A the concentration of species A. The evaluation of the fit for each case was performed in several ways, including a visual evaluation of the fit, the calculation of the root mean square error and plotting and visually evaluating the pulse concentration values in the outlet of the last reactor in series of the model versus the corresponding experimental values. Nevertheless, the area underneath the experimental and model curve were compared in each case investigated, to ensure that the values matched. The root mean square error was calculated with the following Equation:

$$RMSE = \sqrt{\frac{\sum (y_{model} - y_{experimental})^2}{N}} \quad (6.11)$$

where y_{model} and $y_{experimental}$ are the model and experimental concentration values of the tracer respectively, and N is the number of concentration points in the experimental data. The case of 3 CSTRs in series is presented in **Figure 41**. **Figure 41 a)** presents the model concentration at the outlet of the last reactor in series plotted against time, while **Figure 41 b)** presents the model vs

experimental, while also the 45° line is plotted for reference. As seen in **Figure 41 a)**, although the shape of the curve is in relatively good agreement with the experimental data, the model of 3 tanks in series presents a larger deviation from ideality than needed, with the concentration curve of the model data exhibiting a flatter and wider shape than the experimental curve. This deviation is also seen in **Figure 41 b)**, with points drifting away from the 45° line.

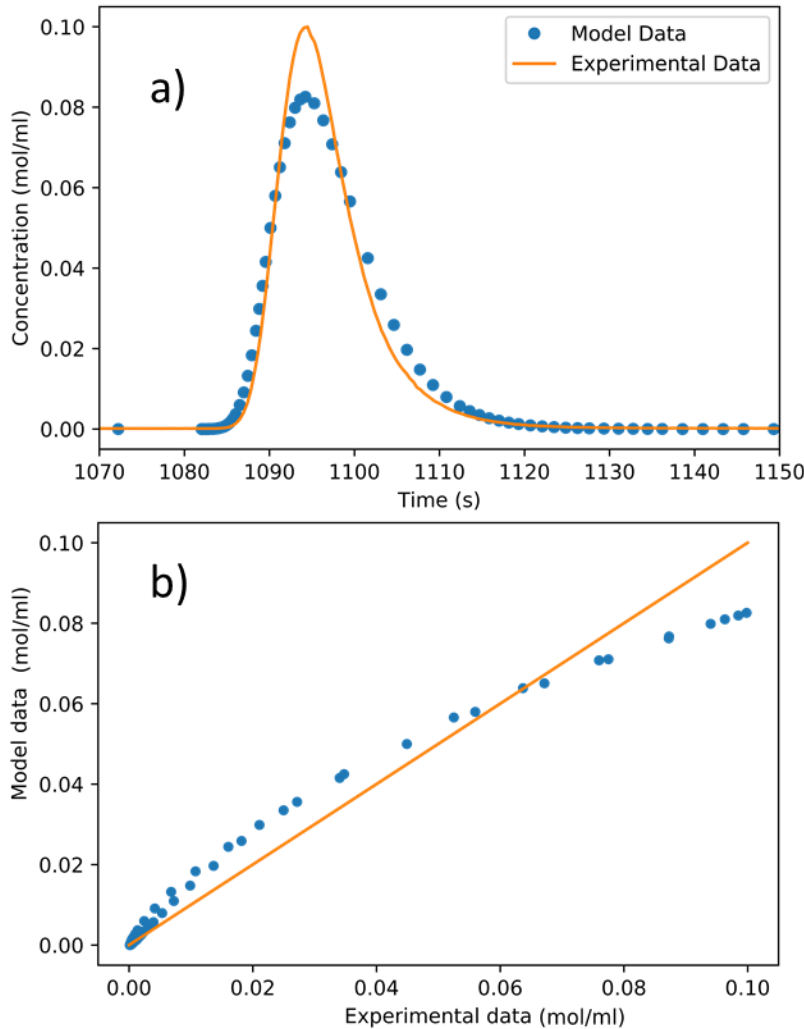


Figure 41: a) Concentration of tracer versus time at the outlet of the last reactor for a 3 CSTRs in series model. b) Model vs experimental CH_3OH concentration at the outlet of the last reactor for a 3 CSTRs in series model.

Consequently, a model with more tanks in series would be a better approach. The model of 4 tanks in series is presented in **Figure 42**. A better fit is observed in **Figure 42 a)**, with the model data curve exhibiting a sharper peak which approaches the experimental data curve. However, the non-

ideality of the system seems to be once again over-predicted, indicating the need for more tanks in series.

Moreover, the improvement of the fit between the 4 and the 3 tanks in series models can be observed by comparing **Figure 41 b)** and **Figure 42 b)**, with more of the points in **Figure 42 a)** being closer to the 45° line. It should be noted that in the case of a perfect fit, all the points should be lying on the 45° line.

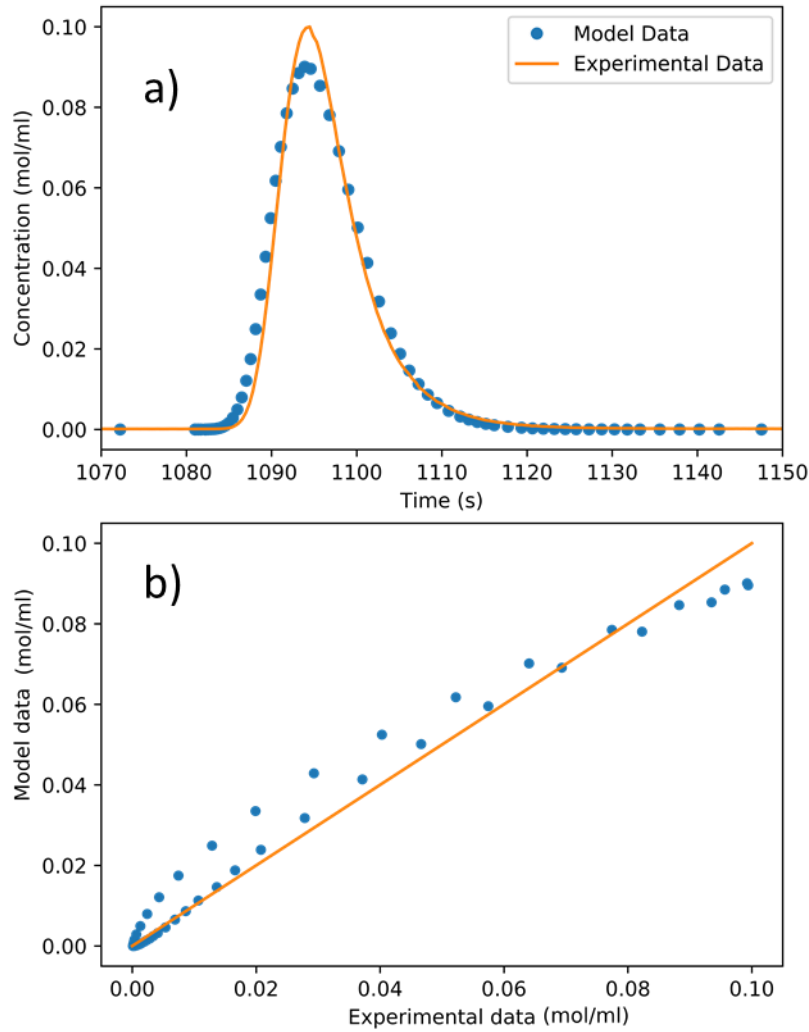


Figure 42: a) Concentration of tracer versus time at the outlet of the last reactor for a 4 CSTRs in series model. b) Model vs experimental CH₃OH concentration at the outlet of the last reactor for a 4 CSTRs in series model.

To further improve the fit, one more tank is added to the series to describe a system which approaches ideality more. The results of 5 CSTRs in series are presented in **Figure 43**. As

displayed in **Figure 43**, very good results are achieved by the addition a fifth tank. More specifically, the model data seems to be almost perfectly approaching the experimental data profile, with the two curves exhibiting the same shape. The deviation between model and experimental data seems to be minimal, which can also be seen in **Figure 43 b)**, where all of the points seem to be very close to the 45° line, with an obvious improvement in comparison to the cases of 3 and 4 tanks in series.

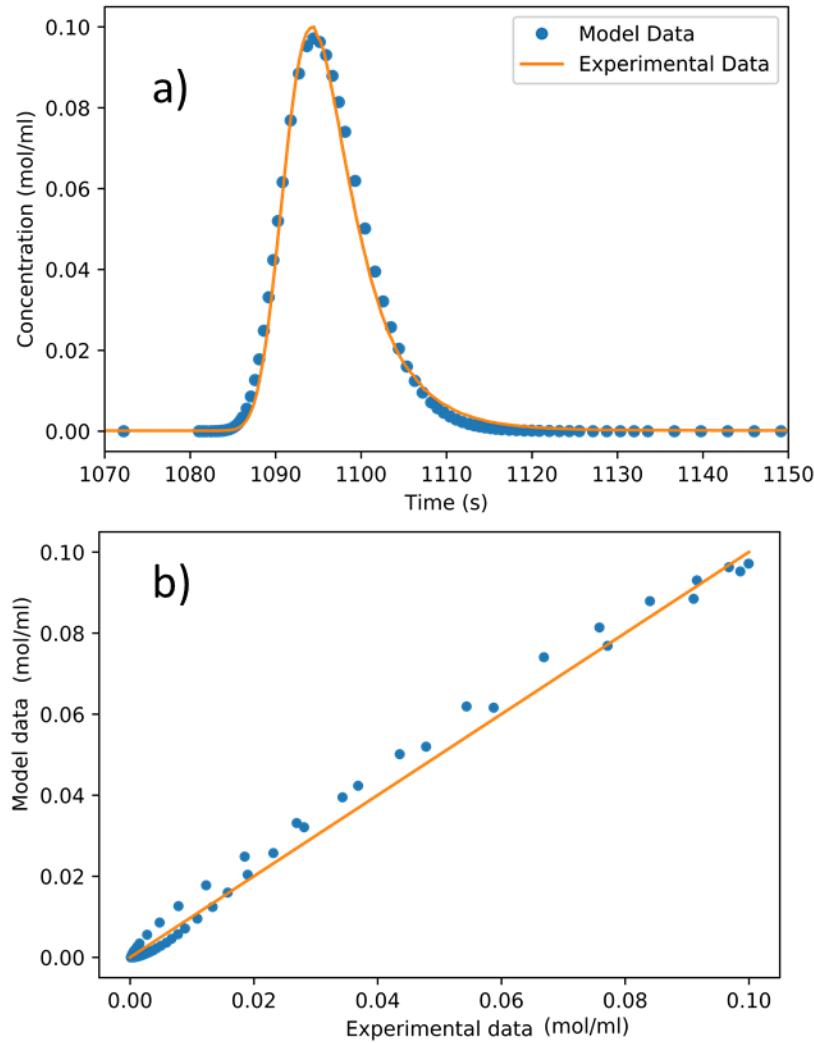


Figure 43: a) Concentration of tracer versus time at the outlet of the last reactor for a 5 CSTRs in series model. b) Model vs experimental CH_3OH concentration at the outlet of the last reactor for a 5 CSTRs in series model.

Although the fit between model and experimental data in the case of 5 CSTRs in series was satisfactory, the case of 6 CSTRs in series was also modelled to assess if there is a potential fit improvement. The case of 6 tanks is presented in **Figure 44**.

As seen in **Figure 44 a)**, adding one more tank to the model resulted in a worse fit, with the model concentration data exhibiting a sharper profile with larger deviation in comparison to the experimental data, indicating that the ideality of the system is in this case overestimated. This can be further observed by **Figure 44 b)**, where the model vs experimental data shows a larger scatter of points in comparison to **Figure 43 b)**.

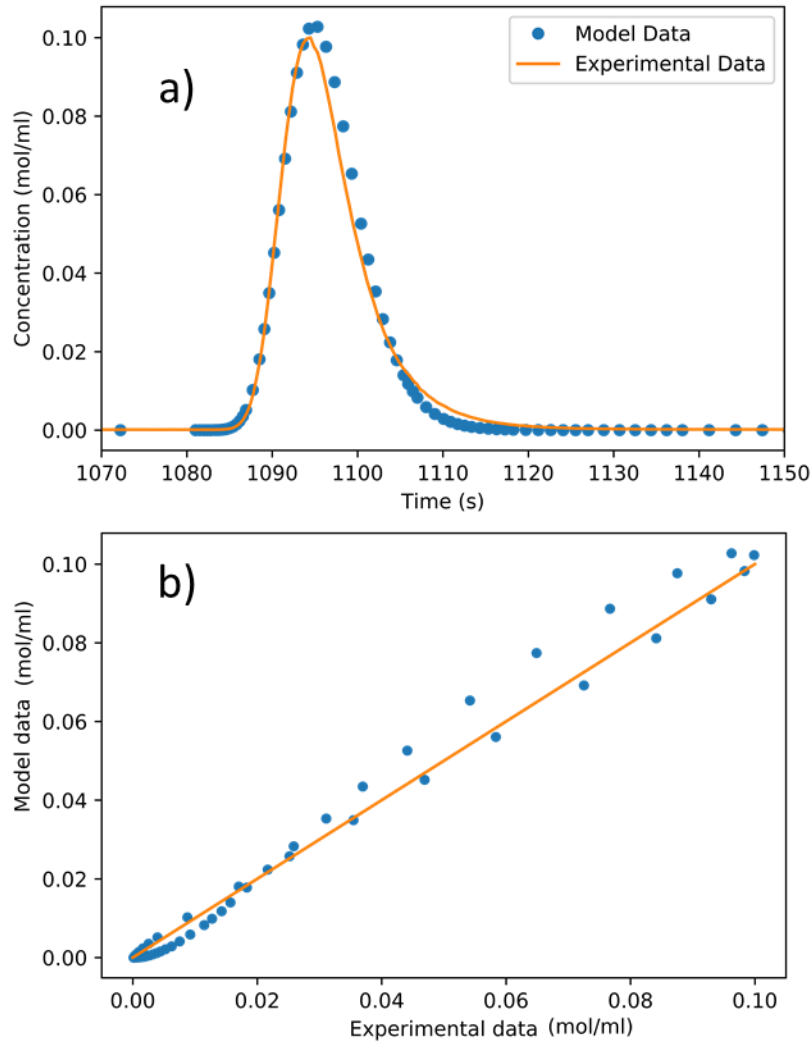


Figure 44: a) Concentration of tracer versus time at the outlet of the last reactor for a 6 CSTRs in series model. b) Model vs experimental CH_3OH concentration at the outlet of the last reactor for a 6 CSTRs in series model.

The visual findings of the comparison between the different model cases were confirmed by the comparison of the Root Mean Square Error for each case. The key performance indicators chosen for comparison of the different cases are presented in **Table 6**.

Table 6: Key performance indicators for different tanks-in-series cases.

	A_{exp} (a.u.)	A_{model} (a.u.)	RMSE (-)
3 CSTRs	1.112	1.109	0.00466
4 CSTRs	1.112	1.109	0.00405
5 CSTRs	1.112	1.110	0.00235
6 CSTRs	1.112	1.106	0.00299

As revealed by **Table 6**, the calculated RMSE values confirm what was visually assessed regarding the experimental and model fit. Specifically, the case of 5 CSTRs in series exhibited the lowest RMSE value among all investigated scenarios, while the calculated area underneath the experimental and model curves had negligible difference in all cases.

As a result, the 5 CSTRs in series model with a reactor volume equal to $V_{\text{system}}/5$ is chosen to be used for all kinetic modelling performed on experimental data.

6.3 Kinetic models

6.3.1 Input of Python models

The 5 CSTRs in series model that was developed was used in the kinetic modelling of the DMTM over a 3% CuMOR. In order to model the reaction and system, a Python routine was developed in which the differential equations describing the inflow, outflow and generation or consumption of each molecule were defined. Considering the overall reaction of the DMTM which is:



the stoichiometry of the reaction is defined inside the Python code. The stoichiometry of the reaction and the differential equations that describe each component are used to calculate the evolution of each of the species over time. According to the findings of Chapter 5, selectivity is assumed to be 100% to the aforementioned products, as no HCHO, CO or CO₂ are observed during reaction.

The concentration of H₂O was taken to be equal to the partial pressure of H₂O at 21°C (2.34 v/v or $1.02 \cdot 10^{-6}$ mol/ml) which was the temperature of the H₂O bubbler (Dortmund Data Bank, 2021). However, the H₂O concentration was not set as a step function in the Python model. As explained in Chapter 5, zeolites have properties as strong desiccants. Consequently, when H₂O vapor is

introduced to the reactor, it is initially adsorbed onto the zeolite until it reaches the maximum adsorption capacity. Upon saturation of the zeolite with moisture, the H_2O concentration level starts to rise until it reaches a steady value which corresponds to the saturation of the helium stream in H_2O vapor. To replicate this fast but not step-like increase in water concentration, the H_2O concentration is introduced to the model via a logistic function. The inputs needed for the logistic function are the maximum point in the y-axis, which is the H_2O concentration calculated, the middle point of the logistic function in the x-axis and the steepness of the rise, which were both set to values that matched the rise of H_2O concentration observed during the experiment. It should, however be noted that the use of a step function for the concentration of water is expected to only have a negligible difference for the modelling of the reaction.

An extra experiment was carried out to provide an estimation of the concentration of pre-adsorbed CH_4 species on the catalyst, which was used in the Python model. The 3% CuMOR was used in CO equilibrium adsorption isotherm measurements using a high pressure volumetric analyser (HPVA-II, Particulate Systems) under an ultra-high vacuum maintained with an oil and turbo pumping station. Samples (~100mg of dry sample) were loaded into the analyser and degassed using an ultra-high vacuum. Single component CO isotherms were measured from 0-1bar at 150°C . The CO used was research grade carbon monoxide provided by BOC. It is assumed that CO is adsorbed onto the active sites and that the interaction between CO and the active sites takes place in a 1:1 ratio, which is further used for the quantification of the pre-adsorbed CH_4 on the catalyst during the DMTM. The measured amounts of adsorbed CO under the pressure of 1bar are assumed to be a good approximation of the amount of CH_4 which is adsorbed onto the catalyst under the CH_4 adsorption step. The molar amount of CH_4 is then divided by the volume of the pure solid of the catalytic bed, which is calculated as explained in a previous section, to obtain the initial concentration of adsorbed CH_4 which is used as input in the Python model. Dr. Arwyn Evans is kindly acknowledged for performing this characterisation and analysing the results of the experiment. It should be noted that the aforementioned approach for the quantification of the pre-adsorbed CH_4 on the catalyst is based on the assumption that the adsorption of CH_4 and CO on the active sites happens in a similar fashion resulting to a similar degree of adsorption. The actual adsorbed amount in the case of CH_4 could exhibit a deviation from the calculated value. Thus, the calculated amount is used as an indication of the maximum capacity of the catalytic active sites at these conditions and as a rough estimation of adsorbed species concentration. The initial

concentration of methane on the catalyst can be set as another fitting parameter in the model fit examination.

The initial concentration of CH₃OH in all cases was equal to zero, as no CH₃OH is present at the initiation of the experiment. As explained previously, the volume of each reactor was set to $V_{\text{system}}/5$ for the case of 5 CSTRs in series used. Adding a reaction (generation) term to Equation (6.10), the generalised form of the equation describing each molecule inside the system is obtained. Equation (6.13) is used with appropriate input in each of the different kinetic model cases to describe each molecule present in the overall reaction, with r_A describing the rate of generation of disappearance of a molecule A due to reaction.

$$\frac{dC_A}{dt} = \frac{nq}{V_{\text{system}}} (C_{A(i-1)} - C_{Ai}) + r_A \quad (6.13)$$

For the case of H₂O all terms of the above equation are relevant, since H₂O is constantly entering and exiting the system, while it also takes part in the reaction. CH₃OH does not enter the system, but is generated during the reaction and also exits the system once generated. Finally, it is important to note that as previously explained, CH₄ is not fed into the system, but is pre-adsorbed onto the catalytic active sites. Consequently, during the reaction CH₄ does not enter nor exit the system, while it takes part in the reaction, being consumed over time. A good way to imagine the role of the catalyst in regards to CH₄ during the reaction would be to think of the catalyst as a CH₄ reservoir that is being depleted as the reaction goes forward.

For each of the cases modelled, the same Equation (6.13) is used to describe each of the species, with appropriate input for each, as explained. For each of the different kinetic cases investigated, the equation of the reaction rate is changed appropriately. This will be explained in more detail in the following sections.

The kinetic model developed suggested is based on a number of assumptions as explained above. The aforementioned assumptions are listed below:

- The H₂O concentration in the model is taken to be equal to the partial pressure of H₂O at 21°C ($1.06 \cdot 10^{-6}$ mol/ml), assuming saturation of the helium stream passing through the water bubbler.

- Selectivity of the process is assumed to be 100% based on experimental findings which showed no production of CO₂ and literature of a similar process which suggests a selectivity of 97%. (Sushkevich et al., 2017)
- The initial concentration of methoxy species on the active sites is set equal to the value of active sites concentration as calculated by CO adsorption. A further assumption is made that during CO adsorption, a 1:1 interaction took place between the CO molecules and the di-copper active sites.
- It is assumed that following CH₄ adsorption and during exposure of the catalyst to H₂O, a portion of methoxy species either desorbs or is displaced by H₂O before reacting to form CH₃OH.

Some of the assumptions listed above are discussed in more detailed in later sections of the present chapter.

6.3.2 Optimisation of scenarios

A simple optimisation protocol was followed for each of the kinetic cases investigated. Optimisation of reaction rate constants took place in three steps. Initially, all inputs regarding initial conditions and reaction rate equations were set in the Python code. Then an additional routine was programmed into the Python code, which could vary each rate constant, k , via interactive sliders over a range of values set by the user. The sliders were used along with a visual evaluation of the fit, to obtain an initial estimation of the range in which k values were investigated.

Subsequently, the reaction rate constants were further investigated and optimised within the chosen range. For each case, several k values in the aforementioned range were set into the model with a small linear step to obtain the CH₃OH concentration profile at the outlet of the reactors in series. The optimal k value in each case was chosen via the least squares method, as shown in Equation (6.14), i.e. by minimising the value of the sum of squared differences between the experimental and model data.

$$\text{Sum of least squares} = \sum (y_{\text{model}} - y_{\text{experimental}})^2 \quad (6.14)$$

For cases with two or more k -values, one of the rate constants was manipulated at a time while the rest were kept constant. Upon optimisation of that constant, it was set to the optimal value and the

optimisation was carried out similarly for the next constant, while keeping the rest unchanged. This protocol was followed until all constants were optimised. Upon optimisation of all k values, the same protocol was iterated starting over from the first constant, until the results of different iterations did not provide different results for the optimal k values. After identifying the optimal rate constant values with this method, these values were used as initial guesses in the final step of optimisation. An objective function was defined inside the python routine, which calculated the least squares between the experimental and model data. Then, an optimisation Python package (`scipy.optimize.minimize`) was used for the minimisation of the objective function by changing the values of the rate constants. The values obtained by the aforementioned sliders routine were used as initial guesses in the final optimisation. Finally, in each different model, the Python model was run with the optimal values and the results were kept as the optimised scenario for that case. An analysis of each of the kinetic cases investigated, along with the results and a comparison of the fits follows in the next sections.

6.3.3 Pseudo-first order reaction

Employing the simplest case and considering the overall reaction which was displayed in Equation (6.12), the kinetic regime of a pseudo-first order reaction was investigated. The reaction rate expressed in the consumption of CH_4 and the production of CH_3OH is given in Equations (6.15) and (6.16) respectively.

$$r_{\text{CH}_4} = -k_1[\text{H}_2\text{O}][\text{CH}_4] \quad (6.15)$$

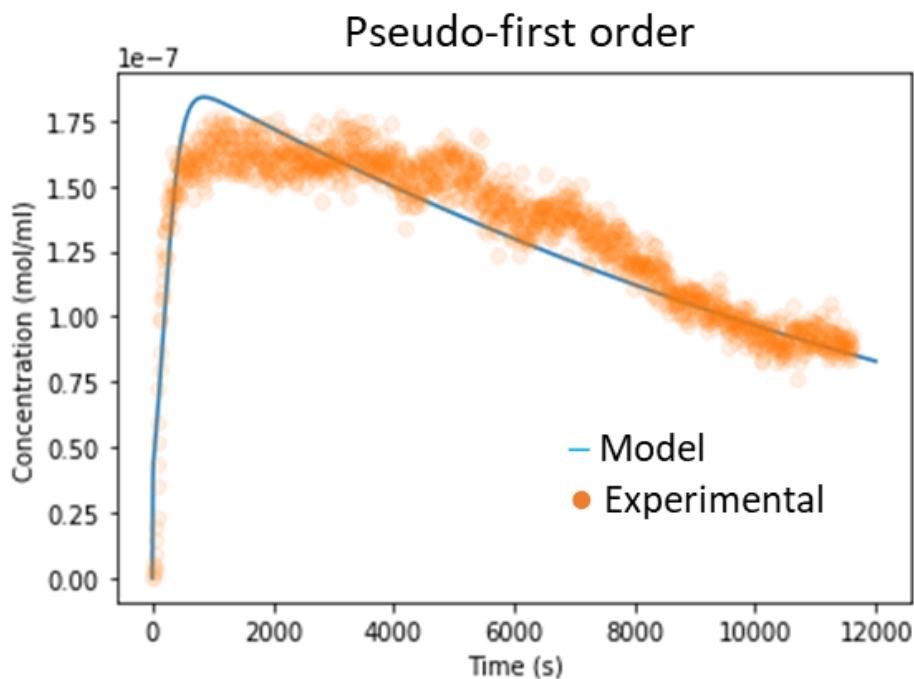
$$r_{\text{CH}_3\text{OH}} = k_1[\text{H}_2\text{O}][\text{CH}_4] \quad (6.16)$$

As seen in Equations (6.15) and (6.16), the rate of reaction includes the concentration of both H_2O and CH_4 . However, the concentration of H_2O , which is fed in excess in comparison to CH_4 , is assumed to have negligible change as the reaction progresses and thus the reaction kinetic regime can be assumed to be pseudo-first order. The reaction constant, k_1 , value was optimised as explained previously. The results of the optimisation of the k_1 value for the case of the pseudo-first order regime are displayed as an example in **Table 7**.

Table 7: Optimisation of k_1 for the pseudo-first order kinetic case.

k_1 (ml/mol·s)	Least squares sum (-)
70	$3.71 \cdot 10^{-13}$
75	$2.75 \cdot 10^{-13}$
80	$2.83 \cdot 10^{-13}$
85	$2.68 \cdot 10^{-13}$
90	$4.22 \cdot 10^{-13}$
95	$5.23 \cdot 10^{-13}$
100	$6.98 \cdot 10^{-13}$

Upon optimisation, the Python model was executed with the optimal value of the reaction rate constant. The model and experimental data of CH_3OH concentration at the system outlet plotted against time are displayed in **Figure 45**.

**Figure 45:** Experimental and model CH_3OH concentration data for a pseudo-first order reaction model.

As seen in **Figure 45**, the pseudo-first order kinetic model displays a relatively good approximation to the experimental data. However, although the pseudo-first order model fits the experimental data adequately in the later stages of the experiment, i.e. after 8000s on stream, the fit at the initial stage of the experiment displays a considerable deviation from the experimental data. Specifically, the first part of the experiment (0-5000s) exhibits a production and desorption of methanol at a relatively constant rate, which is impossible to be described by a simple first-

order kinetic model. Considering the nature of the reaction which involves the dissociative adsorption of CH_4 during interaction with the catalytic active sites, as well as the subsequent reaction of methoxy species with H_2O on the active sites, the pseudo-first order model was highly unlikely to provide a good fit to the experimental data. The pseudo-first order model is a simple approach which could not explain the complicated molecular interactions that occur during the DMTM over a CuMOR catalyst.

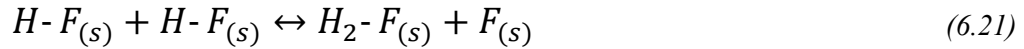
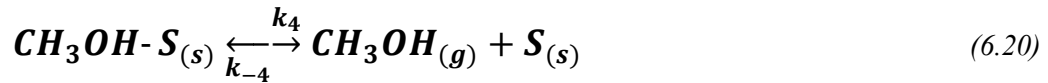
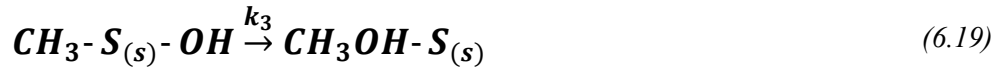
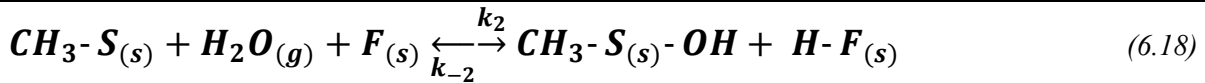
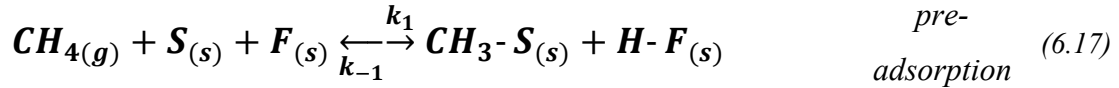
The CH_3OH concentration profile exhibits a rise at the initiation of the experiment until reaching the highest point, at which the concentration stays relatively constant for a considerable amount of time. Subsequently, CH_3OH concentration decreases over time in a trend similar to a first order reaction. This behavior is indicative of a changing order reaction, with zero order behavior at higher CH_4 concentrations and a first order behavior at lower concentrations. Naturally, such a behavior can be only approximated with a more complex kinetic model. A more detailed approach of the kinetic model is discussed in the next section.

6.3.4 Kinetic equations derivation

The development of a kinetic model which can sufficiently describe the reaction needs to be based on experimental observations as well as information reported in the literature. The present section serves to derive the kinetic equations based on the different phenomena occurring in the DMTM over a CuMOR catalyst.

Based on the mechanistic studies reported in the literature, a set of elementary reactions is suggested in the present work which could display the progression of the DMTM reaction over a CuMOR catalyst (Sushkevich et al., 2017). It should be noted, that $\text{S}_{(\text{S})}$ is used to denote the Cu-O-Cu active sites on the catalyst surface, while $\text{F}_{(\text{S})}$ represents the framework sites. Since the di-copper cores are the active sites of interest, kinetic equations will be derived in regards to these sites. As a result, a pseudo-non-dissociative adsorption of CH_4 and H_2O will be assumed on the $\text{S}_{(\text{S})}$ sites in the derivation of the kinetic equations, as the adsorption of each of them does not lead to the simultaneous occupation of two di-copper sites. Moreover, $\text{F}_{(\text{S})}$ sites will be ignored in the derivation of kinetic equations describing the reaction. It is reminded that due to the nature of the reaction, CH_4 adsorption takes place as a separate step prior to the introduction of H_2O into the system. It should also be noted that since the adsorption of water onto zeolitic frameworks takes

place very potently even on framework sites, Bronsted sites are thought to exist in abundance. Of course, $F_{(s)}$ sites which represent framework sites, also exist in abundance, surrounding the di-copper sites. The following elementary reactions describe the adsorption of methyl radicals on the active sites followed by the dissociative adsorption of H_2O on the same site with the concurrent formation of a Bronsted site. The adsorption of a hydroxyl group on the di-copper core leads to the formation of a second Cu-O-Cu bridge. The existence of this active site has been proven in early research into Cu-containing zeolites (Groothaert et al., 2005). The reaction of adsorbed species on the active sites is assumed to be the rate-limiting step, since H_2O exists in abundance and both the adsorption of H_2O and desorption of CH_3OH in the presence of an excess of H_2O are fast and thermodynamically favorable. (Palagin, Sushkevich & Van Bokhoven, 2019)(Mahyuddin et al., 2018)



where k and k_{-} denote the forwards and backwards rate constants of each reaction. The equations which are relevant to the rate of the formation and desorption of CH_3OH , as previously explained, are Equations (6.17) -(6.20). Since the surface reaction is assumed as the rate-limiting step, all other reactions are assumed to be in a quasi-equilibrium state. For the sake of simplification, the above equations are re-written, omitting the terms which are not relevant to the rate of the reaction and representing the reactants with A and B for CH_4 and H_2O respectively. The asterisk sign (*) is used to represent empty Cu-O-Cu sites, while any species followed by an asterisk represent the adsorbed form of the species (e.g., A^* represents adsorbed methyl radicals). Finally, A^*B represents the site

which has adsorbed both species before reaction, while AB^* represents the adsorbed product after surface reaction (CH_3OH_{ads}).



Then, for each reaction which is in equilibrium, the forward rate is equal to the backwards rate, so that the following expressions hold true, while r represents the rate of the reaction:

$$k_1[A][*] = k_{-1}[A^*] \quad (6.27)$$

$$k_2[A^*][B] = k_{-2}[A^* B] \quad (6.28)$$

$$r = k_3[A^* B] \quad (6.29)$$

$$k_4[AB^*] = k_{-4}[AB][*] \quad (6.30)$$

And further solving for surface species concentrations:

$$[A^*] = K_1[A][*] \quad (6.31)$$

$$[A^* B] = K_2[A^*][B] = K_1 K_2[A][B][*] \quad (6.32)$$

$$[AB^*] = \frac{1}{K_4} [AB][*] \quad (6.33)$$

where K denotes equilibrium constants of each process. Taking the total concentration C_s of active sites into consideration, the concentration of all sites is always equal to the occupied sites plus the empty sites (*), so that the following expression holds true:

$$[*] + [A *] + [A * B] + [AB *] = C_s \quad (6.34)$$

Substituting the surface species concentrations into this expression:

$$[*] + K_1[A][*] + K_1K_2[A][B][*] + \frac{1}{K_4}[AB][*] = C_s \quad (6.35)$$

$$[*] = \frac{C_s}{1 + K_1[A] + K_1K_2[A][B] + \frac{1}{K_4}[AB]} \quad (6.36)$$

Substituting this expression into the reaction rate, the rate of CH₃OH production is obtained:

$$r = k_3[A * B] = k_3K_1K_2[A][B][*] \quad (6.37)$$

$r_{CH_3OH} = \frac{C_s k_3 K_1 K_2 [A][B]}{1 + K_1[A] + K_1 K_2 [A][B] + \frac{1}{K_4}[AB]}$	(6.38)
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As previously mentioned, it is widely reported in the literature that the presence of H₂O in the system renders the desorption of adsorbed CH₃OH particularly potent by making it thermodynamically favorable (Mahyuddin et al., 2018)(Shi et al., 2019). As a result, the forward rate of Equation (6.26) describing the desorption of methanol will be very high, so that $1 \gg K_4^{-1}[\text{CH}_3\text{OH}]$. Consequently, the rate equation can be simplified to:

$$r = \frac{C_s k_3 K_1 K_2 [A][B]}{1 + K_1[A] + K_1 K_2 [A][B]} \quad (6.39)$$

Further merging constant values the following expression is obtained:

$$r_{AB} = \frac{k'_1[A][B]}{1 + k'_2[A] + k'_3[A][B]} \quad (6.40)$$

Furthermore, under the suggested reaction regime, since water is fed continuously in abundance, its concentration in the gas phase is assumed to remain constant so that a further simplification can take place in the denominator:

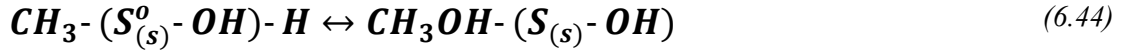
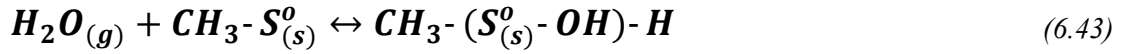
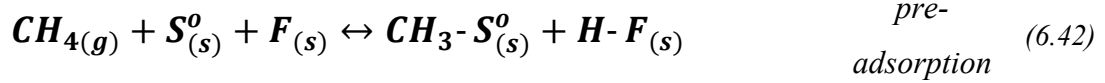
$$r_{AB} = \frac{k'_1[A][B]}{1 + (k'_2 + k''_3)[A]} = \frac{k'_1[A][B]}{1 + k''_2[A]} \quad (6.41)$$

where k'_1 represents the apparent rate constant of the surface reaction of adsorbed species, and k_2'' is a complex term containing the constants describing the adsorption of methane onto the di-copper sites, as well as the adsorption of water on the same sites and the water concentration. It is important to note that only under the constant flow of H_2O in excess it is valid to merge the concentration of water in the gas phase into k_2'' and to simplify the kinetic equations as displayed above.

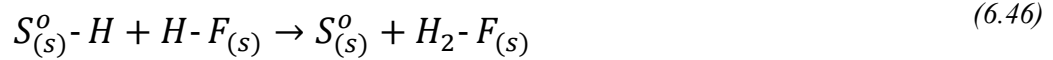
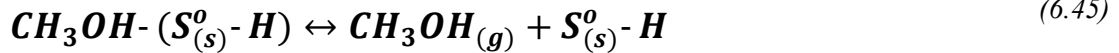
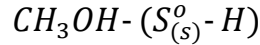
The rate expression derived above is based on the assumption that the adsorbed methoxy radical reacts with a hydroxyl group supplied to the active site during the dissociative adsorption of water. However, literature suggests that the source of oxygen for the formation of the CH_3OH molecule is the oxygen atom bridging the two copper atoms to form the Cu-O-Cu active site. This was reported after isotope mechanistic studies carried out by Sushkevich, Palagin, Ranocchiari, and Bokhoven. The group further suggested that it was the oxygen atoms of water which regenerated the sites following reaction. Following these findings reported in the literature, an alternative sequence of elementary reactions is laid out and kinetic equations are extracted in the same way as previously explained.

It should be noted that in this case, $S^o_{(S)}$ represents the two copper atoms bridged by an oxygen atom, while $S_{(S)}$ represents the site in the absence of the initial oxygen atom. As a result, the expressions $S_{(S)}-O$ and $S^o_{(S)}$ should be considered equal, assuming that the oxygen is bound to the copper atoms by forming an oxygen bridge between them, as is the case following the dissociative adsorption of H_2O on the active site. The alternative elementary steps describing the formation of CH_3OH with the oxygen of the initial site are given below.

Notably, these equations when written in a simplified form, as was done previously, lead to the same equations (Equations (6.23)-(6.26)) as used previously to derive the rate of reaction. As a result the final suggested equations describing the rate of reaction are the same, irrespective of the source of oxygen for CH_3OH formation.



And since $CH_3OH-(S_{(s)}-OH)$ can be written as



The reaction mechanism proposed by the above equations is presented graphically in **Figure 46**. As seen in **Figure 46** a) and b), methane is dissociatively adsorbed onto the di-copper core to form methoxy species, with the concurrent formation of a Bronsted site at a nearby framework position. This dissociative methane adsorption has been proposed and experimentally confirmed by Sushkevich et al. in 2017, who employed Fourier Transform Infrared Spectroscopy (FT-IR) to confirm the linear relationship between the quantity of methoxy species formed during CH_4 adsorption with the quantity of Bronsted sites formed on the aluminosilicate framework (Sushkevich et al., 2017). Upon introduction of water to the system, the dissociative adsorption of water takes place on the same di-copper core. As **Figure 46** c) shows, the dissociative adsorption of water takes place with the formation of a secondary oxygen bridge between the two copper atoms and the adsorption of a hydrogen atom directly on one of the copper atoms of the di-copper core. The possibility of adsorbing one or several water molecules on the di-copper core, where the methoxy species previously formed was confirmed experimentally and computationally by Palagin, Sushkevich & Van Bokhoven in 2019. This is also in agreement with the isotope work carried out by the same research group which confirmed that the oxygen from the water molecule is not the source of oxygen for the formation of methanol. Instead, methanol is formed using the pre-existing oxygen forming the di-copper core, while the oxygen of the di-copper core is replenished by water molecules. Additionally, the possibility of formation of a secondary oxygen

bridge between the copper atoms was proven in early research by Groothaert et al. in 2005, who employed UV-Vis analysis to confirm the existence of a bis(μ -oxo) di-copper core which participated in the DMTM reaction (Groothaert et al., 2005). As further suggested by Palagin, Sushkevich & Van Bokhoven in 2019, the migration of the hydrogen atom adsorbed on one of the copper atoms forming the di-copper core, to the methoxy species is possible, to form methanol, which is subsequently desorbed into the gas phase, as shown in **Figure 46** d) and e). The reaction cycle ends with the formation and desorption of molecular hydrogen from the hydrogen atoms adsorbed during CH_4 and H_2O adsorption, as seen in **Figure 46** f). The formation and desorption of molecular hydrogen has been confirmed both computationally and experimentally in several studies (Sushkevich et al., 2017)(Mahyuddin et al., 2018)(Li et al., 2021).

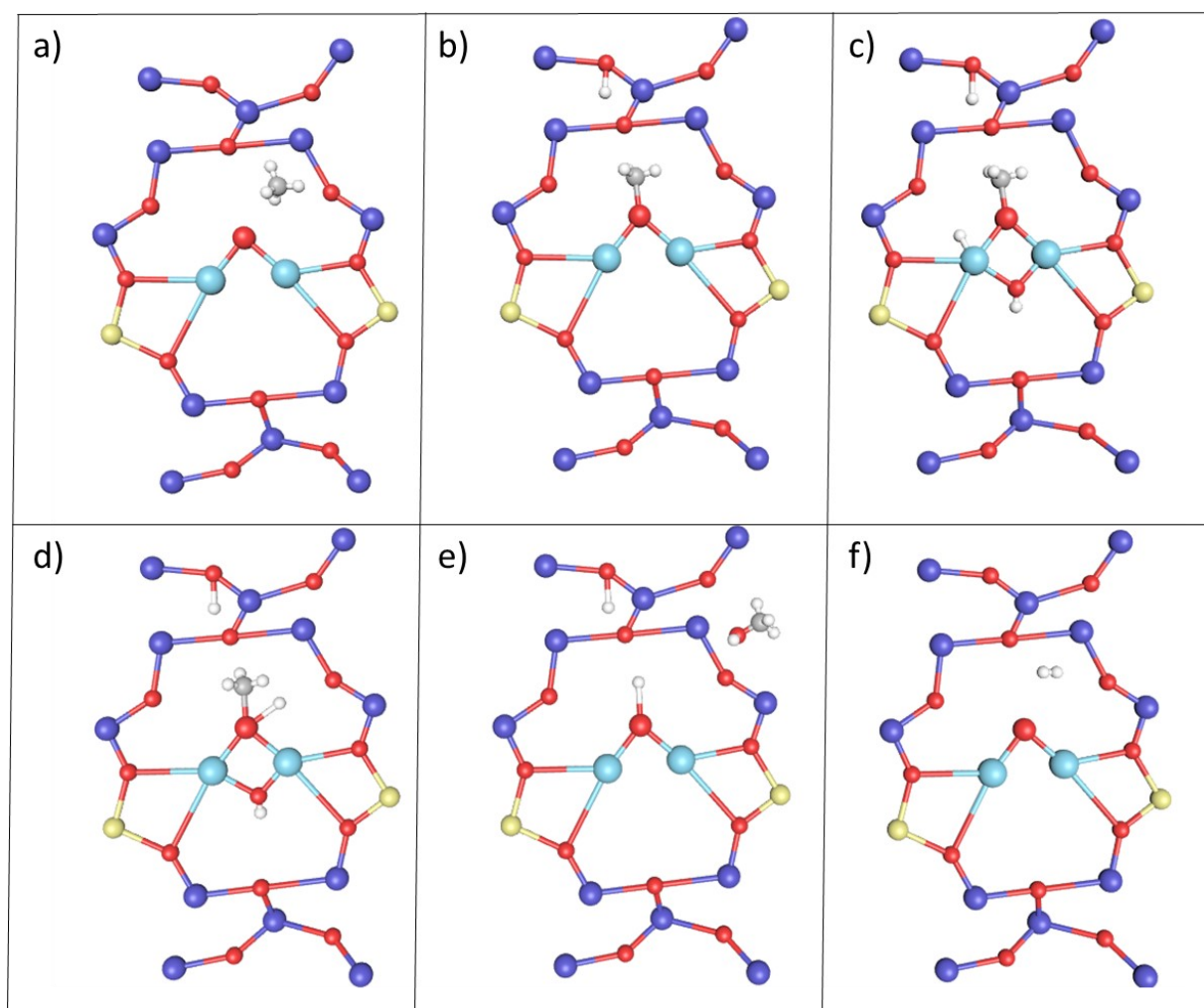


Figure 46: Suggested elementary steps of the DMTM over a di-copper core active site on CuMOR using water as oxidant (structure drawn with the ChemDoodle software).

Since there is evidence to support the sequence of elementary reactions in Equations (6.42)-(6.47), this is the suggested elementary step set, which is used to extract the final kinetic equations. It should be noted that a difference in the mechanism is the participation of the di-copper active site in the formation of H_2 in the case of the second set of elementary reactions. However, this does not affect the rate of reactions nor should it be included in the derivation of kinetic equations describing the methanol production, since it takes place as a separate process and since the reaction is essentially a “single-pass” process, as it happens in a semi-batch fashion. The participation of an oxygen atom which initially exists in the active site itself could indicate towards a Mars van Krevelen mechanism, where a lattice oxygen takes part in the reaction. However, the Mars van Krevelen mechanism proceeds via the formation of product from a gas-phase reactant, after abstracting an oxygen atom from the surface, creating a vacancy. This vacancy is then replenished by the secondary reactant, leading to a redox looping process (Vannice, 2007). Although in the DMTM over CuMOR an oxygen atom is supplied by the active site, the Mars van Krevelen mechanism is not considered to be an appropriate model to represent the reaction in this case. According to a Mars van Krevelen scheme, methanol should be formed in a single-pass fashion after introduction of CH_4 to the catalyst and in the absence of H_2O . However, it has been observed that no CH_3OH is desorbed during CH_4 adsorption, as well as that no CH_3OH is formed in the absence of water. Furthermore, the adsorption of H_2O onto the active site leads to the formation of a second oxygen bridge between the copper atoms, thus leading to no oxygen vacancy being formed throughout the course of reaction, even after the desorption of methanol from the site.

Finally, there is one more important aspect to the progression of the reaction which should be taken into consideration when constructing the rate equations. The affinity of water adsorption on zeolites and specifically onto active sites has been previously discussed and has also been proven experimentally. In fact, the experimental method was designed so, as to avoid the exposure of sites to H_2O before CH_4 would be absorbed onto the active sites. As a result, what needs to be considered when expressing the rate of CH_4 consumption from the active sites is not only the reaction itself, but also an associative desorption of CH_4 from the catalytic active sites before reacting towards the formation of methanol, either naturally or due to water adsorbing on the sites, displacing it in the process. As a result, an additional term representing CH_4 desorption needs to be added to the consumption rate of CH_4 from the active sites. Although the desorption of CH_4 is an associative process which according to the suggested elementary reactions would proceed via the aid of a

hydrogen atom of a nearby Bronsted site, it is considered to be a pseudo-first order process due to the abundance of Bronsted sites.

It should be noted that due to the semi-batch-like nature of the reaction, the CH₄ consumption rate in this case describes the consumption of methoxy species from the catalytic surface, which is denoted as [CH₃*] in the rate equations which were solved in the Python model. Since there is no information about the concentration of methoxy species at the initiation of the experiment with the introduction of water to the system, the initial concentration of the methoxy species was a fitted parameter. After initial fitting of the value for one of the experiments, the same value was used for all other experiments and the value was no longer fitted for experiments which were carried out using catalyst from the same batch, assuming same concentration of methoxy species on the catalyst surface following the same CH₄ treatment. Following the previously detailed derivations and Equation (6.41), the final rate equations describing the consumption of adsorbed methane and the production of methanol are given below.

$$r_{CH_3*} = -\frac{k'_1[CH_3*][H_2O]}{1 + k''_2[CH_3*]} - k_3[CH_3*] \quad (6.48)$$

$$r_{CH_3OH} = \frac{k'_1[CH_3*][H_2O]}{1 + k''_2[CH_3*]} \quad (6.49)$$

where k_3 is the rate constant describing the loss of pre-adsorbed methoxy species from the catalyst due to desorption or due to water displacement.

To evaluate the suggested model and the additional terms, different variations of the kinetic equations are used in the following section. The optimised different cases are compared to conclude on the optimal kinetic model.

6.3.5 Kinetic model cases

The previous section served to derive the kinetic equations which can describe the evolution of reactants and products over time, based on experimental data and literature. Different cases of the derived equations will be discussed and compared in the present section, in an attempt to conclude on which kinetic model is the most suitable to describe the DMTM over a 3% CuMOR catalyst. The cases investigated will be based on the previous analysis and will assess the assumption that

an additional term should be included in the rate equation of $[CH_3^*]$, to describe the desorption of methoxy species before they react with water towards methanol. Additionally, the assumption will be assessed that the desorption of methoxy species, although associative, can be assumed to be a pseudo-first order process. This will be assessed by also investigating the case of squaring the concentration of $[CH_3^*]$ in the added desorption term. Assuming that there is no abundance of Bronsted sites in close proximity of the di-copper active sites, but all Bronsted sites are formed via the dissociative adsorption of CH_4 , the concentration of $[CH_3^*]$ species would match the concentration of $[H^*]$ and thus the concentration of $[CH_3^*]$ species could be squared to describe the associative desorption. The aforementioned cases are presented below.

No additional $[CH_3^*]$ consumption term

The first model to be investigated is the case of no additional consumption term added to the rate of methoxy species. The set of reactions describing the evolution of CH_3^* and CH_3OH are presented below.

$$r_{CH_3^*} = -\frac{k_1'[CH_3^*][H_2O]}{1 + k_2''[CH_3^*]} \quad (6.50)$$

$$r_{CH_3OH} = \frac{k_1'[CH_3^*][H_2O]}{1 + k_2''[CH_3^*]} \quad (6.51)$$

Following the protocol mentioned above, the optimal parameter values of the model, k_1' and k_2'' , are identified. The optimal values of the rate constants of the model are presented in **Table 8**.

Table 8: Optimal parameter values in the case of a model with no additional CH_3^* consumption term.

	Optimised value (-)
k_1' (ml/mol·s)	240
k_2'' (ml/mol)	$1.0 \cdot 10^4$

The model was run with the optimised rate constant values and the experimental and model data for CH_3OH concentration in this case are plotted and displayed in **Figure 47**.

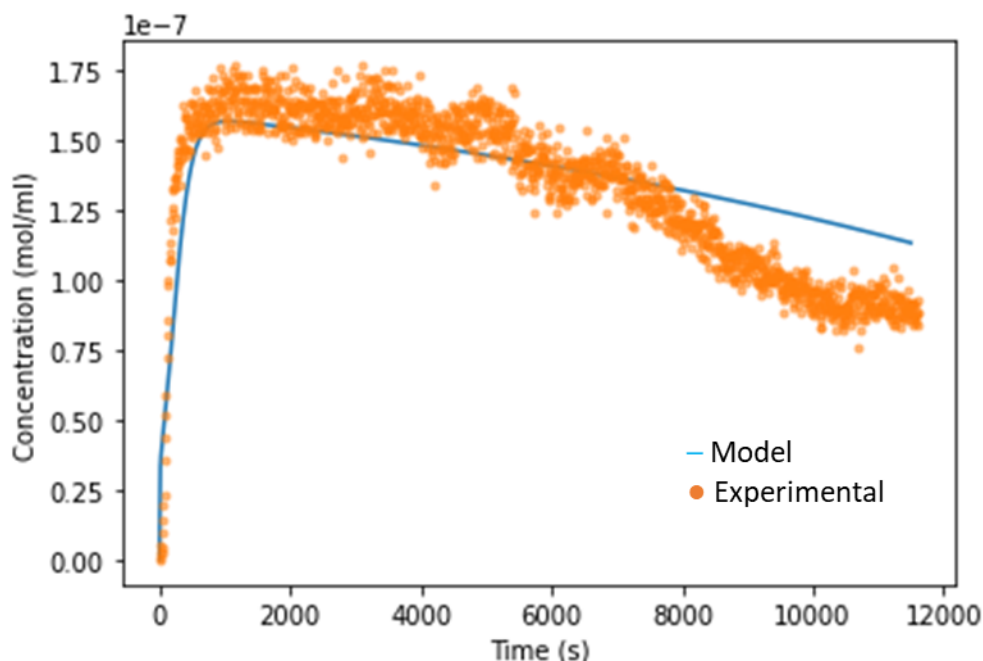


Figure 47: Experimental and model CH_3OH concentration in the case of a model with no additional CH_3^* consumption term.

As seen in **Figure 47**, in contrast to the pseudo-first order model, the model is capable of representing the initial part of the experiment (0-5000s), where the CH_3OH concentration levels remain relatively steady. However, the model exhibits a large deviation from the experimental data in the later stage of the experiment, predicting only a slow drop of the CH_3OH concentration after 5000s on stream. This confirms that a modification of the model is needed to predict a faster drop of the CH_3OH concentration, which, based on experimental findings on the conditions under which the DMTM is performed, is attributed to the desorption of methoxy species before they react towards methanol, since no CH_3OH overoxidation is observed.

Additional $[\text{CH}_3^*]$ consumption term

Following the previous equation derivations as well as the findings of the optimisation in the case with no additional CH_3^* consumption term, the term was added to the rate equation of CH_3^* and the model was optimised. The rates describing the evolution of species in this case are presented below.

$$r_{CH_3^*} = -\frac{k_1'[CH_3^*][H_2O]}{1 + k_2''[CH_3^*]} - k_3[CH_3^*] \quad (6.52)$$

$$r_{CH_3OH} = \frac{k_1'[CH_3^*][H_2O]}{1 + k_2''[CH_3^*]} \quad (6.53)$$

It is reminded that since no side products are experimentally observed at the conditions under which the DMTM is carried out over the 3% CuMOR, no additional consumption term is appropriate to be added to CH₃OH. On the contrary, the consumption term added to the rate of CH₃* is considered necessary to describe the process of desorption of previously adsorbed methoxy species as well as their displacement by water molecules from the gas phase. The addition of this term, which depletes the pre-adsorbed methane from the catalyst at a faster rate, is expected to provide a better fit to the later stage of the experiment. The optimised parameters in this case are presented in **Table 9**.

Table 9: Optimal parameter values in the case of a model with an added CH₃* consumption term.

	Optimised value (-)
k_1' (ml/mol·s)	480
k_2'' (ml/mol)	$2.2 \cdot 10^4$
k_3 (s ⁻¹)	$6.0 \cdot 10^{-5}$

Upon optimisation of the different parameters of the model, the model was run and the results of experimental and model data of CH₃OH evolution over time are presented in **Figure 48**.

As seen in **Figure 48**, the model with the added CH₃* consumption term presents a very good fit to the experimental data. The model predicts the initial CH₃OH concentration plateau at the initial part of the experiment, as well as the sharper methanol concentration decline as the reaction progresses, which leads to the conclusion that an added term which describes the consumption of CH₃* species that were pre-adsorbed on the catalyst should indeed be used to describe the DMTM reaction over a CuMOR catalyst.

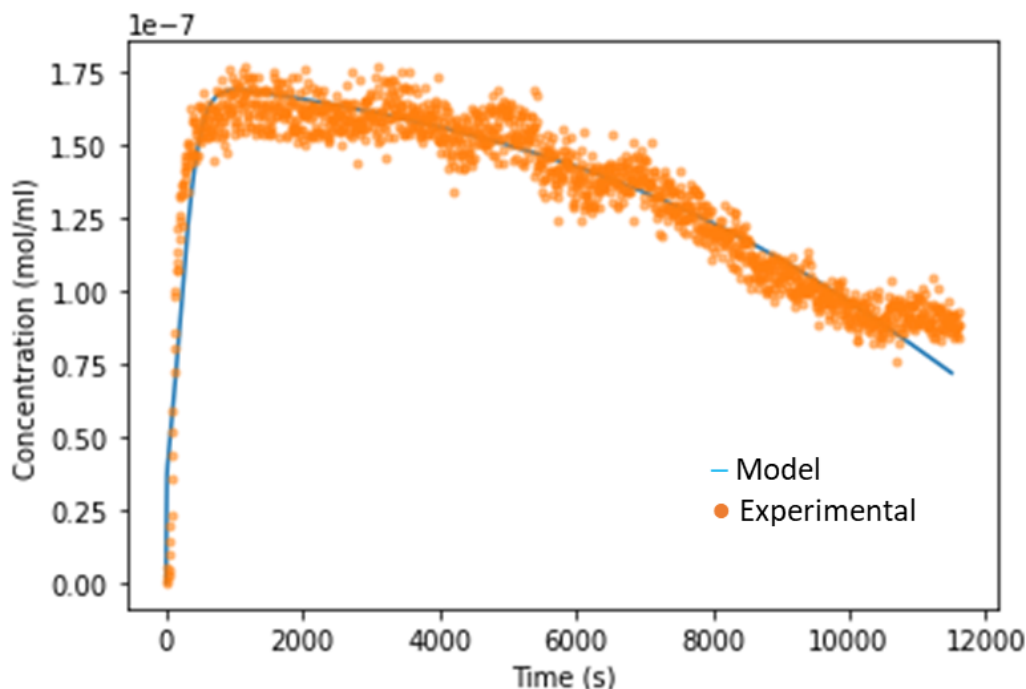


Figure 48: Experimental and model CH_3OH concentration in the case of a model with an added CH_3^* consumption term.

Additional $[\text{CH}_3^*]$ consumption term squared

Although a good fit of the experimental data is achieved with the model with an added consumption term for CH_4 , **Figure 48** indicates that in the last $\sim 1000\text{s}$ of the reaction, a sharper decline of the CH_3OH concentration is predicted by the model in comparison to the experimental data. Although this is an insignificant difference which only has a minor effect on the predicted evolution of CH_3OH over time and only in the very last stage of the experiment, another case was investigated. In this case, the added CH_3^* consumption term was squared, so that it would have a milder effect on the CH_3^* depletion as the concentration of methoxy species on the catalyst decreases. The physical meaning of the squared term was discussed in a previous section. The equations used in this case are presented below.

$$r_{CH_3*} = -\frac{k_1'[CH_3*][H_2O]}{1 + k_2''[CH_3*]} - k_3[CH_3*]^2 \quad (6.54)$$

$$r_{CH_3OH} = \frac{k_1'[CH_3*][H_2O]}{1 + k_2''[CH_3*]} \quad (6.55)$$

The optimised parameters in this case are presented in **Table 10**. The physical meaning of k_3 remains the same, describing the rate of desorption of methoxy species from the catalyst.

Table 10: Optimal parameter values in the case of a model with an added CH_3^* consumption term squared.

	Optimised value (-)
k_1' (ml/mol·s)	490
k_2'' (ml/mol)	$2.2 \cdot 10^4$
k_3 (s ⁻¹)	0.42

Expectedly, the optimised parameters k_1' and k_2'' displayed very similar values to the previous case, while there was a considerable difference in the order of magnitude of k_3 , which was also expected due to the presence of the squared concentration term. The model was run with the optimal values and the experimental and model CH_3OH concentration data are presented in **Figure 49**.

Figure 49 presents a better model fit to the experimental data in comparison to other investigated kinetic model cases. The model predicts well all parts of the experiment, both at the initial CH_3OH concentration plateau, as well as in the later stages when the methanol concentration declines. The quantitative comparison of the various models, as well as an evaluation and discussion on the comparison results follows in the next sections.

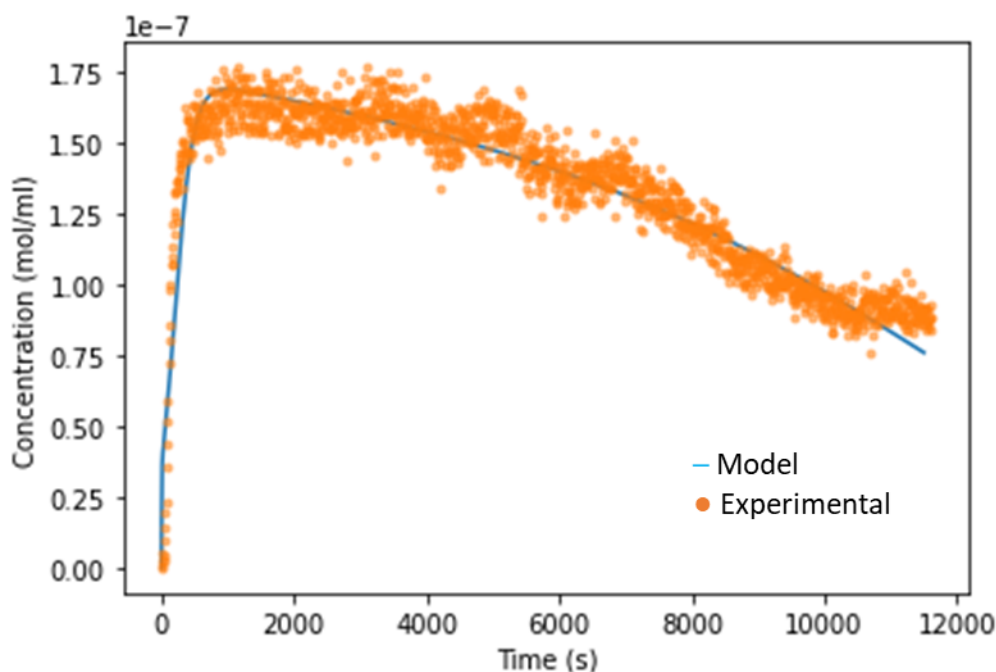


Figure 49: Experimental and model CH_3OH concentration in the case of a model with an added CH_3^* consumption term squared.

6.3.6 Model evaluation

Besides the visual evaluation, a quantitative evaluation of the model fit was carried out to reach conclusions about the suitability of the kinetic models suggested. Each different kinetic model was run with the respective optimised rate constant values and the optimised models were compared. Certain key performance indicators were chosen for the comparison between kinetic models. These key performance indicators and their meaning are listed below.

Sum of least squares

Similarly to the optimisation of the rate constant values in the previous section, the first key performance indicator chosen was the sum of least squares. Equation (6.14) of the sum of least squares can provide with an indication of the relative performance of the model fit when compared to other models. Generally, the sum of least squares value needs to be minimised during model fitting.

$$\text{Sum of least squares} = \sum (y_{\text{model}} - y_{\text{experimental}})^2$$

Root mean square error

The root mean square error (RMSE) used previously for the optimisation of the tanks in series model was also used as a key performance indicator in the evaluation of different model fits. The root mean square error presented in Equation (6.11) acts practically as an indicator of accuracy of the model fit. As the root mean square error is calculated as a mean of the errors of model points in comparison to the experimental points, it essentially displays the deviation of the model from the experimental data. Lower root mean square error values generally indicate a smaller deviation from the experimental data.

$$RMSE = \sqrt{\frac{\sum (y_{model} - y_{experimental})^2}{N}}$$

Experimental vs Model Area under CH₃OH curve

A simple but effective indicator used to assess the validity of the model results was the comparison between the experimental and model area underneath the CH₃OH desorption curve. The area underneath the CH₃OH was obtained by simply integrating the model and experimental curves via a Python routine. Naturally, there should be minimal deviation of the area underneath the model curve from the experimental data curve.

Max relative error (y-axis)

The last key performance indicator employed was the maximum relative error of model points in comparison to the experimental data in the y-Axis (CH₃OH concentration). This key performance indicator was chosen to complement the root mean square error and sum of least squares indicators as it can give a quantitative indication of anomalies in the model fit. As seen in Equation (6.56), this key performance indicator provides the maximum deviation of a point from the experimental data, normalised against the respective experimental data value. This is used to identify specific areas of the model that might exhibit large deviations from the experimental data, even if the overall fit is satisfactory.

$$\text{Max relative error} = \max \left(\frac{|y_{\text{model}} - y_{\text{experimental}}|}{y_{\text{experimental}}} \right) \quad (6.56)$$

The aforementioned key performance indicators were calculated for each of the optimised models. The results are summarised in **Table 11**.

Table 11: Key performance indicators used for evaluation of model fitting.

	Pseudo- first order	No added term	Added CH₃* consumption term	Added CH₃* term squared
Sum of least squares	$2.68 \cdot 10^{-13}$	$2.28 \cdot 10^{-13}$	$1.71 \cdot 10^{-13}$	$1.45 \cdot 10^{-13}$
RMSE	$2.31 \cdot 10^{-8}$	$2.20 \cdot 10^{-8}$	$1.80 \cdot 10^{-8}$	$1.68 \cdot 10^{-8}$
Model area	$1.55 \cdot 10^{-3}$	$1.58 \cdot 10^{-3}$	$1.54 \cdot 10^{-3}$	$1.53 \cdot 10^{-3}$
Experimental area	$1.55 \cdot 10^{-3}$	$1.55 \cdot 10^{-3}$	$1.55 \cdot 10^{-3}$	$1.55 \cdot 10^{-3}$
Max relative error	$3.82 \cdot 10^{-1}$	$3.94 \cdot 10^{-1}$	$3.43 \cdot 10^{-1}$	$3.41 \cdot 10^{-1}$

As seen in **Table 11**, a comparison of the selected key performance indicators confirms what was visually assessed and discussed in the previous section. More specifically, the pseudo-first order model exhibited the worst performance of all investigated fits, confirmed by the RMSE and the sum of least squares, while also having the second largest maximum relative error value. It should be noted that for all models, there was no significant deviation between the model and experimental area underneath the CH₃OH curve.

The model with the added CH₃* consumption term performed considerably better than the model without, again as confirmed by all key performance indicators. As visually seen, the model points of the added term case provided a better approximation to the experimental data, as confirmed by both the sum of least squares and the RMSE. Additionally, the considerable deviation of the model without the consumption term in the later stages of the experiment was indicated by the larger value of the maximum relative error which exceeded that of the pseudo-first order case.

Finally, the best performance among all cases was exhibited by the model with an added CH₃* consumption term squared. Specifically, the sum of least squares and root mean square error values in this case were the smallest among all models, while there was only a small difference in the max relative error between this case and the case of the simple added consumption term. However,

although mathematically providing a better fit to the experimental data, this model is still considered to be not as suitable, taking into consideration the literature and assumptions made in the derivation of the kinetic equations.

6.4 Kinetic parameters estimation

Upon identifying the most suitable kinetic model which describes the DMTM over a 3% CuMOR, more experiments were carried out in an attempt to further validate the model at different temperatures and to extract kinetic parameters.

Following the same reaction protocol, the reaction was carried out at different temperatures inside the range where CH₃OH is desorbed (150-250°C) with 25°C intervals. Thus, the reaction was tested at 150, 175, 200, 225 and 250°C. Following the same protocol explained before, the rate constants of the model with the added CH₃* desorption term were optimised in each different temperature experiment. The optimised model fit of CH₃OH concentration in each case is presented in **Figure 50**. It should be noted that some irregularities in the signal observed as small peaks or dips in **Figure 50** b), c), d) and e) are attributed to mass flow controller momentary faults and hold no experimental significance.

The experimental results observed in **Figure 50** hold interesting information. As observed, at lower temperatures the CH₃OH concentration displays a plateau which remains steady even after a longer exposure of the catalyst to H₂O, whereas, at higher temperatures the plateau shortens or even disappears (in the case of 250°C) as the reaction progresses faster to completion. This, of course, is expected, as with an increase in temperature the reaction rate increases and the depletion of CH₄ species from the catalyst occurs faster.

Additionally, it is reminded that it was proven in experiments presented in earlier sections, that the production of CO₂ begins at temperatures above 200°C. As a result, a faster drop in the concentration of CH₃OH is expected, since CO₂ can be produced not only by a direct oxidation of methoxy species (thus depleting CH₄ species) from the active sites but also the oxidation of CH₃OH itself via methanol steam reforming which starts taking place at 200°C and autothermal reforming which starts taking place at 250°C in the presence of copper-based catalysts. (Iulianelli et al., 2014)(Geissler et al., 2001)

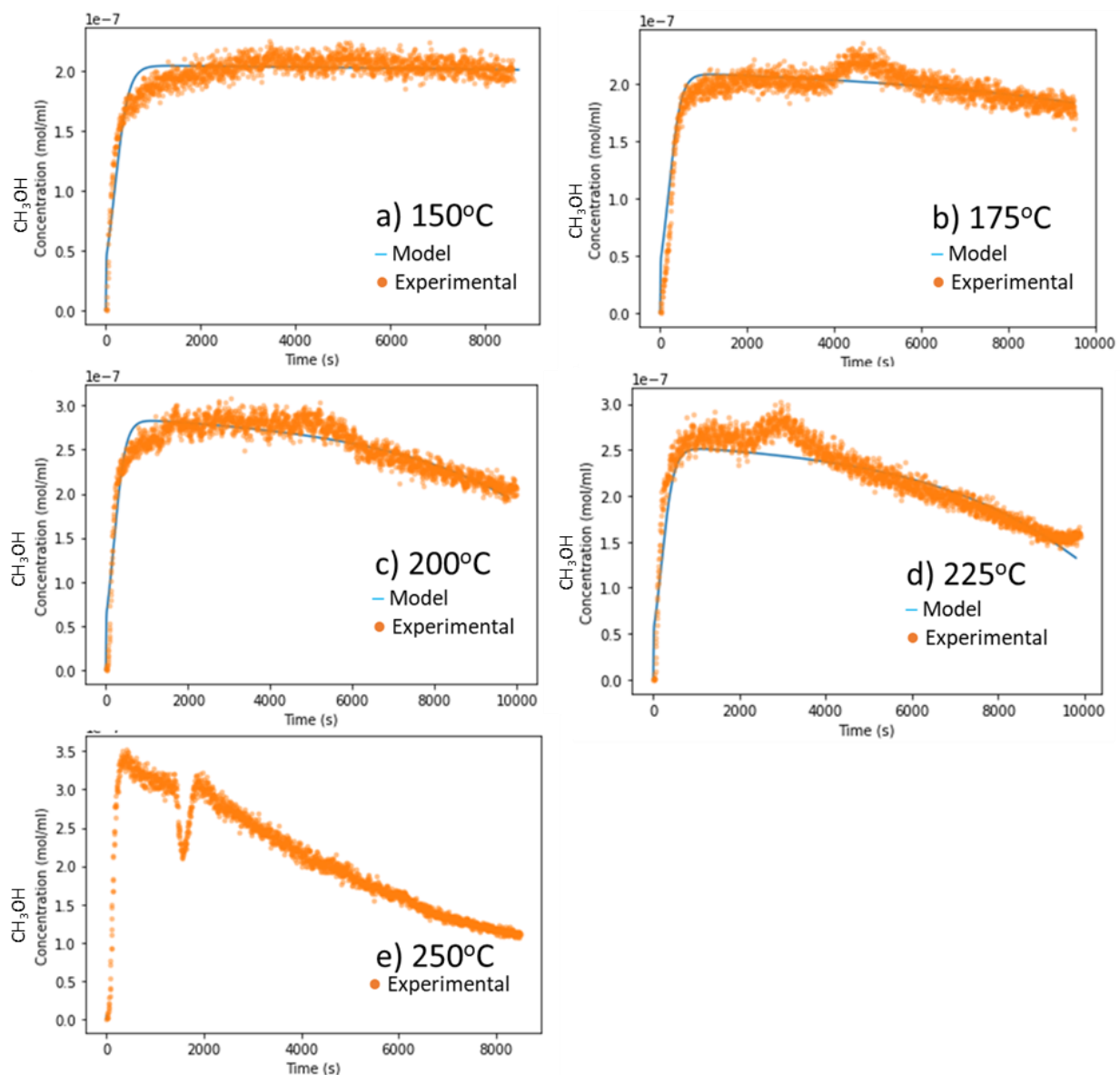


Figure 50: CH_3OH concentration profiles in optimised model with added CH_3^* desorption term at a) 150°C, b) 175°C, c) 200°C, d) 225°C and experimental data for e) 250°C.

The initiation of side reactions which lead to the production of CO_2 lead to a different reaction mechanism above 200°C. As a result, the proposed series of elementary reactions, which only take into consideration the selective direct methane to methanol partial oxidation can be considered valid at temperatures between 150-225°C, where side reactions play an insignificant role. It is noteworthy, that no satisfactory fit could be achieved even by optimising the model parameters in the case of 250°C, as there is a large deviation in the reaction mechanism due to side reactions at

higher T. Additional information is seen in the optimised values of the reaction rate constants, which are presented in **Table 12**.

Table 12: Optimised parameters for the model with an added CH_3^* desorption term in the DMTM at different temperatures.

	k_1' (ml/mol·s)	k_2'' (ml/mol)	k_3 (ml/mol·s)
150°C	420	$1.75 \cdot 10^4$	$1.0 \cdot 10^{-5}$
175°C	460	$1.87 \cdot 10^4$	$9.0 \cdot 10^{-5}$
200°C	680	$1.90 \cdot 10^4$	$1.5 \cdot 10^{-4}$
225°C	620	$1.90 \cdot 10^4$	$2.0 \cdot 10^{-4}$

As seen in **Table 12**, a steady rise of the k_1' value which represents the apparent reaction rate constant is observed in the range of 150-200°C. This is expected, as the reaction progresses faster at higher temperatures. However, the value of k_1' at 225°C is smaller than 200°C, which would not be reasonable in the absence of side reactions. However, as previously explained, due to the further oxidation of CH_3OH to CO_2 , as well as reactions of the methoxy species on the catalyst directly towards CO_2 , a decrease in the observed CH_3OH concentration is expected, which leads to a virtual drop of the observed reaction rate. The value of k_2'' appears to keep a relatively constant value at different temperatures, with a very minor rise observed. It is reminded that k_2'' is a complex term, consisting of several equilibrium constants and the concentration of gaseous H_2O and a direct interpretation of this trend is difficult to be given. It should also be noted that the adsorption of CH_4 takes places in a separate step, which could potentially also influence the effect of temperature in the observed rate constants. The rate constant k_3 representing the associative desorption of CH_4 displays an increase with the rise of temperature, a trend which is expected. It should be noted that k_3 at temperatures above 200°C would not only represent the desorption of methane, but its value would also be affected by side reactions leading to methoxy species not selectively reacting towards methanol, thus displaying a sharper rise.

Since side reactions towards CO_2 drastically change the reaction mechanism above 200-225°C, the proposed kinetic model is considered suitable for the DMTM over a 3% CuMOR in the temperature range of 150-200°C. Since the model is reliable in this range, the optimised k_1 values for 150°C, 175°C and 200°C were used to construct an Arrhenius plot, where the DMTM is isolated in the absence of side reactions. This can be seen in **Figure 51**.

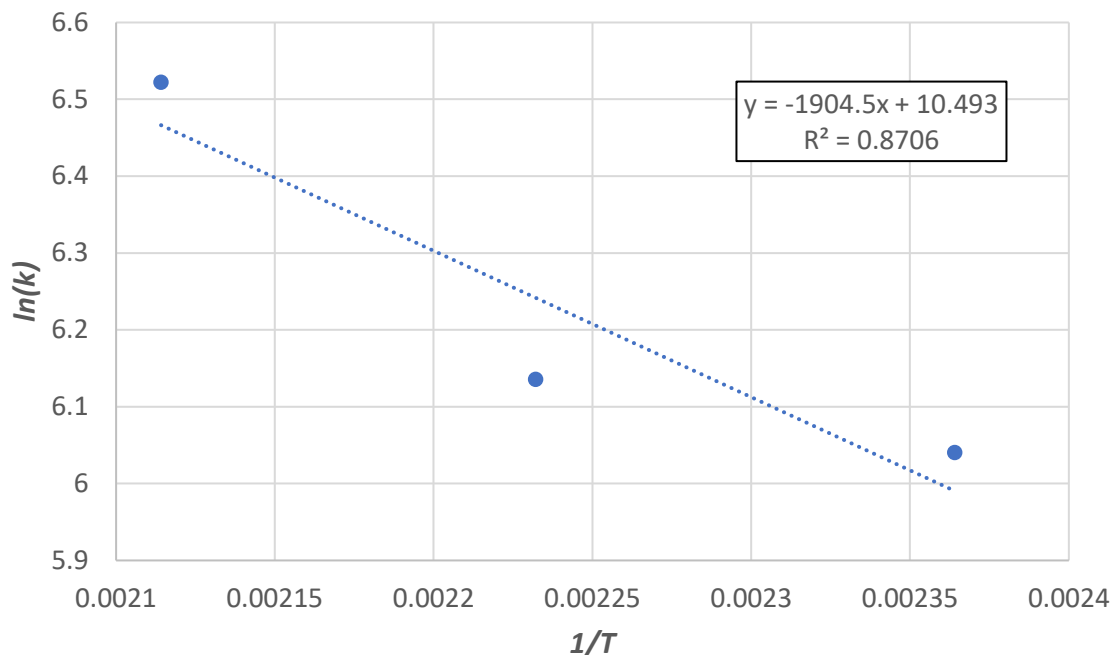


Figure 51: Arrhenius plot for the apparent reaction rate constant in the model with added term in the temperature range of 150-200°C.

With the aid of an Arrhenius plot, the apparent activation energy of the rate limiting step is calculated. This refers to the surface reaction of the methoxy species formed on the di-copper active site with the hydrogen atom adsorbed on the same site during the dissociative adsorption of H_2O , towards the formation of CH_3OH adsorbed on the active site. This is the reaction step described by Equation (6.45). The activation energy of the reaction of methoxy species with gaseous water towards the formation of methanol is calculated to be $E_a=16\text{kJ/mol}$, while the pre-exponential factor k_0 is calculated to be $k_0=3.6.0 \cdot 10^5\text{ml/mol}\cdot\text{s}$. It should also be noted, that if the Arrhenius plot and the activation energy estimation are based on only the 175 and 200°C points, where the model is most accurate, the calculated energy is $E_a=27\text{kJ/mol}$, which is in good agreement with the value reported in literature based on DFT calculations corresponding to the formation of adsorbed methanol on the active sites of 42kJ/mol . Notably, the 175-200°C range is the closest to the 200°C at which both the actual experiment as well as the theoretical calculations are carried out (Mahyuddin et al., 2018).

The calculated activation energy of the reaction of $E_a=27\text{kJ/mol}$ is rather low. However, it is believed that the presence of water in the system plays an important role not only in the selective production of CH_3OH , but also in lowering the energy barrier for the reaction. A DFT study by

Palagin, Sushkevich & Van Bokhoven in 2019 suggested a complex DMTM reaction mechanism on a CuMOR catalyst. The group suggested that water molecules not only adsorb readily on the di-copper active sites, but also on the aluminosilicate framework, while they reported the possibility of at least two water molecules adsorbing on the same di-copper active site. The researchers suggested that the presence of water molecules in abundance stabilise the system via the formation of additional hydrogen bonds during adsorption, thus significantly decreasing activation barriers for elementary steps and rendering the overall reaction thermodynamically feasible. Since H₂O is fed into the water in large abundance in relation to the active sites present on the catalyst, the low activation energies calculated above are attributed to the adsorption of water molecules and formation of stable intermediates like Cu-(OH)₂-Cu, as reported in the aforementioned study (Palagin, Sushkevich & Van Bokhoven, 2019). The low activation energy calculated in the presence of H₂O is also in agreement with the production of CH₃OH being possible at relatively low temperatures (200°C) in the presence of water.

6.5 Discussion

The present chapter served to develop a kinetic model to describe reaction of methane to methanol over a 3% copper mordenite catalyst at the most favorable conditions. A tanks-in-series model was developed and optimised to represent the experimental setup, and several kinetic cases based on experimental findings and literature were investigated in an attempt to reach a satisfactory fit between a model and the experimental data. To ensure the reliability of the kinetic model, the experimental data used for fitting was validated against the results of a similar work in the literature. Additionally, the intrinsic regime of operation of the reactor was confirmed through the calculation of appropriate criteria.

The qualitative and quantitative evaluation of different models led to the conclusions that a pseudo-first order reaction model would never be able to describe the reaction adequately, as it would be a very simplistic approach to the complex interactions between molecules that take part in the reaction and naturally, there was a large deviation in the behavior of the model from the experimental data. Kinetic equations which describe the evolution of different species through the progression of the reaction were developed and tested, to reach the conclusion that a modification in the consumption rate of CH₃* from the catalytic active sites was necessary to describe the

CH₃OH concentration decline in the later stages of experiments. The derived kinetic equations were employed in different variations to assess the fit with experimental in each case.

A simple term was added to the consumption rate of CH₃*, which describes the associative desorption of CH₃* from the active sites before taking part in the DMTM reaction. The necessity of this term became apparent since in its absence, the predicted CH₃OH production rate was considerably higher in the later stages of the experiment than the experimentally observed. The addition of this simple term yielded considerably better results, with the model data adequately approximating the experimental data for the most part of the experimental duration. A small deviation from the experimental data in the very late stage of the experiment led to the investigation of a further variation of the model, with the concentration of CH₃* in the added consumption term being squared. Both the qualitative and quantitative analysis of the fit led to the conclusion that the case of the added CH₃* consumption term squared offered the best fit mathematically among all investigated cases.

However, it is important for a proposed model to not only have a mathematical but also a physical meaning. More specifically, an assumption was made in the development of the kinetic equations about the abundance of Bronsted sites near the active sites, which contribute a hydrogen atom for the associative desorption of CH₄. As a result, the model with the added term squared is dismissed, as the CH₃* desorption process was assumed to be pseudo-first order. Additionally, it should also be considered, that the difference in the model data between the two aforementioned kinetic cases was only marginal and affected the very last part of the experiment, which poses no major significance in the overall progression of the reaction.

Carrying out the reaction at different temperatures, ranging from 150-250°C revealed that the assumption of a selective process towards CH₃OH holds true up to 200°C, while the model was still able to predict the experimental data up to a temperature of 225°C. However, the model was not able to provide any satisfactory fit for the experimental data at 250°C. This is expected, since at higher temperatures the mechanism of the reaction is more complicated, with the overoxidation of methanol in the gas phase being possible through various mechanisms. Furthermore, an overoxidation of CH₃* species to CO or CO₂ might also be possible through a different mechanism on the di-copper active sites. As a result, the recommended kinetic model should be considered valid in the range of 150-225°C to predict the progression of the DMTM over a 3% CuMOR.

Additionally, an Arrhenius plot of the apparent rate of the reaction provided an apparent activation energy of the process which was in excellent agreement with DFT calculations provided in the literature for the reaction.

Concluding, a derivation of kinetic equations led to the evaluation of various models. The investigation revealed that the proposed model with an added term which describes the depletion of a fraction of pre-adsorbed CH_4 species either via desorption or via displacement by water from the gas phase can adequately describe the experimental data obtained for the direct methane to methanol transformation over a 3% CuMOR catalyst in the temperature range of 150-225°C.

7. Industrial concept of the DMTM over a 3% CuMOR catalyst

One important aspect of chemical engineering problems is the scale-up potential of a developed process, as well as the economic feasibility of such a project. It is essential to identify where a laboratorially developed process stands in the current industrial landscape and to set specific targets to be achieved for being competitive to existing technologies. The present chapter aims to develop an industrial concept for the DMTM reaction over a 3% CuMOR, based on the recommended lab-scale process.

The main practical drawback of the developed method is the batch-like nature of the process, which involves the preparation of the catalyst, the methane pre-adsorption and the reaction with water to methanol in three separate, subsequent steps. Batch-like processes are unfavorable for industrial application, and generally continuous processes are preferred and are typically more profitable. To overcome the issue of the non-continuous operation of the lab-scale system, a smart, novel design of three fluidised beds in series is proposed for the DMTM. In the designed process, each reactor carries out one of the steps of the laboratorial process, thus achieving a continuous, looping operation in which the catalyst is continuously transported between the three reactors, to adsorb CH_4 , to catalyse the reaction towards CH_3OH and to be subsequently reactivated. Upon conceptualising the process, it is modelled and optimised with the aid of the ASPEN Tech V11 software, and a complete technoeconomic analysis is carried out, which maps out the economic feasibility with the current performance of the catalyst. Moreover, the cases of different catalyst performances are investigated, so that a target is set for the minimum required catalytic performance, which will serve as a guide for future research on catalysts for the DMTM.

7.1 ASPEN process setup

7.1.1 Black box method and CH_3OH yield basis for simulations

As mentioned in previous chapters, similar experiments to the ones carried out in the present work were carried out by a different research group. In fact, the data obtained in the present work was validated comparing against the aforementioned study of Tomkins et al.. It is reminded that the experimental methods were similar, with the difference being that in the present study the CH_4 adsorption step was carried out under atmospheric pressure, while the aforementioned group performed the adsorption step over a range of pressures from 0.05 to 36bar.

The group concluded that an elevation of the partial pressure of CH₄ during the adsorption step had a considerably beneficial effect on yield, with 36bar of pressure leading to the highest observed CH₃OH yield of 103.3 μ mol $\cdot$ g⁻¹ in the reaction step. Since data has been validated against their experiment with CH₄ adsorption at atmospheric pressure, it is considered appropriate to employ a CH₄ adsorption step carried out at 36 bar and the CH₃OH yield of 103.3 μ mol $\cdot$ g⁻¹ for the simulation of the process in ASPEN. Given the aforementioned single-pass CH₃OH production as well as the total duration of CH₃OH desorption during exposure to H₂O until depletion of CH₃* species from the catalyst, the reaction rate is calculated to be 0.052mol/kg_{cat} $\cdot$ h, which will serve as a basis of comparison for other catalysts and to set a target for future catalytic performance required for a profitable industrial process. (Tomkins, Ranocchiari & Van Bokhoven, 2017)

Since detailed kinetics for different reactant concentrations and different conditions have not been carried out to be used in the ASPEN model, a black box method is considered to be the simplest and most appropriate method. More specifically, the simulation will use representative kinetics which will be deriving results based on the yield reported in the aforementioned study to calculate the production of CH₃OH during the reaction step. The representative reactions and kinetics employed will be explained in more detail in the following sections.

7.1.2 Representative materials

The exact mechanism of the DMTM over CuMOR catalysts is still a topic under debate, with no conclusive results reported in the literature (Li et al., 2021a). However, it is widely accepted that one of the main active sites responsible for the reaction is the extra-framework Cu(II)-O-Cu(II) core. In their work on the selective anaerobic oxidation of CH₄ to CH₃OH, Sushkevich, Palagin, Ranocchiari, and van Bokhoven investigated the reaction mechanism employing various in-situ techniques and DFT calculations. In agreement with other studies in the literature, the group reported that initially, a CH₄ molecule approaches the active site, with the cleavage of a hydrogen atom following. This leads to the formation of methoxy species on the active site, along with the reduction of the active site to a state of Cu(I)-O-Cu(I), as well as the formation of a Bronsted site on a nearby spot on the aluminosilicate framework of the zeolite.

Upon introduction of water, the H₂O molecule approaches and hydrates the active site. Following the formation of methanol, water displaces CH₃OH, leaving behind a hydrated, inactive Cu(I)-

OH₂-Cu(I) site. Consequently, a two-electron reduction follows, with the formation of H₂ and the restoration of the initial state of Cu(II)-O-Cu(II).

Thus, the reaction mechanism progresses through a cycle of subsequent oxidation and reduction of the active sites (Cu(II)-O-Cu(II), to Cu(I)-O-Cu(I), to Cu(I)-OH₂-Cu(I) and back to the initial state of Cu(II)-O-Cu(II)). This looping process keeps the catalyst performing well after several cycles of the reaction performed without any signs of deactivation or performance loss, as reported by Sushkevich, Palagin, Ranocchiari, and van Bokhoven.

The different states of the catalytic active sites are cycled throughout the different steps of the reaction, and as a result, they need to be modelled in ASPEN to obtain the overall process. However, the copper-exchanged mordenite with the Cu-O-Cu sites in different valence states is a very specific material that does not exist in the ASPEN database. Moreover, a material like this would be particularly hard to properly be manually defined in ASPEN.

As a result, the definition and employment of representative materials with the same chemical and physical properties as the 3% CuMOR is considered to be the best approach to this problem. Specifically, the materials of interest that need to be defined, as they are going to be used in the reaction simulations in ASPEN are i) the ready-to-react Cu(II)-O-Cu(II) sites, ii) the catalyst with reduced Cu(I)-O-Cu(I) and adsorbed methoxy intermediates and iii) the spent catalyst with inactive Cu(II)-O-Cu(II) species.

To represent these materials, their chemical composition and valence needs to be considered. The materials chosen to represent the aforementioned catalytic active sites on the mordenite framework are presented in **Table 13**.

Table 13: Physical and representative materials of the DMTM over a CuMOR catalyst.

Physical material	Representative material
Active <i>Cu(II)-O-Cu(II)</i> sites on CuMOR	Copper oxide (CuO)
<i>Cu(I)-O-Cu(I)</i> on CuMOR with methoxy species	Cuprous oxide (Cu ₂ O) + CH ₃ OH (equimolar ratio)
Inactive <i>Cu(II)-O-Cu(II)</i> sites on CuMOR	Cuprous oxide (Cu ₂ O)

The selection of representative materials was made based both on the chemical composition as well as the chemical valence of the actual materials. More specifically, all representative materials

chosen (Cu_2O and CuO) have the same elemental compositions as their physical counterparts during the different reaction mechanism steps. Moreover, the valence of CuO matches the valence of the Cu(II)-O-Cu(II) which it represents, while the valence of Cu_2O matches the valence of the Cu(I)-O-Cu(I) with adsorbed methoxy species, which it represents.

However, having addressed the chemical aspect of the representative materials, it is also important to consider the physical properties of the actual and representative materials. Notably, CuO and Cu_2O have very similar densities (6.3g/cm^3 and 6.0g/cm^3 respectively), while their density differs significantly from the density of the copper-exchanged mordenite (2.1g/cm^3). The density of the catalytic material plays an important role in the design of reactors, as it can affect the fluidisation properties of fluidised bed reactors, the catalyst bed volume, the minimum fluidisation velocity etc.. To address this problem, the density of the representative materials is manually set to match that of the CuMOR. Additionally, a normal particle size distribution with a $10\mu\text{m}$ standard deviation was defined for the catalytic particles with a $D_{50}=500\mu\text{m}$, similar to the particles size distribution used in laboratorial experiments. (National Center for Biotechnology Information. PubChem Database, 2020a)(National Center for Biotechnology Information. PubChem Database, 2020b)(Mindat.org, 2020)

7.1.3 Representative reactions and kinetics

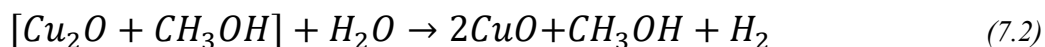
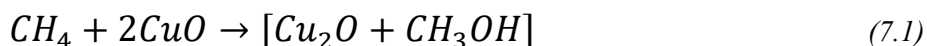
As previously mentioned, the designed industrial process concept involves three reactors in series carrying out each of the individual steps of the laboratorial process. More specifically, the first reactor, R-101, serves for the CH_4 pre-adsorption on the CuMOR, the second reactor, R-102, hosts the partial oxidation of the methoxy species to CH_3OH in the presence of H_2O , while the third reactor, R-103, regenerates the inactive, hydrated catalyst under a flow of air.

As representative materials have substituted the different states of the active sites in the ASPEN model, it is also necessary to appropriately define the equivalent representative reactions and kinetics describing the overall reaction given by Equation (6.12). The representative reactions defined for the representative materials, as well as the respective reactors and conditions of each reaction are presented in detail in **Table 14**. It should be noted that the residence times displayed in **Table 14** refer to the solids, as the solids are cycled through the reactors. The residence times for each reactor are taken from the work of Tomkins et al..

Table 14: Representative reactions and kinetics.

Reactor	T, P	Reaction	Kinetics	Res. time
R-101	200°C, 36bar	$CH_4 + 2CuO \rightarrow [Cu_2O + CH_3OH]$	$r_1 = k_1[CuO]^2[CH_4]$	0.5h
R-102	200°C, 2bar	$[Cu_2O + CH_3OH] + H_2O \rightarrow 2CuO + CH_3OH + H_2$	$r_2 = k_2[Cu_2O][H_2O]$	2.0h
R-103	450°C, 2bar	$2Cu_2O + O_2 \rightarrow 4CuO$	$r_3 = k_3[Cu_2O]^2[O_2]$	1.0h

The reactions carried out in the first two reactors (R-101 and R-102) are practically representative of the overall reaction. The reaction carried out in reactor R-103 is the regeneration of the spent catalyst under a flow of air to prepare the active sites for a new cycle of the reaction and is thus irrelevant to the overall reaction of methane to methanol. It should be noted that in the laboratorial process, helium is typically used to regenerate the catalyst after the first reaction cycle. However, since air is a cheaper material and following the study of Álvarez, Marín, and Ordóñez who concluded that regeneration in air can improve the CH₃OH yields of subsequent reaction cycles, the regeneration under a flow of air is considered a more suitable choice. The reactions carried out in the first two reactors are displayed below:



Adding Equations (7.1) and (7.2), the overall reaction of $CH_4 + H_2O \rightarrow CH_3OH + H_2$ is indeed achieved, in agreement with the literature and the laboratorial process. It should also be noted that a selectivity of 100% is assumed for the reaction based on the lab-scale findings explained in previous sections, since no side products were observed during reaction. This is also in good agreement with the findings of Sushkevich, Palagin, Ranocchiari, and van Bokhoven, who reported a selectivity of the reaction of 97% towards methanol. A selectivity of 100% is also beneficial to the convenience of the simulations as no traces of side products need to be considered, with negligible impact on the final results.

As previously explained, a black box method regarding methanol yield is employed. The methanol yield of $103.3\mu\text{mol/g}_{\text{cat}}$ is used for reactor R-102, while the production of H_2 is assumed to be stoichiometrically proportional to the produced CH_3OH , as dictated by the overall reaction stoichiometry. Considering the aforementioned assumptions, simple power law kinetics are defined for the reactions carried out in each reactor, as seen in **Table 14**. These representative kinetic equations have no direct physical meaning and just serve towards the black box method of achieving the target yields, by manipulating the values of the respective reaction rate constants (k_1 , k_2 , k_3) in each reactor. The reaction rate constants for the reactions carried out in R-101 and R-102 are manipulated and fit to the required values through the ASPEN Design Spec function. The fitting of these values happens via setting a target production rate of methoxy species or methanol respectively in each case (in terms of physical materials). The design specification set in R-101 is the CH_3OH production rate according to the $103.3\mu\text{mol/g}_{\text{cat}}$ reported for a single pass in literature by Tomkins, Ranocchiari and Van Bokhoven in 2017, while the target set in R-102 is the H_2 production rate, which has to match the CH_3OH production rate from the previous reactor. The value of k_3 does not need to be fit, as the kinetics of the regeneration of the catalyst are irrelevant to the process. Considering that the residence time of 1hr is sufficient to regenerate the active sites, a large, arbitrary value is set to the rate constant k_3 .

Although a black-box method lacks the sensitivity and flexibility that detailed kinetics under a range of different conditions and reactant concentrations would provide, it is still an accurate and reliable method to model the process in ASPEN and carry out an economic feasibility study, without any negative impact on the final results.

7.2 Methodology

A basis for the calculation of the economics of the process as well as for the overall feasibility evaluation needs to be set. The present section serves to summarise all protocols used to calculate the expenses of the process and to elaborate on the cost estimation methods regarding all capital and operational costs associated with the proposed industrial process.

7.2.1 Calculation of utilities cost

The operational costs of a plant naturally include specific utilities associated with the operation of different units. The cost of these utilities is calculated based on their price per their respective unit,

as well as the total operation time of the plant. The total uptime of the designed process is calculated as the 80% of the whole duration of a calendar year, as suggested by Coulson and Richardson for a process that involves solids. **Table 15** presents the summary of utilities and their respective costs, as given by the Energy Analyzer of the Aspen Tech software. The software calculates the need of each unit for a specific utility based on the process specifications and uses a database of prices to calculate the final utility requirement and utility cost of each unit. (Aspentech, 2020)

Table 15: Utilities used in the DMTM process and their respective costs.

Utility	Inlet	Outlet	Cost
Electricity	-	-	$7.75 \cdot 10^{-2}$ \$/kWh
High pressure steam	250°C	249°C	$2.50 \cdot 10^{-6}$ \$/kJ
Cooling water	20°C	25°C	$2.12 \cdot 10^{-7}$ \$/kJ
Fired heat	1000°C	400°C	$4.25 \cdot 10^{-6}$ \$/kJ

7.2.2 Calculation of units cost

The calculation of the cost of all the units comprising the process happened in several different ways. The Aspen Capital Cost Estimator (ACCE) is a built-in feature of the Aspen software, which allows for the cost estimation of certain commonly used industrial units. The ACCE employs databases of existing pieces of equipment to give an accurate estimation of cost of a unit in interest based on its size. (AspenTech, 2020)

Additionally, no further estimation is required for commercially available equipment. Instead, the cost of such equipment is directly added to the total capital cost of the process, as given by the respective vendor.

Finally, the cost of manually designed pieces of equipment cannot be estimated by the Aspen Capital Cost Estimator if similar equipment does not exist in the databases. More specifically, the fluidised bed reactors facilitating the different steps of the reaction were manually designed as explained in a further section. As a result, their cost needs to also be manually calculated and added to the overall capital cost.

To calculate the price of such equipment, reference equipment from the literature is used. Employing a correlation given by Coker, the cost of equipment is calculated by comparison to a reference piece of equipment with known capacity and cost. A cost exponent is also applied to directly relate the capacities of the two pieces of equipment. The aforementioned correlation is given below:

$$C_2 = C_1 \left(\frac{Q_2}{Q_1} \right)^m \quad (7.3)$$

where C_2 is the cost of equipment in interest, C_1 is the cost of reference equipment, Q_2 and Q_1 are the capacities of respective pieces of equipment, and m is the cost exponent. However, it is essential to note that the reference equipment cost corresponds to the year when the cost of that piece was documented. This can result in a large deviation from the current market prices for similar pieces of equipment if the cost of reference equipment dates back several years or even decades. Consequently, the price of reference equipment needs to be adjusted to the present via another correlation given below (Coker, 2007):

$$C_1 = C_p \cdot \frac{l_1}{l_p} \quad (7.4)$$

where C_1 is the reference cost in present time used in Equation (7.3), C_p is the cost of reference equipment in the past time, while l_1 and l_p are the Chemical Engineering Plant Index Costs for the respective times, as given in the literature (Jenkins, 2019).

For the calculation of the capital cost of fluidised bed reactors in the present time, reference equipment and respective cost exponents were extracted from the literature (Woods, 2007). More specifically, a 12m^3 fluidised bed reactor with a cost of 5\$ million was used as a reference piece of equipment, with a capacity factor of 0.53. The CEPCI index of the aforementioned reactor was given to be 1000, while a CEPCI index of 603 was used for the present time. The cost of all three fluidised bed reactors of the suggested process were calculated based on the aforementioned data (Woods, 2007) (Jenkins, 2019).

7.2.3 Economic evaluation

The economic evaluation of the project took place in a series of steps as proposed by Dimian in 2003, who lays out the complete methodology, starting from the units of the process in interest as well as the utilities and raw materials needed on an annual basis. It should be noted that the empirical method suggested would fall within the accuracy margin of $\pm 30\%$, which is, however, appropriate for a preliminary investigation. All necessary process units and equipment and their respective utility consumptions are provided by the ASPEN simulation.

Additionally, the cost of raw materials as well as the revenue generated by selling the products is calculated by multiplying the annual amounts needed/generated with their price per unit respectively. The prices for all the materials were found for commercially available products, sold in comparable quantities to industrial needs. It should also be noted that the price of commercially available mordenite was doubled, to account for the extra processing costs to produce the required 3% CuMOR. In the case where several prices were available for products of similar specifications, an average of all quotes was taken. All prices are listed below in **Table 16** (Alibaba.com, 2021a) (Alibaba.com, 2021b) (Christensen, 2020) (EIA, 2021b) (Process Industry Informer, 2015) (Alibaba.com, 2021c).

Table 16: Cost of products and raw materials of the process.

Product	Price
CuMOR	500.00\$/t
Methane	2.65\$/kmol
Helium	30.00\$/m ³
Process water	5.28\$/m ³
Methanol (99.9% wt.)	4.36\$/kg
Hydrogen	9.00\$/kg

The methodology of Dimian breaks down the calculation of all process costs in categories related to the capital costs and the operational costs. The calculation of the capital costs starts with the cost of purchasing all necessary units and uses a series of different factors estimated from similar processes to calculate all additional costs relating to the installation, general commissioning of the plant, and all costs relating to the buildings and land. The factors used were chosen for a process involving both fluids and solids. These can be seen in **Table 17**. All of the aforementioned costs

comprise the Fixed Capital (FC) of the project, while the Working Capital (WC) which is the capital needed to initiate the process is calculated as a fraction of the fixed capital, with a factor chosen for petrochemical processes. The sum of the Fixed Capital and the Working Capital comprise the Total Capital Investment (TCI) required for the process.

Table 17: Summary of costs relating to the capital investment of the project. (Dimian, 2003)

<u>Capital Investment</u>	
Fixed Capital	
<u>Direct Costs</u>	
Purchased Cost of Equipment (PCE)	
Installation	0.39·PCE
Instrumentation & Control	0.13·PCE
Yard improvement & Land	0.16·PCE
Building & Electrical	0.39·PCE
Service, Utility facilities & Piping	0.86·PCE
<u>Indirect Costs</u>	
Construction	0.34·PCE
Engineering, Supervision & Contractor fee	0.50·PCE
Contingency	0.36·PCE
Working capital	0.15·Fixed Capital
<u>Total capital investment</u>	Working Capital & Fixed Capital

Following the calculation of all costs relating to the capital investment, the calculation of the operating costs of the plant is necessary. Following the methodology of Dimian, the annual cost of raw materials is calculated based on the needed amounts multiplied by the price per unit. The total annual revenue (S) is calculated by multiplying the total annual amount produced by all products with their respective price per unit. Similarly the cost of utilities is calculated by multiplying the required amount of each utility with its respective cost. All calculated costs are calculated on an annual basis. Additionally, Dimian provides guidelines for the calculation of workers and shifts needed based on the process equipment, which in the present study was estimated to be 5 shifts with 3 workers working each shift, amounting to a total of 15 shifts to be

considered in the cost. Since there is a large variation of the salary of a plant operator in the United States, an average salary of 28,000\$/y was taken in the calculations (Indeed.com, 2021).

To calculate the total operating costs, besides the plant operators and the necessary supervision costs, annual costs of repairs and maintenance, supplies and research and development, as well as some additional costs need to be considered on an annual basis. Although there is the option in the proposed methodology to consider the plant depreciation in the total operating costs, in the present study the depreciation is considered separately in a later stage. The sum of these costs adds to the Total Operating Costs (TOC). The TOC is also used to calculate the production cost of methanol by a simple division of the produced annual CH₃OH amount with the TOC. The Total Operating Costs are listed below in **Table 18**.

Table 18: Total operating costs and methanol production cost. (Dimian, 2003)

<u>Operating Costs</u>	
Raw Materials	Annual amount · price
Utilities	Sum (Annual utility amount · price)
Operating Labour (OL)	Plant operators · salary
Supervision	0.2 · OL
Repairs/Maintenance	0.05 · FC
Operating supplies, Lab charges, Plant Overhead	0.66 · OL
Equipment insurance	0.01 · PCE
Sales, Administration, Research & Engineering	0.025 · S
Total Operating Costs (TOC)	Sum (Operating costs)
Methanol Production Cost	TOC/CH₃OH annual amount

The final part of the economic analysis protocol was developing the right economic indicators for the evaluation of the project. The profitability analysis is based on taking into consideration the lifetime of the plant, the decline of value of all assets over time and the comparison of the profits made by selling products against the initial investment and operating costs. The calculations, thus, start with the estimation of revenues, S, which was explained previously. The depreciation of assets is considered to be linear, calculated as the fixed capital cost split over the lifetime of the plant,

which for a project like the present one is considered to be at least 20 years, resulting in a 5% depreciation per year.

The net profit before tax is calculated by considering all annual expenses, including the total operating costs and the annual depreciation. To obtain a net profit after tax, a typical tax of 35% is considered. The annual cash flow is calculated as the sum of the net profit after tax and the annual depreciation. The present value of the plant in a given year can then be calculated by also considering an interest rate, which was taken to be 10%. The net present value is calculated as the sum of all present values of the years prior to a given year, from which the total capital investment is subtracted. The payback time for the project is the time needed to recover the total capital investment, while the key indicator, Return of Investment (ROI) is calculated as the division of the net profit after tax by the total capital investment.

It should be noted that a 3-year period was accounted for the complete building and setup of the plant from zero to the first start-up point. The methodology of the profitability analysis is summarised in **Table 19**.

Table 19: Profitability analysis key indicators. (Dimian 2003)

<u>Profitability Analysis</u>	
Sales Revenue (S)	Products annual amount · price
Depreciation (D)	Fixed Capital/Plant lifetime
All Expenses (AE)	Total Operating Costs + Depreciation
Net Profit (before tax) (NP _b)	Sales Revenue – All Expenses
Net Profit (after tax) (NP _a)	NP _b – (NP _b · t)
Cash Flow (CF)	NP _a + D
Present Value (in year n) (PV _n)	CF _n /(1+i) ⁿ
Net Present Value (in year n) (NPV)	$\sum_{n=1}^{n=T} PV_n - TCI$
Payback time	Time to break-even point (recovery of TCI)
Return of investment (ROI)	NP _a /TCI

7.3 ASPEN process design

This section serves to provide with an overview of the process, explaining all of the different steps from the utilisation of raw materials to the suggested catalyst looping technology and the separation of products in high purity. The design of the fluidised bed reactors, as well as all separation units will be discussed in detail.

7.3.1 Process overview

As previously mentioned, the main challenge of the lab-scale DMTM process over the 3% CuMOR was the batch-like nature in which the reaction took place. Generally, batch processes are not favorable for industrial application as they involve numerous shutdowns and start-ups of the process, which are associated with large downtimes in production and high operational costs. To tackle this issue, the suggested process employs a simple yet effective concept of fluidised beds in series, which achieve a continuous, looping operation by cycling the catalyst between reactors, thus allowing all steps of the laboratorial process to take place continuously. Specifically, each reactor is responsible for facilitating each of the three laboratorial process steps. It should be noted that the whole process was modelled with Aspen Plus v11, employing the NRTL method, which is suitable for both polar and non-polar molecules.

The fluidised beds in series comprise the first section of the process. The first reactor in the series, R-101, facilitates the pre-adsorption of CH_4 onto the catalytic active sites. A fresh CH_4 stream joined by any recycled CH_4 from the exit of R-101 is fed continuously to the reactor throughout the process. Heat exchanger E-101 ensures a constant temperature of 200°C for the methane stream entering R-101, which operates isothermally at 200°C . Following CH_4 adsorption, the catalyst moves forward to reactor R-102, in which the DMTM reaction takes place. A fresh, dry helium stream mixes with the recycled helium of the process and a water stream, to form a wet helium stream with the exact composition as the laboratorial process. It should be noted that the choice of helium as a carrier gas was made in an attempt to create a process which exactly replicates the lab-scale process developed in the present study. In practice the choice of helium would be unlikely, and instead another gas like N_2 or Ar would be chosen. However, the choice of a different carrier gas should be complemented with additional experiments to assess the effect of the gas on the final CH_3OH productivity.

The wet helium stream passes through heat exchanger E-102 to reach 200°C and enters R-102, which operates isothermally at 200°C. CH₃OH is formed and desorbed in R-102, while the catalyst is hydrated in the process. Following the reaction in R-102, the spent catalyst proceeds to R-103, which is the reactor responsible for the regeneration of the catalyst. It is reminded that the reactivation of catalyst in laboratorial conditions took place in a temperature programmed fashion up to 400°C. Similarly, the regeneration of the catalyst in R-103 takes place under a temperature of 400°C, under a constant flow of air, which is fed continuously in the process. It should be noted that air is recycled from the exit of R-103 and meets the fresh air feed. E-103 ensures that air entering R-103 is heated to 450°C. The looping of the catalyst between reactors takes place by utilising gravitational forces. More specifically, each fluidised bed reactor is equipped with several cyclones at the top part, which collect the catalyst and move it to the bottom part of the next reactor in the sequence.

As mentioned, the reactor of highest interest is R-102, where the DMTM takes place. The product stream exits R-102 in the vapor phase. The stream consists mainly of He (~0.88 molar fraction), while H₂O, CH₃OH and H₂ exist in the stream in smaller amounts. Since the fraction of the inert helium is so large, it is naturally not favorable to handle the entirety of this product stream in further units of the process, as this would lead to unnecessarily high utility costs. As a result, it is deemed necessary to introduce a splitter S-1, which redirects a large portion of the product stream back to R-102, so that smaller amounts of the product stream are handled by the separation sections downstream. Specifically, S-1 redirects 98% of the total mass entering it to recycle, where it meets with the fresh wet helium stream. It should be noted that during steady state operation, molar fractions of products are so small in the feed entering R-102, that they are considered to have negligible impact to the overall kinetics of the reaction.

In order to achieve an efficient separation of CH₃OH in high purity, while minimising utility expenses, it is essential to separate a large fraction of helium from the aforementioned stream, before the final product separation. Since the stream comprises of He, H₂, CH₃OH and H₂O, the large difference in boiling points between He & H₂ and CH₃OH & H₂O can be used for an easy physical separation. To achieve this, a combination of a sufficiently high pressure and low temperature needs to be met, for a subsequent phase separation. Multi-stage compressor C-101, which is made of a series of compressors and intercoolers, elevates the pressure of the stream to

50bar, while keeping the temperature of the stream to 36°C. The presence of intercoolers, as well as heat exchanger E-104 before C-101 is needed to ensure that the maximum discharge temperature of the streams exiting the compressors will not exceed the allowed 177°C (350F) (Gallick, Phillippi & Williams, 2006). The stream exiting C-101 at 36°C and 50bar, as well as any liquid generated from the intercoolers of C-101 are sent to V-101, where physical separation takes place.

The stream leaving the top of V-101 exists in the vapor phase and comprises mainly of helium (~0.95 molar fraction), with a small fraction of hydrogen, while only trace amounts of methanol and water are present in the stream. The stream is led to hydrogen separator X-101, which achieves a 80% separation of hydrogen at a high purity of >99.99%, while the remaining stream proceeds to mix with the stream recycled by the splitter S-1.

The stream leaving the bottom of V-101 in the liquid phase, comprises of almost equimolar parts of H₂O (~0.47 molar fraction) and CH₃OH (~0.50 molar fraction), with small amounts of He and H₂ present in the stream. The stream is led to the distillation column T-101, which operates at 9 bar and separates the mixture, with water being the bottom product separated at a high purity (>99.5%). Since He and H₂ are present in trace amounts in the feed of the column, it is necessary to use a partial condenser at the top of T-101. The partial condenser ensures the condensation and collection of a large portion of the methanol present in the feed stream at high purity (>99.9%), while the trace amounts of He and H₂ along with a small fraction of CH₃OH are led to the physical separator V-102, which acts as an additional equilibrium step, to be further separated. The largest fraction of CH₃OH present in the stream is collected as a liquid product from the bottom of V-102 at high purity (>99.99%) and meets with the top product of T-101 to form the final product. The remaining trace amounts of CH₃OH, He and H₂ escape from the top of V-102 to the atmosphere. The complete process flowsheet can be seen in **Figure 52**.

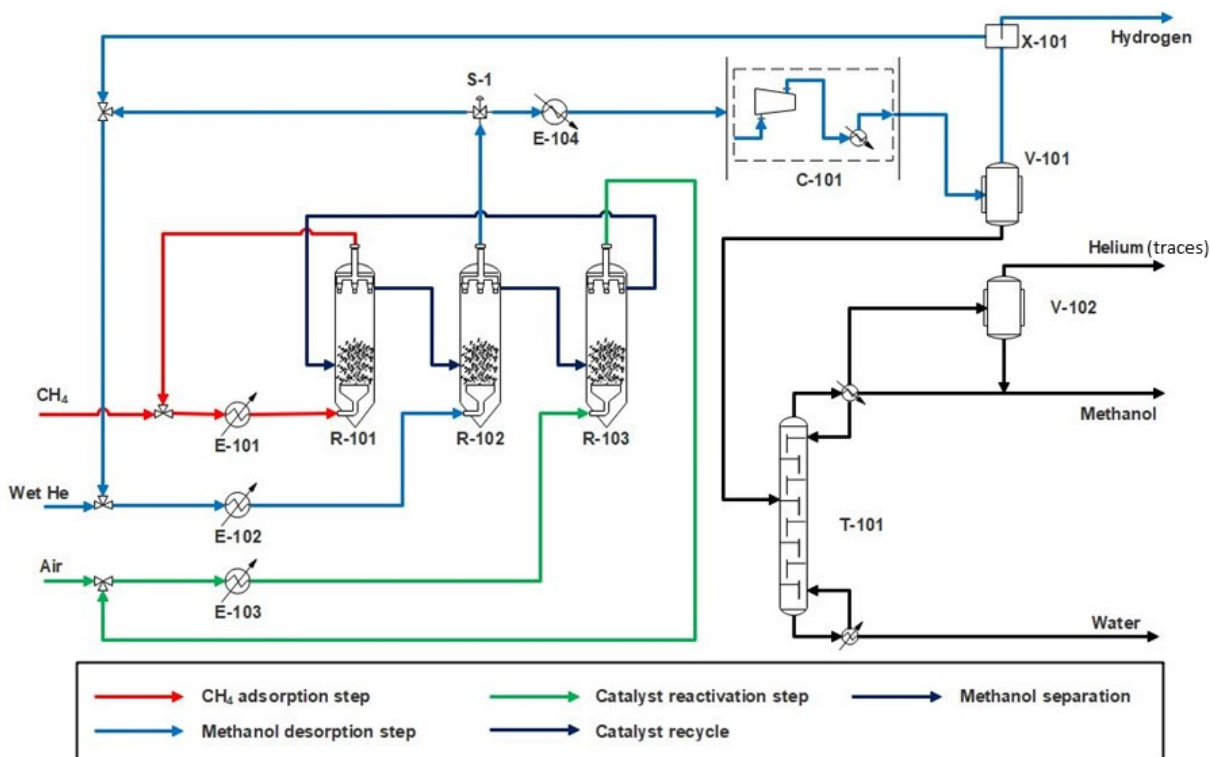


Figure 52: Complete process flowsheet of the DMTM over a 3% CuMOR catalyst industrial concept.

7.3.2 Fluidised bed reactors design

The fluidised bed reactors R-101, R-102, R-103 were manually designed following a simple protocol. The calculations for the reactor design were based on the selection of a catalyst flowrate of 20t/h of catalyst, looping through the three reactors. Additionally, rules of thumb on the design of fluidised bed reactors were used, according to Jördening and Buchholz, who suggested that typical length/diameter ratios of fluidised bed reactors were in the range of 2-5, while 500m³ was suggested as the maximum typical fluidised bed reactor size. The residence time used for each reactor, which refers to the solid particles as they loop between reactors, were taken from the work of Tomkins et al.. It should be noted that the pressure drop inside reactors, as well as the minimum fluidisation velocity, were calculated by Aspen with the aid of the Ergun equation.

Employing all above information, the design of each reactor happened in a series of steps. The bed mass is calculated simply by multiplying the catalyst flowrate (20t/h) with the residence time for each reactor. Considering a bed voidage of 0.5 during fluidisation and the amount of bed mass, dimensions are chosen for the reactor (height, diameter) based on the aforementioned rules of

thumb to accommodate the calculated bed mass. All input is set in Aspen and the pressure drop and minimum fluidisation velocity is calculated by the software.

It is reminded, that a black box method is used to simulate kinetics, in which a target rate of production is set in Aspen. Thus, the target yield in the first reactor is calculated by a multiplication of the catalyst flowrate with the target yield given by literature, to obtain the target CH₃OH production rate. According to stoichiometry, this target production rate of CH₃OH set inside the first reactor exactly matches the consumption rate of CH₄, which has to be re-supplied by the fresh feed during steady-state operation. It should be noted that the recycle streams, as well as their mixing with a fresh feed re-supply, lead to an initial dynamic operation of the system, which is accounted for and simulated with the use of tear streams in Aspen. After initial convergence of the simulation with the aid of tear streams, the simulation then operates in steady state, properly accounting for all recycles. During steady state, the fresh feed streams supply to the process the masses of each component which are being consumed during reaction or, in the case of helium, removed from the process during separation of the product.

The sequential reactor design protocol mentioned above is applied for the design of all three fluidised bed reactors. The details of the fluidised bed reactors is given in the collective **Table 20**, which can be seen below.

Table 20: Summary of fluidised bed reactor design specifications.

	R-101	R-102	R-103
Reactor length	10.0m	14.0m	10.0m
Reactor diameter	2.0m	2.8m	2.3m
Bed mass	10000kg	40000kg	20000kg
Residence time	0.5h	2.0h	1.0h
Min. fluidisation v	0.36m/s	2.21m/s	1.26m/s
Conditions	200°C, 36bar	200°C, 2bar	450°C, 2bar
Volume	31.4m ³	86.2m ³	41.5m ³

It is reminded that the reactions and materials defined inside reactors R-101, R-102 and R-103 are representative and not directly equal to the physical materials of the laboratorial process. This leads to a discrepancy inside the first reactor, R-101, where the virtual methanol product is produced in the form of the representative material $[Cu_2O + CH_3OH]$, which represents the CuMOR with the

formed methoxy species after CH_4 absorption. However, in the Aspen simulation the CuMOR (represented by Cu_2O) and the methoxy species (represented by CH_3OH) do not exist in the same stream, as CH_3OH is produced in the gas phase and Cu_2O is looped as a solid between reactors. In order to tackle this issue, a virtual separation unit is set after R-101, which separates all CH_3OH from the gas phase of the reactor outlet and is led to mix directly with Cu_2O to form the representative material $[\text{Cu}_2\text{O} + \text{CH}_3\text{OH}]$.

Additionally it should be noted that in order to account for pressure drop inside the reactors, a pressure of 2bar is employed, while the operation of the reactors is assumed to happen at roughly atmospheric pressure with negligible impact on the simulation results.

7.3.3 Separation units

Downstream of the reaction section of the flowsheet, a series of simple separations ensure the isolation of products (H_2 and CH_3OH) in high purities, while all unutilised raw materials are recycled back to the process.

Multi-stage compressor C-101 and phase separator V-101

As previously explained, a small fraction of the stream leaving reactor R-102 is led to the multi-stage compressor C-101 and subsequent phase separator V-101 for physical separation of helium and hydrogen from H_2O and CH_3OH . To achieve a physical separation, a sufficiently high pressure and low temperature are needed. Specifically, the separator operates at 50bar and 36°C . To achieve these conditions, a series of 5 compressors in series is employed, which operate isentropically with an equal compression work. Before C-101 and between compressors of C-101, heat exchangers are needed to cool down the streams entering each compressor, to comply with the inlet specifications of the compressor and avoid overheating. Cooling water is used as the cooling utility, with an inlet T of 20°C and an outlet T of 25°C , hence providing a cooling down to 36°C in the inter-streams. Small fractions of the streams condensing between intercoolers, are sent directly to phase separator V-101. The need for several compressors and intercoolers arises, as explained, by the inability to exceed 177°C as the maximum discharge temperature of compressors. Subsequently, the vapor stream leaving the last compressor at 36°C enters the phase separator, where He and H_2 escape the top of the vessel, carrying along them only trace amounts of methanol

and water in the vapor phase. The bottom of V-101 exists in the liquid phase in almost equimolar amounts of water and methanol and only trace amounts of He and H₂.

Hydrogen Separator X-101

The stream leaving the top of V-101 contains a considerable amount of H₂, which needs to be isolated and sold at high purity as one of the process products. However, the molar fraction of H₂ in the stream is particularly small (~4.8%) and its separation from the stream can be difficult. To simplify the separation, a commercially available hydrogen separator is used, which can separate hydrogen from streams with a typical yield of 75-85%. The H2RENEW H2R by Skyre Inc. can isolate H₂ from a stream with a purity of up to 99.99% by electrochemical hydrogen compression. Considering the product specifications and the quantity of hydrogen in the stream in interest, only a single piece is capable of hydrogen separation for the process at steady state. To replicate the hydrogen separator in the Aspen simulation, a simple virtual separator with a 80% efficiency and a separation product of 99.99% purity is designed. (SKYRE Inc., 2020)

Distillation column T-101 and phase separator V-102

The final separation step of the process, which aims to isolate the product CH₃OH in high purity with minimal losses, is the combination of distillation column T-101 and phase separator V-102. An almost equimolar mixture of water and methanol containing traces of H₂ and He enters the 35-stage distillation column at stage 30, which is the optimal feed stage. The distillation column is operated at 9bar, with the reboiler operating at 175°C and the condenser operating at 36°C, with cooling water as the cooling utility of choice. Due to the presence of traces of H₂ and He in the feed stream, it is necessary to employ a partial condenser, which achieves the condensation of the majority of CH₃OH present at the top, as the top liquid product, while the bottom product of the column is water. A design specification is set in Aspen for a 99.9% purity of the top distillate product, while a 99.5% purity is set for the bottom product. The specifications are met by a manipulation of the distillate rate and the reflux ratio of T-101, the final values of which are 2.12kmol/h and 3, respectively. The stream exiting the top of the condenser in the vapor phase is comprised by helium (~0.58 molar fraction) and CH₃OH (~0.41 molar fraction), with small fractions of H₂ and H₂O. The stream enters V-102 which is a physical phase separator at 9bar, operating practically as an additional equilibrium stage. Pure methanol (>99.99% purity) is collected as the liquid bottom product of V-102 and is led to meet with the liquid distillate of T-

101 to form the final methanol product, while the top product of V-102, comprised mostly of helium, escapes to the atmosphere.

7.4 Process optimisation

Basic optimisation was performed on the process to minimise operational and capital costs. Nan Hu is kindly acknowledged for his work in the optimisation of the split ratio and the optimisation of the separation pressure of phase separator of V-101 (Hu, 2020). The present section will lay out the methodology of optimisation of different parameters of the process as well as the results of optimisation. It should be noted that optimisations took place in a sequential order, as they appear downstream of the reactor. Specifically, the split ratio of S-1 was optimised, the optimal split ratio was used to optimise the separation pressure of V-101, and the optimal separation pressure of V-101 was used to optimise the number of stages, the feed stage and the separation pressure of T-101.

7.4.1 Split ratio

As mentioned the first target of optimisation was the split ratio of splitter S-1. The split ratio of S-1 has a large impact on the whole process, as it dictates the amount of material to be handled by all units that follow it, as well as the amounts of materials recycled through the process. Understandably, the split ratio of S-1 has a global impact on the process. As a result, the optimisation of the split ratio took place by setting a global optimisation objective and finding the minimum value. Specifically, to account for the impact of the split ratio on the capital and operational cost, an objective was set which included the annualised capital and operational costs of the process, as well as the CH₃OH produced in a year. It should be noted that the annualised values were the total values divided by the 20 years of plant lifespan. The objective based on which the optimisation of the S-1 split ratio took place can be seen below:

$$\text{Global objective } A = \left(\frac{\text{annualised capital cost} + \text{annual utility cost}}{\text{annual CH}_3\text{OH production}} \right) \quad (7.5)$$

Another parameter considered in the optimisation was the fact that the split ratio should be such at a minimum, that solid entrainment would not happen due to an excessive flow of gas inside of reactor R-102. Several split ratios were investigated ranging from 0.02 to 0.10 with a step of 0.02, while also a split ratio of 1.00 was investigated. Based on the aforementioned constraint, the

optimisation via minimising the global objective of Equation (7.5), showed that a decrease of the split ratio was beneficial to the overall economics of the process, with the value of 0.02 being the minimum acceptable value to avoid solid entrainment in R-102. As a result, a split ratio of 0.02 was used for the simulations. (Hu, 2020)

7.4.2 Separation pressure and multi-stage compressor

Another point of interest in the optimisation of the process was the separation pressure required in the phase separator V-101. The separation pressure of V-101 would affect the number of compressors and intercoolers needed, which in turn would affect the amount of electricity and cooling water utilities costs, as well as the capital cost of C-101 which is used to raise the pressure before V-101. Another thing to be considered in the optimisation of the separation pressure was the methanol recovered from the bottom product of V-101, which is further passed to distillation column T-101 for separation. The capital cost of V-101 would remain unchanged in every scenario so was not considered in the optimisation.

A local objective was set for the optimisation of the separation pressure required in V-101, which took into consideration all the aforementioned parameters. The optimisation objective set for V-101 can be seen below:

$$\text{Local objective } A = \left(\frac{\text{annualised compressor cost} + \text{annual utility cost}}{\text{CH}_3\text{OH recovery rate}} \right) \quad (7.6)$$

The optimisation of the objective shown in Equation (7.6) revealed an almost linear increase of the annualised capital cost with increasing separation pressure, as well as an increase in methanol recovery rates. However, the methanol recovery rate started displaying a plateau after 50bar. The investigated objective displayed a minimum at the separation pressure of 50bar, which was used as the optimal value in further simulations. (Hu, 2020)

7.4.3 Distillation column

An exhaustive approach was taken for the optimisation of distillation column T-101. More specifically, three parameters were optimised via a series of steps, the number of stages, the feed stage and the separation pressure of the column. Three objectives were set for the optimisation of the 3 parameters. Different pressure scenarios were investigated with the pressure ranging from 1-10bar, with a step of 1bar. For each of the scenarios, a different amount of stages was simulated,

from 20-45 stages with a step of 5. A sensitivity analysis was performed on each combination of pressure and number of stages, which changed the feed stage through all stages of the column, from the first to the last. The sensitivity analysis returned the utility required in the column, which was the first objective considered for the selection of the optimal feed stage of each scenario. This objective can be seen below:

$$\text{Local objective A} = (\text{utility need of column}) \quad (7.7)$$

Having identified the optimal feed stage of each different pressure/number of stages combination, the next step of the optimisation was the identification of the optimal number of stages for each T-101 pressure scenario investigated. To assess that, another objective needed to be defined, which would take into consideration the capital cost of T-101 for each different number of stage scenario, as well as the utility costs in the reboiler and condenser in each case. The objective defined for the optimisation of the number of stages for each pressure scenario can be seen below:

$$\text{Local objective B} = (\text{annualised capital cost} + \text{annual utility cost}) \quad (7.8)$$

The minimisation of local objective B provided the optimal number of stages for each different pressure scenario. The final optimisation step was the identification of the optimal separation pressure for distillation column T-101. The targets of the optimisation would be the minimisation of the capital and operational costs of the column, while also another important parameter to be considered was the methanol lost from the top of the subsequent phase separator V-102 in each case. The parameters considered in objective C, used for the final optimisation can be seen below:

$$\text{Local objective C} = \left(\begin{array}{l} \text{annualised capital cost} + \\ \text{annual utility cost} + \\ \text{cost of methanol lost per year} \end{array} \right) \quad (7.9)$$

Simulating all different pressure scenarios with the optimal number of stages and optimal feed stage for each case provided with conclusive answers regarding the ideal separation pressures. **Table 21** displays the collective results of the different scenarios investigated.

Table 21: Collective optimisation table of distillation column T-101.

	Optimal stage	Optimal feed stage	Optimal reflux ratio (-)	Annual utilities (\$/y)	Annualised capital cost (\$/y)	Annual CH₃OH lost (\$/y)	Objective C (\$/y)
1 bar	25	19	1.83	4350	5360	120700	130410
2 bar	30	24	1.66	4260	6900	50070	61230
3 bar	30	24	2.02	4960	6900	31360	43220
4 bar	30	24	2.41	5670	6870	22710	35250
5 bar	35	29	1.95	4990	8300	17720	31010
6 bar	35	29	2.17	5430	8300	14480	28210
7 bar	35	29	2.42	5880	8330	12200	26410
8 bar	35	29	2.69	6390	8330	10520	25240
9 bar	35	30	3.01	6980	8340	9220	24540
10 bar	40	34	2.38	5970	12540	8180	26690

As seen in **Table 21**, an increase in separation pressure of T-101 led to a more efficient separation and as a result, a decrease in the annual quantity of CH₃OH lost through the top of V-102. However, the increase of separation pressure in T-101 also led to increasing capital costs, as expected, accompanied by an increase of utility costs for the cases where the reflux ratio of the column was high. Objective C gave a definitive answer for the optimal separation pressure in T-101, showing a minimum value for the case of 9bar, where the separation of CH₃OH was efficient, while at the same time capital and utility costs were kept to relatively low values. This can be also seen graphically in **Figure 53**.

Following the optimisation of separation pressure, a separation pressure of 9bar with a reflux ratio of 3 was used for distillation column T-101 for all simulations.

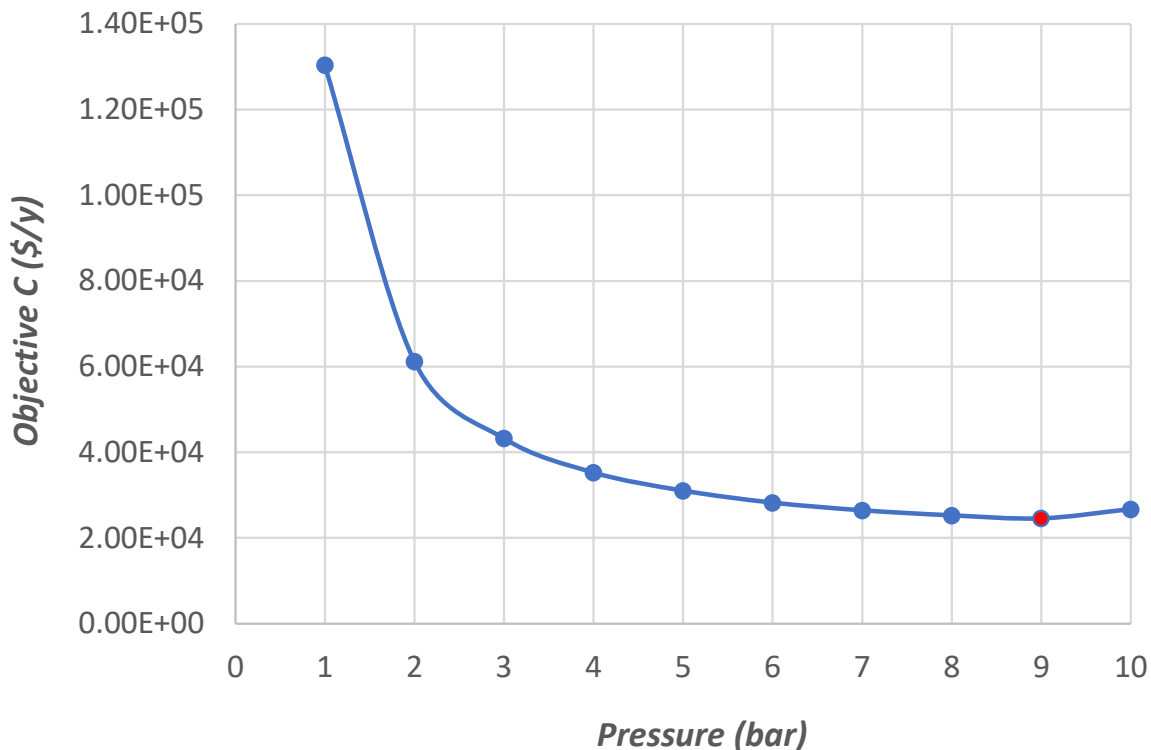


Figure 53: Optimisation of separation pressure of T-101.

7.5 Optimised process results

Following the optimisation of the split ratio of S-1, the separation pressure of V-101 and the various parameters of distillation column T-101, the Aspen simulation was run and the full profitability analysis protocol was applied on the simulation results. The present section serves to provide a summary of the results regarding the process and economics, so that an overview of profitability can be achieved.

Table 22 presents the purchased equipment cost of each unit of the process. As expected, the major capital costs of the process arise from the custom-made fluidised bed reactors, which need to be adequately large to facilitate several tons of the catalyst. In fact, the three reactors represent more than 90% of the total equipment cost. Another considerable contributor to the capital cost is the multi-stage compressor C-101, which is comprised by several compressors and intercoolers.

Table 22: Equipment purchased cost for the optimised DMTM process.

Equipment	Capital Cost (\$)
C-101	1,515,000
E-101	9,000
E-102	15,000
E-103	110,000
E-104	11,000
R-101	5,021,000
R-102	8,573,000
R-103	5,823,000
T-101	167,000
V-101	25,000
X-101	21,000
V-102	16,000
Total	21,306,000

Table 23 presents the annual utility requirements of each unit of the process. As expected, a considerable amount of electricity is needed to power the compressors of C-101, which is the main contributor to the electricity needs of the process. The hydrogen separator X-101 is the only other unit that requires electricity for its operation. While relatively small amounts of energy are required to be supplied by high pressure steam to heat exchanger E-102 which pre-heats the feed of R-102 and to the reboiler in T-101, a large amount of energy is consumed by heat exchanger E-103. This is also expected, since a large amount of air needs to be heated up to 400°C to regenerate the catalyst in R-103. The energy required to pre-heat the air needs to be supplied exclusively by fired heat to achieve such a high temperature requirement. Finally, cooling water is required by several units of the process, with the highest need being represented expectedly by reactor R-101 and the intercoolers of C-101. Reactor 101 needs to operate isothermally at 200°C, while hot catalyst is being continuously passed to it at 400°C by reactor R-103, which is responsible for catalyst regeneration. As a result, a considerable amount of cooling utility is required to ensure a 200°C operation of R-101.

Table 23: Annual utility needs per unit of the process.

	Electricity (kW)	High P Steam (kW)	Fired heat (kW)	Cooling water (kW)
C-101	229	-	-	273
E-101	-	4	-	-
E-102	-	150	-	-
E-103	-	-	660	-
E-104	-	-	-	58
R-101	-	-	-	644
R-102	-	-	-	-
R-103	-	-	-	-
T-101	-	102	-	97
V-101	-	-	-	-
X-101	43	-	-	-
V-102	-	-	-	-
Sum	272	256	660	1072

Table 24 presents the annual costs of utilities based on their annual consumption. Interestingly, although the highest net energy requirement is covered by cooling water, cooling water represents the lowest annual utility cost per year, as it is a cheap utility. Similarly, the considerable amount of energy supplied by fired heat is a relatively small fraction of the total utility cost. On the other hand, electricity and high pressure steam represent the highest fraction of utility costs by a considerable margin, with electricity being the most expensive utility. In fact, electricity costs represent more than 60% of the total utility cost of the process.

Table 24: Annual utility costs of the process.

Utility	Annual consumption (kW)	Annual cost (\$)
Electricity	272	148,000
Fired heat	660	16,000
High pressure steam	256	71,000
Cooling water	1072	6,000

Aside of the purchased cost of equipment, it is essential for the profitability analysis to calculate all costs associated with the building of the plant, including the cost of land, the commissioning

etc. as explained in a previous section. The results of the profitability analysis regarding capital costs, including fixed, working and total capital investment are given in **Table 25**.

Table 25: Total capital investment and associated capital costs.

<u>Capital Investment</u>	
Fixed Capital	88,000,000\$
<u>Direct Costs</u>	
Purchased Cost of Equipment (PCE)	21,306,000\$
Equipment installation	8,310,000\$
Instrumentation & Control	2,770,000\$
Yard improvement & Land	3,410,000\$
Building & Electrical	8,310,000\$
Service, Utility facilities & Piping	18,324,000\$
<u>Indirect Costs</u>	
Construction	7,244,000\$
Engineering, Supervision & Contractor fee	10,653,000\$
Contingency	7,670,000\$
Working capital	13,200,000\$
<u>Total capital investment</u>	101,200,000\$

Following the building of the plant, all costs regarding the annual operation of the plant were calculated, including the amount and cost of required raw materials and the revenues from all products (methanol and hydrogen). These can be seen in **Table 26**. As expected, the main amount of revenues is generated by selling CH_3OH , while some additional revenues are generated from H_2 sales. It should also be noted, that in comparison to utility and capital costs, the cost of raw materials is almost negligible.

Table 26: Annual amount and cost of raw materials and revenues of product sales.

Item	Annual amount	Annual cost/revenue (\$)
CH₄ (raw material)	14,488kmol	38,000
Process H₂O (raw material)	506m ³	3,000
He (raw material)	58m ³	2,000
CuMOR (raw material)	35t	18,000
CH₃OH (product)	456,400kg	1,990,000
H₂ (product)	28,380kg	256,000

To have a better overview of the annual operating costs associated with the production of CH₃OH in the suggested process, the summary of all operational costs is presented below.

Table 27: Summary of operating costs of the DMTM under current catalyst performance.

<u>Operating Costs</u>	
Raw Materials	60,000\$
Utilities	241,000\$
Operating Labour (OL)	420,000\$
Supervision	84,000\$
Repairs/Maintenance	4,400,000\$
Operating supplies, Lab charges, Plant Overhead	257,000\$
Equipment insurance	213,000\$
Sales, Administration, Research & Engineering	56,000\$
Total Operating Costs (TOC)	5,731,000\$/y
Methanol Production Cost	12.6\$/kg

As seen in **Table 27**, the operating costs are prohibitively high for the current performance of the catalyst and the plant capacity investigated. It is seen by the methanol production cost, that the cost to produce a kg of methanol is as high as 12.6\$, which is in fact a much higher cost than the actual selling price of CH₃OH and far from competitive with current alternatives for methanol production which range from 200-800\$/mt (Kajaste et al., 2018). As a result, such a process would never be able to generate profit.

The findings of the profitability analysis listed in **Table 27** are further reinforced with an investigation of other economic indices. Specifically, the calculation of cash flow, net profit after tax, as well as the estimated pay-back time and rate of return of investment give a conclusive picture of the profitability of the process. These economic indices are summarised and presented below in **Table 28**.

Table 28: Economic indices of interest for the profitability of the DMTM.

Economic index	Value
Sales revenue	2,245,000\$/y
Net profit after tax	-5,125,000\$/y
Cash flow	-726,000\$/y
Rate of return of investment (ROI)	-5.1%
Estimated pay-back time	-140y

The investigated economic indices presented in **Table 28** give a definitive answer to the potential of a DMTM process with the current performance of the catalyst. Specifically, due to very high capital and operational costs leading to a high production cost of methanol at the suggested plant capacity, the project could never be profitable. Although there are some sales revenues from CH₃OH and H₂, the process generates negative profits, with a return of investment being impossible in any amount of time. As a result, the process is deemed unprofitable and economically infeasible, given the current performance of the catalyst.

7.6 Heat integration

Heat integration is an essential part of any process design, opening up possibilities for considerable utility cost savings. Specifically, heat integration and appropriate heat exchanger network design utilise the energy of high-enthalpy streams while also cooling them down, to heat up cold streams that require heating. Although Aspen provides the option for a heat integration, it would not be able to include the inter-streams of C-101, while also the accuracy of the heat integration via the routines of Aspen might not be accurate overall. The entire heat integration and heat exchanger network design was manually carried out, including all streams of the process (C-101 inter-streams, reboiler and condenser streams of T-101 etc.).

The procedure that was followed included initially identifying via the Aspen flowsheet the source temperature (T_S) and the target temperature (T_T) of each stream and the calculation of the temperature difference between them (ΔT). Another piece of information collected by the streams was the mass flowrate ($\dot{m}$), as well as the enthalpy change (Q or ΔH) that took place in any heat exchange they participated in. The mass flowrate and the enthalpy change were used to calculate the heat capacity of each stream in interest, which was then directly used in the heat integration process.

Depending on the relationship between T_S and T_T of each stream, the streams were classified as Cold or Hot streams. The summary of the hot and cold streams of the process, along with other information regarding each stream, are presented in **Table 29**.

Two important points should be noted regarding the accurate extraction of stream information in the T-101 condenser and reboiler. The first thing to note is that only phase change takes place in the reboiler without any heating of the stream that enters it. In order to ensure that this assumption was correct, steam table data were used to obtain the latent heat of vaporisation of water (the bottom product is >99.5% purity H_2O) at the given conditions. Using the latent heat of vaporisation and the mass flowrate of the stream entering the reboiler, as given by Aspen, the heat required for only the vaporisation of this stream was calculated and compared to the heat duty of the reboiler as given by Aspen. Indeed, the calculated heat required for vaporisation of the stream entering the reboiler matched the reboiler duty given by Aspen.

Table 29: List of the process streams for heat integration.

Stream	Type	T _s (°C)	T _T (°C)	CP (kW/°C)	Q/ΔH (kW)
E-104	Hot	197.2	36.0	0.36	57.8
C-101e	Hot	177.2	36.0	0.34	47.6
C-101d	Hot	175.3	36.0	0.36	50.3
C-101c	Hot	172.9	36.0	0.39	53.8
C-101b	Hot	170.2	36.0	0.44	58.8
C-101a	Hot	168.3	36.0	0.47	62.1
T-101 cond. a	Hot	132.2	36.0	0.11	10.8
V-101	Hot	36.0	36.0	- (phase change)	218.9
T-101 cond. b	Hot	36.0	36.0	- (phase change)	85.7
Stream	Type	T _s (°C)	T _T (°C)	CP (kW/°C)	Q/ΔH (kW)
E-103	Cold	385.2	450.0	10.19	660.0
E-102	Cold	191.8	200.0	18.20	149.5
E-101	Cold	199.9	200.0	40.00	4.0
T-101 reb.	Cold	175.2	175.2	- (phase change)	101.5

Additionally, it should be taken into consideration that the heat duty of the partial condenser is distributed to the cooling down of the entirety of the stream entering it as well as the condensation of a part of it. In order to account for this, the condenser stream is broken down into two “dummy” streams, “T-101 cond. a” representing the cooling down and “T-101 cond. b” representing the phase change. To calculate the heat required to condense “T-101 cond. b”, a virtual unit was used to condense a known quantity of the distillate methanol. The heat duty of the virtual unit and the mass flowrate of the stream was used to calculate the latent heat of condensation of methanol at the given conditions. The latent heat of condensation of methanol under the given conditions was used to calculate the heat duty required to condense “T-101 cond. b”, considering its mass flowrate given by Aspen. The second dummy stream was then calculated simply as $Q_{\text{total}} = Q_{\text{cool}} + Q_{\text{cond}}$. The heat integration was performed with a minimum allowable temperature approach of $\Delta T_{\text{min}} = 10^\circ\text{C}$. The data of **Table 29** was used to compile and draw the composite curves, given below in **Figure 54**. As seen in **Figure 54**, the heat integration of the process has only marginal potential for utility savings. In fact, a heat integration potential of just **4.3kW** is calculated for the process. The problem for heat integration arises by the fact that although the hot and cold stream energy needs

are relatively similar ($Q_{\text{cold}}=641.5\text{kW}$ and $Q_{\text{hot}}=910.7\text{kW}$), the T_S and T_T of the hot and cold streams exist in completely different temperature regions. This can be better explained by the design of a heat exchanger network for the heat integration of the process, which can be seen below in **Figure 55**.

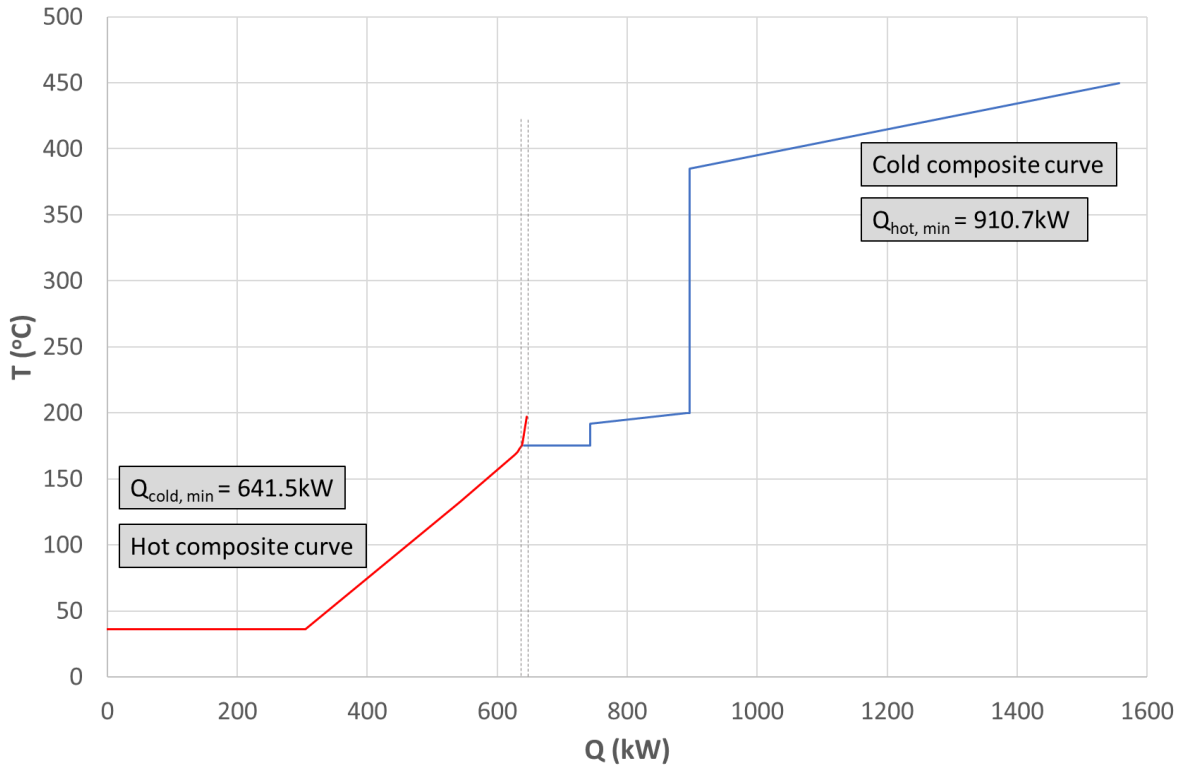


Figure 54: Hot and cold composite curves.

Figure 55 gives a good overview of the challenge for heat integration in the current process. As seen in **Figure 55**, the cold streams of the process all start from relatively high temperatures, while the hot streams have a T_S which does not allow for any heat exchange with the cold streams, especially given the $\Delta T_{\text{min}}=10^\circ\text{C}$, which leads to a $T_{\text{pinch}}=185.2^\circ\text{C}$. The only possible heat integration can take place between the reboiler of distillation column T-101 and the hot stream cooled down by E-104 before entering the multi-stage compressor. However, with the potential for heat exchange between the two streams being only 4.3kW, the consideration of heat integration for the process would be unreasonable, considering that a heat exchanger would need to be designed, purchased, installed and operated, leading to extra capital and operational costs that would take several years to be returned via the heat integration savings. As a result, heat integration should not be considered for the proposed DMTM process.

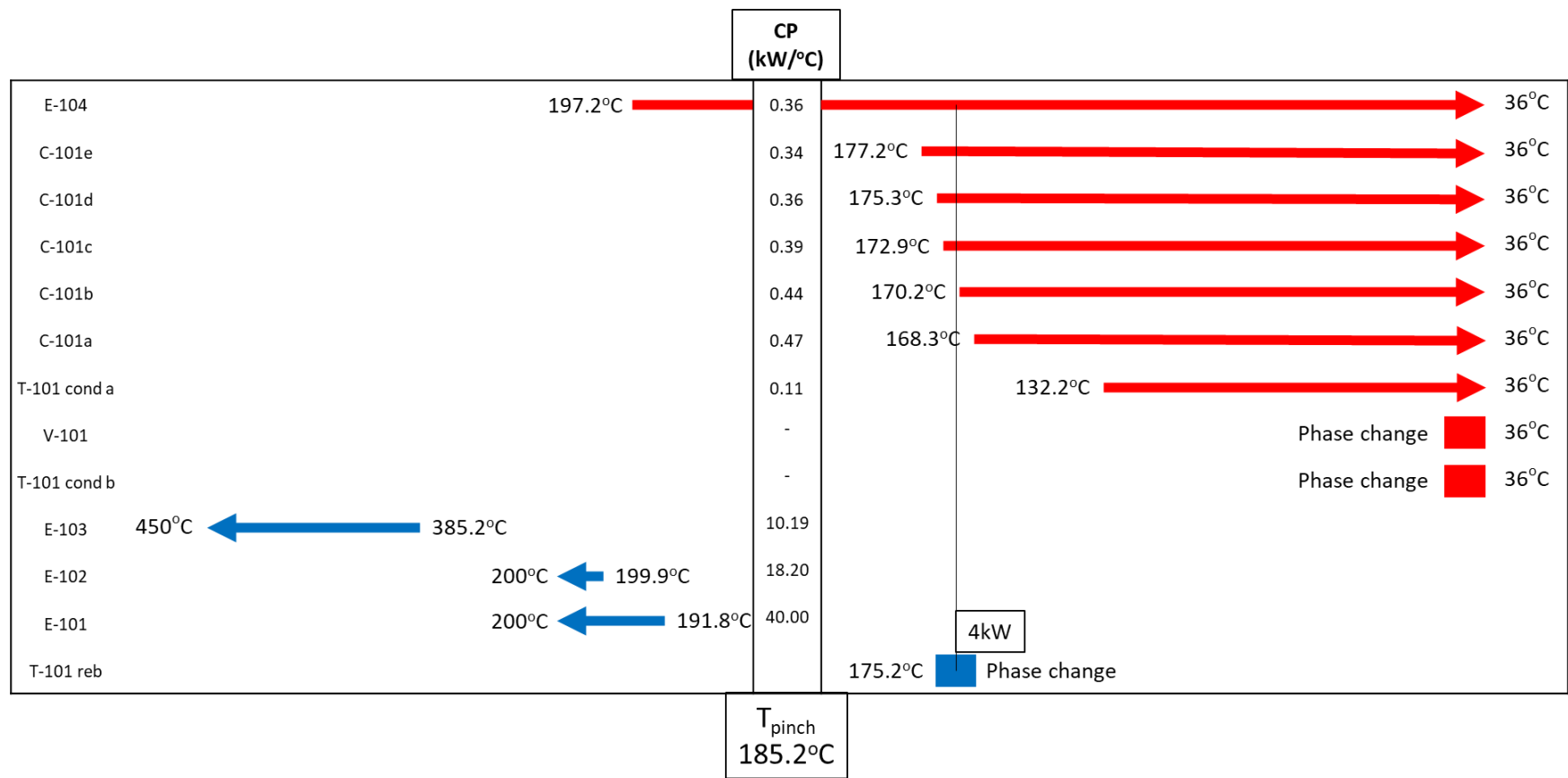


Figure 55: Heat exchanger network design.

7.6.1 Hydrogen utilisation potential

An additional consideration for energy savings is the utilisation of the produced H_2 for covering the fired heat requirements of the process instead of selling hydrogen as a product. A series of calculations regarding the heat requirements of the process, the potential energy that can be supplied by the combustion of H_2 , as well as the comparison of the savings that could be achieved by the combustion of H_2 and the fired utility purchased can lead to conclusions about the profitability potential of his consideration. The summary of results is presented below in **Table 30**.

Table 30: H_2 utilisation potential information.

Cold stream heat-up requirements	915kW
Needs covered by “Fired Heat” utility	660kW
H_2 produced	$11.24 \cdot 10^{-4}$ kg/s
H_2 heat of combustion	$\Delta H_c = 14.2 \cdot 10^4$ kJ/kg (McAllister, Chen & Fernandez-Pello, 2011)
Potential energy by H_2 combustion	$Q_{H_2} = 159$ kW
Annual “Fired Heat” cost	70,800\$/y
Revenues of H_2 sales	255,500\$/y

As seen in **Table 30**, there are several issues regarding the potential of utilising H_2 as a fuel for combustion to cover the “Fired Heat” needs. The first problem arising is the fact that H_2 could only cover about a quarter of the annual needs for “Fired Heat” utilities, thus making it unavoidable to purchase the remainder of the required utility. However, the major issue is that “Fired Heat” is a relatively cheap utility, as opposed to hydrogen which can be sold at a relatively high price to generate a considerable amount of annual revenues. Specifically, the “Fired Heat” utility cost is 70,800\$ per annum while the revenues from H_2 exceed 255,000\$ per year. Additionally, a specially made furnace that could facilitate the combustion of H_2 would also need to be considered, leading to extra capital and operational costs. As a result, it would not make sense to attempt to substitute the purchased “Fired Heat” utility with the combustion of produced H_2 . It is considerably more profitable for H_2 to be sold as a product of high purity along with the produced CH_3OH .

7.7 Case studies

The profitability analysis revealed that the suggested process could never be profitable under the current performance of the catalyst and the presently achieved methanol yields. However, it is important to set a target for the minimum catalyst performance required for a profitable process. A clear picture of the catalyst requirements could help guide the DMTM research to a direction that would allow for an industrially viable DMTM process.

7.7.1 Scenarios of different catalyst performances

In order to assess the industrial potential of the suggested process, different theoretical cases of catalyst performance were investigated. More specifically, a simulation of the process, along with a profitability analysis was carried out for the cases of a catalyst that would yield 10-, 40- and 50 times more CH₃OH in comparison to the present case. The detailed economics for each of these cases could provide an overview of the main bottlenecks of the process as well as set a target for the future development requirements for a catalyst.

The results of the complete profitability analysis of each scenario are summarised below in **Table 31**.

Table 31: Key economic indices for different case scenarios of catalyst performance.

	Present case	10-fold	40-fold	50-fold
Purchased equipment	21,306,000\$	21,680,000\$	23,037,000\$	23,852,000\$
Utility cost	241,000\$/y	718,500\$/y	2,185,000\$/y	2,694,000\$/y
TCI	101,200,000\$	103,000,000\$	109,400,000\$	113,287,000\$
TOC	5,731,000\$/y	7,156,000\$/y	11,840,000\$/y	13,497,000\$/y
Raw materials cost	60,000\$/y	431,385\$/y	1,624,000\$/y	2,024,000\$/y
CH₃OH amount	456t/y	4569t/y	18552t/y	23192t
Sales revenue	2,245,000\$/y	22,450,000\$/y	91,323,000\$/y	114,156,000\$/y
CH₃OH production cost	12.56\$/kg	1.57\$/kg	0.64\$/kg	0.58\$/kg
NP_a	-5,125,000\$	7,031,000\$/y	48,571,000\$/y	62,227,000\$/y
Return of investment rate (ROI)	-5.1%	6.8%	44.4%	54.9%

Another useful index of the case scenarios, that allows for a direct comparison between the different performances of the catalyst is the net present value of the plant in all the years of the plant lifespan. The net present value of the plant in each case over a lifespan of 20 years is presented in **Figure 56**. It should be noted that the timeline begins at year -3, when the building of the plant commences, until it finishes in time $t=0y$.

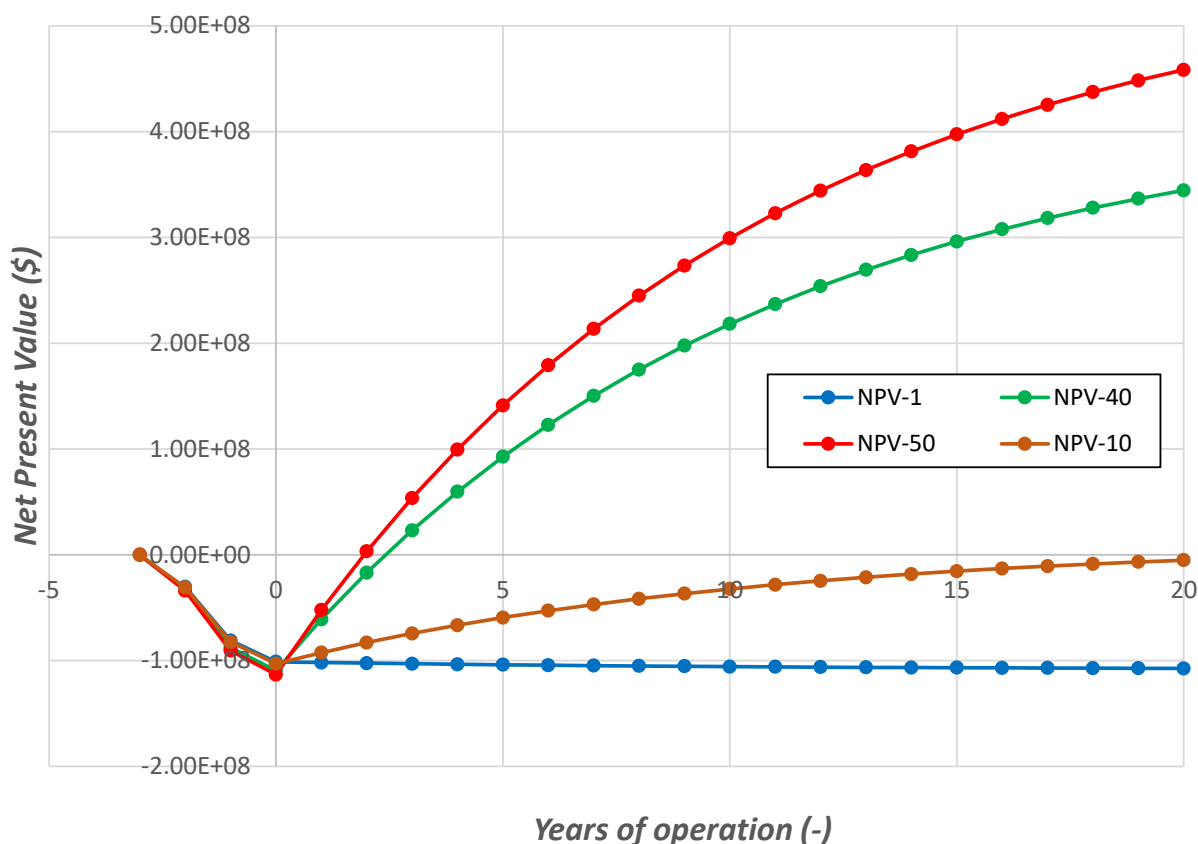


Figure 56: Net present value over the lifespan of the plant for different case scenarios of catalyst performance.

7.7.2 Scenarios results

Table 31 provides some important pieces of information regarding the process costs in different case scenarios. As only the catalytic yield is manipulated in an already established process, there is only a marginal capital cost increase across different scenarios since the quantity of the catalyst and reactor capital costs remain unchanged. The slight increase in capital costs arise from the need for several hydrogen separators in cases of higher catalyst performance, as a single unit would not be sufficient to facilitate the separation. It is reminded that CH_3OH and H_2 are stoichiometrically equally produced during reaction, so consequently a higher yield of CH_3OH would lead to a higher

production of H_2 that would need to be separated from the stream exiting R-102. Although several hydrogen separators would be used in higher catalyst performance scenarios and that could be deemed an unpractical way of H_2 separation, it is estimated that a more elaborate H_2 separation unit design would lead to significant capital and operational costs, without a considerably improved hydrogen separation. As a result, the use of several commercial hydrogen separators could still be the best approach.

On the contrary, a large difference between scenarios is observed in the case of utility and operational costs. This can be explained in several ways. A higher catalyst performance would call for the use of larger quantities of raw materials in the process, which in turn would mean higher utility costs along all units of the process. Additionally, because of larger quantities of materials being fed to the process, a larger split ratio in S-1 would be required to avoid solids entrainment in R-102. This would cause a larger quantity of materials being handled by all units of the process, leading to slightly higher capital costs but considerably higher utility costs. Finally, it is reminded that electricity, which was used in the hydrogen separator X-101 and the multi-stage compressor C-101, was the main contributor to the utility costs of the process by a large margin. As a larger number of hydrogen separators is needed for scenarios of higher catalyst performance, and larger quantities of material need to be handled by multi-stage compressor C-101, electricity costs increase significantly across different case scenarios.

However, as expected, a larger CH_3OH and H_2 yield leads to considerably increased revenues from sales. Moreover, a higher catalytic performance translates to a significant decrease in CH_3OH production cost across scenarios, with the present catalyst performance yielding a 12.6\$/kg production cost, while the 50-fold case exhibits just a 0.58\$/kg production cost. As a result, the profitability margin between scenarios widens dramatically. This can also be seen by the net profit after tax and return of investment rate indices, which also display significant improvement as the catalyst performance increases.

Figure 56 offers a visual overview of the process economics for each scenario. The net present value for each year of operation of the plant is presented for each scenario of catalyst performance. The meeting point of the net present value with the x-axis is considered to be the break-even point of the project. As seen in **Figure 56**, the present case scenario has a negative trend, thus never being able to reach a break-even point. In the case of a 10-fold improved catalyst performance,

although there is an upwards trend for the net present value, even after 20 years of operation of the plant a break-even point is barely not reached, which is an unacceptable economic result for such a project. According to Dimian, Bildea, and Kiss, a small project like the one presented should have a pay-back time of 2-3 years or, in some cases, even smaller.

Interestingly, a 50-fold increased catalytic performance leads to a project with significant profitability, offering a pay-back time of just 2 years of operation. This pay-back time would be considered excellent. However, the 40-fold scenario reaches a break-even point after only 2.5 years, which would also lead to a great investment. Additionally, only a 100\$ million difference is observed in the final net present value of the plant after 20 years of operation between the 40- and 50-fold case. Considering the aforementioned results, the 40-fold improved catalyst performance is thought to be the minimum required performance improvement of the catalyst for a DMTM industrial project of excellent profitability.

7.8 Discussion

The direct methane to methanol conversion has been the topic of heavy research for several decades. Among numerous different materials investigated as potential catalysts for the DMTM, zeolites and copper-exchanged mordenite in particular have been among the best performing materials. In fact, a lab-scale process has been developed which has been able to yield promising amounts of methanol. However, a detailed study on the economic feasibility of such a process has never been carried out and all conclusions regarding industrial viability so far are drawn based merely on the activity and selectivity of catalysts. Since the DMTM reaction is considered to be the “holy grail” of catalysis and would revolutionise the global energy landscape, it is considered essential to properly research into the process economics and draw conclusions on the viability as well as identify weaknesses of the process and potential improvement ground. Ravi et al. in 2019 summarising the current advances of research in the DMTM suggested that the time has come for a thorough feasibility analysis, which would be based on a complete and detailed process flowsheet with actual data, robust material balances and including all energy duties of units. They also suggest that such an analysis, carried out with realistic assumptions, could identify process bottlenecks and guide future research towards an improvement of the process and the potential catalysts.

Although the DMTM over a CuMOR has yielded some of the best results among state-of-the-art research, it poses the major challenge of the lab-scale process being non-continuous but rather have a batch-like nature, carried out in three separate steps. The present study indeed suggests a continuous, looping process, in which the continuous operation is achieved by cycling the catalyst through a series of fluidised catalytic beds, in which the three steps of the laboratorial process are carried out, namely the pre-adsorption of CH_4 , the reaction with H_2O towards CH_3OH and H_2 and the subsequent regeneration of the catalyst. As Ravi et al. suggested in 2019, actual data from the literature were used in a black-box kinetics approach (Ravi et al., 2019).

The concept of three fluidised bed reactors in series was considered to be the best approach in the present study. However, this approach poses certain drawbacks related to the capital and operating costs of the process. Since the catalyst in the suggested process needs to be circulated constantly through the different reactors, an increased capital and operational cost is expected for the inclusion of cyclones at the top of each reactor, which catch the catalyst to move it to the next reactor. Additionally, the mechanical wear of the catalyst caused by the constant transportation between reactors should be considered, potentially leading to a need for a more frequent re-supply of catalyst in the process. Finally, relatively high cooling costs are expected in the present study due to the need to reduce the temperature of the catalyst for the CH_4 adsorption step (200°C) following catalyst reactivation which takes place at a higher T (450°C).

Although the suggested method is associated with the drawbacks mentioned above, it is still believed to be a considerably more viable approach compared to a process based on fixed bed reactors in parallel, each operating all of the lab-scale individual reaction steps, both from an economic as well as from a practical viewpoint. A process involving fixed bed reactors operating in parallel would require a constant change of feed reactants, as well as a change of conditions, since the CH_4 adsorption step is carried out at 36 bar and the regeneration of catalyst step is carried out at a temperature higher than the two other steps of CH_4 adsorption and exposure to H_2O . This would defeat the purpose of a continuous operation and lead to a significant amount of down-time as well as to high operating costs as the reactors would need to be constantly cooled down and reheated to accommodate all reaction steps. Thus, the approach of fluidised bed reactors in series taken in the present study is thought to be the simplest and most cost-effective approach to an industrial DMTM process.

The use of a large abundance of carrier gas inside the process to replicate laboratorial conditions led to the need for a series of separation units, which isolate H_2 to be sold as a side product, as well as CH_3OH in very high purity (99.99% w.t.), while recycling the majority of carrier gas back inside the process. The use of a splitter after the reactor where the production of CH_3OH takes place, which recycles the majority of the stream back to the reactor was necessary, as leading the entirety of the stream to the separation units would impose extremely high and unnecessary utility costs due to the presence of carrier gas in abundance. It was shown that a simple physical separation of He and H_2 from CH_3OH and H_2O after the last reactor was possible after compression. A distillation column operating at slightly elevated pressure was able to isolate the product CH_3OH at high purity with minimal losses, leading to a simple overall process.

Upon establishing a complete process flowsheet on the DMTM over a 3% CuMOR which aimed to provide an actual scale-up of the laboratorial process, the process economics were investigated. Following the complete protocol suggested by Dimian, a thorough profitability analysis of the process was carried out, which calculated several economic indices to obtain a clear picture of the economic potential of the project (Dimian, 2003). The analysis allowed the calculation of the total capital investment, the total operational costs, as well as the profitability analysis including taxes and depreciation of equipment and provided key performance indicators like the net present value after tax, the net present value, the pay-back time and the return of investment. The conclusions drawn from the profitability analysis were that an industrial DMTM process replicating the laboratorially developed reaction over a 3% CuMOR could never be profitable given the current performance of the catalyst, with negative profit being generated throughout the entire lifespan of the plant. The results of the economic evaluation showed that the major capital costs arise, expectedly, from the fluidised bed reactors which dwarfed all other units of the process. The capital cost of multi-stage compressor C-101 was also considerable, although lower than the reactors. Additionally, electricity consumed in C-101 as well as the hydrogen separator X-101 represented the majority of utility costs.

A thorough heat integration revealed that the potential for heat integration of the process is minimal, with only a 4.3kW potential for integration. The small integration potential is attributed to the fact that the cold and hot streams exist in very different, non-overlapping temperature ranges. As a result, heat integration should not be considered for the suggested process, considering that

it would involve also additional capital and utility costs for the installation of an appropriate heat exchanger. Additionally, calculations revealed that the consideration to use the produced H_2 to substitute the purchased fired heat utility is not profitable, since the utility is relatively cheap and considerably more profit can be made by selling H_2 as a product.

To further set a target for the catalyst requirements, different case scenarios were investigated for the performance of the catalyst and consequently the CH_3OH and H_2 yields. More specifically, the complete flowsheet and profitability analysis were investigated for a 10-, 40- and 50-fold more effective catalyst. The results showed that a 50-fold more efficient catalyst in terms of CH_3OH yield would lead to a project with only a 2 year pay-back time, which would be ideal. However, the results of the 40-fold more efficient catalyst are deemed to be still satisfactory, with a pay-back time of 2.5 years, which is considered to be sufficiently short for such a project. Furthermore, the profitability analysis of different scenarios showed that the main cost increases among scenarios arise from utility costs and more specifically from the multi-stage compressor C-101 which in a higher-yield scenario would need to handle more material due to a required higher split ratio in S-1 to avoid solids entrainment in R-102. Additionally, as CH_3OH and inevitably H_2 yield would increase, a much higher number of hydrogen separators would be needed, leading to progressively higher capital and electricity costs.

The findings of the present study strengthens the belief that the current catalyst performance is the bottleneck of the suggested DMTM process over a 3% CuMOR and solidifies the need for more research into a catalytic material that would yield higher amounts of CH_3OH per reaction cycle.

The results of the present economic study regarding the production cost of methanol and profitability over time as well as pay-back time of the project are conclusive. However, some bottlenecks and potential improvements of the process simulation and economic feasibility study need to be discussed. It is reminded that a black-box approach for the kinetics of the reaction was used, employing only the CH_3OH yield given by literature under the given conditions. Although this method offers accurate results, detailed kinetics used inside the reactors would, of course, offer more reliable results. Additionally, using detailed kinetics equations would allow for a manipulation of conditions and reactants concentrations, so that the process could be further optimised and the CH_3OH yields maximised. Moreover, detailed kinetics could provide a better understanding of how the products recycled inside the reactors would affect the production rate of

CH₃OH and information about the validity of the assumption that they minimally influence CH₃OH yields.

Finally, detailed kinetics used inside the reactors would allow for the investigation of a higher H₂O concentration and an appropriate modification of the process. A higher H₂O concentration could lead to significantly shorter reaction times and as a result residence times required inside the reactors. This would lead to significantly lower capital costs for the reactors, as their size would considerably decrease. Additionally, a higher H₂O concentration would lead to lower carrier gas amounts required inside the process, which would lead to significantly lower utility costs for all units, including separation units. It is thus considered that the use of actual materials and kinetics would offer several benefits to the entire process and feasibility analysis.

One more aspect of the process that should not be overlooked is the performance loss of the catalyst. As reported by Sushkevich, Palagin, Ranocchiari, and van Bokhoven, the catalyst displays consistent yields over several cycles of reaction without exhibiting any performance loss. Despite their initial assessment on the catalyst performance loss, no exhaustive study has been carried out on the matter. To account for a potential permanent deactivation of the catalyst that could happen over a long span of time of operation, the present work considered an annual resupply of catalyst equal to 50% of the total catalyst mass looping through the reactors annually. This contributes considerably to the raw materials cost. A detailed study which could provide actual data regarding the necessity of CuMOR substitution and the frequency at which this would need to happen would increase the accuracy of the process economics results.

It is concluded that further research needs to be carried out for the improvement of the current catalyst performance. This should be achieved either by appropriate engineering of existing well-performing materials like the CuMOR to further improve yields, or by exploring new material avenues. However, it is noted that the use of new materials, or maybe even the engineering of current materials, could lead to other ideal process conditions or even completely different processes that could not be directly evaluated with the process concept suggested by the present work. Processes using new materials would need to be conceptualised and simulated and a new economic feasibility would need to be carried out based on a complete simulation that, just like the present study, would make all appropriate assumptions and considerations to reach realistic results.

8. 8MR and zeolite topology influence on the DMTM

Zeolites have been some of the best performing supports in the DMTM for the past decades. They were initially identified as a promising base for the replication of the copper and iron active sites found on the pMMO, which is an enzyme capable of catalysing the DMTM in nature under ambient conditions. Their exceptional performance compared to other materials has been widely reported, with several different frameworks investigated and large effort being put into the identification of the active sites that are responsible for the DMTM over zeolites. However, a less discussed but equally important aspect of the DMTM over zeolites is the topology and geometrical structure of each zeolitic framework, which could play an important role in the formation of the desired active sites that can increase CH_3OH yields. This section aims to target one common characteristic of zeolites that show good results for the reaction towards methanol, which is the presence of an eight-membered ring (8MR) in their framework (Park et al., 2017). It will be attempted to conclude on whether this common characteristic influences the performance of zeolites towards methanol formations, as well as to draw conclusions regarding the aspects of zeolites that can affect their performance in the DMTM.

8.1 Zeolite frameworks and the 8MR

8.1.1 Performance of zeolite frameworks in the DMTM

As previously mentioned, zeolites were employed several decades ago in the research of direct oxidation of methane to methanol. In fact, the MFI framework was the first zeolite reported to produce results in the DMTM by Anderson and Tsai in 1987, with several works following to shed light into the active sites responsible for the reaction. Several years after the initial report of ZSM-5 activity, mordenite was suggested as an improvement with larger yields compared to ZSM-5 and CuMOR has ever since been one of the best performing catalysts in the DMTM to date. (Groothaert et al., 2005)

Since then, and especially in more recent years, several different zeolitic frameworks have been investigated in an attempt to achieve better CH_3OH yields as well as to better understand the reasons of the good performance of zeolites in the reaction and ways to improve it. Some of the common frameworks that were reported to have good activity when exchanged with copper ions were the BEA (beta), FER (ferrierite) and FAU (faujasite) zeolites, which exhibited performance

comparable to the CuZSM-5 they were compared against, while all of them had an inferior performance to CuMOR. (Smeets, Groothaert & Schoonheydt, 2005)

Additionally, some small pore zeolitic frameworks have been reported to show good performance in the DMTM. The reported frameworks, namely SSZ-13 and SAPO-34 (CHA - chabazite), SSZ-16 (AFX) and SSZ-39 (AEI) showed excellent performance, with yields comparable to the then performance of Cu-ZSM5 and CuMOR. It should be noted, however, that the reaction testing method for mordenite was different to the presently best-performing method. Nevertheless, the good performance of the small-pore zeolitic frameworks was notable. (Wulfers et al., 2015)

An interesting and insightful work was recently reported by Park et al. in 2017, which benchmarked the performance of several copper-exchanged zeolitic frameworks in the direct oxidation of methane to methanol. Several frameworks were tested, which included MOR (Mordenite), EON (ECR-1), MAZ (Omega), BPH (UZM-4), LTL, MFI (ZSM-5), HEU, FER (Ferrierite), SZR and CHA (Chabazite). The performance of the zeolitic frameworks was assessed and compared based on the total extracted methanol throughout the experiment. All zeolitic frameworks produced CH₃OH when tested in the reaction, with the MAZ framework exhibiting the best performance among all investigated catalysts (Park et al., 2017). The excellent performance of the Omega (MAZ) zeolite in the DMTM was also reported by Knorpp et al. in 2018, who attributed the improved performance of the framework to the fact that all copper exchanged onto the framework formed active sites inside the pores, in contrast with other frameworks where the copper atoms could form clusters, inactive in the DMTM.

8.1.2 Role of 8MR

Although there are reports of several zeolitic frameworks that perform in the DMTM, it is essential to filter the research and attempt to reach conclusions on the reasons of improved performance among zeolites. Attempting to shed light into the reaction mechanism for each catalyst, intensive research was carried out in the most popular zeolitic supports to identify the nature of active sites as well as their location within the zeolitic framework.

Indeed, Vanelderen et al. in 2015 reported on the location of copper active sites on the frameworks of ZSM-5 and mordenite. They concluded that in the case of ZSM-5, active sites seem to be located in the intersection of 10 membered-rings, while in MOR the active sites form in the 8MR windows

of the side pockets. This was probably the first work that showed comparative evidence that the zeolitic framework itself might significantly influence the formation of sites which are active in the DMTM.

Inspired by this evidence and the conclusion that the zeolitic framework can influence the formation of desired active sites, all reported frameworks in the literature that perform in the DMTM were investigated for common characteristics (Baerlocher & McCusker, 2017). The comparison between different catalysts led to an interesting observation – all the reported frameworks with any performance in the direct oxidation of methane to methanol contain 8MRs in their framework, along with other smaller or larger rings.

The presence of 8MR in all frameworks yielding CH_3OH is considered to not be a coincidence, as the topology of the zeolite dictates the location and proximity of copper atoms to each other and consequently the nature of the formed active site. Grundner et al. in 2015 investigated the nature and location of active sites and concluded that mordenite, in which active sites primarily form in 8MR, provided a well-constrained environment for the active sites which stabilised them and as a result improved their activity in the DMTM. This is in good agreement with the work of Markovits et al. in 2016 who compared the performance of CuZSM-5 and CuMOR, trying to identify the reason of the increased performance of mordenite. The researchers attributed the improved performance of the catalyst to the framework of MOR being a more fertile topology for the formation of productive active sites, as ZSM-5 hosted copper atoms in clusters that were inactive in the reaction in a large proportion. Additionally, they reported that the 8MR in which the copper deposited in the case of MOR provided a better stabilisation of the active site, thus enhancing performance.

Complementing the aforementioned studies, another study investigated the stability of different copper clusters formed intentionally on the mordenite framework, ranging from single atom to 5-copper atom clusters. The researchers concluded that the larger the cluster, the more stable it was. However, it is also reminded that the most active sites for the reaction have reported to be di-copper cores (Palagin et al., 2017). It is thus believed that the 8MR might be providing an ideally sized, well-constrained environment for the formation of the desired active sites, leading to improved performance.

The aforementioned studies were a strong indication that the 8MR could be playing a significant role in the formation of active sites and that conclusions can be reached regarding the ideal topological conditions for the formation of active sites, which could serve as a guide to further engineer materials to maximise catalytic performance in the DMTM.

8.1.3 8MR hypothesis and study aim

Guided and inspired by the research already made in the field of zeolites in the DMTM, but also by the lack of work in the topological comparison between zeolitic frameworks, the present work aims to achieve additional insights that could direct future research.

It is hypothesised that the presence of 8MR in zeolites plays a significant role in their performance in the DMTM. In order to evaluate this hypothesis, the present study aims to isolate the 8MR by investigating zeolitic frameworks that only contain 8MR and smaller rings which could not be hosting copper atoms for the DMTM. The zeolites of interest are GIS, PHI, EDI and MER, which all contain only 4MR and 8MR in their frameworks. The aforementioned frameworks were synthesised, characterised and tested in the DMTM reaction. Moreover, additional experiments were carried out, aiming to enhance the understanding of the zeolitic framework and bottlenecks of their synthesis and use in the DMTM.

Finally, findings will be discussed to reach conclusions that can help drive future research towards the improvement of the overall process, as well as the engineering of future materials with improved performance in the reaction.

8.2 Catalyst synthesis

The synthesised zeolites' molar compositions are summarised below in **Table 32**, as given by the recipes used for their synthesis. It should be noted that the MOH listed in **Table 32** refers to a different metal hydroxide in each case. Specifically, MOH refers to KOH in the case of MER, 75% NaOH and 25% KOH in the case of PHI, and NaOH in the case of GIS. Seong Ho Baek and Zhiyan Qiu are kindly acknowledged and thanked for the synthesis of zeolitic frameworks as well as the analysis of XRF results.

Table 32: Molecular composition of synthesised zeolitic frameworks.

	SiO₂	Al₂O₃	SiO₂/Al₂O₃	H₂O	K₂O	MOH	Time (d)
GIS	8.20	2.05	4.00	173.00	-	10.00	7
EDI	3.00	1.00	3.00	94.50	5.26	-	4
PHI	12.20	2.90	4.21	201.00	-	10.00	4
MER	2.45	0.50	4.90	505.00	-	10.00	7

All synthesised zeolitic frameworks underwent XRD and XRF analysis, as detailed in Chapter 4. XRD analysis was performed on the zeolites before and after each step that could alter their crystalline structure, namely synthesis, calcination, and ion exchange.

Unlike the simple ion exchange method employed for the CuMOR used in earlier experiments, a different ion exchange protocol was used for the synthesised zeolites. Copper ion solutions were created using deionised water and copper nitrate trihydrate, in different molar compositions ranging from 0.001 to 0.05M. For the process of ion exchange, 1.5g of synthesised zeolite was added to 75ml of deionised water and was left under continuous stirring and reflux at a controlled temperature of 50°C overnight. Subsequently, the solution containing the zeolite was filtered and washed repeatedly with deionised water until a neutral pH value was reached. It should be noted that the pH of solutions of different molar concentrations ranged from 4.8-5.7. Finally, the washed, wet zeolite crystals were left to dry overnight in an oven at 100°C and were subsequently calcined. The calcination procedure involved a rise of the temperature at a rate of 3°C/min to 450°C, where the temperature was held for 4h under an environment of static air. Some of the zeolites underwent several cycles of ion exchange (up to 3 cycles) for additional experiments which will be discussed in later sections.

8.3 Synthesised zeolites characterisation

8.3.1 Framework characterisation

Following synthesis and drying, the synthesised zeolites were characterised to confirm their crystalline structure. The XRD patterns of all synthesised frameworks were measured and compared against literature and theoretical XRD patterns. The theoretical, literature and experimental XRD patterns for all structures are presented in **Figure 57** and **Figure 58**.

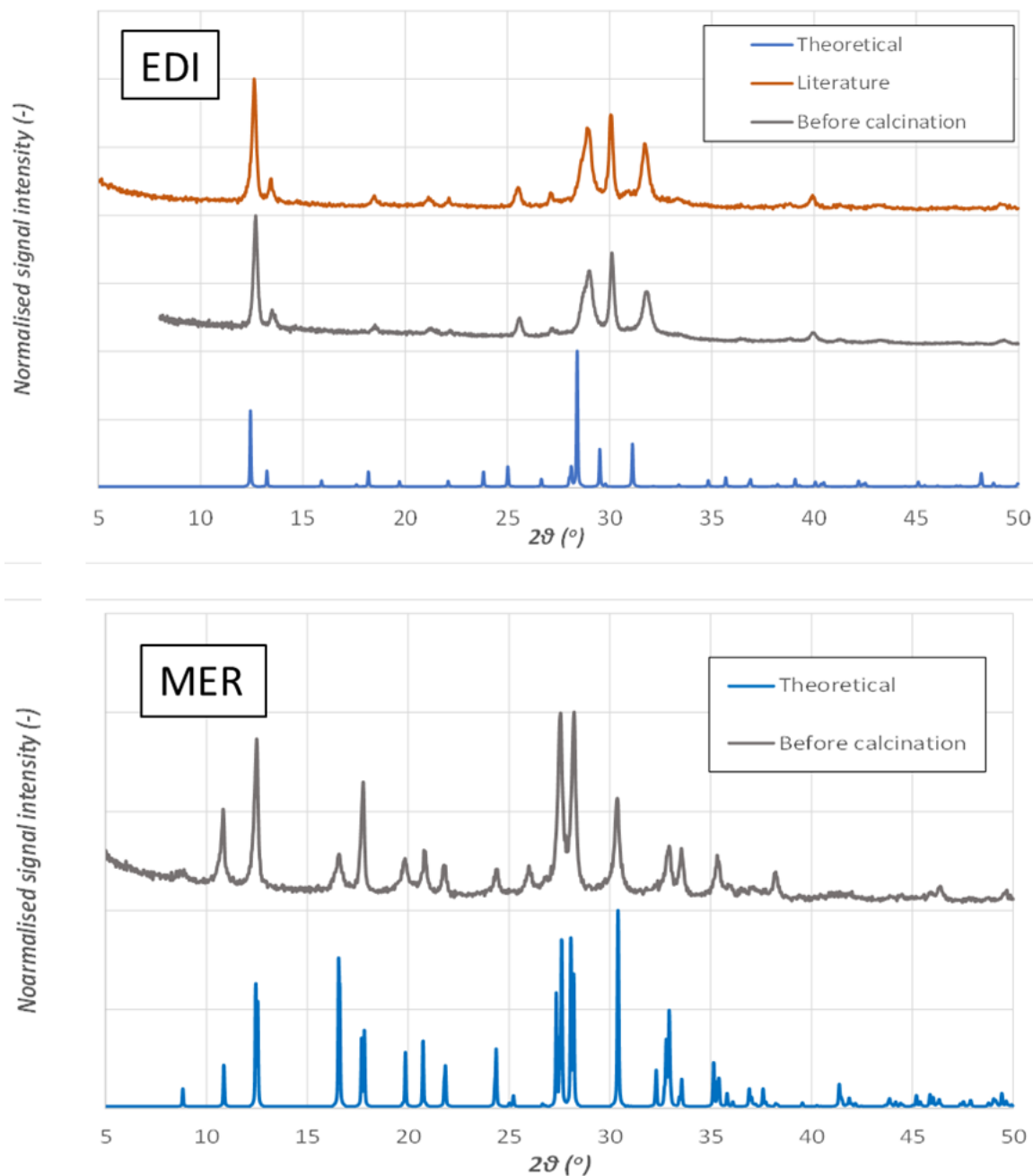


Figure 57: Theoretical, literature and experimental XRD patterns of EDI and MER.

All theoretical patterns were mathematically calculated with the aid of a suitable online-available tool (Database of Zeolite Structures, 2017). In the case of EDI, an additional literature pattern was used for comparison (Robson & Lillerud, 2001).

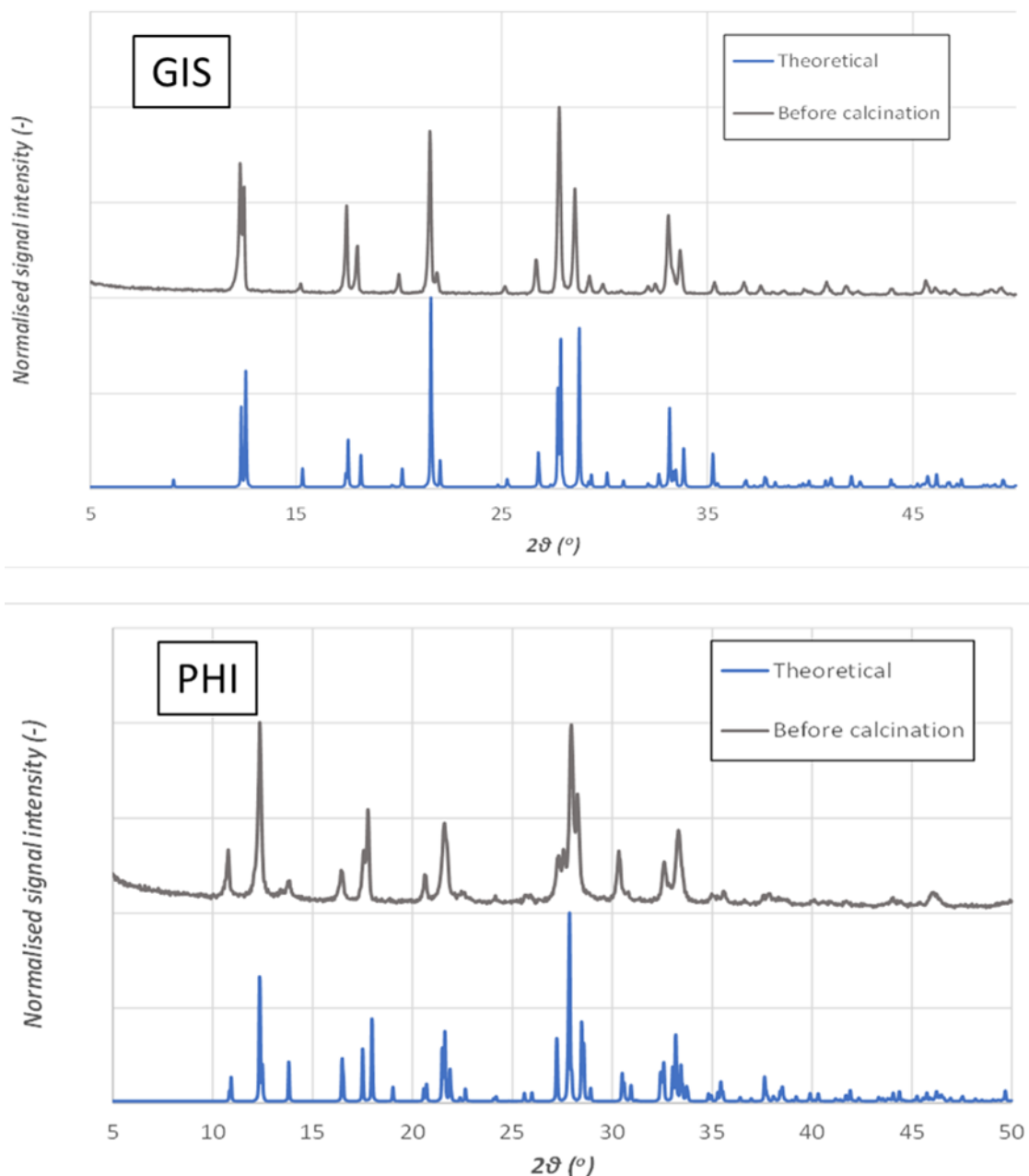


Figure 58: Theoretical and experimental XRD patterns of GIS and PHI.

The patterns seen in **Figure 57** and **Figure 58** confirm that indeed all zeolitic frameworks were synthesised successfully. For all frameworks, the experimentally obtained XRD patterns are in excellent agreement with their theoretical counterparts. In the case of EDI, the theoretical pattern displays a slight difference in intensity proportions for some peaks (at approximately 28, 30, 32°), however, the experimental pattern is in complete agreement with the XRD pattern reported for EDI in literature. It should be noted that all signals presented in **Figure 57** and **Figure 58** have

been normalised and offset values have been added for the sake of presentation of all patterns in one graph.

Following confirmation of all synthesised structures, all zeolites were calcined as described previously. A new XRD analysis of all structures followed after calcination to investigate any potential alteration in their crystalline structure as a result of the thermal treatment.

8.3.2 Characterisation after calcination

The XRD patterns before and after calcination were obtained and compared to identify potential structural changes of the zeolites. The XRD patterns of all zeolitic frameworks are presented in **Figure 59** and **Figure 60**.

As seen in **Figure 59** and **Figure 60**, the patterns of EDI, MER and PHI after calcination display excellent agreement with their before-calcination counterparts. This confirms that the three zeolites have good thermal stability and the thermal treatment did not cause any alteration or collapse of their frameworks. On the contrary, some interesting observations can be made on the XRD pattern of GIS after calcination. Specifically, the first peak of GIS before calcination observed at $\sim 13^\circ$ appears to have slightly shifted after calcination towards 14° . The double peak observed at 17° is no longer present while new small peaks appeared before and after 17° . Additionally, the large, characteristic peaks of GIS around 22° , 27° , 28° and 33° are no longer present after calcination, with many other small peaks appearing at different locations.

This is a clear indication that GIS had poor thermal stability, resulting in a severe alteration of its crystalline structure. As a result, GIS is deemed to be unsuitable for further examination, as well as for use in the DMTM reaction, as high temperatures are involved in the reaction sequence. Generally, hydrothermal stability of zeolites is a sensitive property that needs to be taken into consideration when they are used in catalytic processes, especially when they contain liquid water or vapor. It is also reminded that zeolites are hygroscopic materials which promptly absorb moisture and contain it in their pores. The presence of H_2O along with high temperatures can severely affect the stability of the zeolitic framework, causing it to collapse (Mallada, 2014).

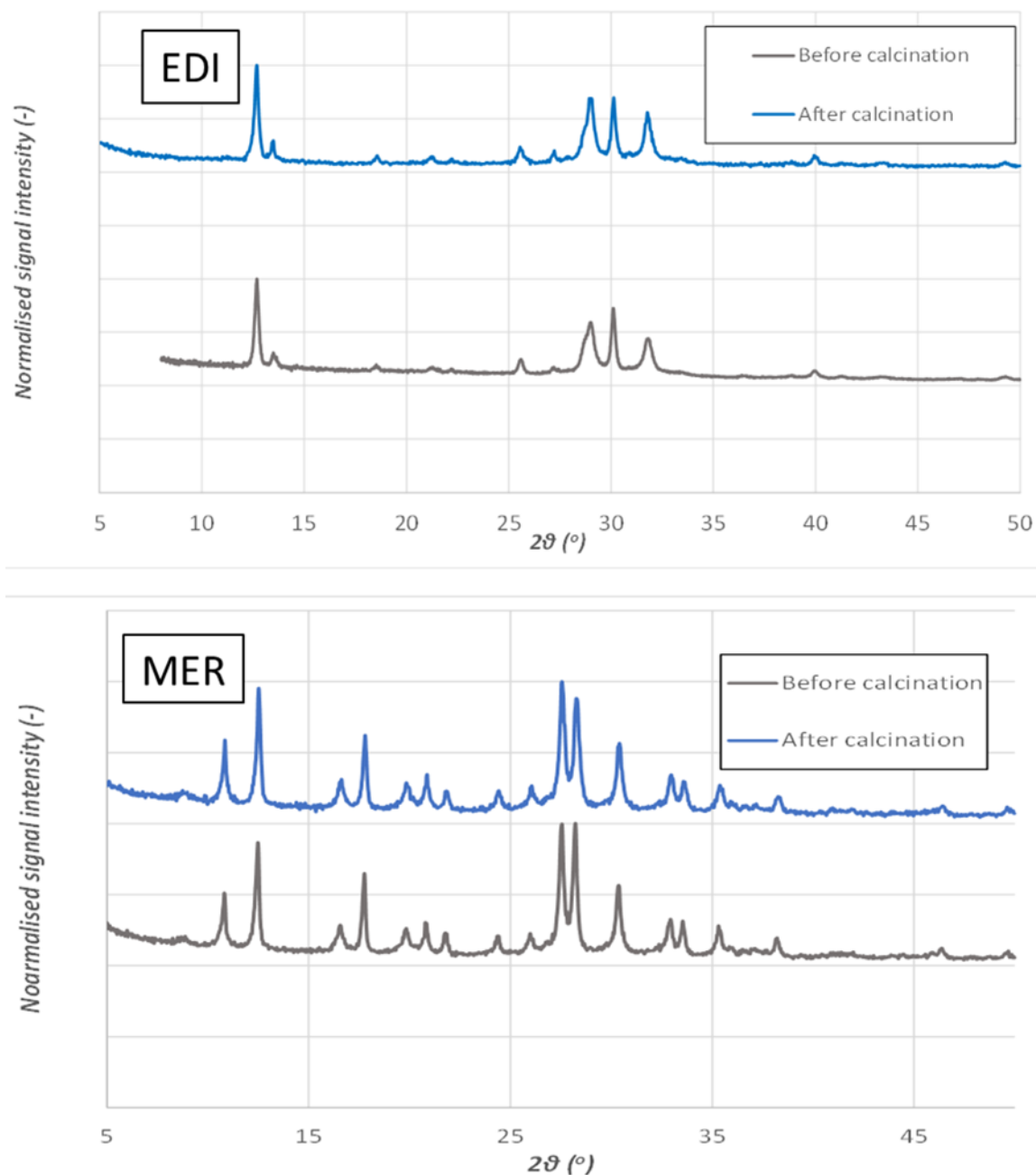


Figure 59: XRD patterns of synthesised EDI and MER before and after calcination.

One of the reasons of good suitability of ZSM-5 and MOR in the DMTM is their good hydrothermal stability even at high temperature and moisture conditions and for prolonged amounts of time (Lutz et al., 2005). These properties allow them to withstand the catalyst activation step which reaches temperatures of 400°C, as well as the prolonged exposure to a wet He stream for CH₃OH extraction for 3 hours or more.

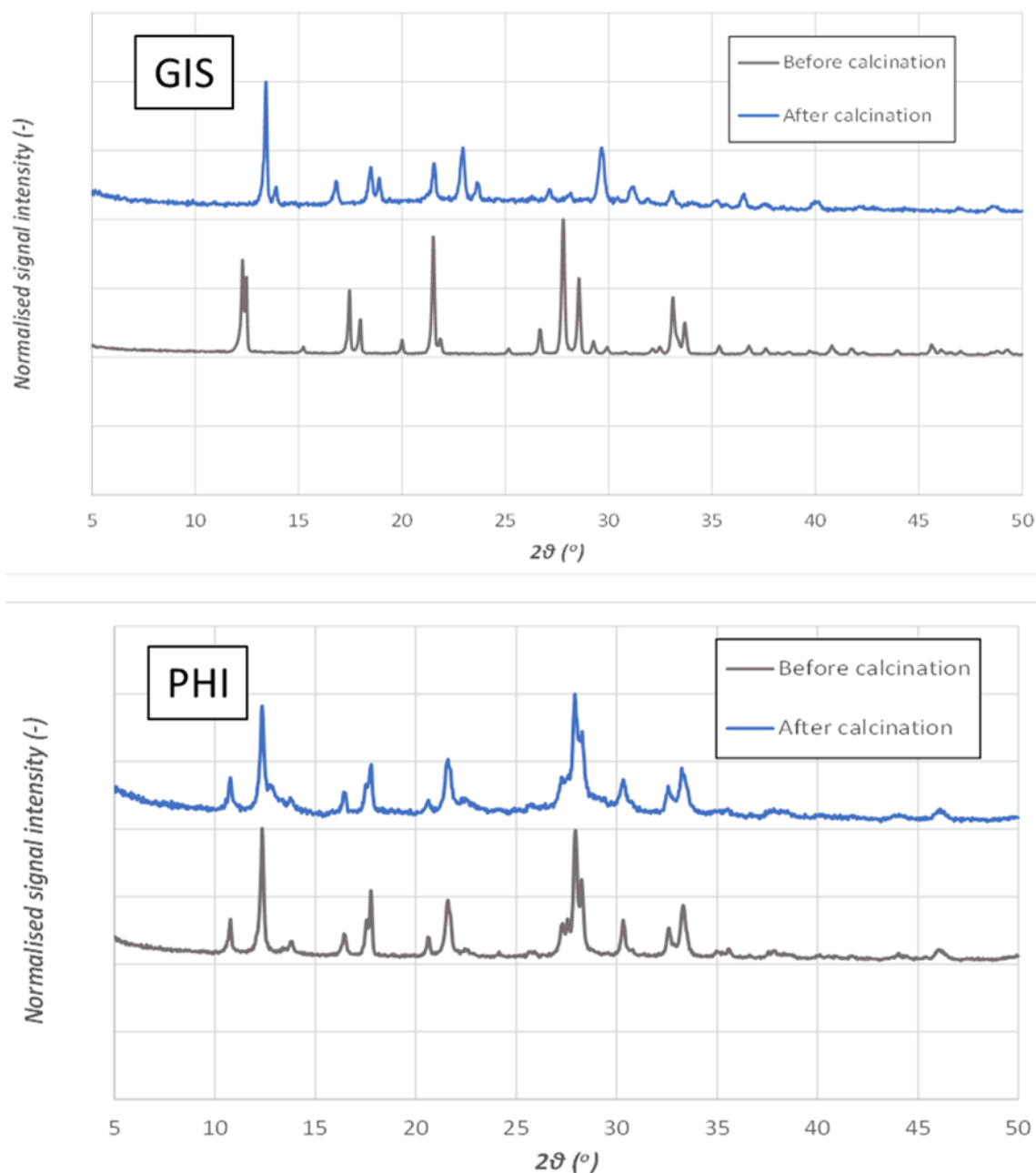


Figure 60: XRD patterns of synthesised GIS and PHI before and after calcination.

It should be noted that thermal stability of zeolites depends heavily on the Si/Al ratio of the framework. Si/Al ratios higher than 3.80 grant very good stability to zeolites, while zeolites with ratios lower than 1.28 show poor stability. The thermal stability of zeolite frameworks with Si/Al ratios that fall between the aforementioned limits cannot be directly predicted (Cruciani, 2006). All synthesised zeolites had Si/Al ratios between 3.00 and 4.80, with GIS having a $\text{SiO}_2/\text{Al}_2\text{O}_3$ of

4.00, which is at the limit of good stability suggested by literature. This can explain the fact that at this Si/Al ratio GIS did not exhibit a good hydrothermal stability.

8.4 Effect of Cu-exchange on the zeolitic framework

8.4.1 Characterisation before and after Cu-exchange

Following calcination, all zeolites were ion-exchanged with copper, as detailed previously. Specifically, all zeolites underwent an ion exchange with a 0.01M solution of Cu^{2+} ions for one cycle and subsequent calcination following the previously detailed protocols. Additionally, in the case of EDI and MER, 0.05M solutions were used for 1 and 3 cycles of ion exchange to further investigate the effect of copper solution concentration and acidity to the framework stability. The details of ion exchange and composition of synthesised and exchanged zeolites as given by XRF analysis are given in **Table 33**. It is reminded that there were severe alterations to the GIS framework following calcination after initial synthesis. As a result, not a complete analysis was carried out after ion exchange on GIS, although it underwent the same process as the other zeolites including ion exchange and reaction testing.

Table 33: Ion exchange and composition details for all zeolitic frameworks.

	XRF SiO ₂ /Al ₂ O ₃	Theoretical SiO ₂ /Al ₂ O ₃	Cycles	Solution concentration	Cu % (w.t.)
GIS	3.8	4.0	1	0.01M	-
PHI	4.1	4.2	1	0.01M	2.88
MER	4.9	4.9	1	0.01M	2.23
			1	0.05M	3.88
			3	0.05M	6.74
EDI	2.7	3.0	1	0.01M	3.07
			1	0.05M	10.96
			3	0.05M	14.26

As seen in **Table 33**, XRF analysis confirms that the zeolitic frameworks have been correctly synthesised, with Si/Al ratios being very close to the theoretical values. Additionally, the solution concentration appears to have a large effect on the degree of ion exchange for the same time of exchange, as the Cu content of zeolites displayed a large increase when treated with a 0.05M

solution as opposed to a 0.01M solution. Additionally, the 3 cycles of ion exchange also appear to achieve a larger copper content on the zeolite as compared to one cycle of ion exchange. However, the sheer presence of copper on the zeolite after copper-exchange is not necessarily due to the formation of active sites, but could also be due to the deposition of copper oxide on the framework. Thus, it is necessary to further analyse the crystalline structure of the zeolites to identify potential changes in their framework and to investigate the presence of other crystalline forms of copper on the framework.

XRD analysis was performed on all zeolites after ion exchange, before and after calcination. The results are presented below in **Figure 61** and **Figure 62**. As seen in **Figure 62**, GIS, the framework of which had presented severe differences to the initially synthesised material after calcination, presented once again a different crystalline structure following ion exchange. Moreover, the crystalline structure further changed after calcination following the ion exchange, with several peaks disappearing, new peaks appearing and a generally more amorphous structure being observed. This behaviour was expected, since the stability of GIS had proven to be poor following the initial calcination after synthesis.

On the contrary, PHI appeared to have an identical XRD pattern before and after ion exchange, thus confirming that no structural changes had taken place on the zeolitic framework during the ion exchange process. However, the calcination of PHI following ion exchange appears to have severely affected the framework, as the PHI pattern seen in **Figure 62** is considerably different before and after calcination, with several peaks disappearing and peaks being present at different locations. As a result, PHI is considered to also be unsuitable to be used in the DMTM under the ion exchange conditions used, which caused an alteration or collapse of the zeolitic framework.

Figure 61 presents the crystalline patterns of EDI and MER following ion exchange under different solution concentrations and different numbers of cycles. As seen in **Figure 61**, EDI displayed excellent stability during ion exchange with a 0.01M solution, with the XRD pattern remaining identical before and after the exchange. Additionally, EDI displayed an almost identical XRD pattern before and after calcination following ion exchange, with only a small intensity difference between the peaks at 30° and 32° being observed. Consequently, EDI exchanged with a 0.01M Cu solution is considered to be suitable for reaction testing, as it still retained its crystalline

structure and the copper ions are assumed to not have deposited on the zeolite as inactive copper oxide species.

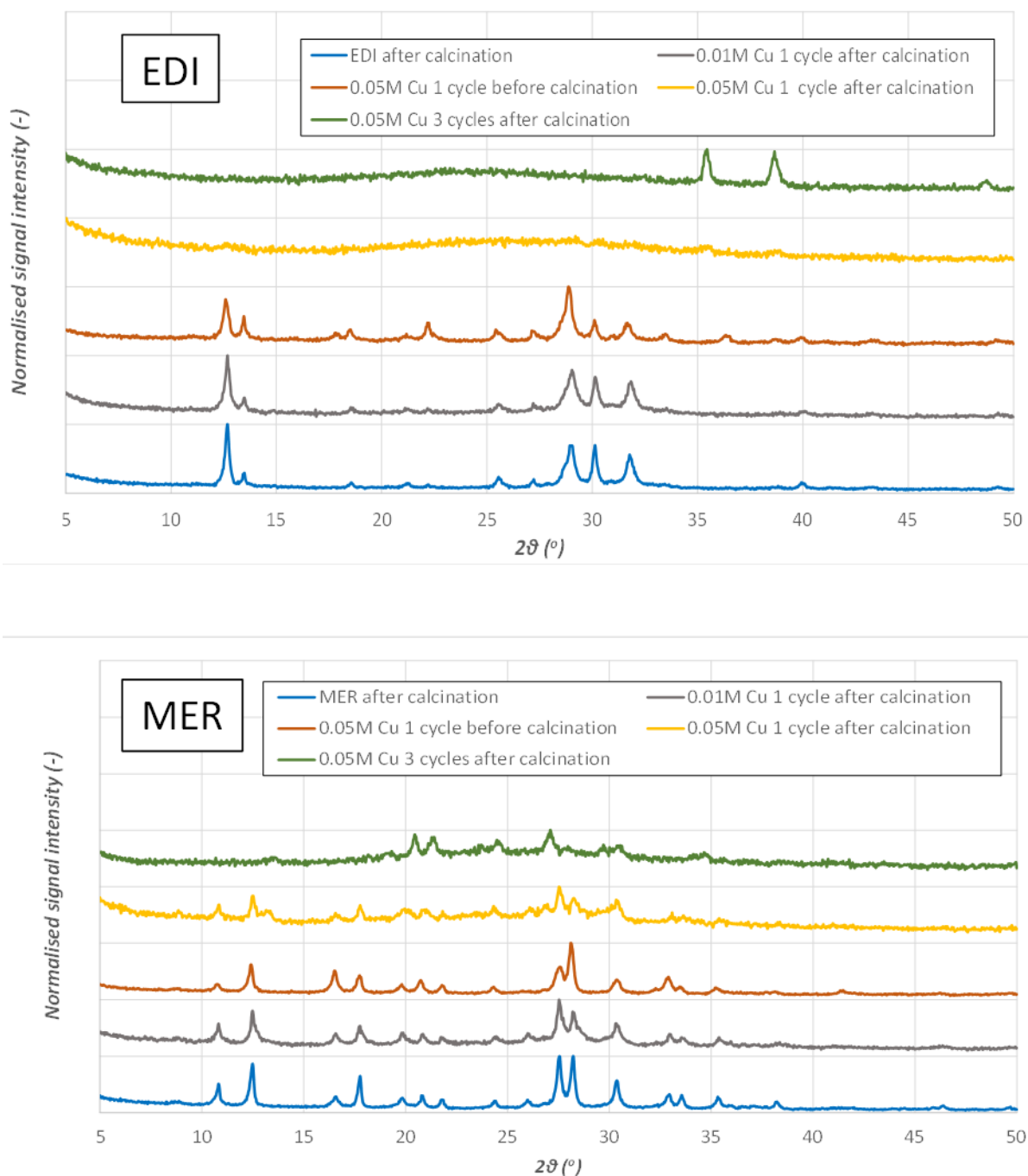


Figure 61: XRD patterns of EDI and MER following copper ion exchange with different solution concentrations, before and after calcination.

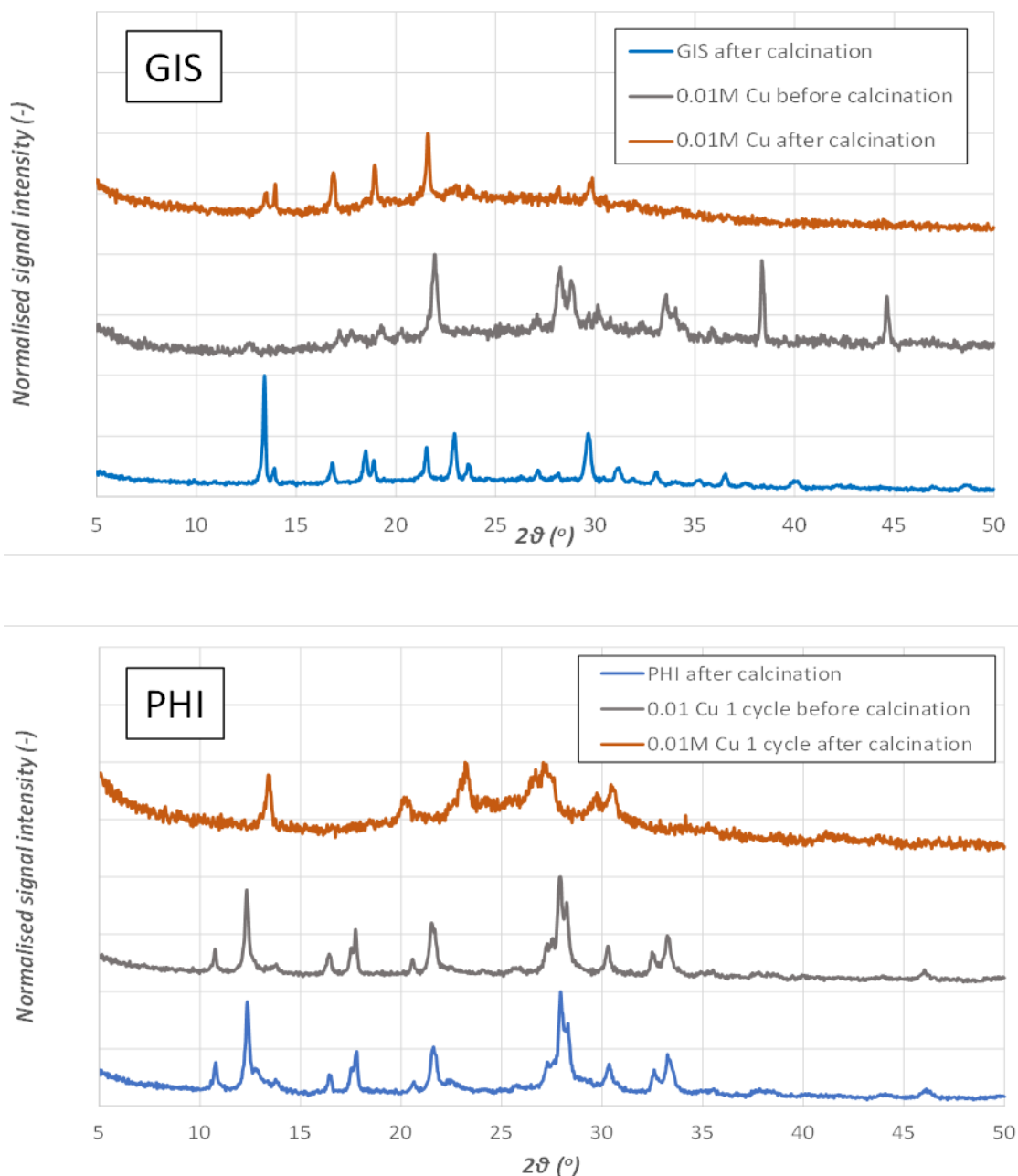


Figure 62: XRD patterns of GIS and PHI following copper ion exchange with different solution concentrations, before and after calcination.

However, the XRD pattern of EDI following 1 cycle of ion exchange with a 0.05M solution displayed a complete loss of crystallinity, with no peaks being present, indicating that the framework had collapsed into an amorphous solid. Interestingly, two peaks were present in the case of 3 cycles of ion exchange of EDI with a 0.05M Cu^{2+} solution. The peaks are located at 35° and 38° , which are characteristic of CuO nanoparticles (Suresh, Karthikeyan & Jayamoorthy,

2016). It is concluded that the 3 cycles of 0.05M Cu^{2+} solution collapsed the framework and left sufficient copper content for the formation of solid copper oxide crystals. As a result, the EDI exchanged with a 0.05M solution is considered to be unsuitable for reaction testing.

Finally, a similar behavior was observed by MER. Specifically, MER displayed excellent stability following ion exchange with a 0.01M solution before and after calcination and was thus considered suitable for reaction testing. Similarly to EDI, the framework of MER seemed to have been severely affected by ion exchange with a 0.05M solution both after 1 and 3 cycles, with the XRD patterns displaying a disappearance of several peaks and displaying a more amorphous picture. None of the 0.05M exchanged MER samples were tested for reaction.

The framework alteration due to ion exchange treatment is also clearly displayed by a microscopic image of the EDI crystals before and after ion exchange. Specifically, images were taken of EDI before and after 1 cycle of ion exchange with a 0.05M solution. These are presented below in **Figure 63**. **Figure 63 a)** displays well defined EDI crystalline structure after synthesis and calcination. In contrast, in **Figure 63 b)** EDI no longer shows a crystalline structure, but rather an amorphous image. This is in good agreement with the findings of the XRD analysis of the same EDI samples.

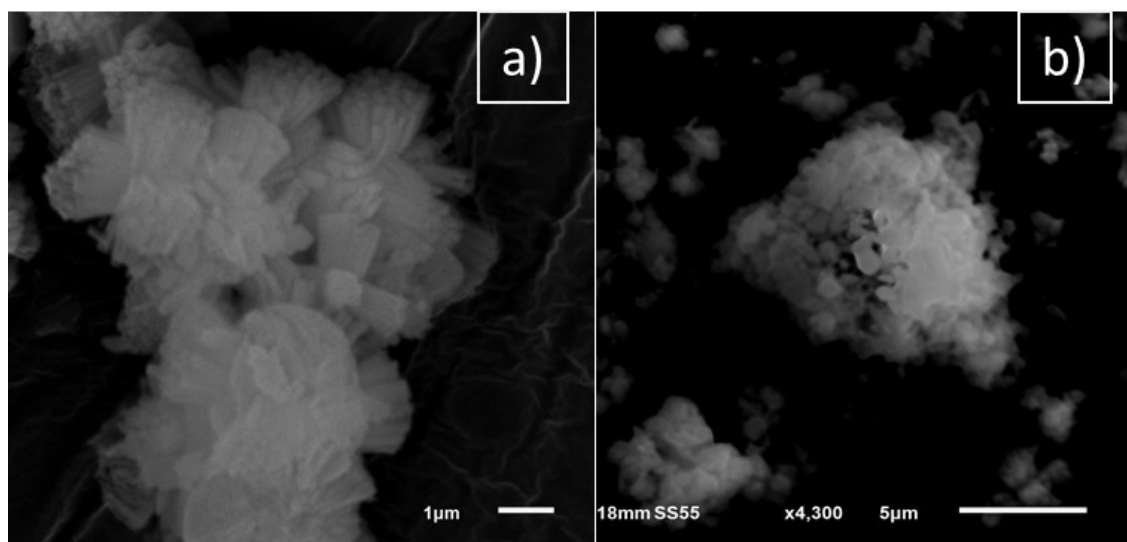


Figure 63: SEM pictures of EDI a) before and b) after ion exchange.

An additional experiment was carried out with EDI, which displayed good hydrothermal stability and stability during ion exchange, to draw conclusions regarding the effect of ion exchange conditions on the copper content of the final zeolite. Specifically, different time of exchange,

temperature and solution concentration conditions were tested for comparison. These can be seen below in **Table 34**.

Table 34: Effect of different ion exchange conditions on final copper content.

Zeolite	T (°C)	Time of exchange	Cu²⁺ concentration	Cu % (w.t.)
EDI	50	overnight	0.001M	0.28
	50	3hr	0.01M	2.70
	20	overnight	0.01M	2.64

As seen in **Table 34**, the solution concentration had a great effect on the final copper content of a zeolite. On the contrary, the change of temperature and duration of ion exchange appeared to have a minimal effect on the final copper content. Considering the large effect of the solution concentration on the degree of ion exchange, there could be a direct link between the solution concentration and the framework destabilisation observed for the zeolites exchanged with 0.05M solutions.

8.4.2 Dealumination and framework stability

It is indicated by the aforementioned findings that there is a correlation between the framework stability of zeolites and the copper solution concentration that was used for their ion exchange. The pH of the different solutions was tested and found to be mildly acidic. It is well documented in the literature, that acidic environments have a direct effect on zeolitic frameworks, as they initiate a process called dealumination. During dealumination, aluminum atoms are removed from their sites in the zeolitic framework, leaving behind defects or “silanol nests” (Dědeček et al., 2009). In fact, dealumination is often used to control and modify the Si/Al ratio of zeolites following their initial synthesis. Several works have reported on the dealumination of common zeolites under different acidic environments, with researchers concluding that the density of silanol nests left by the dealumination process is the deciding factor to the stability exhibited by zeolites in the presence of water under high temperature conditions (Sasongko et al., 2020)(Zhang et al., 2015). Additionally, the intraporous water concentration also plays an important role, which complementing to the concentration of framework defects, can severely destabilise or collapse the zeolitic framework (Prodinger & Derewinski, 2020).

Understandably, the damage to the framework of the synthesised zeolites in the present work is attributed to a dealumination of the framework under the acidic environment of the ion exchange solution. This hypothesis is further reinforced by the fact that the same zeolitic frameworks (EDI and MER) showed good stability before and after ion exchange and subsequent calcination when treated with a lower concentration and hence lower acidity solution (0.01M), but collapsed after treatment with a higher concentration and acidity solution (0.05M), even without calcination. It is hypothesised that in more acidic environments a larger number of framework aluminum is removed from the framework, thus leading to a large concentration of lattice defects and a subsequent destabilisation of the framework that leads to its collapse. This hypothesis explains the XRD findings. It should also be noted that in acidic environments, apart from the aluminum atoms, Si atoms can also be removed from the framework leading to further framework damage. Interestingly, frameworks with a lower Si/Al ratio are more susceptible to destabilisation due to dealumination, since there is a higher abundance of Al atoms that can be removed and leave vacancies behind. Since all synthesised zeolites in the present work had Si/Al ratios ranging from 3.0-4.9, they are considered to be very prone to dealumination. (Silaghi, Chizallet & Raybaud, 2014)

8.5 DMTM reaction results

Following synthesis, calcination ion exchange and subsequent calcination, all zeolitic samples were tested in the DMTM reaction. The reaction protocol used was identical to the protocol used for the 3% CuMOR, detailed in previous chapters. Despite the framework alterations that occurred to GIS and PHI following ion exchange, all zeolites which were treated overnight with a 0.01M Cu^{2+} solution for 1 cycle and at 50°C were tested in the reaction. Additionally, copper-exchanged zeolites were tested in the DMTM reaction for comparison. Specifically, a NH_4MOR ($\text{SiO}_2/\text{Al}_2\text{O}_3=20$) and a NaMOR ($\text{SiO}_2/\text{Al}_2\text{O}_3=13$) were exchanged with a 0.05M solution overnight at 50°C. It should be noted that the aforementioned commercially available mordenite structures had a much higher $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio, and consequently a higher hydrothermal stability, and could tolerate a higher concentration solution (0.05M).

The results of the DMTM for all copper exchanged zeolitic frameworks, as well as their copper content and $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios are presented in **Table 35**.

Table 35: DMTM results for all copper-exchanged zeolitic frameworks.

Catalytic support	Cu % (w.t.)	SiO ₂ /Al ₂ O ₃ ratio	μmol CH ₃ OH/g _{cat}
GIS	-	3.8	-
PHI	2.88	4.1	-
MER	2.23	4.9	-
EDI	3.07	2.7	4.55
NH₄-MOR	1.75	20.0	22.45
Na-MOR	3.41	13.0	11.33

As seen in **Table 35**, among all 4 synthesised zeolites, only EDI was able to produce any methanol during the DMTM reaction with a methanol yield of 4.55 μmol CH₃OH per gram of catalyst. In comparison, NaMOR and NH₄MOR produced 11.33 and 22.45 μmol CH₃OH/g_{cat} respectively. Expectedly, there was no performance in the DMTM by GIS and PHI, the frameworks of which had collapsed during the ion exchange process or the subsequent calcination. However, the MER framework which remained intact following ion exchange did not perform in the DMTM.

8.6 Discussion

Following the hypothesis that the presence of a 8MR in a Cu-exchanged zeolitic framework plays an important role in the DMTM, four different zeolitic frameworks containing only 8MR and 4MR in their structures were synthesised in the present work. Following synthesis, calcination and ion exchange, they were all tested in the DMTM reaction. However, the frameworks of GIS and PHI had previously collapsed following ion exchange. Between MER and EDI, only EDI was able to produce a small amount of CH₃OH, which was considerably smaller in comparison to Cu-exchanged NH₄MOR and NaMOR with different Si/Al ratios.

Although only one of the investigated zeolites was able to produce any CH₃OH, important knowledge and insights regarding zeolites in the DMTM were achieved through the study. One important parameter that seemed to affect several aspects of the zeolites was the Si/Al ratio which comprised their framework. Indeed it has been widely reported that the Si/Al ratio of zeolites can affect their crystal size, their stability, their performance in different reactions (Shirazi, Jamshidi & Ghasemi, 2008)(Golubev et al., 2021). This is understandable, as the Si/Al ratio and consequently the number of Al atoms in the framework dictates the number of valence imbalances of the framework that need to be balanced out by external ions. When exchanged with a desired

metal, these ions become the active sites in different reactions. As a result, the Si/Al ratio of a framework has a direct correlation with the number of active sites that can be deposited on the zeolite. However, this also makes the direct comparison difficult between the results of NH₄MOR (SiO₂/Al₂O₃=20) and a NaMOR (SiO₂/Al₂O₃=13) and the results of EDI which had a considerably lower SiO₂/Al₂O₃ ratio of 2.7.

Additionally, the Si/Al ratio of a zeolite not only influences the number of active sites that can be formed when exchanged with copper, but also the nature of the active sites. Sushkevich, Palagin, and van Bokhoven in 2018 reported that the aluminum content of the zeolitic framework can be manipulated to create monomeric or oligomeric copper active sites, which in turn have different activities in the DMTM. Understandably, higher Si/Al ratios lead to the formation of single atom active sites, while a lower Si/Al ratio leads to the presence of more copper atoms, which form clusters on the zeolitic framework. This hypothesis is further supported by the work of Grundner et al. in 2015, who had reported the same findings.

Mahyuddin et al. in 2018 reported that the formation of the desired di-copper core ([Cu₂(μ-O)]²⁺) required the presence of two Al atoms inside of a 8MR, separated by two Si atoms. This atom orientation would, according to the researchers, lead to the formation of the desired Cu-O-Cu bridge on the framework, which is the catalytic active site of CuMOR in the DMTM. Thus, it is hypothesised that an ideal theoretical Si/Al ratio exists, which, assuming perfect distribution of Al atoms in the framework, would maximise the formation of the desired active sites. Since each different zeolitic framework seems to have a different active site which performs in the DMTM, the suggested “ideal” Si/Al ratio would be characteristic to each zeolite. In the case of CuMOR, where the di-copper core is the desired active site, a Si/Al ratio of 6 would be recommended. This could be the reason of the inferior performance of CuEDI in comparison to CuMOR, as the low Si/Al ratio of 2.7 could have not been ideal for the formation of active sites, and several inactive copper species could have been formed on the zeolite.

The calcination process, which caused the collapse of the GIS framework, highlighted the importance of good hydrothermal stability of zeolites, especially when they are employed as catalysts in processes which involve high temperatures. As previously discussed, the Si/Al ratio of the framework has a direct influence on hydrothermal stability, with lower Si/Al ratio zeolites

appearing to be more unstable, which is expected as they have more valence imbalances, balanced by extra-framework ions.

The ion exchange process indicated the significant effect that the solution concentration and acidity had on the stability of the zeolites. Higher concentrations, which had a more acidic pH value, caused severe dealumination to all zeolites, which was particularly harmful in the low Si/Al ratio zeolites synthesised in the present study. When exchanged with more dilute solutions, EDI and MER exhibited no stability problems even after calcination. Consequently, this is an important factor that needs to be considered in the study of the DMTM over ion-exchanged zeolites.

Although the Si/Al ratio is one of the most deciding features of a zeolite, influencing an array of different parameters, one should not forget the influence of the topological and geometrical characteristics of each framework. As previously discussed, the performance of CuZSM-5 and CuMOR were compared and the researchers found the CuMOR active sites to be well constrained inside the 8MR pores of the framework. They attributed the improved performance of the CuMOR to a good confinement of the active site, which led to a decrease in the activation barrier of the reaction, which agreed with previous works that highlighted that a good confinement might be necessary for higher CH₃OH yields. This argument is also further reinforced by the good performance of some small pore zeolite-like materials, namely SSZ-13 and SAPO-34. The good performance of the materials could be speculated to be due to the good confinement of active sites inside the small pores. (Kvande et al., 2020)

Additionally, the pore size, as well as the general topological structure of the pore and rings on which the active sites form play an important role in the formation of the active site. In a study comparing the performance of several different Cu-exchanged zeolitic frameworks, Mahyuddin et al. in 2017 discussed the effect of the angle of the di-copper bridge angle on the performance of the catalyst in the DMTM. The researchers concluded that apart from the importance of the already discussed confinement of the active site, the Cu-O-Cu angle directly affects the performance of the catalyst in the activation of methane.

Considering the importance of the Cu-O-Cu angle, the 8MR might indeed be a good host for the formation and the good performance of a copper catalytic active site in the DMTM. However, not all 8MRs on different zeolitic frameworks are expected to exhibit the same performance since their three-dimensional structure can differ considerably. More specifically, 8MRs in different

frameworks exist in either regular or bent shapes. This can be seen in a simple schematic representation in **Figure 64**.

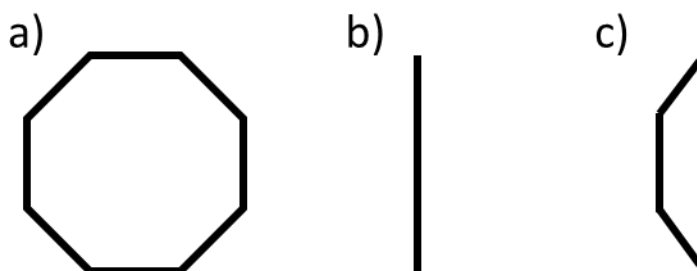


Figure 64: a) 8-membered ring b) regular 8MR as seen from the side c) bent 8MR as seen from the side.

Depending on the location of the Al atoms in the 8MR, the bending of the 8MR can affect the distance between the copper atoms exchanged onto the zeolite and as a result cause a different angle of the subsequently formed Cu-O-Cu bridge which directly affects the CH₃OH yields. This can be seen schematically in **Figure 65**. **Figure 65 a)** presents the formed Cu-O-Cu bridge on the 8MR of a zeolite. Comparing the same di-copper bridge in a regular and a bent 8MR, it can be easily understood that in the case of a regular 8MR the copper atoms would be farther apart to each other, thus leading to a wider bridge angle. On the contrary, a bent 8MR, in which the copper atoms would be closer to each other would lead to the formation of a narrower angle Cu-O-Cu bridge. As a result, the θ angle of the Cu-O-Cu bridge, as well as the θ_{bending} of the 8MR are both considered important factors to the performance of a zeolite in the DMTM.

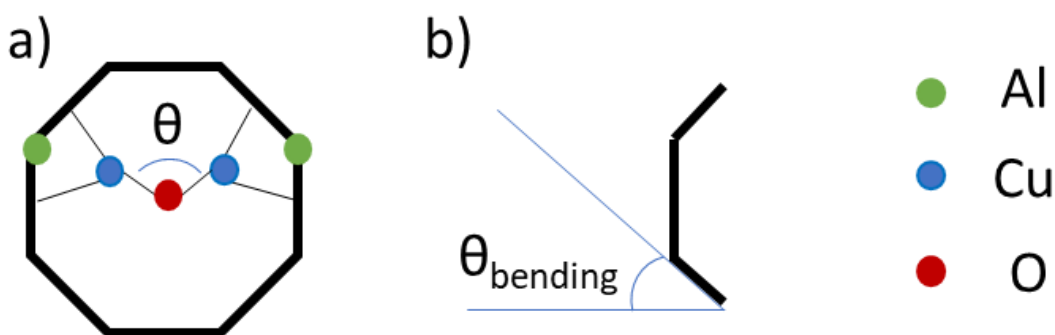


Figure 65: a) Cu-O-Cu bridge on an 8MR of a zeolite b) bent 8MR with a bending angle θ_{bending} .

Considering the importance of the bridge angle and the bending angle of 8MRs, it is useful to compare the geometry of EDI and MER which were tested in the DMTM with different results. It is reminded that while EDI was able to yield small amounts of CH₃OH when tested in the DMTM,

MER did not produce any methanol. The frameworks of MER and EDI are presented in **Figure 66** and **Figure 67** accordingly.

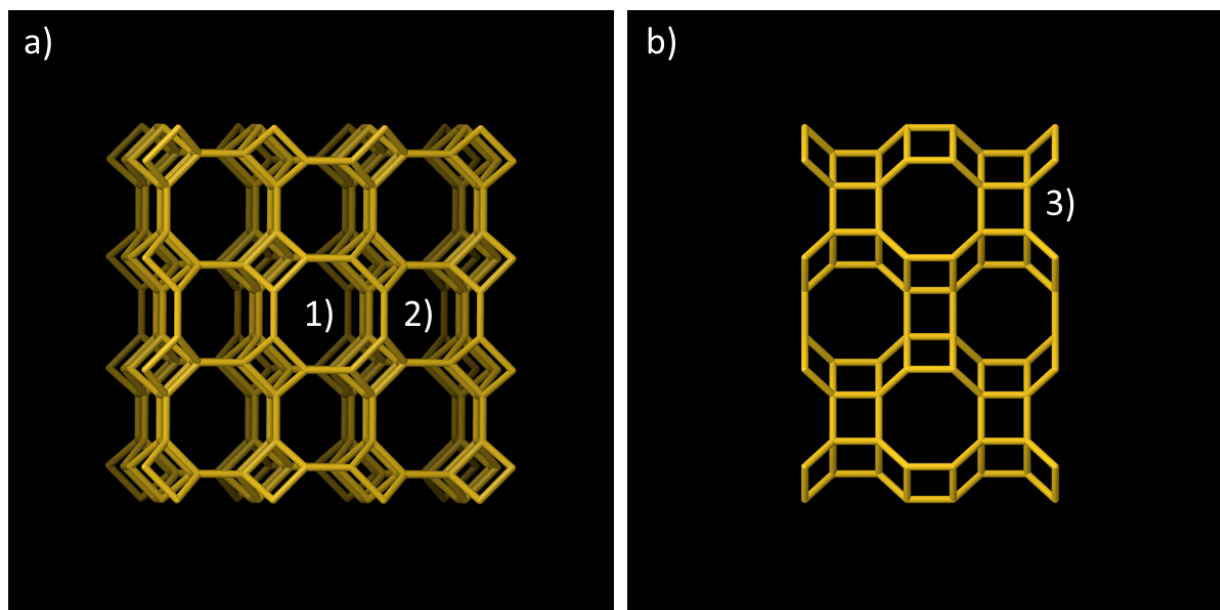


Figure 66: MER as viewed along plane a) [001] and b) [100].

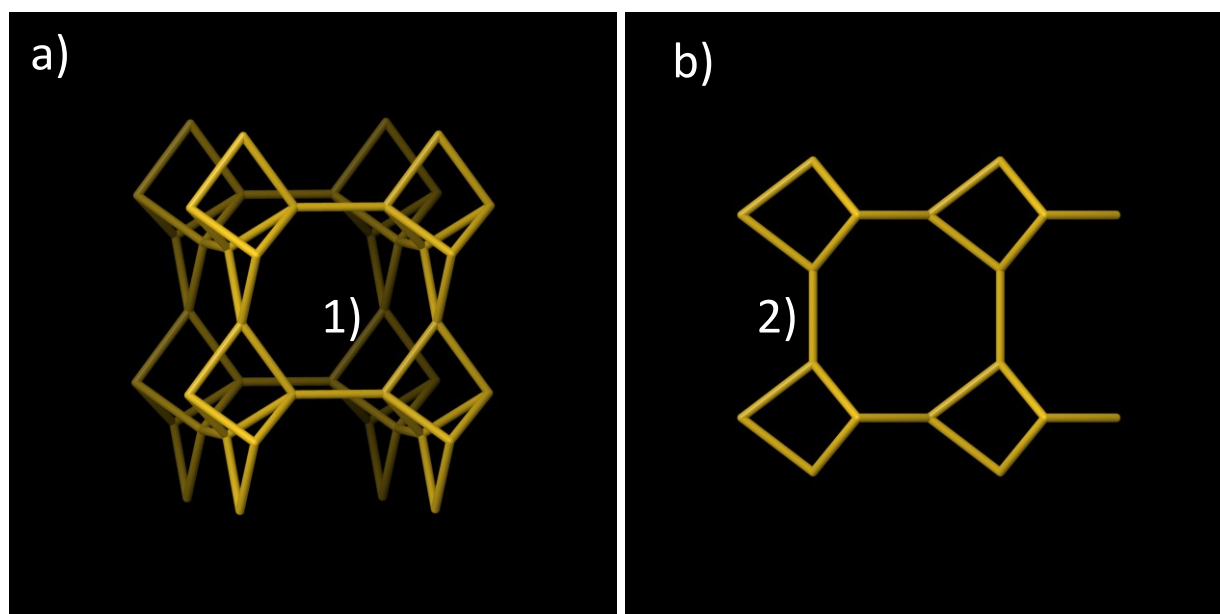


Figure 67: a) EDI 3D structure b) viewed along plane [100].

As seen in **Figure 66**, there are two types of 8MRs in the MER framework, one flat 8MR with a bending angle of 90° (1) and one bent 8MR with a bending angle of 45° (2 and 3). Similarly, EDI also contains 2 types of 8MRs. As seen in **Figure 67**, EDI comprises of a regularly shaped 8MR

(2) and a highly irregular 8MR (1). The irregularly shaped 8MR on EDI has a complex 3D structure with many intersections, which makes it hard to define a bending angle as it bends in several different planes. The regular 8MR of EDI has a relatively small bending angle of approximately 30°.

When comparing the geometries of the two zeolites (EDI and MER), the two major differences is the existence of the irregularly structured 8MR in the case of EDI, as well as the bending angle of the bent 8MRs of the different frameworks, with EDI having a smaller bending angle. These geometrical characteristics of the two zeolites could potentially be the reason of their different performance in the DMTM. Specifically, as previously mentioned a bent 8MR might host the Cu atoms closer together, leading to a smaller Cu-O-Cu bridge angle, which seems to be beneficial for higher CH₃OH yields. A smaller bending angle would lead to more bent 8MR, with the Cu atoms being closer together. As a result, this could be an explanation to the improved performance of the EDI in comparison to MER which has bending angles of 45° in the bent 8MRs and flat 8MRs with an angle of 90°. Additionally, the irregularly shaped 8MRs of EDI with intersections and bends along all planes might be another reason of the improved performance of the zeolite. The copper atoms might exchange on several different positions which are relatively close to each other due to the bends of the framework, thus leading to ideal bonding distances for the Cu-O-Cu bridge. Additionally, the distances between the Cu atoms in the case of the flat and bent rings of MER might be too high for a functional Cu-O-Cu bridge to form, hence the lack of performance of the zeolite in the DMTM.

Building on this hypothesis and the corresponding experimental findings, it is understood that the zeolitic framework itself plays an important role in the formation of the desired active sites in the DMTM. It is essential to investigate and understand the location and nature of active sites in each different zeolitic framework that performs in the DMTM, to further add to the existing knowledge. Understanding all the different factors that affect the performance in the reaction can help to eventually engineer the perfect material, regarding both the catalytic support that hosts active sites as well as the active sites themselves.

8.7 Conclusions and outlook

The present work aimed to understand the influence of the zeolite geometry and topology on its performance in the DMTM. Specifically, the hypothesis was investigated that the 8MRs in zeolitic frameworks are of particular importance for maximising CH₃OH yields. 4 different zeolites were synthesised which contained only 8MRs and 4MRs in their framework, to isolate the effect of the 8MR in the reaction.

Although only one of the zeolites tested was able to produce any methanol, namely EDI, several observations and conclusions were achieved through the study. The calcination process which caused some of the frameworks to collapse highlighted the need for an appropriate Si/Al ratio which would grant the framework enough hydrothermal stability to withstand the elevated temperatures involved in the proposed DMTM reaction sequence. Similarly, the framework stability was heavily affected by the dealumination caused by the mildly acidic solutions used for ion exchange. Extra care needs to be taken particularly in the case of low Si/Al zeolites as these are more prone to the dealumination caused by the acidic medium which causes the frameworks to collapse. As a result, it is essential to identify the stability limits of each framework that is exchanged with copper ions and work with the appropriate solution concentrations. It is concluded that the ion exchange of different zeolites requires special care, with lower ion exchange solution concentrations appearing to ensure the stability of the frameworks, due to minimal dealumination.

Additionally, as reported in the literature, the Si/Al ratio of a zeolite decides the amount and nature of active sites that are formed after ion exchange in extra-framework positions on the zeolite, thus heavily affecting its performance in the reaction. It is speculated in the present study that an optimal Si/Al ratio could exist depending on the zeolitic framework in interest and the active sites which are active for the DMTM on the particular framework.

The confinement of the active sites was also discussed and as literature suggests, active sites appear to have a better performance with a tighter confinement of the active sites, as this appears to lower the activation barrier for the methane activation. The 8MR appears to provide an ideal setting for the formation of active sites for the DMTM (Kvande et al., 2020)(Mahyuddin et al., 2017).

Additional reviewing of the literature as well as observations of the geometry of different frameworks and the analysis of experimental results revealed that the geometry and topology of

each zeolitic framework can have a significant effect on the performance of a Cu exchanged zeolite in the DMTM (Park, Park & Ahn, 2019). Specifically, the fact that the Cu-O-Cu bridge angle affects CH₃OH yields, as well as the fact that 8MR rings can exist in either flat or bent shapes with different bending angles, led to the conclusion that the geometry of each zeolite contributes to the nature of active sites formed. The bending angle of the 8MR can directly affect the Cu-O-Cu bridge angle, which is reported in the literature to have an immediate effect on the performance of the active site in the DMTM. This happens because the Cu atoms on the extra-framework positions can have a shorter distance between them due to the bent shape of the 8MR, which leads to improved CH₃OH yields, as shown by the comparison of experimental results of MER and EDI. Thus, it is essential to identify the desired active sites on each framework by evaluating the activity of different in nature active sites, and to further assess if a particular zeolite topology would be suitable for hosting them.

As discussed in previous chapters, effort needs to be put in future research in the development of a more efficient catalyst in the DMTM. Summarising all above observations, several factors need to be considered when designing a new zeolitic catalyst in the DMTM:

- The Si/Al ratio which can affect the hydrothermal and acidic stability of the zeolite, as well as the degree of dispersion and nature of active sites.
- The number of atoms in the rings comprising a zeolitic framework, as confinement of active sites appears to have an impact on the final CH₃OH yields, with 8MRs appearing to be providing the best environment.
- The identification of desirable active sites on each framework.
- The shape of the 8MR on each framework.
- The Cu-O-Cu bridge angle.

Considering all of the above, the design of a new zeolitic material should aim to first identify the nature of desired active sites (mono-copper, di-copper, tri-copper etc) and aim for a theoretically “ideal” Si/Al ratio for the formation of these sites. At the same time, the Si/Al ratio used should be high enough to ensure hydrothermal and acidic stability to the catalyst, but also low enough for a good dispersion of sites. It is deemed essential for more research to be carried out in identifying the exact nature of active sites which perform in the DMTM for each zeolitic framework, so safer

comparisons and conclusions can be achieved. Finally, theoretical calculations could be carried out to identify the optimal 8MR bending angles and Cu-O-Cu angle.

The first step in designing the “perfect” new catalytic material would be to identify the theoretically optimal design parameters. The previously discussed optimal angles, if identified, could be used along with the optimal Si/Al ratios to design and engineer a new material or to modify existing materials.

The modification of existing materials is limited by several factors, like the acceptable Si/Al limits of each zeolitic framework or the pre-existing and unchangeable geometry of each zeolite, but could still lead to improved results compared to the currently reported. If technologically possible, the engineering of a new material with the exact desired specifications is thought to be the most hopeful route. However, exhaustive research still needs to be carried out to perfectly understand the reaction mechanism for each zeolite as well as the different topological specifications of each framework and how they would affect the DMTM. Additionally, the possibility of engineering a completely new material with the exact specifications needed might be uncertain.

9. *Conclusions and future work*

The present work concerned the direct methane to methanol transformation over zeolitic catalysts. The study investigated several aspects of the DMTM over one of the currently best-performing catalysts, copper-exchanged mordenite. An experimental method was developed, a kinetic model was suggested and an industrial concept of the process was visualised and investigated for economic feasibility. Additionally, the hypothesis that the 8MRs in a zeolitic framework play an important role in the performance of a catalyst in the DMTM was tested, by synthesising several zeolitic frameworks and employing them in the DMTM.

9.1 Conclusions

Different aspects of the DMTM over a CuMOR catalyst were touched on in the present work. The foundation of the work was the conduction of a series of experiments leading to the final experimental method used. Through different experiments, several conclusions were reached regarding the catalyst and the reaction sequence needed to maximise the methanol productivity.

A 3% CuMOR (% w.t.) catalyst displayed the highest methanol productivity and was used in the rest of the experiments. An important observation made was that the production of methanol could not take place in the absence of water, while it was evident from different experiments that in the presence of water, the concentration of produced methanol closely followed the trend of water present in the system. The role of water seems to be two-fold in this reaction, both as a soft oxidant as well as a displacing agent for the methanol once it forms on the catalytic active sites. In both of these ways, water appears to shield methanol from overoxidation, thus leading to a very selective reaction towards the desired methanol, which was confirmed experimentally by no production of CO₂.

Although H₂O seems to play such an important role in the reaction, it was evident that it competes with CH₄ for adsorption onto the same active sites if both molecules are fed to the system simultaneously, with water adsorbing more readily and thus blocking the sites for the adsorption of methane. As a result, co-feeding the reactants leads to no production of methanol. Similarly, introducing water to the system or reducing the catalyst with hydrogen prior to the adsorption of CH₄ leads to no methanol productivity. To overcome this issue, a step-wise reaction sequence is recommended in which first moisture and impurities are removed from the catalyst through the

ramping of the temperature, subsequently a CH_4 adsorption follows on the catalytic active sites, followed by the introduction of water into the system to form and desorb methanol. The full cycle can then be repeated with negligible difference in methanol productivity. A temperature of 400°C is sufficient for the preparation of the catalyst, while the most favorable temperature for isothermal methane adsorption and reaction with water is 200°C . Finally, it was observed that the window for CH_3OH is rather narrow, with methanol being produced only in the range of $150\text{--}250^\circ\text{C}$, with CO_2 starting to be produced at 200°C and continuing to any temperature above. As a result, the isothermal reaction at 200°C displayed a fully selective production of methanol with no carbon dioxide observed.

Further to the development of an experimental sequence, the kinetics of the reaction were investigated. Based on experimental data and observations, as well as evidence reported in the literature, kinetic equations were developed and variations of them were modelled in order to obtain a satisfactory fit to the experimental data. Modelling the different variations of kinetic equations revealed that aside from the derived consumption rate of the methoxy species formed on the catalyst during the CH_4 adsorption, an additional term was necessary to describe a faster decline of the concentration of produced methanol observed. An extra CH_3^* consumption term was added, which described the desorption or the displacement of CH_3^* species by water, before they reacted towards the formation of methanol, thus leading to their faster depletion from the catalytic active sites. The addition of this term led to a good fit between the model and experimental data. It should be noted that an even better mathematical fit was obtained by squaring the aforementioned extra term but was omitted due to a lack of physical meaning.

The suggested kinetic model was investigated in the temperature range of $150\text{--}250^\circ\text{C}$ which is the temperature range of methanol production. The model appeared to adequately predict the evolution of species in the system up to a temperature of 225°C , displaying a significant deviation from experimental data above. This is in good agreement with experimental observations, since above 200°C the reaction does not selectively produce only methanol and side reactions become more prevalent, with a higher CO_2 production at higher temperatures. It is thought that a more complex mechanism takes place at higher temperatures with the overoxidation of both methanol in the gas phase as well as methoxy species directly on the active sites taking place, which the suggested model cannot predict.

As the DMTM over CuMOR catalysts is a topic highly industrially relevant, an industrial process concept was suggested as part of the present thesis. The most important hurdle to overcome in the conceptualisation of the reaction at an industrial scale, was the batch-like, non-continuous nature of the lab-scale reaction. However, in compliance with the fact that the adsorption of methane has to take place prior to the introduction of water to the system, a continuous operation was achieved by a smart design of three fluidised bed reactors in series, each of which carries out one of the lab-scale process steps. The reactors operate in a looping fashion by circulating the catalyst between them.

The process designed in the present study involves a series of simple separations including physical separations and a distillation column operating at slightly elevated pressure. The separations used are able to isolate the reaction products, H_2 and CH_3OH , at high purity, which most of the used reactants as well as the carrier gas are recycled inside the process to minimise losses.

A complete technoeconomic assessment of the process was carried out, which aimed to obtain detailed information regarding the total capital investment as well as operational costs and profitability key indicators of the process. Additionally, the potential of heat integration was explored, which showed that a heat integration of this process should not be considered. This conclusion was reached based on the fact that only a 4.3kW of energy is available for integration due to the process streams existing at different, non-overlapping temperature ranges that do not favor heat integration. Moreover, it was calculated that the produced hydrogen of the process would generate more profit being sold as product, as opposed to being used as a fuel to cover the fired heat utilities.

The technoeconomic analysis clearly showed that under the current catalytic performance, the process could never achieve profitability due to the very high methanol production cost. The main costs of the process arise from the capital investment needed for the fluidised bed reactors, while the main utility costs arose from the electricity used in the multi-stage compressor C-101 and the hydrogen separator X-101. The combination of the relatively high capital and operational costs and the low productivity of methanol under the current performance of the catalyst are prohibitive for the profitability of the process.

In order to assess how far the suggested process is from profitability, the case scenarios of a 10-, 40- and 50-fold more productive catalyst towards methanol were investigated, with the economic analysis of the process taking place for each of these cases. The results of the analysis showed that a 50-fold more productive catalyst would lead to an ideal project with just 2 years of payback time, while a 40-fold more productive catalyst would also lead to an excellent project with a pay-back time of 2.5 years, which is thought to be a realistic target for the future.

Inspired by the need for a more productive catalyst, some more catalysts were synthesised and tested for the DMTM, based on the hypothesis that the presence of an 8MR in the zeolitic framework plays an important role in the productivity of methanol. In order to isolate the effect of the 8MR, four different zeolitic frameworks were synthesised which only contained 4MR and 8MR in their frameworks.

Throughout the synthesis, calcination and ion exchange of the aforementioned catalysts with copper, the framework stability appeared to be a very important factor. The calcination at a high temperature caused the alteration of the GIS framework, while the treatment of all frameworks with mildly acidic copper ion solutions of low concentration followed by calcination caused severe damage to the PHI framework. Additionally, all frameworks collapsed, becoming amorphous solids, when treated with copper ion solutions of higher concentration and lower pH values. This highlights the sensitivity of zeolites to both hydrothermal treatment as well as acidic environments, which lead to the dealumination of the framework and consequent formation of vacancies which lead to the collapse of the framework, a phenomenon more prevalent at lower Si/Al ratio zeolites. Among the synthesised zeolites only MER and EDI retained their crystalline structure after ion exchange and were tested in the reaction, with only EDI producing a small amount of methanol.

It was concluded through this work that the Si/Al ratio of zeolites is an important factor affecting not only the hydrothermal and acidic stability of zeolitic frameworks, but also the number and nature of active sites formed. It is hypothesised in the present work that an ideal theoretical Si/Al ratio could exist for each zeolitic framework in regards to the DMTM, to maximise the formation of desired active sites and also the methanol productivity. It is furthermore concluded that the use of low concentration ion exchange solution is necessary when treating zeolites, as to minimise the effect of dealumination and to ensure the framework stability.

Attempting to identify the reason of different performance between EDI and MER, a geometrical and topological comparison of different zeolitic frameworks was carried out. It was observed that in different frameworks, 8MRs exist in different variations, as they can be flat or bent with different bending angles. Comparing different frameworks and their performance in the DMTM it was concluded that the bending angle of the 8MR can play an important role in the final methanol productivity of the zeolite, as it affects the distance between Cu atoms and as a result the Cu-O-Cu bond angle which has an immediate effect on the catalytic performance. It was concluded that the reason between the different performance of EDI and MER could be the bending of the EDI 8MR, which brings the copper atoms closer together in comparison to the MER so that the desired dicopper core can be formed which is active in the DMTM. Moreover, the confinement of the active site by the 8MR could be another important factor contributing to the good performance of zeolites containing 8MRs in their framework.

9.2 Future outlook

The direct methane-to-methanol transformation is one of the most industrially relevant and attractive topics in the global energy research field. Decades of research have led to important progress, which has brought the industrial application of the DMTM one step closer to realisation. As heavy effort is still dedicated in the development of catalysts and methods which can achieve improved methanol yields, it is important for future research to target the gaps and the still unanswered questions regarding the currently best performing catalysts. Future research should be guided by the findings as well as the shortcomings of previous research, as well as by new ideas and reasonable hypotheses.

The present study touched on several aspects of the DMTM, from its laboratorial application on one of the best performing catalyst to date, CuMOR, to the kinetic study and the industrial application and profitability analysis thereof. Interesting and enlightening findings and conclusions were reached in the present work, and future research is suggested based on them.

As part of the present study, a careful investigation of the most favorable conditions for the DMTM over a CuMOR catalyst took place by carrying out appropriate experiments targeting different aspects of the reaction. This is considered to be an essential step for every catalytic process. Since each catalytic system is unique and the reaction mechanism might differ, it is believed that for all newly reported catalysts in the DMTM, a series of experiments should be performed to identify

the most favorable conditions of the reaction, so that a comparison between catalysts would happen on a basis of maximum CH_3OH production achievable in each system.

To further understand and improve the DMTM over a CuMOR, a more thorough investigation of the effect of temperature on the adsorption process of CH_4 is recommended. A series of experiments of CH_4 adsorption under different temperatures ranging from 25°C to 200°C where the reaction takes place isothermally could indicate if this step could take place more efficiently for the maximisation of methanol yields at a lower temperature. A lower temperature of adsorption could potentially lead to annual energy savings in the suggested industrial process.

An in-situ quantification of active sites could provide valuable information regarding the conversion of adsorbed species. A correlation of the number of active sites with the copper content of the catalyst could provide indirect information regarding the nature of active sites (copper monomers, dimers, trimers, etc.). A more reliable quantification of adsorbed CH_4 in situ could take place by the temperature programmed adsorption and desorption of CH_4 under live monitoring by a mass spectrometer, preferably coupled with gas chromatography characterisation. Additional insight into the nature of active sites could be given by a characterisation of the catalytic material, via extended X-ray absorption fine structure (EXAFS).

It has been shown in the present work that the adsorption of CH_4 needs to take place prior to the exposure of the catalyst to water, to avoid the pre-occupation of sites preventing CH_4 adsorption. Under reaction conditions, the presence of H_2O in the system leads to the formation and desorption of methanol. However, a deeper understanding of the potential of H_2O to displace the previously adsorbed methane species is considered to be essential for the study. An investigation of the displacement of CH_4 by H_2O under different conditions is recommended. Especially focusing on temperatures where the reaction does not take place (under 150°C), a CH_4 adsorption step should take place followed by the exposure of the catalyst to H_2O in the form of either pulses or continuous flow. Monitoring the desorption of any methane during the experiment will provide information about the potential of H_2O to displace CH_4 from the active sites. These findings would enhance the understanding of the reaction and could be used in the further development of the kinetic model.

An important aspect of the performance of different catalysts is their deactivation over prolonged exposure to reaction conditions. A systematic design of accelerated aging experiments of the

catalyst could give information about the loss of performance of the catalyst over time. This could be achieved by exposing the catalyst to exaggerated temperature and humidity conditions in comparison to the reaction conditions for various amounts of time. The subsequent testing of the catalysts in the DMTM could then provide information regarding their deactivation via aging. This would be particularly important to investigate in the case of a zeolitic catalyst, as the stability of zeolites, as discussed previously, can be severely affected by exposure to highly humid environments, especially at elevated temperatures. The findings of these experiments could be further used in the industrial process, to accurately identify the amounts of catalyst needed annually, which would lead to more accurate results during the technoeconomic analysis of the project.

An investigation of the kinetics of the reaction showed that a model with an added consumption term for CH_3^* could provide a good fit for the experimental data. It should be noted that the reaction kinetics were derived in the present work based on a limited number of experiments, carried out under atmospheric pressure and different temperatures and at one H_2O concentration (the concentration of H_2O saturation in moisture at 21°C). Although the proposed model describes adequately the reaction under the conditions of interest (between $150\text{--}225^\circ\text{C}$ where no side reactions are present), it could be beneficial to carry out further sets of experiments on the reaction to investigate the behavior and fit of the suggested model.

The first set of experiments which could be carried out involves varying the partial pressure of methane during the pre-adsorption step. With an appropriate modification of the experimental setup, the partial pressure of methane could be raised while carrying out all other steps of the reaction in the same fashion. A variation of the partial pressure of CH_4 during pre-adsorption is expected to have a direct effect on the initial concentration of CH_3^* species on the catalyst. Since $[\text{CH}_3^*]$ is a fitted parameter in the model, an investigation of the relationship between the partial pressure of CH_4 during pre-adsorption and initial $[\text{CH}_3^*]$ should be performed. Potentially, a correlation could be made which can then be used along with the model for modelling the reaction at different pre-adsorption conditions.

Another important aspect of the DMTM over a 3% CuMOR is the concentration of gaseous H_2O fed over the catalyst. In the present work, only a single concentration of gaseous water was investigated. Although in the step-wise fashion in which the reaction is carried out the

concentration of water remains practically unchanged during the progression of the experiment, it is still one of the terms included in the kinetic model. To obtain a better evaluation of the suggested model, it is recommended that the reaction is carried out at a range of different H_2O concentrations. These experiments could confirm the accurate prediction of the model on the progression of species over time as well as the predicted yield of CH_3OH . Additionally, a correlation between a varying concentration of H_2O and CH_3OH over the same amount of time could be developed, which could also be useful for a further optimisation of the industrial process in ASPEN.

It was observed both experimentally and through the kinetic modelling that the reaction only selectively produces methanol in the range of 150-200°C. The suggested kinetic model is considered invalid above 225°C, as the side reactions which lead to overoxidation products like CO and CO_2 are prevalent at higher temperatures. To obtain a more complete model which also predicts side reactions, considerable modifications on the suggested equations are necessary. Although the overoxidation of CH_3OH itself is possible and expected at higher temperatures via steam reforming (above 200°C) and autothermal reforming (above 250°C) in the presence of copper-based catalysts, the overoxidation of CH_3^* species could be happening via a different mechanism directly on the active sites. Thus, an in-situ investigation of the mechanism at elevated temperatures would be necessary to understand the mechanism of overoxidation and to be able to derive kinetic equations to describe all different phenomena (Iulianelli et al., 2014)(Geissler et al., 2001). Furthermore, once the overoxidation to CO and CO_2 is added to the kinetic model, a comparison of the DMTM at lower and higher temperature could be made. A kinetic analysis as well as a process analysis could reveal whether it would be profitable to compromise on the very high selectivity of the process at 200°C to obtain a faster reaction at temperatures of 225°C and higher, considering the potential need for additional separations.

A smart design of fluidised beds in series reactors was recommended to overcome the hurdle of a non-continuous DMTM process and an industrial concept of the DMTM over a 3% CuMOR was suggested. The process included the separation of all products in high purity and also a full economics and profitability analysis to reach conclusions about industrial feasibility.

The industrial process suggested in the present project was directly inspired and based on the laboratorial DMTM process on a CuMOR which was developed. All conditions and materials of the industrial process designed were taken to be identical to the laboratorial process. As a result,

helium was used as a background gas in the industrial process concept, as no additional experiments were carried out under a different background gas. In practice, helium would be an unlikely choice as a carrier gas in the industry due to economic and practical reasons. However, helium in the suggested process is recycled throughout the process, with only negligible annual losses, which are resupplied to the process through a fresh feed. Additionally, the initial investment in the gas as well as the freshly re-supplied helium, only pose a negligible cost in comparison to the entire process. Nevertheless, it is suggested that for more accurate and industrially applicable results, a different choice of inert gas is made, which could possibly be argon or N_2 . Care should be taken in the case of choosing N_2 as a background gas for the process. It is advised that experiments are carried out to exclude any interaction of N_2 with the active sites which could affect the performance of catalyst in regards to CH_3OH production. In the case of no interference of N_2 with CH_3OH production, it is believed that the use of N_2 as a background gas in the process would produce very similar results as those presented in the present study. This is because the separation steps following the production of methanol in R-102 would need negligible changes, if any. Generally, the choice of a different carrier gas could decrease the costs of the process, both by the costs related to the gas itself, but the changes in process economics are believed to be negligible.

The process was modelled on ASPEN Plus, the database of which did not contain the highly specific CuMOR and the methoxy species which form on its active sites. As a result, representative materials needed to be defined. These materials were used inside of the reactors to simulate representative reactions which were defined to represent the actual reaction in the DMTM over a CuMOR catalyst. The thorough definition of the actual materials with their chemical and physical properties on ASPEN would aid for a simplification of the model without the need for representative materials and could potentially provide improved accuracy to the simulation results.

The kinetic approach used in the reactors was a black-box model which manipulated the rate constants of the representative kinetic equations to achieve a CH_3OH yield taken from the literature. Although the black-box method kinetics are bound to provide an accurate result, it is recommended that detailed kinetic equations are used in the ASPEN simulations. This could create a more flexible ASPEN model which could be investigated and optimised for the industrial process conditions, so that the product yield would be maximised while keeping the process costs to a minimum. Additionally, the suggested kinetic model could be used in the reaction for a

simplification of the model, although this should be approached with care, as it would need to be correctly applied onto the representative materials and reactions or to real materials after they are defined within ASPEN, which could be challenging.

Employing more elaborate kinetic equations in the reactors would also allow for another important optimisation inside the process. It is reminded that the H_2O concentration used in the simulations was the same concentration as the one used in the laboratorial experiments. However, the importance of water presence and concentration and its direct effect on methanol yield was already discussed in previous chapters. The use of detailed kinetics inside the reactors would allow for the use of different water partial pressures inside the reaction, which would lead to higher CH_3OH yields at smaller residence times. Smaller residence times would mean that smaller catalyst masses would be needed inside the reactors, leading to considerably smaller capital and operational costs. Additionally, higher H_2O concentrations would lead to smaller carrier gas fractions inside the process, thus reducing the amount of an inert gas circulating through almost all units of the reaction, and thus reducing the capital and utility costs of these units. It is important to note that the use of higher H_2O partial pressures in the process could dramatically reduce the catalyst required performance as a complete cycle of reaction on catalytic particles would happen in a considerably shorter time. As a result, it is considered very promising to investigate the simulation results from the use of higher H_2O concentrations or even the use of steam, as the feasibility of the process might prove to be much better even with the current catalyst performance.

Regarding the process bottlenecks, the only reasonable option for hydrogen separation was considered to be the commercially available hydrogen separator X-101 used in the process. Although this is an acceptable solution, its capacity was marginally enough to cover the needs of the scenario of the current catalyst performance. As the catalyst performance improves in other scenarios, an increasing amount of H_2 needs to be separated, with the need for several (up to 50) hydrogen separators working in parallel. This is, of course, not a practical solution for industrial application and despite theoretically being an effective method of separation, it would most likely be dismissed in practice, especially for the cases of higher catalyst performance. It is recommended that in future developments of the ASPEN model, an alternative solution for hydrogen separation is investigated.

Similarly to the separation of H_2 , another bottleneck of the process can be considered to be the separation of the large fraction of the carrier gas from the stream exiting the reactor where the reaction takes place, which contains the products of interest. The separation of the carrier gas in the process was achieved through a compression of the stream and a physical separation of the more volatile carrier gas and H_2 , while the traces of the carrier gas remaining were removed from the top of the distillation column T-101. Since the multi-stage compressor C-101 which compresses the stream to a sufficient pressure for physical separation represents one of the major capital and utility costs through its operation, another route should be explored for the potential of separating the carrier gas from the product-containing stream in a cheaper and more efficient way. For such a separation, the use of membranes could be a promising solution. Impressive advances have been made in the field of membranes, which are widely used for a number of separations, so this is considered a solution worth exploring. (Nair et al., 2012)

As far as the process economics and profitability analysis are concerned, the technoeconomic analysis presented in the study is based on a method suggested in the literature, which was developed by correlations derived from existing processes. It would potentially be beneficial for future works to use a number of different economic analysis methods and compare the results, to validate the reliability of the results. Additionally, the price of both raw materials and products could vary based on several factors including the location, the source, as well as the application for which the products (H_2 and CH_3OH) are intended. The results of the technoeconomic and profitability analysis would be more accurate if investigated in a more constrained context, where the specific location of the suggested project, as well as more specific pricings for the materials of interest, are taken into consideration. Parts of the factorial approach of the technoeconomic analysis carried out in the present work could then also be substituted with actual data regarding the cost of land, the total capital and operational costs of the process to provide an analysis with a smaller uncertainty margin.

As previously discussed regarding the laboratorial experimental method, new materials reported for the DMTM would potentially require new processes. Depending on the reaction mechanism in each case, a new process concept would need to be developed that would suit the needs of the newly reported catalyst. The reaction conditions, the sizing of units as well as the separations were designed in this project specifically for the 3% CuMOR catalyst and based on the most favorable

reaction conditions over it as well as on the CH₃OH yields that it can provide. Recent advances in the field report other zeolitic frameworks exchanged with copper which exhibit comparable or even better results than CuMOR. However, the conditions of the reported reactions are considerably different than those of the CuMOR, i.e. CuFAU is reported to be best performing at a temperature of 360°C. This would need to be considered when modelling the DMTM over a CuFAU and the industrial process concepts and simulation results between different catalysts should only be compared for the most favourable conditions of each case. Additionally, new materials which do not exhibit a 100% selectivity towards methanol would potentially call for additional separation steps to separate any side products. Additional separation steps could considerably increase the capital and operational costs of the process. A detailed technoeconomic analysis of the entire process would be required in each case, so that a direct comparison between catalysts would be possible. (Sushkevich & Van Bokhoven, 2019)

An investigation of different zeolitic frameworks took place in the present study. However, two of the four frameworks synthesised collapsed at different stages of their treatment before reaction, leading effectively to only two copper-exchanged zeolitic frameworks being tested in the reaction. Since both the initial number as well as the finally tested number of zeolites was limited, it is recommended that more zeolites of similar specifications are synthesised and tested for the DMTM, to extract safer conclusions regarding the role of the 8MR. The selection of different zeolitic frameworks for synthesis and testing in the DMTM should be based on different factors like their stability under reaction conditions, as well as their framework characteristics. One of the characteristics which should be sought for is the existence of 8MR rings in their structure, preferably in zeolites which do not contain a large variety of different number rings in their framework so that the effect of the 8MR would be indirectly isolated. As seen previously, 8MRs can exist in both flat and bent shapes, which is hypothesised to play an important role in the formation of desired active sites which perform in the DMTM. It is recommended that zeolites with flat and bent MRs are compared against each other, so that conclusions can be made about the validity of the hypothesis. Similarly to the zeolites chosen for the present study, it is recommended that in future zeolites the 8MR effect is isolated by selecting frameworks which contain only 8MR and smaller rings. Specifically, an array of zeolitic frameworks with only 8 and 4MR in their structures are suggested for future investigation. By investigating frameworks with the same ring size, their performance in the DMTM could then be directly related to their pore

structure and the geometry and topology of the rings themselves. The PAU, SBE, ABW, APC, ATN and KFI frameworks all consist of 4MRs and 8MRs. The ATN framework only contains regular 8MRs, ABW and APC contain only bent 8MRs, while PAU, SBE and KFI contain both bent and regular 8MRs in their structure. Having a variety of cases regarding the bending of the 8MR, conclusions could be reached regarding the hypothesis of the bending of the 8MR playing an important role in the Cu-O-Cu angle and thus the performance in the DMTM. (Baerlocher & McCusker, 2017)

The Si/Al ratio of the framework appeared to affect a number of important factors like the number and nature of active sites, and the hydrothermal and acidic stability of the zeolite. It is recommended that for each investigated zeolite, an array of different Si/Al ratios is synthesised and tested for reaction to investigate the effect of the ratio on the final CH₃OH yield. In each catalyst synthesis and ion exchange procedure, it should be kept in mind that the concentration and acidity of the exchange solution can severely affect the stability of the framework through dealumination. It is thus recommended that in each case a variety of solutions is used to identify the limits which each zeolite can tolerate, so that the degree of ion exchange is effectively carried out without jeopardising stability.

It is considered important to conduct a thorough, preferably in-situ investigation of the nature of active sites inside each different zeolitic framework, as well as the investigation of the reaction mechanism in each case. Such a study could shed light into the effect of the 8MR geometry, the pore size and bending angle on the reaction mechanism and final performance of the zeolite in the DMTM. This could further help towards the understanding of the parameters of an “ideal” zeolitic material for the reaction which could be specifically designed. It is hypothesised that a theoretically optimal Si/Al ratio might exist depending on each framework and the corresponding active sites, which would maximise the formation of the desired active sites on the framework. In order to assess this hypothesis, the nature of active sites would need to be characterised in each framework at different Si/Al ratios and further compared to the performance in the DMTM of a framework at different Si/Al ratios. This could provide information about the performance of different in nature active sites in each zeolitic framework and conclude about the existence of a theoretically ideal ratio.

Following on the suggestion that the bending angle of the 8MR can directly affect the bond angle of the Cu-O-Cu bridge and consequently the performance of the active site in the DMTM, it is recommended that DFT analysis and theoretical calculations are conducted to pinpoint the optimal Cu-O-Cu bridge angle based on the currently best-performing catalysts, as well as the required distance between the two Cu atoms on each different framework for the formation of a desired active site. This information would be valuable in the design of new catalysts in the DMTM for improved methanol yields and could be used to predict the activity of a framework in the DMTM.

Based on the finding of the recommended future work, the targeted engineering of new materials could potentially take place. Existing zeolites could be modified to fit the needs of optimal Si/Al ratios or different ion-exchange routes could be explored to achieve the creation of the desired active sites on each framework. Additionally, the synthesis of new zeolitic frameworks with desired specifications could be another possibility. However, it should be kept in mind that each zeolitic framework can exist in a specific Si/Al range, which would be a limitation to the synthesis of new materials or the manipulation of existing ones.

All zeolitic frameworks currently reported in the literature use variations of the lab-scale step-wise process also recommended in the present work, on which also the industrial process concept was based. As a result, the process concept suggested can be used with minimal modifications as a benchmarking tool for present and future catalysts to assess how far from realisation of an economically viable industrial process each new zeolitic catalyst stands. Based on recent works in the literature reporting considerably improved methanol productivities, it is believed that the industrial DMTM over zeolitic catalysts is not far away from realisation (Sushkevich & Van Bokhoven, 2019). This is also showcased by the fact that the case scenario of a 40-fold more productive catalyst achieved a methanol production cost of 0.58\$/kg. which is competitive with the current production cost of methanol in the market, which ranges from 0.2-0.8\$/kg based on method of production and other factors (Kajaste et al., 2018).

It is essential for future work to focus on better understanding all factors which make a catalyst, and especially zeolitic catalyst and the respective active sites, particularly efficient in the DMTM. Although this is not a simple task due to the complexity of zeolitic frameworks and the respective active sites, a careful inspection of each zeolitic framework and the nature of active sites formed on it can provide information on how to design the perfect new catalytic material which will boost

methanol productivity to the target level of a 40-fold better performance that will render the process profitable.

Moreover, heavy effort is being dedicated to the improvement of the catalytic performance between new studies reported in the literature. However, it is important that all newly reported catalysts and lab-scale processes are complemented with respective industrial process concepts and economic analyses, so that their prospective profitability can be directly compared with other materials. This would allow for direct comparisons between catalytic systems different in nature, such as homogeneous and heterogeneous catalysts in the gas and liquid phase.

To summarise, it is recommended that future research should focus on a deeper understanding of the factors affecting the performance of different catalysts in the DMTM, so that the perfect new material can be engineered, while also keeping a close look to the larger scale perspective of finally developing an economically viable and competitive industrial DMTM process, which will open the way for the exploitation of many unused global natural gas reserves.

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11. Appendix

Mass Flow controller calibration

All mass flow controllers used in the present work were calibrated prior of use in any experimental work. Their calibration took place using the appropriate gas in each case. The mass flow controller reading was set to different values in a large range, to achieve different flowrates which were measured via a bubble flowmeter. The graphs below present the correlation of the mass flow controller reading with the actual volumetric flow. As seen in **Figure 68** and **Figure 69**, in all cases a linear relationship between the mass flow controller reading and the increase in flow rate was observed. The linear trendline equation for each case was used in all later experiments to predict the needed flowrate of each gas.

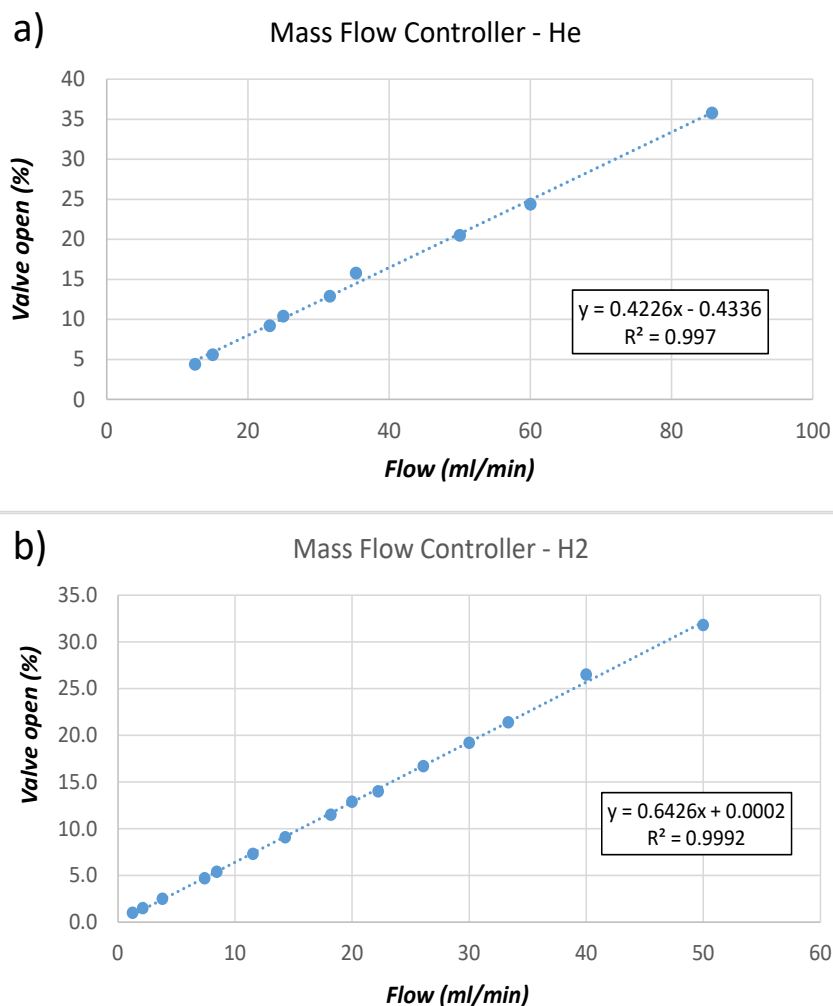


Figure 68: Mass flow controller calibrations for a) Helium and b) H₂.

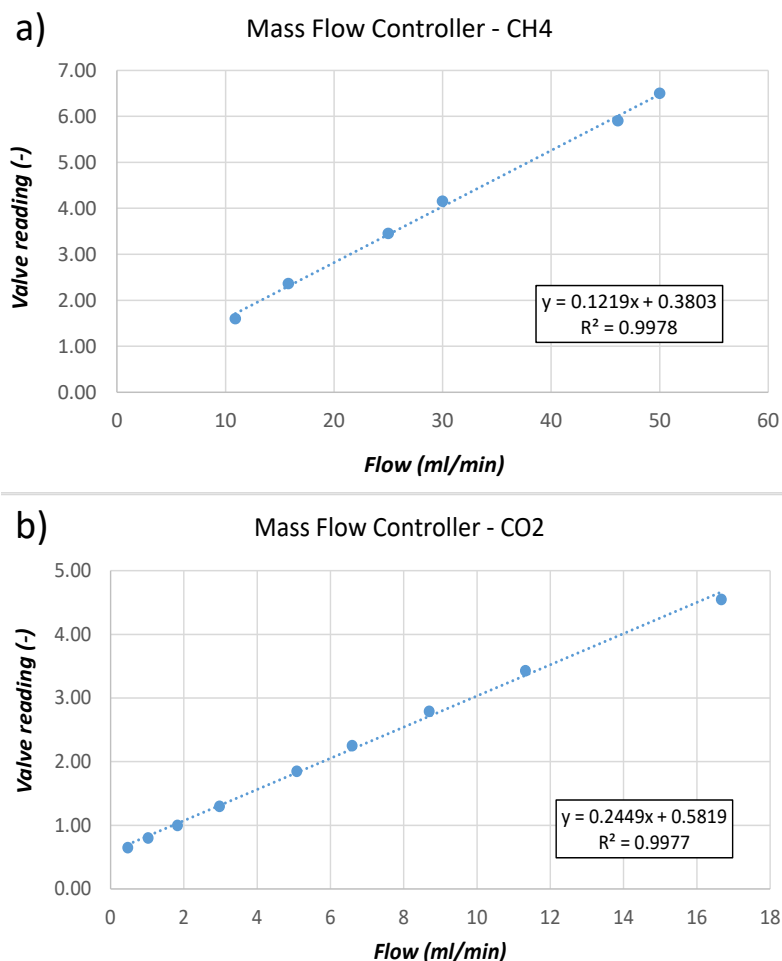


Figure 69: Mass flow controller calibrations for a) CH₄ and b) CO₂.

Temperature control box

To ensure an accurate control of temperature of the catalytic bed, an evaluation of the temperature control box was performed prior to any DMTM experiments. A simple experiment involving the ramping up and ramping down of the temperature of the reactor at a known rate, which was set as a program in the temperature control box, was carried out. Throughout the experiment, the temperature was monitored and readings were manually taken from a thermocouple inside the reactor tube. The theoretically expected temperature readings based on the set ramp rate as well as the manual temperature measurements are plotted against time in **Figure 70** below.

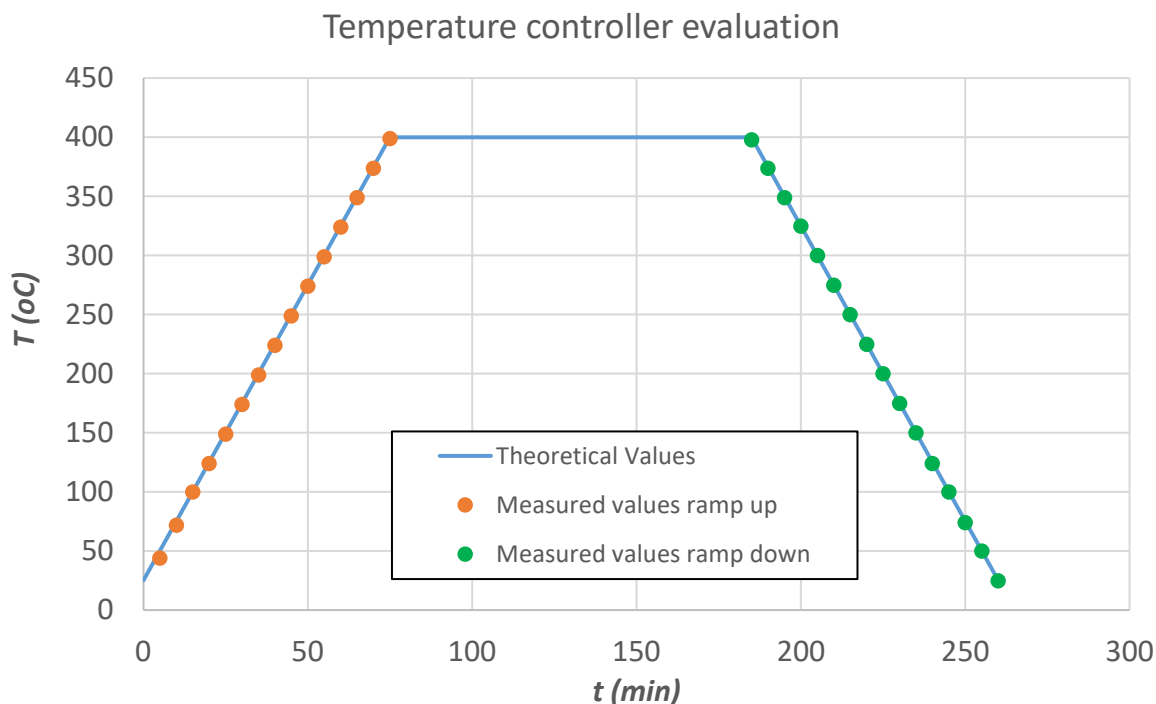


Figure 70: Theoretically expected temperature versus measured temperature during ramp-up and ramp-down.

As seen in **Figure 70**, the theoretical and manually measured temperature values were in excellent agreement. Thus, all programs set in the temperature control box during experiment can be considered reliable.

Quantification calibrations

The mass spectrometer was used for the quantification of species including the product CH_3OH . The protocol used for the quantification of species, as well as a detailed explanation of how the calibration of the quantification is carried out, can be found in a previous section. Following the aforementioned calibration protocol, the calibration for the quantification of CO_2 , CH_4 and CH_3OH took place. **Figure 71** and **Figure 72** present the correlation between the area underneath normalised signals and moles for each molecule.

As seen in **Figure 71** and **Figure 72**, a linear relationship is observed in the case of all molecules, thus ensuring that the quantification of species can be performed reliably following the previously explained protocol.

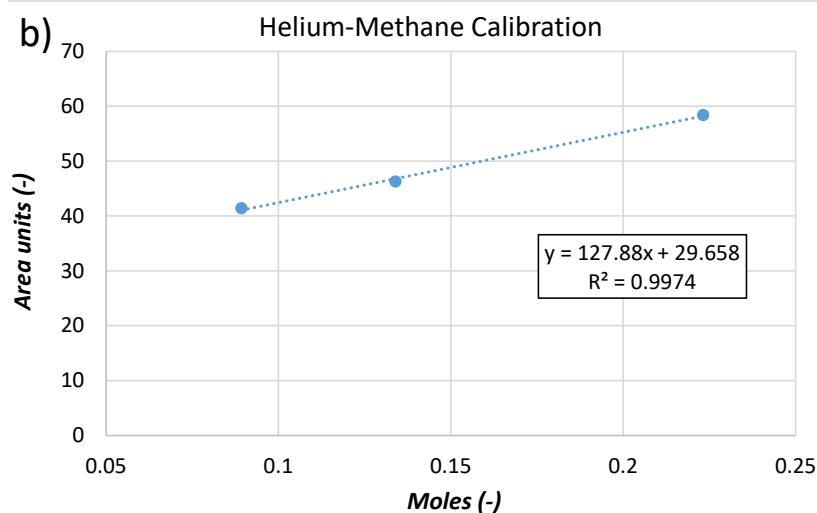
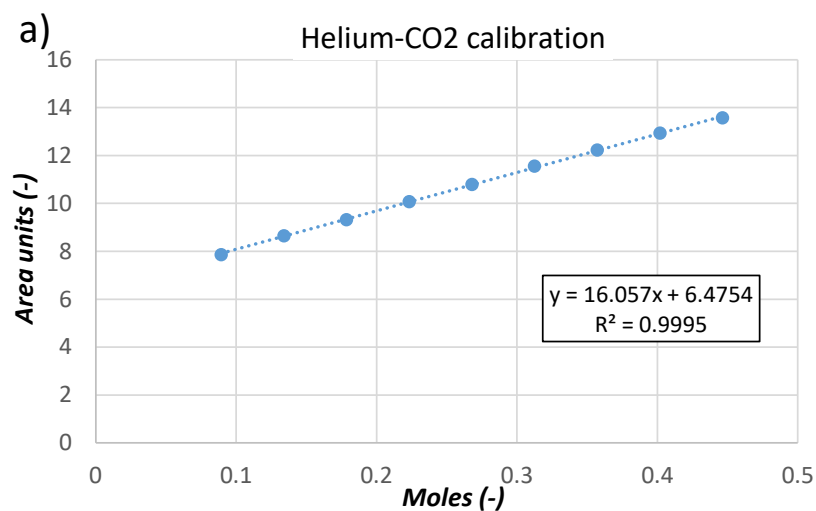


Figure 71: Calibration for the quantification of a) CO₂ and b) CH₄.

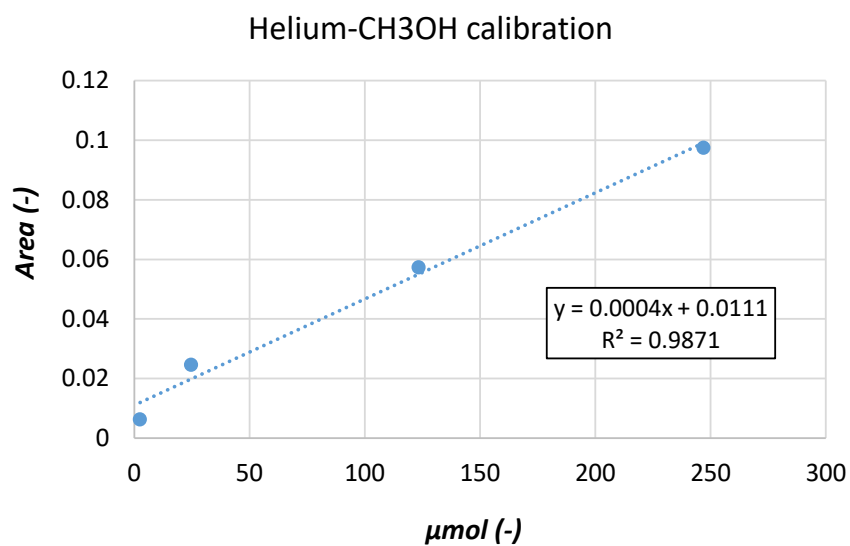


Figure 72: Calibration for the quantification of CH₃OH.

Data validation experiment

The validity of the experimental setup and results was confirmed as explained in a previous section by the comparison of the methanol yield of the 3% CuMOR at the most favorable conditions against data from the literature. The reaction and methanol desorption step of the experiment are presented in **Figure 73**. **Figure 73** presents the signals corresponding to different species (He, H₂O and CH₃OH) plotted against time for the isothermal reaction at 200°C under a flow of wet He, with the H₂O bubbler kept at 40°C for a faster completion of the reaction.

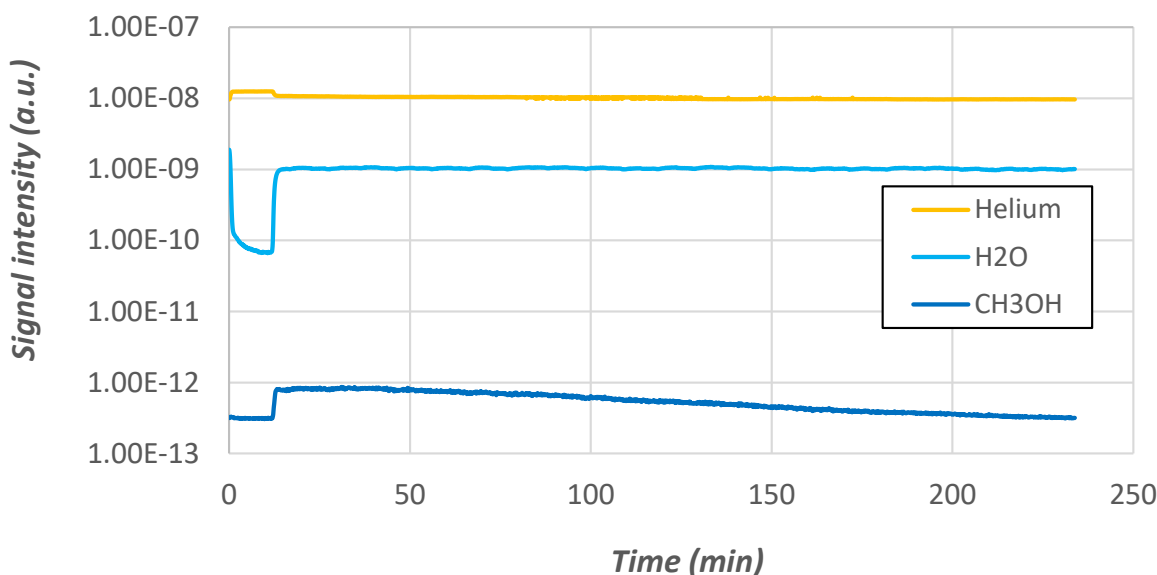


Figure 73: Mass spectrometer signals of He, H₂O and CH₃OH during the reaction step over a 3% CuMOR catalyst under flow of wet helium passing through a water bubbler at 40°C.

EDI DMTM experiment

The DMTM reaction over copper-exchanged EDI yielded CH₃OH in relatively small quantities. The isothermal reaction of methane to methanol over EDI is presented below in **Figure 74** and **Figure 75**. **Figure 74** presents the mass spectrometer signals of different species during the DMTM reaction at 200°C under a flow of wet helium. **Figure 75** presents the corresponding CH₃OH signal of the aforementioned reaction, normalised by the signal of background Helium.

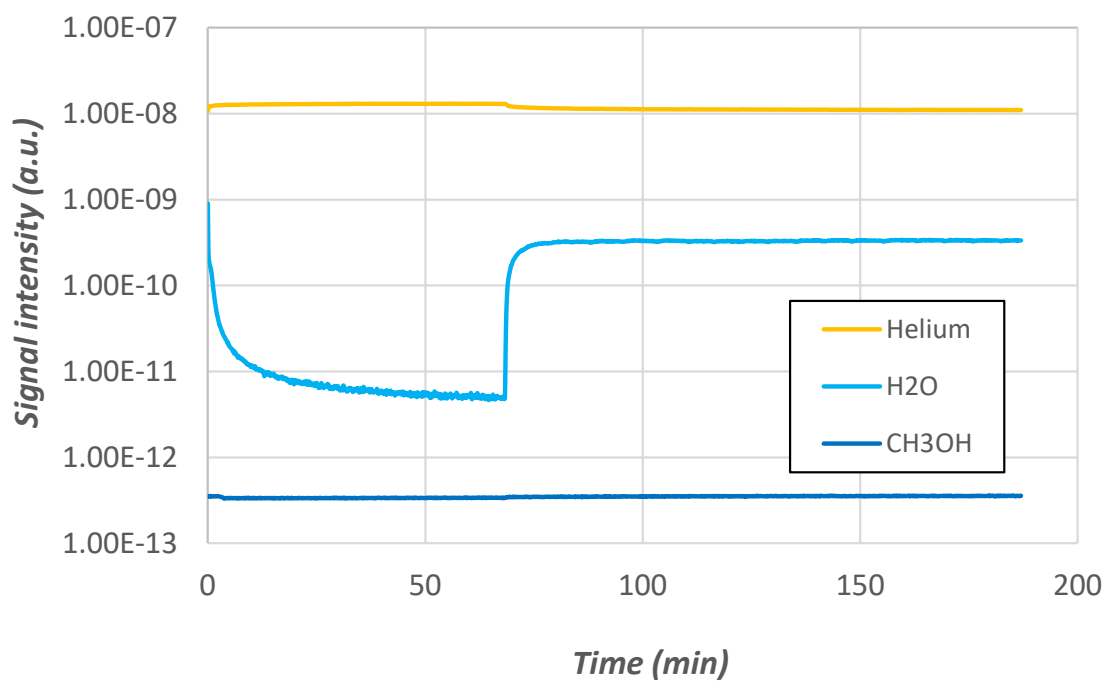


Figure 74: Mass spectrometer signals of He, H₂O and CH₃OH during the reaction step of a copper-exchanged EDI.

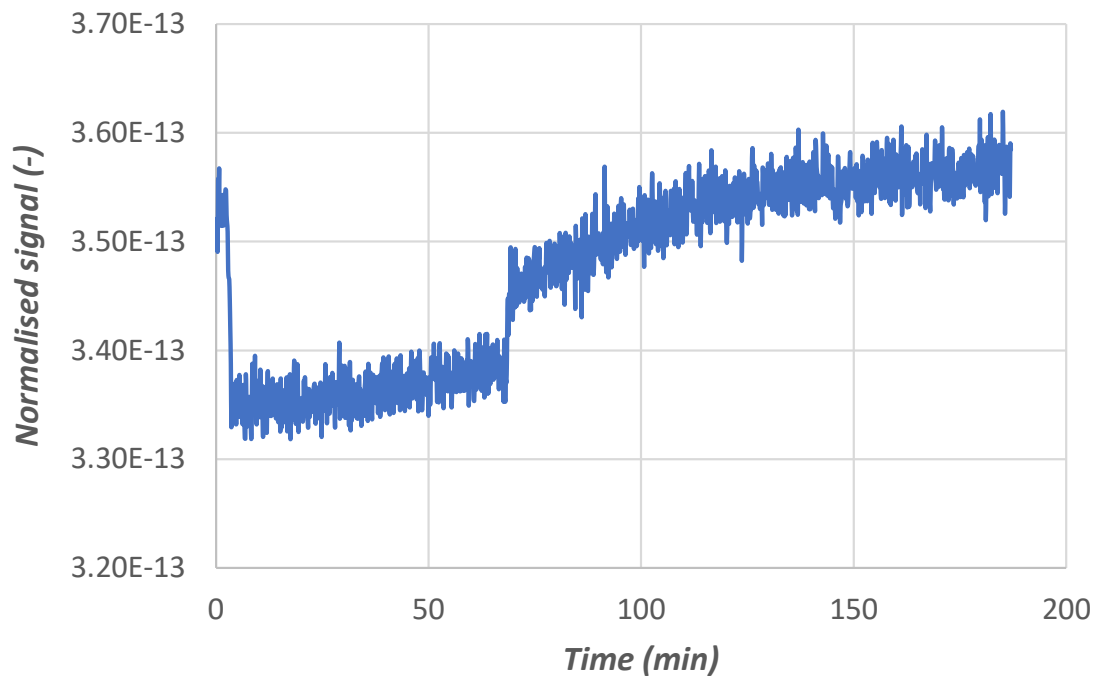


Figure 75: Normalised methanol signal during the isothermal reaction step over a copper-exchanged EDI.

CH₄ equilibrium conversion

The overall reaction of the DMTM using H₂O as oxidant is:



The standard enthalpy of formation $\Delta H^\circ_{f, 25}$ (kJ/mol) and the standard Gibbs free energy of formation $\Delta G^\circ_{f, 25}$ (kJ/mol) of each molecule at 25°C are listed below:

Table 36: Standard enthalpy and Gibbs free energy of formation for the molecules partaking in the DMTM using water as oxidant. (NIST, 2016)

	$\Delta H^\circ_{f, 25}$ (kJ/mol)	$\Delta G^\circ_{f, 25}$ (kJ/mol)
CH ₄ (g)	-74.6	-50.5
H ₂ O (g)	-241.8	-228.6
CH ₃ OH (g)	-200.9	-162.2
H ₂ (g)	0	0

Considering the stoichiometric coefficients of the reaction, the Gibbs free energy and the enthalpy of reaction are calculated:

$$\Delta G^\circ_{25} = \Delta G^\circ_{25, \text{CH}_3\text{OH}} + \Delta G^\circ_{25, \text{H}_2} - \Delta G^\circ_{25, \text{CH}_4} - \Delta G^\circ_{25, \text{H}_2\text{O}} = -162.2 - 0 + 50.5 + 228.6 = 116.9 \text{ kJ/mol}$$

$$\Delta H^\circ_{25} = \Delta H^\circ_{f, \text{CH}_3\text{OH}} + \Delta F^\circ_{25, \text{H}_2} - \Delta F^\circ_{25, \text{CH}_4} - \Delta F^\circ_{25, \text{H}_2\text{O}} = -200.9 + 0 + 74.6 + 241.8 = 115.5 \text{ kJ/mol}$$

The equilibrium constant K_{25} can be calculated using the following relationship:

$$K_{25} = \exp\left(\frac{-\Delta G^\circ_{25}}{RT}\right) = \exp\left(\frac{-116900 \frac{\text{J}}{\text{mol}}}{8.314 \frac{\text{J}}{\text{mol} \cdot \text{K}} \cdot 298\text{K}}\right) = \exp(-47.2) = 3.24 \cdot 10^{-21} = K_1$$

while K_2 is defined to be the equilibrium constant of the reaction at 200°C. Assuming that there is negligible change to the reaction enthalpy at 200°C, the Van't Hoff equation can be used to calculate the value of K_2 :

$$\ln \left(\frac{K_2}{K_1} \right) = \frac{-\Delta H^\circ}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) = \frac{-115500 \frac{J}{mol}}{8.314 \frac{J}{mol \cdot K}} \cdot \left(\frac{1}{473K} - \frac{1}{298K} \right) = 17.25$$

So that:

$$\frac{K_2}{K_1} = e^{17.25} \text{ or } K_2 = 1.005 \cdot 10^{-13}$$

Taking 1 mol of each reactant as a base for calculations and the extent of reaction ξ (mol), the reaction at 200°C is as follows at equilibrium:

	CH ₄ (g)	H ₂ O (g)	↔	CH ₃ OH (g)	H ₂ (g)
Start	1 mol	1 mol		0 mol	0 mol
Equilibrium	1- ξ	1- ξ		ξ	ξ

Considering the stoichiometry of reaction, the equilibrium constant K_2 is related to the activities, α , of molecules that take place in the reaction:

$$K_2 = \frac{\hat{a}_{H_2}^v \cdot \hat{a}_{CH_3OH}^v}{\hat{a}_{CH_4}^v \cdot \hat{a}_{H_2O}^v} = \frac{\hat{\alpha}_{H_2} \cdot \hat{\alpha}_{CH_3OH}}{\hat{\alpha}_{CH_4} \cdot \hat{\alpha}_{H_2O}}$$

The activity of a gas is the ratio of fugacity, f , of said gas in a mixture over the fugacity of the same gas at standard conditions. For ideal gases, the fugacity of a gas is equal to the pressure of the gas in a mixture and the pressure at standard conditions is 1bar. Additionally, the pressure of each gas is equal to the total pressure of the system multiplied by its molar fraction, y , so that finally, the equilibrium constant K_2 can be written in terms of pressure:

$$K_2 = \frac{y_{CH_3OH} \cdot P \cdot y_{H_2} \cdot P}{y_{CH_4} \cdot P \cdot y_{H_2O} \cdot P} = \frac{y_{CH_3OH} \cdot y_{H_2}}{y_{CH_4} \cdot y_{H_2O}}$$

Substituting the molar quantities at equilibrium as listed above and the calculated value of the equilibrium constant:

$$1.005 \cdot 10^{-13} = \frac{\frac{\xi}{2} \cdot \frac{\xi}{2}}{\frac{1-\xi}{2} \cdot \frac{1-\xi}{2}} = \frac{\xi^2}{(1-\xi)^2}$$

Solving the above polynomial, the extent of reaction, ξ , is calculated to be:

$$\xi = 3.17 \cdot 10^{-7} \text{ mol}$$

And considering the base of 1 mol of CH₄ defined previously, the conversion of CH₄ in the reaction with H₂O at 200°C is:

$$\text{CH}_4 \text{ conversion} = \frac{\xi}{1} = 3.17 \cdot 10^{-7}$$

BET Results

BET analysis was carried out on the 3% CuMOR catalysts of Si/Al=13 and Si/Al=20 which were used in the DMTM reaction experiments in the present study. The analysis provided information about the surface area and pore volume of the samples, which were also used in the calculations of the mass and heat transfer limitations carried out via the Eurokin fixed-bed web tool, which will be discussed in more detail below. The results of the BET analysis for the aforementioned catalysts are presented below in **Table 37**.

Table 37: BET results for 3% CuMOR of different Si/Al ratios.

	3% CuMOR (Si/al=13)	3% CuMOR (Si/al=13)
BET surface area (m ² /g)	381.1	415.4
Langmuir surface area (m ² /g)	490.4	535.3
Single point adsorption total pore volume		
of pores with d _p <71.95nm (cm ³ /g)	0.216	0.24
t-plot micropore volume (cm ³ /g)	0.156	0.164
BJH adsorption cumulative volume of		
pores of 1.7nm<d _p <300nm (cm ³ /g)	0.088	0.109

Eurokin tool

As explained in a previous section, an investigation was carried out regarding the intrinsic kinetic regime of the reactor. This was carried out with help of the Eurokin fixed-bed web tool, which can

be used for the assessment of the intrinsic kinetic regime in fixed bed reactors when used for gas-solid heterogeneous catalytic processes. The inputs of the Eurokin web tool as well as the results of the several different criteria relating to mass and heat transfer limitations can be seen below in **Figure 76** and **Figure 77**.

Reaction conditions:		
Catalyst temperature	473	[K] (1)
Total pressure	101.325	[kPa]
Total molar inlet flow	0.0000186	[mol/s]

Properties of catalyst and dilution		
Amount of catalyst	0.4	[g] (2)
Amount of bed dilution	0.00001	[g]
Catalyst pellet diameter	0.178	[mm]
Bed porosity	0.4	[m ³ /m ³ _{bed}]
Cat. internal specific area	381	[m ² /g]
Catalyst pellet porosity	0.22	[m ³ /m ³ _{pellet}]
Catalyst bulk density	840	[kg/m ³ _{bed}]
Catalyst pellet tortuosity	4	[-]
Cat. pellet thermal conduct.	3.63	[W/mK]
Dilution pellet density	0.1	[kg/m ³ _{pellet}]
Dil. pellet thermal conductivity	0.001	[W/mK]

Reactor dimensions:		
Internal reactor diameter	4.57	[mm]
Diameter thermowell	0	[mm]

Reaction rate		
Observed reaction rate	8.8e-7	[mol-A/kg-cat.s] (1)
Reaction order A	1	[-]
Apparent activation energy	150	[kJ/mol-A]
Reaction enthalpy	115.95	[kJ/mol-A]

Calculated values		
Volumetric flow at reaction cond.	7.219e-7	[m ³ /s]
Volumetric flow at STP	2.502e+1	[ml/min]
Superficial velocity	0.04401	[m/s]
Particle Reynolds number	0.03203	
Density mixture	0.11159	[kg/m ³]
Molar volume	3.88e-2	[m ³ /mol]
Pr	0.61222	[-]
Sc	1.17318	[-]
Space time [W _{cat} /(mol-A/s)]	9.190e+2	[kg/s mol]
Weight dilution degree	0.00002	[kg _{dil} /(kg _{cat} +kg _{dil})]
Volume dilution degree	0.25926	[m ³ _{dil} /(m ³ _{cat} +m ³ _{dil})]
Bed cross-sectional area	1.640e+1	[mm ²]
Bed height	3.919e+1	[mm]
Real residence time in bed	3.562e-1	[s]
Total catalyst bed volume	6.429e+2	[mm ³]
Catalyst pellet density	1400.00	[kg/m ³]
Average pore radius	0.825	[nm]
Catalyst solid density	1794.87	[kg/m ³]
Catalyst pore volume	0.15714	[ml/g]
Average pellets thermal cond.	0.0039	[W/m K]
Observed rate constant	3.712e-10	[mol-A/kg-cat.s.Pa-A ⁿ]
Reaction rate per pellet volume	1.232e-3	[mol-A/m _{pellet} ³ .s]
Conversion of A	0.00081	(3)



Physical properties of the components		
General physical properties (mixture values)		
Heat capacity	20.7850	[J/mol K]
Viscosity	2.729e-5	[kg/m s]
Thermal conductivity	0.213930	[W/m K]
(The user should adapt these values accordingly)		

Calculation of Diffusion coefficient (15)		
D(H ₂ O-CH ₄) =	5.943e-5	[m ² /s]
D(H ₂ O-CH ₃ OH) =	4.686e-5	[m ² /s]
D(H ₂ O-He) =	1.881e-4	[m ² /s]
D(H ₂ O),m Wilke eq. =	1.881e-4	[m ² /s]
Do(H ₂ O),m =	1.987e-4	[m ² /s]
f(H ₂ O),app =	0.9532	
Bulk diffusivity: D(H ₂ O),m =	2.085e-4	[m ² /s]
Knudsen diffusivity: D _K (H ₂ O) =	4.100e-7	[m ² /s]

Figure 76: Eurokin fixed-bed web tool inputs and calculated values for the reactor used in experiments of the present work.

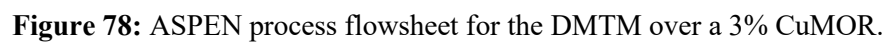
Results concerning transport limitations and other disturbing phenomena

EUROKIN

Pressure drop over the catalyst bed (4)		
Friction factor	26357.30	
Pressure drop over the bed	1254.25	[Pa]
$\Delta P/P$ ratio	1.238e-2	; must be < $(0.2/n) = 0.200$
Criterion OK		
Conditions for the maximum bed dilution (7)		
Relative deviation (Δ)	6.425e-7	
Maximum allowed b	1.000	[vol-dil/vol-tot]
Experimental b	0.259	
Criterion OK		
External mass transport limitation (8)		
Sh	2.147	[-]
Mass transfer coefficient (k_g)	2.51459	[m ³ /m ² s]
$a_v = 6/d_p$	3.371e+4	[m ² /m ³ -pellet]
$C(H_2O)_{bulk}$	6.029e-1	[mol/m ³]
Ca	2.411e-8	; must be < 0.05/n
Efficiency (for n = 1)	1.00000	[-]
Criterion OK		
Radial heat transfer limitation (11)		
Pe_{rf}	8.9046	[-]
$\lambda_{er,0}/\lambda_G$	0.4162	[-]
$\lambda_{er,conv}/\lambda_G$	0.0022	
λ_{er}	0.0895	[W/mK]
Pr (air, 80°C)	0.6850	
$\alpha_{w,0}$	999.6229	[W/m ² K]
$\alpha_{w,conv}$	4.2204	[W/m ² K]
α_w	1003.8433	[W/m ² K]
$ \Delta T(rad) $	4.6293e-4	[K]; must be < 0.620
Criterion OK		
If the temperature of the wall is measured instead of the temperature at the central bed axis, another criterion applies: (11)		
$ \Delta T(rad) $	5.3519e-4	[K]; must be < 0.620
Bi_{wall}	51.2528	[-]
Criterion OK		
Conditions for allowing assumption ideal plug flow behaviour		
Axial dispersion (5)		
$Bo (=Pe_p)$	0.1383	[-]
Constant in criterion	8	
h_{bed}/d_p (minimum required)	0.047	
h_{bed}/d_p (experimental)	220.177	
Criterion OK		
Radial dispersion (6)		
Criterion: d_t/d_p should be at least	8	
d_t/d_p	25.67	
Criterion OK		
Internal diffusion limitation (9)		
$D(eff.)H_2O$	2.251e-8	[m ² /s]
Weisz modulus (Φ)	0.00008	; must be < 0.08
Approximate Thiele modulus (ϕ)	0.00894	[-]
$\tanh(3\phi)$	0.02681	[-]
Approximated efficiency (η)	0.99995	[-]
Criterion OK		
External heat transport limitation (10)		
Nu	2.1185	[-]
Note that Nu may get as low as 0.1 at $Re < 1$ in case of channeling !		
Heat transfer coefficient $\alpha_p = h_w$	2546.13	[W/m ² K]
$ \Delta T(film) $	1.664e-6	[K]; must be < 0.620
Criterion OK		
Temperature gradient within the pellet (12)		
The effect of the internal temperature gradient on the net production rate is smaller than 5% if :		
$ \Delta T(int) $	2.078e-8	[K]; must be < 0.620
Criterion OK		
Adiabatic temperature rise (ΔT_{ad}) (13) (14)		
$\Delta T(ad)$	0.10553	[K]

Figure 77: Results of different calculated criteria for the assessment of mass and heat transfer limitations.

The process flowsheet designed in ASPEN for the DMTM over a 3% CUMOR industrial concept is presented in **Figure 78**.



Zeolitic frameworks

MFI (ZSM-5) and MOR are some of the most important frameworks in the history of zeolites in the DMTM. As discussed in a previous section, the pore structure and geometry as well as the existence of 8-MR inside their zeolitic frameworks renders them active in the conversion of methane to methanol. The zeolitic framework structures of mordenite (MOR) and ZSM-5 (MFI) are presented below in **Figure 79** and **Figure 80**.

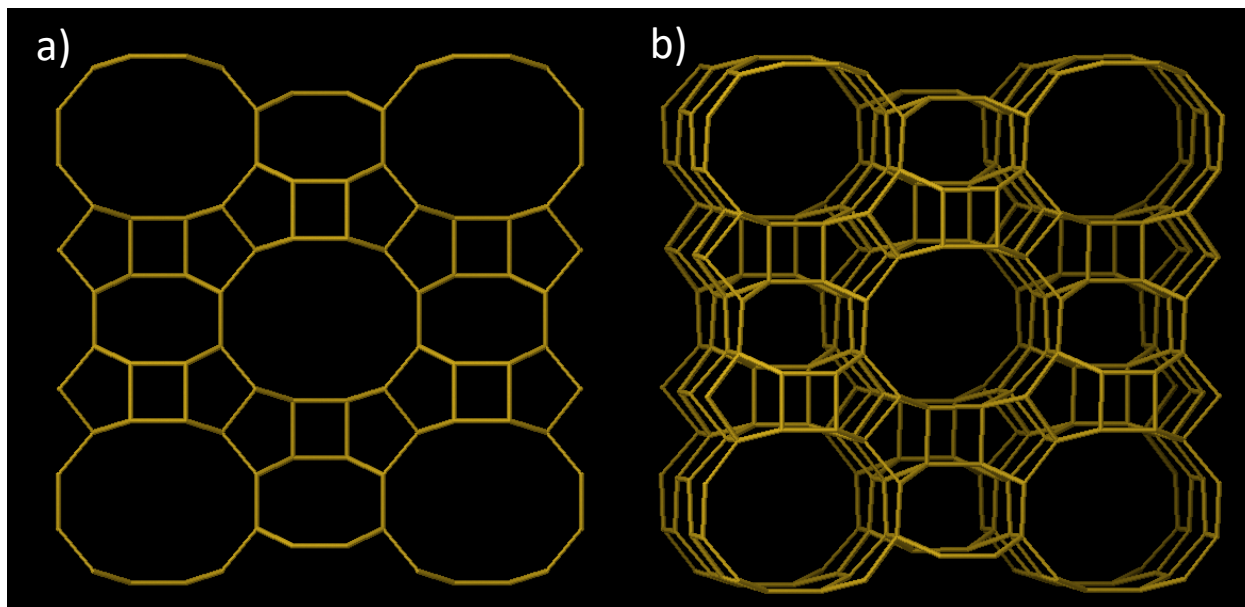


Figure 79: Mordenite as seen a) from the front plane and b) as a 3D structure.

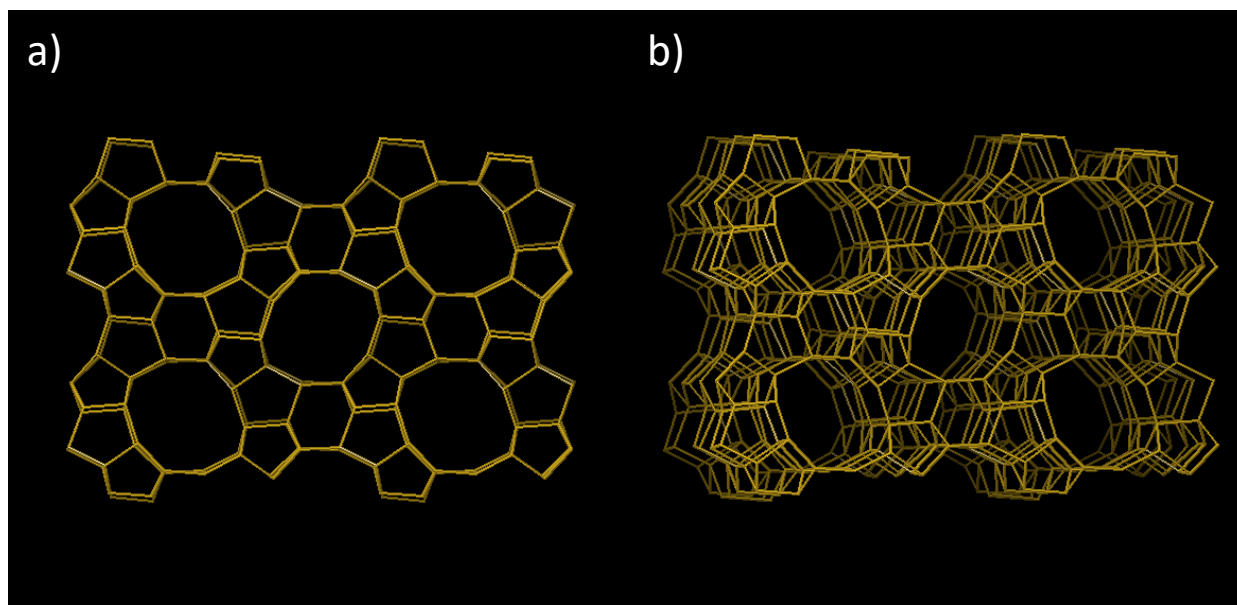


Figure 80: ZSM-5 (MFI) as seen a) from the front plane and b) as a 3D structure.