

Selective Oxidation of Methane to Methanol over ZSM-5 Catalysts in Aqueous Hydrogen

Peroxide: Role of Formaldehyde

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Abstract: The selective oxidation of methane in aqueous hydrogen peroxide over ZSM-5 catalysts with different Si/Al ratios has been investigated. Methyl hydroperoxide was confirmed as the initial product of methane oxidation by a study of product distribution versus reaction time in agreement with previous work. Formaldehyde was identified as an intermediate in the oxidation reaction pathway from MeOOH to formic acid and ultimately CO₂. Hydrogen evolution during the oxidation of methane is reported for the first time. Oxidation of the HCHO intermediate to formic acid was demonstrated to be the source of the evolved hydrogen. HCHO appeared to be the source of low levels of soluble polyoxomethylene. Higher productivity of liquid oxygenated products is reported compared to previous work.

Introduction

The direct selective oxidation of methane to oxygenated products, especially methanol, is one of the most difficult challenges in catalysis which in principle could yield significant economic benefits and a positive environmental impact.^[1,2] Methanol is a platform chemical intermediate and a potential clean fuel in its own right.^[1-3] The high endothermicity of the methane steam reforming process and capital costs of the “indirect” route to methanol has led to continued interest in the possibility of a direct process.^[1,4] Indeed, a “direct” process was patented as early as 1905 by Lance and Elworthy in which methanol was produced from methane and hydrogen peroxide catalyzed by ferrous sulfate.^[5] Methane is the most unreactive hydrocarbon due to its tetrahedral arrangement of four sp³ C–H bonds with filled high-energy orbitals, but no vacant accessible low-energy orbitals. High reaction temperatures are generally needed to activate methane and since the total oxidation pathway of methane to CO₂ and water has a much larger free energy change than its conversion to methanol, the selective production of methanol is kinetically extremely challenging.^[1-10] Consequently, the “direct” methane to methanol process remains elusive despite its evident desirability.

The first aqueous inorganic catalysis system for direct oxidation of methane to methanol was reported by Shilov and coworkers who used the homogenous catalyst system PtCl₄²⁻/PtCl₆²⁻ in which the terminal oxidant was a Pt(IV) complex.^[11] A further system which used O₂ as oxidant was developed by Sen

and co-workers.^[12] Subsequently, several studies of the oxidation of methane using homogeneous catalysts have been made, often in highly concentrated acids such as H₂SO₄ or trifluoroacetic acid.^[11-18] On the whole these homogeneous catalyst systems use solvents that are not environmentally benign; MeOH is not produced in closed catalytic cycles, and the MeOH TOFs tend to be low. In contrast, in nature methane monooxygenases (MMO) are able to produce methanol with 100% selectivity using oxygen as the terminal oxidant at ambient temperatures in water.^[19-22] The active di-iron site and tri-copper cluster sites of the MMOs has prompted considerable research on inorganic biomimetic catalysts, especially Fe or Cu supported on zeolites, which utilize either oxygen (or N₂O) as oxidant.^[22-25] Recent liquid phase studies have sought to use aqueous hydrogen peroxide as an environmentally benign oxidant.^[26-39]

In a series of landmark studies Hutchings and co-workers have shown that ZSM-5 zeolites containing iron as an impurity and Fe-ZSM-5, are effective catalysts for the low temperature oxidation of methane to methanol with aqueous H₂O₂.^[34-37] Methanol TOFs of up to 14 200 h⁻¹ based on the iron content of the zeolites were reported, the largest seen in any previous catalytic system for the partial oxidation of methane.^[34] Based on the study of short reaction times it was shown conclusively that the initial oxidation product was methyl hydroperoxide (MeOOH). The oxidation sites forming MeOOH were identified by DFT calculations and EXAFS to be extra framework iron sites consisting of cationic [Fe₂(μ₂-OH)₂(OH)₂(H₂O)₂]²⁺ species (abbreviated to [Fe₂O₂]²⁺). The loss of an •OH radical from MeOOH was proposed to form an iron-bound methoxy species which following hydrolysis yielded methanol. Methanol was prone to over-oxidation by a non-selective sequential oxidation to give formic acid and CO₂ according to the sequence CH₄ → MeOOH → MeOH → HCO₂H → CO₂.^[34-36] It was also shown that the addition of Cu to Fe-ZSM-5 suppressed formic acid production and increased significantly the methanol selectivity.^[34-36] In a more recent study of methane oxidation over Fe-ZSM-5 and FeCu-ZSM-5, Kalamaras *et al.*,^[38] confirmed the earlier finding by Hammond *et al.*,^[34] that the Si/Al ratio strongly influenced the methanol productivity.

In this contribution we report the study of methane selective oxidation in aqueous hydrogen peroxide over ZSM-5 catalysts where, in contrast to previous work, formaldehyde (in hydrated form CH₂(OH)₂) and hydrogen gas are detected in the products for the first time. In an attempt to rationalize the reaction sequence, methanol, formic acid and an aqueous solution of formaldehyde were individually reacted in hydrogen peroxide in the presence and absence of ZSM-5 catalyst. We show that formaldehyde is a key intermediate in methane selective oxidation leading to the formation of hydrogen and further oxidation products. In addition, a small quantity of water soluble polyoxomethylene appears to be produced which was not reported previously over this catalyst system, and is shown to derive exclusively from the formaldehyde intermediate. The

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Supporting information for this article is given via a link at the end of the document.

present study reports higher total production rates of liquid oxygenate products formed over ZSM-5 than previously published values which may point to physical factors influencing the rate of reaction under some conditions.

Results and Discussion

Four commercial ZSM-5 zeolites with nominal SiO₂/Al₂O₃ ratios of 23, 30, 50 and 80 were used in the study. The properties of the catalysts are given in Table 1. The iron content was found to vary significantly between the various zeolites. In particular, the batch of ZSM-5(50) used had a significantly higher Fe content. The XRD of the zeolites are given in Supporting Information Figure S1 and are consistent with the ZSM-5 structure.

Table 1 Properties of the zeolites

Catalyst	Nominal SiO ₂ /Al ₂ O ₃	Fe /ppm	Surface area /m ² g ⁻¹
ZSM-5(23)	23	224	303.6
ZSM-5(30)	30	174	384.6
ZSM-5(50)	50	342	411.5
ZSM-5(80)	80	240	405.5

As noted in the experimental section, special attention was paid to the reaction and analytical procedures. All experiments were carried out using a purpose-made glass liner reactor and the liquid was stirred using a glass-coated magnetic bar to minimize the possibility of metal leaching into solution from reactor components. A stainless steel thermocouple was in contact with the reaction liquid to measure the reaction temperature. However, it was established in a blank run that this did not contribute to the catalysis of any of the conversions. The reaction temperature was maintained by immersion of the reactor body in a temperature-controlled liquid bath. After the desired reaction time, the reactor was cooled rapidly in ice during which the zeolite catalyst partially settled, and a sample for NMR was withdrawn, prepared, and analyzed within a short time by ¹H NMR. The major part of the study was carried out using ZSM-5(50). A typical ¹H NMR spectrum of the distribution of products from a “standard” methane oxidation experiment (50°C, 10ml, 0.5M H₂O₂, 13.5mg catalyst) over ZSM-5(50) is given in Figure 1. The ¹H NMR spectrum was obtained from an unfiltered sample withdrawn from the reaction mixture. Dissolved methane, methyl hydroperoxide (MeOOH), methanol (MeOH) and formic acid (HCO₂H) are clearly identified. Also present is a low concentration of hydrated formaldehyde or methanediol, H₂C(OH)₂. The chemical shifts of these compounds were validated against the purchased compounds and published values,^[27, 34, 42] and in the case of methyl hydroperoxide also by synthesis of the compound according to a published procedure.^[43] No products were detected under the same reaction conditions in the absence of the catalyst.

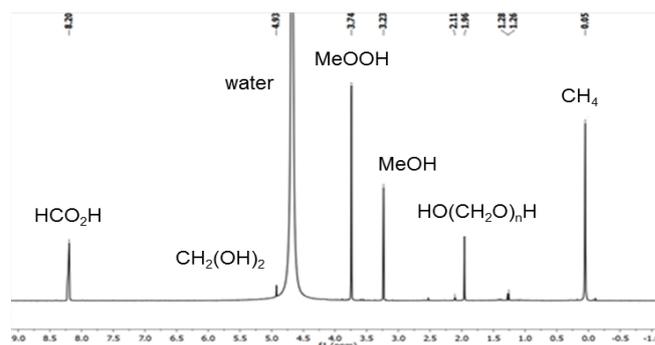


Figure 1. ¹H NMR of methane oxidation products over ZSM-5(50) in 20% D₂O. δ /ppm: (HCO₂H, 8.26), ((HCHO, 4.94(methanediol)), (MeOOH, 3.76), (MeOH, 3.25), (POM; -OH, 1.96), (Me, 0.07). Field 11.74 T.

The ¹H NMR spectrum in Figure 1 also has two notable peaks at 1.95 and 2.1 ppm. We attribute these to water-soluble polyoxomethylenes (POM) which have a molecular formula of HO(CH₂O)_nH. The reported ¹H NMR spectrum of POM species from formaldehyde presents signals at around 1.9-2 ppm (OH) and ca 4.5-5.2 ppm (CH₂-O).^[44-46] The peaks at around 4-5 ppm would have been obscured by the only partially suppressed water signal. In aqueous solution HCHO is known to polymerize to linear POM, where *n* can be as high as 100,^[44-46] and in this respect zeolites are known to promote POM formation.^[47] Low molecular weight POM (*n* < 8) is water-soluble. High molecular weight POM normally forms a white insoluble precipitate at the pH of the samples here, typically at 4 – 5. While the unfiltered samples contained a small white colloidal suspension this was derived from the zeolite catalyst. In a separate experiment, these solid residues were separated by centrifugation, dried, and extracted with *o*-dichlorobenzene. The extract liquid was analyzed by ¹H NMR and GC-MS. POM was not detected leading to the conclusion that higher molecular weight POM was not formed in significant amount at the methane oxidation conditions used. The use of unfiltered samples of reaction products in NMR analysis in the present study reveals the presence of these products from methane selective oxidation over ZSM-5. The amounts of products MeOOH, MeOH, CH₂(OH)₂ and HCO₂H were quantified using externally prepared calibrations. This approach obviated the need to analyze each sample in the presence of an internal standard such as DSA, which was found to be unstable in the residual H₂O₂ in the samples and in any case overlapped with the signal from dissolved methane. The initial calibrations were updated after three months and found to have remained virtually identical confirming that the NMR spectrometer had remained correctly tuned. The liquid product analysis for a standard methane oxidation reaction over ZSM-5(50) is given in Table 2. The water-soluble POM was quantified by assuming their integrated peak areas could be calibrated against hydrated HCHO. Large POM oligomers are insoluble in water and would not be detected by ¹H NMR analysis and even if present would not have contributed to the productivity and selectivity values given in Table 2.

Table 2 Product analysis from methane oxidation over ZSM-5(50)

Catalyst ^[a]	Products ^{[a], [b]} /μmol						Productivity ^[d] mol kg _{cat} ⁻¹ h ⁻¹	X ^[f] %	
	MeOH	MeOOH	HCOOH	CH ₂ (OH) ₂	POM	CO ₂ ^[c]			H ₂ ^[c]
UF	19.0	44.9	98.2	2.3	13.9	<2	10.7	25.5	1.1
F	14.9	53.2	102.6	1.8	5.7	<2	10.9	26.7	1.1
Selectivity ^[e] / %									
UF	11.6	25.2	55.0	1.3	7.8				
F	8.7	29.8	57.6	1.0	3.2				

[a] Reaction conditions: 10 ml, 50°C, P_{CH₄} = 10 bar, [H₂O₂] = 0.5M, catalyst 13.5mg; 1500 rpm; reaction time: 30 min. [b] Analyzed by ¹H NMR; POM = μmol HCHO equivalent. [c] Analysis of the gas phase by GC-TCD & MS. [d] Productivity of liquid products. [e] Liquid product selectivity: mol(product)/mol(total liquid products)x100. [f] Conversion: (total moles C produced)/(initial moles methane)x100. [g] UF = unfiltered sample, F = filtered.

The effect of sample filtration was examined in a standard methane oxidation experiment over ZSM-5(50) after which the sample was cold-filtered through Celite® S to remove any catalyst colloids or particulate matter before NMR analysis. As expected, the solution became clear. Filtration removed the dissolved methane signal in the ¹H NMR. The product analysis over ZSM-5(50) for the filtered sample is given in Table 2. The effect of filtration on the liquid oxygenate product distribution is marginal apart from reducing the amount of polyoxomethylene. In general, the methyl hydroperoxide yield was found to be slightly higher in the filtered samples probably due to the removal of colloidal catalyst entities which were found to continue to slowly catalyze reactions in the NMR tube, producing increasing amounts of formic acid.

In addition to the liquid products, samples of the head space gas were taken and analyzed by GC/TCD using He and Ar as carrier gas, and by MS. Hydrogen was found to be the main gaseous product and is reported for the first time, Table 2. CO₂ was barely detectable in the gas phase. Taking 10ppm as a conservative minimum sensitivity, we estimate the amount of CO₂ in the gas phase is about 0.3μmol. Based on our measured CO₂ solubility in dilute H₂O₂ (0.33 mol.l⁻¹bar⁻¹), we estimate the total CO₂ produced was 2μmol. This level of CO₂ is in reasonable agreement with previous studies of ZSM-5,^[34,35,38] which report a very low yield under these conditions.

The liquid products and selectivities for methane oxidation over other ZSM-5 zeolites, namely ZSM-5(23), ZSM-5(30), and ZSM-5(80), were obtained and are given in Supporting Information Table S2. The liquid product distributions are broadly similar for all the zeolites studied, Table 2 and Supporting Information Table S2. The total amounts of oxygenates produced are much higher for ZSM-5(50) and ZSM-5(30) than ZSM-5(23) or ZSM-5(80). As noted by Kalamaras *et al.*,^[38] and Hammond *et al.*,^[34] a combination of Fe content and acid site density is required for high productivity of oxygenates from methane oxidation since these factors control the amount of extra-framework di-Fe active sites. However, at similar Si/Al ratios, the Fe content appears to be the dominant factor. ZSM-5(23), ZSM-5(30), and ZSM-5(80) zeolites were also found to yield low levels of CH₂(OH)₂ and POM. The gas phase product was analysed for ZSM-5 (30) and found to contain mainly hydrogen with CO₂ being barely detectable.

The present results reveal similarities and several striking differences to the previous work on methane oxidation over ZSM-5.^[34-36] Comparing the liquid product analysis found here with the previous work, the distribution of the main liquid oxygenate products is very similar to those reported by the Hutchings group. For example, the selectivity to MeOOH at similar reaction times in the present results is 27% for ZSM-5(50), Table 2, and 23% for ZSM-5(30), Supporting Information Table S2, compared to 23% reported earlier for ZSM-5(30).^[33, 34] A slightly higher value for MeOOH (43%) was reported for ZSM-5(30) by Kalamaras *et al.*^[38] However, despite this similarity for the main liquid oxygenate products, hydrated formaldehyde and the related POM, which make a small contribution to the product yield as measured by ¹H NMR, were not reported in any of the earlier studies as noted in the above.^[34-36, 38] An important difference is the gaseous hydrogen product reported for the first time in the present work.^[34-36, 38] We note on this point, that the evolution of hydrogen from oxidation of formaldehyde by H₂O₂ is well-known.^[48, 49]

A further striking aspect of the present results is the higher total liquid oxygenate productivity compared to the values reported earlier. Considering just the productivity of MeOOH, MeOH, and HCO₂H, we obtain 24.4 and 20.5 mol kg_{cat}⁻¹h⁻¹, compared to 2.7 and 5.7 mol kg_{cat}⁻¹h⁻¹ reported earlier for ZSM-5(50) and ZSM-5(30) respectively,^[34, 35] and 2.33 mol kg_{cat}⁻¹h⁻¹ reported for ZSM-5(30) by Kalamaras *et al.*,^[38] despite a lower methane pressure (10 bar) being used in the present work. This difference is probably related to several factors. Significantly, the batches of ZSM-5 used in the present study have a higher Fe content (e.g. ZSM-5(50) (342 ppm)), compared to the zeolite samples used in the previous studies: for example ZSM-5(50) = 210 ppm and ZSM-5(30) = 140 ppm,^[34,35] and ZSM-5(30) = 123 ppm.^[38] There are also significant differences in the experimental procedures and analytical methodologies: for example, the analysis of unfiltered samples by NMR in the present work. Interestingly, the total amounts of liquid oxygenate products (MeOOH, MeOH, and HCO₂H) are not too dissimilar from the previous works. For example, 138.7 compared to 77.1 μmol for ZSM-5(30) and 162.1 compared to 36.5 μmol for ZSM-5(50).^[34,35] Admittedly the value for ZSM-5(50) is much higher, but our batch had a much higher Fe content as noted above. The differences in productivity for similar catalysts, therefore, may simply reflect the lower amount of catalyst used in the present

study. This suggests that physical factors may begin to influence the productivity at higher catalyst mass. The methane conversions in the present work are estimated to be around 1%, Table 2 and Supporting Information Table S2, but it is important to note that methane conversion is dependent on the ratio of head space to liquid volume for the particular reactor used.

An interesting feature emerged when the unfiltered samples were analyzed by ^1H NMR and the same samples re-analyzed over time. It was noted that the quantities of dissolved methane, MeOOH and MeOH decreased in the stored unfiltered NMR samples over a period of 1 to 2 days and there was a considerable increase in the relative amount of formic acid. This was attributed to the presence of catalytic material, residual hydrogen peroxide, and dissolved methane in the unfiltered samples (filtration removed almost all the dissolved methane as noted above). In contrast, relatively little change occurred in the product ratios of the filtered samples over the same time. For example, the quantified product HCOOH/CH₃OH ratios derived from the unfiltered and filtered samples were 5.2 and 6.9 respectively when analyzed immediately, and 20.2 and 6.7 respectively for the same samples when re-analyzed 1-2 days later. It seems clear that traces of catalyst, undecomposed H₂O₂ and exposure to air continue to oxidize MeOOH and methanol to formic acid in the NMR tube, emphasizing the need for rapid analysis which was done for the main results presented here.

The effect of reaction time on the reaction products over ZMS-5(50) was investigated by separate runs at 5, 10, 15, 30

min, 1 and 2 hr for which the productivity and selectivity variations are shown in Figure 2 (a) and (b) respectively. The selectivity to MeOOH is observed to fall rapidly from 70% initially at 5min reaction time to around 10% as the reaction proceeds. Consequently, the production of MeOOH passes through a maximum at about 30 min reaction time. Selectivity to CH₂(OH)₂ was about 10% at the shortest reaction time, but fell rapidly to a very low value as the reaction proceeds following the trend in MeOOH selectivity. The selectivity to MeOH increases and levels out finally decreasing very slowly at longer reaction times. HCO₂H productivity and selectivity have low initial values and rise rapidly with reaction time, essentially mirroring the behavior of MeOOH. These trends are in close agreement with the extensive results reported by the Hutchings group.^[34-36] Clearly, the trends identify MeOOH as the primary product formed and its conversion and loss leads to increasing amounts of MeOH and HCO₂H over time, with HCO₂H being the final liquid oxidation product. The present results also indicate that formaldehyde is formed as an early product and it is then rapidly oxidised or undergoes conversion to POM. The direct oxidation of HCHO to give HCO₂H by H₂O₂ is known to occur at H₂O₂ concentrations similar that used here.^[48, 49] The amount of POM found is quite small and it would appear to increase slightly with reaction time, but these low levels make it difficult to establish the trend unambiguously.

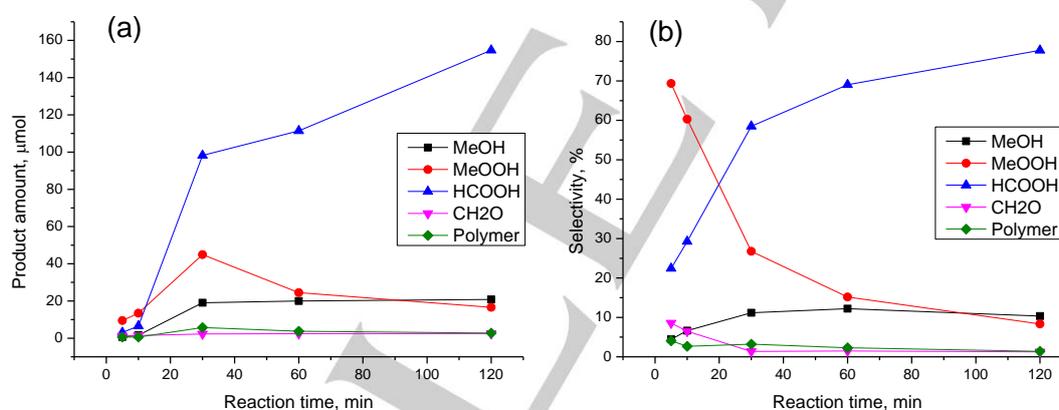


Figure 2. a) Oxygenate production as a function of reaction time b) oxygenate selectivity as a function of reaction time. Conditions: 10 ml, 50°C, $P_{\text{CH}_4} = 10\text{bar}$, $[\text{H}_2\text{O}_2] = 0.5\text{M}$, catalyst 13.5mg, 1500rpm. CH₂O refers to the hydrated form CH₂(OH)₂.

In a separate experiment, the product gas was sampled periodically. Hydrogen was found to build up gradually in the gas phase indicating it was formed throughout the experimental run (Supporting Information Table S3). This is consistent with the source of hydrogen being related to one of the early intermediates in the oxidation reaction sequence and is considered further below. The concentration of CO₂ in the gas phase was very low and barely measurable after 30min reaction time as noted above.

ZSM-5(50) was tested over a range of methane pressure and hydrogen peroxide concentrations. The corresponding oxygenate production and selectivity are given in Figure 3. In general, the productivity of the main liquid oxygenate products and the total productivity (Supporting Information Figure S3) increased with methane pressure as expected. The selectivity to HCO₂H and MeOOH were observed to decrease and increase slightly respectively with increasing methane pressure. This is

consistent with MeOOH being a primary and HCO₂H being a final oxidation product respectively.

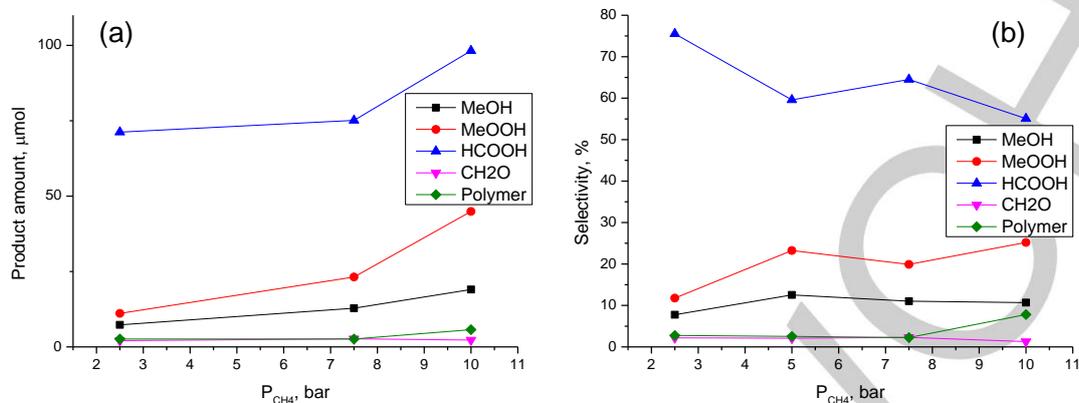


Figure 3 Effect of methane pressure on (a) oxygenate production (b) oxygenate selectivity. Conditions: 10ml, 50°C, $[H_2O_2] = 0.5M$, catalyst 13.5mg, 30 min.

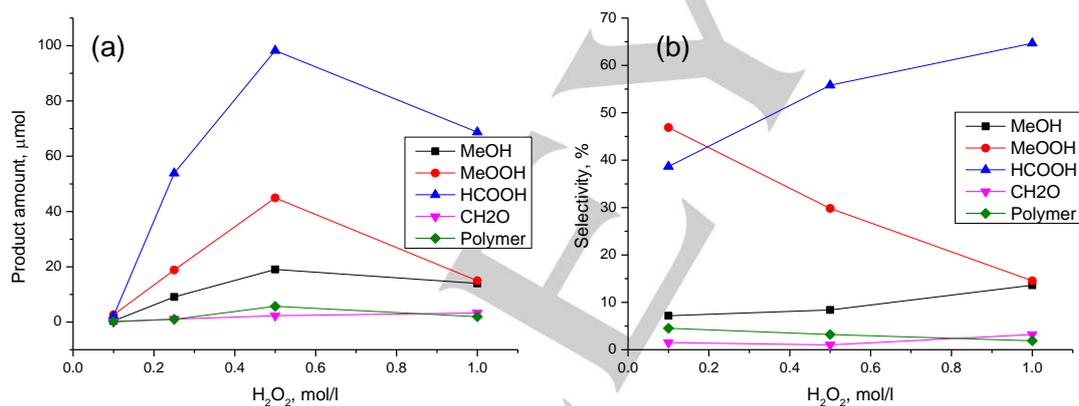


Figure 4. Effect of H_2O_2 concentration on (a) oxygenate production (b) oxygenate selectivity. Conditions: 10ml, 50°C, $P_{CH_4} = 10\text{bar}$, catalyst 13.5mg, 30 min.

The production of the liquid products with increasing H_2O_2 concentration showed a maximum at 0.5mol l^{-1} , Figure 4 and Supporting Information Figure S5. This was due to the greater extent of total oxidation and associated CO_2 production at high H_2O_2 concentrations. Selectivity to MeOOH was greatest at low H_2O_2 concentration consistent with it being the primary product in a sequential oxidation pathway as proposed by Hammond *et al.*^[34, 35]

Reaction of methane oxidation products

The products from methane oxidation were MeOOH, $CH_2(OH)_2$, MeOH, HCO₂H, and CO_2 . As noted above a significant amount of hydrogen gas was also produced throughout the oxidation. To understand this in more detail, the independent oxidation of MeOH, an aqueous solution of formaldehyde, and HCO₂H were investigated at typical methane oxidation conditions over ZSM-5(50) to establish their reactivity and oxidation products. The results are given in Table 3.

Table 3 Oxidation of MeOH, CH₂(OH)₂ and HCO₂H with H₂O₂ over ZSM-5(50)

Entry	Reactants ^[a]	Products/ $\mu\text{mol}^{[b]}$							$\chi^{[e]}$ %
		MeOH	MeOOH	HCOOH	CH ₂ (OH) ₂	POM	CO ₂ ^[c]	H ₂ ^[c]	
1	Methanol	-	0	11.3	0	0	n/d	n/d	23
2	Formaldehyde (aq)	1.2	0	30.2	-	0.029	6	2.98	75
3	Formic acid	0	0	-	0	0	9	-	19
Selectivity ^[d] / %									
4	Methanol	-	0	100	0	0	0		
5	Formaldehyde (aq)	3	-	80.7	-	0.1	16		
6	Formic acid	0	0	-	0	0	100		

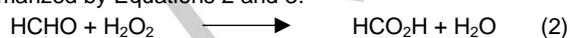
[a] Reaction conditions: Initial concentrations = 5.0mmol/l, 10ml, time = 30min, 50°C. [b] liquid analyzed by ¹H NMR; POM = μmol HCHO equivalent. [c] Gas phase analysis by GC-TCD. [d] Product C selectivity: moles(product)/moles(produced)x100. [e] Conversion (moles C produced)/(initial C moles)x100.

Methanol was oxidized by H₂O₂ to HCO₂H at our “standard” conditions. No H₂ was produced; CO₂ may have been produced in very small amounts and was not quantified. Formic acid was relatively stable over ZSM-5(50) in the presence of H₂O₂ at 50°C (19% conversion) yielding only CO₂ and, importantly, no hydrogen (Eq 1). It is possible this oxidation occurs via a performic acid group on the Fe centres in the ZSM-5 as an intermediate.^[50]



Oxidation of HCHO was carried out using a 37wt% aqueous solution of HCHO stabilized by 15wt% methanol (¹H NMR given in Supporting Information Figure S6). HCHO was rapidly oxidized by H₂O₂ over ZSM-5(50) (Table 3 entry 2: 75% conversion). The main carbon-containing, oxidation products were HCO₂H and CO₂ with a small amount of polyoxomethylene. A minor amount of MeOH may have been produced (3% selectivity), estimated by subtracting the amount of MeOH present in the commercial formaldehyde used from the overall amount of MeOH in the reaction products. Polyoxomethylene was observed only in the oxidation of formaldehyde. It is clear that in the oxidation of methane over ZSM-5, the source of POM is formaldehyde. As noted above, the formation of POM from formaldehyde over transition metal promoted zeolites is known.^[47] More importantly, in contrast to the oxidation of methanol or formic acid, the oxidation of aqueous formaldehyde resulted in H₂ being evolved in significant amounts, Table 3 entry 2. It was confirmed that H₂ was not produced at the “standard” experiment conditions from H₂O₂ and catalyst in the absence of methane or formaldehyde. This demonstrates that ZSM-5(50) does not decompose H₂O₂ to H₂ and O₂ and underlines that the source of H₂ is oxidation of formaldehyde by H₂O₂.

The uncatalysed reaction chemistry of HCHO in acidified aqueous solutions of H₂O₂ was investigated by Fry and Payne in the 1930's.^[48,49] They also reported on the oxidation of methanol and formic acid by H₂O₂. The oxidation of HCHO is summarized by Equations 2 and 3:



These reactions form a basis for understanding the production of hydrogen over ZSM-5. At higher concentrations of H₂O₂ oxidation favours formic acid via Eq 2. Fry and Payne reported

that the production of hydrogen (Eq 3) was favoured at lower concentrations of H₂O₂ typical of the “standard” oxidation conditions used here.^[48, 49] In our methane oxidation experiments, the progressive decrease in the concentration of H₂O₂ caused by its consumption in the oxidation of methane and its decomposition over ZSM-5(50) probably contributes to the promotion of H₂ production from formaldehyde. Oxidation of the aqueous solution of HCHO at “standard” conditions in the absence of catalyst resulted in only a very small conversion (<5%) to formic acid, which is consistent with the homogeneous reaction studies of Fry and Payne done at 60°C.^[48] Overall, this shows that the reactions are mainly catalyzed by the ZSM-5.

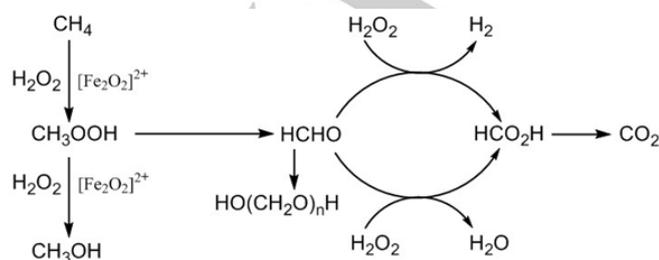
Reaction pathway

In a series of papers Hutchings and co-workers proposed a reaction pathway for methane oxidation over Fe containing ZSM-5 based on sequential oxidation according to the sequence CH₄ → MeOOH → MeOH → HCO₂H → CO₂.^[34-36] These conversions were seen as taking place over binuclear Fe species, [Fe₂O₂]²⁺, in the zeolite. This chemistry was distinguished from methane activation by Fenton's reagent by the proven absence of methyl radicals in the catalytic cycle. The conversion of MeOOH to MeOH was proposed to lead to the release of hydroxyl radicals which then contributed to the further oxidation of MeOH to formic acid. To support this, methanol selectivity was observed to increase in the presence of a ·OH radical scavenger (Na₂SO₃). (In addition, MeOOH and MeOH were proposed to undergo oxidation by minor uncharacterized parallel non-sequential pathways to CO₂).^[34] The experimental results of the present work suggest a more complex reaction network is occurring.

To summarize the main observations from the present work: (a) MeOOH is the initial product from methane oxidation in agreement with previous work; (b) at the conditions used MeOOH is converted to HCHO; (c) HCHO reacts rapidly with hydrogen peroxide to give HCO₂H by two competing processes with different co-products which probably depend on the hydrogen peroxide concentration: to produce water or hydrogen as the co-product; (d) HCHO can polymerize to yield soluble polyoxomethylene; (e) MeOH is oxidized by hydrogen peroxide to HCO₂H.

The above observations are captured in Scheme 1 in which the initial oxidation of methane to methyl hydroperoxide takes place at a binuclear Fe species in the zeolite as proposed by Hutchings and coworkers.^[34-37] The methyl hydroperoxide is then converted to formaldehyde. Whether this takes place by decomposition at the Fe sites or over the acid sites of the zeolite is not clear as both processes are in principle possible and indeed may take place in parallel. The decomposition of MeOOH to formaldehyde is known to occur in the gas phase and in the liquid phase by reactions that depend on the solvent and temperature.^[51-53, 27] In a series of competing reactions, formaldehyde is oxidized over the Fe sites to HCO₂H releasing either water or hydrogen depending on the hydrogen peroxide concentration, and a small proportion of the HCHO is polymerized to soluble polyoxomethylene. In considering the route to methanol, the reduction of MeOOH in solution by NaBH₄ leading to methanol formation is known.^[27] It is tempting, therefore, to assume that MeOOH will react with the evolving hydrogen to yield methanol. However, our attempts to demonstrate this have been largely unsuccessful. In a series of experiments, the oxidation of methane was done under our "standard" conditions for a short time (5 or 10 min) when the selectivity to MeOOH is in the range 60-70% (see above), after which the methane was purged rapidly and replaced with 5 bar of hydrogen for 5 or 15 min. The MeOOH selectivity was observed to drop to a low value and the main product was HCO₂H with little evidence of an increase in methanol selectivity. Overall the result suggests that under methane selective oxidation conditions, MeOOH can be expected to react to form formaldehyde, and undergo oxidation to methanol as proposed by Hutchings and coworkers^[34-37], although the possibility of hydrogenation cannot be completely excluded. A more detailed mechanistic and kinetic study would be required to clarify this complex situation.

The disproportionation of HCHO to MeOH and HCO₂H by the Cannizzaro reaction is a known homogeneous reaction which can also be heterogeneously catalyzed by metal oxides.^[47, 53] In principle, therefore, a Cannizzaro reaction could contribute to the production of MeOH and HCO₂H in the selective oxidation of methane. However, the Cannizzaro reaction is normally catalyzed by base, whereas the reaction mixtures studied here showed weak acidity. Further research would be needed to clarify any such a contribution.



Scheme 1 A simplified methane oxidation reaction scheme over ZSM-5. Oxidation of methanol to formic acid, and possible minor direct oxidation routes from MeOOH and MeOH to CO₂ are omitted for clarity.^[34]

Conclusions

A parametric study of the selective oxidation of methane carried out in aqueous hydrogen peroxide and over ZSM-5 catalysts, showed that the initial oxidation product formed was MeOOH in agreement with the seminal work of the Hutchings and coworkers.^[34-36] ZSM-5 with Si/Al = 50 and 30 were found to be the most active in agreement with the previous work. However, liquid oxygenate productivities were found to be significantly higher for the same ZSM-5, reflecting the generally higher Fe content in the present batch and the lower catalyst mass used. The latter suggests that physical factors may begin to influence productivity at the higher catalyst mass used in previous studies. Hydrated formaldehyde was found in low concentrations. The trends in MeOOH and formaldehyde concentration and selectivity with reaction time are similar indicating that formaldehyde is a reactive product of MeOOH decomposition. Formaldehyde appears to be an important intermediate in the methane selective oxidation pathway catalyzed by ZSM-5. An important feature of our oxidation results was the observation of hydrogen evolution which occurred from the beginning of the oxidation, and is reported for the first time. The evolution of hydrogen was demonstrated to arise from the oxidation of HCHO by H₂O₂. This reaction competes with the oxidation of HCHO to formic acid and water which is favoured at higher hydrogen peroxide concentrations, and the formation of soluble polyoxomethylene. A detailed study of the reaction kinetics is required to clarify the full details of the complex reaction network and the relative importance of individual reactions.

Experimental Section

Catalytic materials and characterisation

Four commercial ZSM-5 (SiO₂/Al₂O₃ mole ratios: 23, 30, 50 and 80) were obtained from Zeolyst International and used as catalysts. The zeolites were activated by calcination in air at 550°C for 3hr prior to use in methane oxidation experiments. Surface area and porosity were determined by N₂ physisorption using a Micromeritics Tristar 3000. XRD was obtained using a PANalytical X'Pert Pro diffractometer (Cu K α radiation). Fe content was determined by ICP by Intertek.

Catalytic reaction

The methane oxidation reactions were carried out in a 50ml stainless-steel autoclave (Parr) using a purpose-made glass liner (50 ml). The glass reactor liners were soaked overnight at repeated intervals in concentrated nitric acid to remove any traces of metals. The reaction temperature was maintained by immersion of the reactor body in a temperature-controlled liquid bath and the reactants were stirred vigorously by glass-coated magnetic bar. Aqueous hydrogen peroxide from Sigma Aldrich (35wt%) was used. In a typical "standard" methane oxidation experiment, de-ionized water (5ml) and catalyst (13.5 mg) was added to the autoclave and heated to 50°C. When the reactor

reached 50°C sufficient diluted H₂O₂ was added to achieve the desired concentration (typically 0.5M in the final liquid volume of 10 ml) avoiding its decomposition during the warm up period. The sealed reactor was then purged with Argon (99.99%, BOC) to remove air, and then pressurized with a 25%CH₄/Argon mixture (BOC) to achieve the desired methane partial pressure, typically 10 bar. After the desired reaction time, usually 30 min, the autoclave was cooled rapidly to 5°C in an ice bath to minimize any further chemical processes and reduce loss of volatile products. In some runs, a GC gas sampling bag was used to collect gaseous products before cooling. After depressurization and purging with argon, the zeolite catalyst was found to have partially settled and a liquid sample was withdrawn and prepared for analysis within a short time by ¹H NMR. The pH of the reaction mixtures was generally found to be in the region of 4-5.

Liquid phase products were analyzed principally by ¹H NMR and occasionally by GC-FID (HP-FFAP capillary column, length 30m, ID 0.32 mm, film 0.25 μm, He carrier gas). The NMR measurements were made at 298K using a Bruker AVANCE III HD 500 spectrometer (11.74 T) running TopSpin 3.2 and equipped with a z-gradient 5mm tunable SmartProbe and a GRASP II gradient spectroscopy accessory providing a maximum gradient output of 53.5G/cm (5.35G/cmA). The spectra were collected at a frequency of 500.13MHz using the Bruker pulse program zgpg30 with a spectral width of 44642.86Hz (89.2ppm) and 262144 data points. A relaxation delay of 1s was employed and the center of the spectrum was placed on the water signal (~4.7ppm). Water suppression was achieved using an 180° selective square shaped pulse (Squa100.1000) of 2ms duration and smoothed square shaped gradients (SMSQ10.100) of 1ms duration and strengths of 31% and 11%. Typically, 512 transients were collected. The data was processed using an exponential function with a line broadening of 0.3Hz and 262144 data points to give a 1st order zero filling. Residual H₂O₂ concentration was determined using Ti(IV)SO₄, which does not react with formaldehyde or hydroperoxides.^[41] Gaseous products were analyzed by GC equipped with a TCD detector using a packed column (Carboxene, length 10ft, 1/8in, ID 2 mm), and Ar or He as carrier gases to determine gas phase H₂, or CH₄ and CO₂ respectively.

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Keywords: methane • oxidation • methanol • ZSM-5 • hydrogen peroxide

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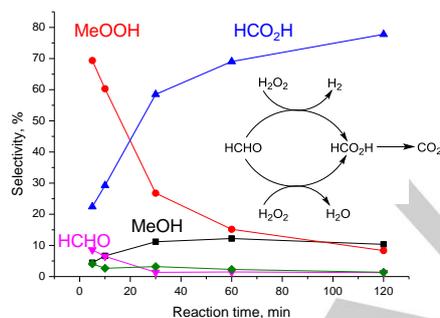
Entry for the Table of Contents (Please choose one layout)

Layout 1:

FULL PAPER

Methane oxidation in H_2O_2 :

Over ZSM-5 methane forms CH_3OOH and a formaldehyde intermediate in the oxidation pathway. Hydrogen is released during the rapid oxidation of HCHO to formic acid over ZSM-5. Polyoxomethylenes are produced in small amounts.



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Selective Oxidation of Methane to Methanol over ZSM-5 Catalysts in Aqueous Hydrogen Peroxide: Role of Formaldehyde