

GOLD CATALYSIS FOR SELECTIVE OXIDATION FOR APPLICATION TO BIO-DERIVED SUBSTRATES

by

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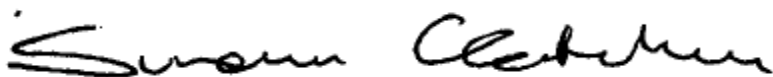
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DECLARATION OF ORIGINALITY

I hereby declare that this thesis was entirely written by me and that all content in this document has been obtained and presented in accordance with the academic rules of Imperial College London. Information derived from the published and unpublished work of others has been appropriately acknowledged and references are given in the list of sources.

A handwritten signature in black ink, appearing to read 'Sumana Chaturvedula', written in a cursive style.

Sumana Chaturvedula

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ABSTRACT

The depletion of fossil resources, the volatility of the oil price market and the urgency to mitigate the effects of climate change have pushed the development in chemical industry for sustainable, energy efficient and economic processes for fine chemical production. Selective oxidation of alcohols using noble metal catalysts is a key catalytic conversion for the production of carbonylic and carboxylic compounds for the chemical, pharmaceutical, automobile or consumer goods industry. Gold based catalysts, in particular, have demonstrated superior performance over commonly employed catalysts or stoichiometric oxidants. Challenges, however, remain to develop not only active and selective catalysts but with a long lifetime for industrial application.

This thesis is based on the study and development of gold based catalyst systems for the selective oxidation of alcohols under mild conditions. The main model compound studied is the selective oxidation of salicyl alcohol to salicyl aldehyde and salicylic acid. Salicyl aldehyde is a very important chemical compound for the production of a range of fine chemicals and chelating compounds with an estimated market capacity of 4000-6000 tonnes/year.

Reactions were carried out in a semi-batch stirred glass reactor under atmospheric pressure using air as oxidant and water as solvent. The setup successfully enabled the direct study of the kinetics and mechanism without influences of mass transport. Studies demonstrated the reaction followed sequential mechanism of first order with the consecutive oxidation of salicyl aldehyde to salicylic acid. The main catalyst system used was gold on powdered activated carbon, prepared by sol-immobilisation using Tetrakis(hydroxymethyl)phosphonium chloride (THPC) as stabiliser. 1wt% Au/C achieved maximum turnover frequency numbers (TOF) of 342 h⁻¹ and selectivities of 79% towards salicyl aldehyde at 100% conversion. The increase in gold loading to 3wt% resulted in a decrease in activity caused by an increased gold particle size. The addition of Pd as second active metal showed the formation of an alloy and a decrease in activity with the increase in Pd amount. The application of the Au/C catalyst system for continuous processing was investigated using gold on granular carbon in a trickle bed reactor.

Base-free selective oxidation of salicyl alcohol was studied via synthesis of MgO dispersed on oxides, in particular hydrotalcites. The basicity, measured by CO₂ adsorption capacity, increased with increased loading of MgO. The catalysts showed potential activity, achieving 59% conversion with 90% selectivity towards salicyl aldehyde.

Table of Contents

DECLARATION OF ORIGINALITY	2
ACKNOWLEDGEMENTS.....	3
ABSTRACT.....	4
1 INTRODUCTION.....	23
1.1 The need for sustainable chemistry.....	23
1.2 Thesis outline	27
2 LITERATURE REVIEW	29
2.1 Catalytic conversion of bio-derived substrates.....	29
2.2 Key catalyst systems for selective oxidation of alcohols	29
2.2.1 Ruthenium, platinum and palladium catalysis.....	30
2.2.2 Gold vs. platinum and palladium	33
2.2.3 Catalyst deactivation.....	35
2.3 Gold for selective oxidation	36
2.3.1 Introduction	36
2.3.2 Structure sensitivity	37
2.3.3 Au on carbon.....	41
2.3.4 Au on oxides.....	42
2.3.5 Mechanism on the catalyst surface	47
2.4 Bimetallic AuPd catalysts	51
2.4.1 Structural properties.....	51
2.4.2 Synergistic effects	53
2.5 Selective oxidation of salicyl alcohol.....	55
3 MATERIALS AND METHODS.....	59
3.1 Chapter introduction	59
3.2 Particle size measurements	59

3.2.1	TEM Transmission electron microscopy	59
3.2.2	EDS Energy dispersive X-Ray spectroscopy.....	60
3.2.3	STEM Scanning transmission electron microscopy.....	60
3.3	Catalyst structure and morphology and product analysis (HPLC)	60
3.3.1	XRD X-Ray diffraction	60
3.3.2	BET Surface area	61
3.3.3	Zeta potential.....	61
3.3.4	TGA Thermogravimetric analysis and CO ₂ adsorption.....	62
3.3.5	ICP Inductively coupled plasma	62
3.3.6	HPLC High performance liquid chromatography	63
3.4	Catalyst preparation	67
3.4.1	Catalyst nomenclature	67
3.4.2	Impregnation.....	67
3.4.3	Sol-immobilisation	68
3.5	Catalyst performance experiments	73
3.5.1	Batch reactor.....	73
3.5.2	Reaction calorimetry.....	76
3.5.3	Trickle Flow reactor.....	78
3.5.4	Calculating catalyst activity.....	82
4	AU/C FOR SELECTIVE OXIDATION OF SALICYL ALCOHOL	83
4.1	Chapter introduction	83
4.2	Reaction network and study of parametric effects	85
4.2.1	Influence of stirring.....	87
4.2.2	Influence of mass of catalyst.....	88
4.2.3	The role of oxygen partial pressure	89
4.2.4	Influence of temperature.....	91
4.2.5	The pH.....	92
4.3	Kinetics and mechanism	95

4.3.1	Order of reaction for selective oxidation of salicyl alcohol	95
4.3.2	Oxidation of salicyl aldehyde	104
4.3.3	Influence of product addition	108
4.3.4	Molecular mechanism on gold surface	112
4.4	Catalyst effects – morphology and properties.....	114
4.4.1	Influence of catalyst preparation method	114
4.4.2	Influence of gold loading.....	117
4.4.3	Influence of catalyst heat treatment	122
4.4.4	Nature of support	125
4.5	Catalyst effects- catalyst performance	127
4.5.1	Influence of preparation method	128
4.5.2	Influence of gold loading and catalyst treatment.....	128
4.5.3	Nature of support	131
4.5.4	Recycle Tests	134
4.6	Chapter summary.....	135
5	MOVING TOWARDS BASE-FREE CATALYSIS	137
5.1	Chapter introduction	137
5.2	Au on alkaline- earth metal oxides	139
5.2.1	Au/MgO and Au/CaO	139
5.3	Au on impregnated oxides	143
5.3.1	Introduction	143
5.3.2	Catalyst morphology and properties	144
5.3.3	Catalyst activity	148
5.4	Au on promoted hydrotalcites.....	149
5.4.1	Introduction	149
5.4.2	Influence of MgO loading.....	149
5.4.3	Effect of gold loading	161
5.4.4	Influence of precursor.....	162

5.4.5	Catalyst deactivation.....	173
5.5	Chapter summary.....	174
6	BIMETALLIC CATALYSIS FOR SELECTIVE OXIDATION OF SALICYL ALCOHOL	176
6.1	Chapter introduction	176
6.2	AuPd on carbon.....	177
6.2.1	Catalyst morphology and properties	178
6.2.2	Catalyst activity	183
6.3	Chapter summary.....	185
7	SELECTIVE OXIDATION OF DIOLS AND TRIOLS.....	187
7.1	Chapter introduction	187
7.1.1	Selective oxidation of 1,2- propanediol	187
7.1.2	Selective oxidation of glycerol	190
7.2	Chapter summary.....	194
8	MOVING FROM BATCH TO CONTINUOUS PROCESSING.....	195
8.1	Chapter introduction	195
8.1.1	Catalyst preparation for trickle bed reactor	195
8.1.2	Effect of LHSV.....	196
8.1.3	Effect of particle size.....	197
8.2	Chapter summary.....	199
9	CONCLUSIONS AND OUTLOOK.....	200
9.1	Key findings of this research	200
9.2	Impact	203
9.3	Outlook	204
10	REFERENCES.....	205
11	APPENDIX.....	211
	A Au/C for Selective Oxidation.....	211
	HPLC analysis.....	211
	Parametric Study (T,p, pH).....	214

Kinetics and Mechanism	216
Influence of product addition	219
Catalytic effects.....	223
B Moving Towards Base Free Catalysis.....	229
Au on oxides.....	229
Au on impregnated oxides.....	230
Au on impregnated HT	233
C Bimetallic catalysis for selective oxidation of salicyl alcohol.....	239
Selective oxidation of diols & triols	244
Selective oxidation of 1,2- propanediol	244
Selective oxidation of glycerol	246
E Moving From Batch to Continuous Processing	248

LIST OF FIGURES

Figure 1-1: Biomass production worldwide [2].	23
Figure 1-2: Model of a bio-based product flow-chart for biomass feedstock according to [3].	25
Figure 2-1: Catalytic conversion routes of bio-derived feedstock to chemicals [20].	29
Figure 2-2: Selective oxidation of 1-octanol to 1-octanal.	31
Figure 2-3: Selective oxidation of 2-octanol to 2-octanal.	31
Figure 2-4: Selective oxidation of cinnamyl alcohol to cinnamaldehyde.	32
Figure 2-5: Reaction and product network for selective oxidation of glycerol [48].	34
Figure 2-6: HRTEM images of most commonly shaped gold nanoparticles exposing crystal facets after annealing at 100° C [62].	39
Figure 2-7: Interactions across interfaces around a gold particle and the contact angle; γ interfacial energy: ms: metal/ support, mg: metal/ gas, gs : support/gas [32].	40
Figure 2-8: Activated carbon pore structure [79].	41
Figure 2-9: Rutile structure of CeO ₂ [90].	43
Figure 2-10: Turnover frequencies for the oxidation of 3-octanol, given as the ratio of moles of 3-octanone per mole of Au per hour, measured at t=10 min [64].	44
Figure 2-11: Double layered structure of hydrotalcite [94].	45
Figure 2-12: Mechanism for selective oxidation of ethanol on Au (111), R= reactant, (TS)= transition state, P= product [118].	48
Figure 2-13 Mechanism for selective oxidation of ethanol on Au (111), R= reactant, (TS)= Transition state, P= Product [118].	49
Figure 2-14: Scheme for adsorption modes for O ₂ on gold. [77].	50
Figure 2-15: Temperature-composition phase diagram of AuPd solid solutions below melting point based on [123]. Curved lines represent order-disorder phase boundaries of the respective composition.	51
Figure 2-16: Particle configuration for Au Pd alloy compositions Au(bright), Pd(dark) after cooling corresponding to 923 atom particles [124].	52
Figure 2-17: Schematic representation of the structure of a bimetallic catalyst with Au (A) and second metal (B) particles [38].	52
Figure 2-18: Schematic representation of the structure of a bimetallic catalyst with alloy and core-shell morphology.	52
Figure 2-19: Modes of action of bimetallic catalysts in selective oxidations: Δ , $\square$ atoms of either Au or group 10 metal involved $\bigcirc$ non-participating atoms [32].	53
Figure 2-20: Modes of action of bimetallic catalysts in selective oxidations: Δ , $\square$ atoms of either Au or group 10 metal involved $\bigcirc$ non-participating atoms [32].	53
Figure 2-21: Modes of action of bimetallic catalysts in selective oxidations: Δ , $\square$ atoms of either Au or group 10 metal involved $\bigcirc$ non-participating atoms [32].	54
Figure 2-22: Selective oxidation of benzyl alcohol.	55
Figure 2-23: Commercial Reimer-Tiemann process.	56
Figure 2-24: Reaction network for salicyl aldehyde a) Dakin-reaction for production of catechol b) etherification and cyclisation to benzofuran, c) reaction with amines to salicylaldehydimine.	57
Figure 3-1: Reactor setup for catalyst reductive heat treatment.	69
Figure 3-2: Setup of a glass batch reactor for the selective oxidation of salicyl alcohol.	74
Figure 3-3: Setup of glass batch reactor (Buchi) setup for selective oxidation of 1,2- propanediol.	76

Figure 3-4: Setup for calorimetric experiments for selective oxidation of salicyl alcohol	78
Figure 3-5: P and ID diagram for the TBR reactor	79
Figure 3-6: Scheme of packed reactor for TBR system.	80
Figure 4-1: General reaction for selective oxidation of salicyl alcohol.....	85
Figure 4-2: Course of reaction for typical experiment for selective oxidation of salicyl alcohol, reaction conditions: $T=50^{\circ}\text{C}$, $p_{\text{total}}=1\text{ bar (air)}$, catalyst 1.5Au/C , $m_{\text{cat}}=0.2\text{g}$, $C_{\text{salicyl alcohol}}=0.04\text{ M}$, $\text{NaOH: salicyl alcohol}=2:1$, $\text{rpm}=1000$	86
Figure 4-3: Mass transport limitation studies on the selective oxidation of salicylic alcohol, $1/r$ (initial) vs $1/m_{\text{cat}}$, reaction conditions: $T=50^{\circ}\text{C}$, $p=1\text{ bar (air)}$, catalyst 1.5Au/C , $m_{\text{cat}}=0.1\text{-}0.4\text{g}$, $C_{\text{salicyl alcohol}}=0.04\text{ M}$, $\text{NaOH: salicyl alcohol}=2:1$, $\text{rpm}=1000$	88
Figure 4-4: Rate of reaction as function of oxygen partial pressure with standard error — linear fit function, reaction conditions: $T=50^{\circ}\text{C}$, $p_{\text{O}_2}=0.21\text{-}1.05\text{ bar}$, catalyst 1.5Au/C , $m_{\text{cat}}=0.2\text{g}$, $C_{\text{salicyl alcohol}}=0.04\text{ M}$, $\text{NaOH: salicyl alcohol}=2:1$, $\text{rpm}=1000$	90
Figure 4-5: Influence of $\text{NaOH}/\text{substrate}$ ratio on conversion, $T=50^{\circ}\text{C}$, $p=1\text{ bar (air)}$, $\text{cat}=1.5\text{ Au/C}$, $m_{\text{cat}}=0.2\text{g}$, $C_{\text{salicyl alcohol}}=0.04\text{M}$, $\text{NaOH: salicylic alcohol}: 3(\bullet), 2(\blacktriangle), 1(\blacktriangledown), 0.5(\blacklozenge), 0(\blacktriangleleft)$, $\text{rpm}=1000$	92
Figure 4-6: Dependency of initial rate of reaction on NaOH concentration, reaction conditions: $T=50^{\circ}\text{C}$, $p=1\text{ bar (air)}$, $\text{cat}=1.5\text{ Au/C}$, $m_{\text{cat}}=0.2\text{g}$, $C_{\text{salicyl alcohol}}=0.04\text{M}$, $\text{rpm}=1000$	93
Figure 4-7: Profile of OH concentration and salicyl acid formation for selective oxidation of salicyl alcohol, reaction conditions: $T=50^{\circ}\text{C}$, $p=1\text{ bar (air)}$, $\text{cat}=1.5\text{Au/C}$, $m_{\text{cat}}=0.2\text{g}$, $\text{NaOH: salicyl alcohol}: 2:1$, $\text{rpm}=1000$	94
Figure 4-8: Plot of first order rate equation based on concentration of salicyl alcohol with standard error — fit function, reaction conditions: $T=50^{\circ}\text{C}$, catalyst 1.5Au/C , $m_{\text{cat}}=0.2\text{g}$, $p=1\text{ bar (air)}$, $C_{\text{reactant}}=0.04\text{M}$, $\text{NaOH: reactant}=2:1$, $\text{rpm}=1000$	97
Figure 4-9: Concentration/ time profile for the selective oxidation of salicylic alcohol: Reaction conditions: $T=50^{\circ}\text{C}$, $p=1\text{ bar (air)}$, catalyst 1.5Au/C , $m_{\text{cat}}=0.2\text{g}$, $C_{\text{salicyl alcohol}}=0.04\text{ M}$, $\text{NaOH: salicyl alcohol}=2:1$, $\text{rpm}=1000$, $\bullet$ salicylic alcohol, $\blacktriangle$ salicylic aldehyde, $\blacktriangledown$ salicylic acid.	99
Figure 4-10: Reaction network with rate constants for the selective oxidation of salicylic alcohol.....	100
Figure 4-11: Origin fitted plot for consecutive reaction of first order for concentration/time profile of salicylic aldehyde, $\blacksquare$ experimental data with standard error, — fit function, experimental data for reaction conditions: catalyst: $T=50^{\circ}\text{C}$, $p=1\text{ bar (air)}$, 1.5Au/C , $m_{\text{cat}}=0.2\text{g}$, $C_{\text{salicyl alcohol}}=0.04\text{M}$, $\text{NaOH: salicyl alcohol}=2:1$, $\text{rpm}=1000$	101
Figure 4-12: Origin fitted plot for consecutive reaction of first order for concentration/time profile of salicylic acid, $\blacksquare$ experimental data with standard error, — fit function, experimental data for, reaction conditions: $T=50^{\circ}\text{C}$, $p_{\text{total}}=1\text{ bar (air)}$, catalyst 1.5Au/C , $m_{\text{cat}}=0.2\text{g}$, $C_{\text{salicyl alcohol}}=0.04\text{ M}$, $\text{NaOH: salicyl alcohol}=2:1$, $\text{rpm}=1000$	102
Figure 4-13: Origin fitted plot for consecutive reaction of first order for concentration/time profile of salicyl aldehyde, $\blacksquare$ experimental data, — fit function, experimental data for, reaction conditions: catalyst: 3Au/C , $T=50^{\circ}\text{C}$, $p=1\text{ bar (air)}$, $C_{\text{salicyl alcohol}}=0.04\text{M}$, $\text{NaOH: salicyl alcohol}=2:1$, $\text{rpm}=1000$	103
Figure 4-14: Concentration/ time profile for the selective oxidation of salicyl aldehyde,	105
Figure 4-15: Origin fitted plot for consecutive reaction of first order for selective oxidation of salicyl aldehyde: concentration/time profile of salicyl aldehyde. $\blacksquare$ Experimental data with error bars, — fit function, experimental data for reaction conditions: catalyst: 1.5Au/C , $T=50^{\circ}\text{C}$, $p=1\text{ bar (air)}$, $C_{\text{salicyl alcohol}}=0.04\text{M}$, $\text{NaOH: salicyl aldehyde}=2:1$, $\text{rpm}=1000$	106

Figure 4-16: : Origin fitted plot for consecutive reaction of first order for selective oxidation of salicyl aldehyde concentration/time profile of salicylic acid, ■ experimental data with error bars, — fit function, experimental data for reaction conditions: catalyst:1.5Au/C, T=50°C, p= 1bar (air) $c_{\text{salicyl alcohol}} = 0.04\text{M}$, NaOH:salicyl aldehyde=2:1, rpm=1000.	107
Figure 4-17: Influence of product addition ($c_{\text{salicylic acid}} = 0.0112\text{ M}$) (——straight line) on selective oxidation of salicylic alcohol, original plot (-----dotted line): 1.5Au/C catalyst, $c_{\text{salicyl alcohol}} = 0.04\text{M}$, $c_{\text{salicylic acid}} = 0.0112\text{M}$, T=323 K, p=1 bar (air), $m_{\text{cat}} = 0.2\text{g}$, salicylic alcohol (■), salicylic aldehyde (●), salicylic acid (▲).	109
Figure 4-18: Origin fitted plot for consecutive reaction of first order for concentration/time profile of salicylic aldehyde, ■ experimental data, — fit function, experimental data for, reaction conditions: catalyst: : catalyst: 1.5Au/C, T=50°C, p=1bar (air), $m_{\text{cat}} = 0.2\text{g}$, $c_{\text{salicyl alcohol}} = 0.04\text{M}$, $c_{\text{salicylic acid}} = , -0.0112\text{ M}$, NaOH:salicyl alcohol: 2:1, rpm=1000.	110
Figure 4-19: Proposed reaction mechanism for liquid phase oxidation of salicyl alcohol under alkaline conditions according to [118].	113
Figure 4-20: 1.5 Au/C prepared by impregnation.	115
Figure 4-21: 1.5Au/C prepared by sol-immobilisation.	115
Figure 4-22: TEM histogram of 1.5Au/C via impregnation.	116
Figure 4-23: TEM histogram of 1.5Au/C via sol immobilisation.	116
Figure 4-24: TEM image of 0.75Au/C.	118
Figure 4-25: TEM image of 1Au/C.	118
Figure 4-26: TEM image of 1.5Au/C.	118
Figure 4-27: TEM image of 3Au/C.	118
Figure 4-28: TEM histogram of 0.75 Au/C.	120
Figure 4-29: TEM histogram of 1Au/C.	120
Figure 4-30: TEM histogram of 1.5Au/C.	120
Figure 4-31: TEM histogram of 3Au/C.	120
Figure 4-32: XRD Diffraction pattern of Au/C catalysts with different gold loading. — activated carbon, bottom— 1.5Au/C, top—3Au/C.	122
Figure 4-33: TEM image 1.5Au/_150°C.	123
Figure 4-34: TEM image 1.5Au/C_350°C.	123
Figure 4-35: TEM image 3Au/C_150°C.	123
Figure 4-36: TEM image 3Au/C_350°C.	123
Figure 4-37: TEM image of 1Au/CeO ₂	126
Figure 4-38: TEM image of 1Au/TiO ₂	126
Figure 4-39: TEM histogram of 1Au/CeO ₂	126
Figure 4-40: TEM histogram of 1Au/TiO ₂	126
Figure 4-41: Influence of Au loading on catalytic activity and selectivity toward the selective oxidation of salicyl alcohol, reaction conditions: T=50°C, p =1bar (air), $m_{\text{cat}} = 0.2\text{g}$, $c_{\text{salicyl alcohol}} = 0.04\text{M}$, NaOH:salicyl alcohol= 2:1, rpm= 1000.	130
Figure 4-42: Selectivity/Conversion plot for selective oxidation of salicyl alcohol on carbon and oxide supported catalysts: 1Au/C, 1Au/CeO ₂ and, 1Au/TiO ₂	133
Figure 5-1: Proposed mechanistic scheme for selective oxidation of salicyl alcohol on an MgO-impregnated surface of HT support material.	138
Figure 5-2: TEM image of 1.5Au/MgO.	140

Figure 5-3: TEM image of 1.5Au/CaO.....	140
Figure 5-4: TEM histogram of 1.5Au/MgO.	141
Figure 5-5: TEM histogram of 1.5Au/CaO.	141
Figure 5-6: TEM image of 1.5Au/0.16MgO-CeO ₂	145
Figure 5-7: TEM image of 1.5Au/0.28 CaO-TiO ₂	145
Figure 5-8: TEM histogram of 1.5Au/0.16MgO-CeO ₂	145
Figure 5-9: TEM histogram of 1.5Au/0.28CaO-TiO ₂	145
Figure 5-10: XRD diffractogram for MgO impregnated CeO ₂ support 0.16MgO-CeO ₂ compared to MgO (ICDD database ID 00-001-1235).	147
Figure 5-11: TEM image of HT support.	151
Figure 5-12: TEM image of 1.5Au/HT.	151
Figure 5-13: TEM image of 1.5Au/0.16MgO-HT.....	151
Figure 5-14: XRD stacked diffractograms of series of MgO promoted HT materials 0.04MgO-HT, 0.08MgO-HT, 0.16MgO-HT, compared to the reference diffractograms of HT (00-014-0191) bottom and MgO (00-001-1235) top.	154
Figure 5-15: Zeta potential measurements of HT■ and 0.16MgO-HT◆ for a pH range form 2-12.....	156
Figure 5-16: Profile for TGA-CO ₂ measurement cycle on1.5Au/0.16MgO-HT step 1-5, total differential weight change (%) against temperature, initial weight m _{cat} =19.5340 mg.	157
Figure 5-17: Concentration/ time profile for the selective oxidation of salicylic alcohol: Reaction conditions: catalyst: 1.5Au/0.16MgO-HT_650, T=50°C, p=1bar (air), C _{salicyl alcohol} = 0.04M m _{cat} = 0.2g, NaOH/reactant=0:1, rpm=1000.....	159
Figure 5-18: XRD diffractograms of HT calcined at 400°C, and 0.16MgO-HT calcined at 400°C with the reference pattern for MgO from the ICDD (00-001-1235)	163
Figure 5-19: TEM image 1.5Au/0.16 MgO-HT_400.	164
Figure 5-20: TEM image 1.5Au/ 0.16 MgO-HT.....	164
Figure 5-21: TEM histogram of 1.5Au/0.16MgO-HT_400.....	165
Figure 5-22: TEM histogram of 1.5Au/0.16MgO-HT.....	165
Figure 5-23: HAADF Image of 1.5Au/0.16MgO-HT a).....	167
Figure 5-24: HAADF Image of 1.5Au/0.16MgO-HT b).....	167
Figure 5-25: BF image of 1.5Au/0.16MgO-HT.....	168
Figure 5-26: BF image of 1.5Au/0.16MgO-HT.....	168
Figure 5-27: HRTEM Image of Au nanoparticles on MgO-promoted HT with different types of shape and orientation, 1-5.....	169
Figure 5-28: Reaction scheme 1 for condensation reaction of salicyl alcohol and salicylic acid.	172
Figure 5-29: Reaction scheme 2 for condensation reaction of salicyl alcohol and salicylic acid.	172
Figure 5-30: Reaction scheme 3 for condensation reaction of salicyl alcohol and salicylic acid.	173
Figure 5-31: TEM image of used catalyst.....	174
Figure 5-32: TEM histogram of used catalyst 1.5Au/0.16MgO-HT.....	174
Figure 6-1: TEM image of 0.75Au0.75Pd/C.....	178
Figure 6-2: TEM image of 1.5Au1.5Pd/C.....	178
Figure 6-3: TEM Histogram of 0.75Au0.75Pd/C.....	179
Figure 6-4: TEM Histogram of 1.5Au1.5Pd/C.....	179
Figure 6-5: X-Ray diffraction pattern of the bimetallic 1.5Au1.5Pd/C , compared to the reference database ICDD for AuPd(below) and including marked reflections according to ICDD for Au and Pd.	181

Figure 6-6: Selected XRD Diffractogram peaks for series of AuPd on carbon catalysts: 1.5Au0.75Pd/C, including the reference peaks for monometallic Au and Pd.	182
Figure 7-1: Reaction pathways and product network for selective oxidation of 1,2- propanediol [47].	187
Figure 7-2: Concentration/time profile for selective oxidation of 1,2- propanediol on 1.5Au/C, reaction conditions: T=50°C, p=1bar, catalyst: 1.5Au/C, m _{cat} = 0.2 g, reactant/Au=1000, 1,2- propanediol: NaOH=1:1, 1,2- propanediol (•), lactic acid (▲), sodium acetate (▼).	188
Figure 7-3: Reaction and product network for selective oxidation of glycerol [48].	191
Figure 7-4: Concentration/time profile for the selective oxidation of glycerol,	192
Figure 8-1: TEM image of 1.5Au/C on granulate (0.60-0.85mm).	196
Figure 8-2: TEM histogram for 1.5Au/C on granulate (0.60-0.85mm).	196
Figure 8-3: Effect of LHSV on conversion and selectivity for selective oxidation of salicyl alcohol in	197
Figure 11-1: Salicyl alcohol calibration HPLC1.	212
Figure 11-2: Salicyl aldehyde calibration HPLC1.	212
Figure 11-3: Salicylic acid calibration HPLC1.	212
Figure 11-4: Salicyl alcohol calibration HPLC2.	213
Figure 11-5: Salicyl aldehyde calibration HPLC2.	213
Figure 11-6: Salicyl acid calibration HPLC2.	213
Figure 11-7: HPLC chromatogram for selective oxidation of salicyl alcohol components (HPLC2).	214
Figure 11-8: Arrhenius plot for determination of the activation energy for the selective oxidation of salicylic alcohol with standard error, — linear fit function, reaction conditions T = 50 -70 °C, p _{total} = 1bar (air), catalyst 1.5Au/C, m _{cat} = 0.2g, C _{salicyl alcohol} = 0.04 M, NaOH: salicyl alcohol= 2:1, rpm= 1000.	214
Figure 11-9: Selective oxidation of salicyl alcohol, reaction conditions T = 50 °C, p _{total} = 1bar (air), catalyst 1.5Au/C, m _{cat} = 0.2g, C _{salicyl alcohol} = 0.04 M, NaOH: salicyl alcohol: 0:1, rpm=1000, • salicyl alcohol, ▲salicyl aldehyde, ▼salicylic acid.	215
Figure 11-10: Selective oxidation of salicyl alcohol, reaction conditions T = 50 °C, p _{total} = 1bar (air), catalyst 1.5Au/C, m _{cat} = 0.2g, C _{salicyl alcohol} = 0.04 M, NaOH: salicyl alcohol= 0.5:1, rpm= 1000, • salicyl alcohol, ▲salicyl aldehyde, ▼salicylic acid.	215
Figure 11-11: Selective oxidation of salicyl alcohol reaction conditions T = 50 °C, p _{total} = 1bar (air), catalyst 1.5Au/C, m _{cat} = 0.2g, C _{salicyl alcohol} = 0.04 M, NaOH: salicyl alcohol= 1:1, rpm= 1000, • salicyl alcohol, ▲salicyl aldehyde, ▼salicylic acid.	215
Figure 11-12: Selective oxidation of salicyl alcohol, reaction conditions T = 50 °C, p _{total} = 1bar (air), catalyst 1.5Au/C, m _{cat} = 0.2g, C _{salicyl alcohol} = 0.04 M, NaOH: salicyl alcohol= 3:1, rpm= 1000, • salicyl alcohol, ▲salicyl aldehyde, ▼salicylic acid.	215
Figure 11-13: Concentration/ time profile for the selective oxidation of salicyl alcohol. Reaction conditions: catalyst: 1.5Au/C, T=50°C, p=1bar, C _{salicyl alcohol} = 0.04 M, nNa ₂ CO ₃ = 1M, rpm= 1000,	216
Figure 11-14: Origin fit plot for determination of initial rate of reaction at t=0 ■ experimental data, — fit function, experimental data for reaction conditions: catalyst: 1.5Au/C, T=50°C, p=1bar, C _{salicyl alcohol} =0.04 M, NaOH: salicyl alcohol 2:1, rpm=1000, •salicyl alcohol.	216
Figure 11-15: Origin fitted plot for consecutive reaction of first order for concentration/time profile of salicyl aldehyde, ■ experimental data, — fit function, experimental data for, reaction conditions: catalyst: 1Au/C, T=50°C, p=1bar, C _{salicyl alcohol} =0.04 M, NaOH: salicyl alcohol 2:1, rpm=1000,•salicyl aldehyde.	217

Figure 11-16: Origin fitted plot for consecutive reaction of first order for concentration/time profile of salicylic acid, ■ experimental data, — fit function, experimental data for, reaction conditions: catalyst: 1Au/C, T=50°C, p=1bar, C _{salicyl alcohol} =0.04 M, NaOH: salicyl alcohol 2:1, rpm=1000, •salicylic acid.	217
Figure 11-17: Origin fitted plot for consecutive reaction of first order for concentration/time profile of salicylic acid, ■ experimental data, — fit function, experimental data for, reaction conditions: catalyst: 3Au/C, T=50°C, p=1bar, C _{salicyl alcohol} =0.04 M, NaOH: salicyl alcohol 2:1, rpm=1000, •salicylic acid.	218
Figure 11-18: Origin fitted plot for consecutive reaction of first order for concentration/time profile of salicyl aldehyde ■ experimental data, — fit function, experimental data for, reaction conditions: catalyst: 1Au/C, T=50°C, p=1bar, C _{salicyl alcohol} =0.04 M, NaOH: salicyl alcohol 2:1, rpm=1000, •salicyl aldehyde ...	218
Figure 11-19: Concentration/ time profile for the selective oxidation of salicyl alcohol + product addition Reaction conditions: catalyst 1Au/C, T=50°C, p=1bar, C _{salicyl alcohol} =0.04 M, NaOH: salicyl alcohol 2:1, rpm=1000, • salicyl alcohol, ▲salicyl aldehyde, ▼salicylic acid.	219
Figure 11-20: Origin fitted plot for consecutive reaction of first order for concentration/time profile of salicyl aldehyde, ■ experimental data, — fit function, experimental data for, reaction conditions: catalyst 1.5Au/C, T=50°C, p=1bar, C _{salicyl alcohol} =0.04 M, NaOH: salicyl alcohol 2:1, rpm=1000, •salicyl aldehyde.....	219
Figure 11-21: Concentration/ time profile for the selective oxidation of salicyl alcohol+product addition, reaction conditions: catalyst: 1.5Au/C, T=50°C, p=1bar, C _{salicyl alcohol} =0.04 M, NaOH: salicyl alcohol 2:1, rpm=1000, • salicyl alcohol, ▲salicyl aldehyde, ▼salicylic acid.	220
Figure 11-22: Origin fitted plot for consecutive reaction of first order for concentration/time profile of salicyl aldehyde, ■ experimental data, — fit function, experimental data for reaction conditions: catalyst 1.5Au/C, T=50°C, p=1bar C _{salicyl alcohol} =0.04 M, NaOH: salicyl alcohol 2:1, rpm=1000, •salicylic acid.....	220
Figure 11-23: HEL Calorimeter reaction plot, injection of reactant after 30 minutes.	222
Figure 11-24: Concentration/ time profile for the selective oxidation of salicyl alcohol. Reaction conditions: catalyst 1.5Au/C, T=50°C, p=1bar, C _{salicyl alcohol} =0.04 M, NaOH: salicyl alcohol 2:1, rpm=1000, • salicyl alcohol, ▲salicyl aldehyde.....	224
Figure 11-25: Concentration/ time profile for the selective oxidation of salicyl alcohol. Reaction conditions: catalyst 0.75Au/C, T=50°C, p=1bar, C _{salicyl alcohol} =0.04 M, NaOH: salicyl alcohol 2:1, rpm=1000 • salicyl alcohol, ▲salicyl aldehyde, ▼salicylic acid.....	224
Figure 11-26: Concentration/ time profile for the selective oxidation of salicyl alcohol. Reaction conditions: catalyst 1Au/C, T=50°C, p=1bar, C _{salicyl alcohol} =0.04 M, NaOH: salicyl alcohol 2:1, rpm=1000, • salicyl alcohol, ▲salicyl aldehyde, ▼salicylic acid.....	225
Figure 11-27: Origin fitted plot for consecutive reaction of first order for concentration/time profile of salicyl aldehyde, ■ experimental data, — fit function, experimental data for, reaction conditions: catalyst 1Au/C, T=50°C, p=1bar, C _{salicyl alcohol} =0.04 M, NaOH: salicyl alcohol 2:1, rpm=1000, •salicyl aldehyde. ..	225
Figure 11-28: Concentration/ time profile for the selective oxidation of salicyl alcohol. Reaction conditions: catalyst 3Au/C, T=50°C, p=1bar, C _{salicyl alcohol} =0.04 M, NaOH: salicyl alcohol 2:1, rpm=1000, • salicyl alcohol, ▲salicyl aldehyde, ▼salicylic acid.....	226
Figure 11-29: Origin fitted plot for consecutive reaction of first order for concentration/time profile of salicyl aldehyde, ■ experimental data, — fit function, experimental data for, reaction conditions: catalyst 3Au/C, T=50°C, p=1bar, C _{salicyl alcohol} =0.04 M, NaOH: salicyl alcohol 2:1, rpm=1000, •salicyl aldehyde. ..	226
Figure 11-30: TEM histogram of 1.5Au/C treated at 150°C.	227
Figure 11-31: TEM histogram of 3Au/C catalyst treated at 150°C.	227

Figure 11-32: Concentration/ time profile for the selective oxidation of salicyl alcohol. Reaction conditions: catalyst 1Au/CeO ₂ , T=50°C, p=1bar, C _{salicyl alcohol} =0.04 M, NaOH: salicyl alcohol 2:1, rpm=1000, • salicyl alcohol, ▲salicyl aldehyde, ▼salicylic acid.....	228
Figure 11-33: Concentration/ time profile for the selective oxidation of salicyl alcohol. Reaction conditions: catalyst 1Au/TiO ₂ , T=50°C, p=1bar, C _{salicyl alcohol} =0.04 M, NaOH: salicyl alcohol 2:1, rpm=1000, • salicyl alcohol, ▲salicyl aldehyde.....	228
Figure 11-34: Concentration/ time profile for recycle test after second run for the selective oxidation of salicyl alcohol. Reaction conditions: catalyst 1.5Au/C, T=50°C, p=1bar, C _{salicyl alcohol} =0.04 M, NaOH: salicyl alcohol 2:1, rpm=1000, • salicyl alcohol, ▲salicyl aldehyde, ▼salicylic acid.....	229
Figure 11-35: Concentration/ time profile for the selective oxidation of salicyl alcohol. Reaction conditions: catalyst: 1.5Au/MgO, T=50°C, p=1bar, C _{salicyl alcohol} =0.04 M, NaOH: salicyl alcohol 0:1, rpm=1000, • salicyl alcohol, ▲salicyl aldehyde, ▼salicylic acid.....	229
Figure 11-36: Concentration/ time profile for the selective oxidation of salicyl alcohol. Reaction conditions: catalyst: 1.5Au/CaO, T=50°C, p=1bar, C _{salicyl alcohol} =0.04 M, NaOH: salicyl alcohol 0:1, rpm=1000, • salicyl alcohol, ▲salicyl aldehyde, ▼salicylic acid.....	230
Figure 11-37: Concentration/ time profile for the selective oxidation of salicyl alcohol. Reaction conditions: catalyst: 1.5Au/0.16MgO-CeO ₂ , T=50°C, p=1bar, C _{salicyl alcohol} =0.04 M, NaOH: salicyl alcohol 0:1, rpm=1000, • salicyl alcohol, ▲salicyl aldehyde, ▼salicylic acid.....	230
Figure 11-38: Concentration/ time profile for the selective oxidation of salicyl alcohol. Reaction conditions: catalyst: 1.5Au/0.16MgO-Al ₂ O ₃ , T=50°C, p=1bar, C _{salicyl alcohol} =0.04 M, NaOH: salicyl alcohol 0:1, rpm=1000, • salicyl alcohol, ▲salicyl aldehyde.....	231
Figure 11-39: Concentration/ time profile for the selective oxidation of salicyl alcohol. Reaction conditions: catalyst: 1.5Au/0.28CaO-CeO ₂ , T=50°C, p=1bar, C _{salicyl alcohol} =0.04 M, NaOH: salicyl alcohol 0:1, rpm=1000, • salicyl alcohol, ▲salicyl aldehyde.....	231
Figure 11-40: Concentration/ time profile for the selective oxidation of salicyl alcohol. Reaction conditions: catalyst: 1.5Au/0.28CaO-TiO ₂ , T=50°C, p=1bar, C _{salicyl alcohol} =0.04 M, NaOH: salicyl alcohol 0:1, rpm=1000, • salicyl alcohol, ▲salicyl aldehyde.....	232
Figure 11-41: Concentration/ time profile for the selective oxidation of salicyl alcohol. Reaction conditions: catalyst 1.5Au/0.28CaO-Al ₂ O ₃ , T=50°C, p=1bar, C _{salicyl alcohol} =0.04 M, NaOH: salicyl alcohol 0:1, • salicyl alcohol, ▲salicyl aldehyde.....	232
Figure 11-42: TEM histogram of 1.5Au/0.28CaO-HT.....	233
Figure 11-43: TEM histogram of 1.5Au/0.28CaO-Al ₂ O ₃	233
Figure 11-44: TEM histogram of 1.5Au/0.28CaO-CeO ₂	234
Figure 11-45: TEM histogram of 1.5Au/0.16MgO-HT.....	234
Figure 11-46: TEM histogram of 1.5Au/0.16MgO-TiO ₂	235
Figure 11-47: TEM histogram of 0.5Au/0.16MgO-HT.....	235
Figure 11-48: TEM histogram of 0.1Au/0.16MgO-HT.....	236
Figure 11-49 EDX of 1.5Au/0.16MgO-HT_400 area 1) without gold (upper) and area2) with gold.	237
Figure 11-50: Concentration/ time profile for the selective oxidation of salicyl alcohol. Reaction conditions: catalyst 1.5Au/0.16CaO-HT, T=50°C, p=1bar, C _{salicyl alcohol} =0.04 M, NaOH: salicyl alcohol 0:1, rpm=1000, • salicyl alcohol, ▲salicyl aldehyde.....	237

Figure 11-51: Concentration/ time profile for the selective oxidation of salicyl alcohol. Reaction conditions: catalyst 0.5Au/0.16MgO-HT, T=50°C, p=1bar, C _{salicyl alcohol} =0.04 M, NaOH: salicyl alcohol 0:1, rpm=1000, • salicyl alcohol, ▲salicyl aldehyde.	238
Figure 11-52: Concentration/ time profile for the selective oxidation of salicyl alcohol. Reaction conditions: catalyst: 1.5Au/0.08MgO-HT, T=50°C, p=1bar, C _{salicyl alcohol} =0.04 M, NaOH: salicyl alcohol 0:1, rpm=1000, • salicyl alcohol, ▲salicylic aldehyde.	238
Figure 11-53: Concentration/ time profile for the selective oxidation of salicyl alcohol. Reaction conditions: catalyst 1.5Au/0.04MgO-HT, T=50°C, p=1bar, C _{salicyl alcohol} =0.04 M, NaOH: salicyl alcohol 0:1, rpm=1000, • salicyl alcohol, ▲salicyl aldehyde.	239
Figure 11-54: XRD diffraction pattern for AuPd (1:1) (ID 01-072-5376).	239
Figure 11-55: XRD diffraction pattern of palladium (ID 00-005-0681).	240
Figure 11-56: Concentration/ time profile for the selective oxidation of salicyl alcohol. Reaction conditions: catalyst: 0.75Au0.75Pd/C, T=50°C, p=1bar, C _{salicyl alcohol} =0.04 M, NaOH: salicyl alcohol 2:1, rpm=1000, • salicyl alcohol, ▲salicyl aldehyde, ▼salicylic acid.	240
Figure 11-57: Concentration/ time profile for the selective oxidation of salicyl alcohol. Reaction conditions: catalyst: 1.5Au1.5Pd/C, T=50°C, p=1bar, C _{salicyl alcohol} =0.04 M, NaOH: salicyl alcohol 2:1, rpm=1000, • salicyl alcohol, ▲salicyl aldehyde.	241
Figure 11-58: Concentration/ time profile for the selective oxidation of salicyl alcohol. Reaction conditions: catalyst 1.5Au0.75Pd/C, T=50°C, p=1bar, C _{salicyl alcohol} =0.04 M, NaOH: salicyl alcohol 2:1, rpm=1000, • salicyl alcohol, ▲salicyl aldehyde, ▼salicylic acid.	241
Figure 11-59: Concentration/ time profile for the selective oxidation of salicyl alcohol. Reaction conditions: catalyst 0.75Au1.5Pd/C, T=50°C, p=1bar, C _{salicyl alcohol} =0.04 M, NaOH: salicyl alcohol 2:1, rpm=1000, • salicyl alcohol, ▲salicyl aldehyde.	242
Figure 11-60: Concentration/ time profile for the selective oxidation of salicyl alcohol. Reaction conditions: catalyst 1.5Pd/C, T=50°C, p=1bar, C _{salicyl alcohol} =0.04 M, NaOH: salicyl alcohol 2:1, rpm=1000, • salicyl alcohol, ▲salicyl aldehyde.	242
Figure 11-61: Concentration/ time profile for the selective oxidation of salicyl alcohol. Reaction conditions: catalyst 1.5Au0.15Pd/CeO ₂ , T=50°C, p=1bar, C _{salicyl alcohol} =0.04 M, NaOH: salicyl alcohol 2:1, rpm=1000, • salicyl alcohol, ▲salicyl aldehyde, ▼salicylic acid.	243
Figure 11-62: Concentration/ time profile for the selective oxidation of salicyl alcohol. Reaction conditions: catalyst 1.5Au0.15Pd/TiO ₂ , T=50°C, p=1bar, C _{salicyl alcohol} =0.04 M, NaOH: salicyl alcohol 2:1, rpm=1000, • salicyl alcohol, ▲salicyl aldehyde, ▼salicylic acid.	243
Figure 11-63: Concentration/ time profile for the selective oxidation of 1,2-propanediol. Reaction conditions: catalyst 1.5Au1.5Pd/CeO ₂ , T=50°C, p=1bar, 1,2 propanediol/Au=1000, NaOH: 1,2- propanediol 1:1, rpm=1000, • 1,2- propanediol, ▲lactic acid.	244
Figure 11-64: Concentration/ time profile for the selective oxidation of 1,2-propanediol. Reaction conditions: catalyst 1.5Au1.5Pd/CeO ₂ , T=50°C, p=1bar, 1,2-propanediol/Au=1000, NaOH: 1,2- propanediol 1:1, rpm=1000, • 1,2- propanediol, ▲lactic acid, ▼acetate.	244
Figure 11-65: : Concentration/ time profile for the selective oxidation of 1,2-propanediol. Reaction conditions: catalyst 1.5Au/CeO ₂ , T=50°C, p=1bar, 1,2-propanediol/Au=1000, NaOH: 1,2- propanediol 1:1, rpm=1000, • 1,2- propanediol, ▲lactic acid.	245

Figure 11-66: Concentration/ time profile for the selective oxidation of 1,2-propanediol. Reaction conditions: catalyst 1.5Au/TiO ₂ , T=50°C, p=1bar, 1,2-propanediol/Au=1000, NaOH: 1,2- propanediol 1:1, rpm=1000 • 1,2- propanediol, ▲lactic acid.	245
Figure 11-67: Reactor Setup (Parr autoclave) for selective oxidation of glycerol.	246
Figure 11-68: Concentration/ time profile for the selective oxidation of glycerol. Reaction conditions: catalyst 1.5Au1.5Pd/C, T=50°C, p=1bar, c _{glycerol} = 0.2M, NaOH:glycerol= 2:1, rpm= 1000, • 1,2 glycerol, ▲ glyceric acid, ▼glycolic acid.....	246
Figure 11-69: Concentration/ time profile for the selective oxidation of glycerol. Reaction conditions: catalyst 1.5Au1.5Pd/CeO ₂ , T=50°C, p=1bar, c _{glycerol} = 0.2M, NaOH:glycerol= 2:1, rpm= 1000, • 1,2 glycerol, ▲glyceric acid, ▼glycolic acid.....	247
Figure 11-70: Concentration/ time profile for the selective oxidation of glycerol. Reaction conditions: catalyst 1.5Au/CeO ₂ , T=50°C, p=1bar, c _{glycerol} = 0.2M, NaOH:glycerol= 2:1, rpm= 1000, • 1,2 glycerol, ▲glyceric acid, ▼glycolic acid.....	247
Figure 11-71: Arrhenius plot for selective oxidation of salicyl alcohol in trickle flow reactor.	248

LIST OF TABLES

Table 2-1: Selective oxidation of 1-octanol [38].	31
Table 2-2: Selective oxidation of 2-octanol [38], [24].	31
Table 2-3: Selective oxidation of cinnamyl alcohol to cinnamaldehyde [38] [24] [42].	32
Table 2-4: Selective oxidation of ethylene glycol on Pt, Pd and Au on carbon catalysts [7] [22, 31].	33
Table 2-5: Selective oxidation of glycerol to glyceric acid on Pt and Au on carbon catalysts [4].	34
Table 2-6: catalyst recycling tests for the selective oxidation of ethylene glycol to glycolic acid [7] [47].	35
Table 2-7: Catalytic test of gold catalysts prepared via metallic sols for selective oxidation of ethylene glycol [31].	43
Table 2-8: Chemical analysis for $(\text{Mg})_{0.665}(\text{Al})_{0.335}(\text{OH})_{1.95}(\text{CO}_3)_{0.149}(\text{H}_2\text{O})_{0.543}$ for calcination temperature range of 300-500°C for 1h in air [106].	46
Table 2-9: Chemical composition, BET surface areas and XRD characterisation of HT [109].	47
Table 2-10: Oxidation of benzyl alcohol a) [119].	55
Table 3-1: Retention times and calibration factors for selective oxidation of salicyl alcohol HPLC1.	64
Table 3-2: Retention times and calibration factors for selective oxidation of salicyl alcohol HPLC2.	64
Table 3-3: Retention times and calibration factors for selective oxidation of 1,2- propanediol on HPLC1.	65
Table 3-4: Retention times and calibration factors for selective oxidation of glycerol on HPLC1.	65
Table 3-5: Precursors used for catalyst preparation via impregnation.	68
Table 3-6: Precursors used for catalyst preparation via sol-immobilisation.	68
Table 3-7: Catalyst series of Au on carbon.	70
Table 3-8: Oxide supports used for gold based catalyst preparation.	70
Table 3-9: List of prepared AuPd on carbon catalysts.	71
Table 3-10: Precursors for MgO promoted catalysts.	71
Table 3-11: MgO promoted HT catalysts.	72
Table 3-12: Operating conditions for batch studies of selective oxidation of salicyl alcohol.	74
Table 3-13: Operating conditions for selective oxidation of 1,2- propanediol.	75
Table 3-14: Operating conditions for runs in Trickle Flow Reactor.	81
Table 4-1: Experimentally determined Activation Energy EA with standard error.	91
Table 4-2: Results for origin fit process for 1.5Au/C catalyst for consecutive reaction of first order function with standard error (SE).	102
Table 4-3: Results for origin fit process for Au/C catalysts with different loading for consecutive reaction of first order function with standard error (SE).	104
Table 4-4: Rate constant k for selective oxidation of salicyl aldehyde.	106
Table 4-5: Influence of product addition on rate constants k_1 and k_2 with standard error (SE).	111
Table 4-6: Properties of activated carbon used for catalyst synthesis.	115
Table 4-7: Comparison of particle diameter for different methods of synthesis for 1.5Au/C catalyst.	116
Table 4-8: Comparison of average particle diameter for series of Au/C catalysts.	119
Table 4-9: TEM results for Au/C catalysts treated at 150°C.	124
Table 4-10: Physical properties of oxide supports.	125
Table 4-11 Impact of preparation method on catalyst performance for the selective oxidation of salicyl alcohol.	128
Table 4-12: Impact of gold loading and treatment temperature on catalytic performance for the selective oxidation of salicyl alcohol.	129

Table 4-13: Influence of nature of oxide support on catalytic activity.	132
Table 5-1: Properties of MgO and CaO as support.	139
Table 5-2: Catalysts prepared on alkaline-earth metal oxide supports.	140
Table 5-3: Average particle diameter for CaO and MgO supported catalysts.	141
Table 5-4: Gold catalysts on alkaline oxide for selective oxidation of salicyl alcohol.	142
Table 5-5: BET surface area of oxide supports used for impregnation.	143
Table 5-6: Catalyst series prepared for CaO and MgO impregnated oxides.	143
Table 5-7: BET values for MgO and CaO impregnated oxide supports.	144
Table 5-8: Average particle diameter for MgO and CaO impregnated catalysts.	146
Table 5-9: Impregnated oxides for the selective oxidation of salicyl alcohol under base-free conditions.	148
Table 5-10: Series of unpromoted and MgO promoted Au/HT catalysts.	150
Table 5-11: Average Au particle diameter for promoted and unpromoted HT.	152
Table 5-12: BET surface areas for MgO promoted HT catalysts.	152
Table 5-13: CO ₂ TGA measurements for MgO promoted HT catalysts.	158
Table 5-14: Effect of MgO loading on initial rate of reaction for the selective oxidation of salicyl alcohol.	160
Table 5-15: Influence of gold loading on MgO promoted HT.	161
Table 5-16: Comparison of BET surface area measurements for 1.5Au/0.16MgO-HT with Mg(OAc) ₂ calcined at 400°C.	162
Table 5-17: Comparison of average gold particle size for catalysts prepared with different Mg-precursors.	165
Table 5-18: Comparison of surface area for 0.16MgO-HT with different precursors.	166
Table 5-19: Comparison of catalytic performance of 1.5Au/0.16MgO-HT catalyst calcined at 400°C and 650°C.	166
Table 5-20: Identified gold particle shapes and orientations of 1.5Au/0.16MgO-HT ₄₀₀	170
Table 6-1: Catalyst series for bimetallic AuPd on carbon catalysts.	177
Table 6-2: Average particle size of AuPd catalyst series compared to monometallic Au and catalysts.	179
Table 6-3: Catalytic activity for series of AuPd bimetallic catalysts for selective oxidation of salicyl alcohol.	184
Table 7-1: Catalytic performance results for Au and AuPd/ C catalysts for the selective oxidation of 1,2-propanediol.	189
Table 7-2: Catalytic performance for Au and AuPd catalysts for selective oxidation of 1,2-propanediol.	190
Table 7-3: Results for Au and AuPd catalysts for the selective oxidation of glycerol.	193
Table 8-1: Effect of varying catalyst particle size on the conversion of salicyl alcohol and selectivity towards salicyl aldehyde.	198
Table 11-1: HPLC analysis parameters.	211
Table 11-2: Calibration factors for HPLC1.	212
Table 11-3: Calibration factors for HPLC 2.	213
Table 11-4: Reaction data as parameters for Langmuir-Hinshelwood rate equation.	221
Table 11-5: Results for parameters $b_1 = k \cdot p_{O_2}$ and $b_2 = K_{acid}$	221
Table 11-6: Thermochemical data for reactants and products for selective oxidation of salicyl alcohol.	222
Table 11-7: Literature data on achieved TOF numbers for selective oxidation of salicyl alcohol [137].	223
Table 11-8: ICP analysis of precursor solution after catalyst preparation 1.5Au/C.	223

Nomenclature

Symbol	Definition	Unit
A	Pre-exponential factor	s^{-1}
BET	Brunauer Emmett Teller Analysis	
c	Concentration	$mol \cdot L^{-1}$
d	Average gold particle diameter	nm
d_t	Minimum throat diameter	m
E_A	Apparent activation energy	$kJ \cdot mol^{-1}$
G	Superficial gas mass flow rate	$kg \cdot s^{-1}$
G'	Gas volumetric flow rate	$mL \cdot min^{-1}$
$\Delta_f H^\circ$	Standard enthalpy of formation	$kJ \cdot mol^{-1}$
$\Delta_R H^\circ$	Reaction enthalpy	$kJ \cdot mol^{-1}$
HPLC	High Performance Liquid Chromatography	
ICP	Inductively Coupled Plasma	
k_{1/2}	Rate constant	$L^*((mol \cdot min)^{-1})$
k	Apparent rate constant	$min^{-1} / min^{-1} g^{-1} / min^{-1} g^{-1} bar \cdot O_2^{-1}$
L	Superficial liquid mass flow rate	$kg \cdot s^{-1}$
L'	Liquid volumetric flow rate	$mL \cdot min^{-1}$
LHSV	Liquid hourly space velocity	h^{-1}
M	Molar mass	$G \cdot mol^{-1}$
m_{cat}	Mass of catalyst	g
n	mol	mol
N_C	Number of circles irrespective of size per unit cross sectional area	N/A
P	Total pressure	bar
pO₂	Partial pressure (oxygen)	bar
R²	Regression coefficient	
r_A	Reaction rate of salicylic alcohol	$mol \cdot m^{-3} \cdot s^{-1}$

rpm	Rotation per Minute	-
SD	Standard Deviation	
S_g	Grain boundary length per unit area	m ⁻¹
S_{t360}	Selectivity at specific time of reaction	[%]
S_x	Selectivity at specific conversion	
SD	Standard Deviation	
σ		
t	Reaction time	min
T	Temperature	°C
TEM	Transmission Electron Microscopy	
TGA	Thermogravimetric Analysis	
θ	Theta, Bragg diffraction angle	
TOF	Turn over frequency	h ⁻¹
u_G	Gas interstitial velocity	m s ⁻¹
v_L	Liquid superficial velocity	m s ⁻¹
V	Volume	L
ρ	Density	kg m ⁻³
σ	Interfacial tension	N m ⁻¹
μ	Viscosity	Pa s
X	Conversion	[%]
XRD	X-Ray Diffraction	

1 INTRODUCTION

1.1 The need for sustainable chemistry

The increasing global demand for energy- in particular in the emerging economies- the finite resources of easily available fossil fuels, challenging exploitation of remaining carbon resources, as well as volatility in the oil price market, have pushed the development of alternative, and sustainable strategies for the supply of energy. The urgency of mitigating the effects of climate change and cutting CO₂ emissions has accelerated research and investment into renewable energy sources such as wind, solar, geothermal, tidal ,wave- and bio-energy [1]. However, as these renewable energy technologies are still very cost intensive and are dependent on subsidies, around 80% of the world's energy consumption and production of chemicals is still derived from fossil resources such as oil, gas and coal [2]. There is an urgent need for the development of environmentally friendly and sustainable processes in chemical industry. This necessitates a paradigm shift from traditional concepts surrounding process efficiency focussing mainly on chemical yield, to processes that emphasize economic value through avoiding the use of toxic/ hazardous substances. Therefore, over the past years, much research has been focused on the development of sustainable cost effective processes, especially in the biomass-to-fine chemicals value chain [3,4]. Their unique properties such as high functionality, biodegradability and compatibility makes them high end valued chemicals. Currently, the global biomass production is estimated around 170 billion tonnes:

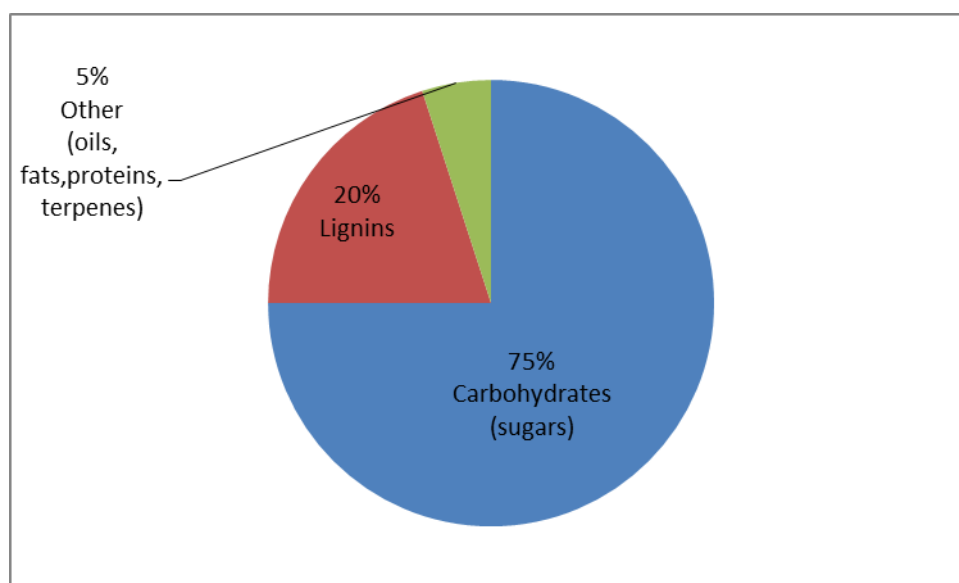


Figure 1-1: Biomass production worldwide [2].

The largest amount around 62% is used for food production, 33% for energy use and around 5 % is used for the production of detergents and chemicals.

Until now, most utilised processes of biomass conversion are based on the gasification for syngas production (CO:H_2), thermochemical liquefaction and /or pyrolysis for the production of bio-oils and acid hydrolysis. In a further process, these chemicals are transformed directly to energy via combustion, or via catalytic conversions to a range of fine chemicals or fuels (Figure 1-2). There is a large potential in the available renewable resources such as lignins, oils and cellulose out of which a large range of bulk chemicals such syngas, ethylene or propylene can be easily obtained. These can be turned into intermediate chemicals such as methanol, styrene or glycerol, which are catalytically converted into higher valued fine and speciality chemicals. Among the many routes for transforming raw materials into fine chemicals the main challenge remains of using renewable raw materials and at the same time also establishing environmentally friendly and efficient conversion pathways. Heterogeneous catalysis is an important transformation route for the chemical industry and has led to the establishment of more effective processes for the production of platform molecules in the chemical and petrochemical industries. These platform molecules can be further derivatised to fine chemicals or intermediates for the pharmaceutical, consumer goods or automobile industry. Heterogeneous catalysis using noble metals in particular is cutting edge technology enabling conversions with high carbon economy and via environmentally friendly pathways causing less waste. Although much research has been done on laboratory scale on the development of efficient catalyst systems, many challenges remain to be resolved, such as catalyst lifetime and stability in order to ensure sustainability for scale-up processes in industry. Therefore, continuous research as well as detailed analysis on the catalyst and reaction mechanism and kinetics and detailed understanding of the behaviour are required to resolve the complex issues.

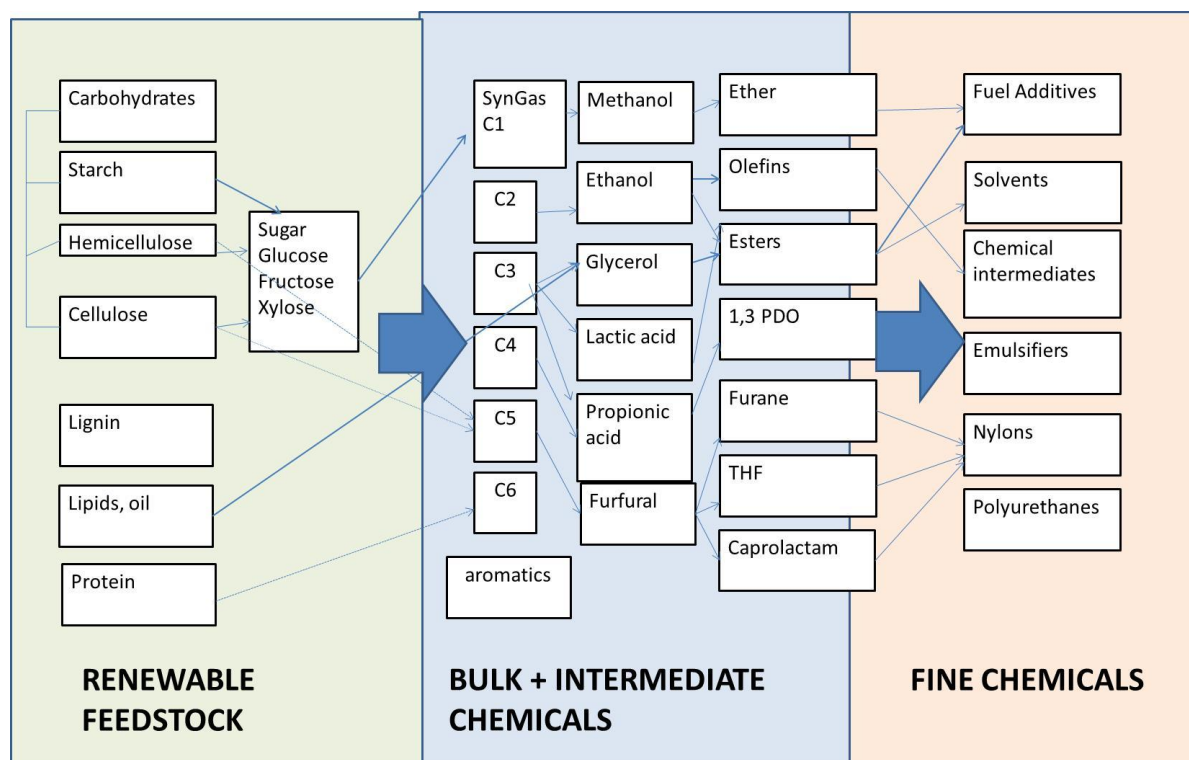


Figure 1-2: Model of a bio-based product flow-chart for biomass feedstock according to [[3]].

One key heterogeneous catalytic technology is selective oxidation. A large range of chemical processes are based on selective oxidation with the functionalization of hydrocarbons as a key application. One important application of the selective oxidation reaction is the selective conversion of alcohols in the liquid phase into their higher functionalised oxygenates, aldehydes and acids. This presents a key technology delivering platform chemicals for the production of pharmaceuticals, fibres or plastic.

Industrial processes still commonly involve the application of harmful and toxic oxidants such as permanganates or chromium salts in stoichiometric quantities, as well as solvents or extreme reaction conditions. These processes cause a risk and environmental impact and often result in a poorer carbon economy due to the formation of by-products and salts. Therefore, these routes extend the number of energy and cost intensive processes based on waste treatment or product separation from the solvent.

The challenge is the development of highly active and selective catalysts as well as sustainable processes, which enable the efficient transformation of a broad range of platform alcohol molecules onto their higher-valued derivatives and intermediates. Furthermore, the sustainability of the process is defined by the mild conditions applied including the use of water as solvent and alternative oxidants such as air, molecular oxygen or hydrogen peroxide [15] [6] [7].

This thesis aims to develop and study a sustainable process for the liquid phase selective oxidation of alcohols to their higher oxygenates. The study includes the establishment of the reaction system and reaction conditions in conjunction with the development and study of effective catalyst systems.

The main reaction hereby investigated is the liquid phase selective oxidation of salicyl alcohol to salicyl aldehyde and salicyl acid under mild conditions. The reactants and products are soluble in water allowing studying the reaction network, kinetics and mechanism in the aqueous phase using water as desirable solvent. The functionality of the molecule is based on a primary alcohol group, with a simple product network enabling an easier study of the selectivity towards the target product salicyl aldehyde. The catalyst system developed and applied is based on supported nanodispersed gold, as its high activity and superior performance over commonly employed noble metal catalysts has been previously demonstrated ^{[8] [9]}. Therefore, this thesis aims at providing a more detailed insight into the reaction mechanism, conditions and the catalyst properties and further integrates all these aspects towards the development of sustainable selective oxidation catalysts. Most of the gold based catalytic reactions require the presence of a base additive in the reaction. This thesis also focusses on the development of a new catalyst design which enables to carry out the selective oxidation under base free conditions.

Furthermore, with an estimated market capacity of 4000-6000 t/y salicyl aldehyde and its derivatives are significant key ingredients and can be used in agricultural chemicals, petroleum chemicals, polymers, fibres, electroplating and perfumes ^[10, 11]. So far, the industrial process is the Reimer-Tiemann Process for the production of salicyl aldehyde from phenol ^[12], requiring the employment of stoichiometric amounts of chloroform and a strong base. Apart from a low product yield, the process causes large amounts of hazardous waste. Therefore, it is of great importance to develop and establish an environmentally friendly route towards a sustainable industrial scale-up for the production of salicyl aldehyde.

1.2 Thesis outline

This thesis is outlined according to the following chapters:

ABSTRACT

The Abstract presents the main objective of the thesis in context with the field of research.

1. INTRODUCTION

The Introduction explains the main context of the area of study providing the justification of the thesis in context with the research.

2. LITERATURE REVIEW

The Literature Review presents background information on key areas of the field of research relevant to the thesis, as well as providing reference data for comparison in the area of study of the thesis.

3. MATERIALS AND METHODS

The Materials and Methods section illustrates and explains the experimental equipment and methodology employed for carrying out the research based on the catalyst systems as well as the liquid phase oxidation experiments.

4.-7. The results and discussion chapters divide into 4 individual chapters:

4. AU/C FOR SELECTIVE OXIDATION OF SALICYL ALCOHOL

This chapter is based on the detailed investigation of the catalyst system Au/C, the reaction mechanism and kinetics of the selective oxidation of salicyl alcohol.

5. MOVING TOWARDS BASE-FREE CATALYSIS

This chapter explores the development of alternative catalyst systems towards carrying out the selective oxidation on Au based catalysts without base additives.

6. BIMETALLIC CATALYSIS FOR SELECTIVE OXIDATION OF SALICYL ALCOHOL

This chapter explores the catalyst performance by adding Pd as second active metal.

7. SELECTIVE OXIDATION OF DIOLS AND TRIOLS

This chapter investigates the application of the developed Au based catalyst systems onto multi-functional alcohols.

8. MOVING FROM BATCH TO CONTINUOUS PROCESSING

This chapter explores the application of the Au/C catalyst system for continuous processing on the selective oxidation of salicyl alcohol.

9. CONCLUSIONS AND OUTLOOK

The Conclusion chapter summarises the key results in context with the field of research, demonstrating the impact of this work and this thesis and providing a future outlook as continuation of this work.

10. REFERENCES**11. APPENDIX**

2 LITERATURE REVIEW

2.1 Catalytic conversion of bio-derived substrates

There are many routes for the transformation of highly functionalised platform chemicals such as alcohols and polyols into fine chemicals. Much research has been going on regarding the catalytic conversion of highly functionalised alcohols such as 1,2-propanediol or glycerol via dehydration or oxidation [13] [14] [15] into a range of chemicals. The figure below presents the scheme for the diverse catalytic conversion routes for glycerol. Since the emerging production of biodiesel as valuable fuel resulted in large quantities of glycerol as a by-product, it became attractive as a raw material [16] [17] [18] [19].

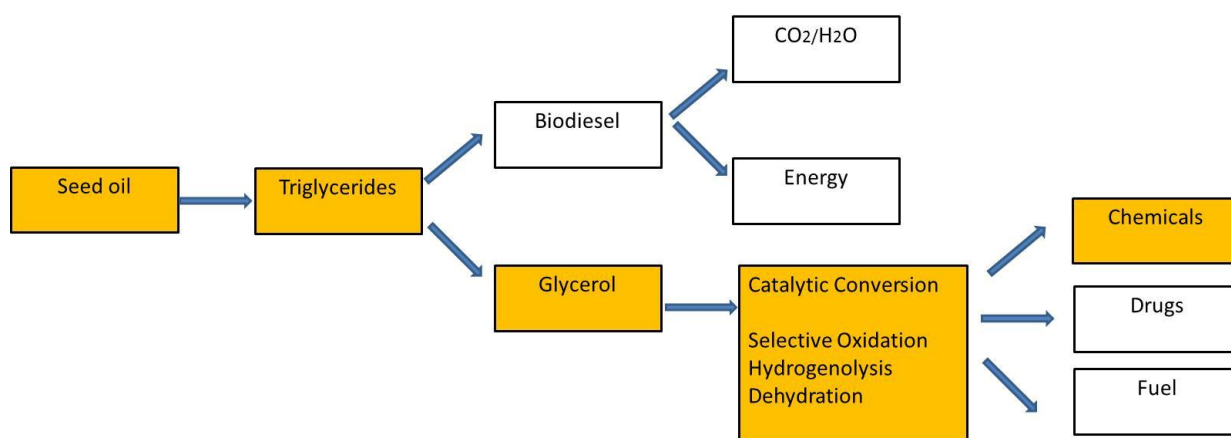


Figure 2-1: Catalytic conversion routes of bio-derived feedstock to chemicals [20].

One of the important catalytic conversion routes is selective oxidation, which enables the conversion of glycerol under mild conditions using air or molecular oxygen into its higher oxygenates such as glyceric acid or dihydroxyacetone based on the catalyst system and the reaction conditions [21] [22] [23] [18] [16]. The big challenge remains to develop an efficient and long lifetime catalyst system to direct the reaction pathway to a maximum yield of the desired products.

2.2 Key catalyst systems for selective oxidation of alcohols

Since the past decades, a diverse range of active metal catalyst systems for the selective oxidation of alcohols has been studied. The most active catalysts were found to be based on platinum group metals in particular on platinum, palladium and ruthenium [24] [25, 26] [27] [28]. It

was found that key parameters such as metal loading, particle size, nature of support and the presence of a second active metal or promoter played a crucial influence on the catalytic activity [18, 29] [30]. In addition, for multi functionalised substrates, some metals showed a higher reactivity towards certain functional groups and thus higher selectivity towards certain products. Some of these catalysts have achieved high yields towards the desired products and a few catalyst systems will be introduced in the following section. Apart from the activity and selectivity, the catalyst lifetime has remained to be a key challenge, which many catalyst systems did not reach due to deactivation. It was later found that nanoparticle gold exhibited superior properties comparing to the conventional platinum group metals. [31] [32, 33] [8] [34] [35].

2.2.1 Ruthenium, platinum and palladium catalysis

The selective oxidation of aliphatic alcohols to aldehydes with molecular oxygen was a very important, but at the same time challenging reaction [36]. Many of the catalyst systems exhibited at some point a loss in activity or selectivity during the reaction caused by poisoning or deactivation. Further, many of the reactions were carried out using organic solvents. For the selective oxidation of primary or secondary aliphatic alcohols to aldehydes with molecular oxygen, ruthenium and platinum based catalysts have shown a high catalytic performance [26] [21] [36] [5]. In particular when promoted with Bi, Pd or Ce, an enhanced effect was observed [17] [21]. The most common method for catalyst synthesis was deposition-precipitation or impregnation followed by reductive treatment yielding small metal particles. In general, Pt based catalysts showed high activity for many of the alcohol oxidations to the respective aldehyde [36] [27] [37], however there was a drop in selectivity, as Pt was active towards the dehydrogenation of the hydrated aldehyde thus leading to the production of carboxylic acid. On the contrary, Ru based catalysts showed higher selectivity towards the aldehyde compared to platinum. The catalytic performance also differed with the type of alcohol functional group, whether primary or secondary. The following examples illustrate the results for the selective oxidation of 1-octanol and 2-octanol to the respective aldehydes. For the primary alcohol function, the platinum based catalyst achieved the highest performance reaching a conversion of 76% and reaching TOF numbers of 142 h^{-1} [38]. However, the catalyst shows poor selectivity based on the dehydrogenation of the aldehyde or also over-oxidation of the catalytic surface leading to other side reactions .

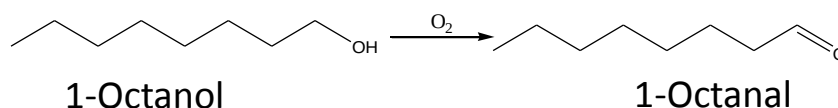


Figure 2-2: Selective oxidation of 1-octanol to 1-octanal.

Table 2-1: Selective oxidation of 1-octanol [138].

Catalyst	T [°C]	Solvent	X [%]	S _{1-octanal} [%]	TOF [h ⁻¹]
5%Pt-1%Bi/Al ₂ O ₃ ^{a)}	60	PhCH ₃	89	85 ^[29]	142
Ru _{0.35} MnFe _{1.5} Cu _{0.15} O _x ^{b)}	20	PhCH ₃	51	100 ^[39]	0.2

Reaction conditions: 15 mmol reactant in toluene, reactant:metal 80:1, 1200 rpm, p= 3 bar air, a) t=6h, b) t= 4h.

For the oxidation of secondary aliphatic alcohol to the respective ketones, the obtained selectivities were higher for many catalyst systems compared to the primary aliphatic alcohol, as no competitive reaction path or formation of by-products were detected.

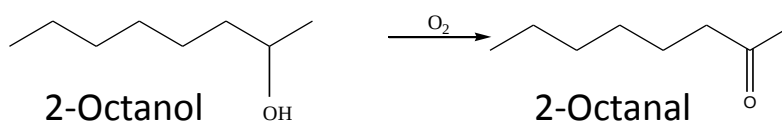


Figure 2-3: Selective oxidation of 2-octanol to 2-octanal.

Hereby, ruthenium based catalysts exhibited higher performances (see Table 2-2) compared to the Pt based catalyst, which showed far lower turnover rates. This could indicate that the oxidation of the secondary alcohol function was much slower, which could also be based on the solvent used and the reaction conditions.

Table 2-2: Selective oxidation of 2-octanol [138], [24]].

Catalyst	T [°C]	Solvent	X [%]	S _{2-octanal} [%]	TOF [h ⁻¹]
1.4% Ru/Al ₂ O ₃	60	None	95	>99	300
5% Pt-1% Bi/Al ₂ O ₃ ^{a)}	60	H ₂ O	78	100	78

Reaction conditions: 15 mmol reactant in toluene, reactant:metal 80:1, 60 C, 1200 rpm, a) pO₂= 1 bar, t= 3h.

For the selective oxidation of primary benzylic alcohols higher TOF numbers and selectivities were achieved with the same catalyst systems. This was based on the fact that the aldehydes were more resistant to further oxidation thus retaining high selectivity. In particular the catalyst based on palladium showed excellent conversions and selectivities. For the oxidation of benzyl alcohol to benzaldehyde, palladium based catalysts have shown a very high activity [40] [41]. Pd supported on aluminium oxide 0.5% Pd/Al₂O₃ was applied and 87% conversion was reached with a selectivity of 95% regarding the aldehyde [25].

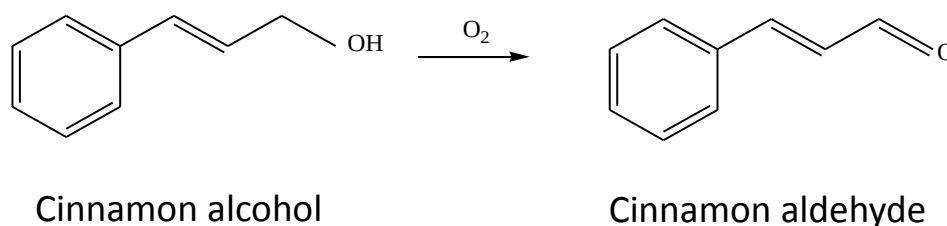


Figure 2-4: Selective oxidation of cinnamyl alcohol to cinnamaldehyde.

For the synthesis of α,β -unsaturated aldehydes such as the oxidation of geraniol to citral or cinnamyl alcohol to cinnamaldehyde, bimetallic catalysts based on Pt and Bi supported on alumina showed high catalytic performance. The Pt-Bi/Al₂O₃ catalyst showed a high performance using water as solvent (Table 2-3):

Table 2-3: Selective oxidation of cinnamyl alcohol to cinnamaldehyde [38] [24] [42].

Catalyst	T [°C]	Solvent	X [%]	S _{cinnamyl aldehyde} [%]	TOF [h ⁻¹]
5%Pt-0.8% Bi/Al ₂ O ₃ ^{a)}	40	H ₂ O	94	>98	144
1.4% Ru/Al ₂ O ₃ ^{b)}	93	PhCF ₃	98	98	27
RuO ₂ ·xH ₂ O ^{b)}	110	PhCH ₃	90	94	5

Reaction conditions: a) alcohol (26 mmol), p_{air} = 1 bar, rpm = 1000, t = 4,83h. b) alcohol (1mmol), PhCF₃ (1.5 mL), pO₂ = 1 bar, t = 2h.

2.2.2 Gold vs. platinum and palladium

The partial oxidation of diols and polyols to their higher oxygenates is a very important transformation route for chemical industry. Many of the products including hydroxyacids and lactones or hydroxyketones are valuable fine chemicals. However, the major challenge is the control of selectivity towards the desired product as the reaction network becomes more complex with multiple functional groups. Furthermore, depending on the catalyst system and active metal, the reactions require the addition of base and pH control as these conditions are crucial for the selectivity. It was found that certain catalyst systems led to different reaction pathways thus decreasing the selectivity toward the desired product. When trying to increase the selectivity the overall rate was affected and lower TOF numbers were achieved.

In the 90s, it was discovered that supported gold nanoparticles were extremely active towards the selective oxidation of alcohols [43] [33, 44-46]. It was demonstrated that gold catalysts delivered high TOF numbers and high selectivities towards the desired product. The following table illustrates the catalytic performance results for the selective oxidation of ethylene glycol using Pt, Pd and Au based catalysts supported on activated carbon [47]. Although Pt/C could transform ethylene glycol quantitatively to glycolic acid, the reaction required controlling certain reaction conditions such as keeping the actual oxygen concentration at the metal surface low at reflux temperature in air (Table 2-4) to avoid over-oxidation of the catalyst surface leading to undesired reaction pathways. It is striking that the gold catalysts achieved by far the highest turnover rates and highest selectivity. When using Pt or Pd on carbon at higher oxygen pressure, a high conversion was achieved but there was a loss in selectivity.

Table 2-4: Selective oxidation of ethylene glycol on Pt, Pd and Au on carbon catalysts [7] [22, 31].

Catalyst	T [°C]	pO ₂ [bar]	TOF [h ⁻¹]	X [%]	S _{Glycolic acid} [%]
5%Pt/C	50	2	475	67	71
5%Pd/C	50	2	500	73	77
1%Au/C	70	2	1000	93	98

Reaction conditions: alcohol (EG) = 0.5 M, EG: metal = 1000 mol/mol, EG/ NaOH = 1 mol/mol, pO₂ = 2 bar, t= 1h.

In general, for the selective oxidation of glycerol, the reaction network is more complex as it depends on whether the primary or secondary hydroxyl group is being activated. Gold based catalysts have shown higher activity and selectivity towards glyceric acid. However, the pH

needed to be maintained at >10 to ensure high activity and selectivity on the gold catalyst surface.

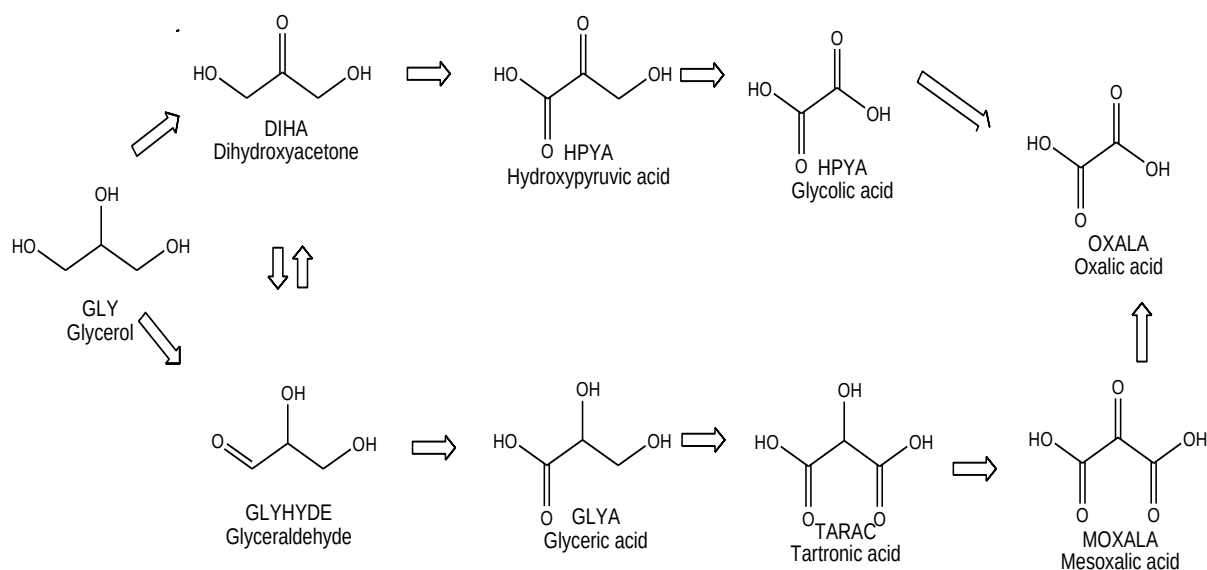


Figure 2-5: Reaction and product network for selective oxidation of glycerol [148].

For Pt and Pd based catalysts, the formation of dihydroxyacetone was preferred under certain reaction conditions [21]. With Pt based catalysts promoted with Bi, it has been shown that, at low pH, the selective oxidation of glycerol occurs through activation of the secondary hydroxyl group leading to the formation of dihydroxyacetone [21]. This molecule can partly transform into glyceraldehyde and via an intermolecular rearrangement to glyceric acid [21] [17] or lead to the formation of glycolic acid. However, the selectivity has been lower compared to gold resulting in a lower yield for glyceric acid.

Table 2-5: Selective oxidation of glycerol to glyceric acid on Pt and Au on carbon catalysts [14].

Catalyst	T [°C]	TOF [h ⁻¹]	X [%]	S _{Glyceric acid} [%]
1%Au/graphite ^{a)}	60	65	84	92
1%Au/C ^{b)}	60	100	56	100
5%Pt/C ^{b)}	60	105	47	74

Reaction conditions: alcohol (glycerol) = 0.6 M a) glycerol: metal = 214 mol/mol, glycerol/ NaOH = 1 / 2 mmol, pO₂ = 6 bar, b) glycerol/ metal = 538 mol/mol, glycerol/ NaOH = 1 / 1 mmol, pO₂ = 3 bar, t = 3h.

The results have also shown that the type of carbon support influences the catalyst activity. In this case activated carbon supported catalysts have demonstrated higher activity rates compared to graphite. Apart from demonstrating high selectivity values, gold based catalysts

have proven to be extraordinary stable catalyst systems and less prone to catalyst poisoning or deactivation.

2.2.3 Catalyst deactivation

Although Pt Pd and Ru based catalysts have proven to be highly active towards the selective oxidation of alcohols and can be used in a broad range for aliphatic and aromatic systems, the major disadvantage is catalyst deactivation [49] [50] [51] [52]. It was discovered that there was a frequent formation of strongly adsorbed by-products during alcohol oxidation on Pt-group metals. These side reactions were based on aldol condensation and oligomerisation of the carbonyl compound leading to a decomposition of the alcohol compound. Overall, this mechanism caused a sintering of metal particles, leaching, over-oxidation and poisoning of the active sites decreasing the overall catalytic performance [53]. Recycling test studies on the selective oxidation of ethylene glycol have found a large deactivation of the Pt and Pd based catalysts compared to Au. In order to mitigate this effect for Pt and Pd, the rate of oxygen supply needed to be lower than the alcohol dehydrogenation to avoid over-oxidation of the catalyst surface.

Table 2-6: catalyst recycling tests for the selective oxidation of ethylene glycol to glycolic acid [7^[47]].

Run	1% Au/C		5% Pt/C		5% Pd/C	
No.	TOF [h ⁻¹]	S [%]	TOF [h ⁻¹]	S [%]	TOF [h ⁻¹]	S [%]
1	430	93	475	79	500	82
2	390	91	450	68	355	70
3	375	92	425	55	325	53
4	380	90	445	48	250	26

Reaction conditions: glycolic acid = 8 mmol, glycolic acid/metal=1000; NaOH/glycolic acid=1;pO₂= 30 bar; T=70°C; t=2h.

The results demonstrated that although Pt/C and Pd/C had higher TOF numbers initially and high selectivity, the selectivity decreased by 50% for Pt and by 70% for the Pd based catalyst. Although the activity of the Pt catalyst remained high, the major loss in selectivity indicated the formation of by-products through side reactions or decomposition of alcohol. Recycling tests on

the Pd catalysts resulted in an overall loss in catalytic activity, causing a drop in TOF numbers by 50% due to possible sintering of particles and blocking of active sites. Furthermore, it has been shown that Pd leached into the reaction solution over time causing catalyst deactivation [5] [36] [54]. Gold, in contrast, retained high selectivity values and high activity, showing a superior performance over time compared to the other metals. This was based on the unique properties of gold nanoparticles and its noble metal character with a high electro chemical potential making it difficult to be oxidised. However, it is known that, as the potential for the first dehydrogenation step of the alcohol on gold is very high, the presence of base in the reaction medium is necessary [55]. As the reactions are carried out in alkaline medium, possible rearrangement mechanisms such as keto-enol tautomerism or the Canizzaro-reaction can therefore influence the selectivity towards the target product. In acidic medium, however, the alcohol will not get oxidised, and leaching of gold into the solution might occur.

2.3 Gold for selective oxidation

2.3.1 Introduction

For a long time gold, as a bulk metal, has been regarded as a poorly active catalyst due to its noble metal properties. High dissociation energies of H₂ and O₂ over bulk and smooth Au surfaces made it inactive for hydrogenation or oxidation. However, these catalysts were prepared by using impregnation and exhibited large particle sizes of >20 nm. In 1995, Haruta et al. demonstrated very high catalytic activity of very small and highly dispersed gold particles on oxide supports of smaller than 5 nm diameter [33, 44] [46] [56] [57]. Their studies on model reactions such as CO oxidation [58] [33] have demonstrated that its unique catalytic performance was crucially dependent on the size and shape of gold particles which were influenced by the catalyst preparation method and catalyst treatment as well as the choice of support material [59] [60-63] [7] [64]. It has been generally agreed that the catalytic activity of gold nanoparticles is in direct relationship to the morphological effects such as size and shape but also electronic effects, induced by the oxidation state of the gold or the charge transfer and interaction between the gold particle and the metal oxide support. It has been suggested that the increasing activity of gold correlated to a decreasing particle size, leading to a higher concentration of low coordinated gold atoms in small particles. It has also been found that gold particles exhibited a particular high activity on reducible oxides such as TiO₂ and CeO₂, indicating the role of the support on the catalytic activity [63] [65, 66] [67].

2.3.2 Structure sensitivity

3.1.1.1 Size control of gold particles

It was shown that most reactions over gold catalysts were dependent on the Au particle size influencing the catalytic activity and also selectivity [68] [8] [69]. Very small gold particles of 5 nm size and well dispersed on the catalyst surface exhibited very high activity [56] [70] [71]. It was found that catalyst particle morphology could be influenced mainly during catalyst synthesis and treatment conditions. The most common methods for the synthesis of Au/C catalysts are impregnation or deposition-precipitation. The precursors used are mainly hydrochloroauric acid HAuCl_4 or gold chloride AuCl_3 [72]:

(1) Impregnation: The support is directly saturated with the metal solution, then dried and activated.

(2) Deposition-precipitation: The gold solution is added to the support and is precipitated as $\text{Au}(\text{OH})_3$ species with NaOH . During the activation process, the gold is reduced to Au (0).

(3) Sol-immobilisation: The gold is reduced to Au (0) in the solution with stabilising and reducing organic compounds (THPC (Tetrakis(hydroxymethyl)phosphonium chloride) or PVA (polyvinylalcohol)/ NaBH_4) and then immobilised onto the support.

It has been shown that the use of reduced metal sol solutions is very efficient to generate small particle sizes especially for supports such as carbon, whereas the deposition-precipitation method leads to an aggregation of particles [73]. Prati et al. studied the influence of the support and the preparation method on the activity of gold catalysts [74]. Several methods for the catalyst preparation were used. For the Au/C catalysts the smallest particle size (3 nm) could be obtained via the sol-immobilisation method with PVA as stabilizing agent. Furthermore, it could be applied to generate monometallic as well as bimetallic metal sol solutions. Hereby, the ratio of the stabilizing agent to gold had a major influence on the effective particle size in the metal sol solution. With THPC as stabiliser, particle diameters of 5.7 nm were achieved. The biggest particles were obtained by the impregnation (10 nm) and incipient wetness impregnation (16.3 nm) method due to the formation of agglomerates. Studies varying the THPC concentration have shown that small particle sizes <5nm are generated using a THPC/au ratio of >1. Even after immobilisation onto the support and catalyst treatment to decompose the stabiliser, the particle size could be controlled [75] [62] [76] [33].

3.1.1.2 Shape and orientation of Au

Studies on Au particles have shown that the size and the shape are key factors influencing the unique catalytic properties^[77]. TEM studies on the shape of gold particles have shown a correlation between the crystallographic surfaces enclosing the particles and the shape. Further, investigations have shown that the typical facets of a face-centred cubic structured metal particle, such as (110), (111), (110) differed in surface atom densities and in the electronic structure and thus were likely to influence the catalyst activity ^[23]. Further the melting temperature of gold was influenced by the crystallite size ^[78]. Furthermore, the shape was likely to be influenced during the process of heat treatment causing a re-orientation of the gold particle towards the formation of the lowest energy. Studies have shown a drastic change in shape during heat treatment at 100°C. While initially, gold particles according to the preparation method were prepared to be spherical and the diameter and distribution remained constant, the particle shape changed. This phenomenon was based on energetic reasons as the spherical single-crystalline particle possibly resulted in a high surface energy with high-index crystal planes. Some of the frequently identified shapes are illustrated in Figure 2-6. The hexagonal (a), the square (b) and the pentagonal shaped (c) particle with the corresponding three dimensional structures of the cubo-octahedron, a cube, and an iso-octahedron are the most commonly observed regular shapes of the Au particle. The facets exposed are (111) and (100) corresponding to the lowest energy surfaces of the Au particle. Furthermore, elongated shaped particles (d) and particles with multiply twinned defects have been observed (f).

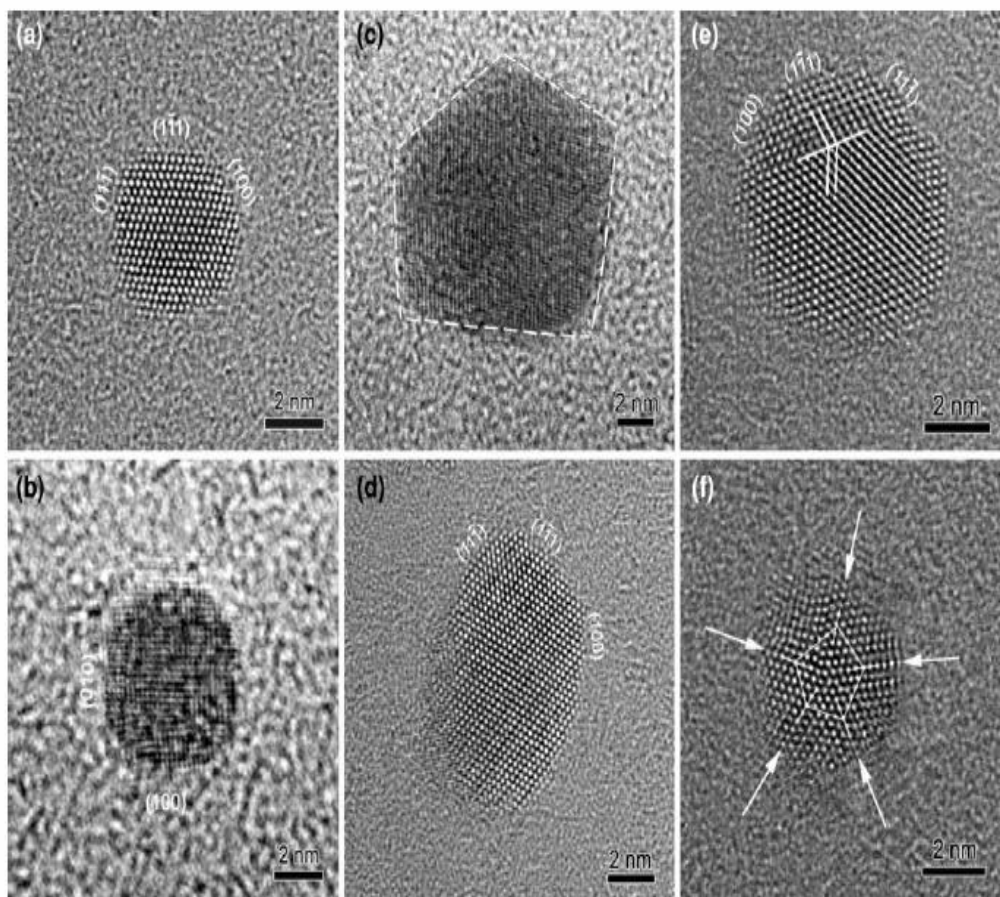


Figure 2-6: HRTEM images of most commonly shaped gold nanoparticles exposing crystal facets after annealing at 100° C [62].

With a further increase in treatment temperature, an agglomeration of gold particles was monitored leading to an increase in average particle size with increased twinned structure. Therefore, the treatment temperature has a key effect on the particle shape and crystal orientation, which have an influence on the catalytic activity.

3.1.1.3 Interaction with the support

Another key factor determining the catalytic activity is the support. The extent to which it determines the structure and stability of small gold particles depends on the fraction of metal atoms directly in contact with it [32].

The particle shape is determined by the contact angle which is expressed by the interfacial energies γ of the 3 surfaces described in the following image:

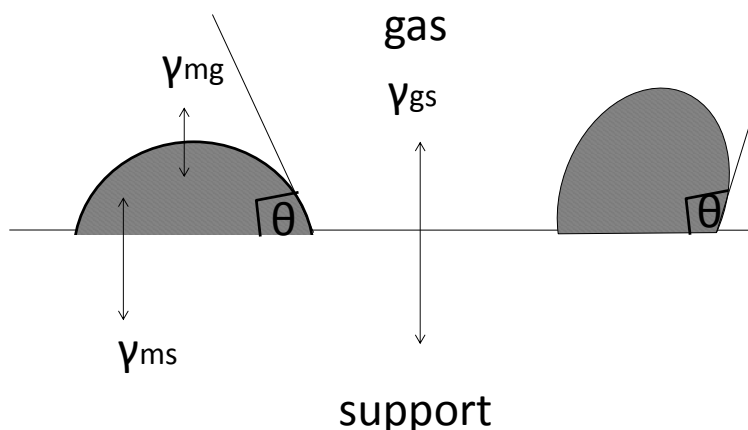


Figure 2-7: Interactions across interfaces around a gold particle and the contact angle; γ interfacial energy: ms: metal/ support, mg: metal/ gas, gs : support/gas [32].

In case the metal support interfacial energy γ_{ms} is large, the metal will wet the oxide surface and the contact area of the particle will be large resulting in hemispherical or truncated cubo-octahedral particles. If γ_{ms} is small then the particle will take a spherical or cubo-octahedron shape. If the energy is increased with all other parameters being constant, the length of the perimeter of the particle increases developing larger flat facets and resulting in a decrease in coordination number [30].

For some materials the reaction and activation takes place at the metal-support interphase rather than on the particle. Thereby, there are different types of metal-support interactions [72]:

- 1) In case of very small metal particles <2 nm, the support can modify the electronic structure of the metal particles, which are the catalytically active phase. This effect can be enhanced through electron transfer for certain oxide supports.
- 2) Through the generation of new active sites at the metal-support interphase, in addition to the adsorption sites on the metal particle itself.
- 3) The formation of a thin oxide layer on the metal particle, in case of a very thin layer, i.e. layer thickness is smaller than a few atoms, this layer can form the catalytic active phase.

The following section will discuss some of the most applied supports for gold based catalysts for selective oxidation and their influence on the catalytic activity.

2.3.3 Au on carbon

Activated carbons are nonhazardous, processed carbonaceous materials consisting of a porous structure and a large internal surface area. They are made on a commercial scale from raw materials such as wood, peat, coconut shells, lignite and hard coal by chemical activation or gas activation. They are commercially available in a variety of cylindrical or pelletized shapes, granular or powdered. All activated carbons are classified and characterised by their type of pores consisting of submicropores ($d \leq 0,8\text{nm}$), micropores ($d = 0.8\text{-}2\text{nm}$) mesopores ($d = 2\text{-}50\text{nm}$) and macropores ($d \geq 50\text{nm}$). The specific inner surface area of commercial activated carbons is in the range of $500\text{ m}^2\text{-}1500\text{ m}^2$. Besides from the element carbon, the material also contains small amounts of oxygen, nitrogen, sulfur and hydrogen bonded in the form of functional groups [79].

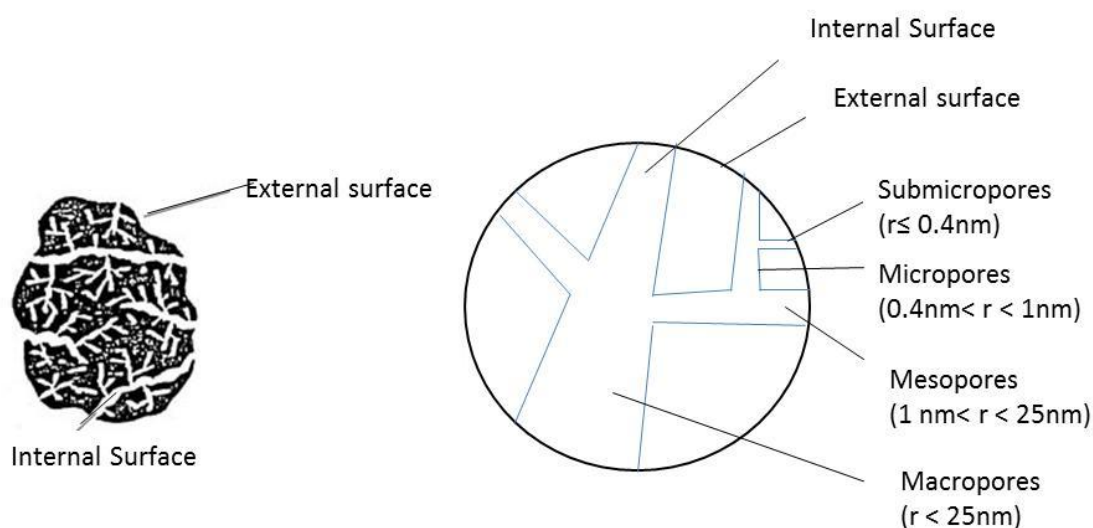


Figure 2-8: Activated carbon pore structure [79].

The large significance of activated carbon as a support for noble metal catalysts is derived from various factors such as its large surface area, its stability in acid/basic media, its high stability at high temperature in absence of air and the possibility of recovery of the active phase by burning off the carbon. Furthermore, the adsorptive properties arise from its porous structure as well as the oxygenated surface groups (i.e. carboxylic, phenolic, lactones, quinones) and chemical composition. These properties can be tailored by the activation process, which allows influencing the pore size and distribution [69]. The pore size distribution determines the surface area but also controls the access of the reactant to the supported metal active site. The surface functional groups influence the acid/base properties and can play a key role in the selectivity of the catalyst. One of the most suitable and effective methods for preparation of

finely dispersed gold particles on carbon is via sol-immobilisation using polyvinylalcohol (PVA) or tetrakis(hydroxymethyl)phosphonium chloride (THPC) [80] [81]. This method delivers uniformly dispersed Au particles with an average size of 5-8nm and a narrow size distribution. Gold on carbon Au/C catalyst systems have been successfully employed for the selective oxidation reaction of a large range of alcohols and polyols [47] [69] [82] [83] [74] [84].

2.3.4 Au on oxides

3.1.1.4 CeO₂ and TiO₂

Au/C catalysts have demonstrated to be very active towards the liquid phase oxidation of alcohols and polyols, however retaining selectivity towards the main product in complex reaction networks is an ongoing challenge. It has been found that gold, when dispersed onto oxide supports such as CeO₂ and TiO₂, exhibited extraordinary catalytic properties [65, 85, 86]. A range of theoretical models have been proposed to explain the high activity: based on the small and controlled gold particles, and the strong interaction (i.e. charge transfer between oxide and gold) and epitaxial contact of the Au particles with metal oxide support which also prevented a major sintering of particles during calcination [87]. Furthermore, some metal oxides contained active sites which were theoretically able to oxidise alcohols in stoichiometric amounts due to the presence of oxygen at the support surface, which introduced a new concept of catalytic active sites on the support. The shape and size of the deposited particles depended on the method but also on the crystallographic phases, surfaces and surface defects. Haruta et al. discovered that highly dispersed gold on selected metal oxides was extremely active for CO oxidation at 200K [44, 56]. Bianchi et al. observed that different preparation methods yielded different attachments of the metal particles to the support [69]. Hereby, the deposition-precipitation method resulted in hemispherical gold particles, whereas the impregnation method produced spherical particles on the TiO₂ (110) support and thus yielded much larger particles [63]. In the case of the CO oxidation, the hemispherical gold particles supported on TiO₂ achieved much higher TOF numbers by four orders of magnitude. This clearly showed that the activity of Au particles on TiO₂ also depended on the contact structure of the particle to the support. Prati et al. have investigated the role of TiO₂ as support for liquid phase oxidation of alcohols in comparison to activated carbon and Al₂O₃ on gold and have found that the same preparation method delivered much smaller average particle diameters on the support [63]. The stronger interaction with the support prevented agglomeration. In the case of activated carbon, however, the highest activity was observed at a larger average particle size. This was

shown to be based on the fact that smaller gold particles were located on the internal surface of carbon making it less accessible for substrates.

Table 2-7: Catalytic test of gold catalysts prepared via metallic sols for selective oxidation of ethylene glycol [31].

Sol precursor	Support	Au particle diameter (in sol) [nm]	Au particle diameter (on support) [nm]	X [%]
THPC/NaOH	γ -Al ₂ O ₃	3.5	3.80	100
THPC/NaOH	TiO ₂	3.5	3.71	100
THPC/NaOH	C	3.5	8.16	90

Reaction conditions: alcohol (EG)= 0.5 M, EG/metal = 1000 mol/mol, EG/NaOH = 1 mol/mol, pO₂ = 2 bar, t= 1 h.

Recently, much research has been done on the design and application of novel structured materials such as TiO₂ nanotubes, which exhibit [88] [89] particularly interesting support properties. CeO₂ has been very attractive as support due to its use as an active component of catalytic converters for the treatment of exhaust gases.

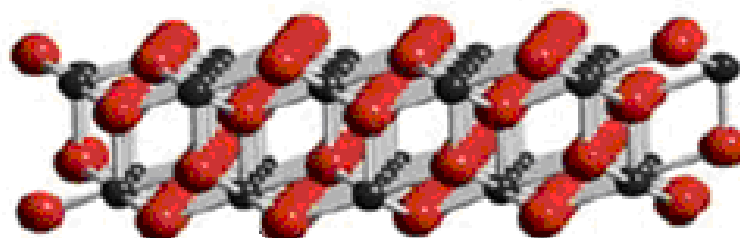


Figure 2-9: Rutile structure of CeO₂ [90].

As a highly reducible oxide with defect structure, leading to the creation and diffusion of oxygen vacancies [91] [58] in the material, CeO₂ is very versatile in its applications including as an oxygen buffer, as catalyst support or as a solid electrolyte. Corma et al. have investigated the performance of Au/CeO₂ catalysts for the liquid phase oxidation of alcohols [92] [87] [58] [61]. Its high surface area and oxygen storage capacity turned the material into an attractive support. The Au/CeO₂ catalysts delivered superior performance over other oxide supports such as TiO₂

and Fe_2O_3 due to an enhanced synergistic effect between Au and CeO_2 . It was further found that in particular small gold particles of 2-5nm size on nanocrystalline CeO_2 (111), turned to be very active and highly selective for the selective oxidation of alcohols in absence of solvent and base, where other catalyst systems reached their limitations, e.g in the case of carbon supported systems [93].

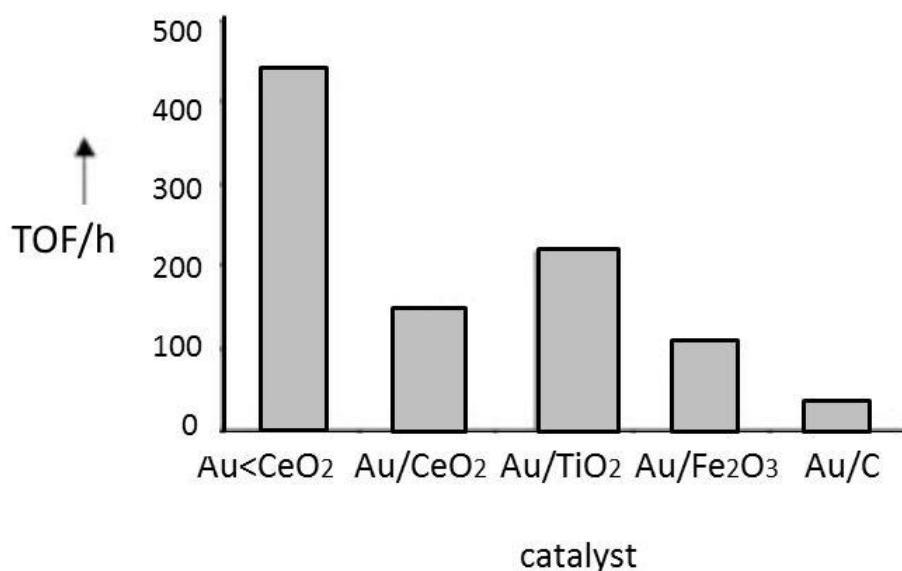


Figure 2-10: Turnover frequencies for the oxidation of 3-octanol, given as the ratio of moles of 3-octanone per mole of Au per hour, measured at $t=10$ min [64].

3.1.1.5 Hydrotalcites

Hydrotalcite (HT)-like compounds are anionic clay minerals and are classified as layered double hydroxides (LDHs). They consist of brucite-like layers and hydroxide and carbonate ions in the interlayers. They have been very attractive for catalytic applications due to their unique properties such as their ion exchangeability in the brucite- and interlayer, their CO_2 adsorption capacity and moreover, and their tunable basicity. The positively charged individual layers constituting the HT structure are of micrometer range in size and nanometer range in thickness [94] [95] [96, 97].

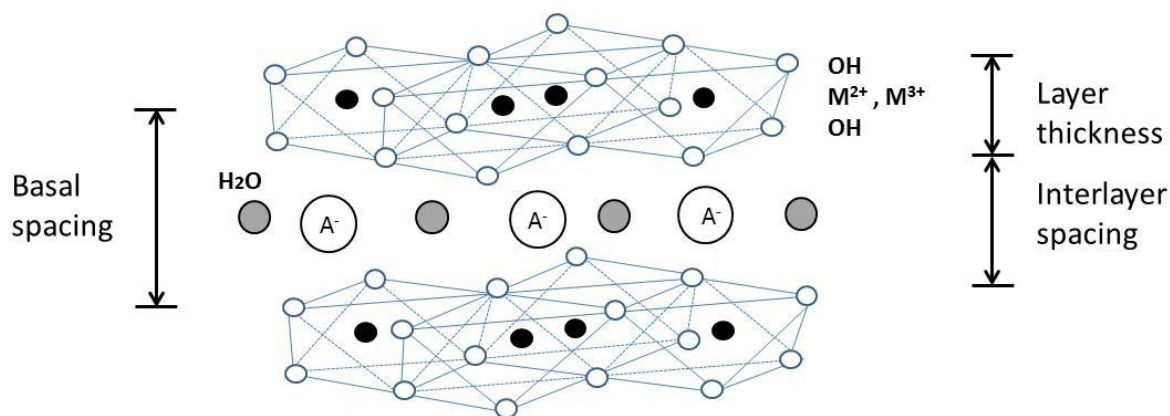


Figure 2-11: Double layered structure of hydrotalcite [194].

These characteristics have made them very versatile and active materials for a large range of applications such as CO₂ adsorption [98] [99] [100] [99] [101] or for liquid phase base-catalysed reactions such as aldol-condensation, or epoxidation of olefins [102] [97,103] [104] [105]. Fresh HT materials are fully hydrated and exhibit low basicity, as the adsorbed water prevents access to basic sites on the surface. Therefore, thermal activation is needed and is also used to modify the basic properties of the material. However, attention should be paid to the fact that the HT material undergoes a structural change when treated under temperature. The thermal behaviour, measured by thermogravimetric analysis, is characterised by various transitions: at lower temperatures, in the range up to approximately 300°C, the loss of adsorbed and interlayer water is observed which is an endothermic and reversible process, retaining the structure. The second step in the range of 300-500°C can be attributed to the loss of hydroxyl groups from the brucite structure. At higher temperatures, multi-weight loss stages can be monitored accounting for the counter anions such as carbonates or nitrates.

The structure of HTs can be analysed by a range of analytical techniques. XRD analysis of uncalcined samples gives information about the layered structure and type of ordering. Depending on the composition of the material, sharp diffraction peaks are often obtained for stoichiometric materials whereas broader lines correspond to less ordered structures and/or the formation of small crystallites. The typical surface area can be obtained by N₂ physisorption (BET) measurements and lies in the range of 100m²/g [94], which refers to the 'external' surface area of this closely packed structure. It has been demonstrated that for HT containing CO₃²⁻ ions, a modification of the structure is observed at temperatures above 350/400°C. As already mentioned, the interlayer water and CO₃²⁻ are removed leading to a decrease in the interlayer spacing (Figure 2-12). If the HT is not further calcined above 400 °C a rehydration with re-expanding the original layer spacing is possible. Studies have shown that after calcination at 400°C for 2 hours both HT and MgO were detected by X-ray diffraction. After

calcination at 400-800 °C, only MgO could be detected. Above 900°C the HT decomposed and two separate oxide phases MgAl_2O_4 and MgO and traces of $\gamma\text{-Al}_2\text{O}_3$ were found [95]. This was also confirmed by studies by Miyata et al. on the chemical analysis on the composition of the hydrotalcite materials. Upon increasing calcination temperature the increase in amount of MgO was shown and after calcination at 400-700°C only MgO could be detected. At 900°C, MgO and the spinel MgAl_2O_4 , and a trace of Al_2O_3 was detected.

Table 2-8: Chemical analysis for $(\text{Mg})_{0.665}(\text{Al})_{0.335}(\text{OH})_{1.95}(\text{CO}_3)_{0.149}(\text{H}_2\text{O})_{0.543}$ for calcination temperature range of 300-500°C for 1h in air [106].

	300°C	400°C	500°C
Weight decrease (%)	12.4	23.8	38.7
Weight from TGA (%)	12.9	22.4	34.1
Al_2O_3 (%)	25.2	27.5	37.0
MgO (%)	39.4	43.0	57.9
CO_2 (%)	9.7	10.6	3.3
H_2O (%)	25.7	18.9	1.8
Molar ratio $\text{CO}_2/(\text{Mg}+\text{Al})$	0.149	0.150	0.034
Molar ratio $\text{OH}/(\text{Mg}+\text{Al})$	19.4	1.31	0.090

In general, the HT materials have shown to be applicable as alkaline support for selective oxidation reactions under mild conditions [37] [107] [108]. The basicity can be further increased by modifying the nature and ratios of the cations $\text{M}^{2+}/\text{M}^{3+}$ or by introducing specific anions in the interlayer [97] [94]. Studies on the ratio of Mg:Al have been done in order to increase the basicity. It was found that ratios up to 5-10 of Mg : Al could be synthesised with the hydrotalcite structure without the segregation of Mg phases. At a higher ratio of 15 Mg:Al, a larger enrichment of MgO phases was observed. Upon calcination at 400°C, these materials transformed and showed diffuse, distorted MgO patterns. Cosimo et al. investigated the structure and surface catalytic properties of hydrotalcite materials with varying Mg:Al content and found that the nature and strength of surface basic sites were very dependent on the composition [109]. For calcined hydrotalcites (CHT) the materials exposed MgO diffraction patterns. At higher amounts of Al also spinel phases are seen. Furthermore, the surface area increased with increasing ratio of Al and decrease in crystallite size.

Table 2-9: Chemical composition, BET surface areas and XRD characterisation of HT [109].

Sample	Al/(Al+Mg) [mol/mol]	Mg [wt%]	Al [wt%]	S _g [m ² /g]	XRD Phase	Crystallite size [Å]	Lattice parameter [Å]
MgO	0	-	-	125	MgO	75	
CHT1	0.11	45.3	6.2	114	MgO	124	4.21
CHT2	0.18	39.7	9.7	184	MgO	91	4.21
CHT3	0.24	34.4	12.1	238	MgO	28	4.21
CHT4	0.47	22.2	21.5	231	MgO	21	4.22
CHT5	0.65	15.0	31.1	298	MgO+MgAl ₂ O ₄	<20	4.21
Al ₂ O ₃	1			388	Amorphous		

Sharma et al. showed that the hydrothermal treatment at increasing temperature and longer ageing time increased the crystallinity and crystallite size of the hydrotalcite significantly [110].

In general, the basic sites on HT materials can be classified into strong sites, involving low-coordinate O²⁻ anions, intermediate basic sites, formed by acid-base pairs, and bicarbonate anions with adsorbed OH species forming weak basic sites on the surface [94]. If the HT material is calcined at high temperatures the O²⁻ sites increase and surface adsorbed OH disappear. HT materials are intensively studied and have a large potential as catalytically active supports for the selective catalytic conversion of alcohols into higher chemical intermediates under mild and base-free conditions [111] [112] [113]. It has been shown that HT supported gold catalysts, with an average particle size of 2.7nm and a narrow size distribution were very active towards the oxidation of alcohols to the corresponding carbonyl compounds with molecular oxygen [111]. However, tuning the properties, in particular the basicity and understanding the behaviour in particular in the liquid phase are still great challenges.

2.3.5 Mechanism on the catalyst surface

Several studies on the mechanistic steps of the liquid phase oxidation on gold catalysts have been done [55] [114]. The mechanism is an oxidative dehydrogenation of the alcohol molecule, analogous to the mechanism on the Pt surface [114]. In particular, the role of the base [30] [68] [115] [116] [117] and the role of the oxygen during the mechanism have been investigated [52, 77, 118]. Studies on the mechanism for the selective oxidation of ethanol to acetaldehyde and acetic acid have revealed information on the role of molecular oxygen and OH. Given the nobility of Au, the

calculated activation barriers for the dissociative adsorption of the OH group were relatively high compared to Pd and Pt e.g. 204 kJ/mol for OH in ethanol. OH bond activation was thus unlikely to occur solely on the metal. The presence of the base in the bulk or on the catalyst surface was therefore necessary to lower the activation barrier to <25 kJ/mol and initiate the first step of the dehydrogenation of the alcohol species [177] [55], which is demonstrated in the following figure:

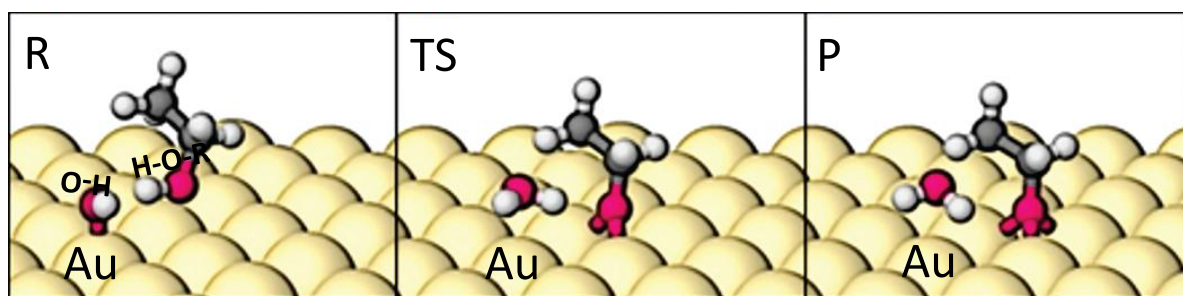
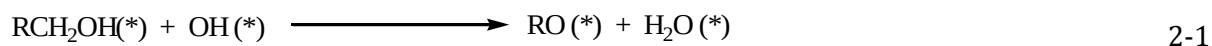


Figure 2-13: Mechanism for selective oxidation of ethanol on Au (111), R= reactant, (TS)= transition state, P= product [118].



Experiments varying the base content have shown a linear correlation of the base and the high activity concluding the abstraction of proton from the primary alcohol function is a rate limiting step. The second step (2) involves the activation of the C-H bond to form the aldehyde species. In the case of gold catalysts, this activation is believed to be facilitated by the presence of OH groups.



The final step is the activation of the aldehyde and incorporation of OH to form the acid via the formation of an alkoxy intermediate which is demonstrated in the following figure (Figure 2-14).

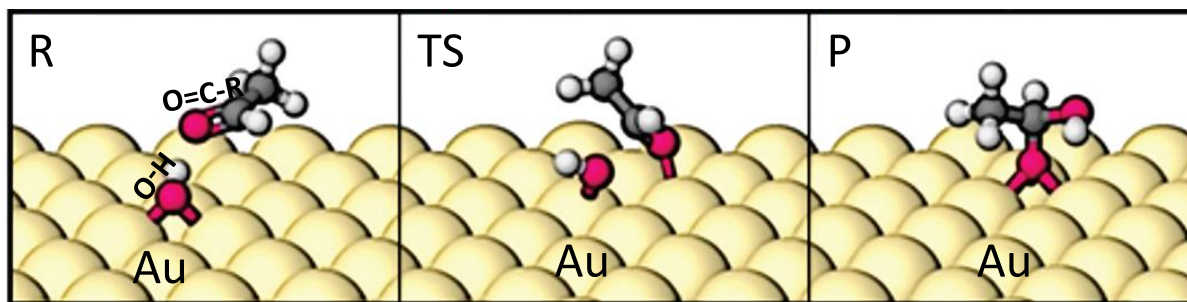


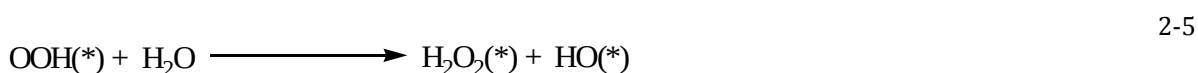
Figure 2-14 Mechanism for selective oxidation of ethanol on Au (111), R= reactant, (TS)= Transition state, P= Product [118].

The activation barrier for this mechanistical step has been calculated to be 45 kJ mol^{-1} due to the energy necessary for restructuring the H-bonding water network around the functional group of the aldehyde and the hydroxide ion enabling their reaction. On the Au(111) surface, the same step resulted in a much lower activation barrier of 5 kJ mol^{-1} [118].

The acid molecule is finally desorbed into the bulk solution liberating the catalytic active site.



The role of the oxygen was believed to be of indirect nature rather than being directly incorporated into the molecule to form the acid as the activation barrier for the O_2 dissociation was calculated to be 105 kJ/mol and therefore unlikely to occur. It was therefore suggested that the activation of the O_2 molecule occurred via the formation of a peroxide and hydrogen peroxide intermediate:



The role of the O_2 was to regenerate of the HO^- species via the reduction with water and by removing the excess negative charge. This process enabled the regeneration of the active metal sites and completing the catalytic cycle. Further detailed investigations on the interaction of the

molecular oxygen on the gold were done by theoretical calculations. Hereby adsorption energies and dissociation energies of molecular oxygen on different gold surfaces and nanoparticles have been calculated considering the molecular geometries and particle morphology [77] [55]. Results have shown that there were three types of adsorption modes of molecular O₂ on gold:

- 1) The weakly interacting end-on model on small, low coordinated gold atoms
- 2) Top-bridge-top mode on all gold surfaces
- 3) Bridge-bridge mode with a specific arrangement of four gold atoms in (100) facets

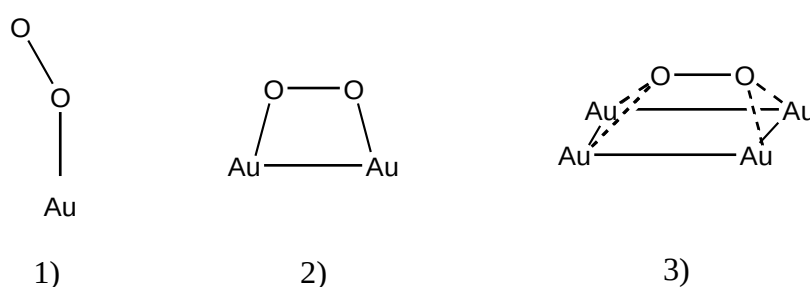


Figure 2-15: Scheme for adsorption modes for O₂ on gold. [77]

The adsorption energies roughly depended on the particle size and on other factors such as the degree of molecular activation towards the O₂ dissociation, the total electron density charge transfer from the catalyst to O₂, the lengthening of the O-O bond and the geometrical conformation of the adsorbed O₂. The highest degree of molecular activation along with the lowest activation barriers were found in bridge-bridge conformers which were exhibited by 100 facets found in small and cuboctahedral shaped Au nanoclusters Au₃₈/Au₁₃.

Experimental studies on the oxidation of benzyl alcohol to benzaldehyde have revealed that activation energies linearly increased with increasing particle size, whereas the adsorption enthalpies decreased. Theoretical calculations had shown that the activity increased with decreasing coordination number. Therefore it was concluded that the activity of gold particles was dependent on the number of uncoordinated Au atoms which was not only based on the particle size but also on the particle geometry and surface roughness. Another important factor was the role of the support, as for some highly structured surfaces, such as TiO₂, the O₂ dissociation took place at the metal-support interphase as they were found to be the most stable active sites.

2.4 Bimetallic AuPd catalysts

2.4.1 Structural properties

The addition of a second active metal such as Pd to Au and the investigation of the effects on the catalytic performance has gained a lot of attention in the recent years [7] [119] [120]. Hereby, the study of the synergistic effects and influence in particular on the reaction performance and selectivity in complex reaction networks was of great interest [121] [122] [48]. The morphology of the bimetallic catalyst was influenced by the preparation method and also by the ratio of Au:Pd. According to the bulk phase diagram, Au-Pd alloys could form at almost all compositions and existed over a large temperature range.

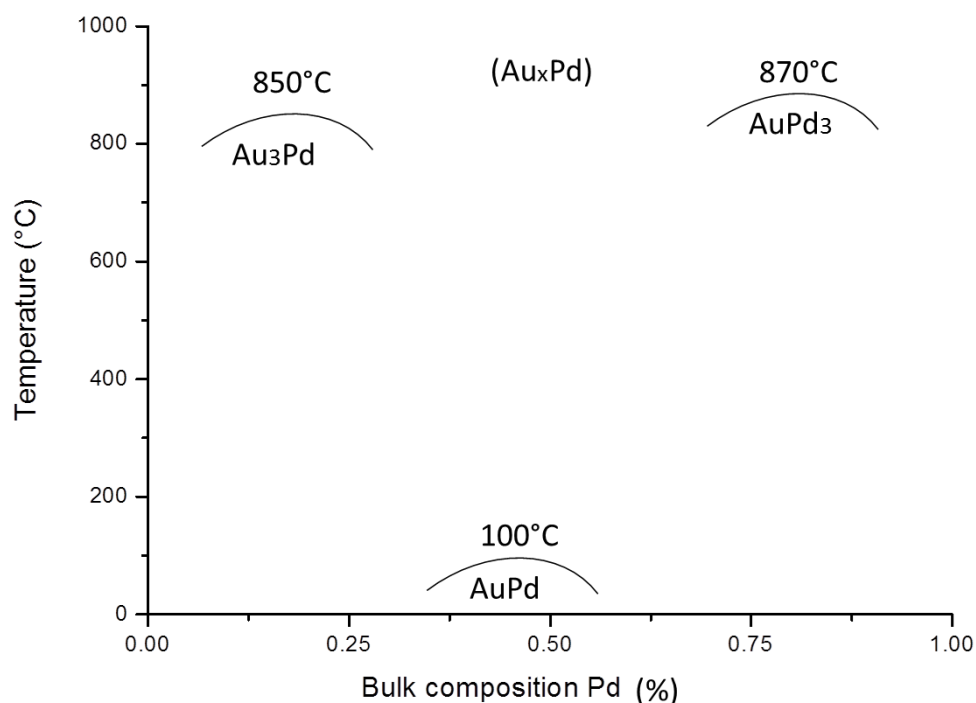


Figure 2-16: Temperature-composition phase diagram of AuPd solid solutions below melting point based on [123]. Curved lines represent order-disorder phase boundaries of the respective composition.

Studies have shown that Au surface segregation is favoured due to its lower surface energies. Studies on the particle shape showed that while the pure metal Au and Pd was found to be isocahedral, the alloy particle showed more complicated morphologies. Furthermore, the surface enrichment of Au leads to a different surface composition and roughness even in 1:1 Au:Pd alloy particles [124].

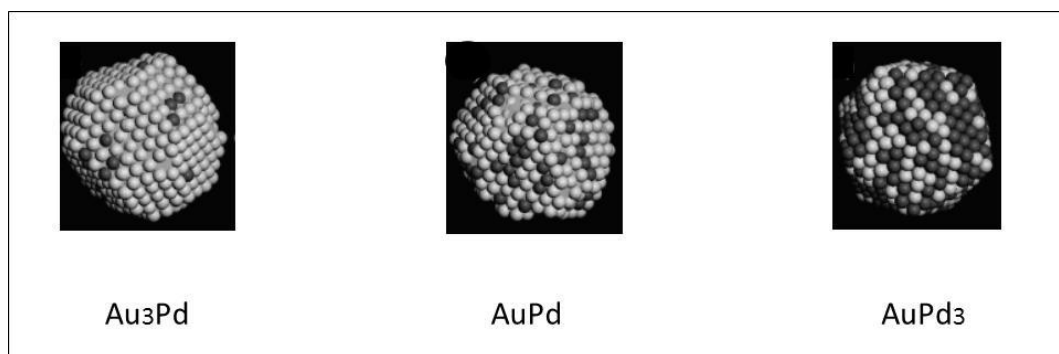


Figure 2-17: Particle configuration for Au Pd alloy compositions Au(bright), Pd(dark) after cooling corresponding to 923 atom particles [124].

The most commonly applied methods for bimetallic catalyst synthesis is based on the 1) successive deposition of the second active metal on gold or 2) the simultaneous deposition and reduction of the metal precursors onto the support [81] [125] [126]. The first method could lead to the formation of adatoms and small particles (multilayer deposition) on the surface of the gold particles (A), to a 'dilution' of the metal particles by the second metal or to single metal clusters on the catalyst surface, which is illustrated in the following figures:

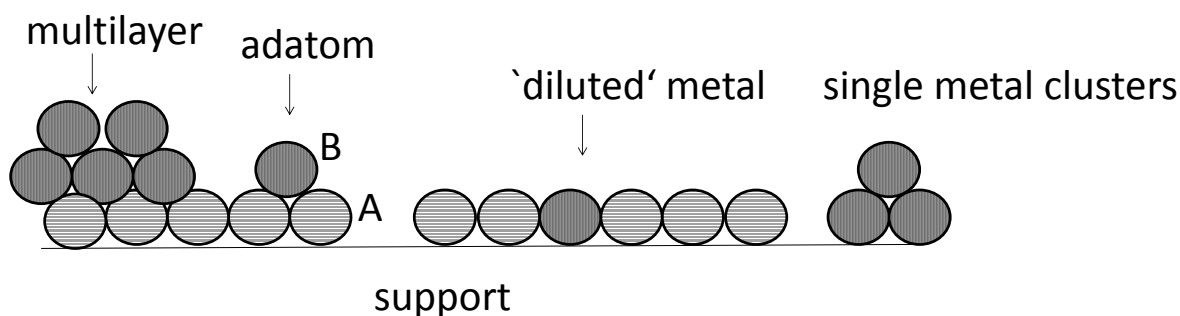


Figure 2-18: Schematic representation of the structure of a bimetallic catalyst with Au (A) and second metal (B) particles [38].

Studies have shown that the employment of the second synthesis method led to the formation of alloy particles, however, core shell structures were also found:

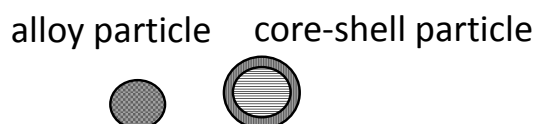


Figure 2-19: Schematic representation of the structure of a bimetallic catalyst with alloy and core-shell morphology.

2.4.2 Synergistic effects

Overall, compared to the monometallic Au system, bimetallic AuPd catalyst systems showed a higher catalytic activity, exhibited better selectivity and a longer catalyst lifetime [127]. The general ‘synergistic’ effect has shown to be based on a shift in electronic and geometric effects among the metals and the support [48] [119]. In a complex reaction network, various mechanistic steps on the catalyst surface could be involved [32]:

- a) In the case of several reaction steps, each one might occur on a different atom or active site. This process involves surface migration and/or desorption and re-adsorption on the surface.

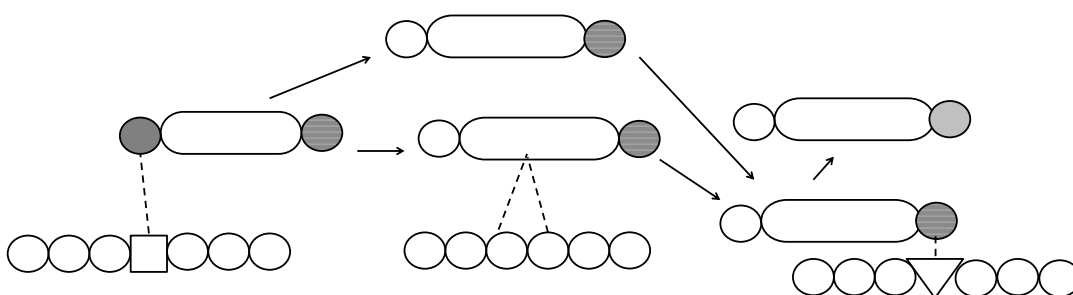


Figure 2-20: Modes of action of bimetallic catalysts in selective oxidations: Δ , $\square$ atoms of either Au or group 10 metal involved $\circ$ non-participating atoms [32].

- b) If a substrate molecule has multiple functionalities they might react at the same time, requiring multiple active sites and the presence of the two metals on the same particle.

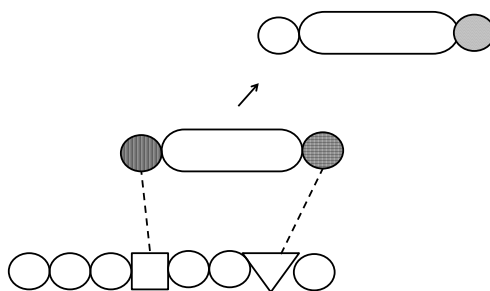


Figure 2-21: Modes of action of bimetallic catalysts in selective oxidations: Δ , $\square$ atoms of either Au or group 10 metal involved $\circ$ non-participating atoms [32].

- c) The ‘dilution’ of metal particles with the second metal can lead to the formation of isolated particles of one active metal, providing the selective operation on one of the functions of the substrate molecule.

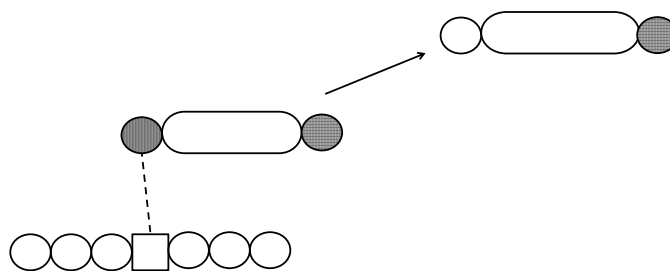


Figure 2-22: Modes of action of bimetallic catalysts in selective oxidations: Δ , $\square$ atoms of either Au or group 10 metal involved $\circ$ non-participating atoms [32].

It was known that in the case of the selective oxidation of glycerol, the reaction pathway and product selectivity was very dependent on the pH of the medium and on the metal employed. The effect of bimetallic catalysts AuPd and AuPt on the catalytic performance in liquid phase oxidation of alcohols, in particular on the product selectivity, has been studied [119] [7]. Factors such as the ratio of the metals and the particle size played key roles in determining the activity. A higher activity was found for the bimetallic catalysts, with a 5-6 fold increase in TOF numbers, showing that there was a strong synergistic effect between Au and Pd/Pt. Regarding the selectivity to the main product glyceric acid, the Au-Pd system exhibited a superior selectivity compared to AuPt, with the overall selectivity increasing in comparison to the monometallic systems. The strong 'synergistic' effect was based on the presence of an alloyed phase. X-ray diffraction analysis and further catalyst characterisation techniques showed a shift in diffraction peak positions compared to the monometallic reference peaks. This was due to a change in the lattice constant and indicated the formation of an alloy type particle. An extensive study of bimetallic AuPd on TiO_2 , Al_2O_3 and C by Hutchings et al. found a variation in particle size and distribution depending on the support. Though all catalysts comprised of mainly small particles of 2-10nm size, the carbon supported AuPd catalyst had a higher density of larger particles >20nm [128, 129] [130]. Moreover, there was a difference in bimetallic particle structure resulting in a Au rich core- Pd rich shell type particle on TiO_2 and Al_2O_3 and a homogeneous alloy particle on the carbon support. XPS analysis had shown that there was a possibility for Pd surface segregation in the alloy particle on oxide supports and the oxidation of PdO leading to phase separation. In the case of carbon, its reducing nature prevented the oxidation of Pd and phase separation. It was therefore proposed that there is a decrease of binding energy between palladium to oxygen on the bimetallic catalyst. Studies on the selective oxidation of aromatic alcohols such as benzyl alcohol with mono and bimetallic Au and AuPd on carbon and oxide supports showed that the TiO_2 and Al_2O_3 supported catalysts showed highest activity and, in contrast to the monometallic Au and Pd catalysts, retained high selectivity towards benzyl aldehyde at high conversions [128] [85] [127]. The solvent furthermore played a significant role

and studies have shown that a higher conversion was observed when using water instead of an organic solvent such as toluene.

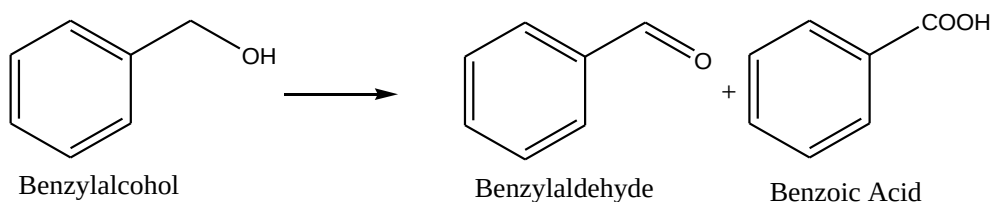


Figure 2-23: Selective oxidation of benzyl alcohol.

Table 2-10: Oxidation of benzyl alcohol ^{a)} [119].

Catalyst	Solvent	X [%]	S Benzyl aldehyde [%]	TOF [h ⁻¹]
1% Au	toluene	0	0	0
1% Pd	toluene	3	94	5
0.73% Au-0.27% Pd	toluene	32	94	54
1% Au	H ₂ O	0	0	0
1% Pd	H ₂ O	18	91	30
0.73% Au-0.27% Pd	H ₂ O	96	94	160

Reaction conditions: benzyl alcohol 0.3 M, benzyl alcohol/metal 1/500 (mol/mol), $T = 333\text{ K}$, $p_{\text{O}_2} = 1.5\text{ bar}$ stirring rate 1250 rpm, $t = 3\text{ h}$.

Supported AuPd alloys have recently become very attractive for the direct synthesis of hydrogen peroxide. It has been found that the H₂O₂ production rate is much higher for AuPd catalysts than for the pure Pd [131] [121] [6], [132]]. These catalysts have high potential for generating H₂O₂ as oxidant not only for reactions such as epoxidation but also for selective oxidation of alcohols [133].

2.5 Selective oxidation of salicyl alcohol

The selective conversion of salicyl alcohol (2-hydroxybenzyl alcohol) is an important chemical route for the production of its higher chemical oxygenates salicyl aldehyde (2-hydroxybenzyl aldehyde) and salicylic acid (2-hydroxybenzoic acid). Until now, no direct transformation from

salicyl alcohol is carried out; the industrial production of salicyl aldehyde and salicylic acid is obtained from phenol.

Salicyl aldehyde

The industrial production of salicyl aldehyde is mainly carried out from phenol (1) in the Reimer-Tiemann process:

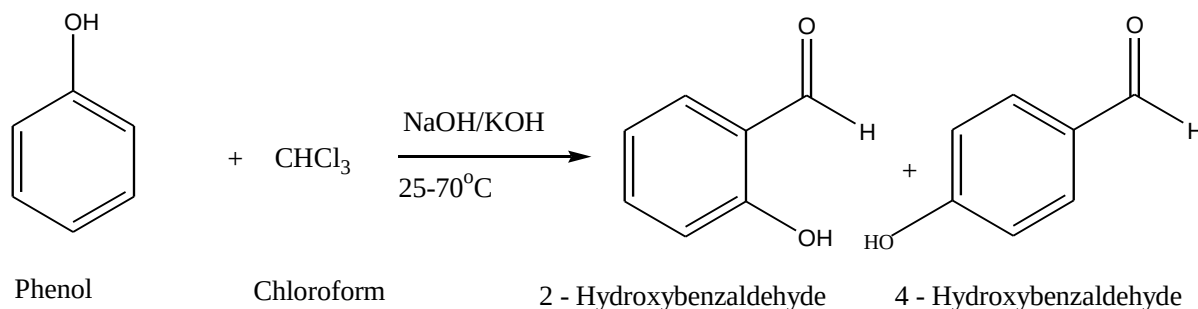


Figure 2-24: Commercial Reimer-Tiemann process.

This reaction requires the application of chloroform and a strong base, KOH. The yield of the product is relatively low requiring large amounts of hazardous chemicals. This process yields 2-hydroxybenzaldehyde (salicyl aldehyde) with 35-40% and the isomer 4-hydroxybenzaldehyde with 8-12% yield.

The product salicyl aldehyde is of large importance to the chemical industry as it is a highly functionalised molecule and can be transformed into a range of other substrates which is illustrated in the following figure (Figure 2-25). Rhone-Poulenc is currently the main producer in Europe and US, the estimated capacity for salicyl aldehyde is around 4000-6000 tonnes/year. Salicyl aldehyde and its derivatives are used as key ingredients in agricultural chemicals, petroleum chemicals, polymers, fibres, electroplating and perfumes [11]. It has been naturally identified as aroma component of buckwheat.

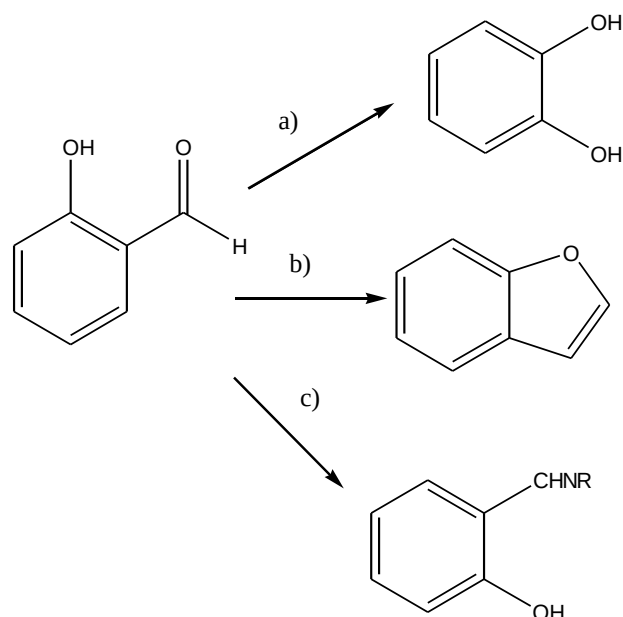
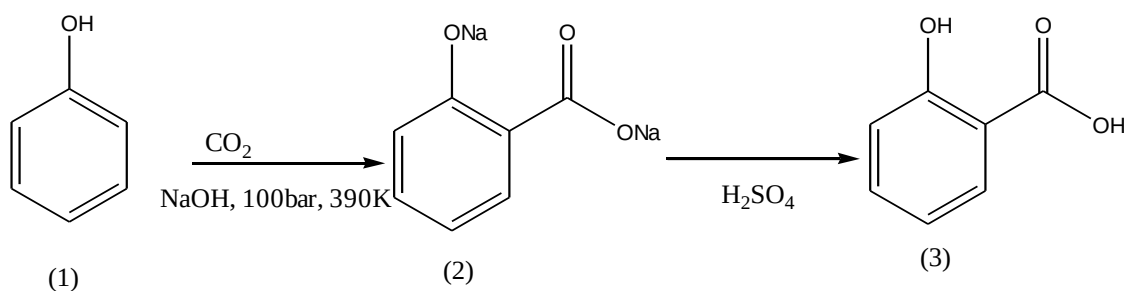


Figure 2-25: Reaction network for salicyl aldehyde a) Dakin-reaction for production of catechol b) etherification and cyclisation to benzofuran, c) reaction with amines to salicylaldehydimine.

Salicylic acid

Salicylic acid and its derivatives are interesting compounds because of their usage for analgesics, antipyretics, and anti-inflammatory agents, used for pharmaceutical products for pain or for treatment of certain skin conditions. Salicylic acid is commercially synthesised from phenol(1) via the Kolbe-Schmitt process to obtain sodium salicylate(2). The salt is further treated with sulphuric acid to obtain salicylic acid (3):



2-7

Salicylic acid does not appear in nature in large amounts, but can be derived from the glucosides of methyl salicylate and salicyl alcohol extraction followed by mild oxidation.

Catalytic oxidation of salicyl alcohol

So far only a few studies have been made on the catalytic oxidation of salicyl alcohol to salicyl aldehyde and salicyl acid. The first patents were made in 1976, claiming to produce high yields salicyl aldehyde in the liquid phase under atmospheric pressure using molecular oxygen and Pt or Pd based catalysts on activated carbon together with a Bi-based co-catalyst. The ratio of reactant:active metal ratio was around 87:1 [134] meaning that relatively high amounts of catalyst were used. Furthermore, large quantities of base, such as NaOH, was used of a ratio of 0.5-3 NaOH:alcohol. Another patented process involved the application of lead Pb as a co-catalyst. The TOF numbers were in the range of 100h^{-1} [135; 136]. Other patents were filed, however, requiring large amounts of co-catalysts based on magnesium, copper or the application of boric acid in nearly stoichiometric amounts. Although the Pt based catalysts on activated carbon showed a high recyclability and stability, the usage of big amounts of hazardous co-catalysts are environmental concerns. Furthermore, much remained unclear regarding the kinetics and mechanism of the reaction. A few studies have been made on the selective oxidation of salicyl alcohol in the liquid phase with molecular oxygen using gold based catalyst systems. Initial TOF rates of around $10\text{-}20\text{ h}^{-1}$ were achieved with Au/Fe₂O₃ and AuZn catalyst systems [137; 138]. The solutions were mostly buffered, and it was found that pH did not influence the rate of reaction. Although the developed and tested catalyst systems proved to be selective towards salicyl aldehyde the reaction resulted in a loss in carbon balance of approximately 20-30 % due to adsorption of the reactant on the catalyst surface.

So far, the commercial processes for the production of salicyl aldehyde are still highly energy and cost intensive. The catalytic conversion processes still require high amounts of co-catalyst and/or high amounts of base. It is therefore of great interest to develop a sustainable, efficient and green process for the production of salicyl aldehyde and salicyl acid from salicyl alcohol.

3 MATERIALS AND METHODS

3.1 Chapter introduction

This chapter explains and illustrates the experimental techniques utilised for obtaining the data for this thesis. This includes the catalyst preparation and characterisation techniques as well as the reaction setup, conditions and analytical equipment for carrying out the selective oxidation experiments.

3.2 Particle size measurements

3.2.1 TEM Transmission electron microscopy

Transmission electron microscopy (TEM) analysis was done to retrieve information on size, shape and the arrangement of Au particles on the catalyst support. The average particle size and distribution of the gold nanoparticles was determined by image analysis using a high-resolution (80-200 kV) Transmission Electron Microscope (JEOL 2010). Samples were prepared by a fine dispersion of 5mg of the powdered catalyst in 1mL ethanol and then depositing 1-2 drops of the fine dispersion onto the copper grid (holey carbon film 300 mesh).

For the obtained bright field images on the Au/C catalyst, the particles with a higher atomic number e.g. ^{197}Au were darker spots compared to the lighter support e.g. ^{12}C . The sample preparation was a very important step, as the image quality was dependent on the density of the dispersion and therefore thickness of the sample on the copper grid. The thinner the sample was, the higher the contrast and resolution became.

The image analysis was performed using the digital micrographs and the image processing software by *Gatan Digital Micrograph* for calibration. Several micrographs (3/4) were taken from different zones of the sample to have a representative sample collection. The particle size and distribution was established by counting and measuring the diameter d_i of about 300-400 particles n_i as well as determining the standard deviation SD [72].

$$SD = \sqrt{\frac{\sum_{i=1}^n a_i^2}{n} - \left(\frac{\sum_{i=1}^n a_i}{n} \right)^2} \quad 3-1$$

Regarding the distribution, there were two types: the number distribution (n_i / d_i) and the surface distribution ($n_i d_i^2 / d_i$) [172]. The surface distribution could give a more accurate account of the fraction of particles which contributed most to the total surface area and therefore to the catalytic properties. The distribution of the particle size is illustrated in the TEM histograms. Although the technique delivered reproducible and representative images of the particle size and distribution of the metal particles, the TEM technique was limited to 2D imaging, as the images were a projection of the plane perpendicular to the electron beam. Other characterisation techniques had to be applied to obtain information about the morphology of the catalyst. Charging of the sample in certain cases caused a drift and made it difficult to focus at high magnification.

3.2.2 EDS Energy dispersive X-Ray spectroscopy

Microanalysis was done using Oxford Instruments INCA EDS 80mm X-Max detector system. This technique in conjunction with the TEM images enabled element identification i.e. the presence of Au particles.

3.2.3 STEM Scanning transmission electron microscopy

STEM analysis was performed using a FEI TITAN 80/300 TEM/STEM instrument allowing the detection of very small metal clusters or even single atoms, through a very small and focused electron beam directed onto the specimen. The annular detectors facilitated the collection of electrons scattered at high angles and enabled HAADF (High Angle Annular Dark Field) imaging. The gold particles appeared bright on a darker background (Z contrast). The samples were prepared the same way as for the TEM analysis.

3.3 Catalyst structure, morphology and product analysis (HPLC)

3.3.1 XRD X-Ray diffraction

X-Ray diffraction (XRD) is an essential analysis technique to obtain information about the structure and morphology of the crystalline phases, crystallite sizes and shapes, bulk defect types and concentration.

Powder X-ray diffraction was performed on the catalysts to obtain information about the particle morphology of the active metals Au and AuPd and on the support morphology, in particular for the oxide supports. The catalysts were measured with a PW3710 Philips X'pert diffractometer using Ni-filtered Cu K α radiation ($\lambda = 1.54178$ Å). Each sample was prepared

as a powdered pellet with a smooth surface. The catalyst amount varied between 150-250 mg. The analysis was performed over a scan range angle of $5-90^\circ 2\theta$ with a step size of 0.0167° . The resulting diffractograms showed the diffraction pattern of the material with the characteristic scattering angles at 2θ . The diffractograms allowed identifying existing phases and particles through comparison of the peak position, sharpness and intensity with the reference database. Theoretically, with sharp and intense reflections, particle sizes of the metal as well as the lattice parameters could be obtained. Additional instrument parameters such as the sample amount, X-ray intensity and apertures played a role in the quality of the diffraction pattern. However, the existence of poorly crystalline and highly divided phase [139] could lead to broad peaks with weak intensity. Further, The limit of detection of gold was dependent on several factors such as particle size, weight fraction or concentration, and the intensity of the continuous scattering from the support [140]. Therefore, in this study, XRD was mainly used as qualitative analysis technique.

3.3.2 BET Surface area

The measurement and evaluation of the surface area and the pore size in relation to the catalyst performance was important. The average Brunauer-Emmert Teller (BET) surface area as well as the pore size and volume of the catalysts were characterised by N_2 -physisorption using a Micromeritics Tri Star 3000 Analyser. Prior to the measurements, the samples were degassed under helium for 6h at $120^\circ C$. The surface area of the samples was determined according to the BET method based on the N_2 adsorption branch, and the mesopore volume was calculated using the Barret-Joyner-Halenda BJH equation.

3.3.3 Zeta potential

Zeta potential measurements were conducted using the ZetaPals Brookhaven Instruments Analyser to measure the potential of the diffuse ions in the boundary layer. The magnitude of the zeta potential gave an indication of the stability of the colloidal system. The zeta potential of the MgO promoted HT material as well as the commercial HT was obtained against the pH. Prior to the measurements, a fine dispersion of the material was dispersed in various aqueous solutions in the range of 2-10 pH. The pH of the solution was adjusted with KOH and HNO_3 . In general, particles with a zeta potential of more than +30mV or less than -30mV were considered to form a stable colloid.

3.3.4 TGA Thermogravimetric analysis and CO₂ adsorption

Thermogravimetric analysis (TGA) of the samples was performed using a Perkin-Elmer TA Q500 Thermogravimetric Analyser. This was done in a temperature range of 30-1000°C on the freshly impregnated and uncalcined HT materials containing earth alkaline salts in order to identify the decomposition profile of the precursor salt. The calcination temperature was set accordingly. Furthermore, for the series of MgO promoted catalysts, TGA analysis with CO₂ adsorption measurements were performed to determine the CO₂ adsorption capacity and obtain information regarding the surface basicity.

The measurement involved a range of sequential cycles and the CO₂ adsorption was performed at low temperature at 70° C. For these experiments, approximately 20-30 mg of each material was heated from 30°C to 400 °C at a rate of 10K/min under N₂. This step was necessary in order to desorb the physisorbed H₂O and CO₂. The sample was held at 400° C for 60 minutes then cooled to 70°C. The gas flow was then switched to CO₂ (5% CO₂/N₂) and then held for 60 minutes. The amount of CO₂ adsorption was determined by change in mass during this cycle. The gas was then switched back to N₂ and kept for 30 minutes. During this cycle most of the loosely physisorbed CO₂ was desorbed. The ramp was then increased to 400°C. The series of promoted HT materials was analysed in order to determine the change in basicity along with the MgO promotion.

3.3.5 ICP Inductively coupled plasma

ICP analysis was performed on the catalysts and the catalyst preparation solution as well as on the reaction solutions after the experiments for quantitative element analysis using the PE Optima 2000 DV instrument. In order to determine the gold content on the oxide catalyst, about 10 mg of the catalyst was digested in 10mL aqua regia HNO₃/HCl (1:3) and in some cases the solution was heated up to 200 °C to ensure complete dissolution. After calibration of the measured elements with the corresponding element standards, the samples were analysed giving an absolute concentration. For the carbon supported catalysts, the filtered solution after immobilisation of the metal sol onto the support was analysed for any amount of metal which remained.

As the detection limit was up to 1ppm even small amounts of leaching during the reaction could be detected. The reaction solutions after the experiment were filtered and analysed by ICP to determine any amount of gold or magnesium as a result from leaching from the catalyst.

3.3.6 HPLC High performance liquid chromatography

The samples from the experiments were analysed using high performance liquid chromatography (HPLC) on a Perkin Elmer Series 200 instrument. Products were separated on a Supelcogel C610H column (300x7.80mm), containing a sulfonated, polystyrene/divinylbenzene packing with spherical particles of 9 μm size. Attached to the column was a guard column to filter impurities and prevent damaging the column. The mobile phase used was 100% of 0.1 wt% phosphoric acid H_3PO_4 and the flow rate was set to 0.8ml/min. The column temperature was 50 $^\circ\text{C}$. Before the analysis, the column was flushed with water to remove remaining chemicals and impurities from the system. The following section included the calibration factors and described the procedure for the analysis of the liquid phase selective oxidation experiments.

3.3.6.1 Selective oxidation of salicyl alcohol

The respective components were salicyl alcohol, salicyl aldehyde and salicylic acid. The main detector was UV VIS detector set to a wavelength of 273 nm. As it was not a diode array detector the analysis was limited to one fixed wavelength which in this case corresponded the adsorption maximum of salicyl alcohol [¹³⁷], as well as high response peaks for salicyl aldehyde and salicyl acid. The concentrations were calculated from the peak area of the chromatograms and the calibration factor of the respective components. For analysis, two HPLC instruments were used HPLC1 and then HPLC2, due to instrumental breakdown of HPLC 1 at a certain point. However, all conditions for analysis remained the same, only the response factors were different. The following tables list the retention times of the products and the calibration factors for both HPLC instruments. A constant amount of internal standard was added to the vials. The results of the HPLC chromatogram were absolute areas, which were used in order to calculate the concentration with the calibration factor. The ratio of the response factor of the internal standard and the component was used to normalize analytical errors and calculate the calibration standard.

Table 3-1: Retention times and calibration factors for selective oxidation of salicyl alcohol HPLC1.

Component	Retention time [min]	Calibration factor
Sodium lactate	10.9	Internal Standard
Salicyl alcohol	37.2	1.63*E-06
Salicyl aldehyde	98.3	3.68*E-07
Salicylic acid	80.3	5.46*E-07

Table 3-2: Retention times and calibration factors for selective oxidation of salicyl alcohol HPLC2.

Component	Retention time [min]	Calibration factor
Sodium lactate	5.1	Internal Standard
Salicyl alcohol	37.2	1.63*E-06
Salicyl aldehyde	98.3	3.68*E-07
Salicylic acid	80.3	5.46*E-07

3.3.6.2 Selective oxidation of 1,2- propanediol

For the selective oxidation of 1,2- propanediol, the detected components were 1,2- propanediol, lactic acid and sodium acetate. The main detector used was Refractive Index (RI). The concentrations were calculated from the peak area of the chromatograms and the calibration factor of the respective components. The following tables list the retention times of the products and the calibration factors for the analysis on the HPLC 1 instrument. A constant amount of internal standard was added to the vials. The results of the HPLC chromatogram were absolute areas.

Table 3-3: Retention times and calibration factors for selective oxidation of 1,2- propanediol on HPLC1.

Component	Retention time [min]	Calibration factor
1-propanol	22.9	Internal Standard
1,2- propanediol	14.6	3.22*E-05
Lactic acid	11.2	3.01*E-05
Sodium acetate	15.0	7.53*E-05

3.3.6.3 Selective oxidation of glycerol

For the selective oxidation of glycerol, the main products detected were glyceric acid and glycolic acid. The main detector used was Refractive Index (RI). The following tables list the retention times of the products and the calibration factors for the analysis on the HPLC 1 instrument.

Table 3-4: Retention times and calibration factors for selective oxidation of glycerol on HPLC1.

Component	Retention time [min]	Calibration factor
1-propanol	22.9	Internal standard
Glycerol	13.1	1.18*E-05
Glyceric acid	11.1	5.84*E-06
Glycolic acid	12.3	1.88*E-05

3.3.6.4 Quantitative analysis

The ratio of the area of the component (obtained by UV signal or RI signal) to the internal standard delivered the response factor f_i :

3-2

$$f_i = \frac{A_i / M_i}{A_{st} / M_{st}}$$

with

f_i response factor of the component

A_i area of component

A_{st} area of internal standard

M_i molecular weight of component

M_{st} molecular weight of internal standard

The response factor normalized all analytical errors occurred during the analysis. With the calibration of each component the calibration factor is obtained f_i which shows the correlation of the area to the concentration in the analysed range.

3-3

$$c_i = \frac{A_i}{f_i * M_i} [\text{mol/L}]$$

c_i concentration of component [mg/mL]

A_i area from UV or RI

f_i calibration factor

M_i molar mass [g/mol]

All calibration plots are listed in the Appendix. With the area obtained by analysis and the calibration factor the concentration can be calculated. It was necessary to verify whether the carbon mass balance equals 100%. The mass balance was calculated the following:

3-4

$$c_0 = \sum_j c_j$$

The sum of the obtained concentrations of the analysed substrates had to correspond to the initial concentration c_0 . The mass balance was calculated to be 95-100%

3.4 Catalyst preparation

3.4.1 Catalyst nomenclature

As a range of catalysts was prepared using different metals, loadings and supports, the following classification system has been set with the following example: 1.5 Au/C

- 1) Loading active metal [wt%] = 1.5
- 2) Active metal = Au
- 3) Support = C

If the support was further modified, such as for the impregnated oxide materials, the catalyst classification was extended with the following example 1.5Au/0.16MgO-HT

- 1) Loading active metal [wt%] = 1.5
- 2) Active metal = Au
- 3) Loading promoter [wt%] = 0.16
- 4) Promoter = MgO
- 5) Support = HT

3.4.2 Impregnation

For the catalyst synthesis, the support was added under stirring to an aqueous solution of the metal precursors. The support used was activated carbon and the gold precursor salt used was HAuCl_4 (Table 3-5). The precursor solution containing the amount of HAuCl_4 according to the desired final loading and was heated to 50°C before the support was added. For a final loading of 1.5wt%, 76 mmol Au /g support was used. The solution was stirred for 2 hours at 50°C . The catalyst was then filtered and washed with DI- H_2O water to remove all chloride and dried at 120°C . For the reduction, the dried catalyst was immersed in an aqueous solution with stoichiometric amount of NaBH_4 1g/0.1g catalyst. Only a few gold and gold catalysts were prepared via impregnation method, as it was difficult to control particle size as discussed in Chapter 4.

Table 3-5: Precursors used for catalyst preparation via impregnation.

Chemical	IUPAC Name	Molecular weight [g*mol ⁻¹]	Supplier
HAuCl ₄	Tetrachloroauric acid, 30 wt%	338.3	Sigma Aldrich
NaBH ₄	Sodium borohydride	37.8	Sigma Aldrich
C	Activated carbon powder, Norrit	12.0	Sigma Aldrich

3.4.3 Sol-immobilisation

Au on carbon

The catalysts were prepared via sol-immobilisation according to reported studies ^[80, 141], where the metal sols containing nanoparticles were formed using THPC as an organic stabiliser and reducing agent. This method enabled the control of particle size during preparation. The following procedure explains the preparation method for a 1.5wt% gold on activated carbon catalyst.

Table 3-6: Precursors used for catalyst preparation via sol-immobilisation.

Chemical	IUPAC Name	Molecular weight [g*mol ⁻¹]	Supplier
HAuCl ₄	Tetrachloroauric acid, 30 wt%	338.3	Sigma Aldrich
THPC	Tetrakis(hydroxymethyl)phosphonium chloride, 80 wt%	190.6	Sigma Aldrich
NaOH	Sodium hydroxide	40.0	Sigma Aldrich
C	Activated carbon powder, Norrit	12.0	Sigma Aldrich

For the sol preparation, 230 mL of DI-H₂O, 11.25 mL of 0.2M NaOH, 4.5 mL of THPC solution (1 mL of THPC in 100mL H₂O) were added under stirring. After 2 minutes, 76 mmol/g catalyst of a HAuCl₄ solution in 5 mL of H₂O was added. This amount corresponded to the ratio of THPC : Au = 1.1 which was constant for all catalyst preparations. There was an immediate change of colour of the solution into dark brown which indicated the formation of the gold sol. The sol solution

was stirred for one hour at room temperature. In the meanwhile, the support was suspended in 100mL/g support of DI-H₂O for 15 min. The gold sol solution was then dropped under vigorous stirring onto the support and stirred for one hour. The catalyst was filtered, washed to remove all chlorine then dried at 120 °C. The dried catalyst was treated and reduced in a glass reactor in H₂/N₂ (25mL/min) at 350°C in a furnace (Figure 3-1). This step was necessary to remove all organic residue of the THPC on the catalyst surface and to ensure all gold is reduced. The gas flow was adjustable with a flowmeter. Based on the setup, the gas could pass through the entire catalyst. The glass reactor was placed in the center of the furnace and furthermore also packed with glass wool at the ends to avoid heat loss. Furthermore, the temperature controlled furnace with suitable dimensions, enabled to maintain a constant temperature profile along the catalyst bed:

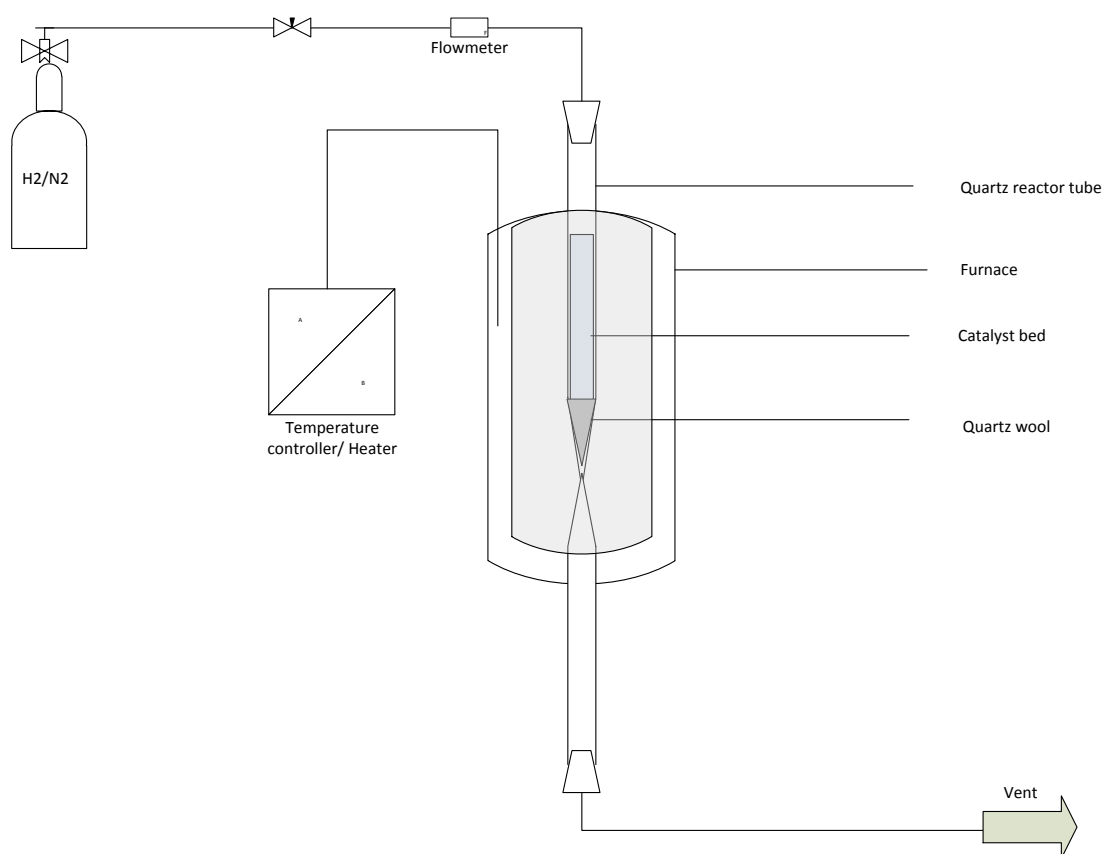


Figure 3-1: Reactor setup for catalyst reductive heat treatment.

The following table (Table 3-7) lists the prepared series of gold catalysts with different metal loading:

Table 3-7: Catalyst series of Au on carbon.

Catalyst	Au [wt %]	n (HAuCl ₄)/g *10 ⁻³ [mol]
0.75Au/C	0.75	38
1Au/C	1.0	51
1.5Au/C	1.5	76
3Au/C	3.0	152

Au on oxide supports

The preparation of monometallic Au on oxide supports was analogous to the preparation for the Au/C system. The only difference was that the solution with the oxide support dispersed in DI-H₂O, was adjusted to a pH of 2, in particular for TiO₂ and CeO₂ [80], before adding the sol to ensure full attachment of the gold onto the support [80]. Experiments without adjusting the pH have shown that the final metal loading was less than the theoretical calculated amount, which was demonstrated by ICP analysis and could be seen during the preparation as the precursor solution remained coloured. The pH adjustment however, was not required for earth metal alkaline supports such as MgO and CaO. The following oxide support materials were used:

Table 3-8: Oxide supports used for gold based catalyst preparation.

Substrate	IUPAC Name	Supplier
CeO ₂	Cerium dioxide	Sigma Aldrich
TiO ₂	Titanium dioxide	Sigma Aldrich
Al ₂ O ₃	Aluminium oxide basic	Sigma Aldrich
MgO	Magnesium oxide	Sigma Aldrich
CaO	Calciumoxide	Sigma Aldrich
HT	Hydrotalcite (3:1 Mg:Al)	Sigma Aldrich

The further catalyst synthesis procedure was as described above for the Au/C system.

AuPd catalysts

The bimetallic AuPd on carbon (AuPd/C) catalysts were prepared using sol-immobilisation [93] analogous to the procedure for monometallic catalyst described above. A precursor solution of

both metal precursors HAuCl_4 and PdCl_2 (palladium chloride 5wt%, (MW = 177.32), Sigma Aldrich) with the concentration according to the theoretical metal loading on the catalyst, was added to the THPC/NaOH solution. The amounts of THPC and NaOH were adjusted accordingly. The further catalyst preparation procedure was as described above for the Au/C system. The prepared series of AuPd on carbon catalysts is listed in the following table:

Table 3-9: List of prepared AuPd on carbon catalysts.

Catalyst	Loading Au [wt%]	Loading Pd [wt%]	n (HAuCl_4)/g catalyst * 10^{-3} [mol]	n (PdCl_2)/g catalyst * 10^{-3} [mol]
1.5Au0.75Pd/C	1.5	0.75	76	70.5
1.5Au1.5Pd/C	1.5	1.5	76	141
0.75Au1.5Pd/C	0.75	1.5	38	141
1.5Pd/C	-	1.5	-	141

MgO-promoted catalysts

The catalysts were prepared by wetness impregnation of the support material with the Mg precursor salts and successive deposition of gold. The following materials were used:

Table 3-10: Precursors for MgO promoted catalysts.

Substrate	IUPAC Name	Molecular weight [g* mol^{-1}]	Supplier
HT	Hydrotalcite commercial (Mg:Al 3:1) $\text{Mg}_6\text{Al}_2(\text{CO}_3)(\text{OH})_{16} \cdot 4\text{H}_2\text{O}$	603.98	Sigma Aldrich
$\text{Mg}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	Magnesium nitrate tetrahydrate	256.41	Sigma Aldrich
$\text{Mg}(\text{OAc})_2$	Magnesium acetate	214.45	Sigma Aldrich

Prior to the impregnation, the HT material was calcined in a glass tube in a furnace at 400 °C in air for the duration of 4h. The glass tube was packed in quartz wool to avoid heat loss. For the following impregnation of a loading of 0.16wt%, 4.88 mmol of the Mg precursor salt was dissolved in 1mL DI- H_2O and then dropped onto 1g of the support. The wet support was dried at

80 °C. The calcination was carried out in the same glass tube in the furnace, the calcination temperature depended on the decomposition temperature of the precursor. For most of the impregnated series $\text{Mg}(\text{NO}_3)_2 \cdot 4 \text{H}_2\text{O}$ was used therefore the temperature was set at 650°C. For the use of $\text{Mg}(\text{OAc})_2$ as precursor, 400°C was used as calcination temperature. The supports were calcined for 2h. After calcination the gold was deposited via the sol-immobilisation method using HAuCl_4 as described earlier. The catalysts were then washed chlorine-free, filtered, dried and treated as above in H_2/N_2 at 350 °C for 2 hours. The following series of gold on MgO promoted supports was prepared.

Table 3-11: MgO promoted HT catalysts.

Catalyst	Au [wt%]	n (HAuCl_4) * 10^{-3} [mol]	n $\text{Mg}(\text{NO}_3)_2 \cdot 4 \text{H}_2\text{O}/\text{Mg}(\text{OAc})_2$ 10^{-3} [mol]
1.5Au/0.04MgO-HT	1.5	76	1.22
1.5Au/0.08MgO-HT	1.5	76	2.44
1.5Au/0.16MgO-HT	1.5	76	4.88

CaO promoted catalysts

A few catalysts with CaO promotion were prepared. The catalysts were prepared by wetness impregnation of the support material with the Ca precursor calcium nitrate hexahydrate, $\text{Ca}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Sigma Aldrich MW=236.15 g/mol). The procedure was analogous to the MgO promoted catalysts described above. The concentrations were calculated for a final loading of 0.28 wt% /g catalyst.

3.5 Catalyst performance experiments

3.5.1 Batch reactor

Selective oxidation of salicyl alcohol

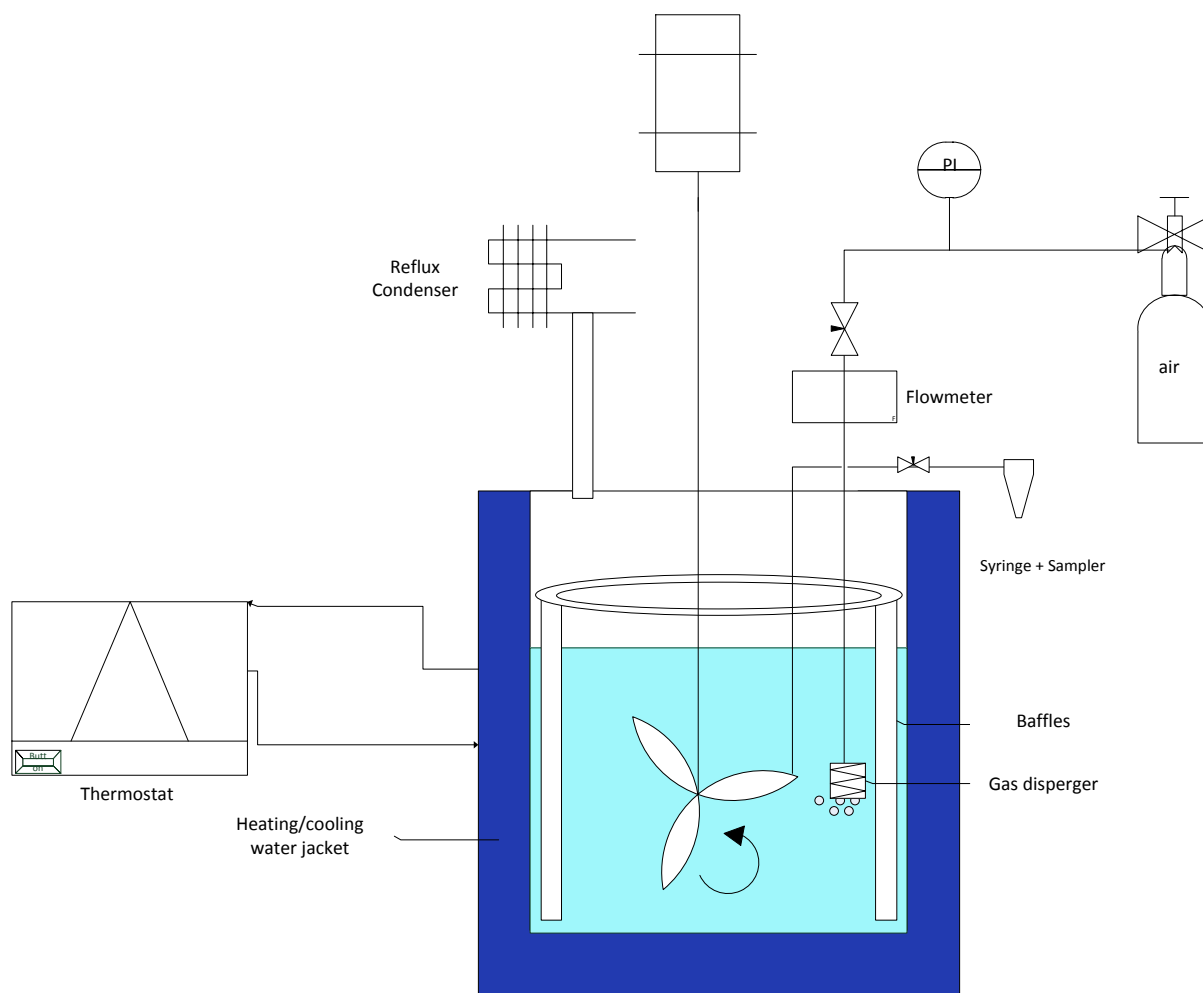
Catalytic tests were performed on the liquid phase selective oxidation of salicylic alcohol with air under mild conditions. Reactions were carried out in a baffled jacketed batch stirred glass reactor. The setup included 4 baffles, which were stationary blades of teflon specifically designed with the dimensions to break up flow caused by the rotating agitator. The reactor was equipped with an overhead stirrer which could go up to an agitation speed of 1000 rpm and ensured a homogeneous concentration and temperature profile of the reaction solution and avoiding the formation of 'dead zones'. The high agitation speed was also necessary in order to disperse the oxygen bubbles in the solution and increase the gas/liquid interphase and ensure a quick transport of the oxygen to the catalyst surface. In addition, a gas dispersing frit was attached to the gas inlet in order to sparge the air bubbles into fine bubbles. The glass reactor had a double wall, the outer wall served as temperature-controlled heating jacket. The water circulation was controlled by a thermostat. Additionally, a reflux condenser cooled by mains water was attached to the reactor. Overall, the reaction setup was systematically designed to be able to study the kinetics reaction rates from the reaction data without underlying mass transport influences.

For a typical reaction, the solvent 100mL H₂O with NaOH (0.04M) was split and approximately 80 mL together with the dispersed catalyst were heated in the reactor under continuous stirring until the desired temperature of 50°C was reached. Then, the reactant salicylic alcohol which was dissolved in 20 mL of the solvent, was injected into the reaction solution marking the initial start of the reaction $t=0$. Samples were taken at regular intervals and filtered with a Millipore filter to remove the catalyst before analysis by HPLC (3.3.6). A series of preliminary experiments to establish optimal reaction conditions were performed i.e. pressure, temperature, mass of catalyst and concentration of base NaOH and the results demonstrated in chapter 4. The operating conditions for the batch reactor studies are listed in the following table (Table 3-12).

Table 3-12: Operating conditions for batch studies of selective oxidation of salicyl alcohol.

m_{catalyst}	0.2g	P_{air}	1 bar
V_{solvent}	0.1L	V_{stirrer}	1000 rpm
$C_{\text{salicylic alcohol}}$	0.04 M	T_{reaction}	50°C
C_{NaOH}	0.08 M	t_{reaction}	360 min

Before starting the catalytic performance experiments a blank run was done to ensure that there was no activity initiated without catalyst (e.g. from the reactor parts itself, contamination through remaining catalyst). Therefore, it could be ensured that the turnover frequency numbers were entirely based on the catalyst.

**Figure 3-2: Setup of a glass batch reactor for the selective oxidation of salicyl alcohol.**

Selective oxidation of 1,2- propanediol

Catalytic tests were performed on the liquid phase selective oxidation of 1,2- propanediol with air under mild conditions. Reactions were carried out in a Buchi glass stirred reactor at 1-3bar gauge pressure. The reactor was equipped with a gas dispersion overhead stirrer to ensure a homogeneous concentration and temperature profile in the reaction solution avoiding the formation of 'dead zones.' Furthermore, the stirrer ensured the fine dispersion of the air bubbles ensuring a maximum gas/liquid/solid interphase and a quick transport of the oxygen to the catalyst surface. The reactor was placed in a water bath at constant temperature, which was controlled by a thermostat. The reaction temperature itself was monitored with a thermocouple inside the reactor. The pressure inside the reactor was shown by a pressure gauge. For the catalytic activity experiment, the solvent 100 mL DI-H₂O with NaOH (c= 0.04M) was divided and 80 mL inserted into the glass reactor. Then the catalyst (0.2g) was added and the solution with the dispersed catalyst heated under continuous stirring until the desired temperature of 50°C was reached. Then the reactant 1,2- propanediol c= 0.15M which was dissolved in 20 mL of the solvent, was added. After stirring for one minute the first sample was taken which marked the initial start of the reaction t=0. Samples were taken at regular intervals and analysed by HPLC (see 3.3.6). The reaction conditions for the oxidation of 1,2- propanediol are listed in the following table (Table 3-13).

Table 3-13: Operating conditions for selective oxidation of 1,2- propanediol.

m_{catalyst}	0.2g	p_{O_2}	1-3 bar
V_{solvent}	0.1L	V_{stirrer}	1000 rpm
$C_{\text{Propanediol}}$	0.15 M	T_{reaction}	50°C
C_{NaOH}	0.30 M	t_{reaction}	300 min

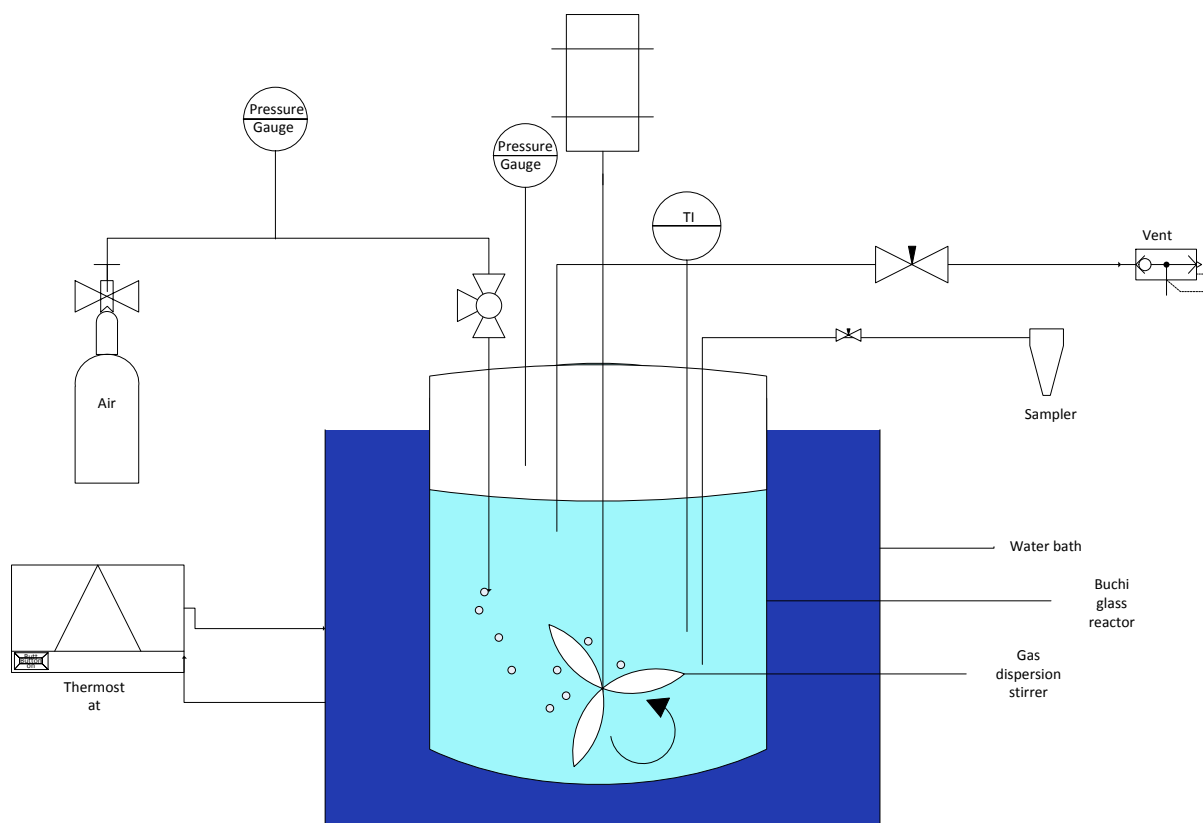


Figure 3-3: Setup of glass batch reactor (Buchi) setup for selective oxidation of 1,2- propanediol.

Selective oxidation of glycerol

A few preliminary experiments were carried out investigating the selective oxidation of glycerol with air under mild conditions. The reactor used was a Parr Instrument stainless steel autoclave operated under atmospheric conditions in batch mode. The reactor setup and conditions can be found in the Appendix.

3.5.2 Reaction calorimetry

A few preliminary calorimetric studies were performed on the selective oxidation of salicyl alcohol to try and determine the heat transfer during the reaction. In general a calorimeter measures the total heat flow rate during a reaction q_{total} (W) and can be expressed as follows [142]:

$$q_{\text{total}} = q_{\text{react}} + q_{\text{mix}} + q_{\text{phase}}$$

3-5

where q_{react} is the reaction heat-flow rate (W), q_{mix} the heat-flow rate occurring due to mixing enthalpies when different fluids are mixed, and q_{phase} is the heat-flow rate due to phase changes (W). The reaction heat flow rate can be expressed as follows (3-6) [143]:

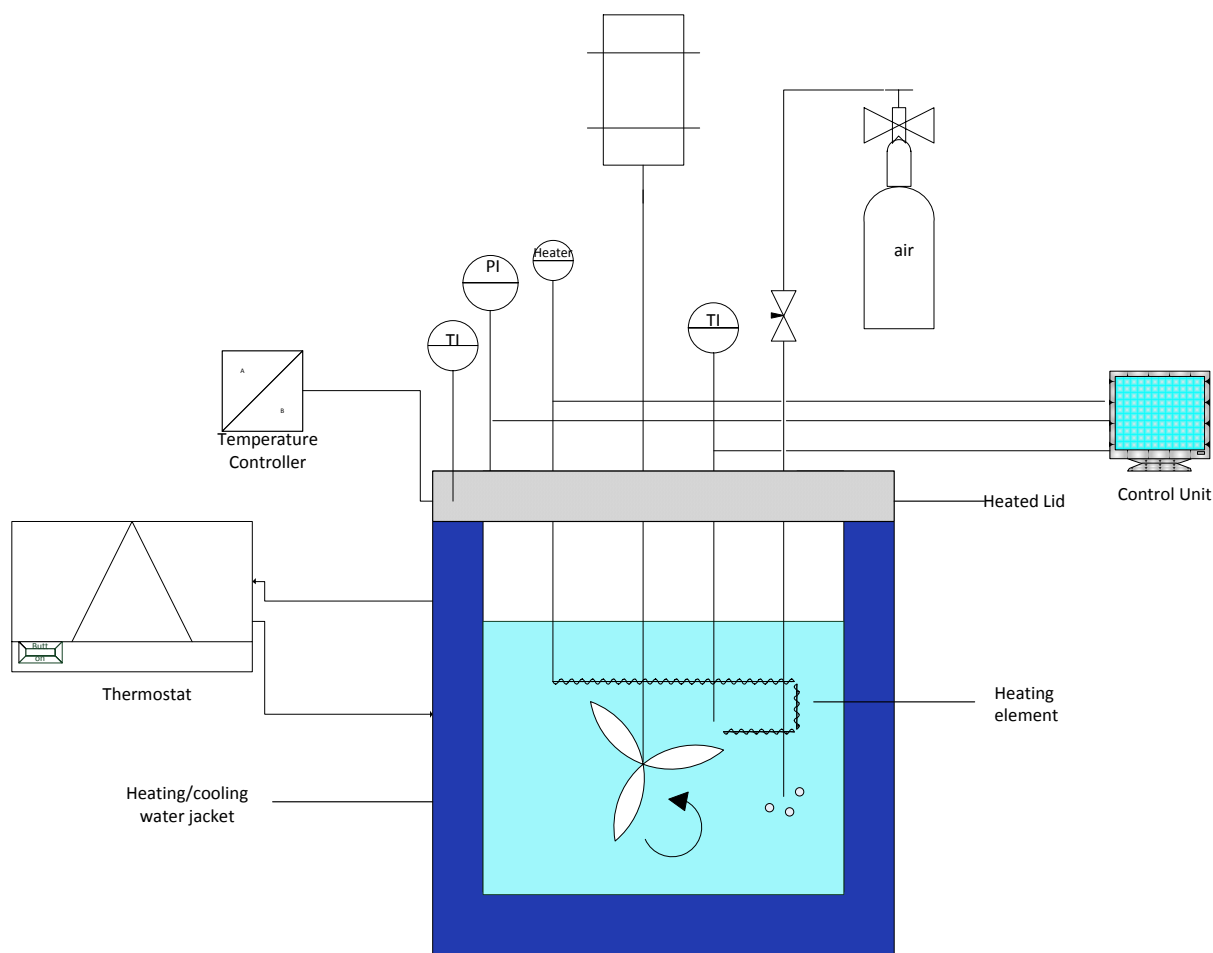
$$q_{\text{react}} = V_r \sum_i d_r H_i \left(\frac{dc_i}{dt} \right) \quad 3-6$$

With V_r presenting the volume of the reaction which is considered constant and ΔH_r being the enthalpy of reaction. For a single step reaction equation with $i=1$ it transforms into:

$$q_{\text{react}} = \Delta_r H^* r_A(t) V_r \quad 3-7$$

The system used was an HEL power compensation reaction calorimeter containing a jacked batch glass reactor and a cooling thermostat operating a constant temperature. The reactor was equipped with an electrical heater and a thermocouple to measure the reaction temperature during reaction. The heat flux of the reaction was measured through the compensation power of the electrical heater used to maintain temperature. The reactor was equipped with a stainless steel lid which was heated to minimise external heat loss. Furthermore the reactor was covered with quartz wool as an external insulation. A gas inlet tube was inserted into the solution to saturate the solvent with oxygen before the reaction.

For a typical experiment with a volume of 30 mL total, the solvent ($\text{H}_2\text{O} + \text{NaOH}$) was divided and 20mL together with the dispersed catalyst were heated in the reactor. The heating temperature was set to 50°C, with the heating lid set to 55°C and the cooling temperature was set to 20°C. It should be noted that due to an faulty heating element, the capacity of the heating element was limited and therefore the temperature could not be reached. The reactor temperature and heating compensation was monitored. At the same time air was dispersed into the solution for about half an hour. Once the temperature was constant the air supply was closed and the reactant salicyl alcohol, dissolved in the remaining 10mL of the solvent, was injected into the solution. A temperature drop was observed upon injecting the reactant. The plot of the monitored power compensation and heat of reaction against time can be found in the Appendix.



E-11

Figure 3-4: Setup for calorimetric experiments for selective oxidation of salicyl alcohol

The experiments did not deliver any quantitative valuable data due to also the limited heat capacity of the heating element.

3.5.3 Trickle Flow reactor

The selective oxidation of salicyl alcohol was carried out under trickle flow conditions. This was done jointly with the MSc student Chieng Ching Chong. Suitable reaction conditions were established based on precedent studies in the batch reactor using a granular type catalyst and also on existing work on the selective oxidation of glycerol in a trickle flow reactor [121]. Several preliminary steps such as the flow rates and calibration, the reactor design and the determination of the trickle flow regime were required before carrying out the experiments, which are outlined in the MSc thesis [144].

3.5.3.1 Reactor Design

The reactor was a stainless steel tube of the dimensions 300 mm × 10 mm which was detachable from the unit. The temperature in the reactor was controlled by a cooling jacket connected to an external thermostat and the reactor inlet temperature was controlled by trace heating the inlet pipes. The product outlet was collected in two sampling vessels which were cooled with circulating cooling liquid to ensure complete condensation of products. The catalyst bed temperature was measured by inserting a thermocouple through the bottom of the reactor until it touched the quartz wool at the interface of the packed bed and glass beads. Fixing a thermocouple inside the catalyst bed was not possible as it would risk disrupting the trickle flow. To minimise heat loss the entire reactor and the feed lines were well insulated to avoid heat loss before entering the reactor.

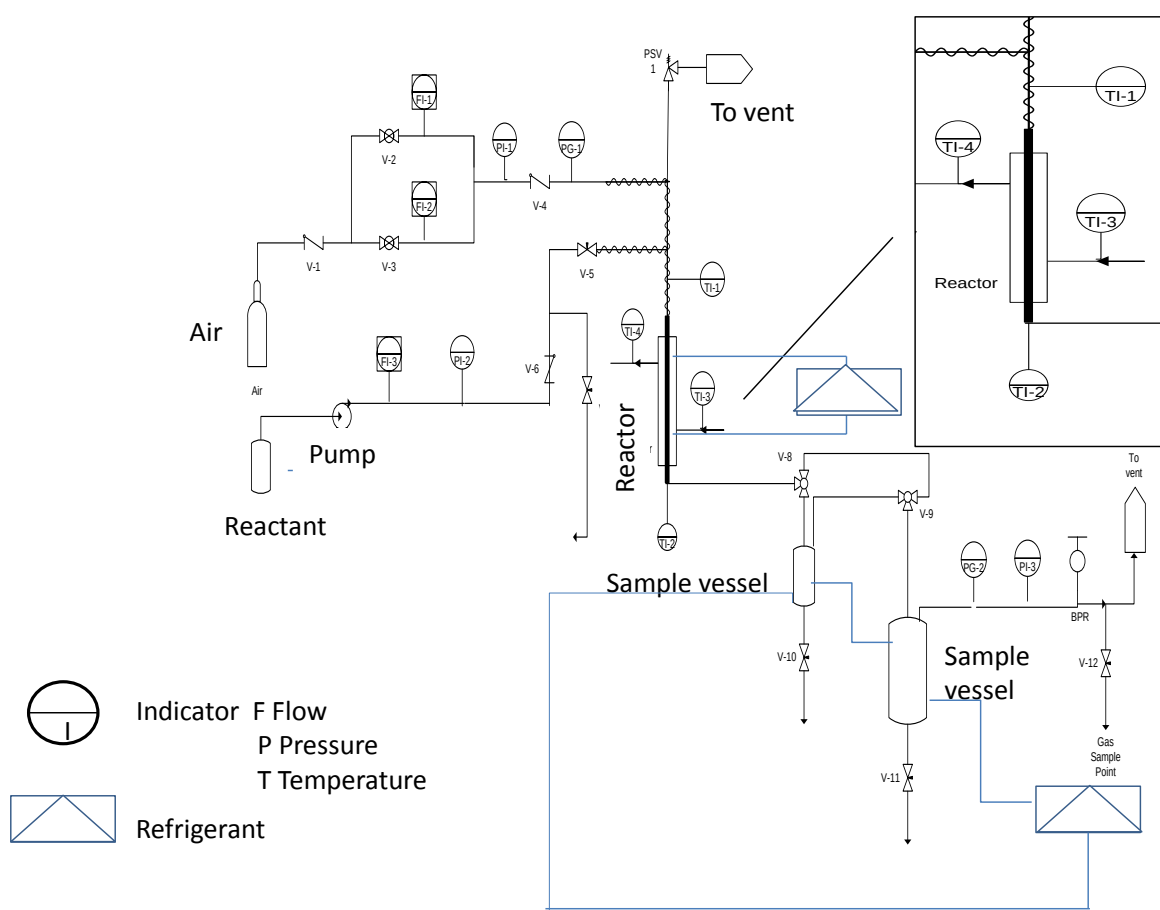


Figure 3-5: P and ID diagram for the TBR reactor

1) Catalyst loading

For a uniform heat transfer, the catalyst bed was placed in the centre of the reactor and packed with silica carbide and quartz wool. The catalyst itself approximately 1g of the catalyst 1.5Au/C

was diluted with silica carbide to 10 mL which acted as an inert material. Glass beads were used on either side of the catalyst bed to ensure that the fluid was preheated to the desired reaction temperature before it entered the catalyst bed.

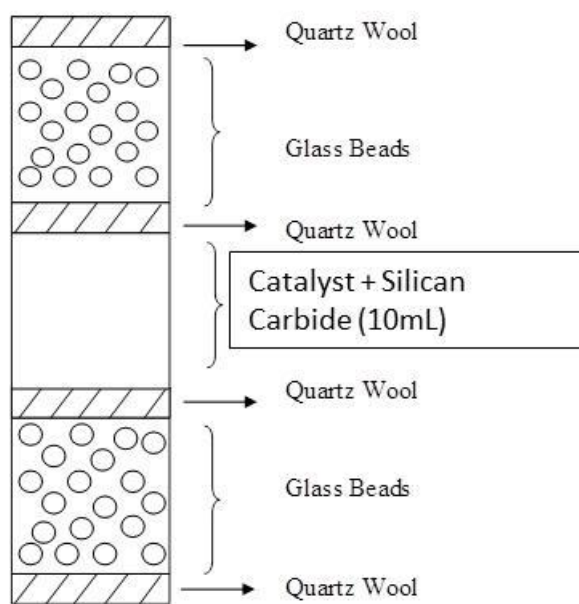


Figure 3-6: Scheme of packed reactor for TBR system.

2) Reactor start up

The reactor was connected and the water was pumped through the jacket until the desired temperature was reached. The temperature of the inlet flow was set through the PID controlled pre-heater. The refrigeration unit was set to 4 °C to ensure full condensation of the products in the collection vessels. The gas flow rates of air and N₂ were set to reach the desired oxygen partial pressure. Experimental studies investigating the influence of pressure have led to an optimal operating total pressure of 8 bar.

3) Reactor operation

After reaching steady state, the sampling vessels were drained. For the first sample, the product was collected over a period of 1 hour. Then the valve of the vessel was opened carefully to collect the sample in a tube. The vessel was drained again. In case of the formation of gaseous

products, the gas was collected using a 0.5 L gas sampling bag. The following table summarizes the different operating conditions applied for the set of experiments.

Table 3-14: Operating conditions for runs in Trickle Flow Reactor.

$T (^{\circ}\text{C})$	(bar)	LHSV (h^{-1})	$L' (\text{mL min}^{-1})$	$G' (\text{mL min}^{-1})$	$\text{O}_2\text{:Alcohol}$
80	1.68	1	0.17	108	131
40	0.21	1	0.17	96	131
60	0.21	1	0.17	102	131
80	0.21	1	0.17	108	131
40	0.105	1	0.17	96	65
40	0.21	1	0.17	96	131
40	0.42	1	0.17	96	261
40	0.21	0.5	0.08	96	261
40	0.21	1	0.17	96	131
40	0.21	2	0.33	96	65

After every run, the reactor was removed and the packing emptied. The system and sampling vessels were flushed with DI- H_2O to remove any remaining residues of previous runs. The liquid samples were analysed by HPLC. The sample preparation and analysis were carried out according to 3.5.1 for the batch reactor studies.

It was assumed that the Trickle Flow Reactor operates as a Plug Flow Reactor thus the following expression was applied:

$$F_{A0} \frac{dX}{dV} = -r_A \quad 3-8$$

$$-\ln(1 - X) = k \frac{V}{L'} = k\tau \quad 3-9$$

whereby L' is the liquid flow rate of alcohol in mL min^{-1} while τ is the residence time of the reactant in the reactor.

3.5.4 Calculating catalyst activity

The following section gives the general equations utilised for the calculation of the catalytic activity.

The conversion X of the reactant and the selectivity S_i towards a product and the yield (Y) are calculated the following:

$$X = \frac{c_0 - c_t}{c_0} * 100\% \quad 3-10$$

with c_0 being the concentration of the reactant at $t=0$ and c_t the concentration of the reactant at a specific time. The selectivity is expressed as

$$S_i = \frac{c_i}{\sum_j c_j} * 100 \quad 3-11$$

The yield of the respective component i is obtained the following:

$$Y_i = S_i * X \quad 3-12$$

The turnover frequency number is defined the number of times n that the overall catalytic conversion takes place per catalytic site per unit time, for a fixed set of reaction conditions. In this context, the number of active sites corresponds to the amount of metal loading on the catalyst surface ^[145].

3-13

4 AU/C FOR SELECTIVE OXIDATION OF SALICYL ALCOHOL

4.1 Chapter introduction

This chapter presents a broad and fundamental study of the gold on carbon (Au/C) catalyst system and its application on the main model reaction, the selective oxidation of salicyl alcohol. All reaction components are water soluble, so that the reaction could be performed in aqueous solution under mild conditions. The first task was to set up a suitable reactor system and optimise the conditions for carrying out the experiments and to ensure that consistent and reliable data were obtained. This included the application of a suitable catalyst preparation method which delivered the desired properties for the Au/C catalyst system i.e small and finely dispersed gold particles. For the Au/C catalyst system, the synthesis chosen was sol-immobilisation using THPC (tetrakis(hydroxymethyl)phosphonium chloride) as organic stabiliser, which has not been as commonly applied ^[141] as compared to other methods ^[146] ^[147] ^[148] ^[149].

1. Parametric study

The reaction was performed under mild conditions in a baffled glass stirred batch reactor under continuous flow of air. The typical course of reaction for the selective oxidation of salicyl alcohol with the products obtained on the selected Au/C reference catalyst are discussed. Furthermore, the general carbon mass balance of the reaction is evaluated as well as the catalytic performance quantified by introducing conversion/selectivity rates and turnover frequencies. Based on this type of evaluation, all following catalyst performances are assessed. In the set of tasks, the investigation of the influence of reaction conditions and parametric factors is presented. This study was essential to identify any mass transport limitations and set the suitable reaction conditions. Hereby, the influences of stirring speed, reaction temperature T , oxygen partial pressure pO_2 , pH and catalyst mass are assessed. The results are evaluated in the context of previous published studies on related selective oxidation reactions.

2. Investigation of kinetics and mechanism

After establishing the reaction conditions, studies were extended to investigate the kinetics and the mechanism of the reaction. Hereby, it was important to identify the order of reaction and the type of mechanism involved i.e. parallel or consecutive for the formation of products. The results are discussed and initial rates of reaction are used for activity evaluation. A kinetic equation based on sequential first order reaction has been tried to fit to the experimental data in order to determine the rate constants k_1 and k_2 . The study further extends to the investigation the effect of product addition on the rate of reaction. Possible adsorption effects or other side reactions influencing the catalytic performance are discussed.

In a different approach to determine the kinetics, reaction calorimetry was used as technique to study the thermochemistry of the reaction. However, based on limitations of the reactor setup this approach did not deliver valuable results. For the future outlook it is an attractive technique, which is described in the Materials and Methods chapter, to evaluate the kinetics and mechanism of the reaction. The general reaction profile (power compensation and reaction temperature against time) can be found in the Appendix.

3. Study of catalytic effects

The third part of this study focuses on the catalytic effects of the Au/C system on the selective oxidation of salicyl alcohol. Hereby, the impact of the gold particle morphology on the catalytic performance is thoroughly investigated. Effects such as the catalyst preparation method, reproducibility as well as treatment temperature and metal loading are studied. A range of characterisation techniques were utilised to determine the physical chemical properties (surface area and pore size and volume) of the catalyst and the surface morphology in particular the gold particle size and distribution. The catalyst characterisation data is essential to explain and discuss the overall catalytic effects on the selective oxidation of salicyl alcohol.

In an extended study of the catalytic effects the influence of the support was investigated and is discussed, for which a few conventional oxide supported catalysts such as Au on CeO_2 and TiO_2 were synthesised and applied for selective oxidation of salicyl alcohol. The catalyst systems were characterised and the structural morphology as well as the performance compared with the carbon supported catalysts.

4.2 Reaction network and study of parametric effects

This section discusses the typical reaction network for the selective oxidation of salicyl alcohol. As illustrated in the introduction, the partial oxidation of salicyl alcohol leads to the formation of its higher oxygenates salicyl aldehyde and salicylic acid as presented in Figure 4-1:

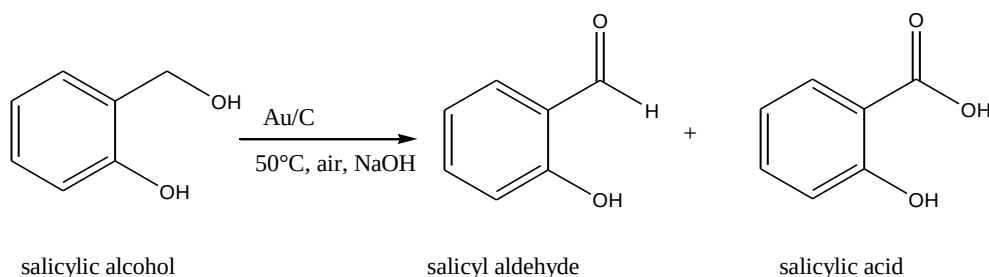


Figure 4-1: General reaction for selective oxidation of salicyl alcohol.

In general, the selective oxidation of salicyl alcohol gives two products: salicyl aldehyde and salicylic acid, which is in agreement with previous studies on this reaction ^[137]; no other products in the liquid or gas phase were detected. The mass balance was 95-100% at all stages of the reaction. The following figure illustrates a typical course of reaction of all detected components for the selection of salicyl alcohol on 1.5wt% Au/C (1.5Au/C) in the presence of base in water at 50°C.

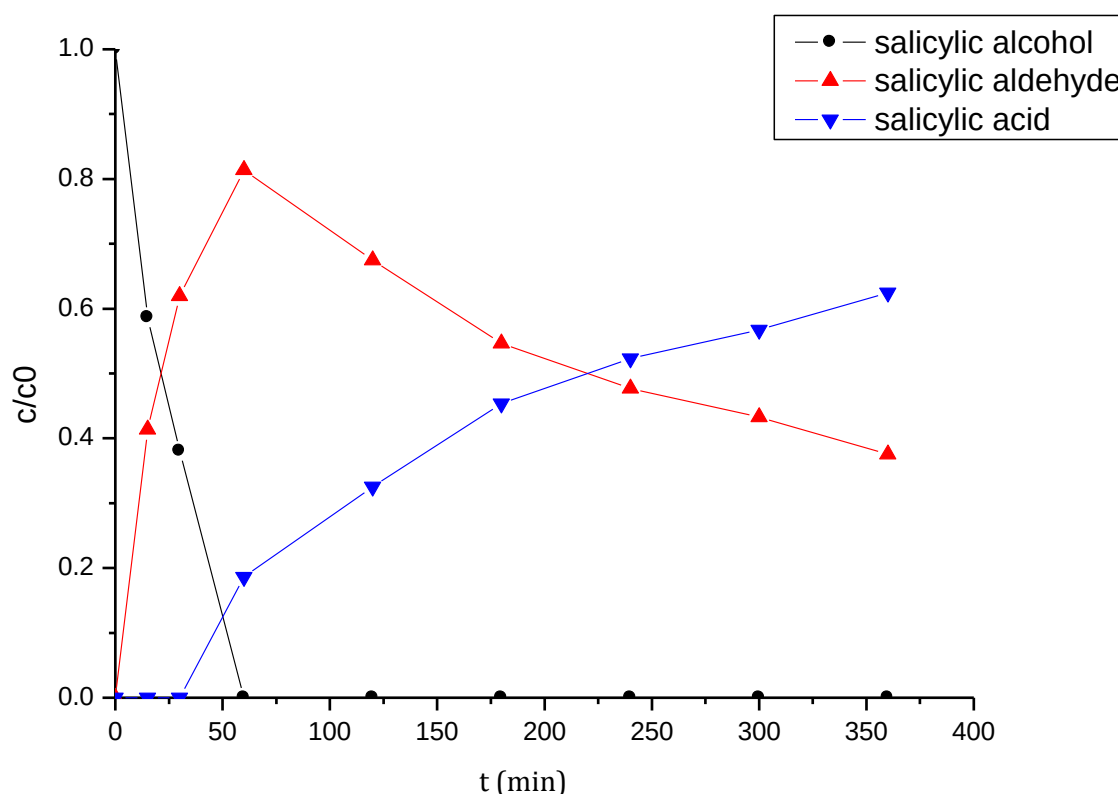


Figure 4-2: Course of reaction for typical experiment for selective oxidation of salicyl alcohol, reaction conditions: $T=50^{\circ}\text{C}$, $p_{\text{total}}=1\text{bar}$ (air), catalyst 1.5Au/C , $m_{\text{cat}}=0.2\text{g}$, $c_{\text{salicyl alcohol}}=0.04\text{ M}$, $\text{NaOH: salicyl alcohol}=2:1$, $\text{rpm}=1000$.

In this graph, the normalized concentration c/c_0 is plotted against the reaction time. Samples were taken at specific intervals during the reaction giving typically 7-9 data points per run. There is only a slight imbalance of concentration of salicyl alcohol at the beginning of the reaction $t=0$, which is probably caused by adsorption on the catalyst support surface. However, this was within the mass balance of 95-100%. The concentration of salicyl alcohol shows full conversion after 60 minutes.

It can also be seen that the formation of salicyl aldehyde is detected already at the beginning of the reaction whereas the formation of salicylic acid only appears at higher conversions of salicyl alcohol. At higher conversion it can also be seen that salicyl aldehyde reaches a peak concentration and then decreases while the concentration of salicyl acid increases at the same time indicating a possible sequential reaction, where salicyl aldehyde gets oxidised further to salicylic acid. At lower conversions, the amount of salicyl alcohol converted in a specific amount of time corresponds to the amount of salicyl aldehyde produced within the same time. This occurs therefore at the same rate which means that the reactant salicyl alcohol directly forms

salicyl aldehyde within the limits imposed by the carbon balance. The results demonstrate an overall higher efficient conversion reaction and carbon economy compared to the previous studies by Milone et al. [^{137, 138}] who observed a negative carbon balance from the beginning of the reaction of 20 wt% caused by adsorption of the reactant. Furthermore, for catalysts with higher gold loading >1wt %, they reported that the yield of salicyl aldehyde decreased due to adsorption on the catalyst surface.

In order to analyse and compare the impacts and effects on the catalyst performance for the series of experiments, the initial rates at $t=0$ were determined as there was no product influence and could therefore be directly obtained (see Appendix). Furthermore, to quantify the catalytic performance, the catalytic activity was expressed in conversion mostly after the reaction time at 360 min X_{t360} % and selectivity towards salicyl aldehyde at the time t or at a specific conversion X . In order to compare the catalytic performance of catalyst systems with different metal loadings, the initial turnover frequency number TOF h^{-1} was used which was defined as the moles of product (salicyl aldehyde) formed within the first 0.5h per number of total active metal sites on the support. In this case the total moles of active metal Au on the support was used (see also Materials and Methods).

4.2.1 Influence of stirring

It was important to ensure good mixing to avoid the formation of concentration or temperature gradients and to keep the catalyst in suspension. Therefore, the reactor was equipped with an overhead stirrer which could be operated at a high stirring speed of 1200 rpm and which had a stirring propeller with specified dimensions in order to ensure vigorous mixing of the reaction solution. Furthermore, as explained in the Materials and Methods section, the reactor was equipped with four baffles in order to break the boundary layer adjacent to the reactor wall, enhance the mixing and thus avoid the formation of so-called 'dead zones'. Furthermore, the high stirring speed was also necessary to disperse the air bubbles in the solution to ensure a maximum surface at the gas/liquid interphase. The stirring rate was set to 1000 rpm based on reference studies on the variation of the stirring speed for similar reaction systems in water, such as the selective oxidation of glycerol [¹⁴¹]. Studies showed that stirring speed rates of >600 rpm were sufficient to ensure a homogeneous mix of the solution [¹⁵⁰].

4.2.2 Influence of mass of catalyst

As the selective oxidation of salicyl alcohol was based on a gas-liquid-solid reaction system, it was important to identify any mass transport limitations. These limitations can occur at the gas/liquid or liquid/solid interphase. Therefore, the influence of the catalyst loading in the reaction on the initial rate of reaction for the selective oxidation of salicyl alcohol was studied. For this purpose, the catalyst mass was varied between 0.1-0.4 g while keeping all other reaction conditions constant. In a regime without mass transfer limitation, when the rate is controlled by the chemical reaction, the initial rate of reaction should increase proportionally with the catalyst mass which should result in a linear plot going through the origin. Figure 4-3 shows a plot of $1/\text{initial rate of reaction}$ against $1/\text{mass of catalyst}$ [151] [152].

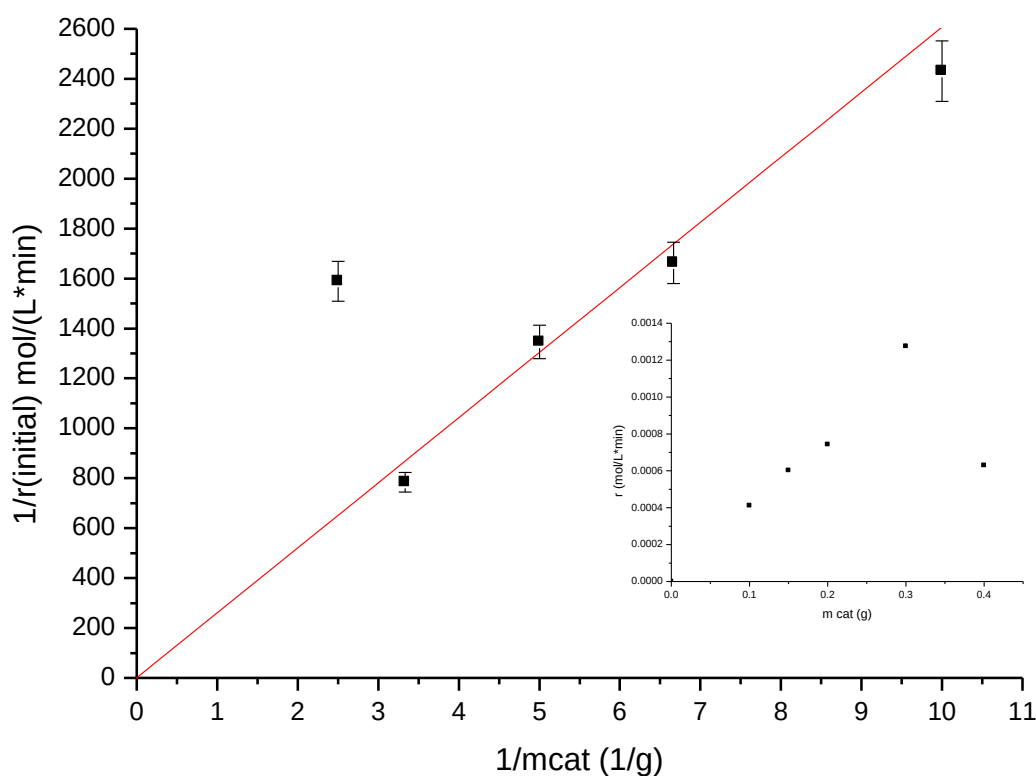


Figure 4-3: Mass transport limitation studies on the selective oxidation of salicylic alcohol, $1/r(\text{initial})$ vs $1/m_{\text{cat}}$, reaction conditions: $T=50^\circ\text{C}$, $p=1\text{ bar}$ (air), catalyst 1.5Au/C, $m_{\text{cat}}=0.1\text{-}0.4\text{ g}$, $C_{\text{salicyl alcohol}}=0.04\text{ M}$, NaOH: salicyl alcohol= 2:1, rpm= 1000. The inserted small plot illustrates rate r vs mass of catalyst m_{cat} .

The plot shows a linear graph going through zero for a catalyst mass range of 0.1-0.3g. When increasing the catalyst mass to 0.4g the value for the rate of reaction strongly deviates. In case of presence of mass transport limitations, the graph would lead to an interception. However, the rapid decrease in rate can be caused by an interplay of combined factors: one possibility might

be the poor catalyst suspension in the reactor, decreasing the liquid/solid interphase and therefore the overall rate. Another effect could be based on transport limitations at the gas/liquid interphase i.e the transport of molecular oxygen into the liquid is much slower compared to the reaction. Therefore, the role of the oxygen partial pressure was analysed and will be discussed in the following section. The results demonstrate that for the operating conditions and catalyst loading used in the experimental series, the reaction was clearly in a non-transfer limited regime and therefore kinetically controlled.

4.2.3 The role of oxygen partial pressure

The next step was to investigate the role of the oxygen partial pressure on the reaction. This work was done jointly with the MSc student Chieng Ching Chong in the Buchi autoclave, which allowed to run the experiments at increased pressure (see Materials and Methods).

Previous studies on the role of oxygen have demonstrated its importance in the mechanism for selective oxidation of alcohols, based on regenerating the OH species and re-oxidising the metal-hydride species, which is discussed in detail (section 4.3).

In a separate experiment, it has been shown that no significant activity is observed in the absence of oxygen. For the catalytic experiments, the air is sparged into the solvent before the reactant is injected, in order to saturate the solution. The air is kept at a continuous flow at atmospheric pressure throughout the reaction and it is assumed that the solvent stays saturated. The concentration of oxygen is therefore constant compared to the concentration of the reactant. The reaction remains first order in the concentration of the reactant. However, the dependency of the rate of reaction on the oxygen partial pressure was evaluated experimentally by changing the total pressure of air and measuring the initial rate of reaction. This was also important in order to verify whether there were any underlying limitations, i.e diffusion controlled processes of the oxygen transport through the bulk phase on to the catalyst surface.

The initial reaction rate in dependency of the oxygen partial pressure is illustrated in Figure 4-4.

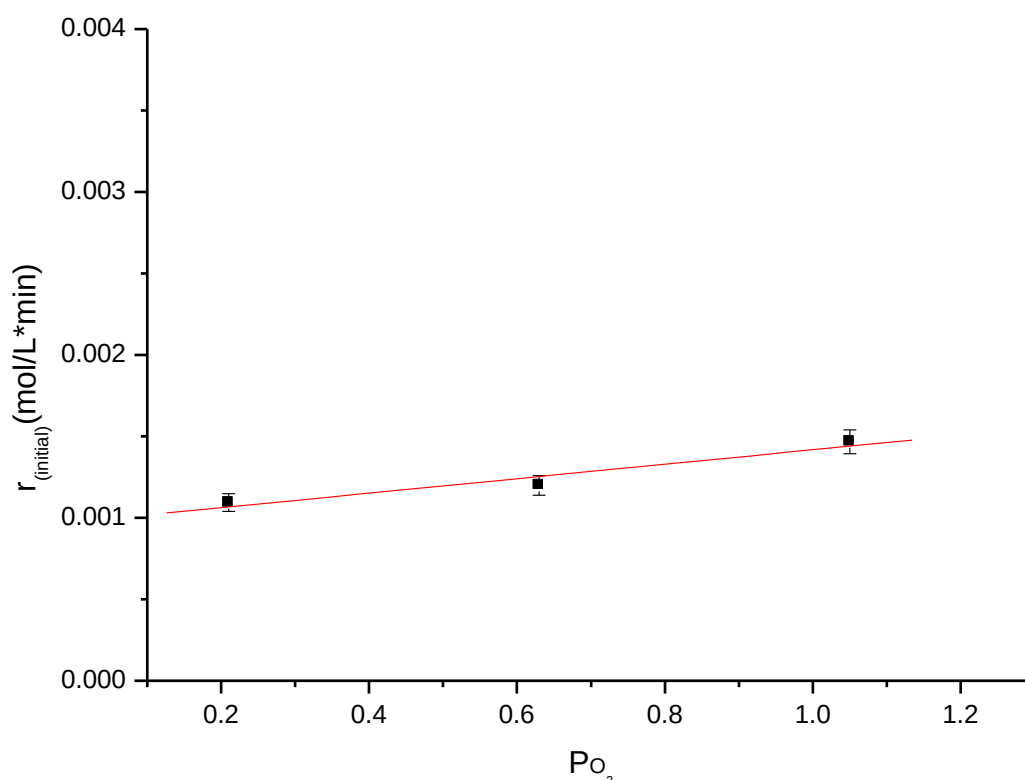


Figure 4-4: Rate of reaction as function of oxygen partial pressure with standard error — linear fit function, reaction conditions: $T=50^{\circ}\text{C}$, $p_{O_2}=0.21\text{--}1.05$ bar, catalyst 1.5Au/C , $m_{\text{cat}}=0.2\text{g}$, $c_{\text{salicyl alcohol}}=0.04\text{ M}$, $\text{NaOH: salicyl alcohol}=2:1$, $\text{rpm}=1000$.

The data shows only a slight increase in the initial rate of reaction within the first 15 minutes with a slope of 0.011 from the inset (see Appendix) when the oxygen partial pressure is increased from 0.2 to 1.05 bar. Theoretically, the oxygen solubility in water is approximately 6 mg/L (1.9×10^{-4} mol/L) at 35°C [153]. The initial rate of reaction is 1.1×10^{-3} mol/L*min. This means that the converted concentration of reactant is 6 times larger than the concentration of the dissolved oxygen at atmospheric pressure. When increasing the partial pressure of oxygen to 1.05 bar, the concentration of dissolved oxygen increases, however, the rate of reaction seems nearly unaffected. This might indicate that the oxygen is not directly involved in the reaction mechanism and that the diffusion of oxygen onto the catalyst surface is not the rate limiting step. The mechanistic role of the oxygen will be discussed in 4.3.4. The study has demonstrated that the selective oxidation of salicyl alcohol is essentially independent of the oxygen partial pressure. It has further been demonstrated that the increase in oxygen partial pressure did not affect the selectivity towards the product salicyl aldehyde. Additionally, the air was sparged at a gas flow rate of $50\text{ cm}^3/\text{min}$ through a microporous frit in order to achieve a

high dispersion of small air bubbles in the liquid phase increasing the gas/liquid interphase. Tests without the application of the microporous frit have shown that the initial rate of reaction was slightly lower due to the larger bubble size. It was concluded that with the microporous frit in place and the high stirring speed, an increase in the oxygen flow rate would not enhance the rate of reaction as there were no apparent mass transport limitations of the gas into the liquid, and the oxygen solubility is maintained throughout the reaction.

4.2.4 Influence of temperature

The effect of temperature on the rate was studied by varying the reaction temperature and monitoring the impact on the conversion. The work was done jointly with the MSc student Chieng Ching Chong. To evaluate the dependency of the rate constant on the temperature, the Arrhenius plot was used which is given in the Appendix. The slope indicates a proportional correlation of the reaction rate with the temperature. The activation energy determined was 56.98 kJ/mol. The value is in accordance with previous findings by Milone et al. on the selective oxidation of salicyl alcohol on Au/ Fe₂O₃ [137] which is shown in the following table:

Table 4-1: Experimentally determined Activation Energy EA with standard error.

E _A experimental [kJ*mol ⁻¹]	SE E _A [kJ*mol ⁻¹]	E _A literature [137] [kJ*mol ⁻¹]
56.98	8.456	54.34 to 62.70

For heterogeneous catalysed reactions in the liquid phase, the values of activation energy are typically between 50-100 kJ*mol⁻¹. Studies on the activation energy for the oxidation of benzyl alcohol carried out in the liquid phase have reported values of 42 kJ*mol⁻¹ showing that the results achieved here were in a comparable range [55].

4.2.5 The pH

Research on the selective oxidation of alcohols on gold based catalyst systems, particularly on activated carbon, have demonstrated the necessity for the presence of a base. This was based on studies on the mechanism in which the hydroxide ions of the base alleviated the hydrogen abstraction of the alcohol. Studies have shown that this step was found to be rate determining to the reaction [114], [5]. This was supported by other studies on the oxidation of glucose over gold supported on carbon which have shown that the alcohol molecule was not able to adsorb on the carbon supported gold surfaces. Therefore, the initial deprotonation was necessary to initiate the first step and adsorb the alcohol onto the catalyst surface.

For the study of the selective oxidation of salicyl alcohol, NaOH was used as it was a strong base and easy soluble in water. The dependency of the initial rate of reaction on the base concentration was investigated. For this purpose, the ratio of the base NaOH to reactant was varied and the influence on the conversion detected (Figure 4-5). For all concentrations of base, the mass balance reached was 95-100%.

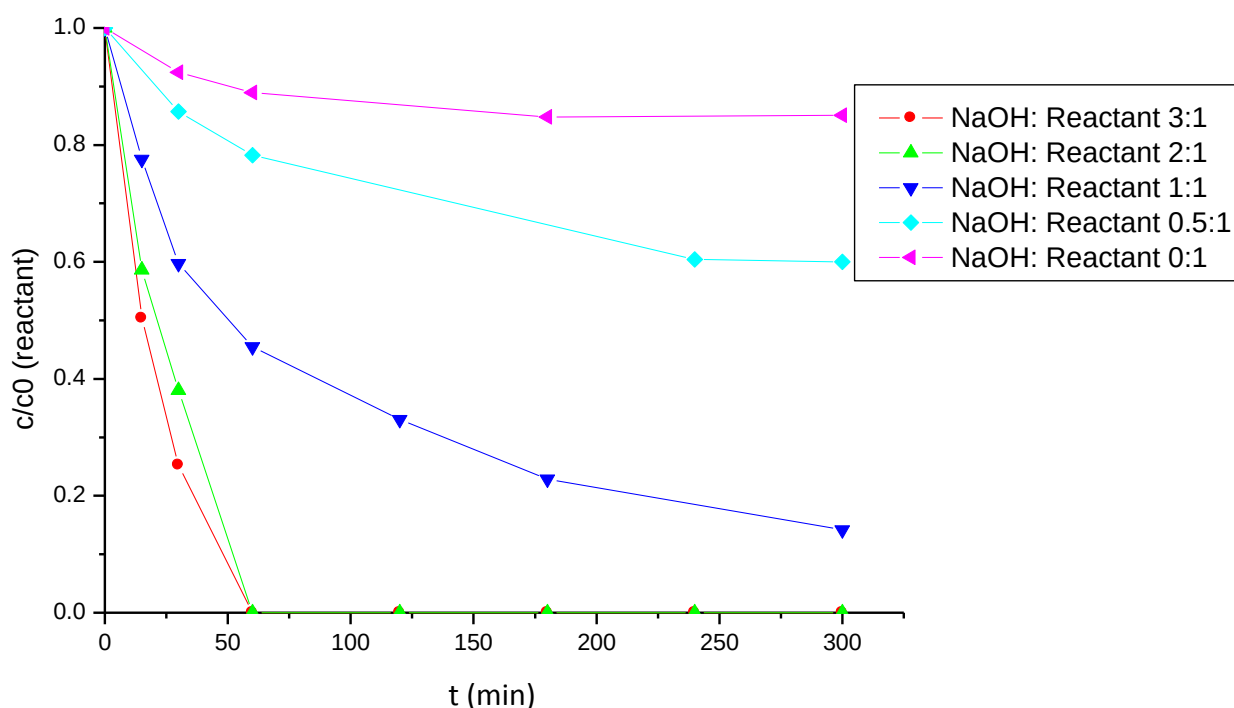


Figure 4-5: Influence of NaOH/substrate ratio on conversion, $T=50^{\circ}\text{C}$, $p=1$ bar (air), $\text{cat}=1.5$ Au/C, $m_{\text{cat}}=0.2\text{g}$, $c_{\text{salicyl alcohol}}=0.04\text{M}$, NaOH: salicyl alcohol: 3(●), 2(▲), 1(▼), 0.5 (◆), 0(◄), rpm = 1000.

The results demonstrate a strong influence of the base concentration on the conversion rate of salicyl alcohol for the investigated ratio of NaOH/reactant 0-3/1. At a ratio of 2 :1 NaOH: salicyl alcohol the rate of conversion approaches nearly a maximum. A further increase in base does not enhance the activity significantly. This is illustrated in the following figure showing the plot of initial rate of reaction against the concentration of base NaOH:

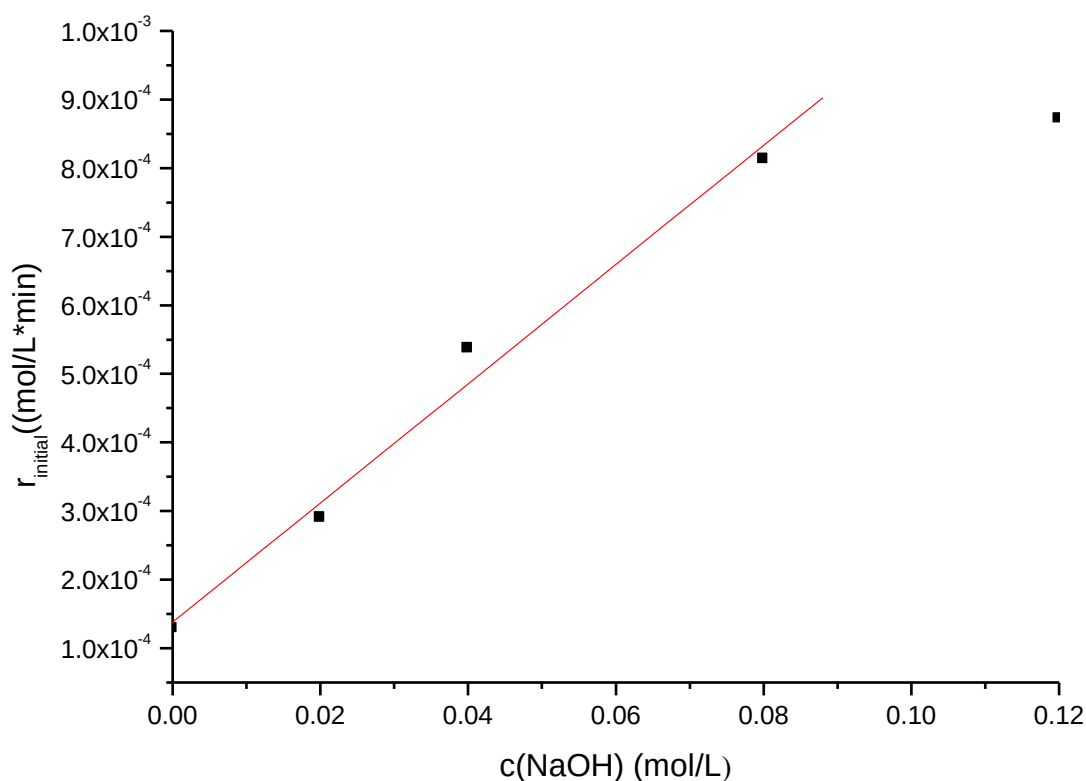


Figure 4-6: Dependency of initial rate of reaction on NaOH concentration, reaction conditions: T=50°C, p=1 bar (air), cat=1.5 Au/C, m_{cat}= 0.2g, c_{salicyl alcohol} = 0.04M, rpm=1000.

However, the base concentration did not affect the selectivity towards salicyl aldehyde at comparable conversion levels. The conversion/ time plots are given in the Appendix. The amount of base used for the experimental series for the selective oxidation of salicyl alcohol is 2:1 NaOH, ensuring high conversion rates. This study has shown the necessity of the presence of a base for carbon supported gold based catalyst system, as it has been already reported in other studies on comparable selective oxidation reactions on gold catalysts in the aqueous phase [141]. Milone et al. [138] found that, for the selective oxidation of salicyl alcohol on AuFe catalysts, the reaction rate was independent of the pH in the bulk medium and therefore claimed the activation of the alcohol molecule occurred solely on the catalytic surface. However,

the solution was mostly buffered with Na_2CO_3 leading to a basic reaction medium. In neutral solution, the pH decreased due to the formation of salicylic acid. In order to verify the impact of the formation of salicylic acid, the pH was measured during the course of reaction, as OH^- species were likely to be consumed through the formation of salicylic acid and subsequent deprotonation of the acid. In addition, the OH^- species involved in the initial deprotonation of the reactant, were supposedly regenerated on the catalyst surface according to the mechanism (see 4.3.4). However, a decreased regeneration rate of OH^- species could cause an effect of overall pH. Other reported studies on comparable systems, such as the selective oxidation glycerol under mild conditions, have carried out the experiments under control of pH via titration, due to the formation of glyceric acid lowering the overall pH [141]. The following graph illustrates the change in concentration of OH^- ions determined via the measurement of the pH of the reaction solution for the selective oxidation of salicyl alcohol with a ratio of NaOH :salicyl alcohol 2:1 against the concentration of salicylic acid formed during the reaction. The error bar for the OH^- concentration is based on the relative measurement error of the pH.

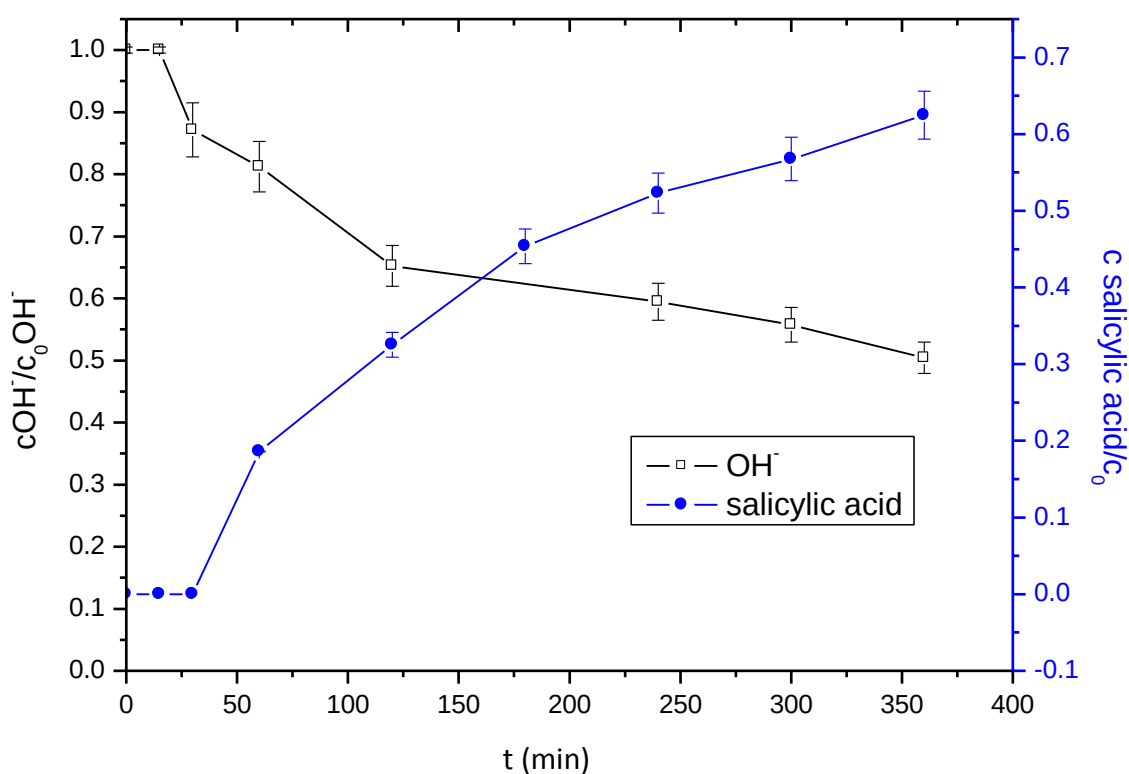


Figure 4-7: Profile of OH^- concentration and salicyl acid formation for selective oxidation of salicyl alcohol, reaction conditions: $T = 50^\circ\text{C}$, $p = 1\text{ bar}(\text{air})$, cat 1.5Au/C mcat=0.2g, NaOH : salicyl alcohol: 2:1, rpm= 1000.

The results show that the amount of hydroxide ions in the bulk solution decreases over time to approximately 50% of the initial OH^- concentration. The plot suggests that the formation of salicylic acid consumes the hydroxide ions, due to the strong acidic nature of salicylic acid ($\text{pK}_\text{a}=2.75$ [154]). Further, for the deprotonation of salicyl alcohol, the OH^- -species are possibly consumed faster than they are regenerated causing an overall decrease in pH. Another reason might be the adsorption of OH^- on the catalyst surface already at the beginning of the reaction when salicylic acid is not yet formed. The adsorbed OH^- could still act in the catalytic cycle. However, as pointed out earlier in Figure 4-5, a higher increase in NaOH in solution to 3:1 does not increase the initial rate of reaction significantly. The effect of decrease in pH could, also impact the further oxidation of salicyl aldehyde to salicylic acid.

An alternative approach was investigated by using Na_2CO_3 as base additive and buffer instead of NaOH. The use of the buffer Na_2CO_3 had also been reported in previous studies on the selective oxidation of salicyl alcohol by Milone et al., carrying out studies in a pH range of 7-11 and claiming that the conversion of salicyl alcohol was not influenced by the basicity of the solution [137]. Here, however, the initial rate of reaction achieved with the 1M Na_2CO_3 solution was much lower compared to the NaOH catalysed reaction. The effective pH reached with 1M Na_2CO_3 was lower compared to 0.08M NaOH due to the weaker basicity. The poorer solubility, however, limited the amount of Na_2CO_3 to be applied for this reaction.

The lack of the amount of initial OH^- ions could therefore result in a lower catalytic activity. Additionally, the CO_3^{2-} ion could possibly involve in the catalytic cycle by adsorbing on the catalyst surface and blocking active sites.

4.3 Kinetics and mechanism

4.3.1 Order of reaction for selective oxidation of salicyl alcohol

Based on the studies of the parametric influences on the reaction rate it was shown that under the conditions used, the measured concentration of the reactant followed first order kinetics in the concentration of salicyl alcohol [SalOH]. The following equations give the mechanistic steps of oxidation of salicyl alcohol to salicyl aldehyde including the oxygen activation (4-1) the deprotonation of salicyl alcohol (4-2) and the β -hydride elimination to form salicyl aldehyde (4-3):



With SalOH being salicyl alcohol, SalO⁻ being the deprotonated form of the alcohol and SalCHO being salicyl aldehyde. Assuming 4-1 and 4-2 are in equilibrium, 4-3 is the rate determining step which involves the β-H abstraction to form aldehyde:

$$r = k_3 [\text{SalO}^-] \cdot \theta_{\text{O}}^2 \quad 4-4$$

With θ_{O} being the coverage of molecular oxygen on the catalyst surface.

$$K_2 = \frac{K_{\text{O}_2} P_{\text{O}_2}}{(1 + K_{\text{O}_2} P_{\text{O}_2})^2} \quad 4-5$$

and the equilibrium constant via 4-2 leading to the following term:

$$K_2 = \frac{[\text{SalO}^-]}{[\text{OH}^-][\text{SalOH}]} \quad 4-6$$

The following expression for the rate of reaction is obtained:

$$r = k_3 K_2 [\text{OH}][\text{SalOH}] \frac{K_{\text{O}_2} P_{\text{O}_2}}{(1 + K_{\text{O}_2} P_{\text{O}_2})^2} \quad 4-7$$

Once the concentration $[\text{SalO}^-] \gg [\text{SalOH}]$ then the rate becomes only dependent on the concentration of the alcohol. The amount of base $[\text{OH}^-]$ was in excess compared to the amount of salicyl alcohol. The following expression can be used for expressing the first order rate equation with $[A]$ being the concentration of the reactant salicyl alcohol:

$$[A] = [A]_0 \exp(-k_1 t) \quad 4-8$$

By taking the logarithm from equation the linear form was obtained:

$$\ln \frac{[A]}{[A]_0} = -k_1 * t \quad 4-9$$

By plotting the term $-\ln(1-X)$ for salicyl alcohol against the reaction time the rate constant k can be obtained from the slope:

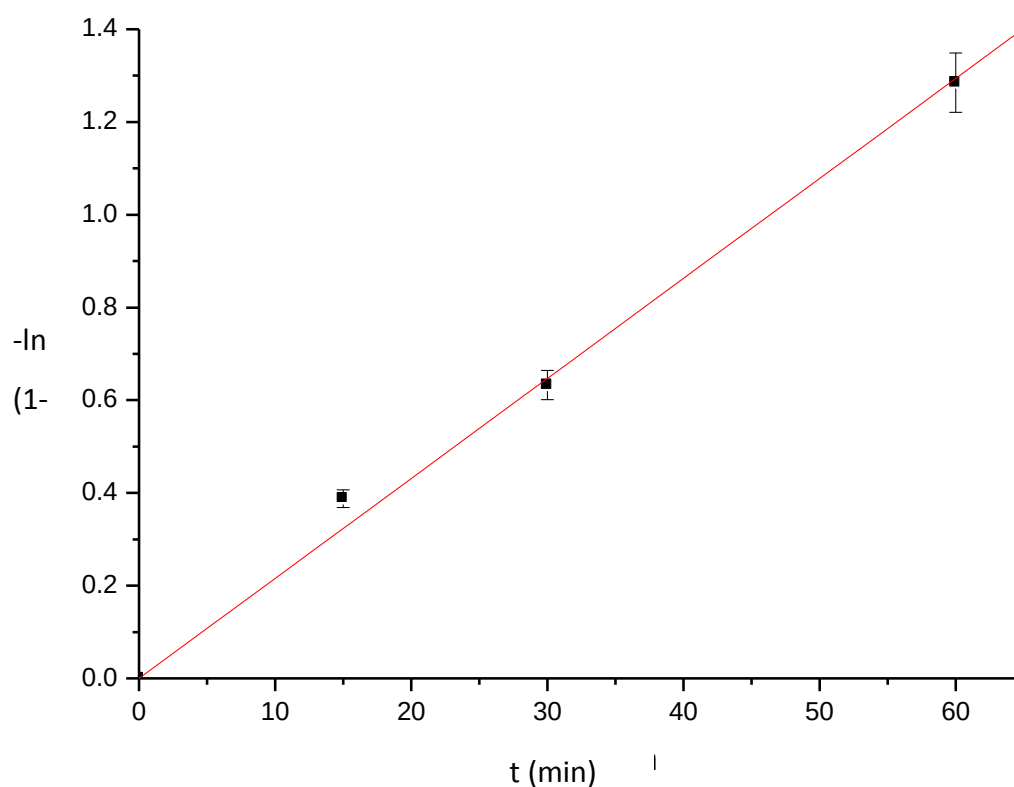


Figure 4-8: Plot of first order rate equation based on concentration of salicyl alcohol with standard error — fit function, reaction conditions: $T=50^{\circ}\text{C}$, catalyst 1.5Au/C, $m_{\text{cat}}= 0.2\text{g}$, $p=1\text{ bar (air)}$, $c_{\text{reactant}}= 0.04\text{M}$, NaOH: reactant= 2:1, rpm=1000.

The results are also in accordance with the studies by Milone et al. [137] who demonstrated a first order dependence of the rate of reaction on the concentration of the reactant. Studies on the selective oxidation of benzyl alcohol on gold based catalysts revealed that the initial rate of

reaction is independent of the oxygen pressure at the investigated range of 0.2-3 bar. This indicates that the re-oxidation of the metal hydride by the molecular oxygen proceeds quickly and is not rate-controlling [16].

As already illustrated and pointed out by the data and the course of reaction, the selective oxidation of salicyl alcohol is assumed to follow a consecutive reaction of first order. The next step was to investigate this more closely by determining the rates constants and by comparing the theoretical rate equation of a consecutive reaction to the experimental data.

4.3.1.1 Sequential reaction kinetic analysis

As already introduced at the beginning of this chapter, the course of reaction for the selective oxidation of salicyl alcohol indicates a consecutive mechanism which is illustrated again in the following figure (Figure 4-9). From the beginning of the reaction, salicylic alcohol is directly oxidised to salicylic aldehyde, the desired product of the reaction. However, at higher conversions the formation of salicylic acid is observed. Once the conversion of salicylic alcohol reaches 100% a maximum yield of 72% of salicylic aldehyde is obtained. Beyond that point the concentration of salicylic aldehyde decreases and a simultaneous increase in formation of salicylic acid is detected. The concentration/time profile strongly suggests a reaction mechanism following a consecutive reaction of pseudo first order where the salicylic aldehyde is being further oxidised to salicylic acid.

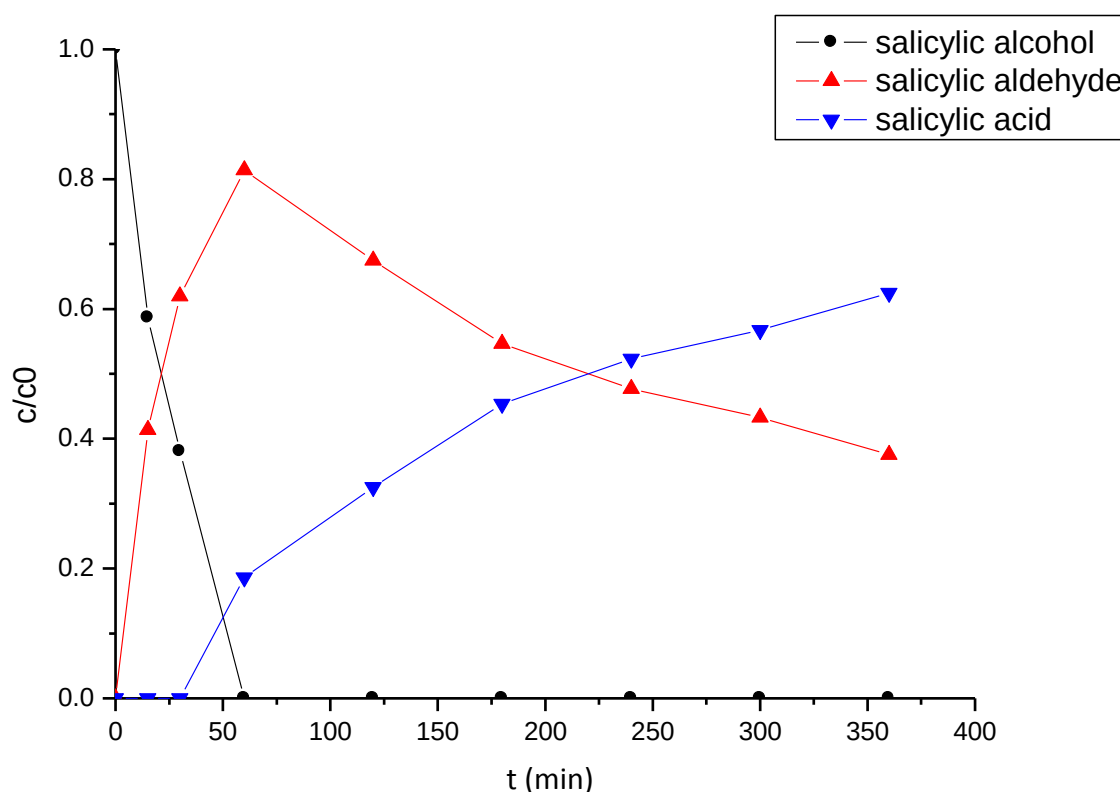


Figure 4-9: Concentration/ time profile for the selective oxidation of salicylic alcohol: Reaction conditions: $T=50^{\circ}\text{C}$, $p=1$ bar(air), catalyst 1.5Au/C , $m_{\text{cat}}= 0.2\text{g}$, $c_{\text{salicyl alcohol}}= 0.04$ M, $\text{NaOH: salicyl alcohol}= 2:1$, $\text{rpm}= 1000$, ●salicylic alcohol, ▲salicylic aldehyde, ▼salicylic acid.

4.3.1.2 Mechanistic aspects

There are two routes leading to the formation of salicylic acid, a) by oxidation of salicyl aldehyde via re-adsorption of the aldehyde onto the catalyst surface b) by direct oxidation of salicyl alcohol to salicylic acid on the catalytic surface via a possible intermediate. As mentioned earlier, after full conversion of salicyl alcohol is reached and the peak concentration of salicyl aldehyde is passed, the formation of salicyl acid occurs through route a). At lower conversions the formation of salicylic acid might occur through route b). This can be verified by determining the rate constants for the formation and disappearance of all 3 components which will be discussed in the following section.

In the next step the theoretical rate equation for a consecutive mechanism is applied and the theoretically calculated data compared with the experimentally achieved data. It was assumed as before that reaction rate is independent of the oxygen pressure in the pressure range of 0.2-3 bar.

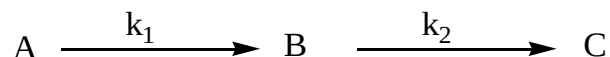


Figure 4-10: Reaction network with rate constants for the selective oxidation of salicylic alcohol.

4.3.1.3 Rate equations

With the expressions for the first order rate equation for the concentration of salicyl alcohol [A] salicyl aldehyde [B] and salicylic acid [C]:

$$d[A]/dt = -k_1 \cdot A \quad 4-10$$

$$d[B]/dt = k_1 \cdot A - k_2 \cdot B \quad 4-11$$

$$d[C]/dt = k_2 \cdot B \quad 4-12$$

And through integration of these expressions, the following equations are obtained:

$$[A] = [A]_0 \exp(-k_1 t) \quad 4-13$$

$$[B] = \frac{k_1 \cdot A_0}{(k_2 - k_1)} \left(\exp\{-k_1 \cdot t\} - \exp\{-k_2 \cdot t\} \right) \quad 4-14$$

$$[C] = [A]_0 \left[1 - \left\{ 1/(k_2 - k_1) \right\} \left\{ k_2 \exp(-k_1 t) - k_1 \exp(-k_2 t) \right\} \right] \quad 4-15$$

The theoretical equation for [B] expressing the formation and disappearance of salicyl aldehyde was used, in order to determine the two rate constants k_1 and k_2 . As for the consecutive reaction, it was more important to obtain the overall rate given by the rate constant compared to the initial rate of reaction. The following graph presents the experimental data and the fit obtained:

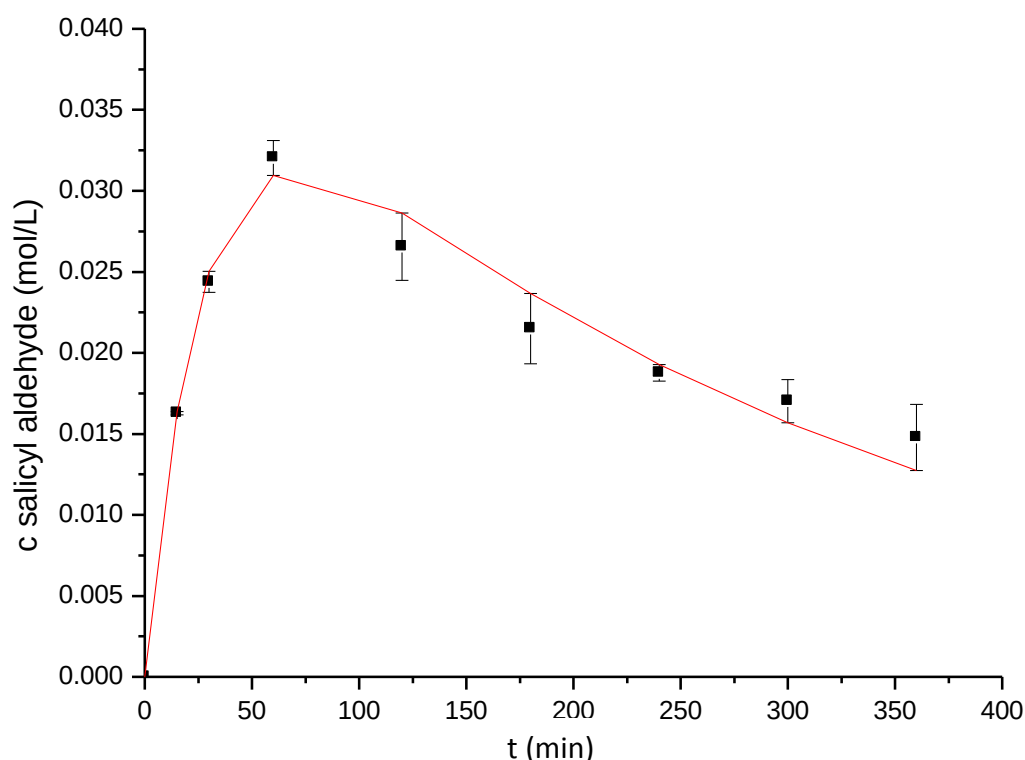


Figure 4-11: Origin fitted plot for consecutive reaction of first order for concentration/time profile of salicylic aldehyde, ■ experimental data with standard error, — fit function, experimental data for reaction conditions: catalyst: $T=50^{\circ}\text{C}$, $p=1\text{bar}$ (air), 1.5Au/C , $m_{\text{cat}}=0.2\text{g}$, $c_{\text{salicyl alcohol}}=0.04\text{M}$, $\text{NaOH:salicyl alcohol}=2:1$, $\text{rpm}=1000$.

The black data points in Figure 4-11 present the experimental data for concentration of salicyl aldehyde with standard error. For the fitting process, a set of estimated parameters for k_1 and k_2 was inserted for initiation. The red graph represents the theoretical fit corresponding to the course of reaction of salicyl aldehyde according to a consecutive rate equation. The calculated error for the fitted data is also marked in the plot. The fitted plot shows that consecutive first order reaction corresponds well to the obtained experimental data for the salicyl aldehyde. The values for k_1 and k_2 are presented in the following table (Table 4-2). In order to verify the consistency of the fit process, k_1 was determined separately through the expression for $[A]$ $k_{1[A]}$, corresponding to the disappearance of salicyl alcohol. Accordingly, k_2 was obtained separately through the expression $[C]$ $k_{2[C]}$, describing the formation salicylic acid (see Table 4-2). The following figure illustrates the experimental data for the course of concentration of salicylic acid with the applied fit according to equation for $[C]$:

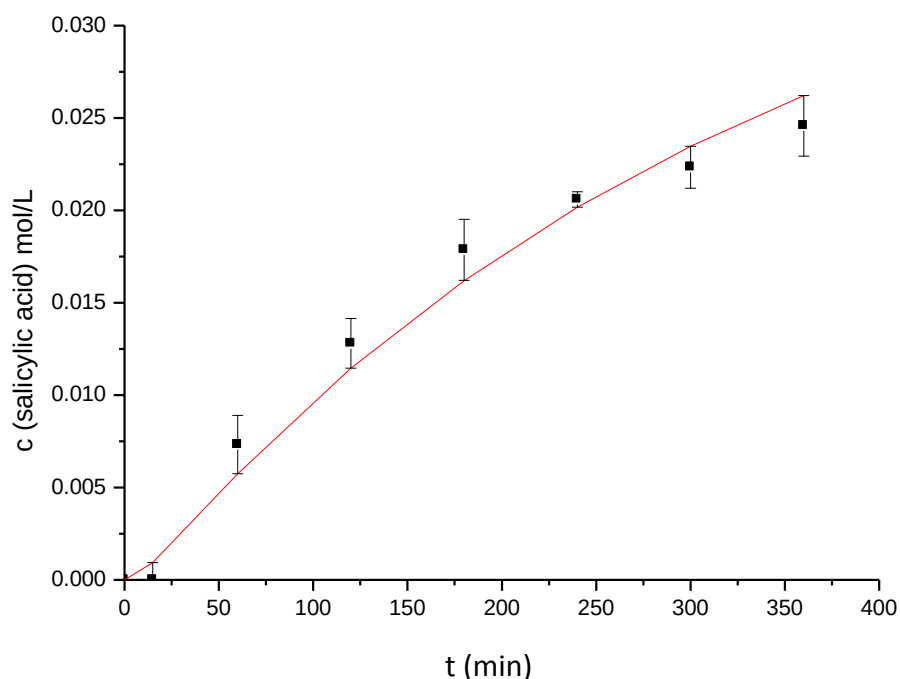


Figure 4-12: Origin fitted plot for consecutive reaction of first order for concentration/time profile of salicylic acid, ■ experimental data with standard error, — fit function, experimental data for, reaction conditions: $T=50^{\circ}\text{C}$, $p_{\text{total}}=1\text{bar}$ (air), catalyst 1.5Au/C, $m_{\text{cat}}=0.2\text{g}$, $c_{\text{salicyl alcohol}}=0.04\text{M}$, NaOH:salicyl alcohol= 2:1, rpm= 1000.

The figure shows that the consecutive first order reaction model corresponds well to the obtained experimental data for the salicylic acid.

Table 4-2: Results for origin fit process for 1.5Au/C catalyst for consecutive reaction of first order function with standard error (SE).

catalyst	$k_1\text{ (B)}$ (SE) *[10 ⁻³] [h ⁻¹]	$k_1\text{ [A]}$ (SE) *[10 ⁻³] [h ⁻¹]	$k_2\text{ [B]}$ (SE) *[10 ⁻³] [h ⁻¹]	$k_2\text{ [C]}$ (SE) *[10 ⁻³] [h ⁻¹]
1.5Au/C	36.4 (2.8)	38.0 (4.5)	3.45 (0.18)	3.04 (0.25)

Reaction conditions: $T=50^{\circ}\text{C}$, $m_{\text{cat}}=0.2\text{g}$, $p=1\text{bar}$ (air), $c_{\text{salicyl alcohol}}=0.04\text{M}$, NaOH:salicyl alcohol= 2:1, rpm=1000.

From the results it can be seen that k_1 is larger than k_2 an order of magnitude. Furthermore, the value for the formation of k_1 obtained via [B] $k_{1[B]}$ corresponds to the value of k_1 obtained through expression [A] $k_{1[A]}$ within error. Therefore, the rate of disappearance of salicyl alcohol corresponds to the rate of formation of salicyl aldehyde confirming the previous observations. In conclusion, the formation of salicylic acid has to occur through salicyl aldehyde. The results for k_2 show that the value $k_{2[B]}$ representing the disappearance of salicyl aldehyde corresponds well to $k_{2[C]}$ based on the formation of salicylic acid within error.

The study was extended to investigate the influence of gold loading on the kinetics and rate constants k_1 and k_2 . Hereby it was important to investigate whether the reaction still followed sequential mechanism on the Au/C catalyst with different particle surface morphology. The catalyst effects and structural morphology will be discussed in section 4.4. The data appears to follow a consecutive order, therefore, the same function was applied to the course of concentration for salicyl aldehyde and is illustrated in the following figure. The rate constants k_1 and k_2 were determined using the theoretical equation for [B] and again compared with the values obtained via equation [A] and [C] (Table 4-2).

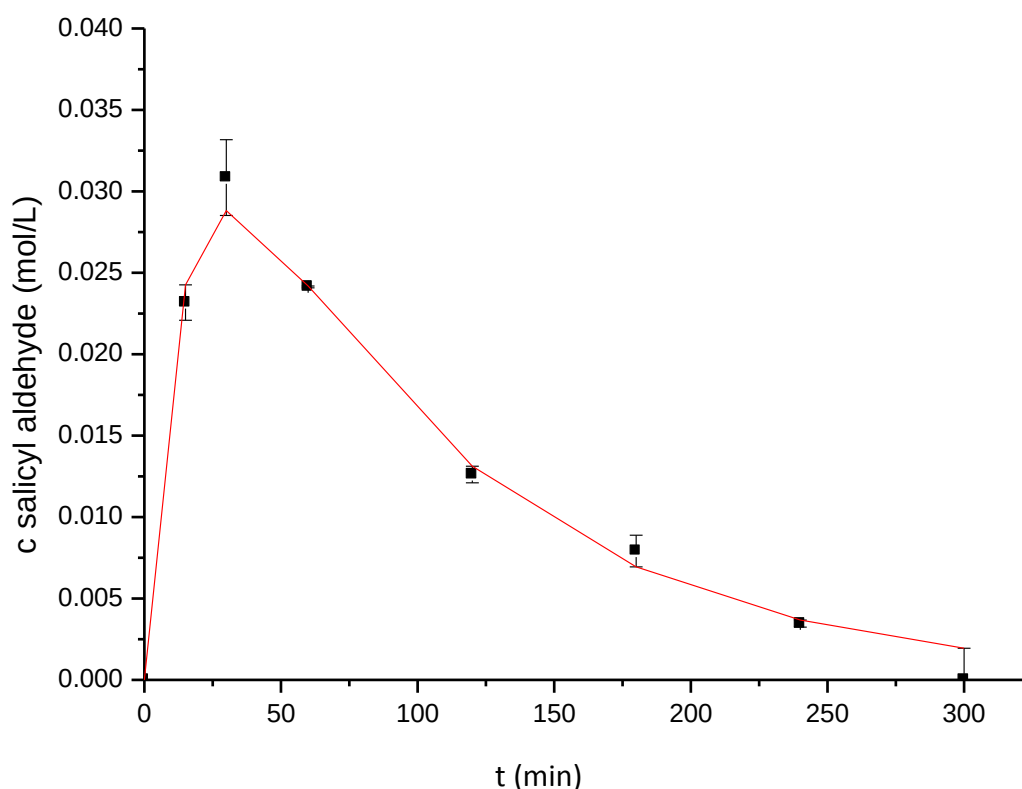


Figure 4-13: Origin fitted plot for consecutive reaction of first order for concentration/time profile of salicyl aldehyde, ■ experimental data, — fit function, experimental data for, reaction conditions: catalyst: 3Au/C, T=50°C, p= 1bar (air) $c_{\text{salicyl alcohol}} = 0.04\text{M}$, NaOH:salicyl alcohol=2:1, rpm=1000.

From the table it can be seen that the values for the rate constant k_1 and k_2 determined by [B] comply well with the corresponding rate constants $k_{1[A]}$ and $k_{2[C]}$, for all gold loadings.

Table 4-3: Results for origin fit process for Au/C catalysts with different loading for consecutive reaction of first order function with standard error (SE).

Catalyst	$k_{1(B)} \text{ (SE)}$ *[10 ⁻³] [h ⁻¹]	$k_{1(A)} \text{ (SE)}$ *[10 ⁻³] [h ⁻¹]	$k_{2(B)} \text{ (SE)}$ *[10 ⁻³] [h ⁻¹]	$k_{2(C)} \text{ (SE)}$ *[10 ⁻³] [h ⁻¹]
1Au/C	19 (1.3)	20.9 (2.2)	2.94 (0.15)	2.0 (0.15)
1.5Au/C	36.4 (2.8)	38.0 (4.5)	3.45(0.18)	3.04 (0.25)
3Au/C	73 (6.5)	87 (42)	10.59 (0.55)	10.68 (1.12)

Reaction conditions: T=50°C, m_{cat}=0.2g, p= 1bar (air), C_{salicyl alcohol} = 0.04M, NaOH:salicyl alcohol= 2:1, rpm=1000.

Furthermore, the ratio k_1/k_2 remains constant within error for all catalysts. It can therefore be concluded the selective oxidation of salicyl alcohol follows sequential kinetics of first order for all Au/C catalysts investigated.

4.3.2 Oxidation of salicyl aldehyde

The direct oxidation of salicyl aldehyde to salicylic acid was carried out using the same catalyst 1.5Au/C with the same reaction setup and conditions. Based on the preceding studies, it was assumed that the oxidation of salicyl aldehyde to salicylic acid followed a first order rate equation. The rate constant was determined according to equation 4-13. The following graph illustrates the concentration/ time profile for the catalytic conversion of salicyl aldehyde with the 1.5Au/C catalyst in presence of a base at 50°C.

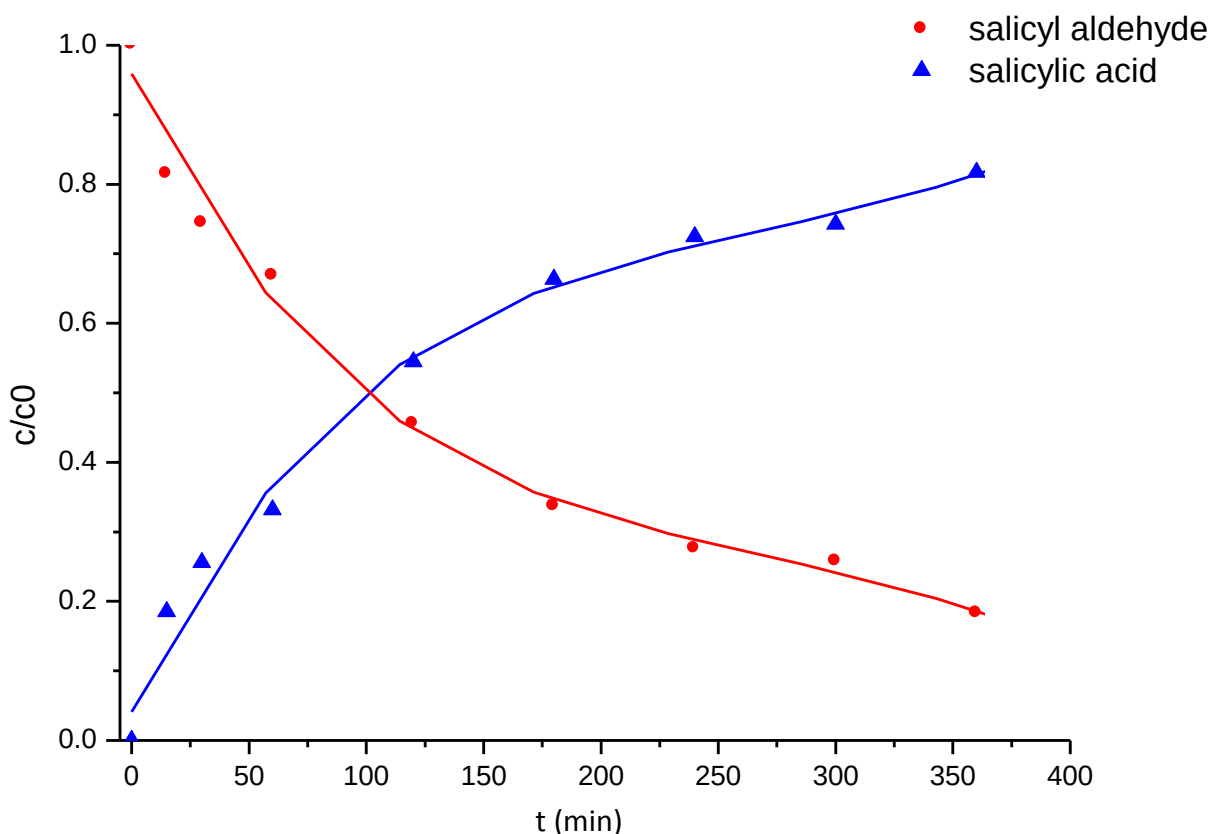


Figure 4-14: Concentration/ time profile for the selective oxidation of salicyl aldehyde,
 reaction conditions: $T=50^{\circ}\text{C}$, $p=1\text{bar}(\text{air})$, catalyst 1.5Au/C , $m_{\text{cat}}=0.2\text{g}$, $c_{\text{salicyl aldehyde}}=0.04\text{M}$, $\text{NaOH:salicyl aldehyde: } 2:1$, $\text{rpm}=1000$, $\blacktriangle$ salicylic aldehyde, $\blacktriangledown$ salicylic acid.

The product detected was salicylic acid and no other product formation in the gas or liquid phase was observed. The carbon mass balance of the reaction was 95-100%.

It can be seen that the conversion of salicyl aldehyde proceeds much more slowly compared to the conversion of salicyl alcohol. The rate constant k describing the disappearance of salicyl aldehyde was determined by applying a fit function with equation 4-13 with $[A]$ being the reactant salicyl aldehyde. It was important to identify whether the rate is inhibited by any other process i.e. adsorption which decreases the activity. Another reason could be a partial deactivation of the catalyst which decreases the performance.

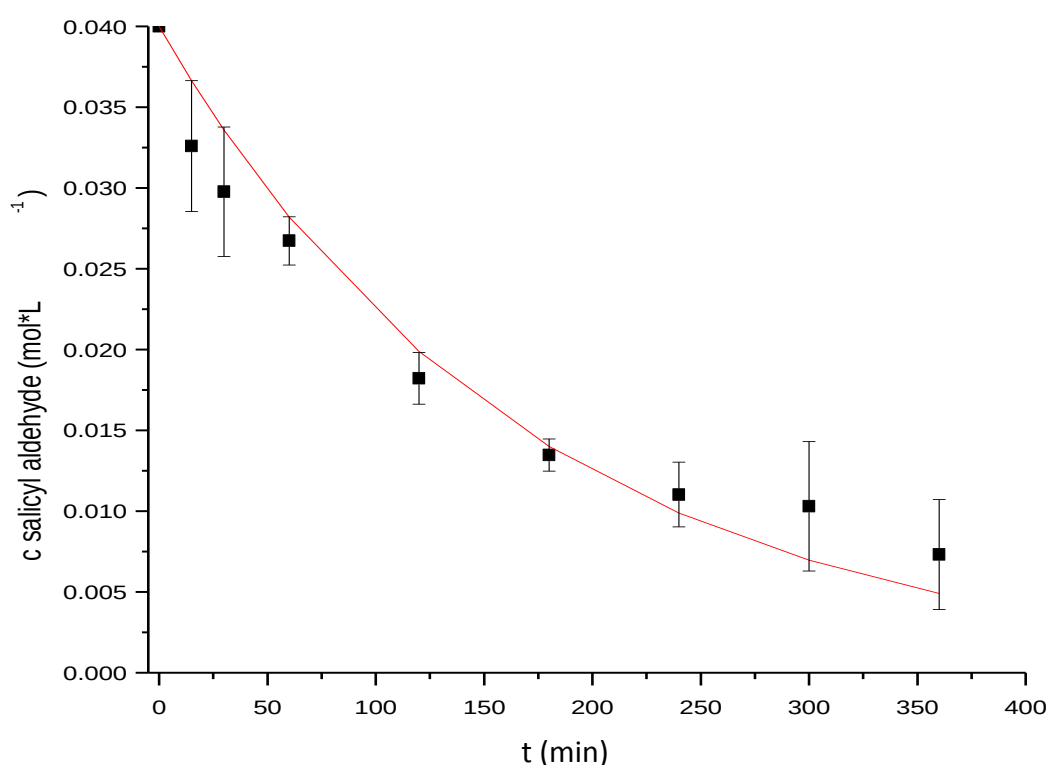


Figure 4-15: Origin fitted plot for consecutive reaction of first order for selective oxidation of salicyl aldehyde: concentration/time profile of salicyl aldehyde. ■ Experimental data with error bars, — fit function, experimental data for reaction conditions: catalyst:1.5Au/C, T=50°C , p= 1bar (air) $c_{\text{salicyl alcohol}} = 0.04\text{M}$, NaOH:salicyl aldehyde=2:1, rpm=1000.

The rate constant was additionally calculated via the concentration of [B] corresponding to the formation of salicylic acid. The graph for the formation of salicylic acid and the fit function are illustrated in the Figure 4-16.

Table 4-4: Rate constant k for selective oxidation of salicyl aldehyde.

Catalyst	$k_{[A]}$ *[10 ⁻³] [h ⁻¹]	$k_{[B]}$ *[10 ⁻³] [h ⁻¹]
1.5Au/C	5.83 (0.48)	5.83 (0.48)

Reaction conditions: T=50°C, $m_{\text{cat}}=0.2\text{g}$, p= 1bar (air), catalyst: 1.5Au/C, T=50°C, p=1bar (air), $m_{\text{cat}}=0.2\text{g}$, $c_{\text{salicyl aldehyde}}=0.04\text{M}$, NaOH:salicyl aldehyde: 2:1, rpm=1000.

The results show that the rate for the disappearance of salicyl aldehyde corresponds to the rate of formation of salicylic acid.

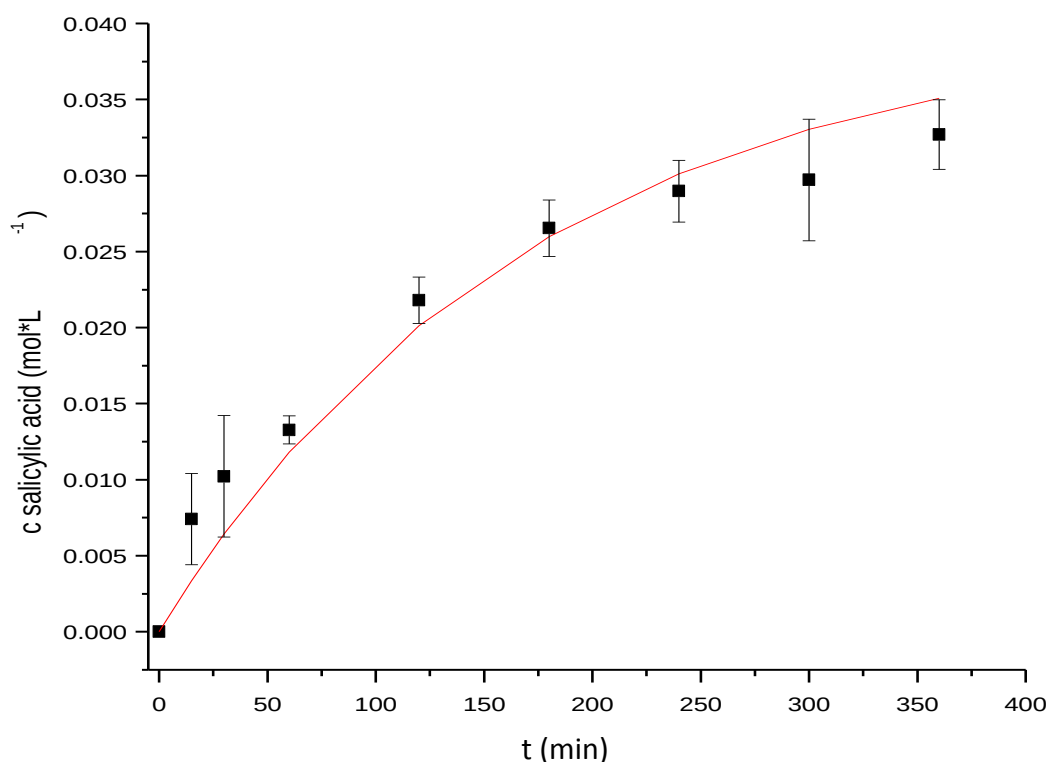


Figure 4-16: : Origin fitted plot for consecutive reaction of first order for selective oxidation of salicyl aldehyde concentration/time profile of salicylic acid, ■ experimental data with error bars, — fit function, experimental data for reaction conditions: catalyst:1.5Au/C, T=50°C, p= 1bar (air) $c_{\text{salicyl alcohol}} = 0.04\text{M}$, NaOH:salicyl aldehydel=2:1, rpm=1000.

It can be seen that k is smaller by one order of magnitude compared to k_1 with the same catalyst and the same reaction conditions applied. This shows that under the investigated conditions, the selective oxidation of salicyl aldehyde to its higher oxygenate salicylic acid proceeds at a much slower rate compared to the selective oxidation of salicyl alcohol to salicyl aldehyde.

Comparing the rate constant k to the rate constant k_2 in Table 4-2 this value is slightly higher, which is based on the higher initial concentration of 0.04M but of the same degree of order. This shows that for the investigated catalyst system, the rate for the selective oxidation of salicyl aldehyde to salicyl acid, in a sequential mechanism or separate reaction, proceeds independently at a slower rate. This effect appears to apply in general for the investigated Au/C catalyst system. However, to investigate whether this applies to the metal loading of 1.5wt% additional reaction data of catalyst systems with different gold loadings would need to be

included to verify it is independent of the Au surface morphology. The investigation so far is based on a simple reaction equation model and does not consider other effects which could influence or decrease the rate such as adsorption and catalyst deactivation effects. Therefore, the study was extended to investigate the effect of product adsorption which is presented in the following section.

4.3.3 Influence of product addition

So far, the study of the consecutive mechanism has been based on a simple first order model equation. This enabled the calculation of the overall rate and rate constants k_1 and k_2 . As already discussed above, the rate constant k_2 corresponding to the disappearance of salicyl aldehyde and formation of salicylic acid, is always much smaller than k_1 . A possible reason might be caused by underlying effects such as irreversible product adsorption affecting the rate. In order to investigate this more closely, a series of experiments was conducted by adding the product salicylic acid at the beginning of the reaction, while keeping the other reaction conditions the same as in 4.3.1. The concentration of added product corresponded to the minimum yield of salicylic acid at the beginning of the reaction and the maximum yield at the end of the reaction according to Figure 4-9. In case of product adsorption, a loss in concentration of salicylic acid causing a mass imbalance should be detected. The catalyst applied for this set of experiments was 1.5Au/C. The concentration of the reactant salicyl alcohol was also varied and the initial rate of reaction determined, which is given in the Appendix. The quantitative analysis resulted in a mass balance of 90-100% and a 5-10% loss of the theoretically expected concentration of initially added salicylic acid.

The following figure compares the time/concentration profiles of the reactant and products with and without product addition. For the plot, the added product salicylic acid was subtracted from course of concentration of the formation of salicylic acid with the initially adsorbed amount of 5-10 wt% taken into account. After analysing the course of reaction for all components it can be seen that the reaction still followed a sequential mechanism at a slower rate.

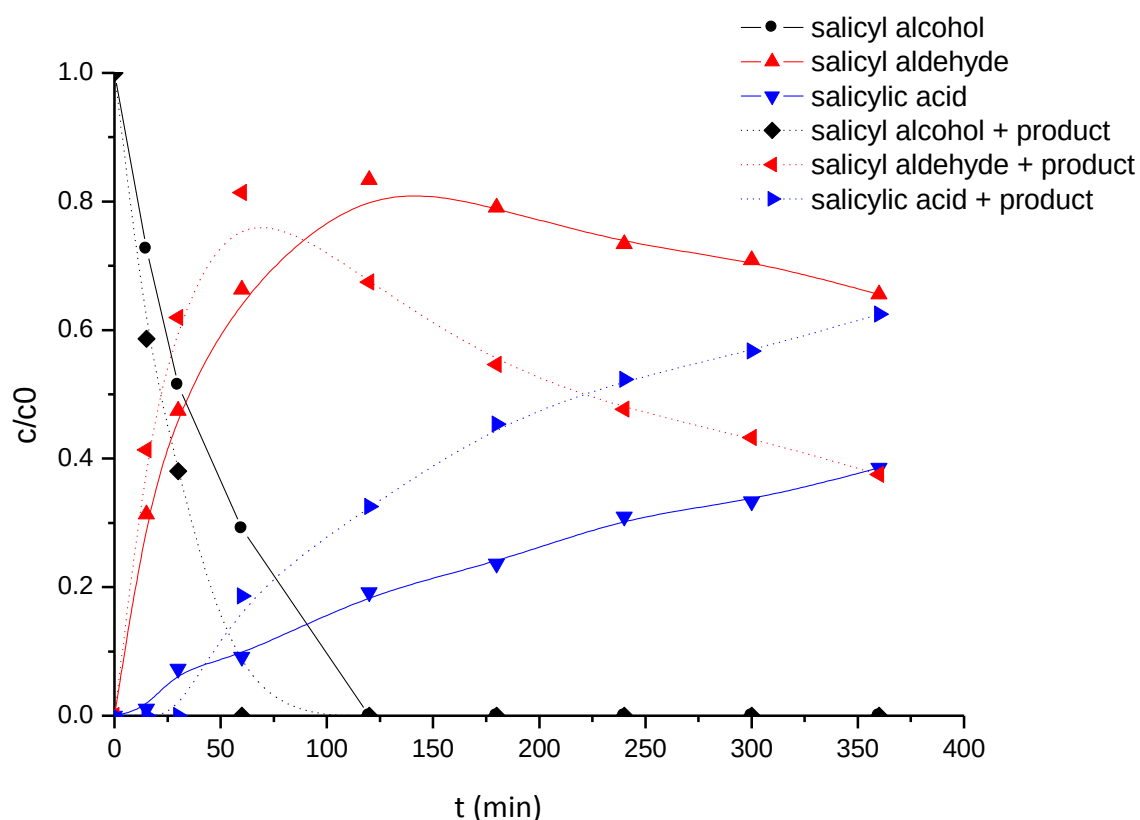


Figure 4-17: Influence of product addition ($c_{\text{salicylic acid}} = 0.0112 \text{ M}$) (—straight line) on selective oxidation of salicylic alcohol, original plot (-----dotted line): 1.5Au/C catalyst, $c_{\text{salicyl alcohol}} = 0.04\text{M}$, $c_{\text{salicylic acid}} = 0.0112\text{M}$, $T = 323 \text{ K}$, $p = 1 \text{ bar}$ (air), $m_{\text{cat}} = 0.2\text{g}$, salicyl alcohol (■), salicyl aldehyde (●), salicylic acid (▲).

The kinetics of the reactions and the rate constants k_1 and k_2 were determined with the fit function as discussed in 4.3.1.3 for $[B]$ corresponding to the concentration of salicyl aldehyde. Hereby, it was important to see whether the reaction still followed sequential kinetics under the influence of product addition.

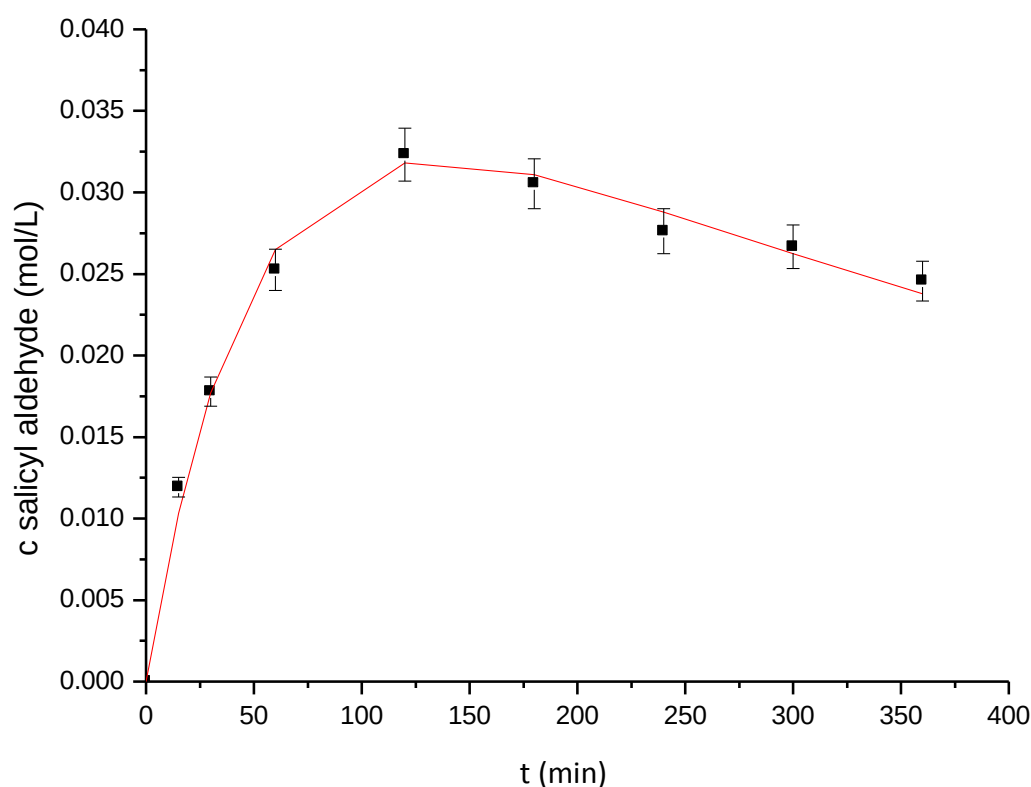


Figure 4-18: Origin fitted plot for consecutive reaction of first order for concentration/time profile of salicyl aldehyde, ■ experimental data, — fit function, experimental data for, reaction conditions: catalyst: 1.5Au/C, T=50°C, p=1bar (air), $m_{\text{cat}}=0.2\text{g}$, $c_{\text{salicyl alcohol}}=0.04\text{M}$, $c_{\text{salicylic acid}}=0.0112\text{M}$, NaOH:salicyl alcohol: 2:1, rpm=1000.

The black data points present the experimental data for the course of concentration of salicyl aldehyde with product addition. The graph shows that the selective oxidation of salicyl alcohol with product addition corresponds well to the sequential reaction kinetics. The results for the rate constants are given in the following table (Table 4-5):

Table 4-5: Influence of product addition on rate constants k_1 and k_2 with standard error (SE).

Catalyst	c salicylic acid added [mol*L ⁻¹]	$k_{1[B]}$ (SE) *[10 ⁻³] [h ⁻¹]	$k_{2[B]}$ (SE) *[10 ³] [h ⁻¹]
1.5Au/C	0	36.4 (2.8)	3.45 (0.18)
1.5Au/C	0.0112	20.2 (0.98)	1.68 (0.08)
1.5Au/C	0.0245	8.1 (1.1)	2.25(0.35)

Reaction conditions: T=50°C, m_{cat}=0.2g, p= 1bar(air), catalyst: 1.5Au/C, T=50°C, p=1bar(air), m_{cat}=0.2g, C_{salicyl alcohol}=0.04M, C_{salicylic acid} = 0-0.0245 M, NaOH:salicyl alcohol: 2:1, rpm=1000.

The values obtained for the rate constant k_1 , corresponding to the disappearance of salicyl alcohol and the formation of salicyl aldehyde decrease rapidly with increasing amount of added product. However, the product addition does not seem to affect the rate constant $k_{2[B]}$ to the same extent. As the amount of base was not changed for this set of experiments, the addition of salicylic acid at the beginning of the reaction might cause a decrease in pH due to the acidic nature of salicylic acid (pKs = 2.75 [154]) which leads to a decrease in rate of reaction based on the linear correlation on the concentration of OH⁻(see 4.2.5). The initial concentration of 0.08 M NaOH would decrease through the addition of 0.0245 mol/L of salicylic acid thus lowering the initial rate up to 30% according to Figure 4-6. Another cause for the decrease in rate could be the blockage and deactivation of active sites due to the initial adsorption of the product or even side reactions taking place on the catalyst surface i.e. condensation reactions between salicyl alcohol and salicylic acid. However, as no side products were detected in the solution, the only other possibility is that the side products are retained on the catalyst surface. To test this hypothesis, further analysis of the catalyst surface is required.

To determine the adsorption effect on the rate of reaction, a Langmuir-Hinshelwood type kinetics was considered. However, as the adsorption was mainly dominated by salicylic acid and the adsorption effects of the reactant salicyl alcohol and the product salicyl aldehyde were too low, the rate was mainly dependent on the concentration of salicyl acid. Therefore the LH kinetic approach was not representative of this reaction system and kinetics and did not deliver the expected results (see Appendix).

This study has shown that the presence of excess salicylic acid has an effect on the catalytic performance. The conversion to the acid is low in the range of alcohol conversion and only plays

a role once the salicyl aldehyde is sequentially oxidised. Therefore the reaction still appears to follow sequential kinetics of first order.

4.3.4 Molecular mechanism on gold surface

The parametric study on the reaction rate for the selective oxidation of salicyl alcohol has supported the proposed consecutive reaction mechanism on the Au/C catalyst. The investigation of the influence of the amount of base on the initial rate of reaction demonstrated the essential role of the OH^- species for the initial deprotonation of the alcohol. Furthermore, the study of the influence of oxygen partial pressure has proven experimentally that the presence co-adsorbed oxygen species on the surface was necessary as there was almost no conversion observed in the absence of oxygen. Based on the experimental results and the suggested mechanism in previous reported studies ^[118], the scheme for the consecutive mechanism for the selective oxidation of salicyl alcohol is illustrated in Figure 4-19. The mechanism involves several elementary steps. The initial steps include the adsorption of the salicyl alcohol molecule on the active gold site, the activation of the O-H bond by the gold particle and the actual deprotonation of the alcohol by OH^- forming water. This illustrates the direct correlation of the OH^- ions with the initial reaction rate. The concentration of OH^- ions is in excess as they are also regenerated by the adsorbed molecular oxygen. In addition, as discussed in 4.2.3, the rate of reaction for the given conditions is independent of the oxygen partial pressure. The rate of reaction is therefore only dependent on the concentration of salicyl alcohol at the initial stage of reaction. In the next step (2), the C-H bond activation takes place at the active site, with a subsequent β -H elimination and formation of salicyl aldehyde.

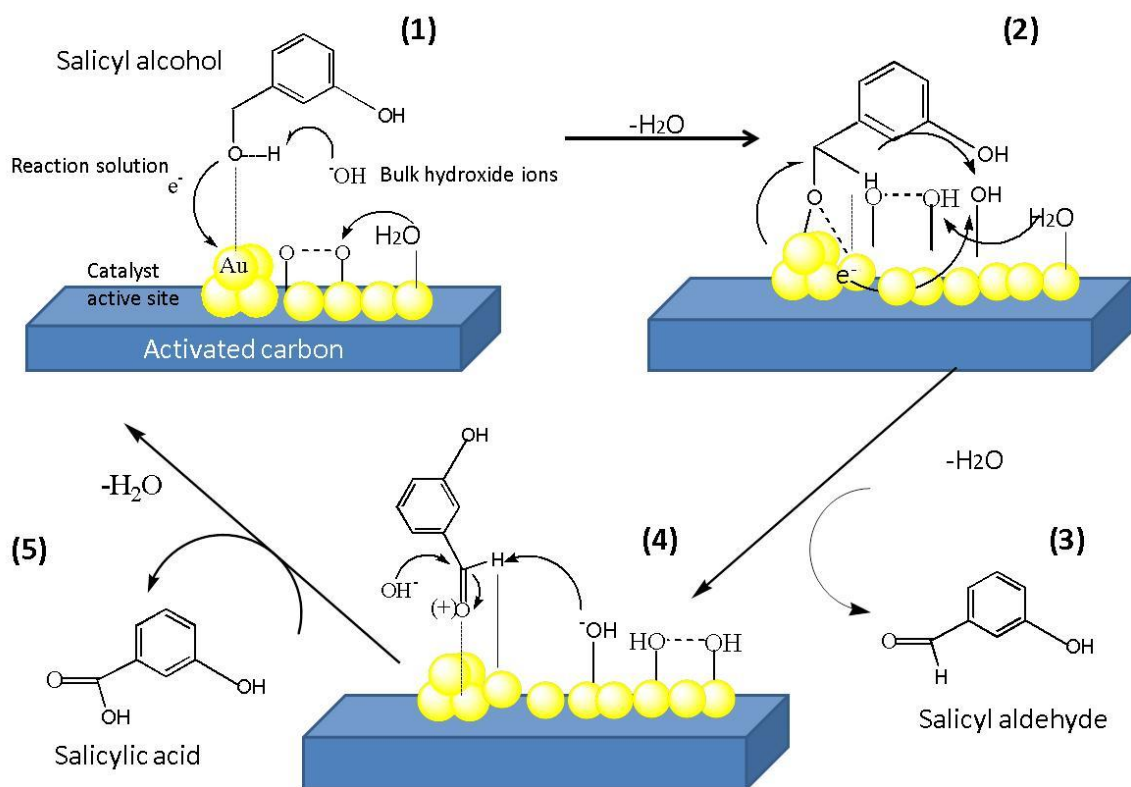
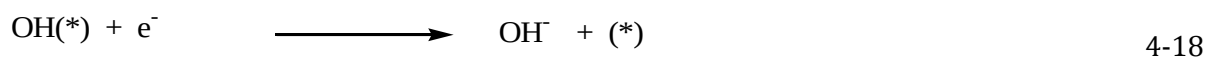
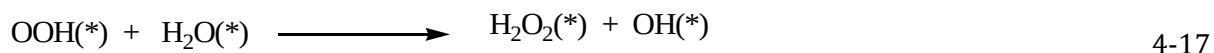
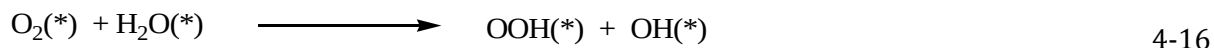


Figure 4-19: Proposed reaction mechanism for liquid phase oxidation of salicyl alcohol under alkaline conditions according to [118].

The adsorbed oxygen molecule plays an important role in this mechanism by regenerating OH^- ions via the reduction with water via formation of peroxide species as well as the removal of electrons added to the surface during the adsorption of OH^- . It becomes clear that no significant activity is detected in absence of oxygen. However, oxygen is still not expected to directly incorporate into the reactant for the formation of salicylic acid, as the molecular dissociation of oxygen on gold has high activation barriers [118].



The third step is based on the desorption of salicyl aldehyde into the bulk reaction solution (3). This concentration is detected by HPLC. Following this, salicyl aldehyde is re-adsorbed onto the

catalyst surface and the C-O bond activated by the gold followed by a nucleophilic attack (4) of the OH^- to form salicylic acid. Hereby, OH^- can be from the reaction solution or from adsorbed OH^- on the catalyst surface. Finally, salicylic acid is desorbed into the reaction solution which is detected by HPLC (5).

4.4 Catalyst effects – morphology and properties

So far, this chapter has focused on the parametric studies and influences on the kinetics and rate of reaction. The next step was to understand the influence of the catalyst properties on the catalyst performance towards selective oxidation of salicyl alcohol.

Previous extensive studies on gold based catalyst systems for selective oxidation have demonstrated the strong structural sensitivity of the catalytic performance (see Literature Review). This section focuses on the surface and structural properties of the catalyst composition, the catalyst morphology such as the gold particle size, type and distribution. Further, its interaction with the support were investigated.

The first part focuses on the influence on the surface morphology presenting characterisation techniques such TEM, BET and XRD as described in Materials and Methods:

1. Catalyst preparation method
2. Metal loading
3. Catalyst treatment
4. Nature of the support

The second part describes and discusses the impact of the catalyst morphology on the catalytic activity, in particular the turnover frequency numbers and selectivity towards the main product salicyl aldehyde.

4.4.1 Influence of catalyst preparation method

Two different catalyst preparation methods were studied: impregnation and sol-immobilisation. The procedure is described in the part Materials and Methods. The sol-immobilisation method enabled the control of the particle size during the preparation of the reduced metal sol through the organic stabiliser THPC. The catalyst had to be treated at 350°C to decompose the stabiliser.

For all catalyst syntheses, the main support used was activated carbon. The original shape was pellets. However, for the synthesis it was ground to powder. The following table lists the main features of the powdered support.

Table 4-6: Properties of activated carbon used for catalyst synthesis.

Support	Grain size original [cm]	Grain size for synthesis [μm]	S _{BET} powder [m ² *g ⁻¹]	Pore diameter Powder [nm]	Pore volume Powder [cm ³ *g ⁻¹]
Activated Carbon Norrit	0.3-0.6	150-250	755	5.9	0.53

Based on reported studies about the unique properties of small gold particles (see Literature Review), the aim here was to synthesise a catalyst with gold particles of approximately 5nm size homogeneously dispersed on the catalyst surface. In an initial step, the catalyst preparation method was investigated under the criteria particle size, particle distribution and reproducibility. The reproducibility of the method was investigated by preparing multiple batches and determining the final metal loading by ICP (see Materials and Methods) and performing a catalyst characterisation of the various batches.

The catalysts were initially prepared with 1.5wt% gold loading and were analysed by TEM to compare the average size and distribution of the gold particles (Figure 4-20 and Figure 4-21).

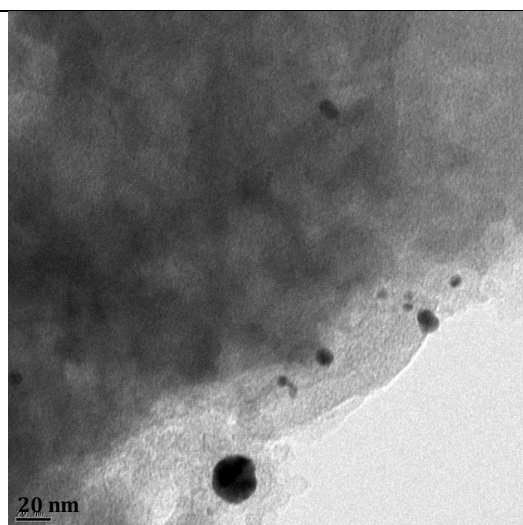


Figure 4-20: 1.5 Au/C prepared by impregnation.

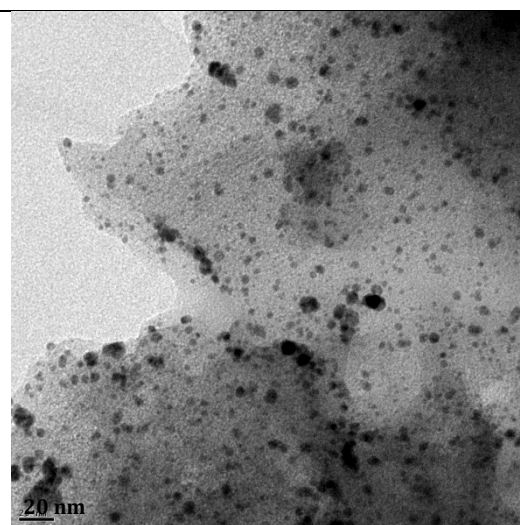


Figure 4-21: 1.5Au/C prepared by sol-immobilisation.

The TEM images consist of dark spherical spots on a grey background. Based on other reported studies as well as spectroscopic analysis (EDX), the black spherical spots were identified as gold particles on the carbon support (grey background). Although the contrast of the elements depended on the molecular weight, the final image could have a poor contrast due to the thickness of the sample. In some cases no particles could be distinguished as the sample image was black. Therefore, it was important to analyse multiple (3-4) images in order to get a representative characterisation of the sample. The two representative images of both catalysts show a strong difference in their surface morphology. It is clearly demonstrated that the sol-immobilisation method gave small gold particles and a homogeneous distribution on the catalyst surface. For the catalyst prepared by impregnation, the distribution appeared inhomogeneous, as there were large areas with less or no gold particles. The particles were partly much larger and thus resulted in a wider distribution. To evaluate the properties more precisely, the gold particle size was determined as an average of the particle diameter and its distribution (see Materials and Methods).

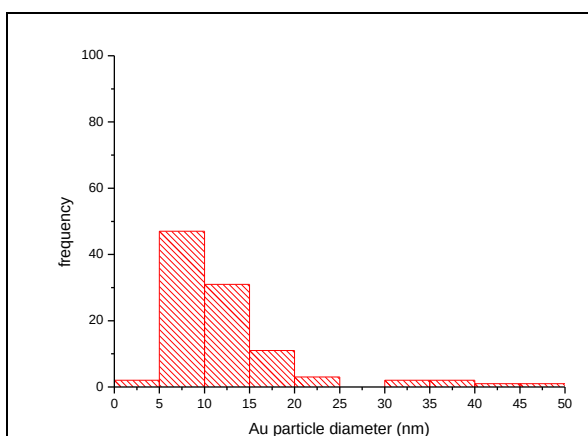


Figure 4-22: TEM histogram of 1.5Au/C via impregnation.

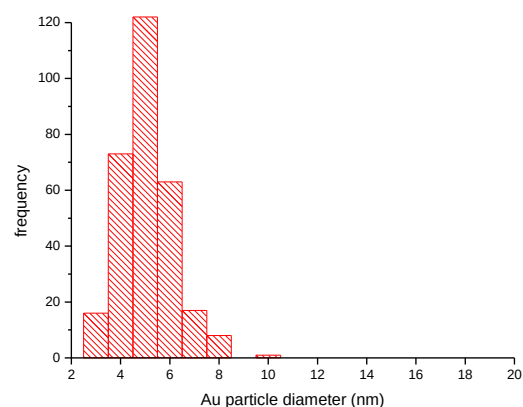


Figure 4-23: TEM histogram of 1.5Au/C via sol immobilisation.

The average determined particle diameter and the standard deviation SD of the mean particle size (see Materials and Methods) for both catalyst systems is presented in the following table:

Table 4-7: Comparison of particle diameter for different methods of synthesis for 1.5Au/C catalyst.

Catalyst	Preparation method	Au average particle diameter [nm]	SD Au average particle diameter [nm]
1.5Au/C	Impregnation	12.7	5.16
1.5Au/C	Sol-immobilisation	5.1	1.1

It can be seen that the impregnation method delivered an average particle size of 12.7 nm with a wide distribution (Figure 4-22) and the sol-immobilisation method successfully produced finely dispersed gold particles of 5.17nm diameter and a narrow size distribution. Furthermore, the sol-immobilisation method maintained high reproducibility regarding the metal loading, gold particle diameter and distribution, which is due to the organic stabiliser. Therefore, this method was used for all further catalyst preparation throughout this study.

These findings are in agreement with other reported studies on Au/C preparation methods where classical preparation methods such as impregnation and deposition precipitation delivered poorly dispersed catalysts with large particle sizes, whereas with sol-immobilisation using PVA or THPC small and disperse gold particles of 5nm size were obtained ^[73] ^[81]. These catalysts also demonstrated superior catalyst performance towards the selective oxidation of alcohols i.e. 1,2- propanediol. The study on the catalytic performance is discussed in section 4.5.

4.4.2 Influence of gold loading

The influence of the loading was investigated with particular focus on the particle diameter or particle size, the size distribution and the catalytic performance. For this purpose a series of catalysts with different metal loading, prepared by sol-immobilisation, was characterised by TEM and XRD. The representative TEM micrographs of the catalyst series are presented in the following figures (Figure 4-24-Figure 4-27). For comparison, the TEM micrograph of the presented 1.5Au/C catalyst is included. The TEM images show that the gold particles are evenly dispersed on the catalyst surface for all metal loadings. For the lower metal loadings 0.75-1.5wt%, the particles seem to be of similar spherical shape and particle size. For the 3Au/C catalyst, however, there are larger elongated agglomerates of particles on the catalyst surface.

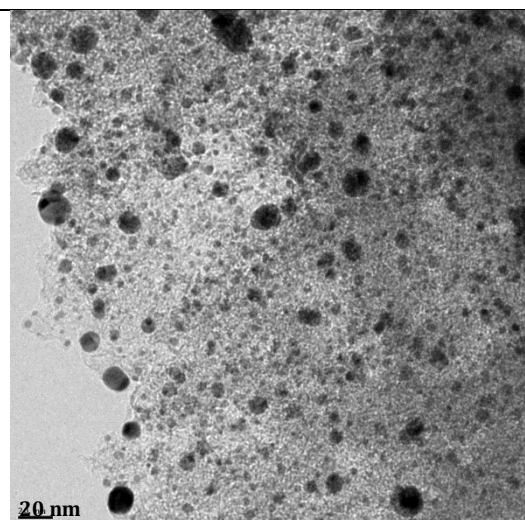


Figure 4-24: TEM image of 0.75Au/C.

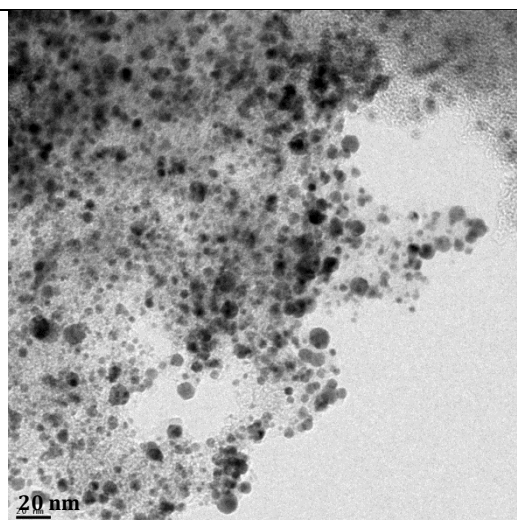


Figure 4-25: TEM image of 1Au/C.

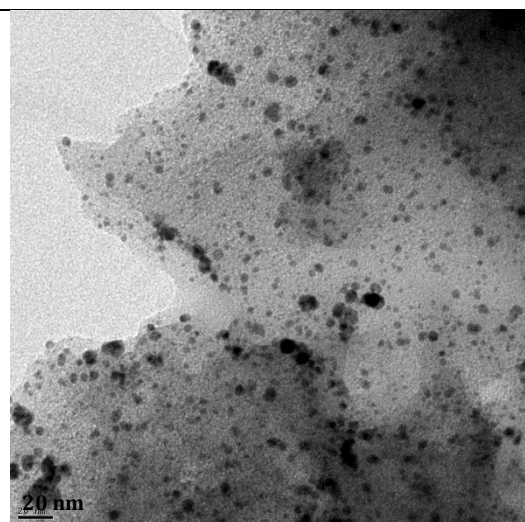


Figure 4-26: TEM image of 1.5Au/C.

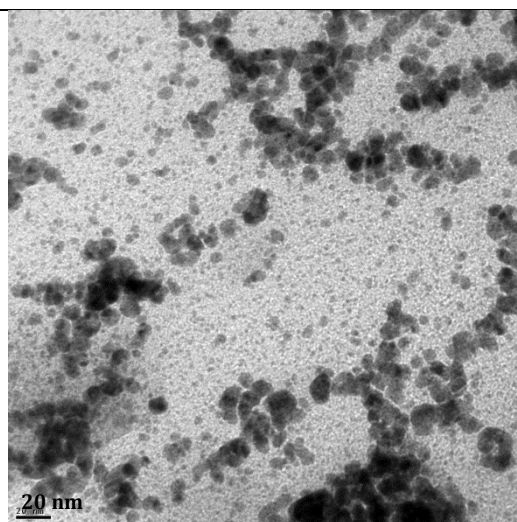


Figure 4-27: TEM image of 3Au/C.

The average particle diameter was determined and the results listed in the following table (Table 4-8). In addition, the particle size distribution was determined with particular focus on the amount of small particles from 3.5-5.5nm, which were expected to determine the catalyst activity.

Table 4-8: Comparison of average particle diameter for series of Au/C catalysts.

Catalyst	Au [wt%]	Au average particle diameter [nm]	SD Au average particle diameter [nm]	Fraction 3.5-5.5 nm [%]
0.75Au/C	0.75	4.94	1.67	73
1Au/C	1	5.34	1.61	83
1.5Au/C	1.5	5.07	1.1	83
3Au/C	3	8.33	2.30	20

For metal loadings between 0.75-1.5 wt% Au, an average particle diameter of around 5nm was obtained which is also reflected in the fraction of particles of 3.5-5.5nm size. The 0.75Au/C catalyst has a slightly smaller fraction of 3.5-5.5 nm particles due to the existence of even smaller particles <3.5nm. Overall, no significant changes in particle size and distribution are shown in this range. For the 3Au/C catalyst, the particle size distribution becomes very broad with the fraction of 3.5-5.5nm particles only comprising of 20% of the total amount of particles. The average particle size determined for this catalyst was 8.33nm. The particle size distribution is illustrated in the following TEM histograms (Figure 4-28-Figure 4-31).

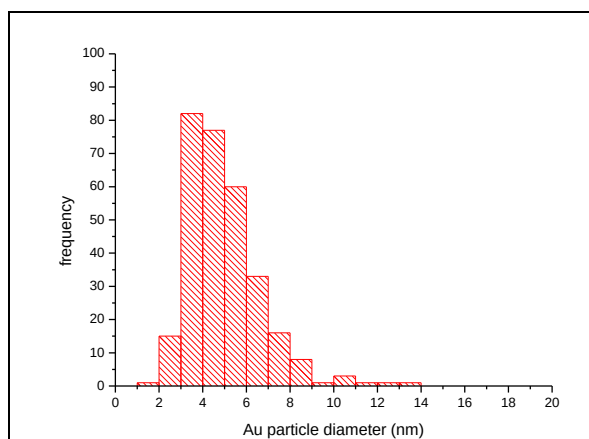


Figure 4-28: TEM histogram of 0.75 Au/C.

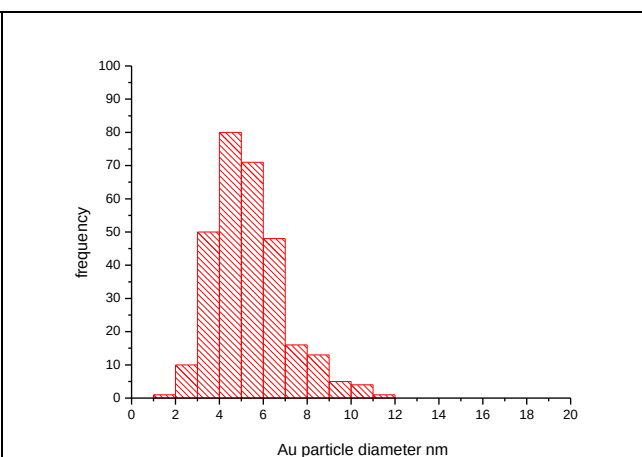


Figure 4-29: TEM histogram of 1Au/C.

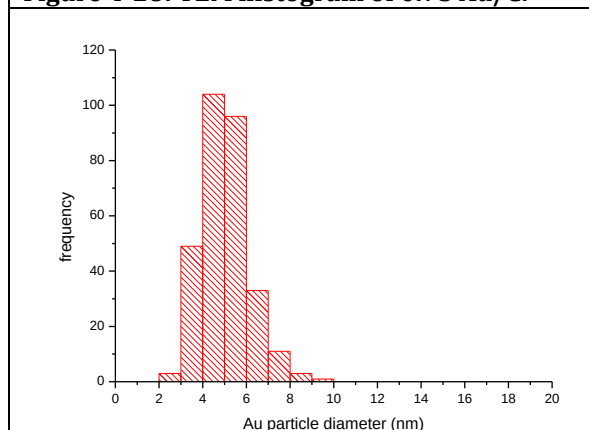


Figure 4-30: TEM histogram of 1.5Au/C.

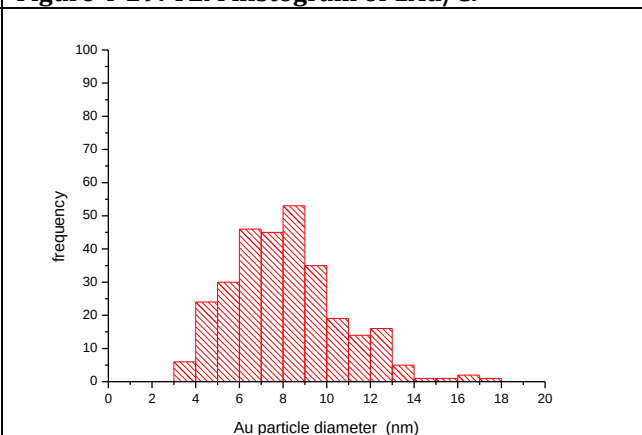


Figure 4-31: TEM histogram of 3Au/C.

Although THPC acts as stabiliser to control particle size, an effect of agglomeration when increasing the gold loading to 3wt% is observed. It is important to identify the cause or mechanism which causes the formation of agglomerates or larger particles which can occur either in the metal sol solution during catalyst preparation or during the activation and treatment step. The activation temperature can cause a sintering of particles. This effect will be evaluated and discussed in the next section 4.4.3. Related studies reported on Au/C catalysts have shown that the immobilisation of the metal sol onto the support already increased the average Au particle diameter [155]. This effect could be enhanced with an increased gold loading. Other reported studies claimed there was no impact on the particle size or distribution with the gold loading. However, the investigated range was very low 0.25-1wt% [10].

A different approach to obtain information about the particle size is through X-ray diffraction. As a larger amount of sample is analysed at the same time, the results could lead to more representative values. At first, the reference catalyst 1.5Au/C was analysed by XRD as well as the activated carbon itself as background. The characteristic diffraction peaks of the crystalline

gold are the most intense reflection at $38^\circ 2\theta$ corresponding to the (111), followed by 44.4° and $64.6^\circ 2\theta$, corresponding to (200) and (220) planes, respectively [156]. The gold particle size can theoretically also be determined by the width of a half peak height with the Scherrer equation:

$$d = 0.9\lambda / \beta \cos \theta \quad 4-19$$

With β being the width of the half peak height and d the particle diameter and θ the Bragg angle. The only distinguishable diffraction line given from the Au of the catalysts is at $38^\circ 2\theta$, the peak at $44.4^\circ 2\theta$ is not distinguishable from the underlying peak of the carbon support. For the 1.5 Au/C (Figure 4-32), the peak is of very low intensity. This is due to the combination of the low weight percentage of the catalyst causing the weak peak intensity and also on the small particle size which causes a broadening of the diffraction lines as described in other reported studies [157] [158]. Other reports on Au on TiO_2 have also shown that only particles with a size larger than 5 nm, generated observable diffraction peaks [159].

As all other catalysts with a loading in the range of 0.75-1.5 wt% had an average determined particle size of approximately 5nm, the XRD pattern was expected to be similar. With an increase in gold loading to 3wt% the intensity of the Au reflection at $38^\circ 2\theta$ increases. This agrees with the fact that for larger particles the diffraction line becomes sharper. This is in correspondence to the average particle diameter obtained through TEM analysis. Furthermore, the reflection at 64.6° becomes slightly visible, however, the peak is very broad. The peaks were too broad and not distinct enough from the support so that it would become difficult to determine the half height peak width for calculating the average particle size. The XRD diffractogram in this case only delivered a qualitative analysis of the catalyst morphology confirming the trends determined by TEM.

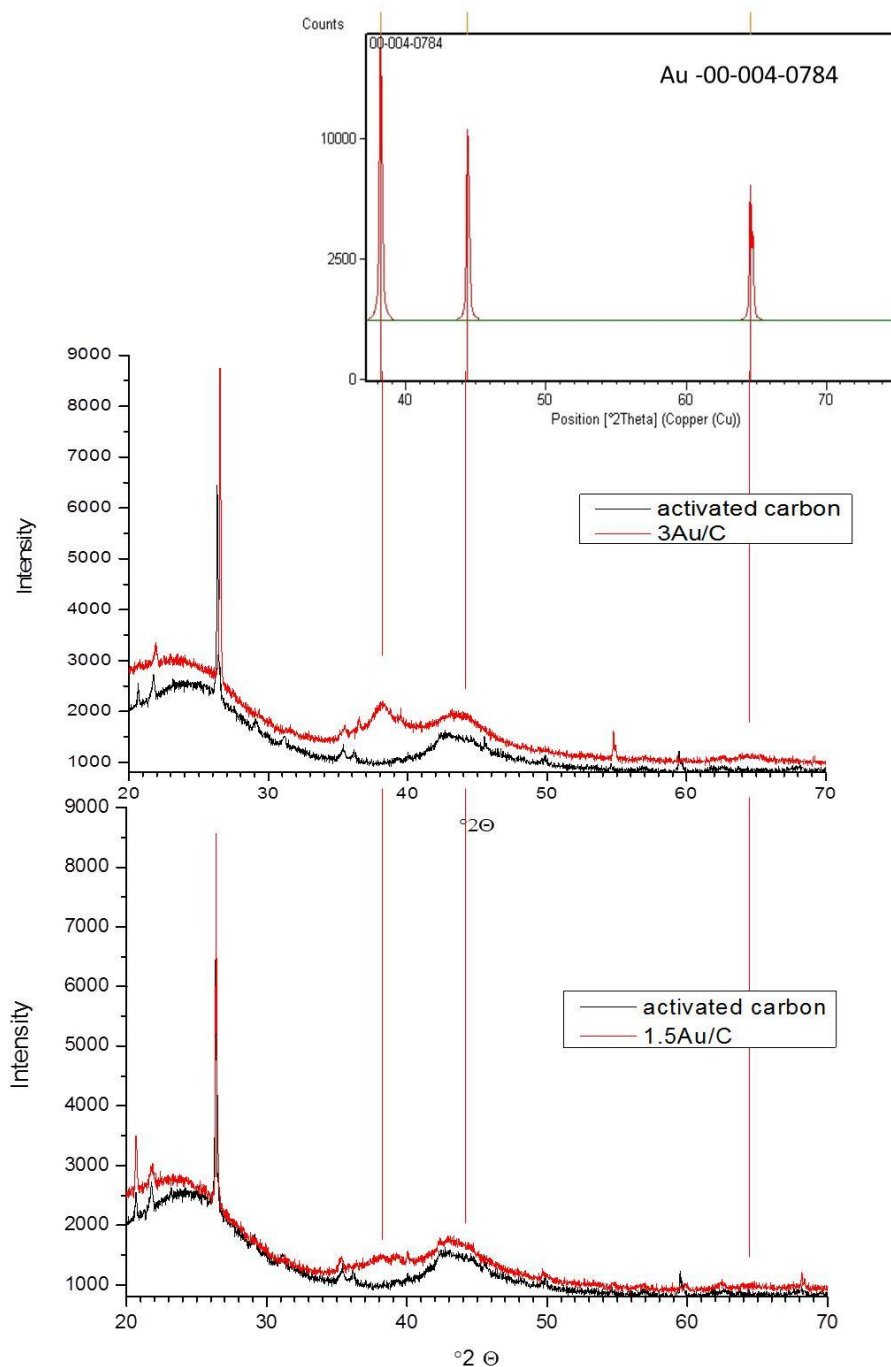


Figure 4-32: XRD Diffraction pattern of Au/C catalysts with different gold loading. — activated carbon, bottom— 1.5Au/C, top— 3Au/C.

4.4.3 Influence of catalyst heat treatment

The study on the influence of the gold loading has shown that for loadings in the range of 0.75-1.5wt% the average particle size and distribution remained relatively constant around 5nm (Table 4-8). However, for a higher loading of 3wt% a size increase of more than 60% to 8.3 nm

was observed. This effect could be based on the catalyst treatment which is carried out at high temperatures of 350°C causing agglomeration of Au particles. It has also been reported in the literature that [18] the increase in heat treatment temperature leads to an increase in Au particle size through agglomeration. Another reason could be the formation of larger particles in the metal sol during catalyst preparation and during immobilisation onto the support. In this case, the control of particle size by the organic stabiliser would not be as efficient for higher metal loadings. In order to study this effect closer, the catalyst was treated at a lower temperature of 150°C and investigated by TEM. Furthermore, the fresh and untreated catalyst was also analysed separately by TEM. However, for the fresh catalysts, the existence of the organic stabiliser on the surface caused side effects such as charging and drifting, therefore images could not be evaluated. The following figure shows the images of the 1.5Au/C catalyst and 3 wt% Au catalyst treated at 150°C and 350°C, respectively, for comparison.

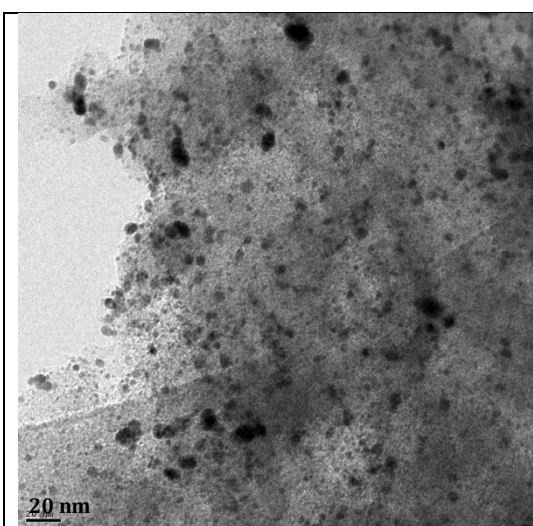


Figure 4-33: TEM image 1.5Au/_150°C.

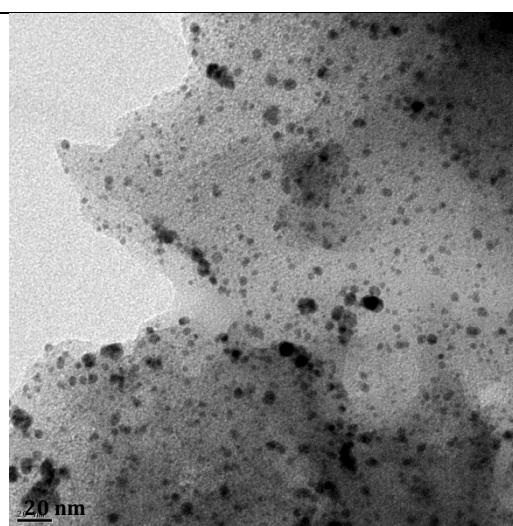


Figure 4-34: TEM image 1.5Au/C_350°C.

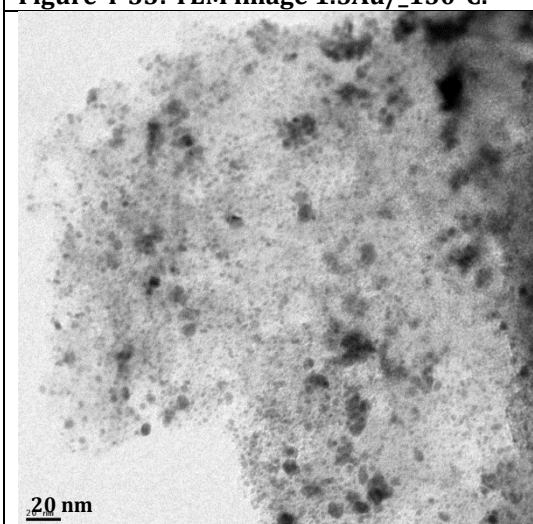


Figure 4-35: TEM image 3Au/C_150°C.

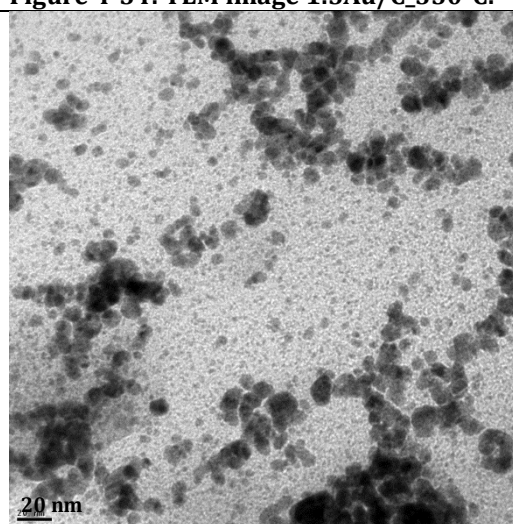


Figure 4-36: TEM image 3Au/C_350°C.

The images show that for the 1.5Au/C catalyst the difference in treatment temperature does not have an apparent effect on the catalyst particle morphology. In contrast, the TEM image for the 3Au/C catalyst treated at 150°C reveals a much finer dispersion of smaller particles, whereas at 350°C, as discussed earlier, the existence of large agglomerates becomes apparent. The average particle size and distribution of the catalysts treated at 150°C was obtained. The TEM histograms of the particle size distribution are presented in the Appendix. The main results are listed in the following table (Table 4-9):

Table 4-9: TEM results for Au/C catalysts treated at 150°C.

Catalyst*	Au average particle diameter (350°C) [nm]	Au average particle diameter (150°C) [nm]	SD Au average particle diameter (150°C) [nm]	Fraction 3.5-5.5 nm (150°C) [%]
1.5Au/C	5.1	6.1	2.6	65
3Au/C	8.3	7.1	2.3	50

*TEM results for 0.75Au/C and 1Au/C n.a.

The results show for the 1.5Au/C catalyst, the average particle size remains constant within error at a lower treatment temperature. The temperature does not affect the catalyst with the lower gold loading 1.5Au/C within error. For the 3Au/C catalyst the average particle size decreases only slightly and can be considered almost constant within error. However, the striking fact is that the fraction of smaller particles 3.5-5.5 nm increases from 20% to 50% which means that the catalyst treated at lower temperature has a larger fraction of smaller particles as can be taken from the TEM histograms (see Appendix). Therefore, the agglomeration of particles occurred during catalyst treatment. For the 1.5Au/C catalyst, the fraction decreases from 83% to 65% which is due to the fractional existence of even smaller particles <1.5-3.5nm, which is shown in the particle size distribution (see Appendix). These very small particles partially sinter during the catalyst treatment and form a larger fraction of particles of approximately 5nm thus narrowing the size distribution [Figure 4-30]. The effect of particle size enlargement through heat treatment was also reported in other studies investigating gold based catalyst systems such as 1Au/TiO₂, where a significant growth from 3.5–3.9 to 8–10 nm was observed at temperatures of 250°C [148].

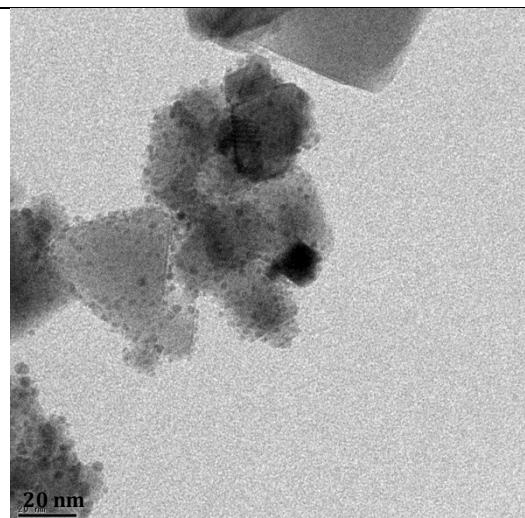
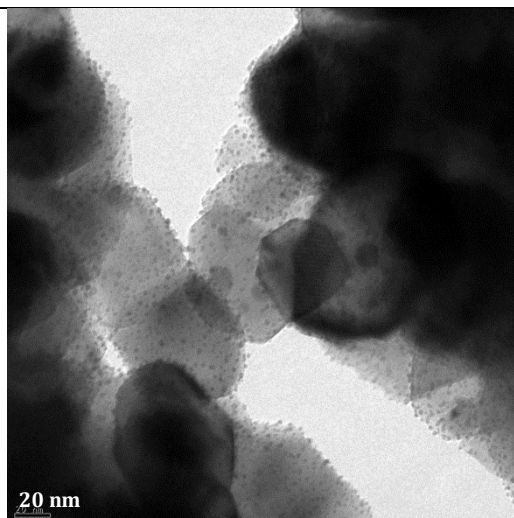
4.4.4 Nature of support

So far, the effect of gold particle size and distribution of the catalytic performance have been mainly discussed. The remaining factor influencing the catalytic activity was, as outlined in the introduction, the effect of the catalyst support, which was investigated in a set of preliminary experiments by supporting Au on conventional oxides such as CeO_2 and TiO_2 and testing them for selective oxidation of salicyl alcohol. The catalysts were prepared by sol-immobilisation as described earlier (Materials and Methods). The following table lists the properties of the applied materials.

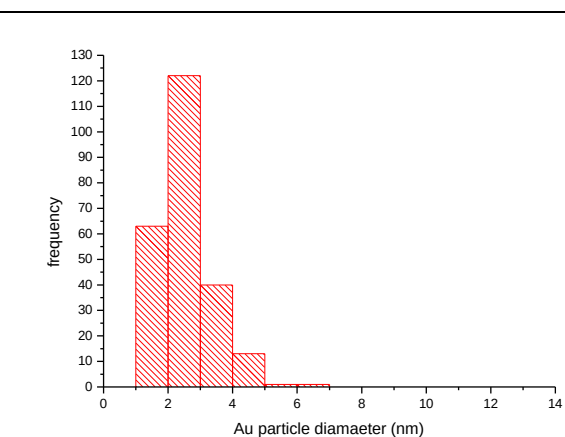
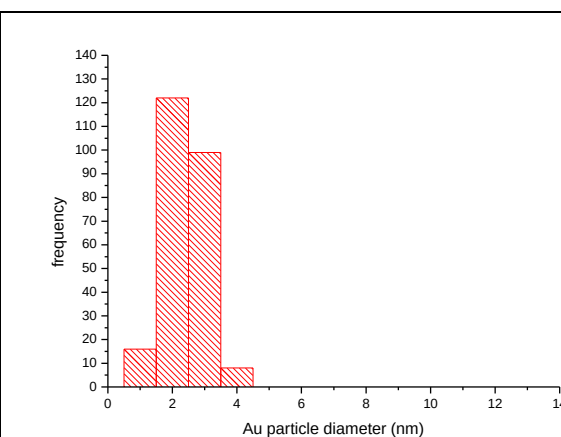
Table 4-10: Physical properties of oxide supports.

Support	grain size [nm]	S_{BET} [$\text{m}^2 \cdot \text{g}^{-1}$]	BJH adsorption Pore diameter [nm]	pore volume [$\text{cm}^3 \cdot \text{g}^{-1}$]
Ce(IV) oxide CeO_2	nanopowder <50nm	26	14.82	0.098
Ti(IV)oxide TiO_2	nanopowder	150	n.a	n.a

For direct comparison with the most active Au/C catalyst, the oxide material catalysts were prepared with 1wt% gold loading. TEM analysis was performed on the 1Au/ CeO_2 and 1Au/ TiO_2 catalyst and representative images are shown in the following figures (Figure 4-37 and Figure 4-38). It is striking that for both catalysts the gold particles are evenly distributed on the surface of the structured support and appear to be of homogeneous size. Therefore a narrow size distribution indicates a stronger metal support interaction.


 Figure 4-37: TEM image of 1Au/CeO₂.

 Figure 4-38: TEM image of 1Au/TiO₂.

The average particle size and distribution was determined and is illustrated in the following TEM histograms.


 Figure 4-39: TEM histogram of 1Au/CeO₂.

 Figure 4-40: TEM histogram of 1Au/TiO₂.

The histograms show that both catalysts have gold particles of a very small size and narrow distribution. The average particle diameter is around 2.5 nm and therefore 50% of the particle size of 1Au/C catalyst. The catalyst was prepared via the same sol-immobilisation technique as the 1Au/C catalyst, and was similarly treated and activated at 350°C. Therefore, the significant difference is based on the strong interaction between support and gold particles, which could play a role during the deposition of gold particles during sol-immobilisation. As already mentioned in the introduction, the metal-support interaction i.e. Au-oxide interphase and Au-

oxide charge-transfer has a large impact on the particle size, shape, catalytic activity and selectivity. The immobilisation and adsorption of the reduced gold particles, which are assumed to be negatively polarized [¹⁶⁰], on the support is described as electrostatic interaction with the positively charged support.

Furthermore, as described in the methodology, the immobilisation onto oxide supports was carried out at a low pH below the isoelectric point of the supports in order to enhance the adsorption. Once adsorbed onto the structured TiO₂ surface layer, the particles interact strongly with the support and do not migrate to form larger agglomerates. Even during the catalyst treatment at 350°C, the particles retain their shape and size, which indicates the strong interaction with the support. Other reported studies have also demonstrated that their catalyst 1Au/TiO₂ prepared by sol-immobilisation resulted in average Au particles of 2-3 nm [⁶³]. This effect stands in contrast to the Au/C catalysts, which underlie influences of particle agglomeration.

4.5 Catalyst effects- catalyst performance

The following section focuses on the impact of structural effects of the catalyst on the catalytic performance. In order to determine the conversion and turnover frequencies, it was important to verify that all catalytic conversion of salicyl alcohol was achieved exclusively by the gold on the catalyst and not by the carbon support. For this reason an experiment with just the support was carried out. The results obtained demonstrated that no catalytic activity takes place solely on the activated carbon support. Therefore, all catalytic activity is referred to the gold. The next step was to investigate the predominant properties such as average diameter, the distribution and the interaction with the support with respect to their impact on the catalytic performance, i.e conversion and selectivity.

The presented and discussed catalyst systems from the previous section were tested for selective oxidation of salicyl alcohol under the set conditions (see Materials and Methods). The following section illustrates the results for these different catalysts based on preparation method, gold loading and catalyst treatment temperature. The catalytic activity is expressed in conversion X_t in % after the specified reaction time $t = 360$ minutes, the selectivity towards salicyl aldehyde S in % at a specific conversion rate and initial turnover frequency values TOF in h^{-1} . As the TOF number is based on the active metal sites, it is assumed that the amount of Au in moles corresponds to the amount of available metal sites.

4.5.1 Influence of preparation method

The catalyst prepared by sol-immobilisation method achieved a 6 times higher performance in terms of TOF compared to the catalyst prepared by impregnation (Table 4-12). The low performance is likely to be caused by the increased average Au particle size and poorer dispersion on the surface

Table 4-11 Impact of preparation method on catalyst performance for the selective oxidation of salicyl alcohol.

catalyst	Preparation method	Treatment temperature [°C]	Au average particle diameter [nm]	Initial rate of reaction r *10 ⁻³ [mol/L*min]	X _{t360} [%]	S _{sal.aldX30} [%]	TOF* [h ⁻¹]
1.5Au/C	Impregnation	350	12.7	0.068	31	100	53
1.5Au/C	Sol-immobilisation	350	5.1	1.09	100	100	320

Reaction conditions: T=50°C, p =1bar (air), m_{cat}=0.2g, c_{salicyl alcohol}= 0.04M, NaOH:salicyl alcohol= 2:1, rpm= 1000.

***TOF after 0.5h.**

The results are also in agreement to previous reports on the effects of preparation method, where the pore impregnation method, compared to sol-immobilisation, led to large particles of >300 nm and thus resulted in a low catalytic activity in comparable selective oxidation reactions [73].

4.5.2 Influence of gold loading and catalyst treatment

Table 4-12 illustrates the impact of the gold loading on the catalytic performance as well as treatment temperature. Regarding the gold loading, the highest performance based on the TOF number was achieved by the 1Au/C catalyst with a TOF number of 342h⁻¹ followed by 1.5Au/C with a value of 320 h⁻¹.

Table 4-12: Impact of gold loading and treatment temperature on catalytic performance for the selective oxidation of salicyl alcohol.

catalyst	Treatment temperature [°C]	Au average particle diameter [nm]	Initial rate of reaction r *10 ⁻³ [mol/L*min]	Xt ₃₆₀ [%]	S _{sal aldX30} [%]	TOF* [h ⁻¹]
0.75Au/C	350	4.9	0.29	78	100	255
0.75Au/C	150	n.a	0.28	64	100	189
1Au/C	350	5.1	0.79	100	100	342
1Au/C	150	n.a	0.56	100	100	269
1.5Au/C	350	5.1	1.09	100	100	320
1.5Au/C	150	5.1	0.97	100	100	287
3Au/C	350	8.3	1.11	100	100	149
3Au/C	150	7.1	1.04	100	100	176

Reaction conditions: T=50°C, p =1bar (air), m_{cat}=0.2g, c_{salicyl alcohol}= 0.04M, NaOH:salicyl alcohol= 2:1, rpm= 1000.

*TOF after 0.5h

Compared with the results of the reference catalyst 1.5Au/C, when reducing the gold loading by 50%, i.e. for the 0.75Au/C catalyst, the activity decreases by 20%. Although the 0.75Au/C catalyst has the smallest average gold particles and therefore better dispersion, the lower performance might be due to the reduced number of available active metal sites. Therefore, even though the gold catalyst had homogeneously distributed particles of small size and narrow distribution, the catalytic performance did not necessarily increase linearly. When doubling the gold loading to 3wt%, the activity decreases by almost 56%. The low performance is based on the increased gold particle size of 8.3 nm. Other reported studies on the effect of the particle size on the catalytic performance have shown the activity of small gold particles <5nm was based on the presence of low-coordinated gold atoms [155]. The small particle size plays a role in lowering the activation energies and also facilitating the bonding with oxygen of the alcohol group of the reactant due to the presence of edge or corner sites. Therefore, an increase in particle size of the gold particles, leading to agglomerates and larger clusters of gold atoms, could hinder the adsorption of the reactant, consequently decreasing the rate of reaction.

For the impact of the treatment temperature, the results show an overall decrease in catalytic activity when reducing the treatment temperature to 150°C. This effect applies to all catalysts within the lower range of loading 0.75-1.5Au/C. This is due to the fact that the stabilizing agent THPC still remained on the catalyst surface possibly blocking catalytic active sites. However, the

3% Au/C catalyst shows a slight increase in catalytic activity when treated at 150 °C. Here, two effects seem to interplay influencing the catalytic activity: the treatment temperature affecting the average particle size and the removal of the organic residual to avoid blocking catalytic active sites. Hereby, other reported studies on 1Au/TiO₂ prepared by sol-immobilisation have shown that the heat treatment at 250°C leads to an increase in catalyst activity due to the removal of the residual on the catalyst surface and unblocking active sites [148].

The next key factor to investigate was the influence of the particle size on the selectivity. As can be seen from the results in Table 4-12, the selectivity towards salicyl aldehyde is 100% at conversion of 30% for all gold loadings, as no salicylic acid is formed at low conversions. The following figure presents the selectivity towards salicyl aldehyde reached for each catalyst at 100% conversion.

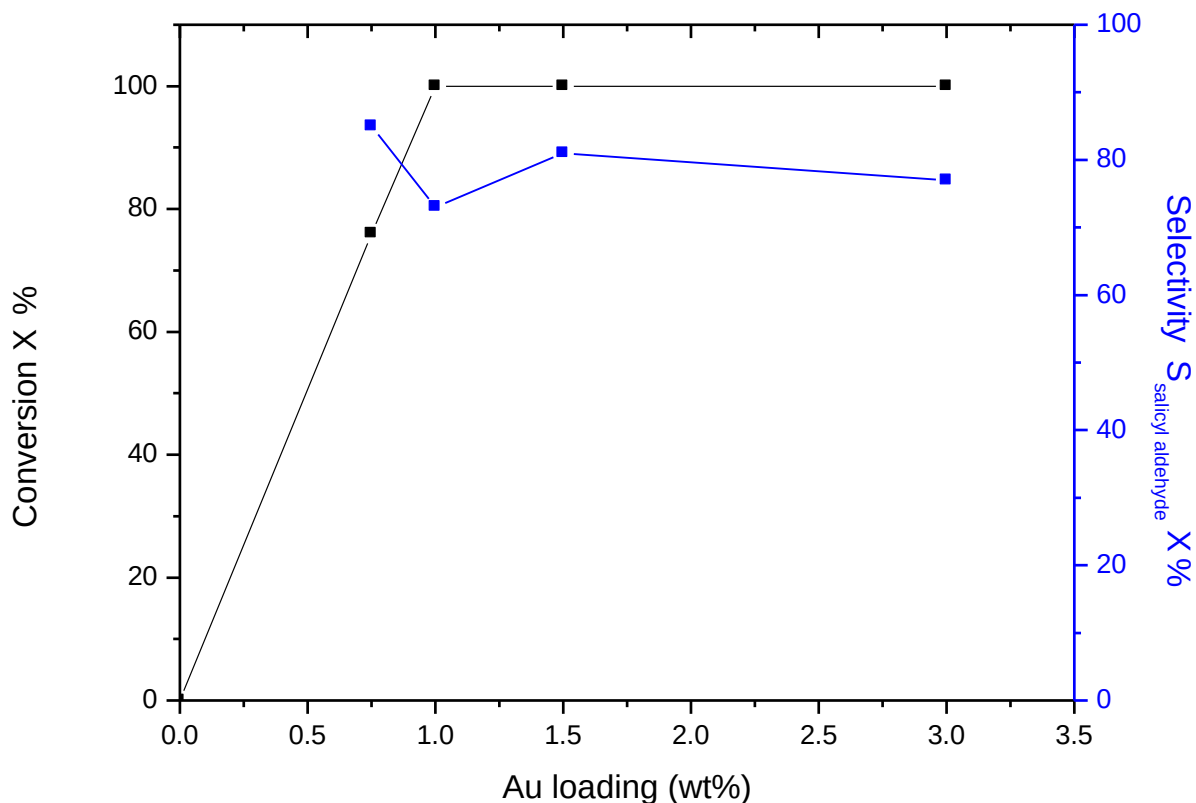


Figure 4-41: Influence of Au loading on catalytic activity and selectivity toward the selective oxidation of salicyl alcohol, reaction conditions: T=50°C, p =1bar (air), m_{cat}=0.2g, C_{salicyl alcohol}=0.04M, NaOH:salicyl alcohol= 2:1, rpm= 1000.

It can be seen that the selectivity towards salicyl aldehyde at 100% conversion remains relatively constant between 73-85% for all gold loadings. The values correspond to the samples taken at regular intervals during the course of reaction. Therefore, the exact time when 100% full conversion is reached between two samples can only be approximated. After reaching full conversion of salicyl alcohol, the selectivity towards salicyl aldehyde drops drastically with an increased gold loading. For 3Au/C, salicyl aldehyde has been fully oxidised after 360 minutes and only salicylic acid is detected (see Appendix).

In conclusion, the influence of catalyst preparation and temperature on the particle size and catalytic activity have been demonstrated in this section. The observed loss in catalytic activity with higher metal loading is therefore based on the increase in average particle size of the catalyst ^{[55],[77]} with the decrease in number of low coordinated Au atoms and loss in active sites. Furthermore, larger particles are likely to have increased adsorption energies leading to a decrease in catalyst activity.

These results are comparable to what has been found in other reported studies such as for the selective oxidation of glycerol, where an increase in particle size for Au/C catalysts caused a decrease in catalytic activity ^[48]. This effect was also based on the loss of low-coordinated Au atoms for the bigger particles making it more difficult for the reactant molecule to adsorb on the catalyst. Other reported studies on the selective oxidation of salicyl alcohol ^[137] showed that when increasing the gold loading above 1 wt% the selectivity towards salicyl aldehyde decreased due to product adsorption. Studies on similar oxidation reactions such as the selective oxidation of glycerol in the presence of 1wt% Au/C as a function of particle size have demonstrated a drastic decrease in catalyst activity when the gold particle size increased from 5nm to 17 nm based on the preparation method ^[48], however, an increase towards the selectivity of glyceric acid was observed.

4.5.3 Nature of support

To investigate the impact of the oxide supports on the catalytic performance the catalysts were tested for the selective oxidation of salicyl alcohol. The following table (Table 4-13) presents the main results including the average Au particle size. Furthermore, for comparison with the Au/C catalyst system, the particle fraction of the 3.5-5.5nm diameter is also presented.

Table 4-13: Influence of nature of oxide support on catalytic activity.

Catalyst	Au average particle size [nm]	SD Au average particle size [nm]	Fraction 3.5-5.5nm [%]	X _{t360} [%]	TOF* [h ⁻¹]
1Au/C	4.97	1.61	73	100	342
1Au/CeO ₂	2.48	0.84	23	90	142
1Au/TiO ₂	2.37	0.59	7	42	26

Reaction conditions: T=50°C, p=1bar (air), m_{cat}=0.2g, c_{salicyl alcohol} = 0.04M, NaOH:salicyl alcohol= 2:1, rpm= 1000.

*TOF after 0.5h

The results show that the catalytic activity achieved in TOF numbers by the oxide supported catalysts is much lower compared to the Au/C catalyst. Although the 1Au/TiO₂ catalyst has on average the smallest gold particles, it exhibits the lowest performance with a TOF number of 26h⁻¹. In contrast, the 1Au/CeO₂ reaches TOF numbers of 142 h⁻¹ and is therefore in a comparable dimension to the Au/C catalyst. The superior activity of the CeO₂ supported catalysts over the TiO₂ based catalyst can be based on the unique properties of CeO₂ i.e the presence of atomic or molecular oxygen on the catalyst surface, which could enhance the catalytic mechanism and increase the performance. In addition, the fraction of 3.5-5.5nm particles decreases drastically for the 1Au/TiO₂ catalyst due to the existence of smaller particles < 2nm. In this case, very small gold particles <3.5 nm might not have the optimised properties and structural geometry to enhance the selective oxidation of salicyl alcohol. Another reason might be that the very small particles are in very small pores and places inside the catalyst surface which are inaccessible for the reactant molecule. The contact interface between the particle and the oxide support, the electronic and charge transfer effects also play an important role in influencing the activity (2.3.4).

The impact on the selectivity towards salicyl aldehyde is illustrated in a selectivity/ conversion profile within the 360 min reaction time for the 1Au/C, 1Au/TiO₂ and 1Au/CeO₂ in Figure 4-42 in the presence of a base.

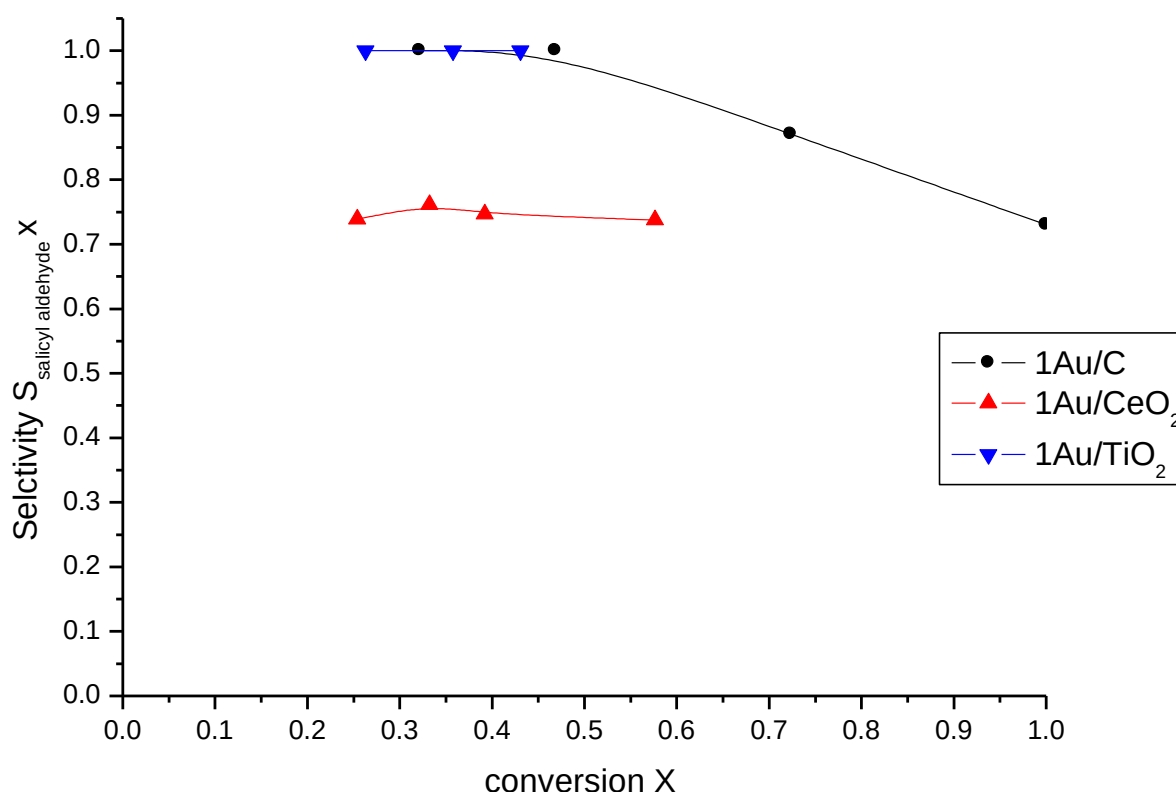


Figure 4-42: Selectivity/Conversion plot for selective oxidation of salicyl alcohol on carbon and oxide supported catalysts: 1Au/C, 1Au/CeO₂ and, 1Au/TiO₂.
 Reaction conditions: T=50°C, p=1bar (air), m_{cat}=0.2g, c_{salicyl alcohol}= 0.04M, NaOH/reactant= 2:1, rpm= 1000.

It can be seen that the selectivity towards salicyl aldehyde for the TiO₂ and C supported catalyst systems are 100% within the lower conversion range of 20-50%. After that the formation of salicylic acid is detected for the 1Au/C system. For the CeO₂ supported catalyst, however, the selectivity towards salicyl aldehyde in the same conversion range is lower due to an enhanced formation of salicylic acid. This effect is probably due to the oxygen storage capacity of CeO₂ which can therefore promote the formation of salicylic acid, through release of oxygen from the support to the catalyst surface. Hereby it would be important to investigate the kinetics, whether the selective oxidation of salicyl alcohol still followed sequential kinetics or whether another mechanism i.e. parallel conversion is taking place.

However, these are only preliminary experiments and the overall performance regarding the conversion and turnover frequency is much lower compared to the carbon supported gold catalyst. As these catalyst systems did not achieve the expected performance for the liquid phase oxidation of salicyl alcohol under the investigated conditions, they were not studied more

extensively in this context. However, other reported studies have revealed interesting catalyst properties based on similar reactions. Au/CeO₂ was applied as an efficient catalyst in the selective aerobic oxidation of aldehydes in the liquid phase to the respective acids and have demonstrated high catalytic performance over other oxide supported catalysts. This was based on the small gold particle size of 4-4.5 nm and also on the oxygen activated species formed on the support in particular on nanocrystalline CeO₂ [192]. Other reported work on the selective oxidation to benzyl alcohol under solvent-free conditions, pO₂ = 10 bar, has shown high performance of 1Au/TiO₂ demonstrating superior selectivity to benzaldehyde compared to 1Au/C.

The application of these materials as oxide supports will be further investigated in a different context of catalyst design (Chapter 5).

4.5.4 Recycle Tests

The lifetime and stability of the Au/C catalysts was tested by applying the catalyst 1.5Au/C for 3 consecutive runs under the same reaction conditions. After each run the catalyst was filtered, washed and dried before being applied. TEM analysis was done on the used catalyst to monitor any possible particle agglomeration and an increase in particle size. The reaction solutions were analysed by ICP to identify any leaching of gold.

The results show that no leaching of the gold into the reaction solution is detected. The average particle size was determined and is 6 nm (SD 3.1 nm) and therefore is nearly constant within error. However, the formation of larger particles is observed, resulting in a larger size distribution, which is illustrated in the TEM histogram in the Appendix. For the catalytic performance, a complete disappearance of salicyl alcohol is observed, however the expected yields of the products salicyl aldehyde and salicylic acid are not reached and the appearance of an unknown product peak is detected instead. Overall, the recycle experiments result in a large mass imbalance. In order to identify the product, the reaction solution was neutralized followed by an extraction of the organic phase. After removing the solvent, the organic residue was analysed by GC-MS. The results indicate the formation of a condensation product (see Appendix). This will be discussed in detail in the following chapter, where the same effect of a condensation reaction was encountered on an oxide supported catalyst system (5.4.5). The cause of the side reaction might be based on the blocking of catalyst active sites due to adsorption of reactants from the previous run or large amounts of base adsorbed on the catalyst surface. Other reported studies on the selective oxidation of benzyl alcohol have also detected amounts

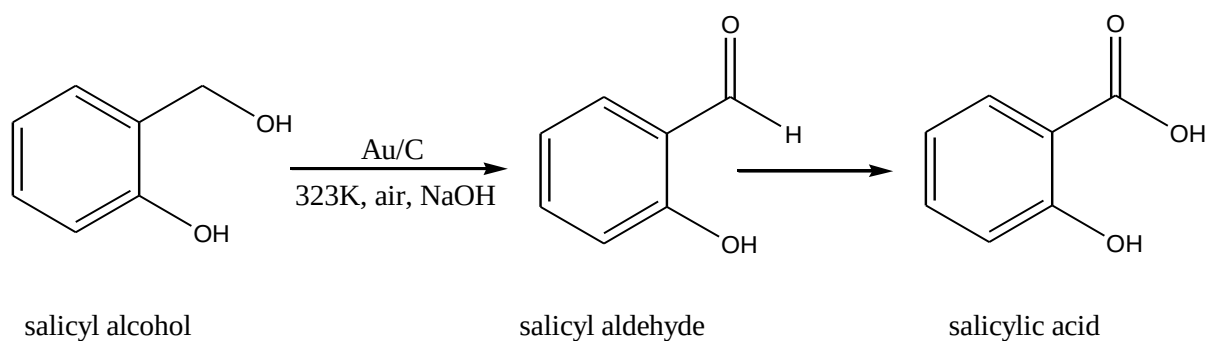
of benzyl benzoate, an esterification product of benzoic acid and the reactant benzyl alcohol [148].

However, it should be noted that for the preliminary recycle experiments, the catalyst was only washed with water and dried before being applied. Therefore, the recycle process might have not been effective enough to remove any organic or alkaline components on the catalyst surface. In case of a recycling treatment including heat treatment in order to decompose and desorb adsorbed species on the catalyst surface, the overall performance might be retained. Further investigations regarding this aspect will have to be carried out in future. The experimental conversion/ time data for the recycle experiments can be found in the Appendix.

4.6 Chapter summary

This chapter laid out a detailed study of the Au/C catalyst system and its application on the main model reaction, the selective oxidation of salicyl alcohol. The investigation covered three fundamental aspects: a) the setup of a suitable reactor system and parametric study b) the investigation of the kinetics and reaction mechanism c) study of the catalytic effects. The study of the parametric effects has set the optimal reaction conditions for carrying out the liquid phase oxidation of salicyl alcohol and obtaining the data without underlying effects based on mass transport limitations from the gas to liquid phase and liquid to solid phase. Therefore, for the following investigations, the kinetics and mechanism as well as the catalytic effects could be directly correlated to the reaction performance and obtained data. Furthermore, the mass balance of the reaction was 95-100%, which was analysed and quantified by HPLC as described in Materials and Methods.

The investigation of the kinetics and mechanism has demonstrated the reaction followed a consecutive reaction of first order. The general reaction network is therefore based on the oxidation of salicyl alcohol to salicyl aldehyde and consecutive oxidation to salicylic acid.



This mechanism was confirmed by the rate constants showing the rate of disappearance of salicyl alcohol is equivalent to the rate of formation of salicyl aldehyde and the disappearance of salicyl aldehyde corresponding to the formation of salicylic acid. Further, the study on the oxidation of salicyl aldehyde confirmed these rates. Further effects such as product adsorption were also studied and discussed and it was found that upon the addition of the product salicylic acid the rate constants decreased, particularly affecting k_1 which decreased by 60%, whereas the rate constant k_2 , corresponding to the disappearance of salicyl aldehyde, was less affected. The decrease in activity is likely to be caused by the decrease in OH⁻ which would lead to a 25% lower rate. Further blockage of active sites through adsorption of salicylic acid, or possible side reactions taking place on the catalyst surface are additional factors leading to a decrease in activity. Moreover, it was demonstrated that the reaction still followed sequential kinetics of first order.

The third section focused on the catalytic effects in particular the particle size and distribution as well as the nature of the support. The key drivers affecting the particle size and distribution were identified as preparation method and catalyst treatment. It was found that the sol-immobilisation method was very effective and delivered reproducible catalysts with small and highly dispersed gold particles. The results have shown that the 1 wt% and 1.5 wt% Au on carbon system, with the smallest average particle size and highest dispersion demonstrated the highest catalyst activity with TOF numbers of 342 h⁻¹ and 320 h⁻¹. The selectivity towards salicyl aldehyde was in the range of 73% and 83%, respectively, at 100% conversion of salicyl alcohol. Upon increase of gold loading the catalyst activity decreased due to agglomeration and increase of particle size. The effect of catalyst treatment showed that a decrease in treatment temperature lead to a decrease in activity due to the remaining organic stabiliser on the catalyst surface.

Overall, the results exceeded the catalytic performance reported by previous studies on the selective oxidation of salicyl alcohol by a factor of 40-50 [137]. It was furthermore demonstrated that the selectivity was not affected significantly by the gold loading and particle size. It was also shown that the application of conventional oxide supports such as CeO₂ and TiO₂ had a strong impact on the catalyst surface morphology achieving very small Au particles of 2.3 nm diameter. Hereby, Au/CeO₂ showed lower selectivities towards salicyl aldehyde, enhancing the formation of salicylic acid at lower conversions, which could possibly impact the reaction kinetics.

Challenges remain to be further investigated and optimised such as the catalyst recycling and increase of lifetime.

5 MOVING TOWARDS BASE-FREE CATALYSIS

5.1 Chapter introduction

The development of alternative and sustainable pathways for the production of fine chemicals has become a major challenge. The selective oxidation of alcohols to their higher oxygenates on noble metal catalysts is a key technology. Based on the unique catalytic properties, supported gold catalysts have become very attractive demonstrating superior catalytic performance, high selectivity as well as a long lifetime. The catalyst performance hereby is strongly dependent on the Au particle size and distribution and the interaction with the support. These properties can be influenced by the preparation method and the choice of support, which was investigated in the previous chapter. Hereby it was also demonstrated that the conversion rate correlated to the amount of base used. These results are in accordance with the studies in the literature on the Au/C system for selective oxidation of alcohols (see Chapter 4). Furthermore, the use of base such as NaOH proved to be effective, however caused high basicity of the reaction solution of pH >12 which poses an environmental concern.

This chapter aims to develop alternative routes to substitute the base by including the basicity into the catalyst itself. This approach is taken by using alkaline-earth metal oxides such as CaO and MgO to generate OH groups on the catalyst surface which are directly involved in the mechanism. This is illustrated in the following figure (Figure 5-1) based on a gold on MgO (Au/MgO) surface [111]. The mechanism is analogous to that on Au/C surface as discussed earlier, whereby the bulk OH species is replaced by the OH associated to the alkaline-earth metal oxides on the catalyst surface.

(1) The initial step involves the activation of the OH bond followed by the deprotonation through the OH groups associated to the alkaline-earth metal oxide i.e. MgO on the catalyst surface. The excess negative charge is taken by the Au and then taken by the molecular oxygen.

(2) The second step is based on the C-H bond activation from the gold with a consecutive beta-hydride elimination to form salicyl aldehyde. Studies have shown that the activation and cleavage of the C-H bond is the rate-determining step. It has been demonstrated that the reactivity depends on the particle size, thus smaller Au particles exhibit higher activity due to their coordinatively unsaturated state [108].

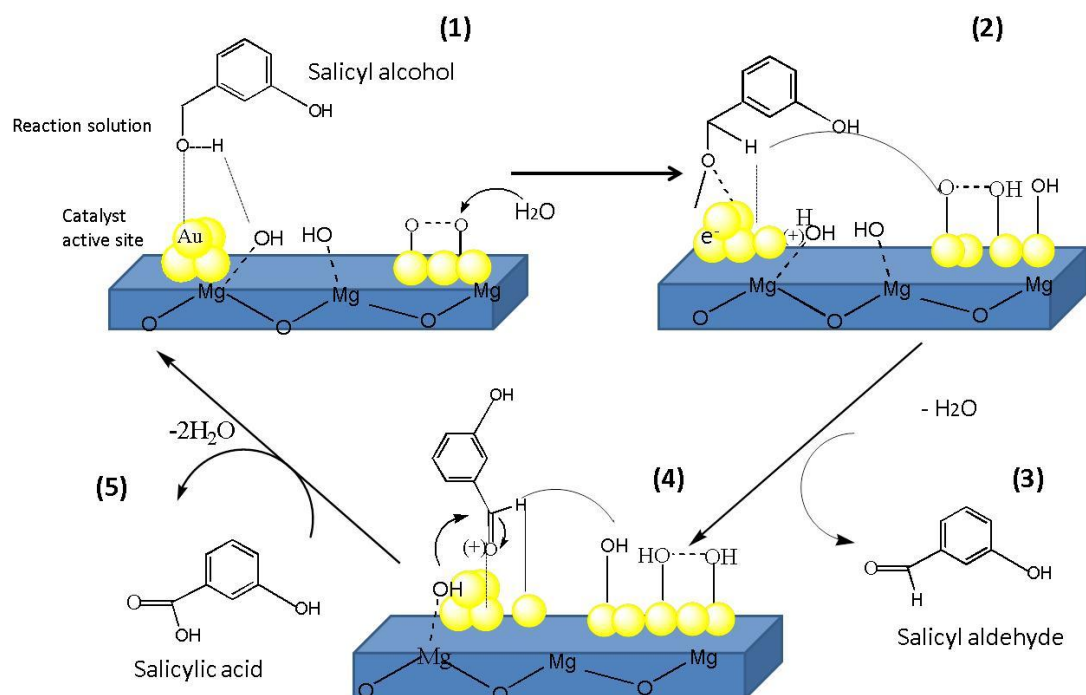


Figure 5-1: Proposed mechanistic scheme for selective oxidation of salicyl alcohol on an MgO-impregnated surface of HT support material.

The third step involves the desorption of salicyl aldehyde (3) and the oxidation of the hydride by the adsorbed oxygen species on the catalyst surface. For the formation of salicylic acid, the salicyl aldehyde is re-adsorbed onto the catalyst surface (4) and the C-O bond activated on the gold particle. The nucleophilic attack of the OH group is likely to occur through the OH species associated to the alkaline-earth metal oxide on the catalyst surface [118]. It is thus important that the basic Mg-OH sites and the gold active sites are in the proximity of each other so the dehydrogenation and the C-H bond activation can occur easily. The final step involves the desorption of the salicylic acid (5) and the regeneration of the active site. The regeneration occurs via the oxidation of the hydride through the adsorbed oxygen or hydroxide species on the gold particle which lead to the formation of hydrogen peroxide or water, respectively. The regeneration of the OH species associated with the alkaline-earth metal oxide surface can occur through adsorption of water. The following approach was taken to design a catalyst with basic surface sites:

1) Au on alkaline-earth metal oxides

The direct approach for the design of basic catalysts was to utilise the alkaline earth oxide materials directly as a support and to deposit the gold onto it. For this purpose, the commercially available oxides, CaO and MgO were used as supports. The catalysts were

characterised based on their structural morphology and properties and stability in the liquid phase with regards to leaching effects.

2) Au on impregnated oxides

The aim was to disperse and at the same time stabilize the alkaline-earth metal oxide on a structured oxide support such as CeO_2 and TiO_2 , which already showed attractive properties (see Chapter 4). This could also decrease the risk of possible leaching of the earth alkaline material into the solution. The catalysts were investigated and evaluated based on their catalytic performance and stability towards the selective oxidation of salicyl alcohol.

3) Au on impregnated hydrotalcites

In a further step, the application of complex metal oxides such as hydrotalcites with basic properties as supports was evaluated. These materials were further impregnated with MgO to enhance the basicity.

The structural morphology was investigated using XRD. CO_2 -TGA measurements were performed to obtain information about the CO_2 adsorption capacity correlating to the basicity of the materials. The effect of the basicity on the catalyst performance was tested on the selective oxidation of salicyl alcohol. Further impacts such as the gold loading and precursor effects were also investigated.

5.2 Au on alkaline- earth metal oxides

5.2.1 Au/MgO and Au/CaO

In general, the alkalinity of the earth metal oxides increases in the following order: $\text{MgO} < \text{CaO} < \text{SrO} < \text{BaO}$. SrO and BaO , however, dissolve completely in H_2O with formation of the respective hydroxides and are therefore considered not stable for this application as support. Therefore, the common oxides MgO and CaO have been applied as catalyst supports (Table 5-1):

Table 5-1: Properties of MgO and CaO as support.

Support	Grain size [nm]	S_{BET} [$\text{m}^2 \cdot \text{g}^{-1}$]	Pore volume [$\text{m}^3 \cdot \text{g}^{-1}$]
CaO	< 160nm	15.1	n.a
MgO	< 50 nm	2.3	n.a

The catalysts were prepared via sol-immobilisation as described in the part of Material and Methods. The final gold metal loading was 1.5wt%, which was confirmed by ICP analysis (see Materials and Methods).

Table 5-2: Catalysts prepared on alkaline-earth metal oxide supports.

Catalyst	wt% Au
1.5Au/CaO	1.5
1.5Au/MgO	1.5

The catalytic activity was studied for the selective oxidation of salicyl alcohol, as discussed in (5.2.1.2).

5.2.1.1 Catalyst morphology

The catalysts 1.5Au/MgO and 1.5Au/CaO were prepared by sol-immobilisation. The following figure presents the TEM images for the MgO and CaO supported Au catalysts together with the particle size distribution.

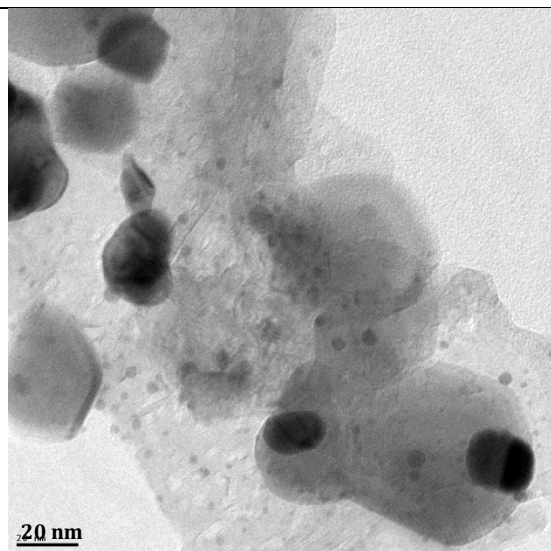


Figure 5-2: TEM image of 1.5Au/MgO.

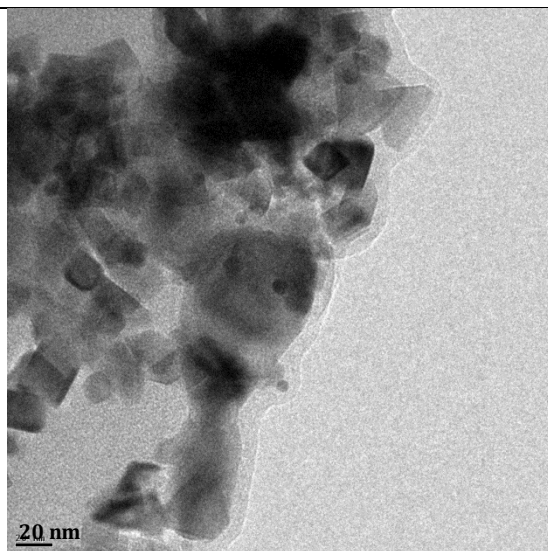
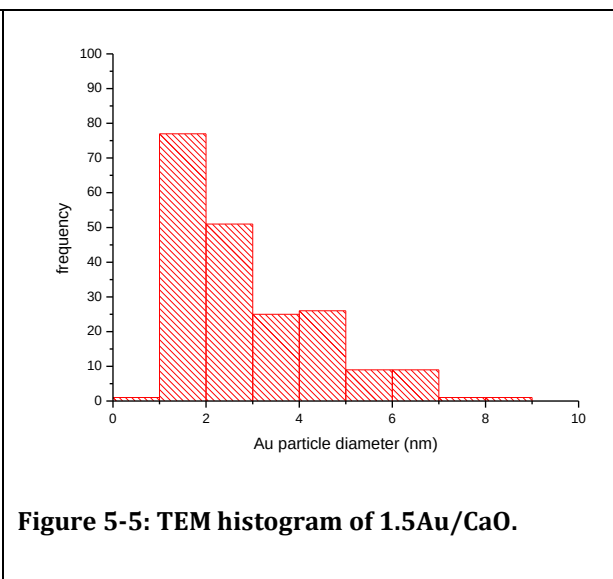
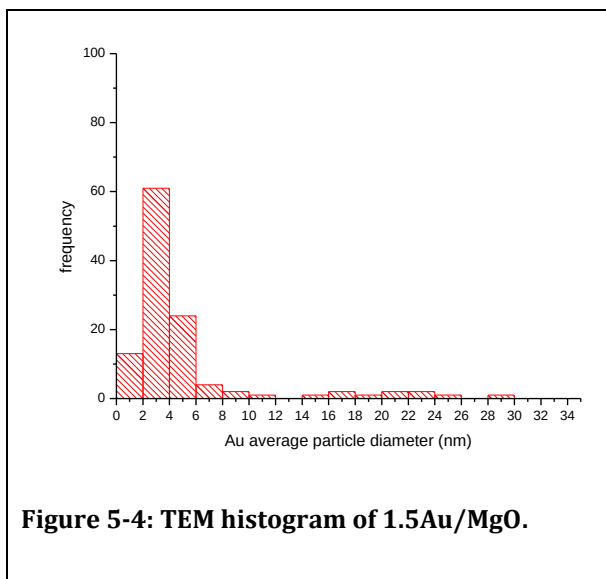


Figure 5-3: TEM image of 1.5Au/CaO.



It can be seen that the gold particles on the MgO support consist of a broader size distribution with particles >20 nm compared to the CaO supported catalyst. The average determined particle diameter for 1.5Au/MgO is 4.98 nm, almost double compared to the 1.5Au/CaO catalyst with an average particle diameter of 2.8 nm.

Table 5-3: Average particle diameter for CaO and MgO supported catalysts.

Catalyst	Au average particle diameter [nm]	SD Au particle diameter [nm]
1.5Au/MgO	4.98	3.32
1.5Au/CaO	2.81	1.23

This particle enlargement is due to agglomeration taking place during the catalyst preparation and moreover catalyst heat treatment. This is also based on the smaller BET surface area of MgO so that the Au particles are not as dispersed as on the CaO surface and tend to agglomerate more easily.

5.2.1.2 Catalyst activity

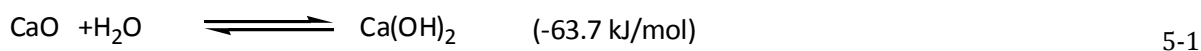
The catalyst performance was tested for the selective oxidation of salicyl alcohol under mild conditions without the presence of a base. The following table presents the results for the MgO and CaO supported catalysts expressed in conversion after 360 minutes X_{t360} and selectivity towards salicyl aldehyde at 30% conversion $S_{salald X30}$. In addition, the amount of leaching of Mg and Ca as well as Au in the reaction solution relative to the entire catalyst is also given.

Table 5-4: Gold catalysts on alkaline oxide for selective oxidation of salicyl alcohol.

Catalyst	X _{t360}	S _{salald-X30}	m (Mg /Ca) /m _{cat}	m Au/m _{cat}
	[%]	[%]	[wt%]	[wt%]
1.5Au/MgO	65	100	30.1	<1
1.5Au/CaO	37	100	53.5	<1

Reaction conditions: T=50°C, p=1bar(air), c(sal.alc) = 0.04 M, NaOH: salicyl alcohol: 0:1, rpm = 1000.

The 1.5Au/MgO catalyst shows a higher catalyst performance compared to the CaO supported catalyst despite the lower alkalinity. Both catalysts show an extremely high amount of leaching analysed by ICP. The CaO supported catalyst exhibits the highest leaching leading to an effective loss of >50% of the catalyst during the reaction. The leaching for CaO is higher compared to MgO. This effect is likely caused by the higher solubility of CaO in water (1.2g/L at 30°C) compared to MgO (0.086 g/L at 30°C) and a highly exothermic reaction (2):



However, for both catalysts at the reaction time of 6 hours, the active metal gold does not leach proportionally into the solution along with the leached support indicating that the leaching process occurs from the inner support rather than from the surface.

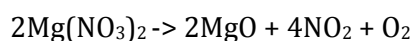
In order to make these catalyst systems sustainable and stable for the liquid phase oxidation in water, it was important to suppress leaching. Studies by Milone et al. have applied comparable alkaline-earth metal oxide supported Au catalysts such as AuCa on Ca(OH)₂/CaO for the selective oxidation of salicyl alcohol and buffered the solution with Na₂CO₃ in order to reduce the solubility of Ca [138]. However, this approach implied the application of an additional additive such as Na₂CO₃ which would need to be separated again from the reaction solution. Furthermore, the CO₃²⁻ might adsorb on the catalyst surface and influence the catalyst activity. The effect of buffering was investigated in this study and will be discussed at a later stage.

A new approach was taken by designing a catalyst with the surface properties and basicity of an alkaline-earth metal oxide but dispersed on a stable support.

5.3 Au on impregnated oxides

5.3.1 Introduction

The aim was to promote structured and high surface area oxides such as TiO_2 or CeO_2 with the alkaline-earth metal oxides CaO and MgO . The catalysts were prepared by impregnating the supports with the nitrate precursor salts $\text{Ca}(\text{NO}_3)_2$ and $\text{Mg}(\text{NO}_3)_2$ followed by calcination at 650°C in air to decompose the nitrate and obtain the alkaline- earth metal oxide (see Materials and Methods). The calcination temperature was set according to the decomposition temperature region obtained through TGA analysis.



The following table lists the properties of the utilised supports for impregnation.

Table 5-5: BET surface area of oxide supports used for impregnation.

Support	Grain size [nm]	S_{BET} [$\text{m}^2\cdot\text{g}^{-1}$]	Pore size [$\text{m}^2\cdot\text{g}^{-1}$]	Pore volume [$\text{m}^2\cdot\text{g}^{-1}$]
CeO_2	< 50	26	14.82	0.098
TiO_2	< 50	150	n.a	n.a
Al_2O_3	< 50	155	n.a	n.a

Based on the average pore volume of the supports and the solubility of the precursor, a maximum final loading in wt% of MgO and CaO was obtained:

Table 5-6: Catalyst series prepared for CaO and MgO impregnated oxides.

Catalyst	Au [wt%]	MgO [wt%]	CaO [wt%]
1.5Au/0.16MgO- CeO_2	1.5	0.16	
1.5Au/0.16MgO- TiO_2	1.5	0.16	
1.5Au/0.16MgO- Al_2O_3	1.5	0.16	
1.5Au/0.28CaO- CeO_2	1.5		0.28
1.5Au/0.28CaO- TiO_2	1.5		0.28
1.5Au/0.28CaO- Al_2O_3	1.5		0.28

Hereby, the theoretical loading of MgO and CaO was assumed to correspond to the final actual loading based on the catalyst preparation and calcination procedure in air which ensured complete decomposition of the nitrate salt into the respective oxide.

5.3.2 Catalyst morphology and properties

TEM analysis was performed on the catalysts to determine the average particle size and distribution of the Au particles. BET analysis was done to evaluate the change in surface area upon impregnation and calcination. Further, a few XRD measurements were performed to investigate the structural and morphological changes due to impregnation with alkaline-earth metal oxides. The following table lists the impregnated supports after calcination and the values for the BET surface area.

Table 5-7: BET values for MgO and CaO impregnated oxide supports.

Catalyst	BET surface area [m ² /g]	Pore size [nm]	Pore volume [m ² /g]
0.16MgO-CeO ₂	14.82	27.12	0.10
0.16MgO-TiO ₂	31.04	21.6	0.17
0.16MgO-Al ₂ O ₃	93.90	6.95	0.16
0.28CaO-CeO ₂	7.13	38.5	0.07
0.28CaO-TiO ₂	0.82	46.58	0.01
0.28CaO-Al ₂ O ₃	54.48	12.26	0.17

The results show that the surface area decreases drastically upon impregnation with MgO and CaO together with a decrease in pore volume. This was particularly evident for the TiO₂ supported materials compared with the unpromoted supports. This effect can be based on the filling in or blockage of micropores of the original support due to impregnation by MgO/CaO crystallites or due to sintering during the calcination process. The stronger decrease in surface area for the CaO impregnated supports is due to the higher loading. The following images show the representative TEM micrographs of the Au particle on the MgO and CaO impregnated oxide supports. Further images of the catalyst series of impregnated supports can be found in the Appendix.

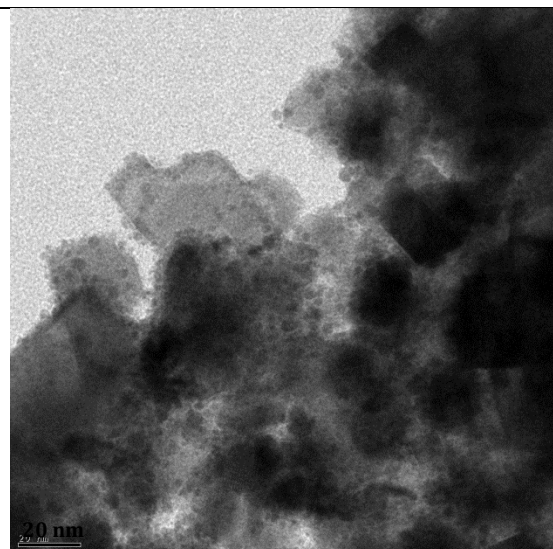


Figure 5-6: TEM image of 1.5Au/0.16MgO-CeO₂.

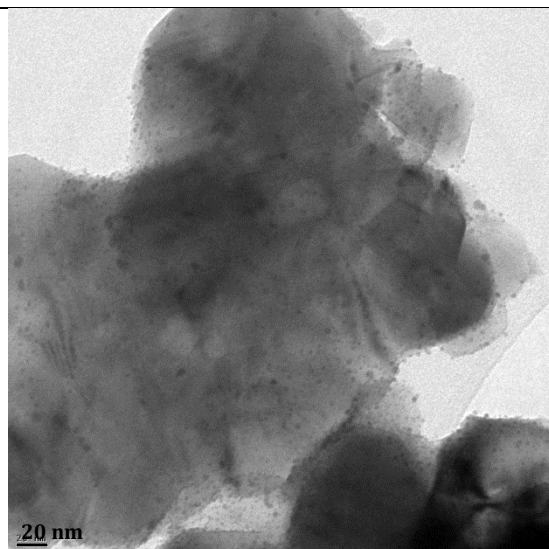


Figure 5-7: TEM image of 1.5Au/0.28CaO-TiO₂.

At first glance, the Au particles appear very small and of narrow size distribution, and homogeneously distributed on the support particle. The catalyst surface morphology in terms of size and distribution shown in the TEM histograms of Au particles appears to be similar to that of the 1Au/CeO₂ and 1Au/TiO₂ catalyst discussed in (4.4.4).

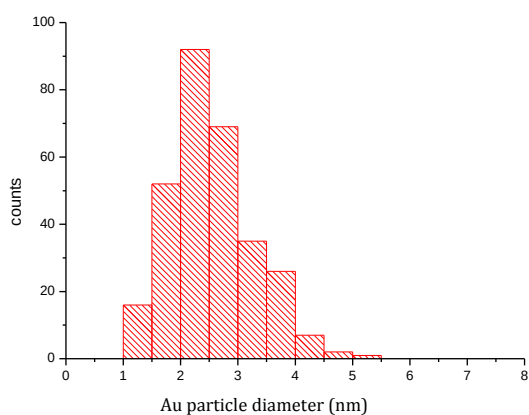


Figure 5-8: TEM histogram of 1.5Au/0.16MgO-CeO₂.

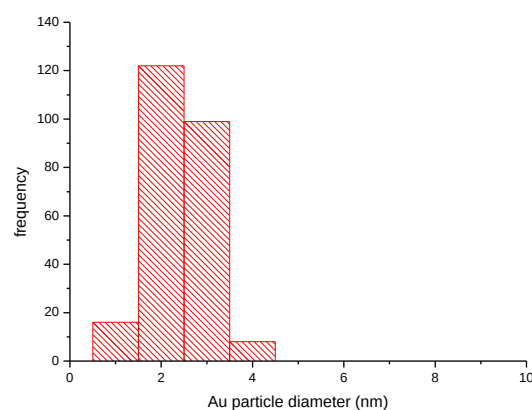


Figure 5-9: TEM histogram of 1.5Au/0.28CaO-TiO₂.

The determined average particle sizes are listed in the following table (Table 5-8). The presence of MgO cannot be identified at first sight from the TEM images. For this purpose, XRD diffraction patterns were obtained to give more detailed information. The results for the Au particle size show that the promoted CeO₂ and TiO₂ catalysts have the smallest Au particle size 2.37-2.6nm. These values correspond to the average Au particle size on the unpromoted Au/CeO₂ and

Au/TiO₂ catalyst discussed earlier (see Chapter 4). This indicates that the underlying support predominantly influences the Au particle size and distribution rather than the promoted MgO or CaO. The narrow size distribution indicates a strong interaction with the support preventing an agglomeration of the particles. The largest average particle size is obtained with the Al₂O₃ supported catalyst. The effect on the catalyst performance will be discussed in the following section.

Table 5-8: Average particle diameter for MgO and CaO impregnated catalysts.

Catalyst	Au average particle diameter [nm]	SD Au particle diameter [nm]	Fraction 3.5-5.5nm Au particles [%]
1.5Au/0.16MgO-CeO ₂	2.48	0.63	22.2
1.5Au/0.16MgO-TiO ₂	2.5	0.5	15.9
1.5Au/0.16MgO-Al ₂ O ₃	n.a	n.a	n.a
1.5Au/0.28CaO-CeO ₂	2.62	0.60	52.8
1.5Au/0.28CaO-TiO ₂	2.37	0.49	43.6
1.5Au/0.28CaO-Al ₂ O ₃	4.98	1.33	70

XRD diffraction was performed exemplary on the MgO promoted CeO₂ support 0.16MgO-CeO₂. The following figure illustrates the promoted support 0.16MgO-CeO₂ compared to the reference pattern of MgO obtained from the ICDD database (00-001-1235). The reference reflections for MgO are marked red in the sample diffractogram. For comparison, diffraction pattern of the pure CeO₂ is illustrated as well. The figure shows that the diffraction pattern of the MgO promoted CeO₂ material is nearly the same to that of the pure CeO₂ support.

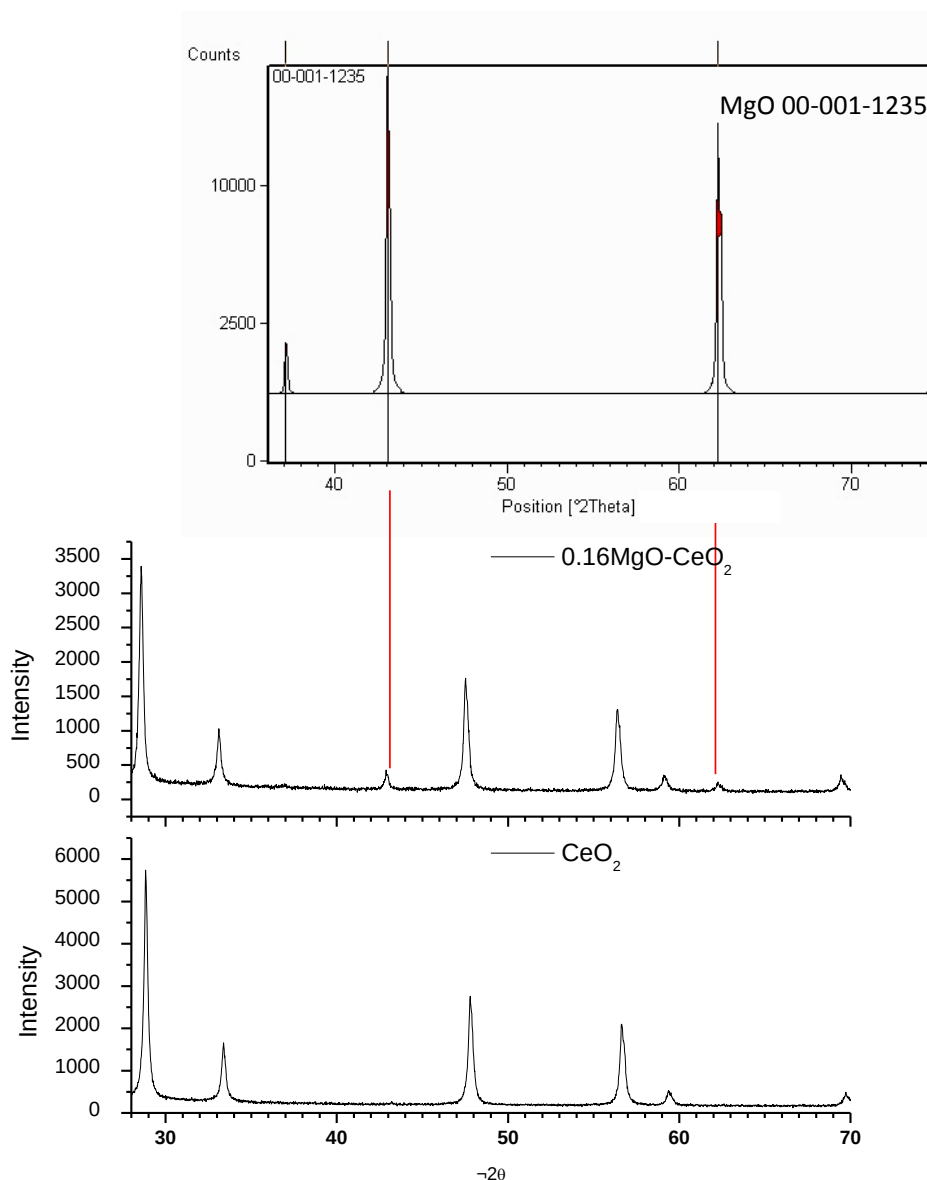


Figure 5-10: XRD diffractogram for MgO impregnated CeO_2 support 0.16MgO-CeO_2 compared to MgO (ICDD database ID 00-001-1235).

Both patterns show sharp peaks at the same positions. Only for the promoted support the overall intensity is slightly lower. However, as expected, the crystallinity and structure of the underlying CeO_2 support is not largely influenced by the MgO promotion and calcination as CeO_2 is a highly structured and temperature stable support. The peaks at 43° and 63° 2θ correspond to MgO, demonstrating the presence of MgO on the support surface, however, they are of low intensity and broad shape. The low intensity is likely to be based on the low loading of MgO. The broad shape could indicate the presence of very small and dispersed MgO crystallites on the CeO_2 surface. Furthermore, the BET results show that the surface area decreases by nearly 50% upon impregnation with MgO, however, the pore size and volume remain nearly constant. This

could mean that the MgO crystallites are located on the CeO₂ pores rather than being dispersed in the pores, which would affect the pore size and volume. This was only a preliminary examination of the MgO promoted CeO₂ support and further investigations regarding the other promoted oxides of the series would need to be carried out. The next step was to investigate the catalytic performance of the promoted catalysts towards the selective oxidation of salicyl alcohol.

5.3.3 Catalyst activity

The series of CaO and MgO promoted catalysts were tested for the base-free selective oxidation of salicyl alcohol under mild conditions (see Materials and Methods). The results for the conversion of salicyl alcohol after 360 minutes and the selectivity towards salicyl aldehyde after 360 minutes are presented in the following table (Table 5-9). In addition, the amount of leached Mg/ Ca relative to the total catalyst is given as well as the Au leached into the reaction solution.

Table 5-9: Impregnated oxides for the selective oxidation of salicyl alcohol under base-free conditions.

Catalyst	Xt ₃₆₀ [%]	S _{sal} aldehydet ₃₆₀ [%]	m(Mg/Ca)/m _{cat} [wt%]	mAu /m _{cat} [wt%]	pH
1.5Au/0.16MgO_CeO ₂	22	100	9	<0.1	8.2
1.5Au/0.16MgO_TiO ₂	<1	100	10	<0.1	8.7
1.5Au/0.16MgO_Al ₂ O ₃	21	100	n.a	<0.1	n.a
1.5Au/0.28CaO_-CeO ₂	9	100	14	<0.1	n.a.
1.5Au/0.28CaO_-TiO ₂	<1	100	15	<0.1	n.a.
1.5Au/0.28CaO_-Al ₂ O ₃	8	100	n.a	<0.1	n.a

***Reaction conditions: T=50°C, p=1 bar (air), m_{cat}=0.2g, c(sal.alc)= 0.04 M, NaOH/reactant: 0:1, rpm=1000.**

The results show that the catalysts in total exhibit relatively low catalyst activity, the maximum conversion reached is 22% by 1.5Au/0.16MgO-CeO₂. This is likely to be caused by the low concentration of basic sites on the catalyst support, as the direct correlation of the conversion rate with the base concentration has been demonstrated earlier (Chapter 4). All catalysts show a considerable amount of leaching of the promoted CaO and MgO into the reaction solution, which corresponds to almost 50% of the initial promoted earth alkaline metal oxide which

could lead to a fast deactivation of the catalyst. The leaching is possibly caused by a weak interaction of the alkaline-earth metal oxide with the support and further driven by the exothermic reaction with water. The CaO promoted catalysts show an overall lower activity compared MgO promoted catalysts despite of the higher loading and stronger alkalinity. This could be based on a different surface morphology of the CaO compared to MgO promoted catalysts with larger agglomerated crystallites forming with an inhomogeneous distribution. Although both alkaline-earth metal oxides have the same crystal structure, the difference in performance is likely to be based on a synergistic effect between MgO/CaO and Au, charge transfer effects and the smaller size of the MgO crystallites. Further, the TiO₂ support, shows no significant activity irrespective of the promotion of alkaline-earth metal oxide. This could also be based on a weaker metal-support interaction. Further studies regarding the electronic structure of the catalyst surface would have to be carried out. Overall, the alkaline-earth metal oxides especially supported on CeO₂ show potential for base-free selective oxidation of salicyl alcohol. However, further investigations would need to be carried out aiming to increase the performance and decrease leaching.

5.4 Au on promoted hydrotalcites

5.4.1 Introduction

This section extends the study of earth alkaline promoted catalysts to using more complex structured materials such as hydrotalcites. As introduced in the Literature Review the materials are double-layered hydroxides, and the flexibility in the structure based on the possibility of interchange of the anions and cations to obtain the desired catalyst properties have made them very attractive as catalyst materials. In this study, the Mg-Al based hydrotalcite materials with a ratio of 3:1 Mg:Al are discussed for the selective oxidation of salicyl alcohol and promoted with MgO to further enhance the basicity. Hereby, the influence of MgO promotion on the basicity and catalyst activity are discussed and investigated as well as gold loading under the aspects of whether a lower loading and higher dispersion have any effect on the activity.

5.4.2 Influence of MgO loading

The materials were prepared by promoting hydrotalcite (HT) with the nitrate precursor salt Mg(NO₃)₂ followed by a calcination at 650°C in air to decompose the nitrate and obtain the alkaline-earth metal oxide (see Materials and Methods). Prior to the preparation the HT material was calcined in air at 400°C. After impregnation, the calcination temperature was set

according to the decomposition temperature region obtained through TGA analysis. The gold was deposited via sol-immobilisation. The following series of promoted HT materials was synthesised:

Table 5-10: Series of unpromoted and MgO promoted Au/HT catalysts.

Catalyst	Au loading [wt%]	MgO loading [wt%]
1.5Au/HT	1.5	-
1.5Au/0.16MgO-HT	1.5	0.16
1.5Au/0.08MgO-HT	1.5	0.08
1.5Au/0.04MgO-HT	1.5	0.04

Hereby, the theoretical loading of MgO was assumed to correspond to the actual loading based on the catalyst preparation and calcination procedure in air ensuring the full decomposition of the precursor and formation of the oxide.

5.4.2.1 Catalyst morphology

The catalyst characterisation was based on the properties of the promoted support itself and the Au surface morphology of the support. Hereby it was important to determine the influence of the HT on the size and distribution of Au particles and the impact of MgO promotion of the HT support on the Au particle size and distribution. For this purpose TEM analysis was performed on the pure HT support, the unpromoted 1.5Au/HT and the promoted 1.5Au/0.16MgO-HT support. The representative micrographs are illustrated in the following figures:

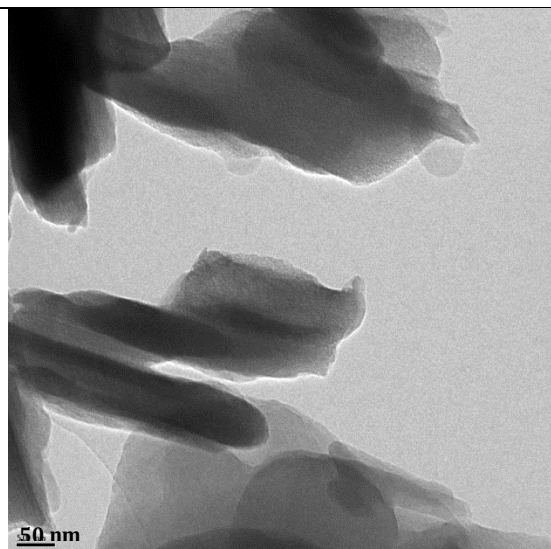


Figure 5-11: TEM image of HT support.

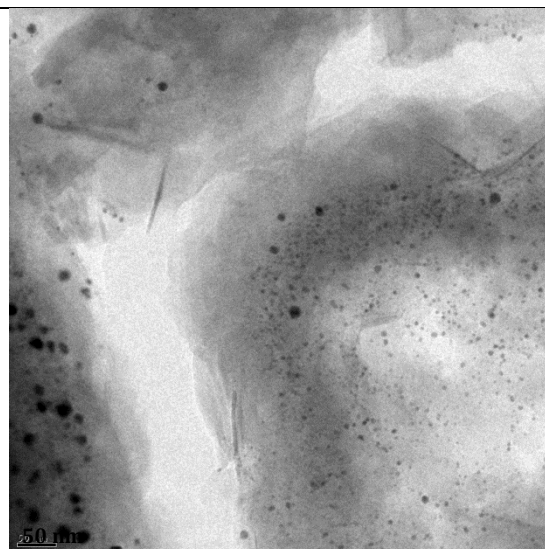


Figure 5-12: TEM image of 1.5Au/HT.

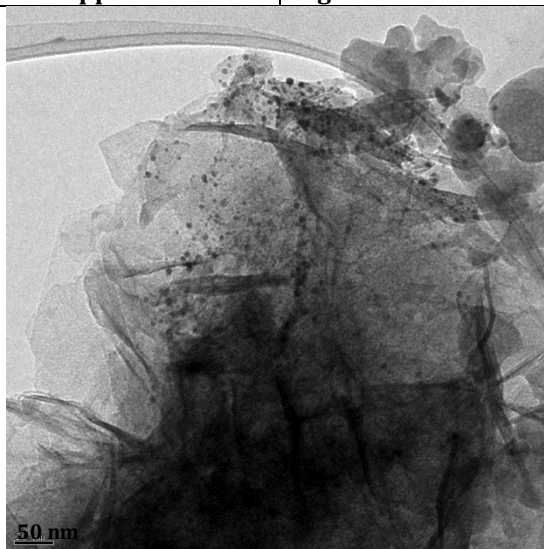


Figure 5-13: TEM image of 1.5Au/0.16MgO-HT.

For the unpromoted 1.5Au/HT support, the gold particles appear to be of small size, and evenly distributed over certain areas, however, some areas do not seem to be containing any gold particles. For the promoted 1.5Au/0.16MgO-HT support, the size and distribution of Au particles seem to be similar. It is possible that the gold deposits on specific areas on the HT support are based on the support morphology, i.e pore size and surface charge. Further, for the promoted HT catalyst it can be seen that the support changes into a fibre-type material compared to the pure HT. This can also influence the deposition of Au onto the material. This phenomenon will be further investigated and discussed based on additional EDX and STEM analysis (see 5.4.4). The average Au particle size for the unpromoted HT and the MgO promoted HT catalyst was determined. It can be seen that the average Au particle size increases only

slightly for the catalyst with the highest MgO promotion. It was therefore assumed that the Au surface morphology is independent of the amount of promoted MgO.

Table 5-11: Average Au particle diameter for promoted and unpromoted HT.

Catalyst	Au loading [wt%]	Au average particle size [nm]	SD Au average particle size [nm]
1.5Au/HT	1.5	5.50	1.5
1.5Au/0.16MgO-HT	1.5	6.27	1.73

The next step was to investigate the structural morphology of the support and the basicity with the impact of MgO loading. For this purpose, the MgO impregnated materials were analysed by N₂-physisorption. The following table lists the average BET surface areas for the series of MgO promoted HT materials together with the values for the original support material calcined at 400°C.

Table 5-12: BET surface areas for MgO promoted HT catalysts.

Catalyst	S _{BET} [m ² *g ⁻¹]	Pore size [nm]	Pore volume [m ³ *g ⁻¹]
HT	130.40	2.40	0.09
0.16MgO-HT	16.84	7.80	0.04
0.08MgO-HT	42.50	9.04	0.19
0.04MgO-HT	80.01	11.29	0.42

The results show that the surface area decreases with an increase in MgO promotion. This is possibly based on the blocking of micropores of HT which can be caused by the formed MgO crystallites. Further, the average pore size increases which might be based on agglomeration during catalyst calcination resulting in a larger pore size distribution. The effect on the catalyst basicity and performance towards the selective oxidation of salicyl alcohol will be discussed in the next section. Related reported studies on HT materials have shown that calcination in air leads to further decrease in surface area due to sintering of the newly formed small MgO crystallites in the presence of the H₂O vapour produced upon calcination and decomposition [109]. Other studies have shown that the removal of CO₂ leads to formation of high porosity with an increase in surface area [110].

As discussed in the Literature Review, a major factor influencing the structural morphology of HT is the thermal treatment at high temperature. Therefore, the unpromoted HT was also

calcined individually at 650°C resulting in a decrease in surface area to 20m²/g. Another important factor to be considered is ageing. In general, due to exposure to the atmosphere, the HT material adsorbs H₂O and CO₂ resulting in a change of the surface area over time. Related studies have shown that the BET surface area decreased with increased ageing time and hydrothermal treatment temperature [110].

X-ray diffraction was performed on the series of MgO promoted catalysts to obtain information on the influence of the MgO promotion on the structural morphology. In general, the HT materials are double layer close packings of OH anions in which cations M²⁺/³⁺ occupy alternate octahedral sites. Such M-OH are edge shared forming infinite layers of brucite type [95] stacked above each other. CO₃²⁻ and H₂O molecules occupy the interlayer spacings balancing electroneutrality. The diffraction pattern shows sharp basal reflections at lower angles and broader reflections at higher angles. [95]. The existence of both sharp and diffuse non-basal reflections is interpreted as an indication of a partially disordered structure, with defects above all in the stacking superposition of the regular unit layers. Furthermore, small and defect, anisotropically shaped-rich crystallites cause significant line broadening [95]. Especially in layered structures, a lot of stacking defects among the reflecting planes (crystallite size broadening) as well as defects due to an increased spacing (strain or deformation broadening) are seen, which cause a line broadening in the diffractogram based on the difference in particle size. This can be expressed with the following equation (5-2):

$$\Delta(2\theta) = \lambda / L \cos \theta \quad 5-2$$

With $\Delta(2\theta)$ being the width of the reflection peak L the thickness of the crystallite, λ the wavelength and θ the Bragg angle. The following diffractogram shows the diffraction patterns of the pure HT as well as the series of MgO promoted HT materials. The reference reflection positions for pure MgO are marked in red and the reference pattern for HT is given for comparison.

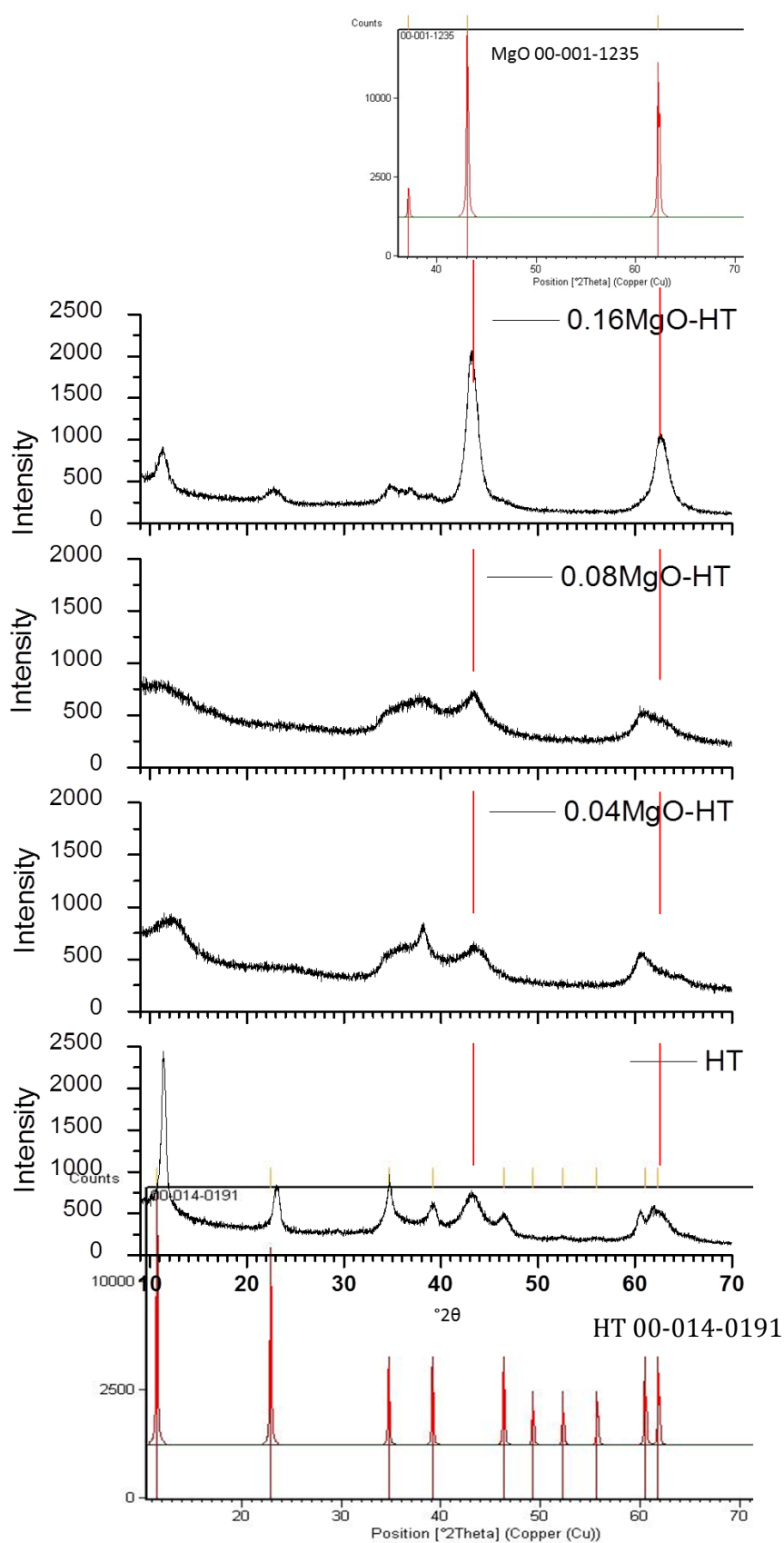


Figure 5-14: XRD stacked diffractograms of series of MgO promoted HT materials 0.04MgO-HT, 0.08MgO-HT, 0.16MgO-HT, compared to the reference diffractograms of HT (00-014-0191) bottom and MgO (00-001-1235) top.

The diffractogram shows that upon increasing MgO promotion and calcination, the underlying HT structure slowly disappears and transforms into a MgO-like structure. Furthermore, the peaks are very broad indicating the presence of small and defect structured particles. As discussed earlier, according to the thermal behaviour of HT, higher temperature causes the loss of interlayer H_2O and CO_2 . It can also be seen that at lower MgO loadings the peaks indicating the original HT material are very broad and diffuse and also slightly shifted to the reference pattern of HT. This could indicate a possible transitional, amorphous phase between HT and MgO caused by MgO dispersed into the structure of the HT changing the lattice parameters and thus creating a shift in scattering angles. Another reason could be the crystallization of MgO occurring via intermediate structures. Related studies have shown that the thermal decomposition and transformation of $\text{Mg}(\text{OH})_2$ to MgO occurs via the formation of a defect layer of $\text{Mg}(\text{OH})_2$ with smaller cell dimensions prior to the re-crystallisation to the cubic structure characteristic of MgO [110]

With the highest loading at 0.16 wt% the MgO peaks become sharp and distinct indicating the presence of well crystallised MgO. This could be caused by the increased amount of MgO resulting in precipitation of MgO crystallites on the surface and agglomeration of these crystallites upon calcination or a mixed oxide structure of MgO with Al. The agglomeration is also caused by the loss of surface area upon impregnation and calcination. This is also in agreement with studies by Sharma et al. [110] showing that the crystallite size increases with increasing temperature. Previous reported studies on the composition of Mg-Al based hydrotalcite materials have shown that certain structures are only retained with specific molar ratios of Mg/Al of 2-3, however some metastable homogeneous compounds with ratios 1-4 have been reported [106]. Any composition outside these ratios could cause precipitates of separate hydroxides, carbonates and hydroxycarbonates. Regarding the thermal behaviour, the results of this study conform to studies on the thermal behaviour of HT, wherein after calcination at 300°C for 2 hours the diffraction pattern shows the existence of both HT and MgO. Upon the increase of the calcination temperature to 400-800°C, only peaks corresponding to the MgO diffraction lines are observed [97].

The next section investigates the further properties of the MgO promoted HT materials, including the surface charge/ zeta-potential and in particular the CO_2 adsorption capacity. The zeta potential gives information about the intensity of particle surface charge and the stability of the colloid solution. The following figure shows the measurements for the zeta potential against the pH for the unpromoted HT and promoted HT with the highest MgO loading. The isoelectric point is reached when the zeta potential is nearly zero. The figure shows that for the analysed pH range of 2-12, the zeta potential decreases with increasing pH but the isoelectric point has

not been reached. Upon extrapolating the trend, the zeta-potential would be reached at a pH value of around 13. Other studies have shown ^[161] that the point of zero charge potential for MgO occurred at $\text{pH } 12.5 \pm 0.5$. The values for the measured zeta potential are nearly the same for the unpromoted and promoted HT.

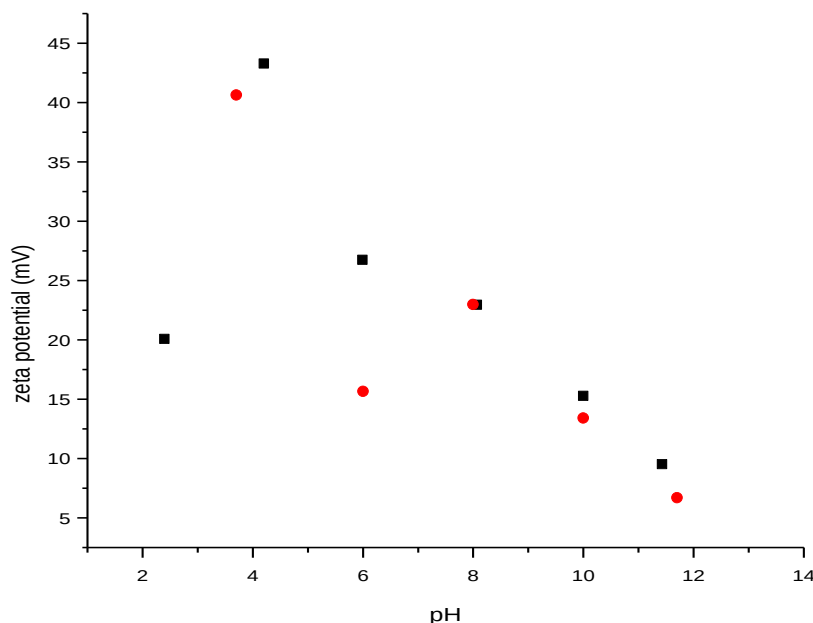


Figure 5-15: Zeta potential measurements of HT■ and 0.16MgO-HT◆ for a pH range from 2-12.

In general, a relatively high zeta potential value around 40-60 mV indicates a relatively stable colloid. Although there is a linear trend for the course of zeta potential values, it can be seen that a few values fall out of line. This is caused by a fluctuation of the value for zeta potential indicating that the colloid was not stable. This could have been also caused by a quick settlement of particles due to their heavy weight. Another factor could be the hydration of the material as shown in previous reported studies on hydrotalcite materials, whereby the isoelectric point of oxides could shift up in about 1.5-2.5 pH units with the hydration degree ^[162].

5.4.2.2 Catalyst basicity

In order to obtain information on the alkaline properties of the MgO impregnated HT materials, the CO_2 adsorption capacity was investigated through CO_2 -TGA measurements. Hereby, the

analysis was performed on the catalysts with the gold deposited on the MgO promoted HT supports. As discussed in the Literature Review, the CO₂ adsorption is an indicator for the basicity of the catalyst surface. The measurements were performed as described in Materials and Methods, and the maximum temperature chosen for the measurement cycle was 400°C in order not to evoke a structural transformation of the HT during the measurement. As a reference, the original HT material was tested several times for CO₂-adsorption in order to establish the temperature profile of the measurement. A typical adsorption profile is illustrated in the following figure (Figure 5-16:

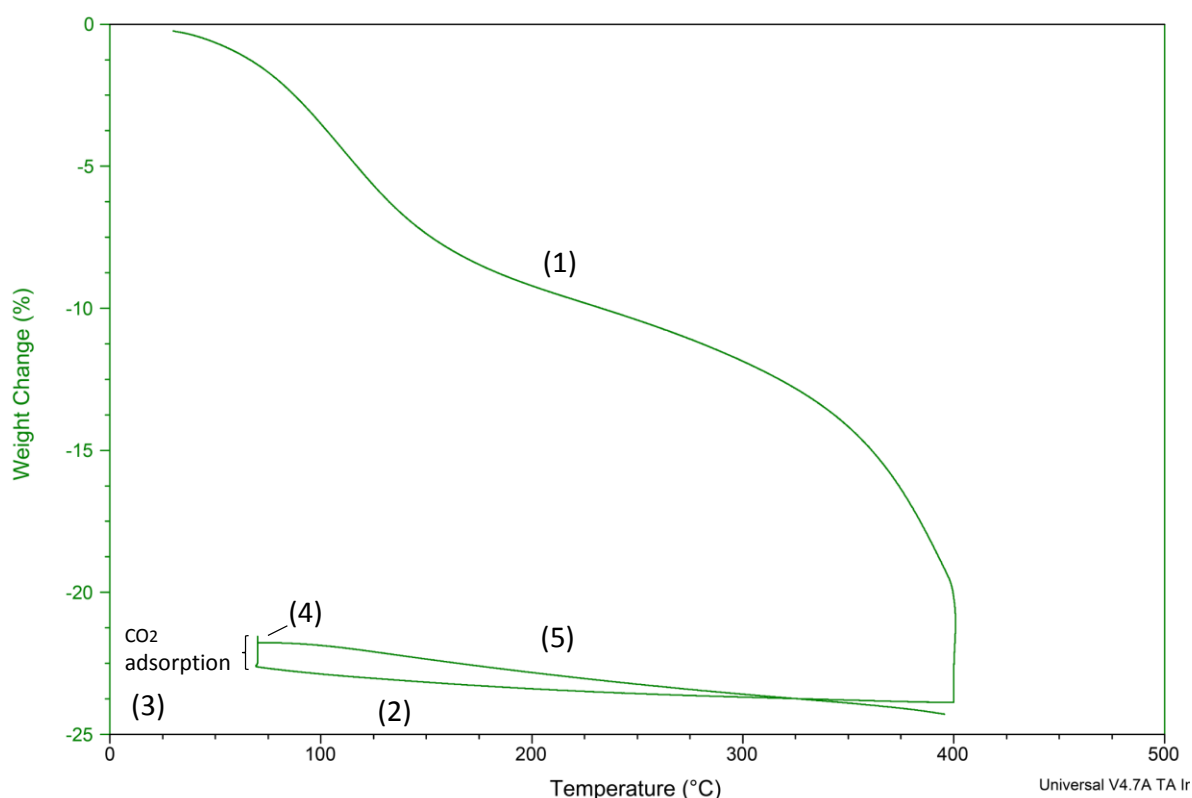


Figure 5-16: Profile for TGA-CO₂ measurement cycle on 1.5Au/0.16MgO-HT step 1-5, total differential weight change (%) against temperature, initial weight m_{cat} =19.5340 mg.

As discussed earlier, the HT material is sensitive to ageing resulting in a loss of BET surface due to adsorption of CO₂ and H₂O from the atmosphere. Thus for the TGA cycle measurements, samples were degassed at 400 °C in a flow of N₂ for 1h (1) before lowering the temperature under N₂ (2) and switching to CO₂ to carry out the CO₂ adsorption measurement at 70 °C (3). During this cycle the catalyst exhibits gradual weight loss of around 20-25 wt%, which mainly corresponds to the loosely-held physisorbed H₂O in the interlayer space and some initial decarbonation [100].

It can be seen that when exposing the catalyst to CO₂ the weight increases. This can be based on two types of adsorption: low temperature CO₂ adsorption via physisorption and high temperature adsorption of CO₂ via chemisorption. The latter is an indicator for the surface basicity of the catalyst material. Following the CO₂ adsorption step, the measurement cycle is set to 70°C under N₂ marking the desorption step (4). During this cycle a loss of about 15 wt% of the adsorbed CO₂ can be observed. This weight loss could correspond to the amount of loosely physisorbed CO₂ on the catalyst surface. Finally, when the temperature is increased gradually up to it 400°C (5) all adsorbed CO₂ is already desorbed at a temperature of 330°C. This loss presents the stronger chemically adsorbed CO₂ on the catalyst surface. Further weight loss at around 400°C is monitored which indicates the additional desorption of H₂O from the initial material. The following obtained results present the overall amount of adsorbed CO₂ (Table 5-13) together with the determined surface area of the catalyst expressed by $m_{CO_2}/(m_{cat} \cdot S_{BET}$ surface area).

Table 5-13: CO₂ TGA measurements for MgO promoted HT catalysts.

Catalyst	S_{BET} *10 ⁻³ [m ² *g ⁻¹]	m_{CO_2}/m_{cat} *10 ⁻³ [mg/mg]	$m_{CO_2}/S_{BET} \cdot m_{cat}$ (SD) *10 ⁻³ [mg*m ⁻²]
HT	130.01	0.92	7.11(0.34)
Au/HT	32.01	0.62	19.40 (0.34)
1.5Au/ 0.16MgO-HT ₋	5.10	0.69	136.42 (0.38)
1.5 Au/0.08MgO-HT	11.91	0.67	56.15 (0.18)
1.5 Au/0.04MgO-HT	18.90	0.68	36.25 (0.1)

The results show that the absolute amount of adsorbed CO₂ remains relatively constant for all MgO promoted HT materials. The pure HT has the highest value of CO₂ capacity which is based on the high surface area. The relative adsorbed CO₂ based on the BET surface area shows that the highest capacity is reached for the catalyst with the highest MgO promotion. Therefore, the results correspond with the expected trend of an increased basicity with an increase in MgO promotion. Other studies on HT materials have shown that samples with a higher ratio of Mg showed higher intrinsic basicity and, further, that calcination at higher temperatures of 700°C show higher basicity compared to pure MgO [108]. Therefore, the alkalinity of the calcined and

MgO impregnated support is expected to increase even further and possibly exhibit a higher catalytic performance, which will be discussed in the following section.

5.4.2.3 Catalyst activity

The series of MgO-promoted HT materials was tested for the selective oxidation of salicylic alcohol under mild and base-free conditions. As already demonstrated through CO₂-TGA measurements, the materials exhibit basic properties correlating with the promotion of MgO. The basic surface sites are in this case substituting the role of the conventional base additive in the bulk solution, such as NaOH. The following figure (Figure 5-17) shows a typical concentration/ time profile for the selective oxidation of salicyl alcohol on the 1.5Au/0.16MgO-HT catalyst. The products detected were salicylic aldehyde and salicylic acid. No other products were detected in the gas or liquid phase. The carbon mass balance reached was 95-100% at all times.

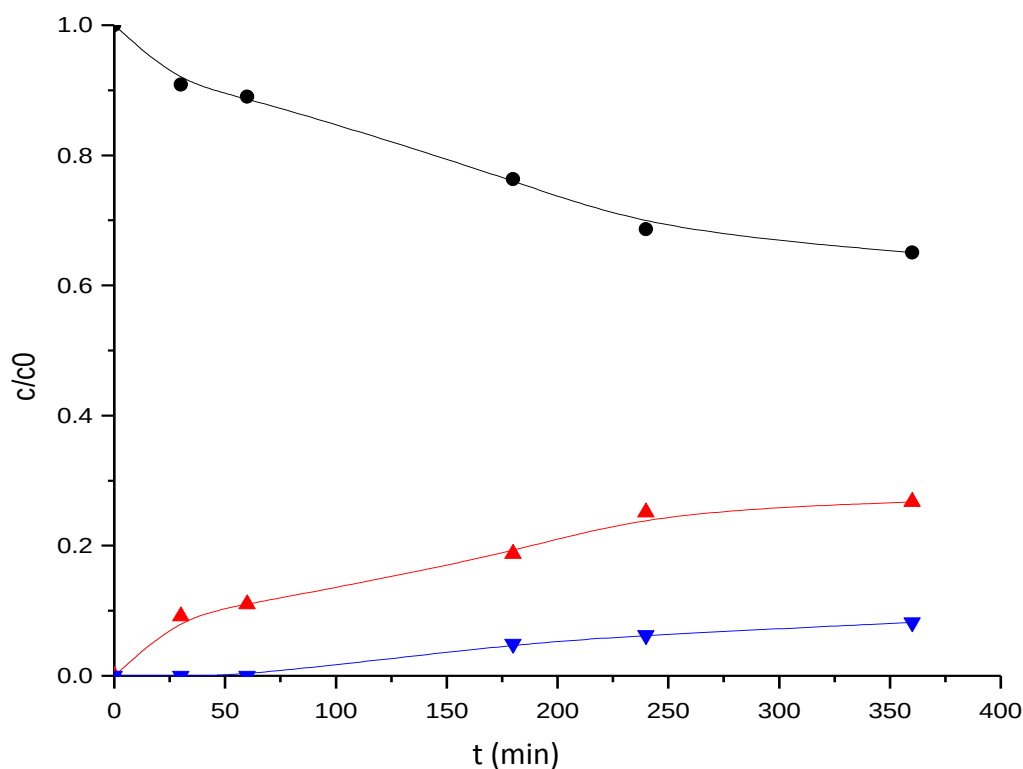


Figure 5-17: Concentration/ time profile for the selective oxidation of salicylic alcohol: Reaction conditions: catalyst: 1.5Au0.16MgO-HT_650, T=50°C, p=1bar (air), $c_{\text{salicyl alcohol}} = 0.04\text{M}$ $m_{\text{cat}} = 0.2\text{g}$, NaOH/reactant=0:1, rpm=1000.

●salicyl alcohol, ▲salicylic aldehyde, ▼salicylic acid.

The main product is salicyl aldehyde, which is detected at the beginning of the reaction at low conversions. The formation of salicylic acid is observed after 1h, also at low conversions. It is therefore possible that salicylic acid directly forms through conversion of salicyl alcohol through a parallel mechanism. This is due to the enhancement of the formation of salicylic acid on the catalyst surface possibly due to available OH species or O_2^{2-} from the MgO on the catalyst surface. Results by previous reported studies on the selective oxidation of salicyl alcohol have reported a parallel mechanism using $CaCO_3$ as support reaching selectivities of 15% towards salicylic acid at 90% conversion [138]. The following table lists the results achieved for the conversion of salicyl alcohol after 360 minutes and the selectivity towards salicyl aldehyde at low conversions of 20% together with the initial rate of reaction. In addition, the amount of leaching of Mg of the total catalyst and Au into the reaction solution determined by ICP is also listed:

Table 5-14: Effect of MgO loading on initial rate of reaction for the selective oxidation of salicyl alcohol.

Catalyst	Initial rate of reaction [mol/(L*min)]	X_{t360} [%]	$S_{salald \cdot X20}$ [%]	Mg/ m_{cat} [wt%]	Au/ m_{cat} [wt%]	pH
1.5Au/HT	n.a	<5	100	n.a	n.a	n.a
1.5Au/0.16MgO-HT	1.2*E-04	35	90	5	<0.1	8.6
1.5Au/0.08MgO-HT	4.6*E-05	22	100	3	<0.1	8.1
1.5Au/0.04MgO-HT	3.9*E-05	10	100	3	<0.1	7.6

Reaction conditions: catalyst 1.5Au0.16MgO-HT, T=50°C, p=1bar (air), $c_{salicyl\ alcohol}$ = 0.04M, NaOH:salicyl alcohol 0:1, rpm=1000.

The highest catalytic activity is exhibited by the 1.5Au/0.16MgO-HT catalyst with the highest MgO promotion. This can already be seen in the initial rate of reaction, which is 2.6 times higher compared to the catalyst 1.5Au/0.08MgO-HT. The selectivity towards salicyl aldehyde is lower due to the enhanced formation of salicylic acid which might be based on the increased oxygen species on the catalyst surface. However, this is only the case for the catalyst with the highest MgO promotion. It is questionable whether this effect can be attributed to the presence of MgO on the surface, as the pure MgO support itself does not show enhanced activity towards the formation of salicylic acid (see 5.2.1.2). Overall, the pure Au/HT catalyst shows the lowest catalytic activity towards the selective oxidation of alcohol. The results show the catalyst activity is dependent on the loading of MgO on the catalyst surface.

The overall leaching of Mg corresponding to MgO is around 3-5 wt% of the total catalyst material. This would mean a loss of up to 20-40% of total amount of the promoted MgO. For the catalyst with the highest activity, the highest amount of leaching is observed, corresponding to the increased pH of the solution. Here the question arises, whether the catalytic activity, especially the initial step of the deprotonation of the alcohol was evoked by the bulk OH⁻ species generated from the leaching of MgO into the solution. It should be noted that for all catalysts the amount of gold leaching is less than 1 wt% and therefore negligible. In conclusion, the most active MgO promoted HT catalyst was 1.5Au/0.16MgO-HT with the highest amount of impregnation. However, some key issues need further investigation such as the influence of MgO on the catalyst morphology and the mitigation of the leaching effect.

5.4.3 Effect of gold loading

This section investigates the influence of the Au particle size and dispersion on the catalyst morphology and activity. Hereby, the gold loading was varied between 1.5-0.1wt%. TEM analysis was performed on the catalysts to determine the average particle size and the results are shown in the following table (Table 5-15). The catalyst activity was tested for the selective oxidation of salicyl alcohol under base free conditions. The results are expressed in TOF numbers and the selectivity towards salicyl aldehyde at low conversions of 20%. The TEM images can be found in the Appendix.

Table 5-15: Influence of gold loading on MgO promoted HT.

Catalyst	X_{t360} [%]	$S_{\text{salicyl aldehyde}} X_{t360}$ [%]	TOF [h ⁻¹]	Au average particle diameter [nm]	SD average particle diameter [nm]
1.5Au/0.16MgO-HT	35	90	115	6.27	1.73
0.5Au/0.16MgO-HT	2	100	5	3.32	1.01
0.1Au/0.16MgO-HT	<1	100	<2	2.24	0.56

Reaction conditions: catalyst 1.5Au/0.16MgO-HT, T=50°C, p=1bar (air), $C_{\text{salicyl alcohol}} = 0.04\text{M}$, NaOH:salicyl alcohol 0:1, rpm=1000.

* TOF after 0.5h

The results show that the average Au particle size decreases with metal loading due to higher dispersion of the particles on the catalyst surface and therefore lower tendency for agglomeration. However, the catalyst performance decreases drastically upon decrease of metal loading. A possible cause for this effect might be different particle geometry and surface

roughness due to the smaller size or also the fact that due to the small size the particles might be dispersed into micropores, which are less accessible for the substrate molecule. Similar effects were seen for the Au/C catalyst where a decrease in loading to 0.75wt% led to the formation of very small gold particles <3nm and showed a decrease in activity (see Chapter 4).

5.4.4 Influence of precursor

The commonly used precursor was $\text{Mg}(\text{NO}_3)_2$, which was practical in application due to its high solubility in water and full decomposition in air at high temperature. However, a high calcination temperature was needed to decompose the NO_3 species and form MgO causing changes on the original hydrotalcite support. As an alternative solution, another precursor was used, in this case magnesium acetate $\text{Mg}(\text{OAc})_2$ was chosen which decomposed at lower temperature. However, it was important to ensure that no organic residue such as acetic acid of the precursor, remained on the support which could impact the catalyst activity. The calcination temperature was set to 400°C after analysis of the thermal profile via TGA. The calcination temperature corresponded to the temperature at which the HT retained its morphology. A preliminary catalyst was prepared with a loading of MgO of 0.16wt% calcined at 400°C. The following table gives the data for the BET surface area measurements and the pore size.

Table 5-16: Comparison of BET surface area measurements for 1.5Au/0.16MgO-HT with $\text{Mg}(\text{OAc})_2$ calcined at 400°C.

Catalyst	Precursor	Calcination Temp. [°C]	S_{BET} [m ² *g ⁻¹]	Pore size [nm]	Pore volume [m ³ *g ⁻¹]
1.5Au/0.16MgO-HT_400	$\text{Mg}(\text{OAc})_2$	400	29.7	16.7	0.12
1.5Au/0.16MgO-HT	$\text{Mg}(\text{NO}_3)_2$	650	18.9	7.8	0.04

The results show that the BET surface area for the material impregnated with the new precursor calcined at 400°C is larger by around 50% with a greater average pore size compared to the impregnated HT calcined at 650°C. This difference is likely to be based on the lower sintering effect of MgO crystallites and decreased blocking of the pores of the HT material. XRD measurements were done to determine the impact of the MgO promotion on the HT support. The figure below illustrates the stacked diffractograms of the HT support and the MgO promoted HT calcined at 400°C. In addition, the reference pattern for HT calcined at 400°C as well as MgO from the ICDD are presented. The reference diffraction lines for pure MgO are marked red in the patterns.

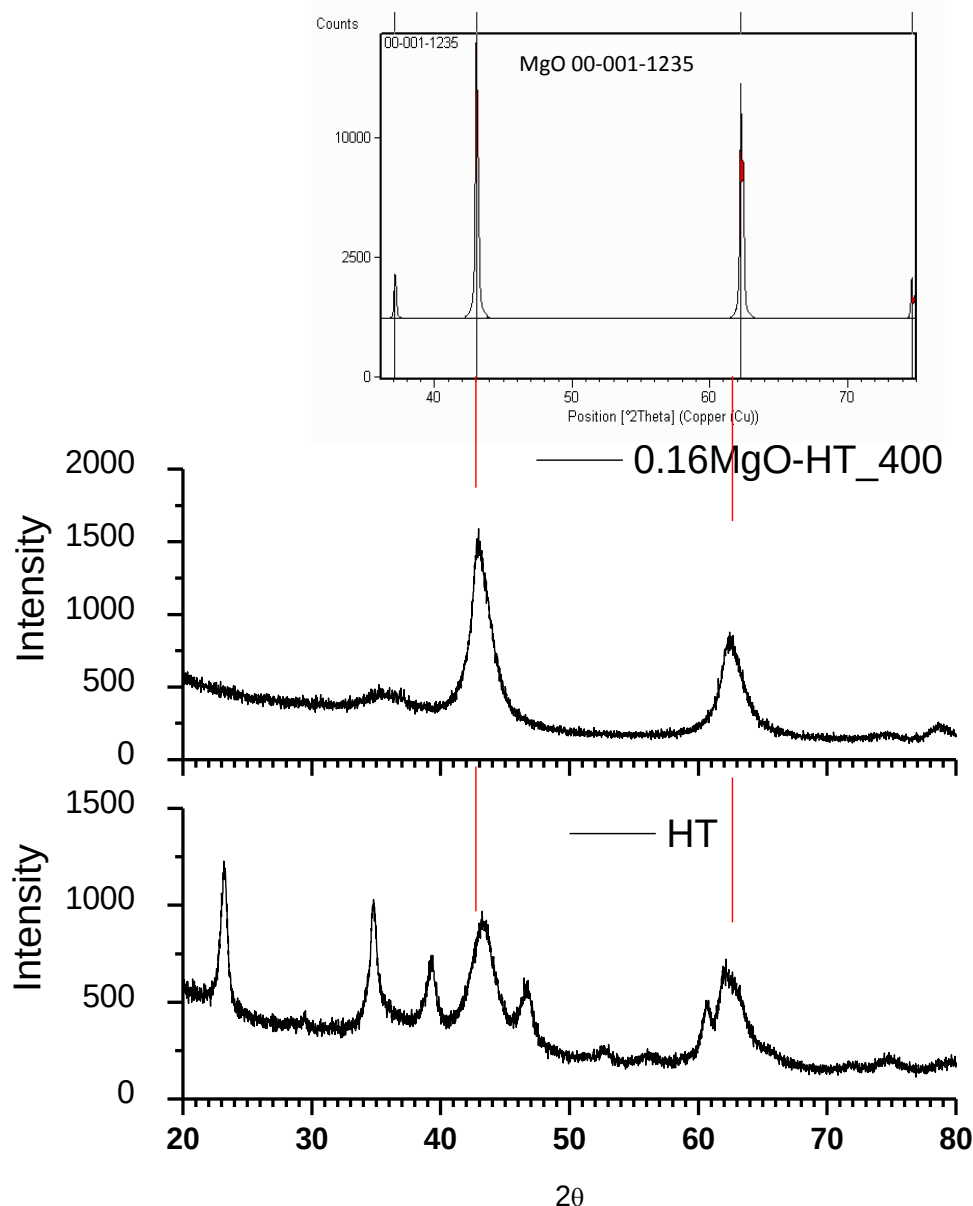


Figure 5-18: XRD diffractograms of HT calcined at 400°C, and 0.16MgO-HT calcined at 400°C with the reference pattern for MgO from the ICDD (00-001-1235) .

The diffractogram shows, similar to the HT promoted with the magnesium nitrate precursor, that the pattern of HT disappears and the characteristic diffraction lines for pure MgO become predominant. Assuming that the structure of HT is mostly retained when calcined at 400°C, the peaks indicate the formation of an MgO phase at the catalyst surface. This can be based on larger MgO crystallites or precipitates formed on the surface. Although the surface area of this material is by 50% larger compared to the same material with a larger dispersion of MgO crystallites, the diffraction peak shape and width is nearly the same as that for the catalyst prepared with the previous precursor. It was important to analyse whether the application of the different

precursor caused any changes during the catalyst preparation in particular the deposition of the gold onto the catalyst surface. Transmission electron microscopy analysis was done in order to retrieve information on size, shape and arrangement of the gold particles. The following figures present the TEM images of the 1.5/0.16MgO-HT catalysts calcined at 400°C and 650°C.

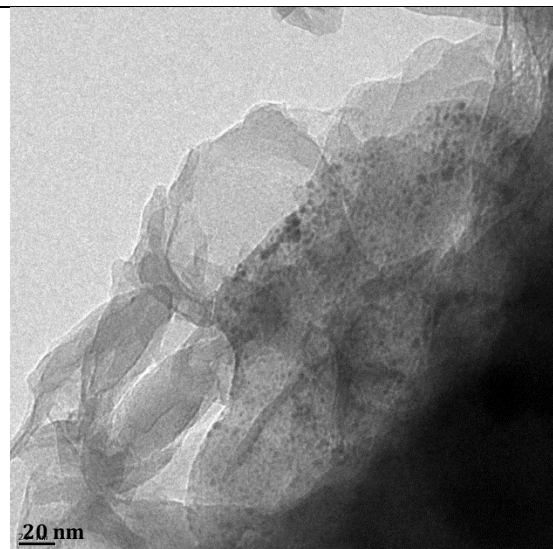


Figure 5-19: TEM image 1.5Au/0.16 MgO-HT_400.

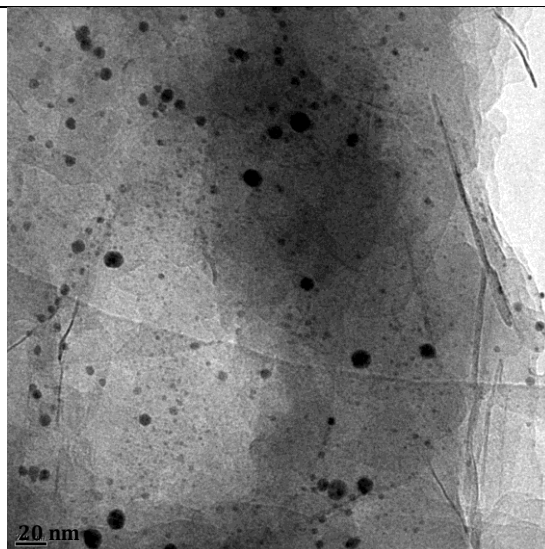
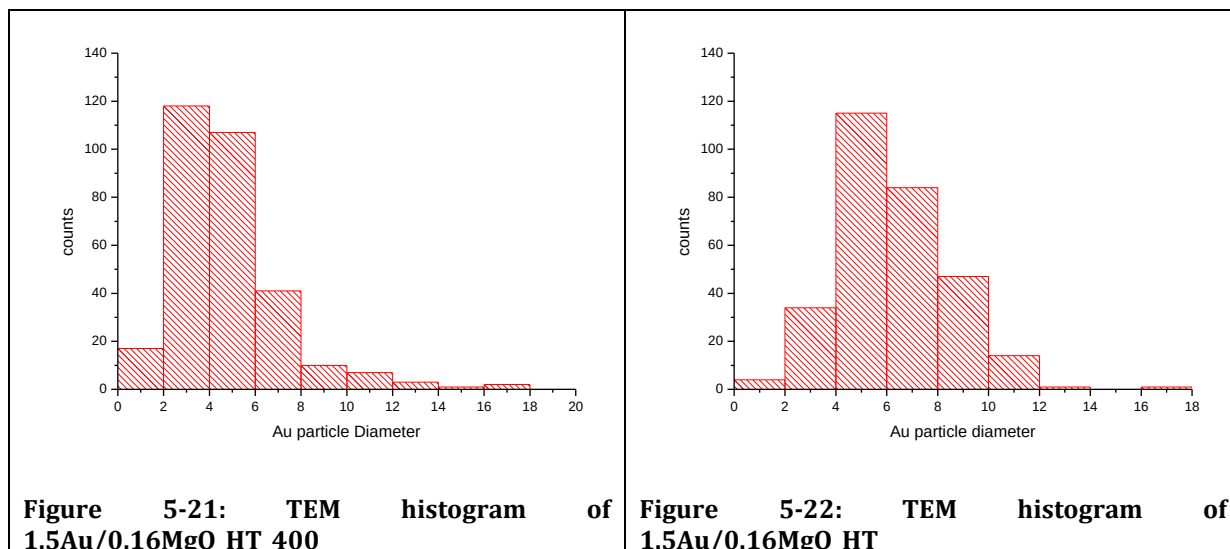


Figure 5-20: TEM image 1.5Au/ 0.16 MgO-HT.

Both images show very small and disperse gold particles. For both catalysts, some areas of the catalyst do not seem to be populated by gold particles. EDX measurements could not detect Au either (see Appendix). High resolution STEM was done on the 1.5Au/0.16MgO-HT_400 catalyst to obtain more information, which is discussed in the following section. The average Au particle diameter and the distribution for the catalyst with the new precursor was determined and the results are presented compared to the previous determined particle diameter for the 1.5Au/0.16MgO-HT catalyst.



The results show that the average particle size for the catalyst is smaller with 4.56 nm and a slightly narrower distribution compared to the corresponding catalyst with the common precursor. This can be based on the different surface morphology influencing the particle deposition during catalyst preparation, such as the larger surface area leading to a higher dispersion of the particles and therefore lowering agglomeration of particles during catalyst heat treatment. Another effect could also be a different surface morphology and different charge of the catalyst due to a different dispersion of the promoted MgO on the surface.

Table 5-17: Comparison of average gold particle size for catalysts prepared with different Mg-precursors.

Catalyst	Au average particle diameter [nm]	SD Au average particle diameter [nm]
1.5Au/0.16MgO-HT	6.27	1.73
1.5Au/0.16MgO-HT_400	4.56	1.56

To determine the difference in basicity, the CO₂ adsorption capacity was measured and the results are presented in the following table.

Table 5-18: Comparison of surface area for 0.16MgO-HT with different precursors.

Catalyst	Calc. Temp. [°C]	S _{BET} [m ² *g ⁻¹]	Pore size [nm]	Pore volume [m ³ *g ⁻¹]	mCO ₂ /*m _{cat} *S _{BET} (SD) *10 ⁻³ [m ² mg ⁻¹]
1.5Au/0.16MgO-HT_400	400	29.7	16.7	0.12	157.4 (0.20)
1.5Au/0.16MgO-HT	650	18.9	7.8	0.04	136.4 (0.38)

The catalyst calcined at 400°C shows a higher CO₂ adsorption capacity which is likely to be based on the higher surface area of the materials and higher dispersion of the MgO leading to a higher amount of CO₂ adsorption. The catalyst performance was tested for the selective oxidation of salicyl alcohol under base free mild conditions. The following table lists the results for the conversion achieved after 360 min, the selectivity towards salicyl aldehyde at 20% conversion as well as the leaching of Mg and Au into the reaction solution. The catalyst performance results are listed below:

Table 5-19: Comparison of catalytic performance of 1.5Au/0.16MgO-HT catalyst calcined at 400°C and 650°C.

Catalyst	Initial rate of reaction [mol*/L*min ⁻¹]	X _{t360} [%]	S _{Sal.aldX20} [%]	Leaching Mg of catalyst [wt%]	Leaching Au of catalyst [wt%]	pH
1.5Au/0.16MgO -HT_400	2.9*E-04	59	90	4	<0.1	8.4
1.5Au/0.16MgO-HT	1.2*E-04	35	90	5	<0.1	8.6

Reaction conditions: catalyst 1.5Au/0.16MgO-HT, T=50°C, p=1bar (air), c_{salicyl alcohol}= 0.04M, NaOH: salicyl alcohol 0:1, rpm=1000.

The results show that the catalyst 1.5Au/0.16MgO-HT_400 achieves a higher performance compared to the 1.5Au/0.16MgO-HT catalyst reaching a conversion of 59% after 360 minutes. This could be based on the higher basicity of the catalyst, the higher dispersion of MgO and also higher dispersion of gold particles on the surface. Further, the selectivity towards salicyl aldehyde at low conversion is 90% and therefore the same for both catalysts. The leaching of MgO is only slightly less, it remains in the same range for both catalysts.

Additional Scanning Transmission Electron Microscopy was performed allowing the investigation of extremely small particles including the arrangement of their atoms and their degree of order that could not be obtained by TEM images. This technique, as introduced in Materials and Methods, provided very high resolution images with a very good contrast image of the gold (bright yellow) on the support (grey) as seen in the High Angle Annular Dark Field images (HAADF) in the following figure (Figure 5-23). However, as the support did not have a clear crystal orientation, a proper alignment was not possible based on the fact that the material is a mixed double-layer hydroxide and the orientation was not entirely in plane. Therefore, atomic resolution of the gold particles was not possible. A general idea of the shape is shown in Figure 5-24 where the particles form hexagonal-shaped cluster. However, the image and contrast were not absolutely clear.

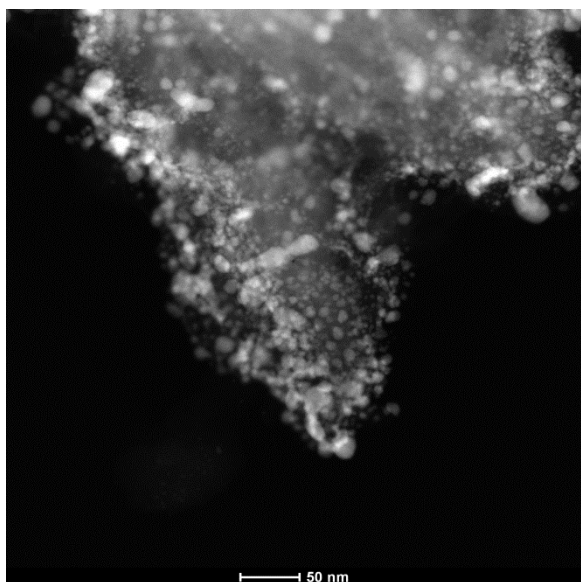


Figure 5-23: HAADF Image of 1.5Au/0.16MgO-HT a)

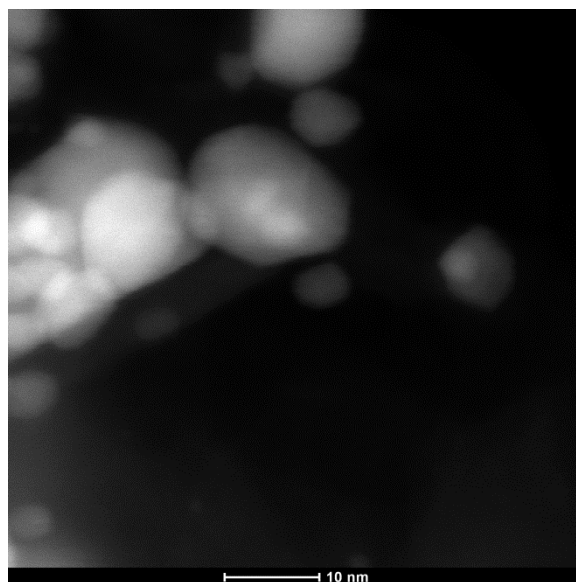


Figure 5-24: HAADF Image of 1.5Au/0.16MgO-HT b)

The very bright particles represent overlapping gold clusters. Further information about the particle shape could be obtained with high resolution Bright Field (BF) images. A high magnification bright field image of the catalyst reveals hexagonal shaped gold particles. The contours of the particles are sharp and clear. In addition, very high resolution BF microscopy on the same area showed the lattice planes of the individual particles which is illustrated in the following figures (Figure 5-25 and Figure 5-26).

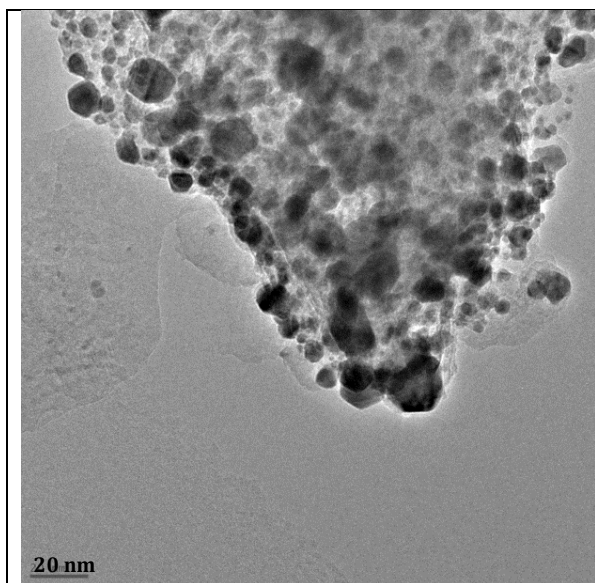


Figure 5-25: BF image of 1.5Au/0.16MgO-HT.

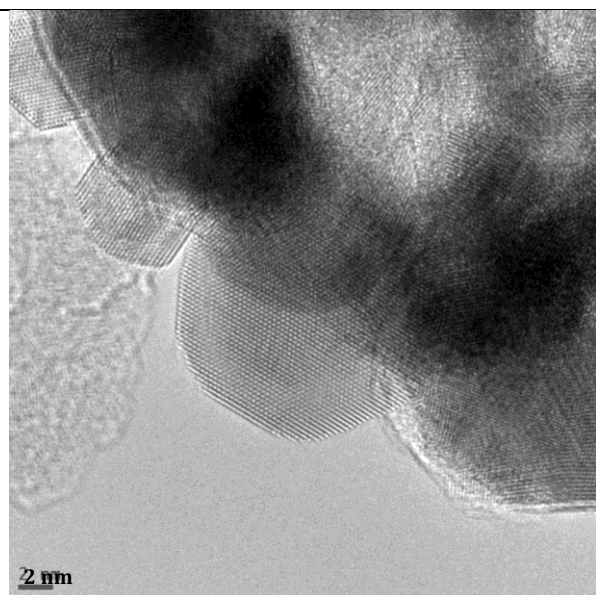


Figure 5-26: BF image of 1.5Au/0.16MgO-HT.

Some particles formed hexagonal shapes and other clusters were of round shapes. Studies showed that for a spherical single-crystalline particle, its surface must contain high-index crystallography planes, which possibly result in a high surface energy. Upon treatment at higher temperature of the gold particles, they underwent a re-organization process and to form lowest energy. For the most common crystal structure of Au, face-centered cubic (fcc) gold, the planes with the lowest surface energy were [111] followed by [100] exhibiting the second lowest energy faces. Studies have shown that especially after treatment under higher temperature around 200°C or over, these planes form the facets of most gold particles [162].

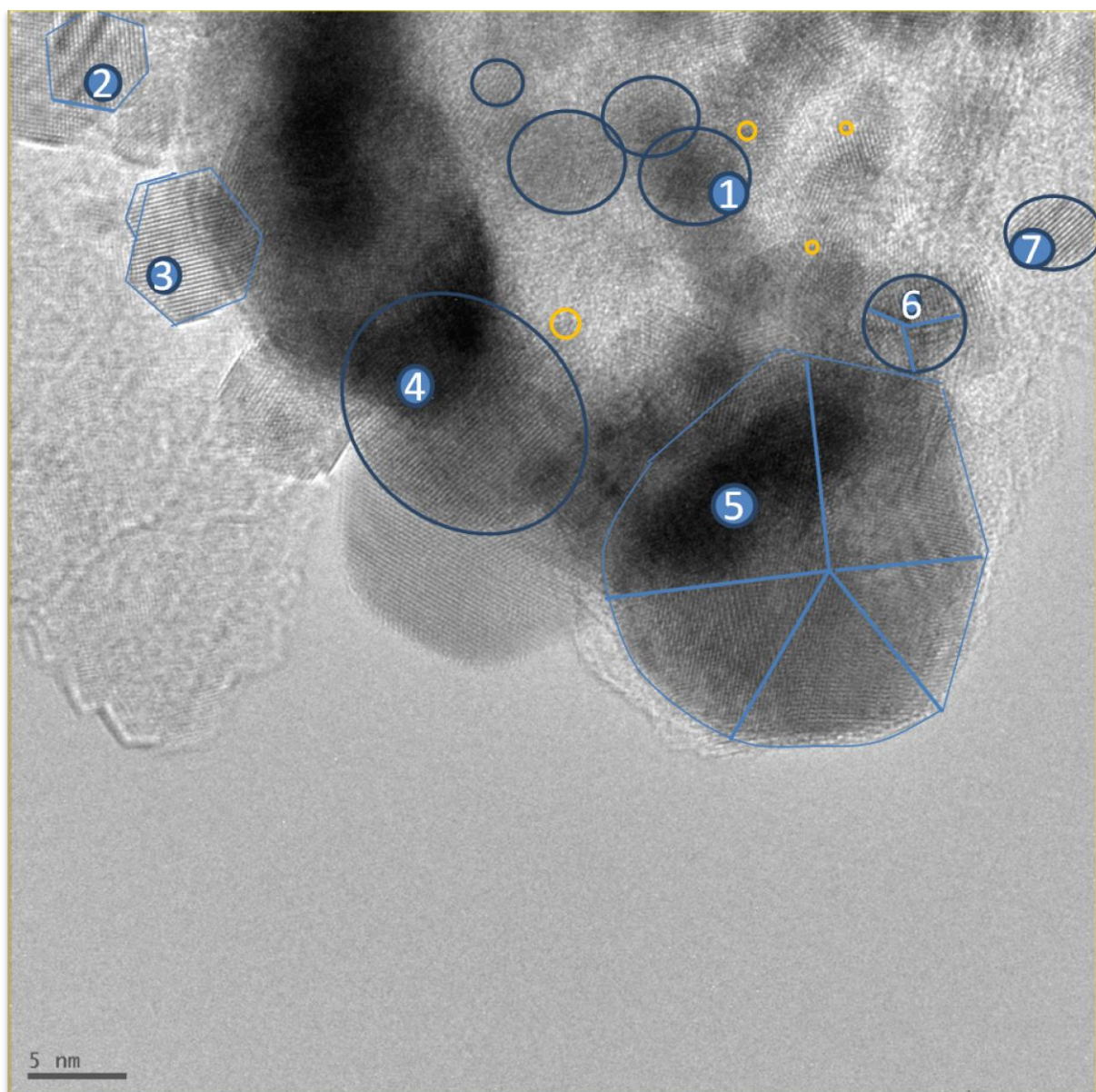


Figure 5-27: HRTEM Image of Au nanoparticles on MgO-promoted HT with different types of shape and orientation, 1-5.

High magnification of very thin areas of the catalyst allowed obtaining high resolution images of the lattice planes of the gold particles. Various types of shapes could be identified and assigned to different crystal orientations based on previous crystallographic studies of gold particles [62]. The darker spots on the image represent overlapped gold particles and clusters stacked upon each other. Some contrasts of particles seem stronger than others, which is also due to the different location on the support. Therefore, it may be possible that the gold deposits in different areas and layers is due to a different surface morphology or surface charge. This could lead to very low concentration of Au in certain areas which are below the detection level of EDS.

The following gold particle shapes according to the HRTEM image (Figure 5-27) have been identified:

Table 5-20: Identified gold particle shapes and orientations of 1.5Au/0.16MgO-HT_400.

Type	Shape	Particle diameter [nm]	Lattice facets
1	spherical	4	(100), (111)
2	Regularly hexagonal	5	(100)
3	Regularly hexagonal	6	(200)
4	Large elongated shaped	12	(200)
5	Large hexagonal-type	15	Multiply twinned
6	Round shaped	4	Multiply twinned
7	elongated	4	(200)

The most common and regular shapes found in small gold particles are, single crystalline, spherical shaped (particle type 1) and these particles were likely to correspond to a cuboctahedral shape symmetry close in shape to Wulff constructions [163]. These particles have an average diameter of around 3-5 nm. Their lattices reveal facets of (110) and (111) as it is most commonly known [164]. Furthermore, the image shows the existence of extremely small spherical type nanoparticles of around 1 nm or less which can be seen by the orange marked particles, which were also revealed in the HAADF images. The second frequently monitored particle shape for this catalyst was the regular hexagonal shaped gold particle. Further types referred to larger and elongated shaped particles (3 and 4). Lattice facets of (200) can be observed, however some parts of the particle seem to reveal more than one facet and the contours of the particle could not be clearly distinguished. The other shapes (particle 5 and 6) referred to multiply twinned particles [62]. These multiply twinned particles have a much larger diameter compared to the average particle diameter determined. In general, as discussed earlier, gold nanoparticles have been mostly observed as cubo-octahedral fcc structures, or singly or multiply twinned fcc structures [78].

It has further been demonstrated that the shape of gold particles changed under treatment temperature. The shapes transform from the initials spherical as it had been synthesised, to faceted shapes. With an increase of temperature the shapes evolved into irregular or defect structures, such as elongated shapes or multiple twinned shapes due to energetically preferred re-organization [62]. This effect was also observed in this study. The organic stabiliser THPC was the main agent factor to control the particle size and shape to be spherical in particular on carbon. However, as the gold particles were exposed to high temperature treatment to fully

decompose all organic residues, the particles were likely to re-organize and form irregular shapes.

Another phenomenon regarding Au particles on MgO, is that of the sinking in of very small gold particles into the support material. This effect is caused by a difference in surface energies, if the surface energy of the support substrate is less than of the particle. In this study, as the HT material was promoted with MgO such an effect could possibly occur [132].

In summary, the HRTEM analysis allowed to identify single crystal gold particles and their exposed lattice facets. However, the charging of the sample made it difficult to go to even higher atomic resolution of the gold clusters. Only those lattice planes, which were orientated with a zone axis aligned with the electron beam could be seen.

The gold particles analysed on the MgO promoted HT support compose of a variety of shapes, from spherical and regularly hexagonal to irregular elongated and multiply twinned shapes. With increase in particle size the shapes evolve to more irregular and multiply twinned forms. All of the particles mostly exposed facets of (111) and (100), however, facets of (200) were also observed. The results are in accordance with the diffraction pattern obtained by XRD. The characteristic gold peak of 38.2 corresponds to the (111) lattice. This diffraction peak becomes more prevalent with increasing gold particle size due to particle agglomeration, meaning that bigger particles expose more (111) lattice planes.

The catalytic activity is very dependent on size and particularly shape and orientation of the gold particle. Only certain exposed facets will be catalytically active in the reaction due to adsorption energies and molecular conformational stabilities with the components during the reaction. The relative amount of edge, corner and surface atoms also vary with the gold particle size. According to previous studies on O₂ activation on gold nanoparticles, the cuboctahedral gold particle corresponds to the gold cluster Au₃₈ exposing the facets (111) and (100) [177]. Certain facets would be catalytically less active or have high surface adsorption energies. Especially for the selective oxidation with molecular oxygen on gold it has been found that certain surfaces of gold particles are energetically preferred for the dissociation of O₂. However, it was also discovered that the catalytic activity also occurs at the metal-support interface [155].

5.4.4.1 Effect of buffering

The catalytic performance studies on the liquid phase selective oxidation have shown that the gold on MgO promoted HT systems are active, however, a large amount of leaching into the reaction solution was observed. To counteract the effect of leaching, the reaction solutions were buffered with 0.1M Na₂CO₃. Although initially the formation to the aldehyde was monitored, there was a loss in mass balance of around 30% which increased as the amount of the reactant salicyl alcohol decreased rapidly without forming salicyl aldehyde or salicylic acid (see Appendix). Furthermore, the formed salicyl aldehyde disappeared over time and the formation of a new unidentified product was observed. The product mix was extracted with an organic solvent and then analysed by GC-MS. A peak of m/z ratio of 228 (see Appendix) was detected indicating the formation of a condensation product of the aldehyde and the alcohol. One possible product with that molecular weight would be benzyl salicylate Figure 5-28, which would correspond to an ester formation. However, this would require the abstraction of methanolate group CH₂OH from the benzene ring. It is questionable whether this is likely to happen as the mechanism destabilizes the aromatic benzene ring which requires overcoming high activation energy. The alternative pathway would occur via water abstraction of the alcohol group and formation of a ketone condensation product (Figure 5-29). A third possible pathway is the formation of an ether product (Figure 5-30).

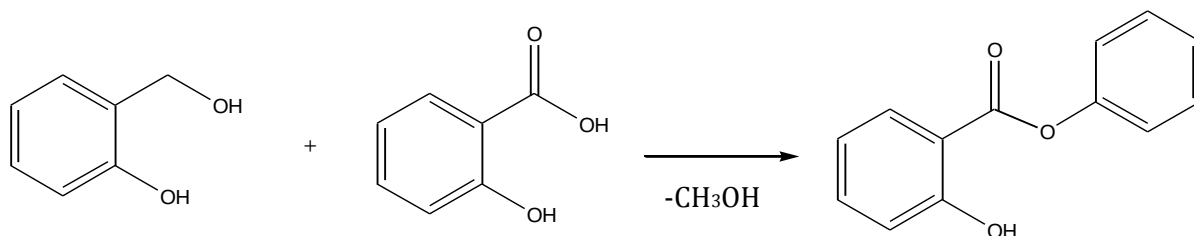


Figure 5-28: Reaction scheme 1 for condensation reaction of salicyl alcohol and salicylic acid.

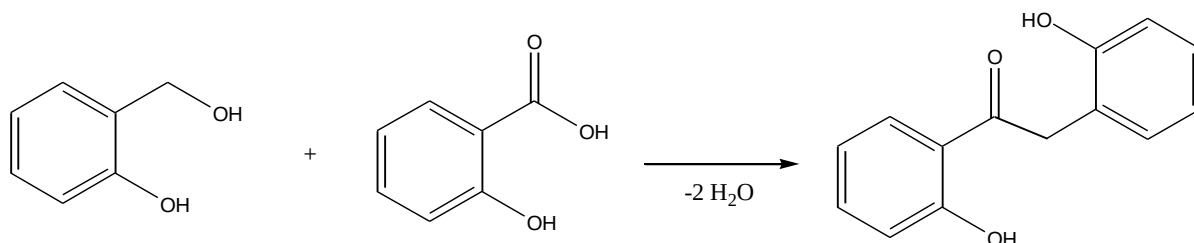


Figure 5-29: Reaction scheme 2 for condensation reaction of salicyl alcohol and salicylic acid.

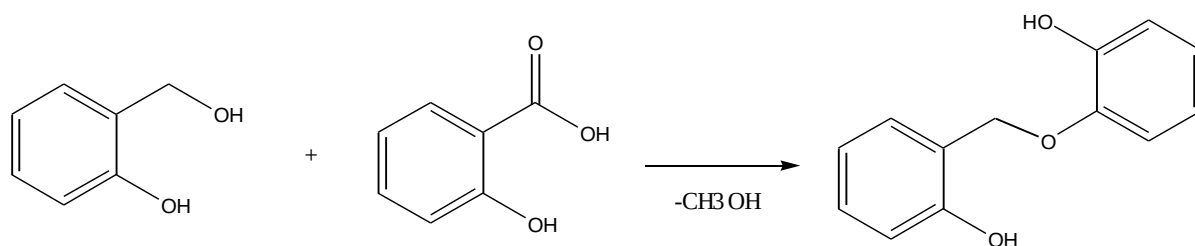


Figure 5-30: Reaction scheme 3 for condensation reaction of salicyl alcohol and salicylic acid.

The main cause leading to this type of reaction was the addition of Na_2CO_3 which caused a condensation reaction most likely due to product adsorption and blocking of the catalyst active sites. Due to the presence of Na_2CO_3 , a high amount of OH^- was present in the bulk solution which could further activate the molecules and facilitate the dehydration. This effect would be in agreement with other studies showing HT materials to be very active for condensation reactions [102]. Other studies on a similar compound, benzyl alcohol, with Au on HT catalysts reported an ester as a by-product [97].

5.4.5 Catalyst deactivation

MgO promoted HT catalysts have so far demonstrated catalyst activity towards the base-free liquid phase selective oxidation of salicyl alcohol under mild conditions. However, as leaching was observed for each run, it was important to determine the catalyst stability. Therefore recycle tests and catalyst characterisation of the used catalyst were done. For the recycle tests, the catalyst with the highest performance 1.5Au/0.16MgO-HT was washed with H_2O and applied for 3 recycle consecutive runs for the selective oxidation of salicyl alcohol. TEM microscopy was performed as well to obtain information about the particle size and distribution (Figure 5-32). The results show that average particle size is larger by 50% for the used catalyst after 3 cycles of runs. The particle size distribution is wider which is based on the agglomeration of particles.

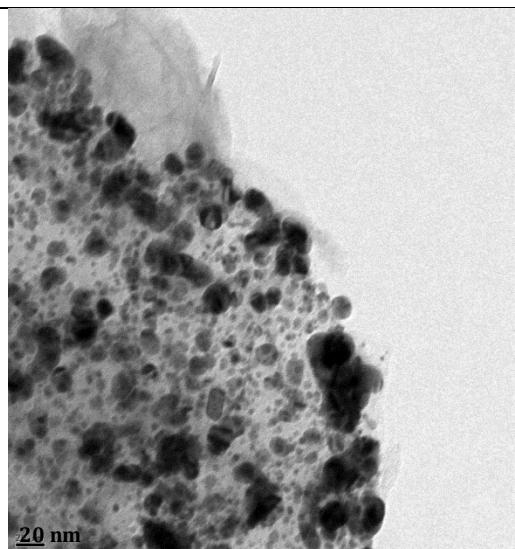


Figure 5-31: TEM image of used catalyst 1.5Au/0.16MgO-HT.

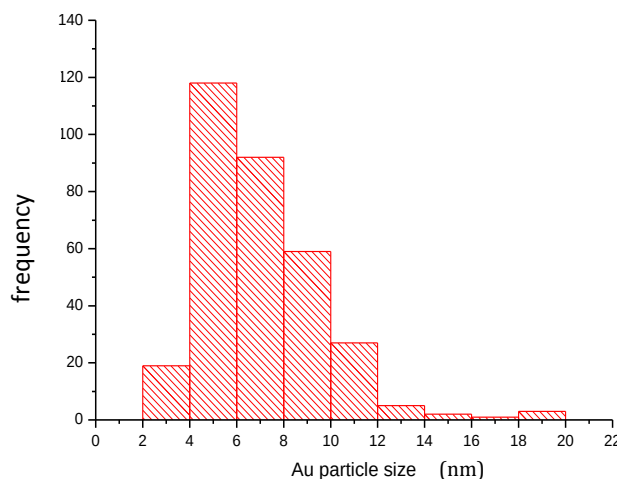


Figure 5-32: TEM histogram of used catalyst 1.5Au/0.16MgO-HT.

Following the experimental series, the used catalyst was tested by TGA analysis to determine CO₂ adsorption capacity. Hereby, the same analysis cycle was applied as for the previous analysed samples (see Materials and Methods). The overall CO₂ adsorption was equivalent to 99% of its initial capacity. The results clearly demonstrate that the basic surface sites remain present on the catalyst surface and active towards low temperature CO₂ adsorption.

The catalyst activity decreases rapidly after several consecutive runs. The poor performance could be caused by blocked surface sites through adsorption of products and increased average Au particle diameter. It should be noted that the catalyst was not re-calcined at 400 °C to desorb any H₂O or CO₂ from the atmosphere or reaction solution before recycle experiments to avoid agglomeration of gold particles.

5.5 Chapter summary

This chapter focused on the investigation and evaluation of alkaline catalyst materials to be able to carry out the selective oxidation of salicyl alcohol under base-free conditions. The materials were based on earth alkaline metal oxides such as CaO and MgO. Based on a few preliminary studies on the use of pure CaO and MgO as support, where a the high effect of leaching was observed, the catalyst design was modified to obtain a stabilized system and dispersed alkaline-earth metal oxide on a structured support. The idea was to provide OH sites on the support surface to initiate the deprotonation of the alcohol. The materials were studied based on their

morphology and properties and their activity towards the liquid phase oxidation. The impregnated oxides showed potential activity delivering very small and highly dispersed Au particles of narrow distribution. However, the catalyst performance was very low with a high amount of leaching observed. For the MgO promoted HT materials the results showed a structural change upon increase of loading towards an MgO phase. This could have been caused by larger crystallites forming with higher MgO promotion or also a precipitation of MgO on the support surface enhanced through the high calcination temperature. Furthermore, the basicity of the catalyst series was investigated and there was a direct correlation of the CO₂ adsorption capacity and the amount of MgO impregnation. The catalysts were also tested for the selective oxidation of salicyl alcohol and the results corresponded to the expected trends, of a higher catalytic performance with higher CO₂ adsorption capacity.

Another Mg precursor was used for impregnation of HT material enabling calcination at 400°C at which the original HT structure was retained. Structural analysis showed a diffraction pattern corresponding to MgO. The catalyst also had a higher surface area and contained smaller Au particles. Further, this system was more active compared to the previous catalyst with the same MgO promotion with the common nitrate precursor achieving 59% conversion and selectivity values of 90% towards salicyl aldehyde with TOF numbers of 115h⁻¹. However, even here leaching was observed. Buffering the reaction solution with Na₂CO₃ caused a side reaction leading to a condensation product. Further investigations would need to be done regarding mitigation of leaching and increase in the catalyst lifetime.

6 BIMETALLIC CATALYSIS FOR SELECTIVE OXIDATION OF SALICYL ALCOHOL

6.1 Chapter introduction

This chapter comprises of an extension on the Au/C catalyst system in Chapter 4. The study investigates the effects of the addition of a second active metal on the main catalyst system Au/C and discusses the impact on the selective oxidation of salicyl alcohol.

For the selective oxidation of alcohols, monometallic Au/C catalysts have delivered high activity and selectivity towards the desired product. Known for their long catalyst lifetime, lower deactivation through leaching and poisoning, they have demonstrated superior performance in many cases over other conventionally applied metals such as palladium or platinum. However, in certain cases, studies have shown that, where monometallic Au catalysts reached their limits in terms of activity and selectivity, bimetallic catalysts with added metals such as palladium have enhanced the performance significantly [165] [119, 120] [7, 127, 166]. In those cases it was often shown that Au and Pd formed an alloy particle revealing new catalytic properties based on synergistic effects [125] of the alloy particle. The new properties were dependent on many factors such as the preparation method, metal ratio or the support [122] [166].

For the selective oxidation of salicyl alcohol, this work has demonstrated a high catalytic activity achieved by the monometallic Au/C catalyst system, however some effects seem to impede the further enhancement of the performance. At 100% conversion of salicyl alcohol, the maximum selectivity towards salicyl aldehyde is only 85% due to the consecutive oxidation to salicylic acid (see Chapter 4). Another effect is the increase in particle size by 60% with the increase in gold loading due to agglomeration of the gold particles (see Chapter 4) causing a drastic decrease in activity. Although particle agglomeration is not observed for oxide supported Au/TiO₂ catalyst, the catalyst performance is much lower and therefore not comparable.

Therefore, in order to attempt to alleviate these effects, bimetallic catalysts on carbon were synthesised. The focus was on the catalyst system containing the active metals gold and palladium, as its enhanced properties based on the alloyed nature and superior performance over monometallic gold catalysts in comparable selective oxidation reactions have been demonstrated [7] [120] [122] [167]. The study is composed of two main parts including the investigation of the catalyst morphology and properties and the impact on the catalyst performance towards the selective oxidation of salicyl alcohol.

6.2 AuPd on carbon

The aim was to synthesise an alloyed AuPd on carbon catalyst using the same activated carbon (Norrit) as for the Au/C catalyst series (Chapter 4) and using sol-immobilisation with THPC as organic stabiliser to control particle size. The bimetallic AuPd catalysts were prepared adding both metal precursors simultaneously to the solution to generate a bimetallic AuPd sol (see Materials and Methods). This method provided the conditions for the generation of fine and disperse particles as seen for the Au/C catalysts (Chapter 4) and it has also been reported in other studies that one-step sol generation lead to the formation of alloy particles [183] [48]. The amount of organic stabiliser was adjusted accordingly to the metal amount, however, the formation of agglomerates due to a higher metal loading in the sol-solution could be possible. Other methods for preparation of bimetallic catalysts, such as the successive deposition of the metals onto the support were used in other studies, however, this method could cause the formation of segregated monometallic ad-atoms and agglomerates leading to a heterogeneous metal composition on the catalyst surface (see 2.4).

A series of AuPd catalysts were prepared by changing the ratio of Au:Pd, which are listed in the following table (Table 6-1). The total content of metal did not exceed 3 wt% so that the results in particular for the surface morphology of the catalyst were comparable to the monometallic Au/C catalysts discussed in Chapter 4. ICP analysis of the sol-solution after the catalyst preparation was done and no significant amounts of Au or Pd were found in the solution so that the experimental loading corresponded to the theoretically calculated loading.

Table 6-1: Catalyst series for bimetallic AuPd on carbon catalysts.

Catalyst	Loading Au [wt%]	Loading Pd [wt%]	Ratio Au:Pd
0.75Au0.75Pd/C	0.75	0.75	1:1
1.5Au/0.75Pd/C	1.50	0.75	2:1
0.75Au/1.5Pd/C	0.75	1.50	1:2
1.5Au/1.5Pd/C	1.50	1.50	1:1
1.5Pd/C	0	1.50	0:1

A few catalysts have been prepared using oxide supports such as CeO₂ and TiO₂. Their catalyst performance data can be found in the Appendix.

6.2.1 Catalyst morphology and properties

TEM analysis was performed in order to determine the average particle size and distribution of the metal on the support. In case of the formation of an alloy structure, the particle size was not expected to increase. However, due to the catalyst reductive treatment at 350°C used in the present study, agglomeration was possible especially for higher loadings as already seen for the monometallic Au/C series (see 4.4.2). The following figures show the TEM images of the 0.75Au0.75Pd/C catalyst and the 1.5Au1.5Pd/C catalyst.

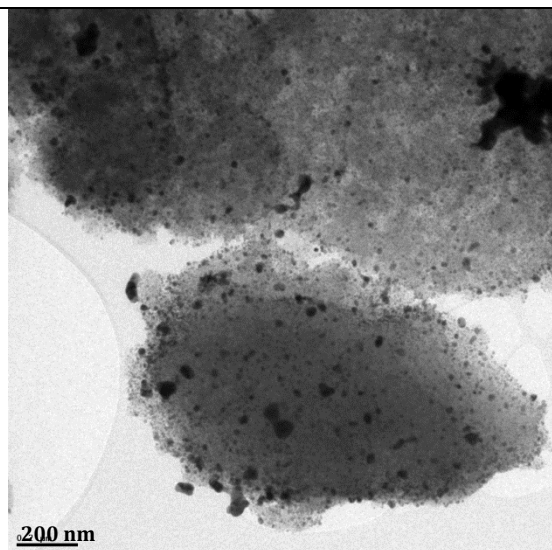


Figure 6-1: TEM image of 0.75Au0.75Pd/C

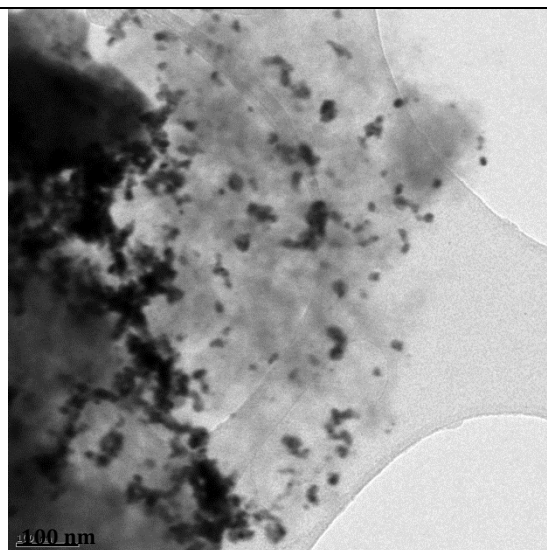


Figure 6-2: TEM image of 1.5Au1.5Pd/C

The dark spots represent the metal particles, although a distinction between Au and Pd cannot be made from the TEM images. The images show that with an increase in loading, the particle size appears to increase and the formation of agglomerates is observed.

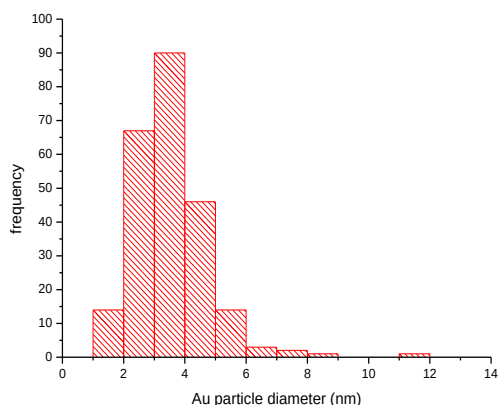


Figure 6-3: TEM Histogram of 0.75Au0.75Pd/C

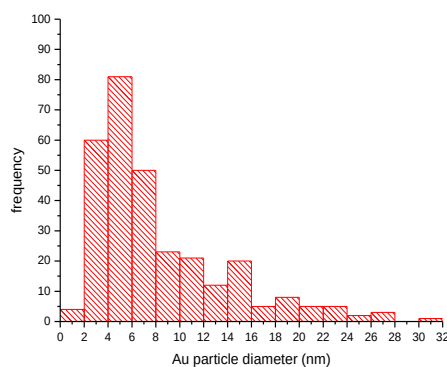


Figure 6-4: TEM Histogram of 1.5Au1.5Pd/C

The TEM histograms show a very narrow size distribution for the 0.75Au0.75Pd/C catalyst and a very broad distribution with particle diameters up to 30 nm for the 1.5Au1.5Pd/C catalyst. The following table lists the determined average particle sizes of the AuPd/C catalyst series together with the fraction of particles from 3.5-5.5 nm. For direct comparison, the previously determined average particle diameters for the monometallic gold catalysts are included as well.

Table 6-2: Average particle size of AuPd catalyst series compared to monometallic Au and catalysts.

Catalyst	Total metal loading [wt%]	AuPd average particle diameter [nm]	SD AuPd average particle diameter [nm]	Fraction 3.5-5.5nm [%]
0.75Au0.75Pd/C	1.50	3.51	0.9	63
1.5Au0.75Pd/C	2.25	4.96	2.17	42
0.75Au1.5Pd/C	2.25	4.76	1.92	50
1.5Au1.5Pd/C	3.0	8.10	4.25	47
1.5Au/C	1.5	5.07	0.83	83
3Au/C	3.0	8.33	2.04	20
1.5Pd/C	n.a	n.a	n.a	n.a

The results show that for the bimetallic catalysts, the smallest average particle size occurs for the 0.75Au0.75Pd/C catalyst. When comparing the results for the average particle diameter with the monometallic Au catalysts with the same total metal loading, the 0.75Au0.75Pd/C catalyst has a much smaller average particle size compared to 1.5Au/C. This could be based on a stronger interaction with the support, preventing agglomeration during the catalyst preparation and heat treatment step. Further, the formation of other particle types such as core-shell structures is also possible. For the 1.5Au1.5Pd/C catalyst, a particle size of 8.1 nm is obtained with a very large size distribution which is similar to the Au/C catalyst with the equivalent metal loading of 3w%. Therefore, at higher loading the presence of palladium does not prevent particles from agglomeration.

XRD analysis was performed on the AuPd catalyst series to investigate the nature of the bimetallic particles. According to the phase diagram ^[123], Au-Pd is miscible at all compositions and forms homogeneous alloy particles. The figure below presents the diffractograms of the bimetallic 1.5Au1.5Pd/C catalyst with activated carbon as background, compared with the reference database for the Au:Pd 1:1 alloy (ICDD 01-072-3756). In addition, the positions of the reflections for the monometallic Au and Pd are also marked as reference. As already discussed in Chapter 4, the most characteristic reflection for the monometallic gold is at 38° 2 θ . For the monometallic palladium, the most significant reflection has been identified according to the International Centre for Diffraction Data (ICDD 00-005-0681) corresponding to 40.12° 2 θ (see Appendix). For the alloyed particle with the composition 1:1 Au:Pd, this corresponding reflection lies in between at 39.17° 2 θ .

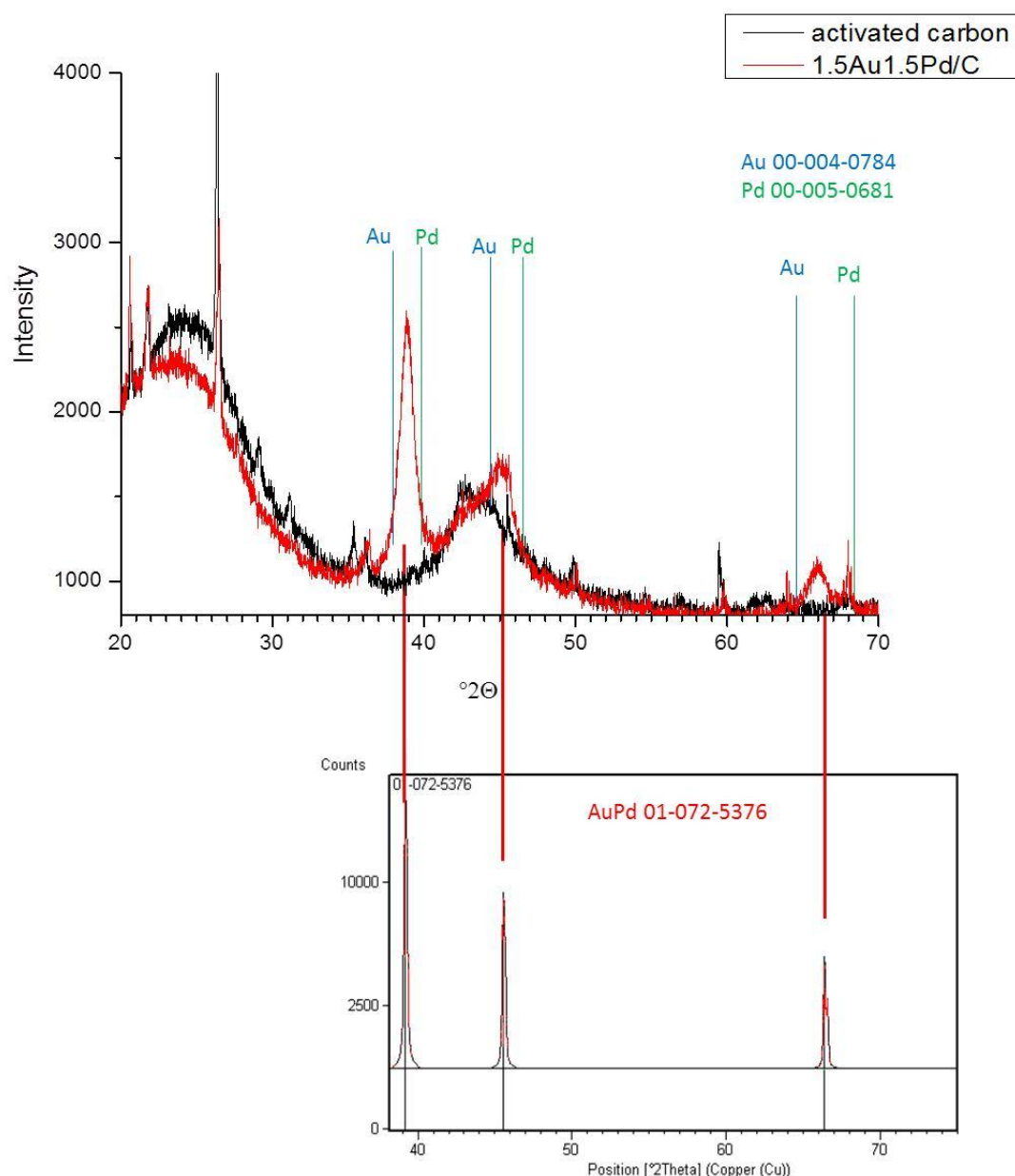


Figure 6-5: X-Ray diffraction pattern of the bimetallic 1.5Au1.5Pd/C , compared to the reference database ICDD for AuPd(below) and including marked reflections according to ICDD for Au and Pd.

From the diffraction pattern of the bimetallic 1.5Au1.5Pd/C (1:1) catalyst it can be seen that the positions of the reflections indicate intermediate scattering angles between those of the monometallic Au and Pd peaks and seem to correspond well to the reference pattern for the 1:1 AuPd alloy. However, as the peak positions for the monometallic and alloy phase are very close and the reflections, and in particular the reflections at 45° and 66° are very broad, a co-existence of segregated monometallic particles cannot be excluded. Other studies on bimetallic AuPd catalysts prepared by sol-immobilisation on carbon have shown that a Au:Pd ratio of 1:1 led to particles of 1-5nm average size and with a mixture of icosahedral, decahedral and cub-

octahedral morphology. Many of these particles showed random compositions of AuPd alloys and very small particles of 2nm showed an enrichment of Au ^[168]. Other reported studies confirmed the same trend that the while all particles were AuPd alloys, the smallest particles were Au-rich, whereas the largest particles tended to be Pd-rich ^[169]. In this diffractogram, the most intense diffraction peak is at 39.17 °2θ corresponding to the (111) lattice plane according to ICDD. The overall intensity of the diffraction pattern for the 1.5Au1.5Pd/C catalyst is much higher compared to the monometallic Au diffraction pattern of the 3 Au/C catalyst with the same total metal loading and average particle diameter (see 4.4.2). This could be based on the existence of larger particles taken from the wider size distribution, however, according to the position of the scattering angles, as discussed above, these particles would likely have an alloy composition. The following figure shows the comparison of the diffraction peak at 39.17 °2θ for the series of AuPd catalysts (Figure 6-6). In addition, the peak positions for monometallic Au and Pd are marked as reference.

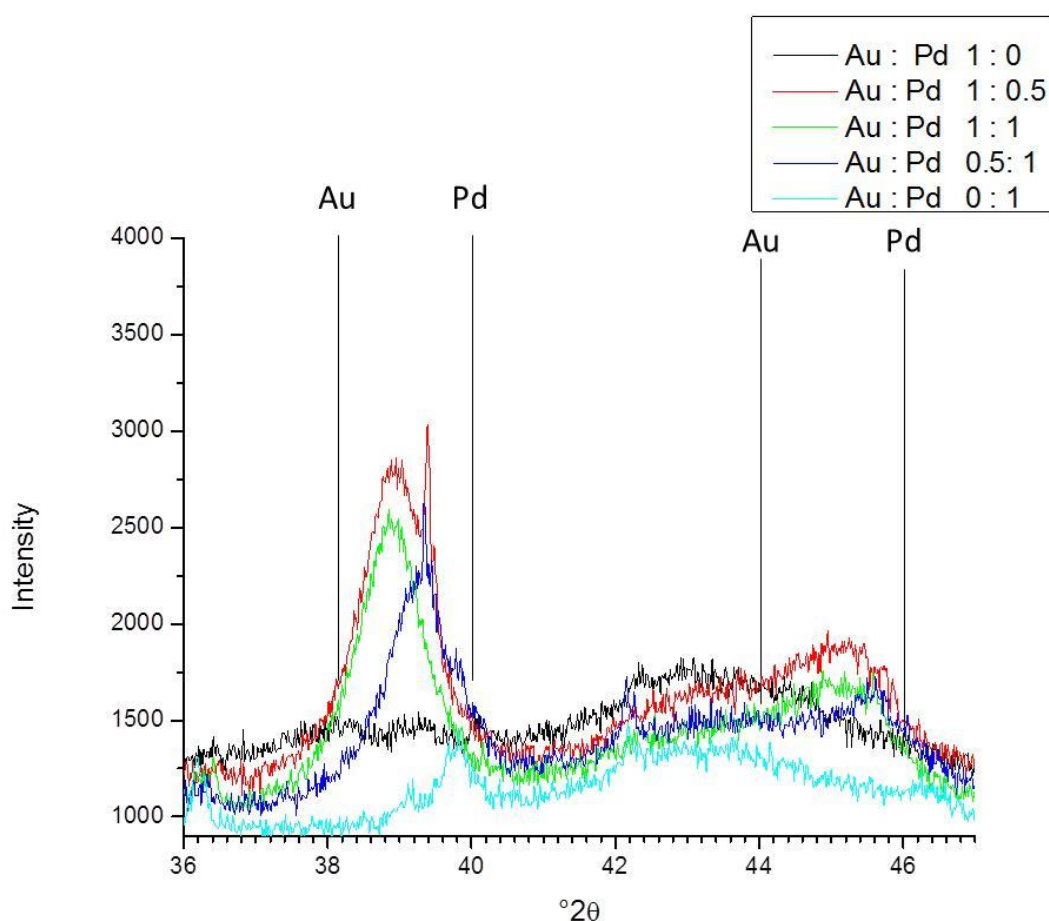


Figure 6-6: Selected XRD Diffractogram peaks for series of AuPd on carbon catalysts: 1.5Au0.75Pd/C (), 1.5Au1.5Pd/C(), 0.75Au0.15Pd/C(), 1.5Pd/C() including the reference peaks for monometallic Au and Pd.

It can be seen that with an increasing ratio of Pd there is a shift of the peak towards Pd. This could mean that the particle changes its composition and becomes Pd-rich changing the lattice constant. Another possibility is that segregation may take place resulting in a core-shell particle structure with a thick Pd shell [120]. However, further investigations such as high resolution TEM images with element mapping would need to be carried out in order to determine the exact particle composition and to also determine the influence of heat treatment on the particle composition.

In general, previous reported studies have shown the existence of various types of structures with increased surface roughness when alloying Au and Pd [166]. This is influenced by the type of preparation method and by the heat treatment. Furthermore, the lower surface energy of Au for 1:1 Au:Pd leads to surface enrichment by Au when increasing the catalyst treatment temperature [170]. Other studies have shown that the synthesis of bimetallic AuPd catalysts prepared by sol-immobilisation leads to the formation of alloy particles, however, a higher molar fraction of Pd caused the formation of larger, Pd rich particles at the surface with a different structural morphology [122].

6.2.2 Catalyst activity

To determine the influence of the bimetallic catalyst particles on the catalyst activity, the series was tested for selective oxidation of salicyl alcohol under mild conditions in the presence of base. The results are expressed in conversion after 360 minutes and the selectivity towards salicyl aldehyde at 30% and 100% conversion (Table 6-3). In addition, the previous obtained results for the monometallic Au/C catalysts are listed as well as 1.5Pd/C catalyst together with the determined average particle size.

In general, the products detected were salicyl aldehyde and salicylic acid, no other products were found in the gas or liquid phase. The mass balance reached was 95-100% at all times. The concentration / time plots (see Appendix) show, as seen for the reaction on monometallic Au/C catalysts, that the formation of salicyl aldehyde is detected at the beginning of the reaction and the formation of salicylic acid is detected only at higher conversions.

Table 6-3: Catalytic activity for series of AuPd bimetallic catalysts for selective oxidation of salicyl alcohol.

Catalyst	Au average particle size [nm]	X _{t360} [%]	S _{sal.ald X30} [%]	S _{sal.ald X100} [%]	TOF [h ⁻¹]*
1.5Au/C	5.1	100	100	80	320
0.75Au0.75Pd/C	3.5	100	100	81	118
1.5Au0.75Pd/C	4.9	100	100	83	35
0.75Au1.5Pd/C	4.8	52	100	-	11
1.5Au1.5Pd/C	8.1	65	100	-	5
1.5Pd/C	n.a	16	100	-	7
3Au/C	8.3	100	100	78	149

Reaction conditions: T=50°C, p= 1bar (air), m_{cat}= 0.2g, c_{salicyl alcohol}= 0.04 M, NaOH: salicyl alcohol= 2:1, rpm= 1000.

* TOF values after 0.5h

Compared to the monometallic catalysts, the catalytic performance of the bimetallic catalysts is based on the particle morphology and dispersion and moreover electronic effects based on the bimetallic nature of the particles. The results show that the 0.75Au0.75Pd/C catalyst achieves the highest performance reaching full conversion and TOF numbers of 118 h⁻¹. The poorest performance is achieved by the 1.5Au1.5Pd/C catalyst. Although both catalysts have the same ratio Au:Pd of 1:1, the difference in catalytic performance is likely to be based on the increased particle size due to higher metal loading or possible enrichment of Pd in the particles. In contrast, for the catalysts 1.5Au0.75Pd/C and 0.75Au1.5Pd/C, both with the same metal loading and an average particle size of approximately 5 nm, the catalyst activity decreases with a higher ratio of Pd. The diffraction pattern also confirms that the particles enrich in Pd on the surface. The selectivity towards salicyl aldehyde is 100% at low conversions of salicyl alcohol for all catalysts and up to 83% at 100% conversion for the 0.75Au0.75Pd/C catalyst. Therefore, no significant increase in selectivity is given with the addition of palladium. The pure Pd catalyst shows the lowest catalyst performance, and all Pd-rich catalysts show a lower performance effectively due to electronic effects. This becomes more evident for the catalyst with the highest metal loading 1.5Au1.5Pd/C compared to 3 Au/C where both catalysts have approximately the same average particle size but the monometallic catalysts shows a far superior performance. In addition, the existence of very large particles > 20 nm leading to a wider size distribution are also likely to cause a decrease in activity.

As the activation barrier for the alcohol group on Pd is lower than on Au, theoretically the OH bond activation of the alcohol should occur more readily. The low performance of Pd the can

therefore be based on electronic effects. Another reason could also be increased deactivation due to the over-oxidation of Pd, which has been observed by other studies [114]. In addition, the catalysts show very small particles which could be less accessible for the substrate molecule depending on the location in the catalyst pore.

Few AuPd catalysts on oxide supports such as 1.5Au1.5Pd/CeO₂ and 1.5Au1.5Pd/TiO₂ were prepared by sol-immobilisation and tested for the selective oxidation of salicyl alcohol under mild conditions in the presence of base. The concentration against time plots can be found in the Appendix. The overall results showed a higher activity of the oxide supported bimetallic catalysts 1.5Au1.5Pd/CeO₂ reaching TOF numbers of 64 h⁻¹ and 1.5Au1.5Pd/TiO₂ achieving TOF of 54 h⁻¹ compared to the carbon supported 1.5Au1.5Pd/C catalyst. This is likely to be based on the stronger interaction of the bimetallic particles with the oxide support leading to synergistic effects at the metal-support interphase. Further characterisation on the particle size and distribution of the oxide supported catalysts need to be done. However, there was a decrease in selectivity especially for the 1.5Au1.5Pd/CeO₂ catalyst. As CeO₂ is known to have a good oxygen storage capacity due to its defect structure and vacancies, these morphological and structural properties could therefore promote the further oxidation to salicyl acid and decrease the selectivity (see Appendix). Other studies have demonstrated the superior performance of oxide supported AuPd alloy catalysts over carbon supported AuPd alloy catalysts in comparable selective oxidation reactions [120]. The application and performance of AuPd on oxide catalysts will be discussed again in Chapter 7.

6.3 Chapter summary

In summary, the overall activity of the catalysts in the selective oxidation of salicyl alcohol is strongly influenced by the structural composition of the metal particles. In contrast to previous reported studies showing that the addition of Pd to Au enhanced the catalytic activity and stability in comparable selective oxidation reaction; this study revealed a decrease in activity due to the addition of palladium especially for higher gold loadings.

Although having the same average particle size compared to monometallic 3Au/C catalyst, the 1.5Au1.5Pd/C catalyst showed a much broader particle size distribution. This indicates that the intended particle size control with the sol-immobilisation method was less effective for the bimetallic catalysts with higher loading. Whether the larger size particles were generated in the sol or formed due to agglomeration during catalyst heat treatment, needs to be investigated. Also the exact composition of the large particles -whether alloy or segregated monometallic- needs to be further characterised.

The position of the XRD diffraction peaks for the 1:1 AuPd corresponded to intermediate scattering angles between those of the monometallic Au and Pd peaks indicating the overall formation of alloy particles. With the increase in Pd, a shift of the reflections towards Pd occurred indicating an enrichment of Pd in the particles. Another possibility is the formation of core-shell structures with a Pd shell or the segregation of Pd particles on the bimetallic particles. The overall catalytic performance decreased upon addition of palladium to the gold catalyst which is likely to be based on the change in the lattice parameters and electronic properties of the alloy phase. The selectivity towards salicyl aldehyde did not enhance upon the addition of palladium. In conclusion, the results demonstrated that gold is more active in the selective oxidation of salicyl alcohol under the given conditions.

The results therefore stand in contrast to previous reported studies where an enhancement of catalytic activity was achieved by adding Pd to Au/C supported catalysts compared to the monometallic Au/C catalysts ^[23] ^[122]. Additional investigations regarding the exact composition of the bimetallic particles need to be carried out in order to find out how the addition of the Pd changes the electronic structure of the particles. Further, the catalyst preparation method would need to be optimised to narrow the particle size distribution and increase the catalyst activity.

7 SELECTIVE OXIDATION OF DIOLS AND TRIOLS

7.1 Chapter introduction

This chapter is based on the investigation of the gold based catalyst systems on other alcohol compounds with increased functionality such as diols and triols. The substrates selected were 1,2- propanediol, as water soluble functional diol and glycerol as highly functionalised polyol. The reactions were carried out under mild conditions using a batch reactor with comparable setup and conditions to the selective oxidation of salicyl alcohol (see Materials and Methods). The product network was more complex, however, as various studies on the selective oxidation of 1,2- propanediol and glycerol on gold based catalysts have already been reported [6] [47] [171] [83] [10]] the achieved results could be directly compared and the transferability evaluated.

7.1.1 Selective oxidation of 1,2- propanediol

The following scheme illustrates the reaction pathway and product network for the selective oxidation of 1,2- propanediol.

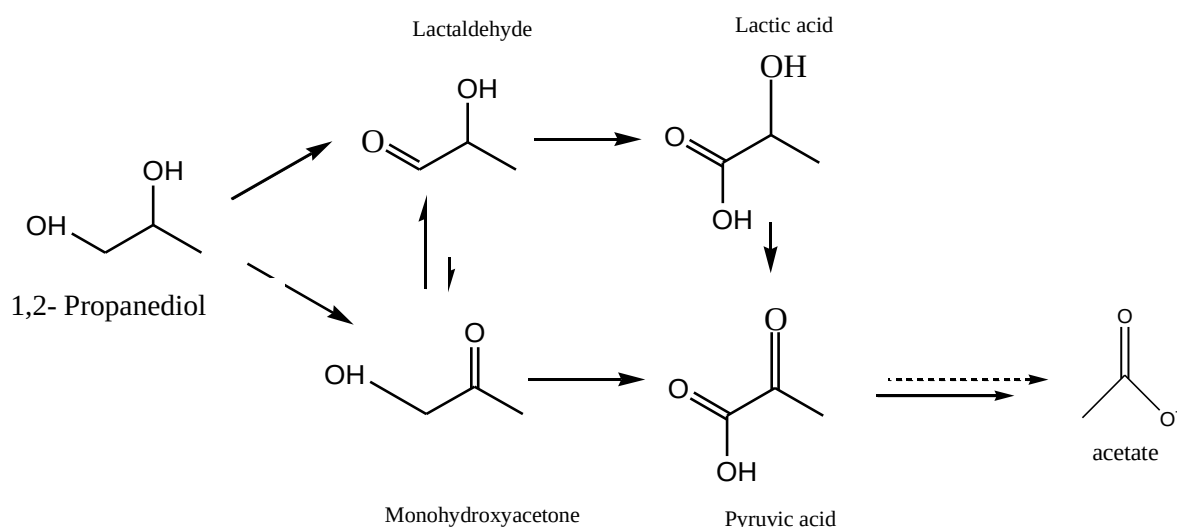


Figure 7-1: Reaction pathways and product network for selective oxidation of 1,2- propanediol [147].

According to the general reaction network, there are two possible pathways for the selective oxidation of 1,2- propanediol leading to lactic acid: a) Through the oxidation of the primary alcohol function via the formation of lactate aldehyde as intermediate or b) through the oxidation of the secondary alcohol group and formation of monohydroxyacetone with

subsequent intramolecular reaction to lactic acid (Canizzaro reaction). The experiments were carried out in a Buchi glass batch reactor system as described in Materials and Methods. The reactor setup was also equipped with a high performance overhead gas dispersion stirrer, which was set to 1000 rpm, and dispersed the air bubbles. Further, a temperature-controlled water bath ensured a homogeneous temperature and concentration profile and avoiding the formation 'dead zones'. Furthermore, for the experiments, the ratio of 1,2- propanediol Au = 1000 : 1 was used which was adapted to what has been employed by other studies ^[193] ^[47]. The following graph illustrates the general concentration/time profile for the selective oxidation of 1,2- propanediol under mild conditions on the 1.5Au/C catalyst in the presence of a base:

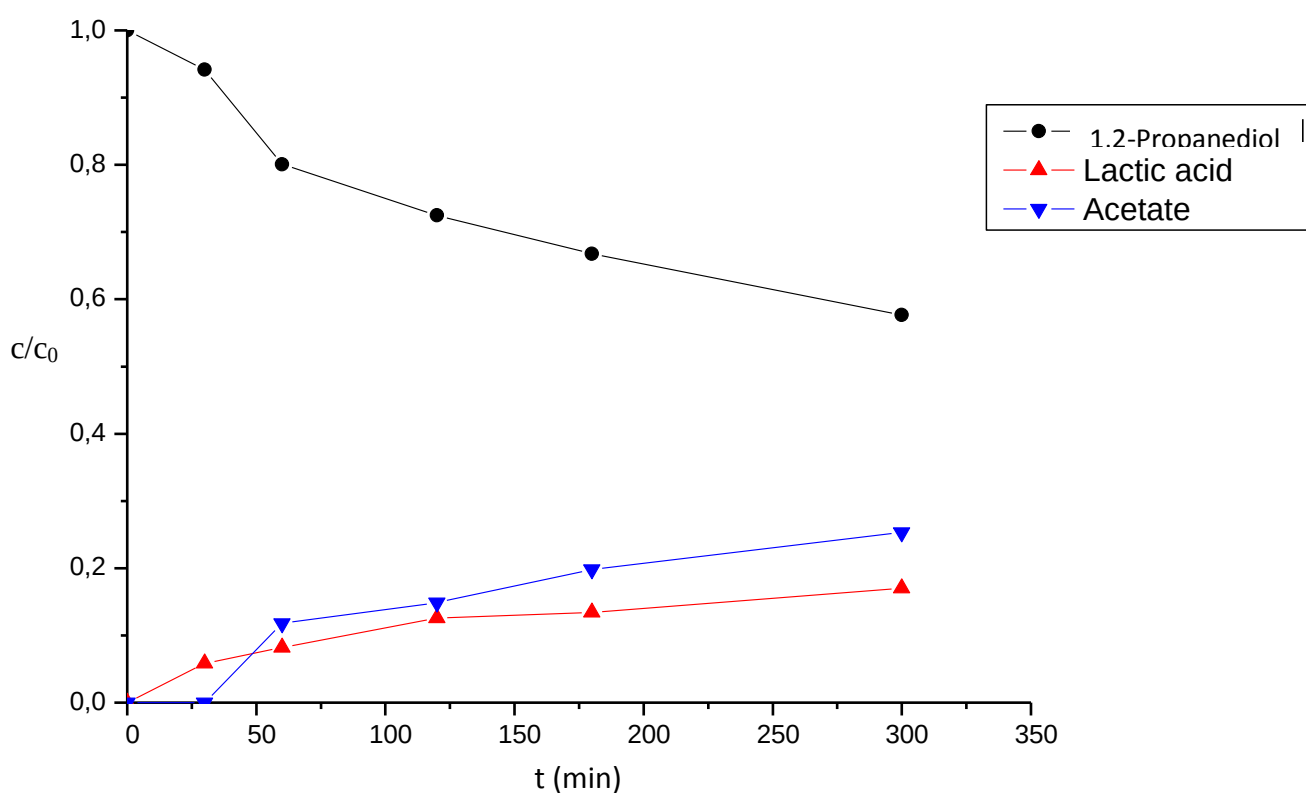


Figure 7-2: Concentration/time profile for selective oxidation of 1,2- propanediol on 1.5Au/C, reaction conditions: T=50°C, p=1bar, catalyst: 1.5Au/C, m_{cat} = 0.2 g, reactant/Au=1000, 1,2- propanediol: NaOH=1:1, 1,2- propanediol (●), lactic acid (▲), sodium acetate (▼).

The main products detected were lactic acid, which was target product, and acetate; no further products in the gas or liquid phase were found. The carbon mass balance reached was 95-100% at all times. The plot shows that the formation of lactic acid is detected from the beginning of the conversion of 1,2- propanediol, however, the formation of acetate is observed at low

conversions already. This indicates a possible parallel reaction taking place where the primary and secondary hydroxy group of the alcohol are being targeted. The formation of acetate would in this case occur through the decomposition of hydroxyacetone as found in other studies^[167] or through oxidative scission of pyruvic acid ^[47]. A few of the monometallic Au and bimetallic AuPd catalysts which had been prepared, characterised and investigated for the selective oxidation of salicyl alcohol (see Chapter 4 and 6) were employed for the selective oxidation of 1,2- propanediol under mild conditions. The following table lists the results for the conversion X_t after 300 minutes, the selectivity towards lactic acid $S_{\text{lactic acid}}$ after 300 minutes, as well as the normalized TOF number in $\text{h}^{-1} / \text{pO}_2$ compared to some key results from other reported studies. Further, the previously determined average Au particle sizes of the catalysts are also included.

Table 7-1: Catalytic performance results for Au and AuPd/ C catalysts for the selective oxidation of 1,2- propanediol.

Catalyst	Au average particle size [nm]	X_{t300} [%]	$S_{\text{Lactic acid } t 300}$ [%]	TOF**/ pO_2 bar [h^{-1}]
1.5Au/C	5.1	32	53	86.1
1.5Au1.5Pd/C	8.1	25	100	38.1
3Au/C	8.3	40	63	68.2
1.5Au/C	4.7	100	98	260 ^{[172]a)}
2.5Au2.5Pd/C*	~6	91	96	2.1 ^[167]

Reaction conditions: $T=50^\circ\text{C}$, $\text{pO}_2=0.21\text{bar}$, $m_{\text{cat}}=0.2\text{g}$, $c_{1,2\text{-propanediol}}=0.15\text{M}$, 1,2 propanediol: Au=1000, rpm=1000.

a) 30 bar O_2

* $T=60^\circ\text{C}$, 1,2- propanediol : Au=500

** TOF after 5h

From the results it can be seen that the achieved conversion on the monometallic 1.5Au/C catalyst is far lower compared to the achieved activity of the 1.5Au/C under comparable conditions reported by other studies. In addition, the selectivity towards lactic acid for the 1.5Au/C is very low and only reaches 53% already at low conversion of 32%, whereas 1.5Au/C reported by other studies retains 98% selectivity at 100% conversion. The large difference in activity could be based on the Au surface morphology and also based on a different type of activated carbon used. Furthermore, the high availability of oxygen through high oxygen partial pressure increases the formation of lactic acid. The bimetallic 1.5Au1.5Pd/C catalyst shows a 100% selectivity towards lactic acid already at low conversions.

The addition of Pd therefore increases the selectivity of the catalyst. The alloy nature of particles (see Chapter 6) could block the oxidation of the secondary hydroxy group leading to acetate. A few preliminary experiments were carried out using oxide supported Au and AuPd catalysts as introduced earlier (see Chapter 6).

Table 7-2: Catalytic performance for Au and AuPd catalysts for selective oxidation of 1,2-propanediol.

Catalyst	Au average particle size [nm]	X _{t300} [%]	S _{Lactic acid t300} [%]	TOF ^{**} /pO ₂ [h ⁻¹]
1Au/CeO ₂	2.48	14	100	40.4
1Au/TiO ₂	2.37	10	100	17.1
1.5Au1.5Pd/CeO ₂	n.a	35	100	9.81
1.5Au1.5Pd/TiO ₂	n.a	52	84	36.1

Reaction conditions: T=50°C, pO₂=0.21bar, m_{cat}= 0.2g, c_{1,2-propanediol}= 0.15M, 1,2-propanediol:Au=1000, rpm=1000.

****TOF after 5h**

Comparing the results for the monometallic Au catalysts in Table 7-1 and Table 7-2, it can be seen that the oxide supported catalysts show an overall lower performance compared to the carbon supported catalysts. The addition of palladium to gold, in particular on TiO₂, results in an increase in catalytic performance compared to the monometallic Au/TiO₂. All investigated oxide supported catalysts show high selectivity towards lactic acid. This is in agreement with other reported results, showing that Au/CeO₂ supported catalysts prepared by sol-immobilisation show a higher selectivity towards lactic acid [63, 167]. This can be based on the strong metal support interaction influencing the metal particle and interphase with the support and blocking the activation of the secondary hydroxy group.

7.1.2 Selective oxidation of glycerol

For the selective oxidation of glycerol, the complexity of product network increases which is illustrated in the following figure:

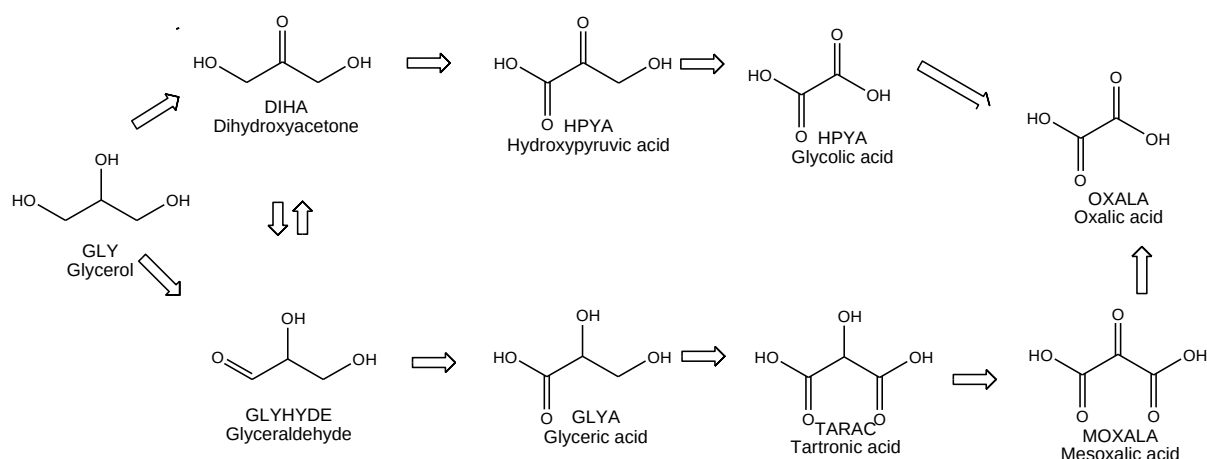


Figure 7-3: Reaction and product network for selective oxidation of glycerol [48].

According to previous reported studies on the selective oxidation of glycerol, there are two main oxidation pathways: a) the oxidation of the primary hydroxyl group leading to glyceric acid and higher oxygenates via glyceraldehyde as intermediate; b) the oxidation of the secondary hydroxyl group forming dihydroxyacetone which can transform to glyceraldehyde or hydroxypyruvic acid leading to glycolic acid. The reaction pathway is mainly dependent on the type of active metal and also the reaction conditions i.e pH. Studies have shown that with Au based catalysts, at a high pH, the primary hydroxy group is being oxidised with glyceric acid as main end product [74] [173] [121]. The second reaction pathway takes place at low pH using active metals based on Pt[18].

For this study, a few preliminary experiments were carried out applying the mono- and bimetallic Au and AuPd catalysts as studied and discussed for the selective oxidation of salicyl alcohol (Chapter4 and 6). The following figure (Figure 7-4) illustrates the typical concentration/ time profile for the course of reaction for the selective oxidation of glycerol under mild conditions on 1.5Au/C catalyst in the presence of base.

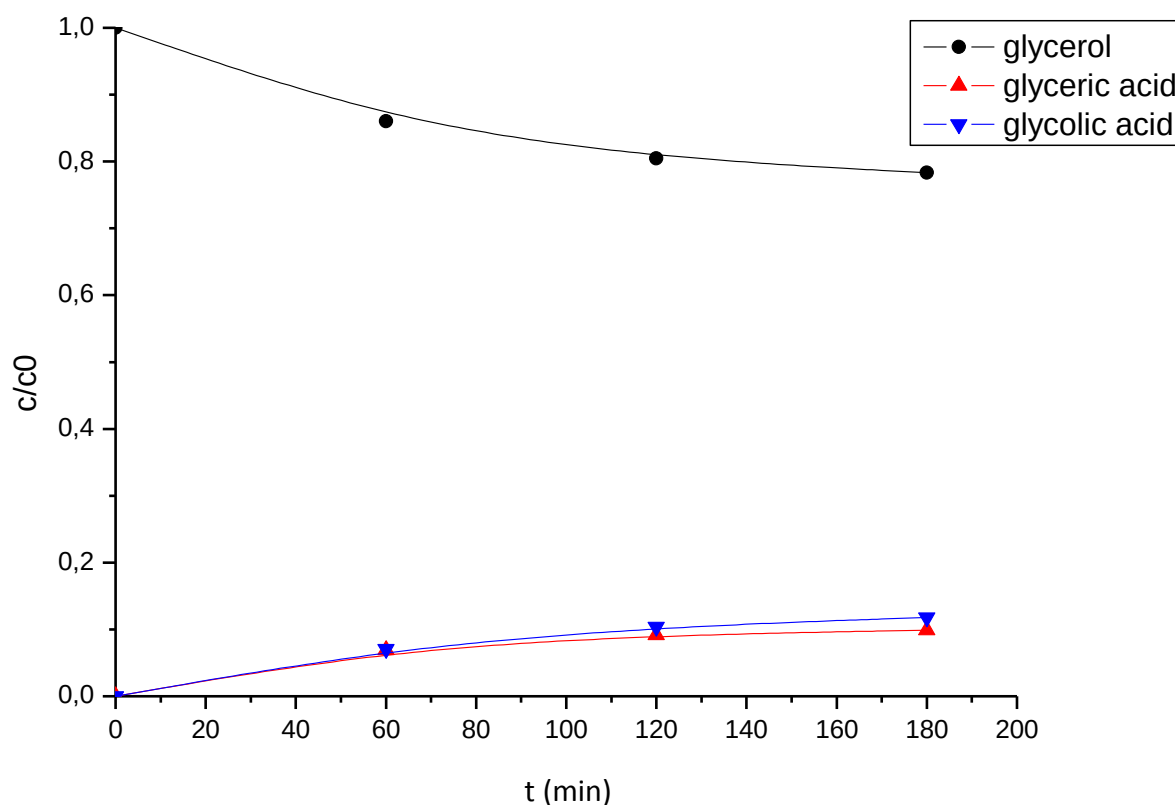


Figure 7-4: Concentration/time profile for the selective oxidation of glycerol, reaction conditions: $T = 50^{\circ}\text{C}$, $p = 1\text{bar (air)}$, $\text{cat} = 1.5\text{Au/C}$, $m_{\text{cat}} = 0.2\text{g}$, $c_{\text{glycerol}} = 0.2\text{M}$, $\text{NaOH:glycerol} = 2:1$, $\text{rpm} = 1000$.

The products detected were glyceric acid and glycolic acid, no other products in the gas or liquid phase were found. The carbon mass balance reached was 95-100% at all times. The figure shows that while the concentration of glycerol decreases, the formation glyceric acid and glycolic acid is detected simultaneously from the beginning of the reaction. According to the reaction network, this would imply a parallel reaction mechanism, taking place where the primary and secondary hydroxy groups are oxidised. The following table lists the results for the selective oxidation of glycerol at 300 minutes, the selectivity to glyceric acid at 300 minutes and the TOF numbers expressed $\text{h}^{-1} / p\text{O}_2$ by the partial pressure of oxygen.

Table 7-3: Results for Au and AuPd catalysts for the selective oxidation of glycerol.

Catalyst	Au average particle size [nm]	X ₃₀₀ [%]	S _{Glyceric acid300} [%]	TOF*/pO ₂ bar[h ⁻¹]
1.5Au/C	5.07	22	45	85.3
1.5Au1.5Pd/C	8.1	13	75	66.7
1.5Au/CeO ₂	2.45	17	53	59.2
1.5Au1.5Pd/CeO ₂	n.a	28	81	28.8
1.5Au/C	n.a.	100	45.2	363 [7]

Reaction conditions: T=50°C, p =1 bar(air) , m_{cat}=0.2 g, c_{glycerol}= 0.2M, NaOH: glycerol =2:1, rpm=1000.

*TOF after 5h

The results show that the highest activity is achieved by the monometallic 1.5Au/C catalyst reaching TOF numbers of 85 h⁻¹. Compared with what has been reported by other studies on the 1.5Au/C catalyst system, the activity is lower by a degree of order. However, it should be noted that the reaction conditions applied are different, such as the employment of higher amounts of base leading to higher conversion rates, based the correlation of the rate of reaction with the OH⁻ concentration which has been demonstrated for the selective oxidation of glycerol [141] as well as the selective oxidation of salicyl alcohol (in Chapter 4).

The results further show that selectivity towards glyceric acid in this study is low in particular for the monometallic Au catalysts. It can be seen that addition of palladium increases the selectivity towards glyceric acid. Overall, this preliminary study suggests that the monometallic gold catalysts are active but less selective towards the oxidation of the primary alcohol group in glycerol under mild conditions[7]. This is in agreement with other reported studies on the selective oxidation of glycerol, showing that the selectivity towards glyceric acid on AuPd alloy catalysts is higher compared to monometallic Au catalysts [174]. Other studies on the glycerol oxidation have shown that a strong synergistic effect is reached by bimetallic AuPd catalyst supported on carbon resulting in a much higher activity, which is uniquely attributed to the presence of alloy particles [166]. However, as seen from previous reported studies, the results are very dependent on the particle size effect, ratio of metals and reaction conditions used. Therefore, further studies on the particle composition and size effect would need to be carried out in order to understand the catalyst activity and impact on the product distribution.

7.2 Chapter summary

This chapter presented a preliminary study to investigate the transferability of the gold based catalyst system onto the liquid phase selective oxidation of complex alcohol substrates. The substrates selected were 1,2- propanediol and glycerol both giving a complex reaction and product network.

Overall, the study showed that the reaction could be carried out under mild conditions using air as oxidant and water as solvent. For the selective oxidation of 1,2- propanediol, the highest activity was achieved with the monometallic 1.5Au/C catalyst reaching TOF numbers of 86 h⁻¹. However, the monometallic catalyst appeared to be less selective towards the oxidation of the primary alcohol group leading to the formation of the target product lactic acid. The addition of Pd to the gold catalyst decreased the catalytic activity, however the catalyst showed higher selectivity towards lactic acid. For the selective oxidation of glycerol, the highest catalytic performance was obtained with the monometallic Au/C catalyst with TOF numbers of 85 h⁻¹, with selectivities of 45% at 22% conversion. A large increase of selectivity towards the main product glyceric acid was observed upon addition of palladium.

In summary, the results so far suggest that the monometallic Au/C catalyst is less selective towards the oxidation of the primary alcohol group of poly functional alcohols leading to the oxidation of the secondary group. The addition of Pd to Au increases the selectivity towards the oxidation of the primary alcohol function for all investigated supports i.e. carbon and oxide. In comparison with previous reported studies, the results for activity and selectivity differ based on the reaction conditions used.

Further investigations would need to be carried out on the catalyst surface and particle morphology of the mono and bimetallic catalysts in order to understand its impact on the catalyst activity and product distribution.

8 MOVING FROM BATCH TO CONTINUOUS PROCESSING

8.1 Chapter introduction

To demonstrate the applicability for larger scale reactors and investigate long-term stability of the catalyst system, the Au/C catalyst system was applied in a trickle bed reactor on the selective oxidation of salicyl alcohol under continuous flow. This study was done in collaboration with a MSc student Ching Chieng Chong. The main catalyst system hereby applied was 1.5 Au/C. The challenge was to prepare the catalyst in a suitable form i.e. in particulate matter and to further achieve small and disperse gold particles on this support comparable to the Au surface morphology of the powdered Au/C catalyst (Chapter 4). The support was the same activated carbon (Norrit) used as for the powdered catalyst (see Chapter 4) and was crushed and sieved according to the required grain sizes. The aim was to obtain comparable activity and selectivity towards the selective oxidation of salicyl alcohol to what had been achieved from the batch reactor studies using the Au/C catalyst system (see Chapter 4). Therefore, an important part was the investigation of the impact of the catalyst grain size on the activity and selectivity. Parametric studies regarding the effect of temperature, oxygen partial pressure and residence time were carried out and the results are illustrated in the MSc Thesis [144]. According to the study, the optimum test conditions applied were $T=80^{\circ}\text{C}$, $p\text{O}_2=0.21\text{bar}$, $\text{LHSV}=0.5$.

8.1.1 Catalyst preparation for trickle bed reactor

Based on the dimensions of the reactor, the catalyst bed was fixed to a total volume of 10 cm^3 out of which the active catalyst was 1g diluted with silica carbide to 10 cm^3 . The active catalyst required to be of specific granular size suitable to these dimensions for which a granular 0.6-0.85 mm was selected. The catalyst was prepared via sol-immobilisation, and the gold sol was immobilised on the granulate particles. TEM analysis was performed in order to verify whether the support grain size influenced the deposition of gold particles. The following figures present the TEM image and the Au particle size distribution of the granulate catalyst 1.5Au/C with a grain size of 0.6-0.85 mm.

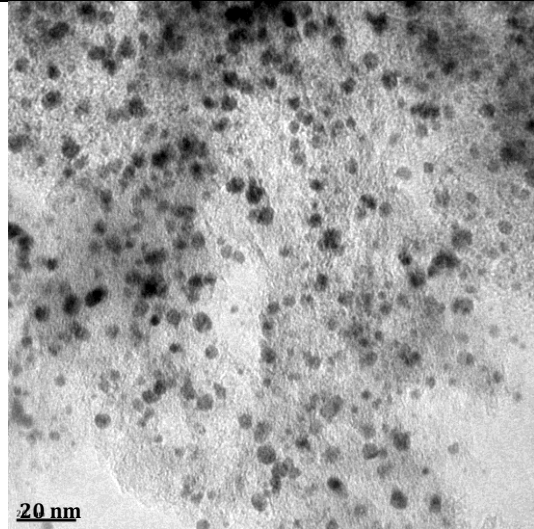


Figure 8-1: TEM image of 1.5Au/C on granulate (0.60-0.85mm).

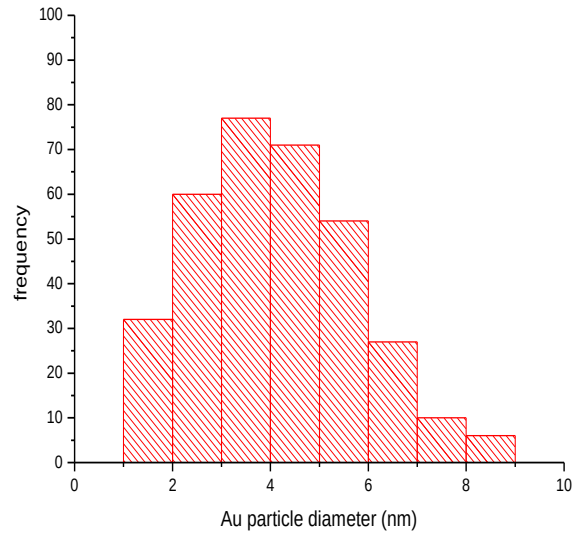


Figure 8-2: TEM histogram for 1.5Au/C on granulate (0.60-0.85mm).

The average determined Au particle diameter is 4.1 nm (SD=2.56 nm) and comparable to what has been achieved on the powdered 1.5Au/C catalyst with 5.07 nm (SD=1.1). The particle size measurements were only performed on the grain size of 0.60-0.85mm, however, it was assumed that the particle size and distribution remained constant within error for the larger grain sizes.

8.1.2 Effect of LHSV

The following design equation for a plug flow reactor was used:

$$F_{A0} \frac{dX}{dV} = -r_A \quad 8-1$$

$$-\ln(1-X) = k \frac{V}{L'} = k\tau \quad 8-2$$

For this set of experiments, the liquid flow rate of salicyl alcohol was varied to investigate the impact of LHSV (ratio of the hourly volume of liquid per unit processed to the volume of catalyst per unit) on the performance.

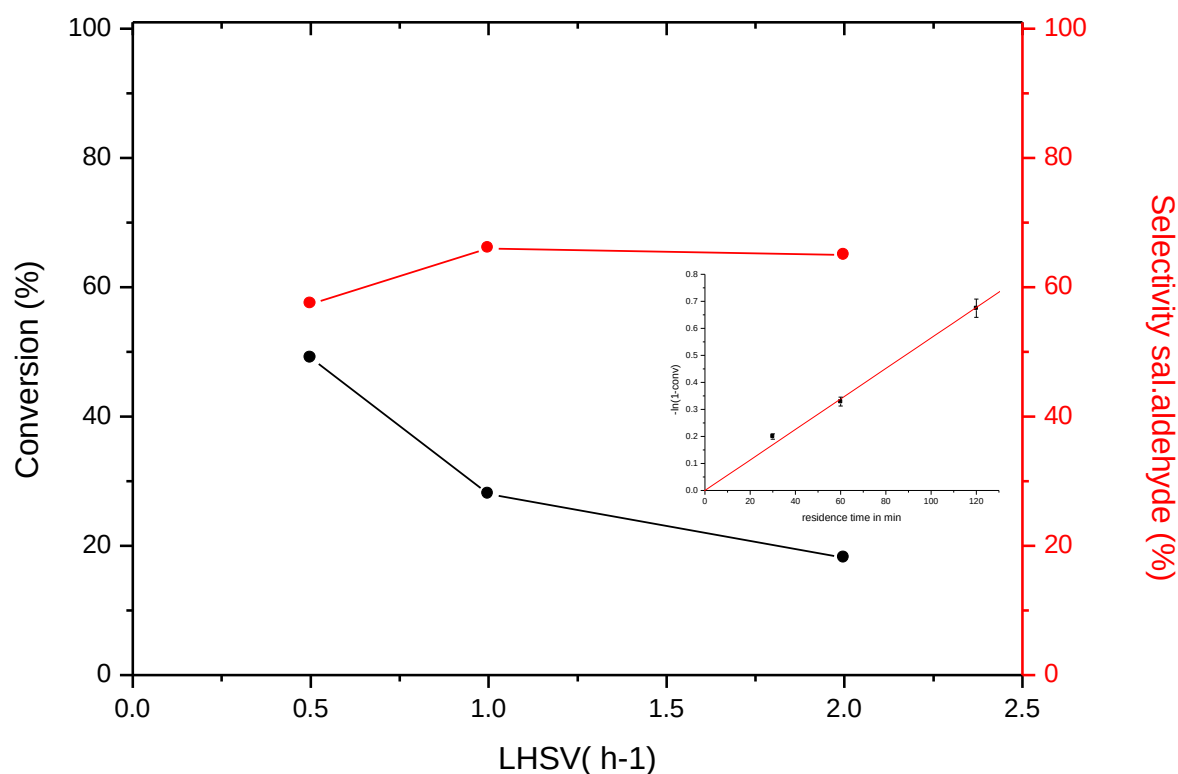


Figure 8-3: Effect of LHSV on conversion and selectivity for selective oxidation of salicyl alcohol in trickle flow reactor, and first order plot $-\ln(1-\text{conv})$ vs. residence time): reaction conditions: $T=40^{\circ}\text{C}$, $p\text{O}_2=0.21$ bar, catalyst= 1.5Au/C , $m_{\text{cat}}=1\text{g}$ grain size $0.6\text{--}0.85\text{ mm}$ (in 10mL silica carbide), $c_{\text{salicyl alcohol}}=0.04\text{ M}$, $\text{NaOH}:\text{salicyl alcohol}=2:1$, ● conversion salicyl alcohol ● selectivity salicyl aldehyde.

The plot $-\ln(1-\text{conv})$ for salicyl alcohol against the residence time in the reactor shows that the selective oxidation of salicyl alcohol follows first order kinetics under continuous conditions. The plot shows that the LHSV has a strong effect on the conversion of salicyl alcohol. With an increase in LHSV to 2 and effective decrease of the residential time of the reactant, the conversion drops by 65%. At the same time the selectivity towards salicyl aldehyde increases only slightly so it is nearly independent of the LHSV [175].

8.1.3 Effect of particle size

The next step was to investigate the impact of the catalyst granulate size on the catalyst performance. In general, the rate-controlling step in a trickle-bed reactor can be based on several processes: a) mass transfer of oxygen at the gas/liquid interphase b) mass transfer of the substrate molecules through the liquid film covering the catalyst pellets, (c) diffusion and reaction processes within the liquid filled catalyst pores and (d) intrinsic kinetics of the

reaction. It is known that the reaction concentration at interphase between catalyst surface/liquid film is strongly influenced by simultaneous diffusion and reaction within the catalyst pellets [176]. Previous studies by Le Nobel and Choufoer in a trickle-bed reactor representative of the Shell hydro- desulfurisation process [177], found that a reduction in catalyst size increased the reaction rate, indicating pore diffusion limitations.

The following table (Table 8-1) shows the results obtained on the conversion of salicyl alcohol and selectivity towards salicyl aldehyde for varying the catalyst grain size (0.6-4mm). In addition, the BET surface area as well as the pore diameter and volume of the granular support are listed.

Table 8-1: Effect of varying catalyst particle size on the conversion of salicyl alcohol and selectivity towards salicyl aldehyde.

Catalyst grain size	S_{BET}	Pore volume	Pore size	X	$S_{\text{salicyl aldehyde}}$
[mm]	[$\text{m}^2 \cdot \text{g}^{-1}$]	[$\text{cm}^3 \cdot \text{g}^{-1}$]	[nm]	[%]	[%]
0.6 – 0.85	703	0.43	2.4	99.6	36.7
> 0.85	683	0.39	2.4	55.4	74.7
4 *	653	0.42	2.5	32.6	75.6

Reaction conditions: $T=40^\circ\text{C}$, $p_{\text{O}_2}=0.21\text{bar}$, $\text{LHSV}=0.5\text{ h}^{-1}$, $\text{catalyst}=1.5\text{Au/C}$, $\text{mcat}=1\text{g}$, $\text{C}_{\text{salicyl alcohol}}=0.04\text{ M}$, $\text{NaOH:salicyl alcohol}=2:1$.

* - uncrushed cylindrical granulates

The results demonstrate that there is a strong decrease in conversion with an increase in catalyst grain size indicating the presence of mass transport limitation through pore diffusion. For the catalyst with the smallest grain size almost full conversion is reached with a LHSV of 1 h^{-1} . The low selectivity towards salicyl aldehyde is caused by over-oxidation to salicylic acid. It is possible that the wetting of the catalyst is not fully reached so that oxygen has a greater access to the catalyst active centre and can lead to direct over-oxidation of salicyl aldehyde. The results for the BET measurements only show a slight decrease in overall surface area and the pore volume and pore size appear to be constant. The apparent activation energy for the trickle flow reactor was determined to be 32.5 kJ/mol (see Appendix for Arrhenius plot) and therefore almost 60% lower compared to the value from the batch reactor studies with 56.9 kJ/mol . If suggested diffusion is a significant limitation, then the observed rate constant is proportional to D_{eff}/r_p and the apparent activation energy is $E_a = (E_D + E)/2$. If mass transfer limitations are present in the liquid film as well as in the catalyst pores, the experimental determined apparent

activation energy should range within that value for a pore diffusion limited and bulk diffusion limited reaction [176].

8.2 Chapter summary

This chapter presented a preliminary investigation on the application of the Au/C catalyst system in a continuous reactor system i.e. trickle bed reactor for the selective oxidation of salicyl alcohol. The main challenge was to design the catalyst with comparable properties in terms of Au particle size and distribution compared to the powdered 1.5Au/C catalyst applied for the batch reactor studies and to obtain preliminary data regarding the catalyst activity and selectivity.

It was demonstrated that the selective oxidation of salicylic alcohol under continuous operating conditions in the trickle flow reactor followed first order kinetics. The catalyst activity results showed a decrease in catalyst activity with an increase in the catalyst grain size indicating mass transport limitations based on pore diffusion. The catalyst with the smallest grain size achieved nearly full conversion, however, the selectivity towards salicyl aldehyde was only 37% due to over oxidation to salicylic acid. Overall, the catalyst selectivity was lower compared to the powdered catalyst. Reasons might be based on a partial wetting of the catalyst grains, enabling a higher access of the oxygen leading to direct over-oxidation of salicyl aldehyde.

This chapter has shown the limitations in application of the Au/C catalyst system in a trickle bed reactor. Further investigations would need to be carried such as the increase of pore volume or the application of structured support in order to eliminate mass transport limitations and successfully establish the Au/C catalyst for continuous processing.

9 CONCLUSIONS AND OUTLOOK

9.1 Key findings of this research

The main objective of this research work was the study of gold based catalyst systems on the liquid phase selective oxidation of alcohols to their higher oxygenates based on:

- The establishment of a suitable reactor system and optimal conditions to carry out the reaction under mild conditions
- The study of the kinetics and mechanism
- The investigation of catalyst effects with focus on Au/C
- The approach towards base-free selective oxidation through catalyst development
- The transferability from batch to continuous processing and catalyst requirements
- The relevance of the Au/C catalysis to other platform alcohols

The main reaction investigated was the selective oxidation of salicyl alcohol, with salicyl aldehyde, the target product and salicylic acid. The solubility of the reactant and products in water, together with the simple product distribution and the relative speed of the reaction, enabled to plan and perform the study in a reasonable time span. The studies were carried out in a temperature-controlled jacketed glass batch reactor, and its specific design included a high agitation overhead stirrer to ensure a homogeneous concentration and temperature profile throughout the experiment and baffles with specific dimensions to break the boundary fluid layer during the reaction. Furthermore, the reactor contained a gas dispersion frit to finely disperse the air bubbles, as well as a reflux condenser. The reaction conditions were critically investigated to ensure that influences of mass transport were eliminated for the performed experiments. Based on the establishment of the reaction system and conditions, the investigation regarding the mechanism and kinetics as well as the catalytic performance were carried out. For all experiments, mass balance of 95-100% was reached at all times and, in contrast to previous reported studies on this reaction, only small amounts of initial adsorption were detected within the limits of mass balance.

The study based on the kinetics and mechanism demonstrated the initial dependency on the base at low conversion. The kinetic analysis showed the reaction followed a consecutive mechanism with salicyl aldehyde being oxidised to salicylic acid. The mechanism applied to all Au/C catalysts with different loadings.

The most active catalyst system was 1wt% Au/C achieving maximum TOF numbers of 342h^{-1} and selectivities of 79% at 100 % conversion. Compared to previous results reported on this

reaction the performance was higher by 40 times. Structure sensitivity of the Au/C catalysts was studied showing that the catalyst treatment temperature and gold loading impacted the particle size and distribution, which in turn influenced the catalytic performance. The catalyst activity decreased with increasing average particle size.

The study based on the base-free selective oxidation has shown that, while pure alkaline-earth metal oxides showed high amounts of leaching, when dispersed and impregnated on oxides, especially hydrotalcites, this effect was mitigated. For the MgO impregnated hydrotalcite series, the basicity of the catalysts, measured by CO₂ adsorption, increased with the amount of MgO. Analysis on the morphology of the support indicated the formation of MgO particles or precipitates on the support surface. This effect was also caused by the decrease in surface area upon calcination of the support. The catalyst 1.5Au/0.16MgO-HT with the highest CO₂ adsorption capacity showed the highest activity reaching initial TOF numbers of 115 h⁻¹ and selectivities of 90% at 56% conversion.

The synthesis of bimetallic AuPd on carbon catalysts led to a wider particle size distribution compared to monometallic Au/C catalysts with the same total metal loading. This effect could be caused by the formation of a mix of mono- and bimetallic particles. X-Ray diffraction patterns showed a shift of the diffraction lines indicating the existence of alloyed particles. The catalyst performance for bimetallic AuPd catalysts decreased with an increase in Pd content reaching maximum TOF numbers of only 118h⁻¹. The selectivity towards salicyl aldehyde remained relatively constant for the different ratios of Au: Pd.

The applicability of the Au/C catalyst on the selective oxidation of 1,2- propanediol and glycerol was analysed. The main products were lactic acid and glyceric acid, respectively, which implied the oxidation of the primary alcohol function. Amongst the employed catalysts, the Au/C catalyst showed the highest activity. However, the performance compared to the selective oxidation of salicyl alcohol was lower by a degree of order, achieving initial TOF numbers of only 86h⁻¹ for the selective oxidation of 1,2- propanediol and 85h⁻¹ for the selective oxidation of glycerol. Selectivity values were very low towards the target products in multi-functional alcohols, as the Au/C system appeared to be non-selective towards the activation of the primary alcohol group. Therefore, for the selective oxidation of glycerol, the selectivity reached was only 46% at maximum of 22% conversion towards the main product glyceric acid. For the selective oxidation of 1,2- propanediol, the selectivity was only 57% at maximum of 30% conversion. The here obtained values for catalyst activity in terms of TOF numbers were lower by two degrees of order compared other reported studies on the same reactions in the aqueous phase on Au/C.

However, the results were based on different reaction conditions and cannot be directly correlated.

The application of the Au/C catalyst for continuous processing was tested using a trickle flow reactor. For this purpose, the catalyst was prepared in particulate form with specified grain sizes (0.6-0.85 mm) which were suited to the dimensions of the reactor. The catalysts were prepared using the same sol-immobilisation method as for the powdered catalyst achieving small and dispersed gold particles on the granular particles. Studies on the reaction conditions showed that an increase in LHSV did not cause a significant increase in selectivity. The study showed the reaction was mass transfer limited caused by pore diffusion.

9.2 Impact

Au/C catalysts have demonstrated the highest performance on the selective oxidation of salicyl alcohol. However, limitations of this catalyst system regarding the application for continuous processing have been identified. The strong mass transfer effects with an increase in grain size impedes the general applicability for trickle bed reactors. Alternative strategies would require the change in pore size of the support through possible treatment or the application of structured carbon material. The challenge is to obtain a homogeneous Au surface morphology on the new carbon material.

The study on the base free catalysis is an important field of research towards green catalytic conversion. This study has evaluated the usage of alkaline-earth metal oxide based catalysts and shown the potential and the limits in application for selective oxidation in the aqueous phase. Pure alkaline-earth metal oxides such as MgO, having a high basicity, and being successfully employed as Au/MgO catalysts for CO oxidation, are not suitable for selective oxidation reactions in water due to the high amount of leaching. Buffering the solution to mitigate leaching is likely to cause side effects such as condensation reactions. However, the employment of MgO based catalysts for reactions in the organic phase is possible. A plausible solution is the dispersion of alkaline-earth metal oxides on stable supports such as oxides, as it was presented in this work. The dispersion is dependent on the surface morphology of the support. Especially hydrotalcite materials have shown suitable support properties due to their large surface area and flexibility in structure as well as basic nature and their applicability as support for liquid phase reactions has been reported. Depending on the amount, the dispersion of alkaline-earth metal oxides is likely to generate metal oxide precipitates on the support surface rather than a homogeneous layer on the support. Increasing the amount of MgO will cause larger precipitates to form and might risk leaching. The task is the control of the dispersion of oxide to achieve reproducible properties of the catalyst and to achieve maximum reaction rates by increasing the basicity.

The study of gold based catalysts for the selective oxidation of other platform molecules such as 1,2- propanediol and glycerol has shown that Au/C is the most active catalyst system which has been in accordance with other studies. However, the Au/C catalyst system reaches limitations due to a loss in selectivity with an increased complexity of reaction network. Application for continuous processing of selective oxidation reactions of multifunctional platform molecules on Au/C would require different measures to control the selectivity through a different catalyst design and questions, the practicality for Au/C as applicable selective oxidation catalyst.

9.3 Outlook

The development of the catalyst system for base-free selective oxidation is an important step towards the establishment of green catalytic conversion. Further development on the dispersion and stabilisation of the oxide the support needs to be done in order to minimise leaching and deactivation. Probe reactions in the batch system on more complex molecules need to be done to understand the performance in complex reaction networks. The catalyst can then be tested for continuous processing with the investigation of catalyst grain size and mass transfer effects. Eventually the materials should be stable and selective and applicable to complex bio-derived substrates such as sugars and lignins.

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11 APPENDIX

A Au/C for Selective Oxidation

HPLC analysis

$$Y = B * X$$

Y= area (UV/RI)

X= concentration (mol/L)

C= (calibration factor)

Table 11-1: HPLC analysis parameters.

Column	SUPELCOGEL-610H (30 cm × 0.78 cm)
Temperature	50°C
Flow rate	0.8 mL/min
Detection	UV VIS (273 nm), Refractive Index
Analysis run time/sample	120 min
Sample volume total	1.5 mL
Sample volume reaction sample	0.25 mL
Internal standard volume	0.1 mL

A) Selective Oxidation of Salicyl Alcohol HPLC1

Salicyl alcohol calibration

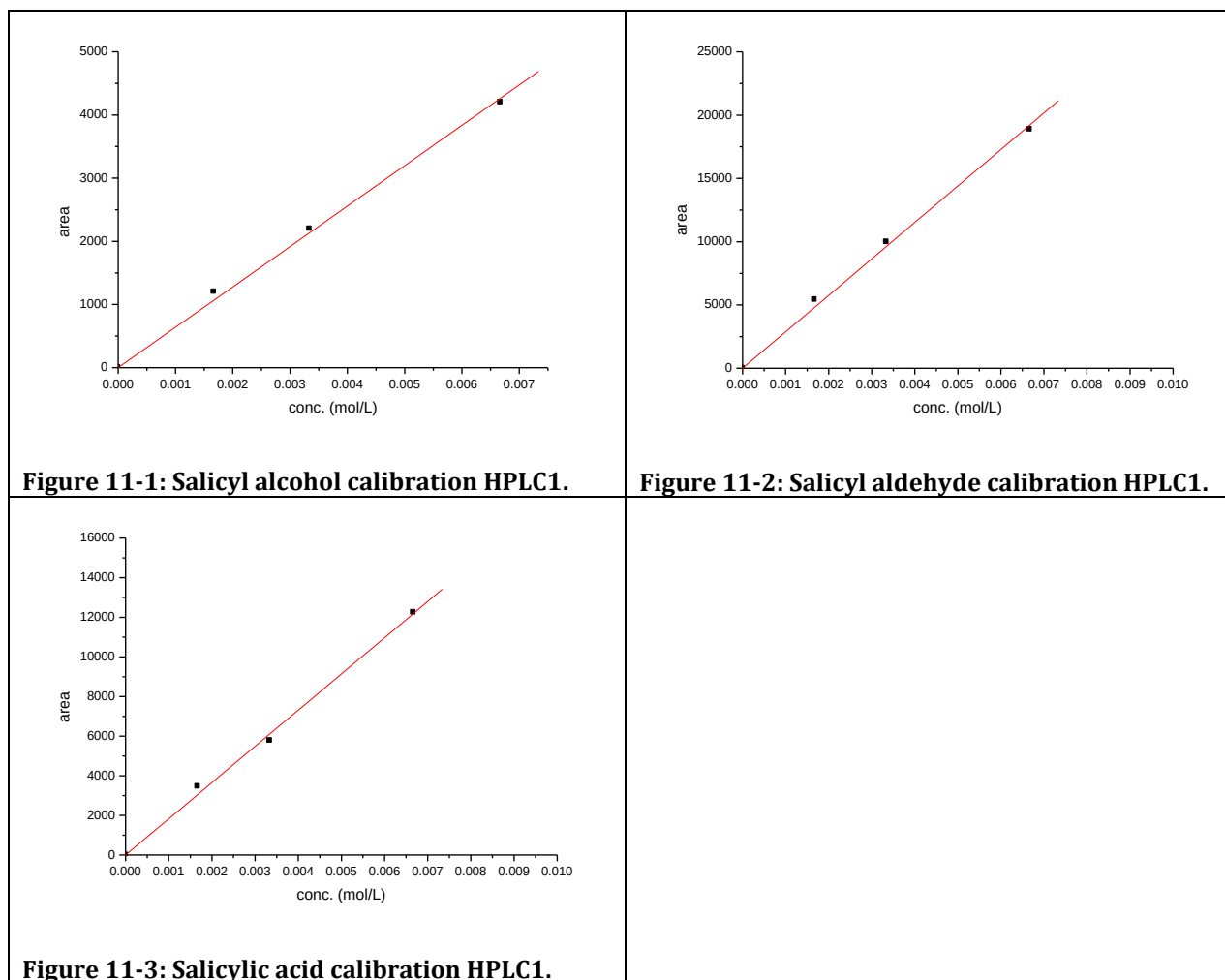


Table 11-2: Calibration factors for HPLC1.

component	B	SD	R ²
Salicyl alcohol	1.63*E-06	12136.50	0.99
Salicyl aldehyde	3.68*E-06	59386.29	0.99
Salicylic acid	5.46*E-07	39538.98	0.99

B) A) Selective Oxidation of Salicyl Alcohol HPLC2

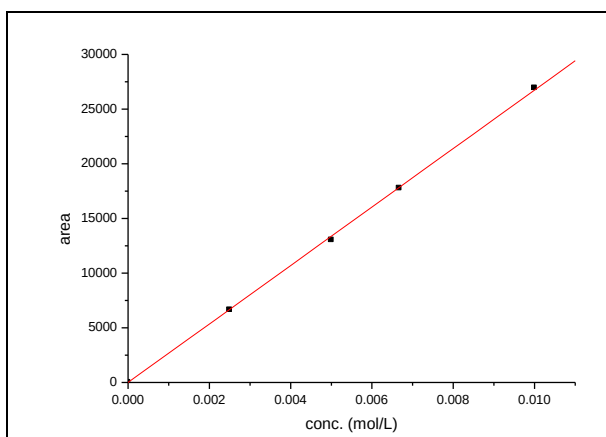


Figure 11-4: Salicyl alcohol calibration HPLC2.

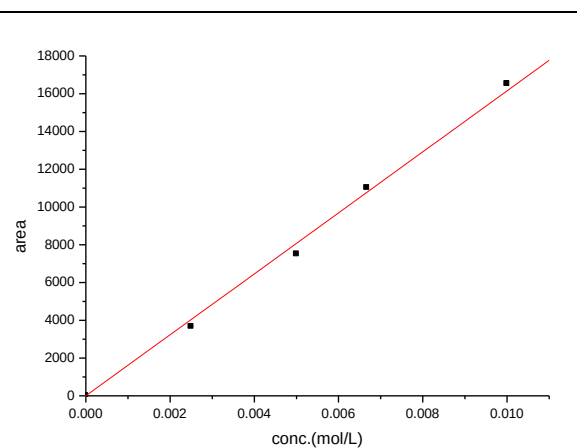


Figure 11-5: Salicyl aldehyde calibration HPLC2.

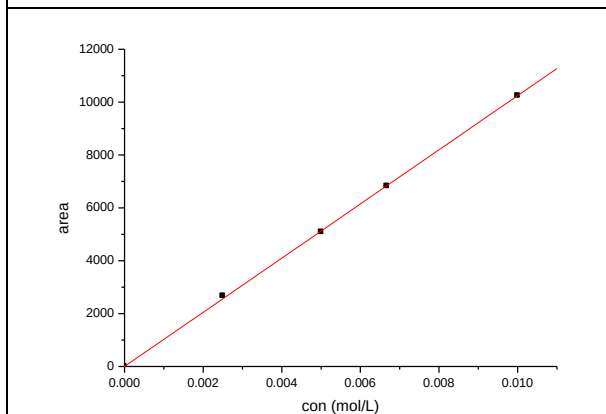


Figure 11-6: Salicyl acid calibration HPLC2.

Table 11-3: Calibration factors for HPLC 2.

Component	B	SD	R ²
Salicyl alcohol	2.67E6	19955.75	0.99
Salicyl aldehyde	1.62E6	39222.04	0.99
Salicyl acid	1.03E6	5946.13	0.99

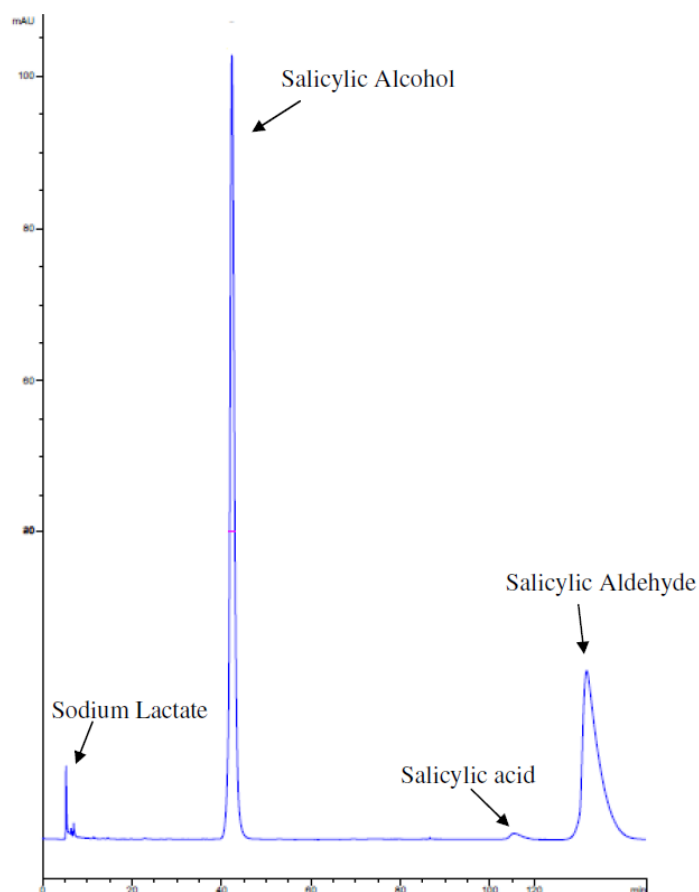


Figure 11-7: HPLC chromatogram for selective oxidation of salicyl alcohol components (HPLC2).

Parametric Study (T,p, pH)

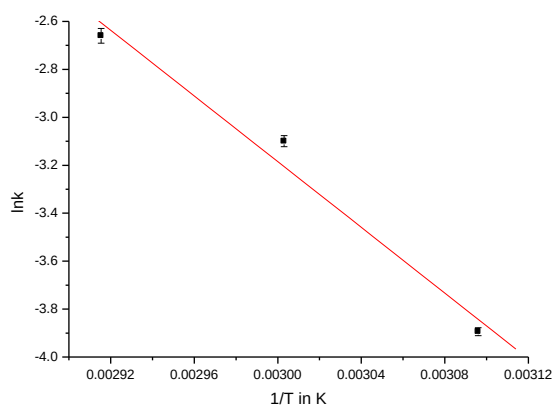


Figure 11-8: Arrhenius plot for determination of the activation energy for the selective oxidation of salicyl alcohol with standard error, — linear fit function, reaction conditions $T = 50 - 70\text{ }^{\circ}\text{C}$, $p_{\text{total}} = 1\text{ bar}$ (air), catalyst 1.5Au/C, $m_{\text{cat}} = 0.2\text{ g}$, $c_{\text{salicyl alcohol}} = 0.04\text{ M}$, NaOH: salicyl alcohol = 2:1, rpm = 1000.

Effect of pH

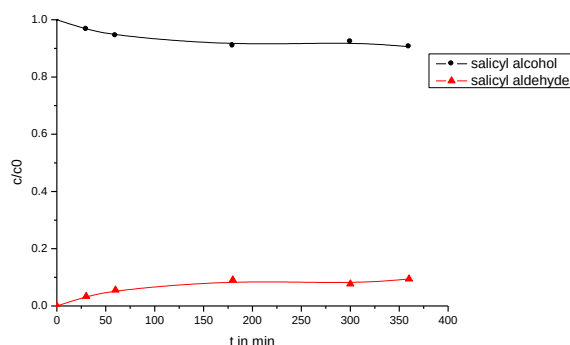


Figure:11-9: Selective oxidation of salicyl alcohol, reaction conditions $T = 50\text{ }^{\circ}\text{C}$, $p_{\text{total}} = 1\text{ bar}$ (air), catalyst 1.5Au/C , $m_{\text{cat}} = 0.2\text{ g}$, $c_{\text{salicyl alcohol}} = 0.04\text{ M}$, $\text{NaOH: salicyl alcohol} = 0:1$, $\text{rpm} = 1000$, • salicyl alcohol, ▲ salicyl aldehyde, ▼ salicylic acid.

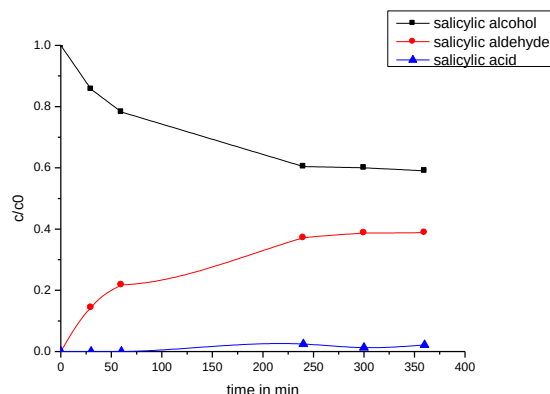


Figure 11-10: Selective oxidation of salicyl alcohol, reaction conditions $T = 50\text{ }^{\circ}\text{C}$, $p_{\text{total}} = 1\text{ bar}$ (air), catalyst 1.5Au/C , $m_{\text{cat}} = 0.2\text{ g}$, $c_{\text{salicyl alcohol}} = 0.04\text{ M}$, $\text{NaOH: salicyl alcohol} = 0.5:1$, $\text{rpm} = 1000$, • salicyl alcohol, ▲ salicyl aldehyde, ▼ salicylic acid.

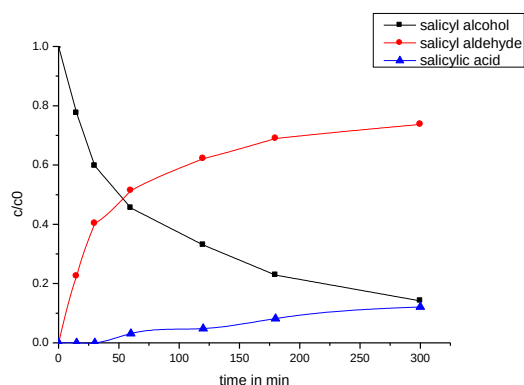


Figure:11-11: Selective oxidation of salicyl alcohol reaction conditions $T = 50\text{ }^{\circ}\text{C}$, $p_{\text{total}} = 1\text{ bar}$ (air), catalyst 1.5Au/C , $m_{\text{cat}} = 0.2\text{ g}$, $c_{\text{salicyl alcohol}} = 0.04\text{ M}$, $\text{NaOH: salicyl alcohol} = 1:1$, $\text{rpm} = 1000$, • salicyl alcohol, ▲ salicyl aldehyde, ▼ salicylic acid.

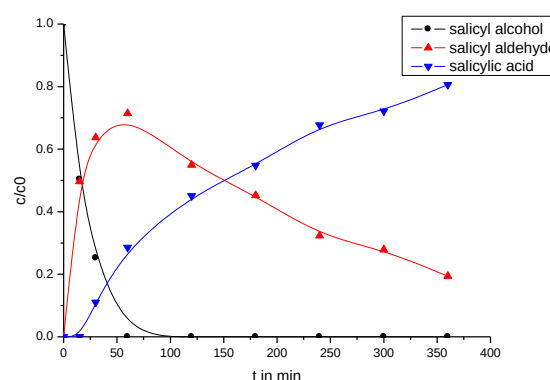
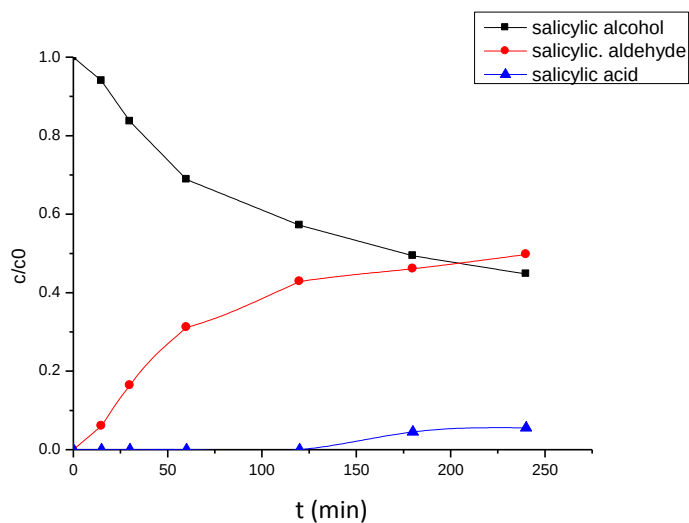


Figure 11-12: Selective oxidation of salicyl alcohol, reaction conditions $T = 50\text{ }^{\circ}\text{C}$, $p_{\text{total}} = 1\text{ bar}$ (air), catalyst 1.5Au/C , $m_{\text{cat}} = 0.2\text{ g}$, $c_{\text{salicyl alcohol}} = 0.04\text{ M}$, $\text{NaOH: salicyl alcohol} = 3:1$, $\text{rpm} = 1000$, • salicyl alcohol, ▲ salicyl aldehyde, ▼ salicylic acid.

Selective oxidation of salicyl alcohol with 1M buffered solution Na_2CO_3



**Figure 11-13: Concentration/ time profile for the selective oxidation of salicyl alcohol. Reaction conditions: catalyst: 1.5Au/C, $T=50^\circ\text{C}$, $p=1\text{bar}$, $c_{\text{salicyl alcohol}}=0.04\text{ M}$, $n_{\text{Na}_2\text{CO}_3}=1\text{M}$, $\text{rpm}=1000$,
 • salicyl alcohol, ▲ salicyl aldehyde, ▲ salicylic acid.**

Kinetics and Mechanism

Determining initial rate of reaction

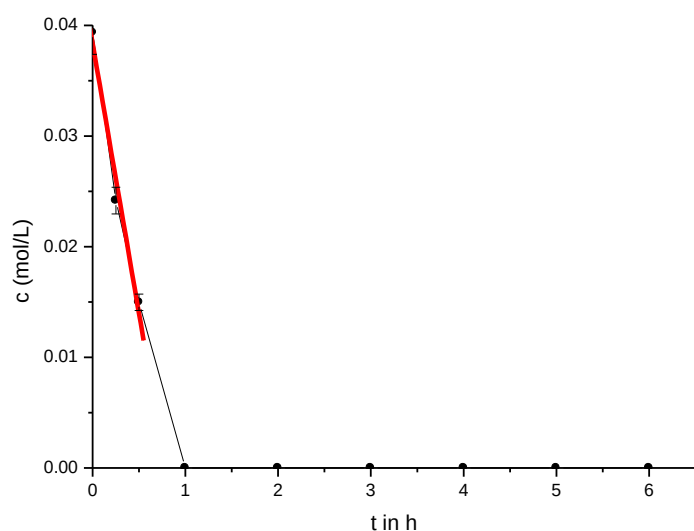


Figure 11-14: Origin fit plot for determination of initial rate of reaction at $t=0$ ■ experimental data, — fit function, experimental data for reaction conditions: catalyst: 1.5Au/C, $T=50^\circ\text{C}$, $p=1\text{bar}$, $c_{\text{salicyl alcohol}}=0.04\text{ M}$, $\text{NaOH: salicyl alcohol } 2:1$, $\text{rpm}=1000$, • salicyl alcohol.

1Au/C

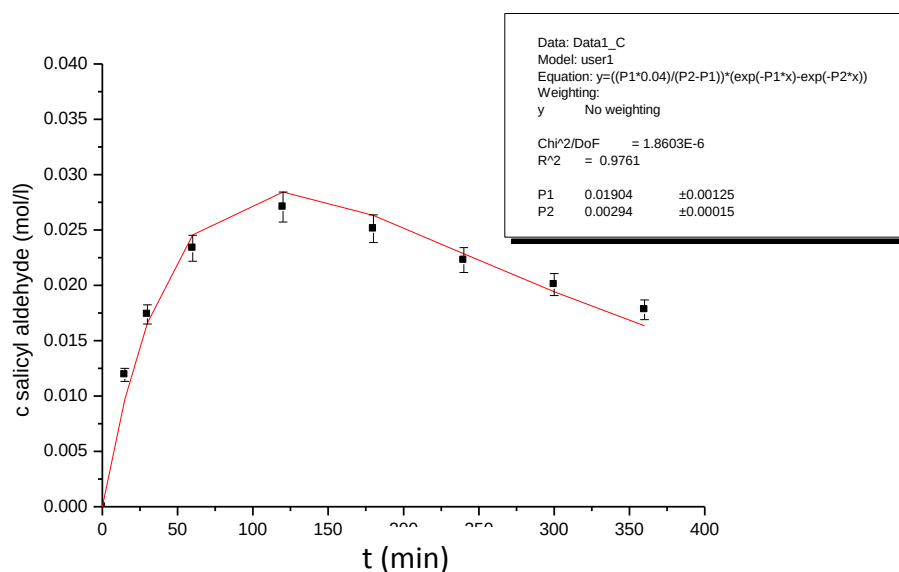


Figure 11-15: Origin fitted plot for consecutive reaction of first order for concentration/time profile of salicyl aldehyde, ■ experimental data, — fit function, experimental data for, reaction conditions: catalyst: 1Au/C, T=50°C, p=1bar, $c_{\text{salicyl alcohol}}=0.04$ M, NaOH: salicyl alcohol 2:1, rpm=1000, salicyl aldehyde.

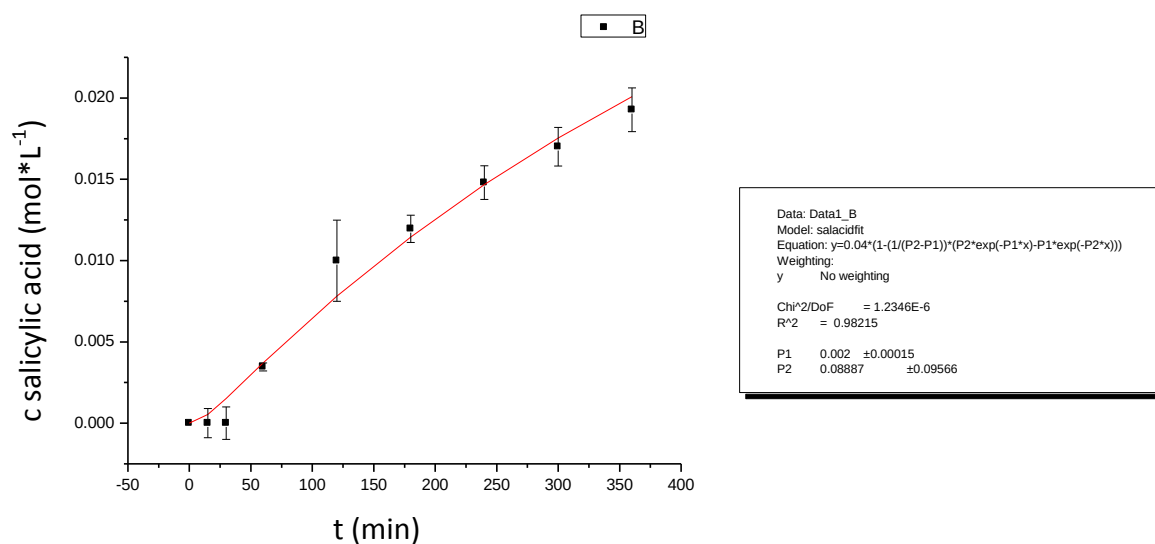


Figure 11-16: Origin fitted plot for consecutive reaction of first order for concentration/time profile of salicylic acid, ■ experimental data, — fit function, experimental data for, reaction conditions: catalyst: 1Au/C, T=50°C, p=1bar, $c_{\text{salicyl alcohol}}=0.04$ M, NaOH: salicyl alcohol 2:1, rpm=1000, salicylic acid.

3Au/C

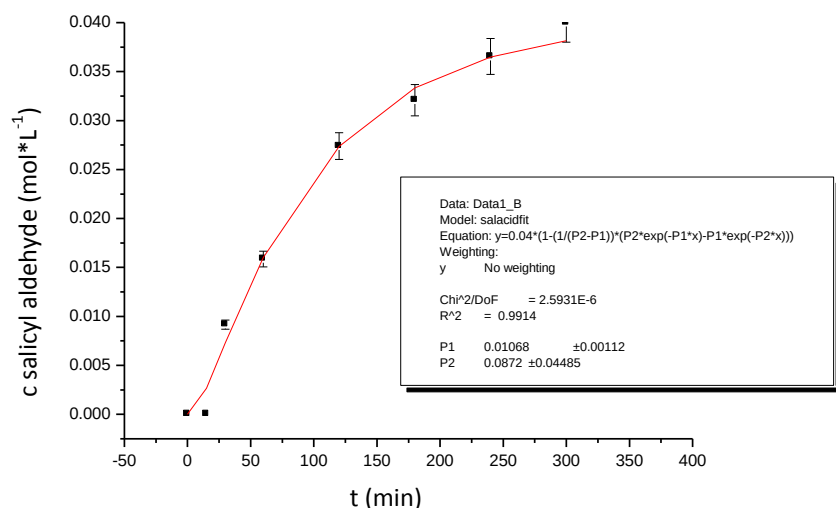


Figure 11-17: Origin fitted plot for consecutive reaction of first order for concentration/time profile of salicylic acid, ■ experimental data, — fit function, experimental data for, reaction conditions: catalyst: 3Au/C, T=50°C, p=1bar, $c_{\text{salicyl alcohol}}=0.04$ M, NaOH: salicyl alcohol 2:1, rpm=1000, •salicylic acid.

Selective oxidation of salicyl aldehyde:

$$\text{Equation: } y = ((0.04) * \exp(-P1 * x))$$

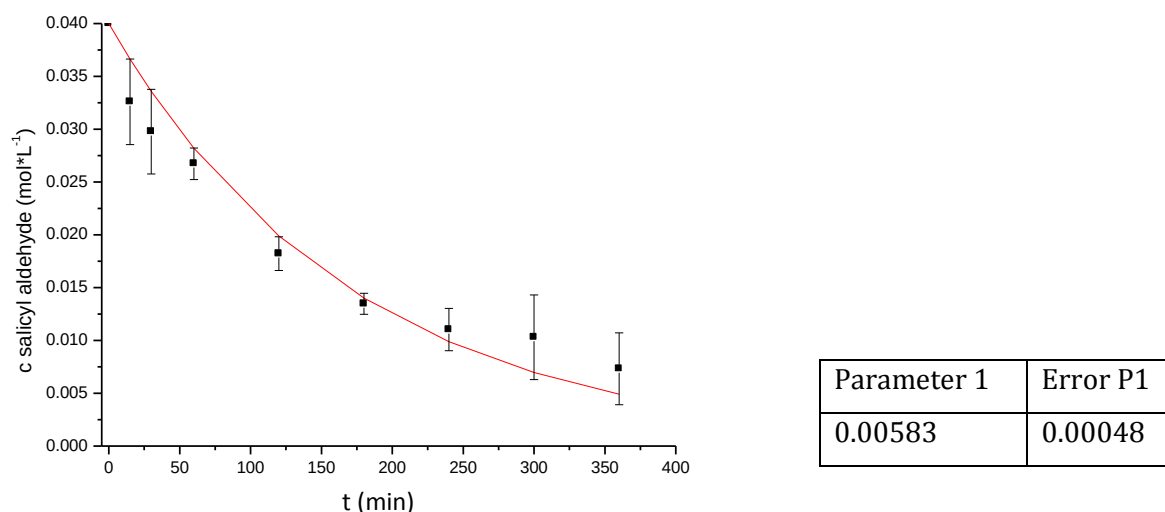


Figure 11-18: Origin fitted plot for consecutive reaction of first order for concentration/time profile of salicyl aldehyde ■ experimental data, — fit function, experimental data for, reaction conditions: catalyst: 1Au/C, T=50°C, p=1bar, $c_{\text{salicyl alcohol}}=0.04$ M, NaOH: salicyl alcohol 2:1, rpm=1000, •salicyl aldehyde

Influence of product addition

Selective oxidation of salicyl alcohol + c sal.acid added ($0.0112 \text{ mol} \cdot \text{L}^{-1}$)

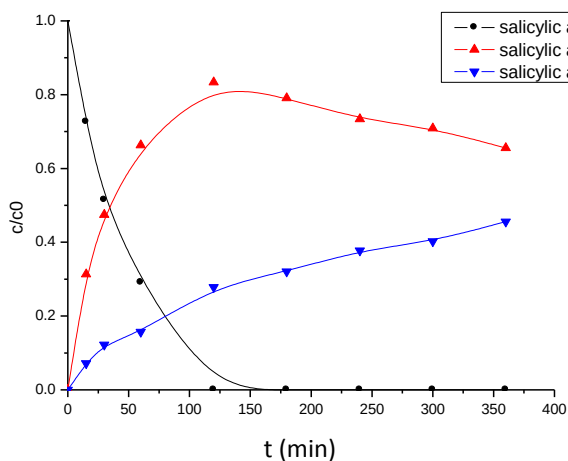


Figure 11-19: Concentration/ time profile for the selective oxidation of salicyl alcohol + product addition Reaction conditions: catalyst 1Au/C, $T=50^{\circ}\text{C}$, $p=1\text{bar}$, $c_{\text{salicyl alcohol}}=0.04 \text{ M}$, NaOH: salicyl alcohol 2:1, rpm=1000, • salicyl alcohol, ▲ salicyl aldehyde, ▼ salicylic acid.

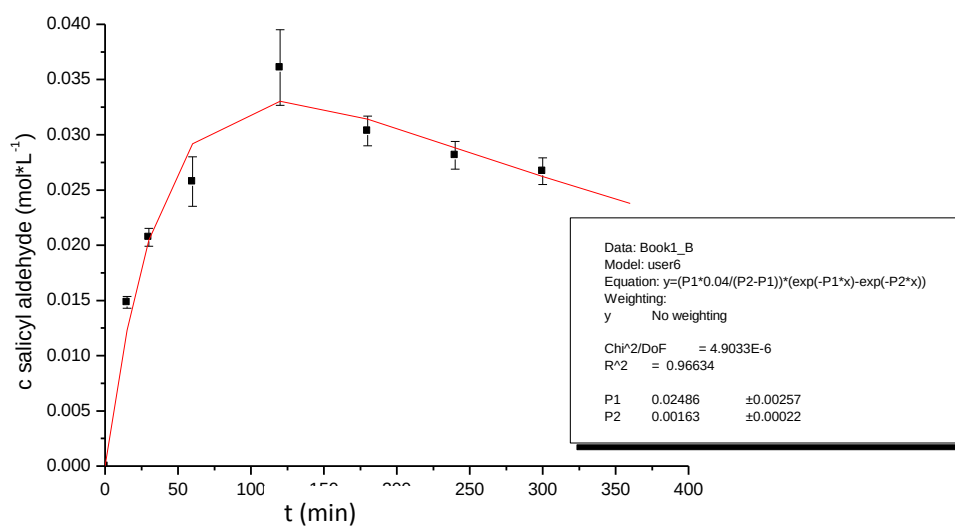


Figure 11-20: Origin fitted plot for consecutive reaction of first order for concentration/time profile of salicyl aldehyde, ■ experimental data, — fit function, experimental data for, reaction conditions: catalyst 1.5Au/C, $T=50^{\circ}\text{C}$, $p=1\text{bar}$, $c_{\text{salicyl alcohol}}=0.04 \text{ M}$, NaOH: salicyl alcohol 2:1, rpm=1000, • salicyl aldehyde.

Selective oxidation of salicyl alcohol + c sal.acid added ($0.0245 \text{ mol} \cdot \text{L}^{-1}$)

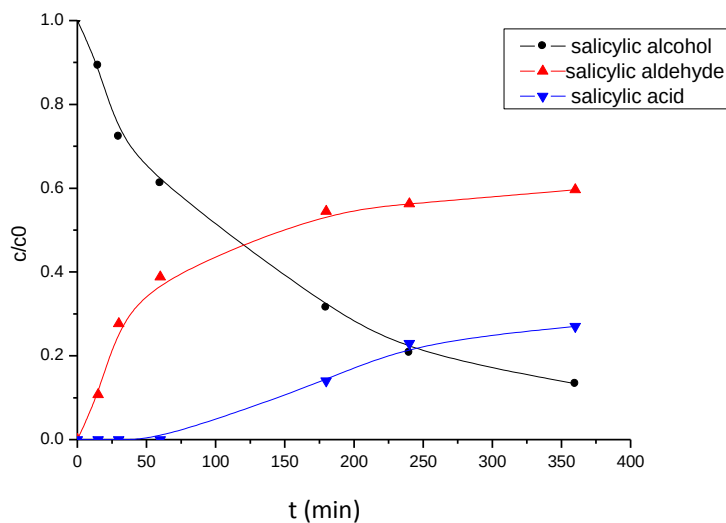


Figure 11-21: Concentration/ time profile for the selective oxidation of salicyl alcohol+product addition, reaction conditions: catalyst: 1.5Au/C, $T=50^{\circ}\text{C}$, $p=1\text{bar}$, $c_{\text{salicyl alcohol}}=0.04 \text{ M}$, NaOH: salicyl alcohol 2:1, rpm=1000, • salicyl alcohol, ▲ salicyl aldehyde, ▼ salicylic acid.

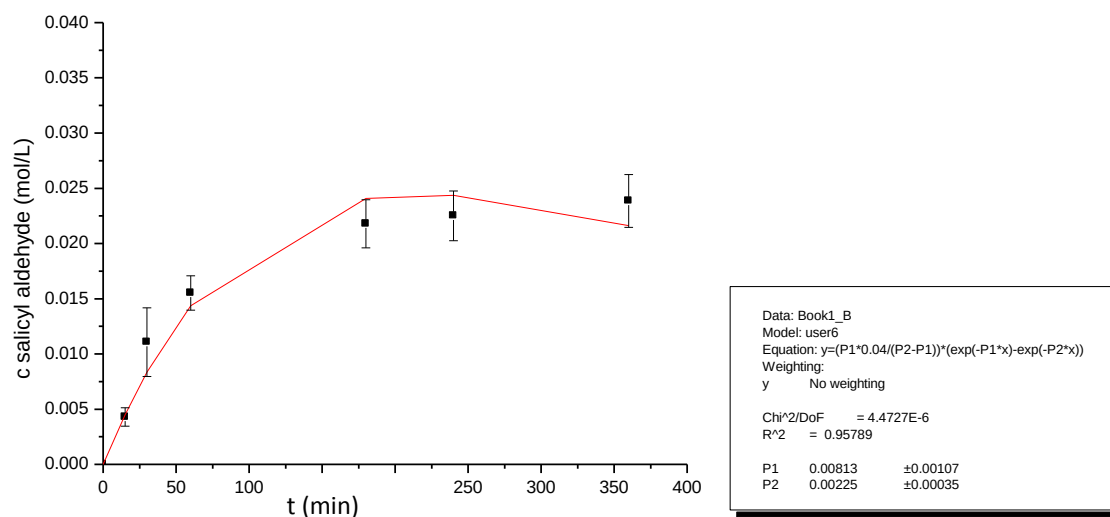


Figure 11-22: Origin fitted plot for consecutive reaction of first order for concentration/time profile of salicyl aldehyde, ■ experimental data, — fit function, experimental data for reaction conditions: catalyst 1.5Au/C, $T=50^{\circ}\text{C}$, $p=1\text{bar}$, $c_{\text{salicyl alcohol}}=0.04 \text{ M}$, NaOH: salicyl alcohol 2:1, rpm=1000, •salicylic acid.

Langmuir-Hinshelwood equation for influence of salicylic acid product addition:

$r =$	$\frac{k \cdot p_{O_2} \cdot c_{\text{reactant}}}{(1 + K_{\text{acid}} \cdot c_{\text{acid}})}$
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Table 11-4: Reaction data as parameters for Langmuir-Hinshelwood rate equation.

c(sal.alcohol) [mol*L ⁻¹]	c(sal.alcohol)/m catalyst [mol/(L*g)]	initial rate r for salicylic alcohol *10 ⁻⁴ [mol/L*L*min]	initial concentration c(sal.acid) [mol/L]	initial conc.(sal.acid)/mass of catalyst [mol/(L*g)]
0.04	0.2	10.85	0	0
0.04	0.2	4.35	0.0114	0.057
0.04	0.2	7.63	0.0057	0.0285
0.02	0.1	5.89	0.0114	0.057
0.06	0.3	5.99	0.0114	0.057

Table 11-5: Results for parameters b1 = k*pO₂ and b2=K_{acid}.

b1	b2 K _{acid}	*p value (t-test) b1	*p value (t-test) b2	*conf. interval b1	*conf. interval (95%) b2	RSS *10 ⁻⁶	VAR *10 ⁻⁷	F- test
0.13	109.8	0.0151	0.167	0.0870	192.49	3.69*	7.39	0.136

Reaction Calorimetry

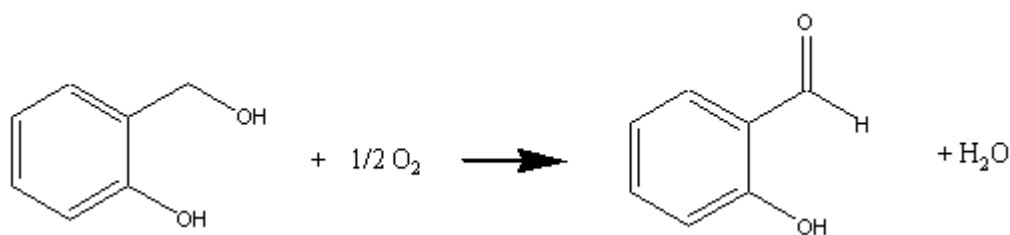


Table 11-6: Thermochemical data for reactants and products for selective oxidation of salicyl alcohol.

ΔH_f° salicyl alcohol [kJ* mol^{-1}]	ΔH_f° salicyl aldehyde [kJ* mol^{-1}]	$\Delta H_f^\circ \text{H}_2\text{O}$ [kJ* mol^{-1}]	ΔH_R° [kJ* mol^{-1}]
-390 [178]	-296 [179]	-285.83	-191
-377.7 [180]	-283.2 [181]	-285.83	-191

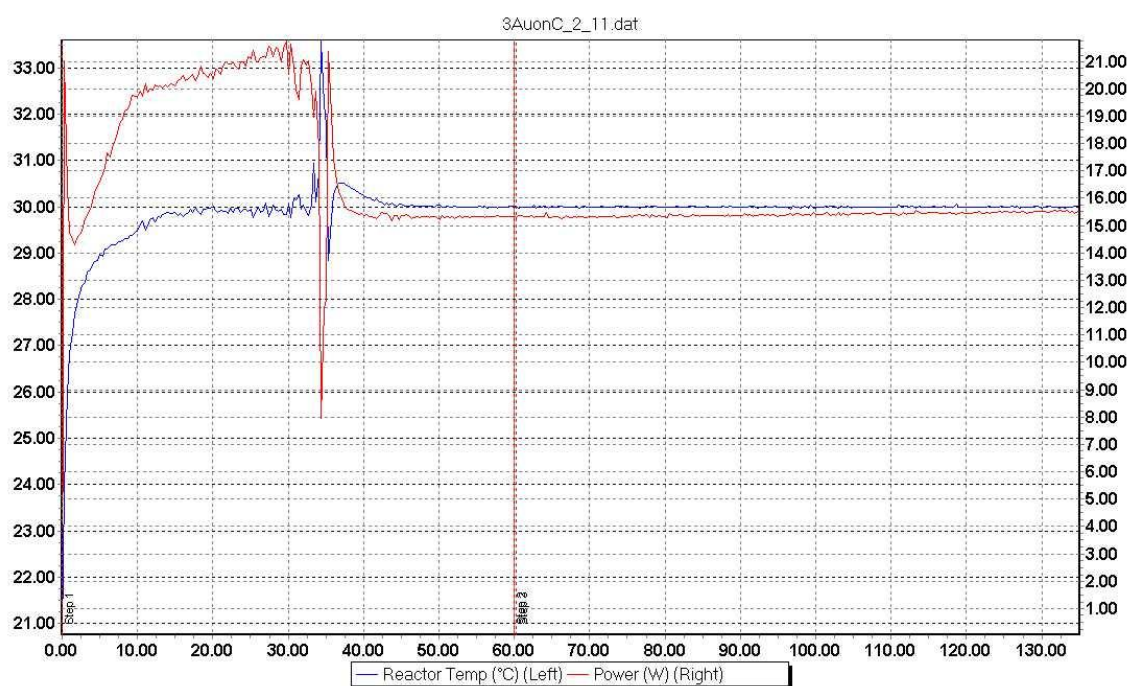


Figure 11-23: HEL Calorimeter reaction plot, injection of reactant after 30 minutes.

Catalytic effects

Table 11-7: Literature data on achieved TOF numbers for selective oxidation of salicyl alcohol [137].

catalyst	wt% Au	n Au [mol] *10 ⁻⁵	n product [mol]*10 ⁻⁵	TOF [h ⁻¹]
Au/Fe ₂ O ₃	0.46	2.53	13.75	5.43
Au/Fe ₂ O ₃	1.26	1.92	16.5	8.59
AuZn	1.7	4.32	38.5	8.92

ICP analysis for catalyst 1.5Au/C: measurement of filtered Au sol solution after deposition.

Table 11-8: ICP analysis of precursor solution after catalyst preparation 1.5Au/C.

Analysis	m Au [mg*L ⁻¹]	m Au in solution [mg]	m Au total catalyst [theor.] [mg]	m Au total catalyst exp. [mg]	m Au theor/exp
1	0.033	0.0165	45	44.98	0.99
2	0.034	0.017	45	44.98	0.99

Influence of preparation method

1.5Au/C via impregnation

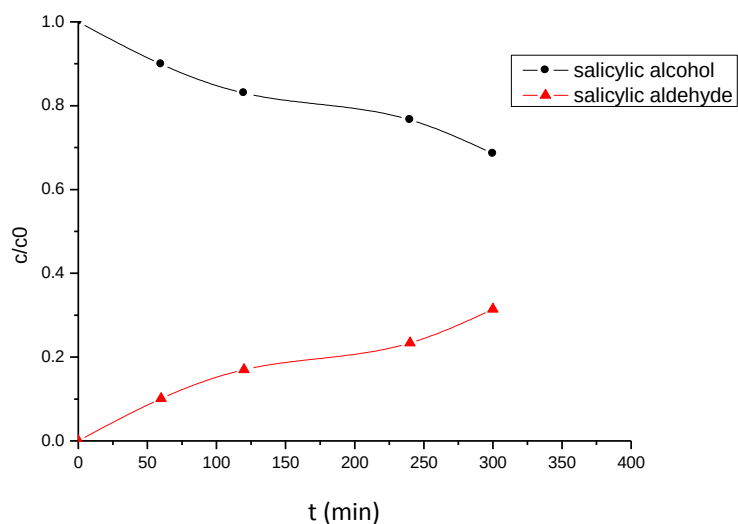


Figure 11-24: Concentration/ time profile for the selective oxidation of salicyl alcohol. Reaction conditions: catalyst 1.5Au/C, T=50°C, p=1bar, $c_{\text{salicyl alcohol}}=0.04$ M, NaOH: salicyl alcohol 2:1, rpm=1000, • salicyl alcohol, ▲ salicyl aldehyde.

Influence of gold loading

0.75Au/C

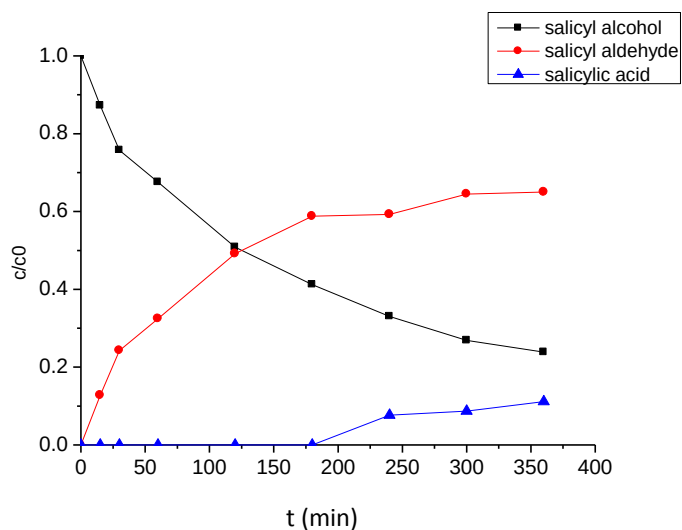


Figure 11-25: Concentration/ time profile for the selective oxidation of salicyl alcohol. Reaction conditions: catalyst 0.75Au/C, T=50°C, p=1bar, $c_{\text{salicyl alcohol}}=0.04$ M, NaOH: salicyl alcohol 2:1, rpm=1000 • salicyl alcohol, ▲ salicyl aldehyde, ▼ salicylic acid.

1Au/C

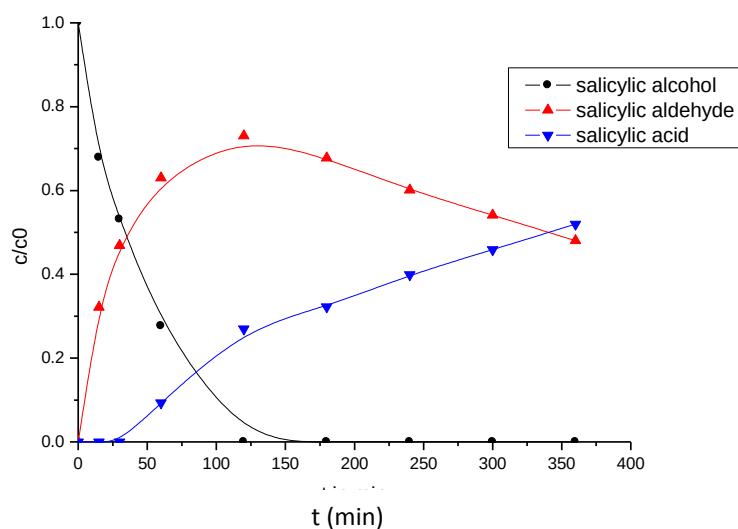


Figure 11-26: Concentration/ time profile for the selective oxidation of salicyl alcohol. Reaction conditions: catalyst 1Au/C, T=50°C, p=1bar, $c_{\text{salicyl alcohol}}=0.04$ M, NaOH: salicyl alcohol 2:1, rpm=1000, • salicyl alcohol, ▲ salicyl aldehyde, ▼ salicyl acid.

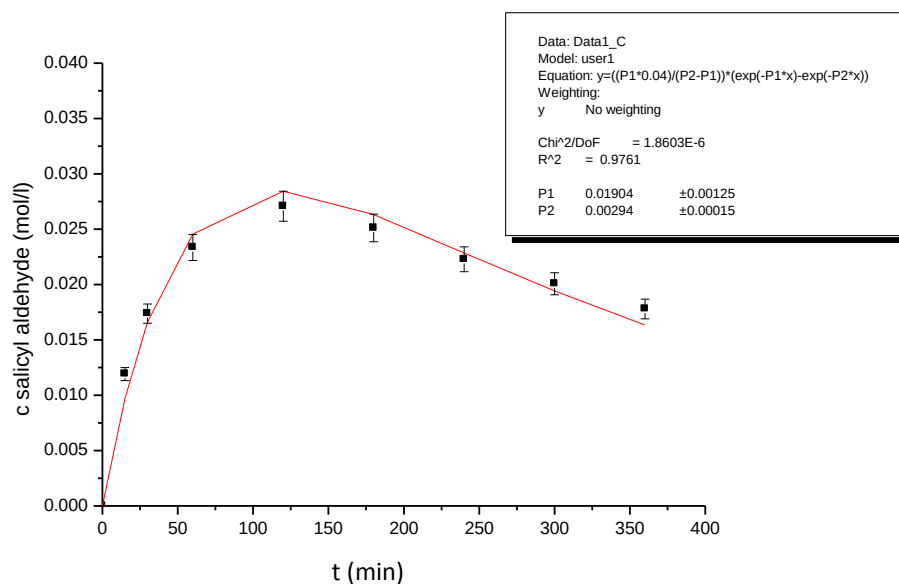


Figure 11-27: Origin fitted plot for consecutive reaction of first order for concentration/time profile of salicyl aldehyde, ■ experimental data, — fit function, experimental data for, reaction conditions: catalyst 1Au/C, T=50°C, p=1bar, $c_{\text{salicyl alcohol}}=0.04$ M, NaOH: salicyl alcohol 2:1, rpm=1000, • salicyl aldehyde.

3Au/C

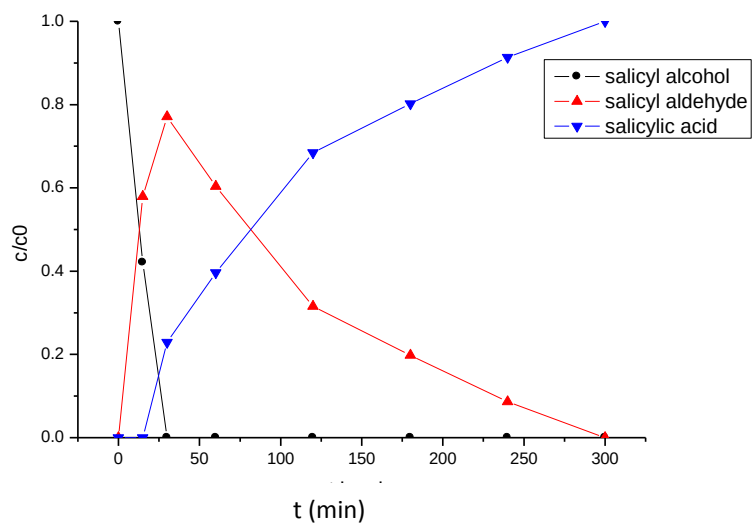


Figure 11-28: Concentration/ time profile for the selective oxidation of salicyl alcohol. Reaction conditions: catalyst 3Au/C, T=50°C, p=1bar, $c_{\text{salicyl alcohol}}=0.04$ M, NaOH: salicyl alcohol 2:1, rpm=1000, • salicyl alcohol, ▲ salicyl aldehyde, ▼ salicylic acid.

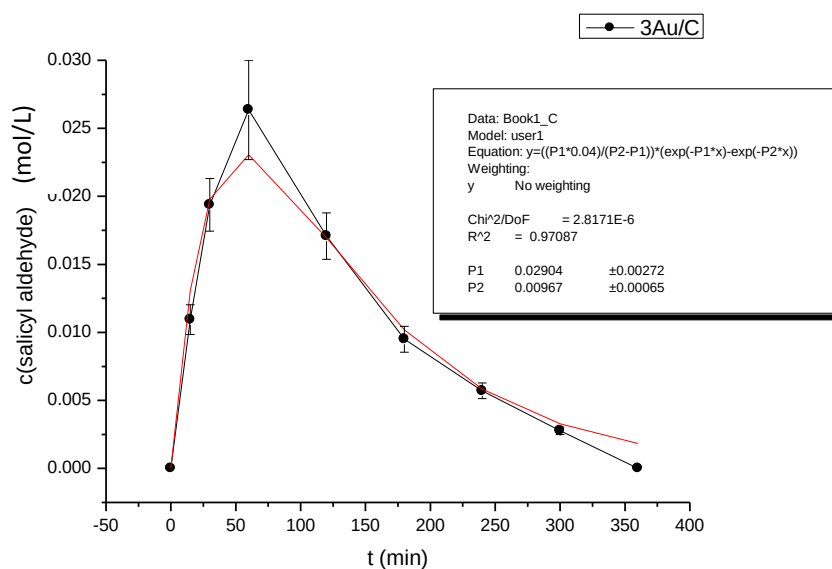


Figure 11-29: Origin fitted plot for consecutive reaction of first order for concentration/time profile of salicyl aldehyde, ■ experimental data, — fit function, experimental data for, reaction conditions: catalyst 3Au/C, T=50°C, p=1bar, $c_{\text{salicyl alcohol}}=0.04$ M, NaOH: salicyl alcohol 2:1, rpm=1000, • salicyl aldehyde.

1.5Au/C treated at 150°C

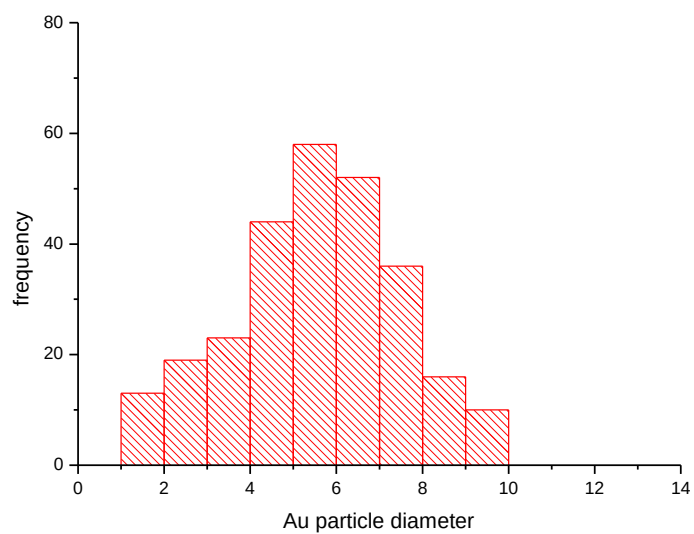


Figure 11-30: TEM histogram of 1.5Au/C treated at 150°C.

3Au/C treated at 150°C

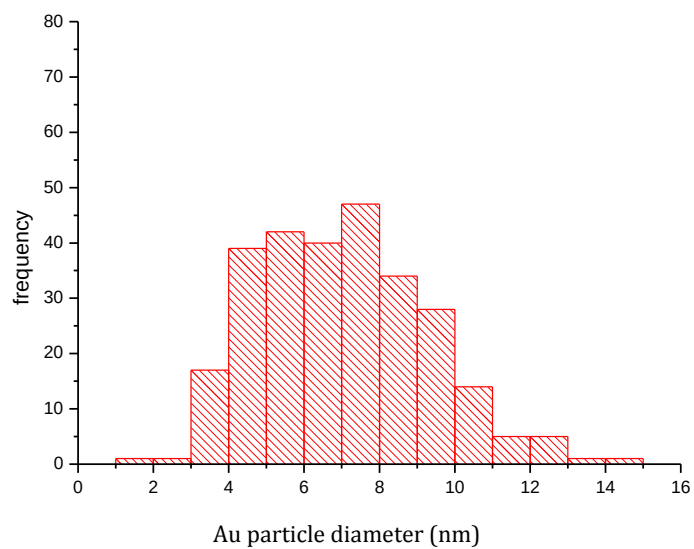


Figure 11-31: TEM histogram of 3Au/C catalyst treated at 150°C.

Au on oxide supports

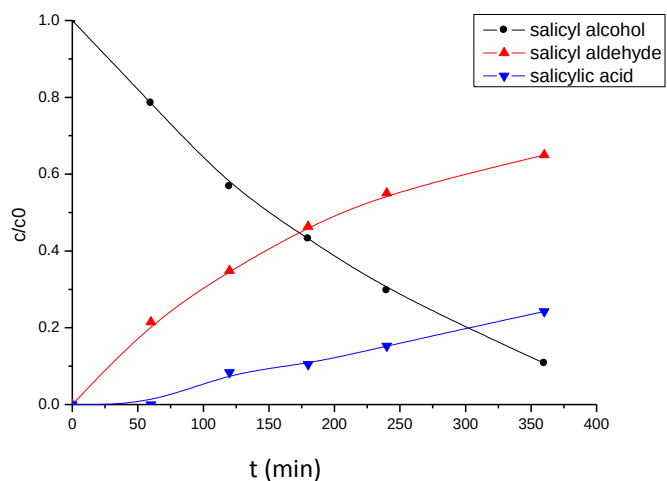
1Au/CeO₂

Figure 11-32: Concentration/ time profile for the selective oxidation of salicyl alcohol. Reaction conditions: catalyst 1Au/CeO₂, T=50°C, p=1bar, $c_{\text{salicyl alcohol}}=0.04$ M, NaOH: salicyl alcohol 2:1, rpm=1000, • salicyl alcohol, ▲ salicyl aldehyde, ▼ salicylic acid.

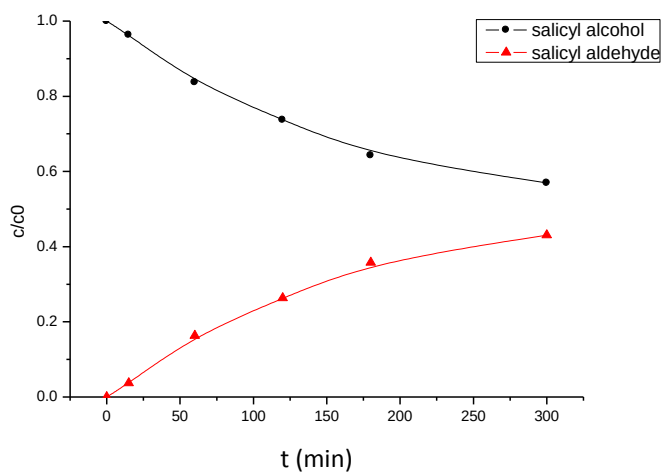
1Au/TiO₂

Figure 11-33: Concentration/ time profile for the selective oxidation of salicyl alcohol. Reaction conditions: catalyst 1Au/TiO₂, T=50°C, p=1bar, $c_{\text{salicyl alcohol}}=0.04$ M, NaOH: salicyl alcohol 2:1, rpm=1000, • salicyl alcohol, ▲ salicyl aldehyde.

Recycle tests

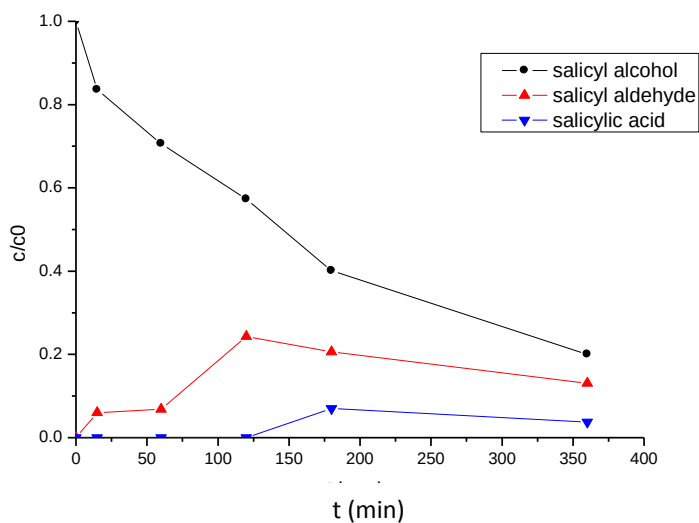


Figure 11-34: Concentration/ time profile for recycle test after second run for the selective oxidation of salicyl alcohol. Reaction conditions: catalyst 1.5Au/C, $T=50^{\circ}\text{C}$, $p=1\text{bar}$, $c_{\text{salicyl alcohol}}=0.04\text{ M}$, NaOH: salicyl alcohol 2:1, rpm=1000, • salicyl alcohol, ▲ salicyl aldehyde, ▼ salicylic acid.

B Moving Towards Base Free Catalysis

Au on oxides

1.5Au/MgO

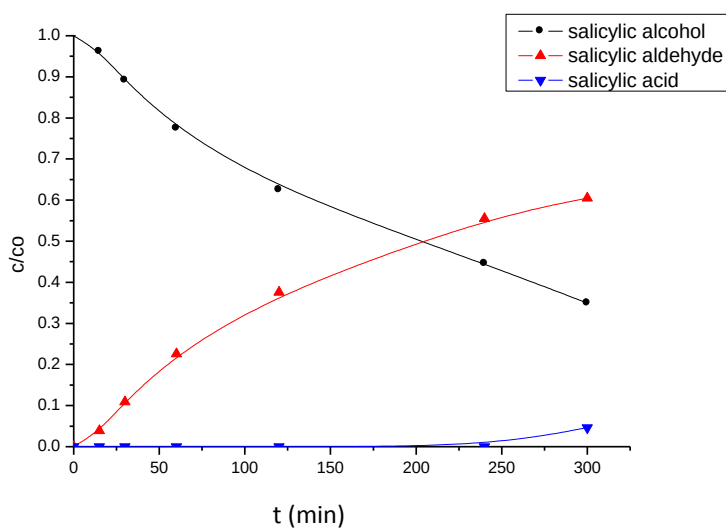


Figure 11-35: Concentration/ time profile for the selective oxidation of salicyl alcohol. Reaction conditions: catalyst: 1.5Au/MgO, $T=50^{\circ}\text{C}$, $p=1\text{bar}$, $c_{\text{salicyl alcohol}}=0.04\text{ M}$, NaOH: salicyl alcohol 0:1, rpm=1000, • salicyl alcohol, ▲ salicyl aldehyde, ▼ salicylic acid.

1.5Au/CaO

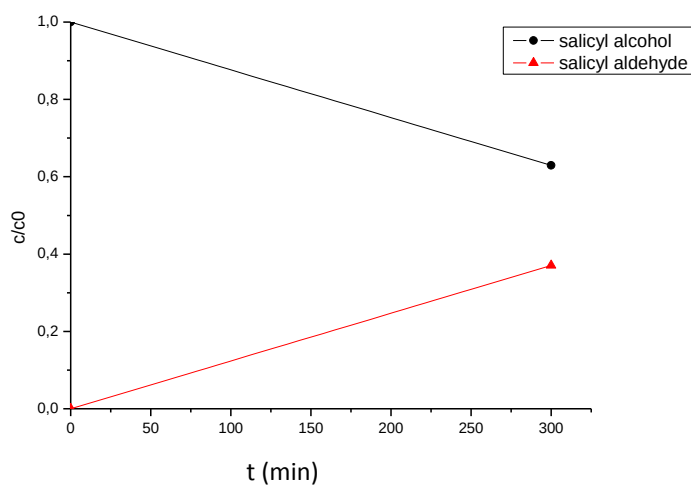


Figure 11-36: Concentration/ time profile for the selective oxidation of salicyl alcohol. Reaction conditions: catalyst: 1.5Au/CaO, T=50°C, p=1bar, $c_{\text{salicyl alcohol}}=0.04$ M, NaOH: salicyl alcohol 0:1, rpm=1000, • salicyl alcohol, ▲ salicyl aldehyde, ▼ salicylic acid.

Au on impregnated oxides

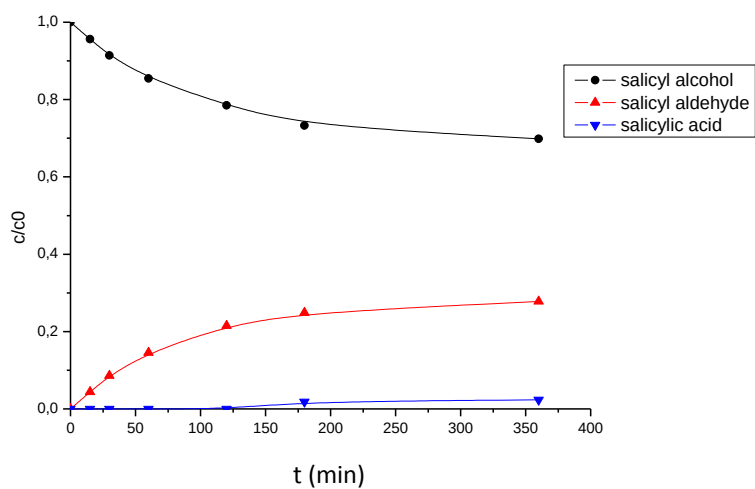
1.5Au/0.16MgO-CeO₂

Figure 11-37: Concentration/ time profile for the selective oxidation of salicyl alcohol. Reaction conditions: catalyst: 1.5Au/0.16MgO-CeO₂, T=50°C, p=1bar, $c_{\text{salicyl alcohol}}=0.04$ M, NaOH: salicyl alcohol 0:1, rpm=1000, • salicyl alcohol, ▲ salicyl aldehyde, ▼ salicylic acid.

1.5Au/0.16MgO-Al₂O₃

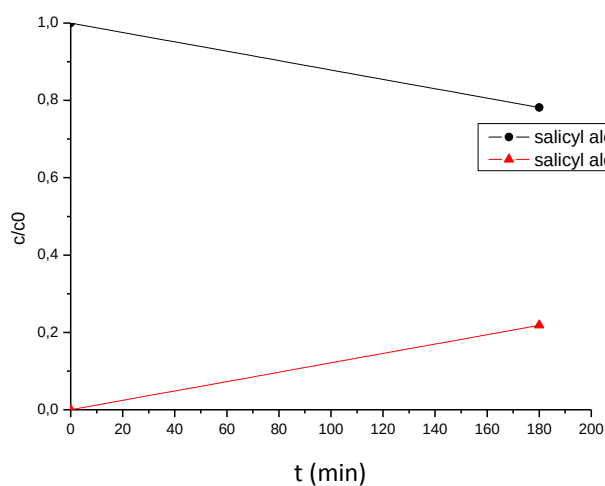


Figure 11-38: Concentration/ time profile for the selective oxidation of salicyl alcohol. Reaction conditions: catalyst: 1.5Au/0.16MgO-Al₂O₃, T=50°C, p=1bar, $c_{\text{salicyl alcohol}}=0.04$ M, NaOH: salicyl alcohol 0:1, rpm=1000, ● salicyl alcohol, ▲ salicyl aldehyde.

1.5Au0.28CaO-CeO₂

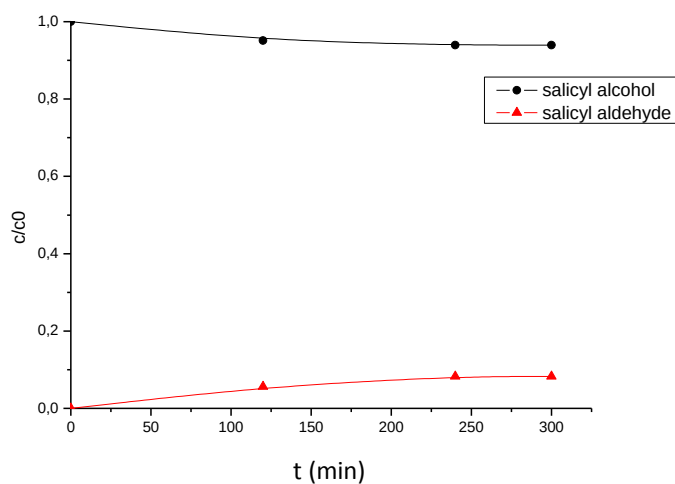


Figure 11-39: Concentration/ time profile for the selective oxidation of salicyl alcohol. Reaction conditions: catalyst: 1.5Au/0.28CaO-CeO₂, T=50°C, p=1bar, $c_{\text{salicyl alcohol}}=0.04$ M, NaOH: salicyl alcohol 0:1, rpm=1000, ● salicyl alcohol, ▲ salicyl aldehyde.

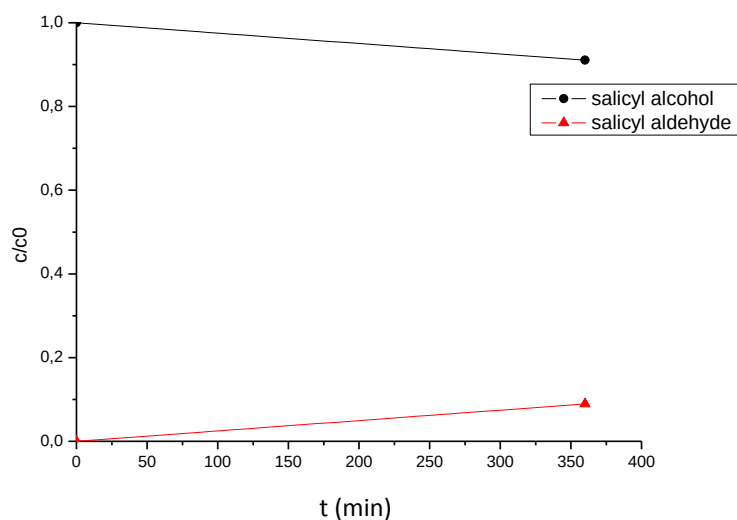
1.5Au/0.28CaO-TiO₂

Figure 11-40: Concentration/ time profile for the selective oxidation of salicyl alcohol. Reaction conditions: catalyst: 1.5Au/0.28CaO-TiO₂, T=50°C, p=1bar, $c_{\text{salicyl alcohol}}=0.04$ M, NaOH: salicyl alcohol 0:1, rpm=1000, ● salicyl alcohol, ▲ salicyl aldehyde.

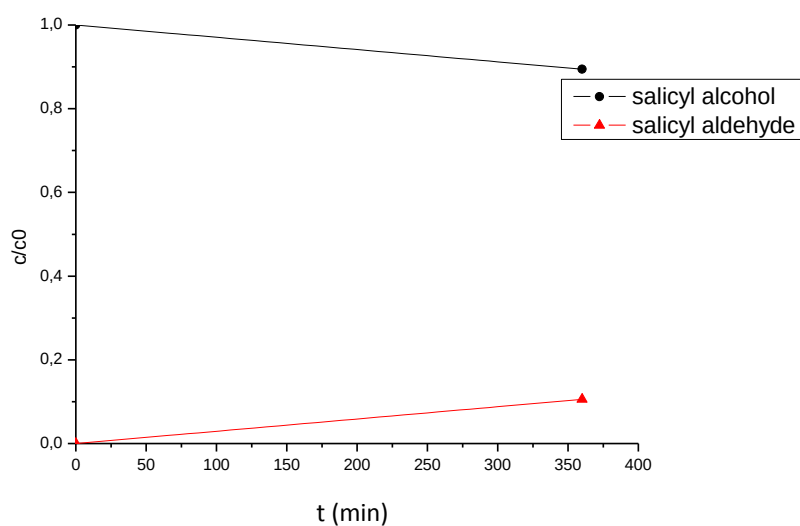
1.5Au/0.28CaO-Al₂O₃

Figure 11-41: Concentration/ time profile for the selective oxidation of salicyl alcohol. Reaction conditions: catalyst 1.5Au/0.28CaO-Al₂O₃, T=50°C, p=1bar, $c_{\text{salicyl alcohol}}=0.04$ M, NaOH: salicyl alcohol 0:1, ● salicyl alcohol, ▲ salicyl aldehyde.

Au on impregnated HT

1.5Au/0.28CaO-HT

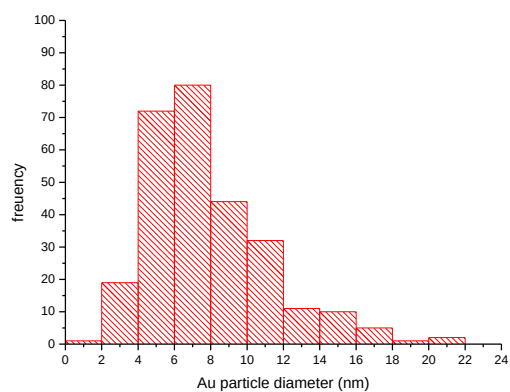


Figure 11-42: TEM histogram of 1.5Au/0.28CaO-HT.

1.5Au/0.28CaO-Al₂O₃

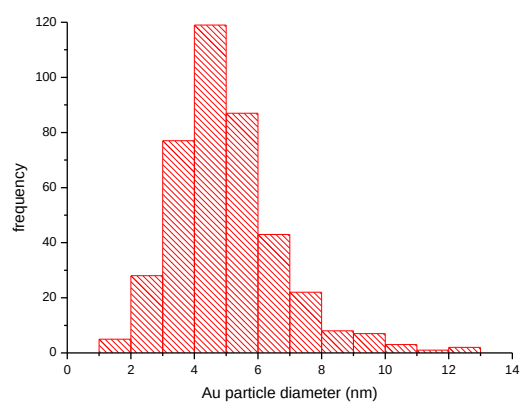
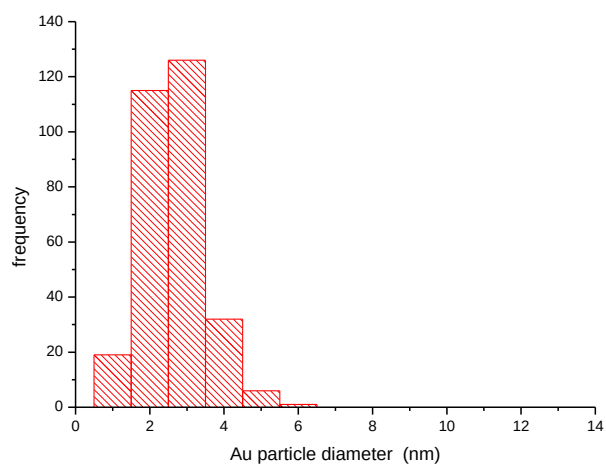
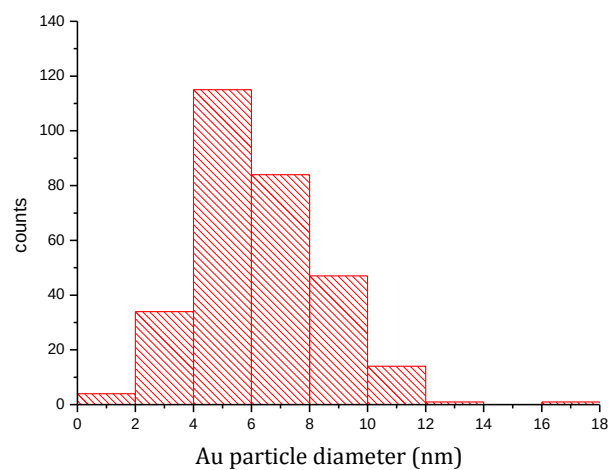


Figure 11-43: TEM histogram of 1.5Au/0.28CaO-Al₂O₃

1.5Au/0.28CaO-CeO₂**Figure 11-44: TEM histogram of 1.5Au/0.28CaO-CeO₂****1.5Au/0.16MgO-HT****Figure 11-45: TEM histogram of 1.5Au/0.16MgO-HT.**

1.5Au/0.16MgO-TiO₂

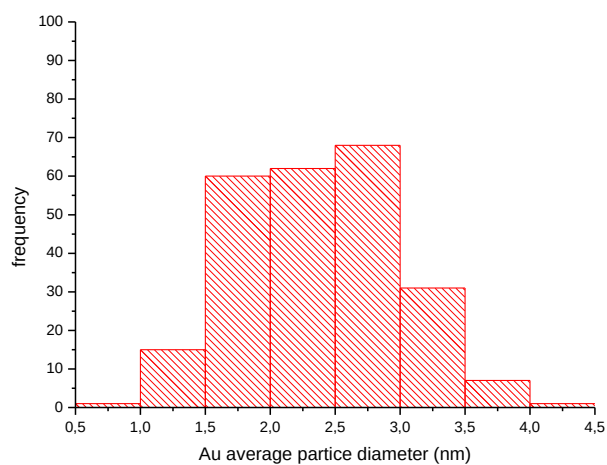


Figure 11-46: TEM histogram of 1.5Au/0.16MgO-TiO₂.

0.5Au/0.16MgO-HT

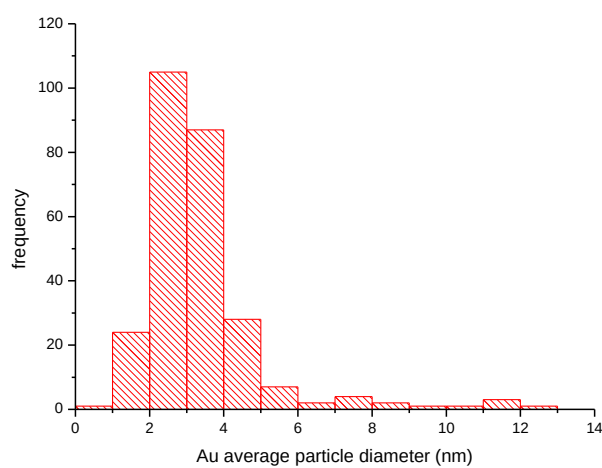


Figure 11-47: TEM histogram of 0.5Au/0.16MgO-HT.

0.1Au/0.16MgO-HT

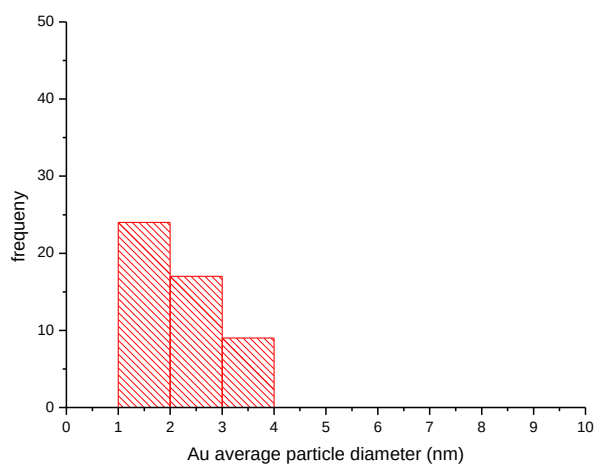
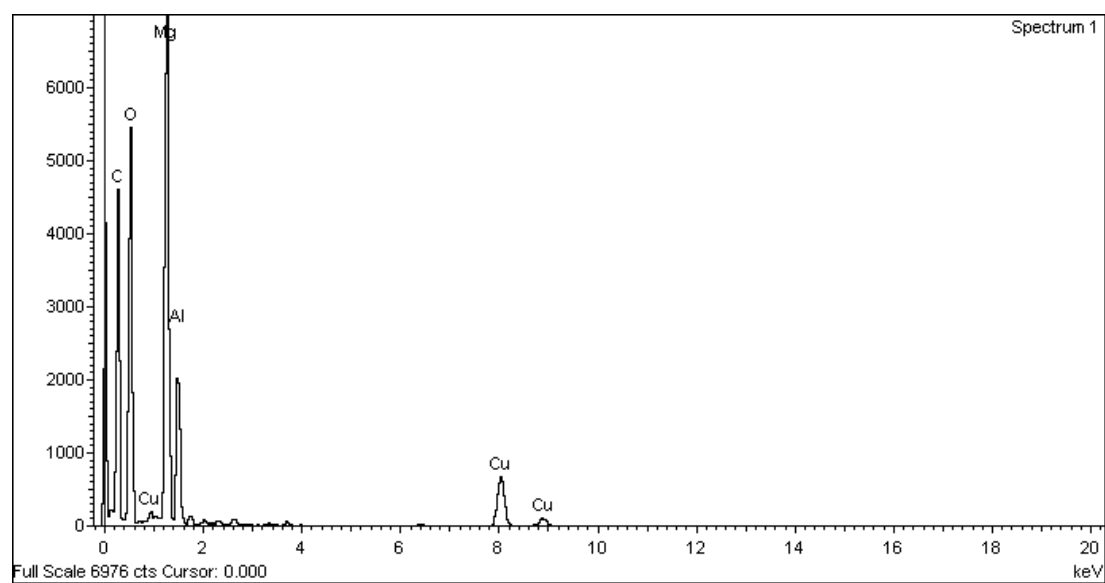


Figure 11-48: TEM histogram of 0.1Au/0.16MgO-HT.



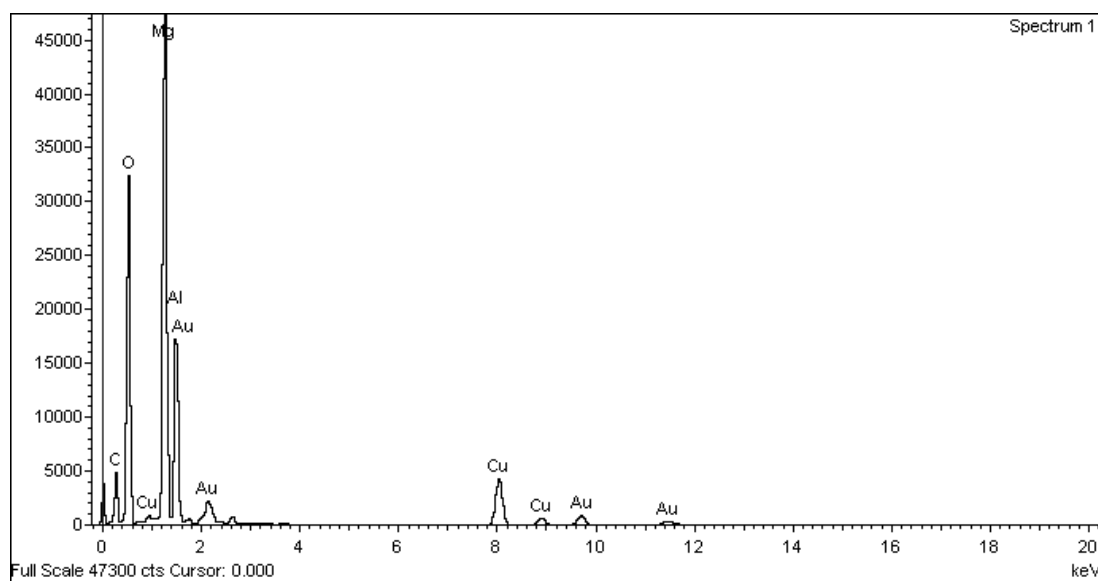


Figure 11-49 EDX of 1.5Au/0.16MgO-HT_400 area 1) without gold (upper) and area2) with gold.

1.5Au/0.28CaO-HT

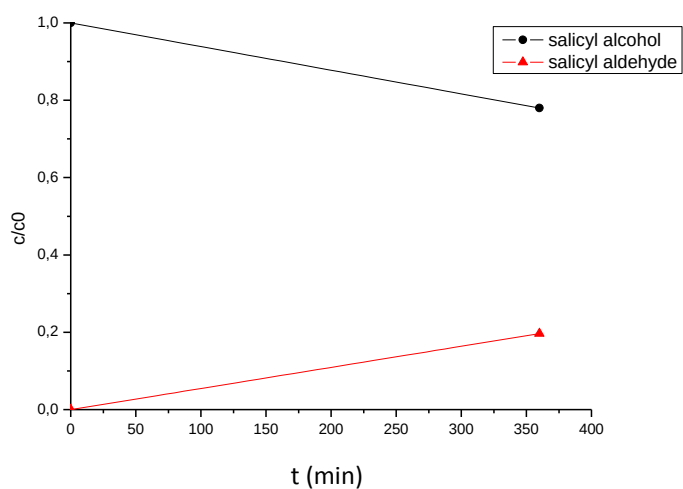


Figure 11-50: Concentration/ time profile for the selective oxidation of salicyl alcohol. Reaction conditions: catalyst 1.5Au/0.28CaO-HT, $T=50^{\circ}\text{C}$, $p=1\text{bar}$, $c_{\text{salicyl alcohol}}=0.04\text{ M}$, NaOH: salicyl alcohol 0:1, rpm=1000, • salicyl alcohol, ▲ salicyl aldehyde.

0.5Au/0.16-MgO-HT

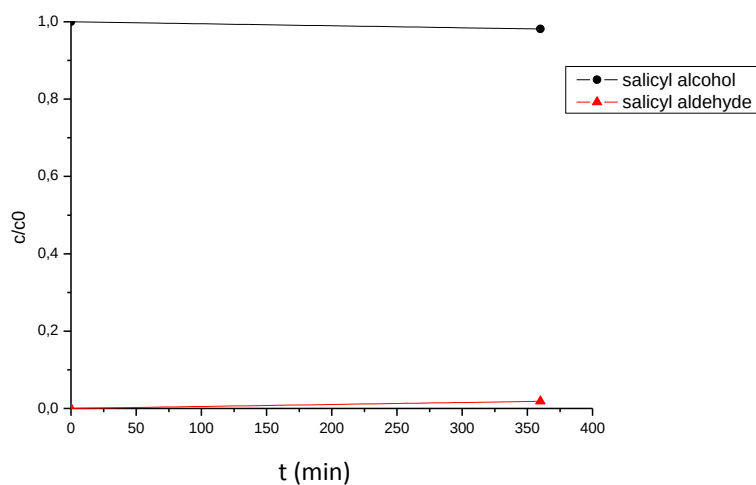


Figure 11-51: Concentration/ time profile for the selective oxidation of salicyl alcohol. Reaction conditions: catalyst 0.5Au/0.16MgO-HT, T=50°C, p=1bar, $c_{\text{salicyl alcohol}}=0.04$ M, NaOH: salicyl alcohol 0:1, rpm=1000, ● salicyl alcohol, ▲ salicyl aldehyde.

1.5Au/0.08MgO-HT

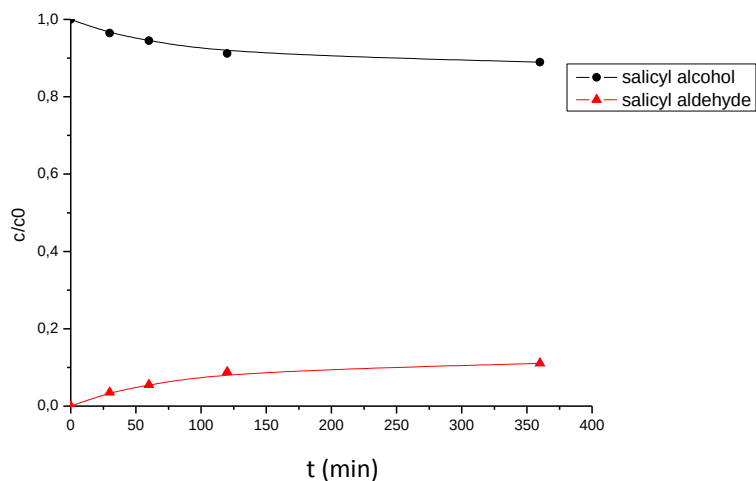


Figure 11-52: Concentration/ time profile for the selective oxidation of salicyl alcohol. Reaction conditions: catalyst: 1.5Au/0.08MgO-HT, T=50°C, p=1bar, $c_{\text{salicyl alcohol}}=0.04$ M, NaOH: salicyl alcohol 0:1, rpm=1000, ● salicyl alcohol, ▲ salicylic aldehyde.

1.5Au/0.04MgO-HT

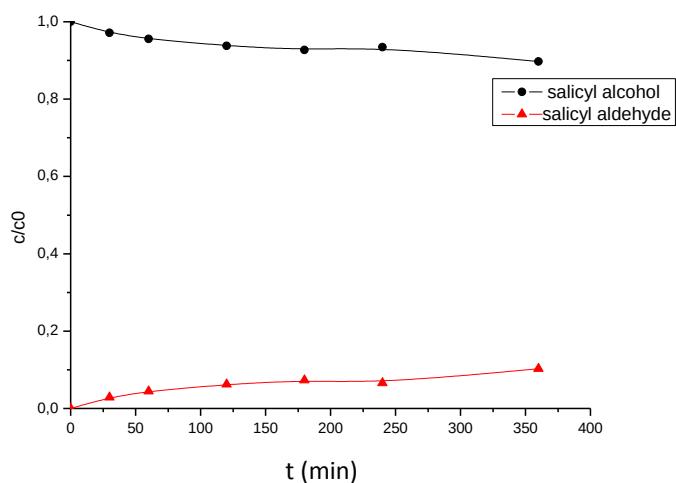


Figure 11-53: Concentration/ time profile for the selective oxidation of salicyl alcohol. Reaction conditions: catalyst 1.5Au/0.04MgO-HT, T=50°C, p=1bar, $c_{\text{salicyl alcohol}}=0.04$ M, NaOH: salicyl alcohol 0:1, rpm=1000, • salicyl alcohol, ▲ salicyl aldehyde.

C Bimetallic catalysis for selective oxidation of salicyl alcohol

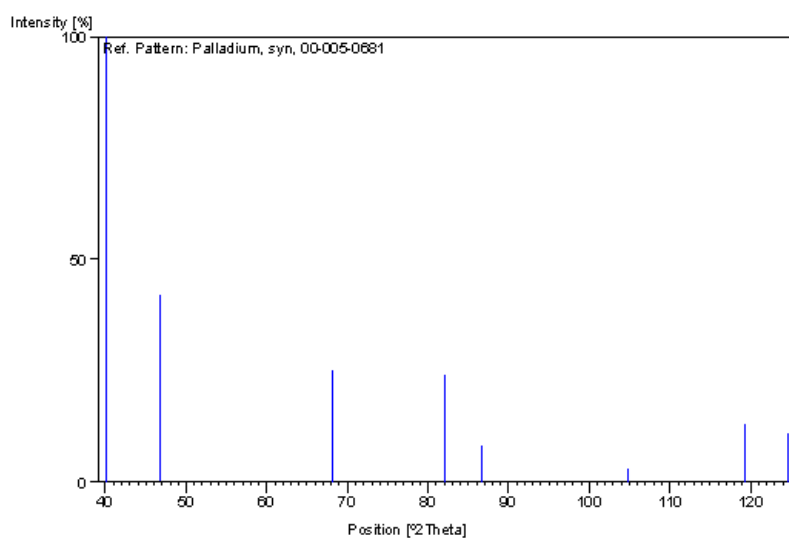


Figure 11-54: XRD diffraction pattern for AuPd (1:1) (ID 01-072-5376).

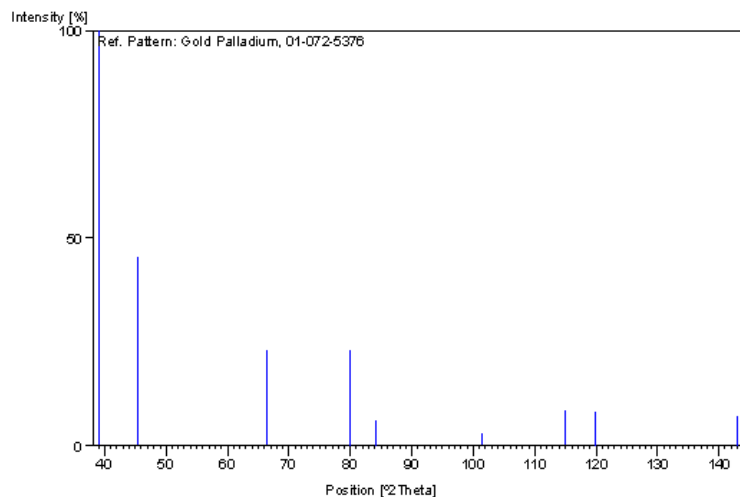


Figure 11-55: XRD diffraction pattern of palladium (ID 00-005-0681).

Catalytic performance

0.75Au0.75Pd/C

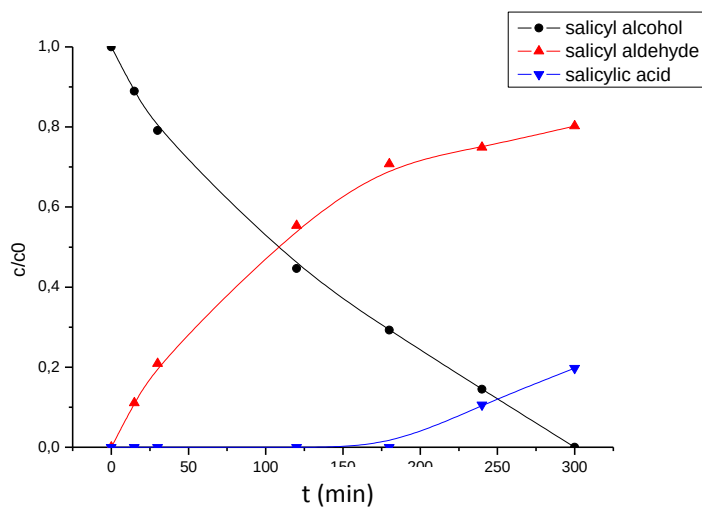


Figure 11-56: Concentration/ time profile for the selective oxidation of salicyl alcohol. Reaction conditions: catalyst: 0.75Au0.75Pd/C, $T=50^{\circ}\text{C}$, $p=1\text{bar}$, $c_{\text{salicyl alcohol}}=0.04\text{ M}$, NaOH: salicyl alcohol 2:1, rpm=1000, ● salicyl alcohol, ▲ salicyl aldehyde, ▼ salicylic acid.

1.5Au1.5Pd/C

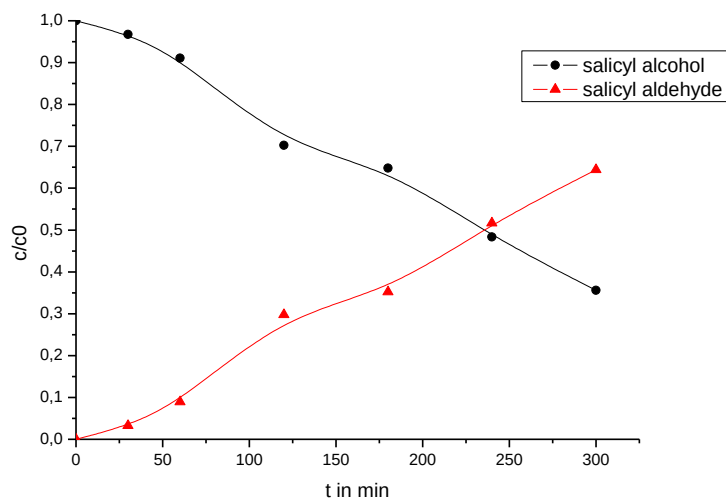


Figure 11-57: Concentration/ time profile for the selective oxidation of salicyl alcohol. Reaction conditions: catalyst: 1.5Au1.5Pd/C, T=50°C, p=1bar, $c_{\text{salicyl alcohol}}=0.04$ M, NaOH: salicyl alcohol 2:1, rpm=1000, • salicyl alcohol, ▲ salicyl aldehyde.

1.5Au0.75Pd/C,

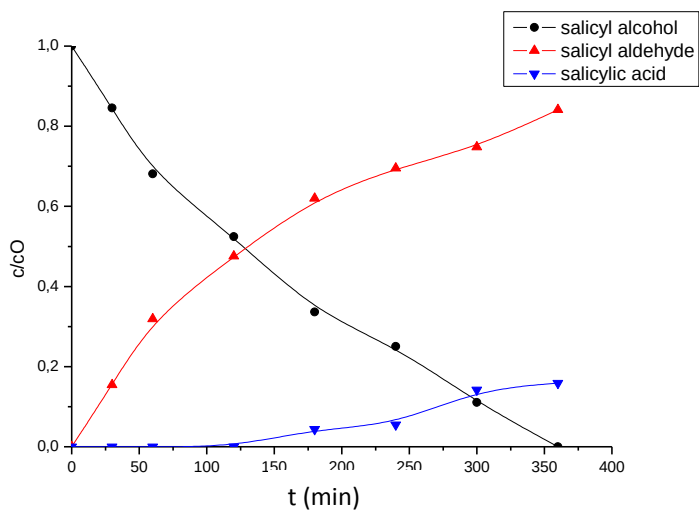


Figure 11-58: Concentration/ time profile for the selective oxidation of salicyl alcohol. Reaction conditions: catalyst 1.5Au0.75Pd/C, T=50°C, p=1bar, $c_{\text{salicyl alcohol}}=0.04$ M, NaOH: salicyl alcohol 2:1, rpm=1000, • salicyl alcohol, ▲ salicyl aldehyde, ▼ salicylic acid.

0.75Au1.5Pd/C

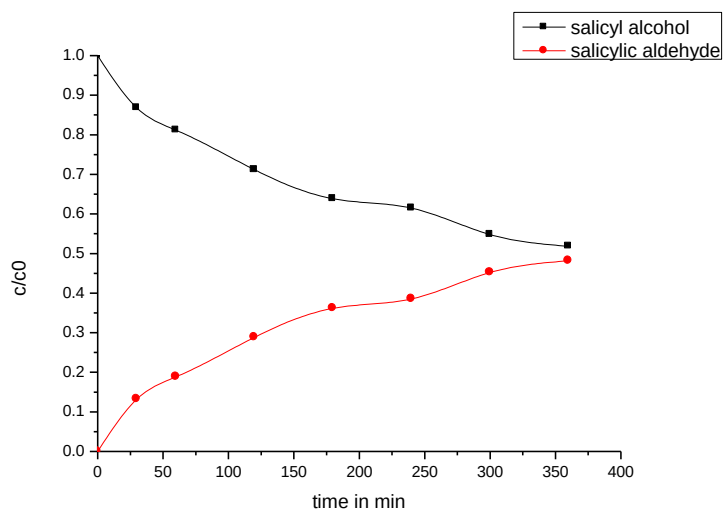


Figure 11-59: Concentration/ time profile for the selective oxidation of salicyl alcohol. Reaction conditions: catalyst 0.75Au1.5Pd/C, T=50°C, p=1bar, $c_{\text{salicyl alcohol}}=0.04$ M, NaOH: salicyl alcohol 2:1, rpm=1000, ● salicyl alcohol, ▲ salicylic aldehyde.

1.5Pd/C

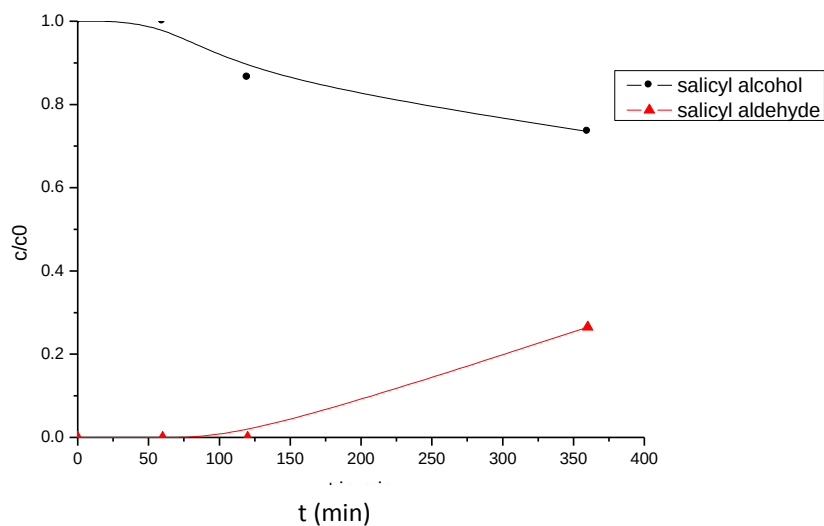


Figure 11-60: Concentration/ time profile for the selective oxidation of salicyl alcohol. Reaction conditions: catalyst 1.5Pd/C, T=50°C, p=1bar, $c_{\text{salicyl alcohol}}=0.04$ M, NaOH: salicyl alcohol 2:1, rpm=1000, ● salicyl alcohol, ▲ salicylic aldehyde.

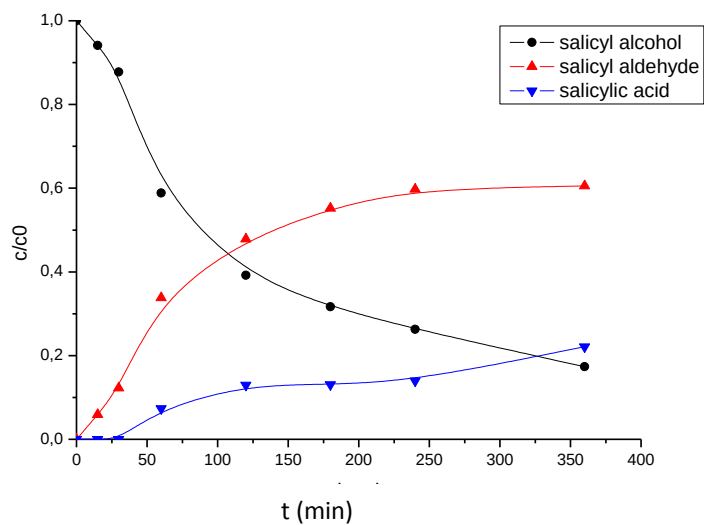
1.5Au0.15Pd/CeO₂

Figure 11-61: Concentration/ time profile for the selective oxidation of salicyl alcohol. Reaction conditions: catalyst 1.5Au0.15Pd/CeO₂, T=50°C, p=1bar, $c_{\text{salicyl alcohol}}=0.04$ M, NaOH: salicyl alcohol 2:1, rpm=1000, • salicyl alcohol, ▲ salicyl aldehyde, ▼ salicylic acid.

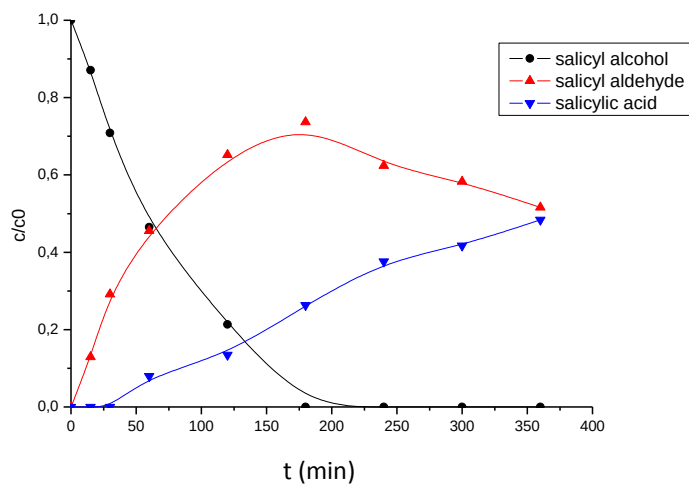
1.5Au0.15Pd/TiO₂

Figure 11-62: Concentration/ time profile for the selective oxidation of salicyl alcohol. Reaction conditions: catalyst 1.5Au0.15Pd/TiO₂, T=50°C, p=1bar, $c_{\text{salicyl alcohol}}=0.04$ M, NaOH: salicyl alcohol 2:1, rpm=1000, • salicyl alcohol, ▲ salicyl aldehyde, ▼ salicylic acid.

Selective oxidation of diols & triols

Selective oxidation of 1,2- propanediol

1.5Au1.5Pd/CeO₂

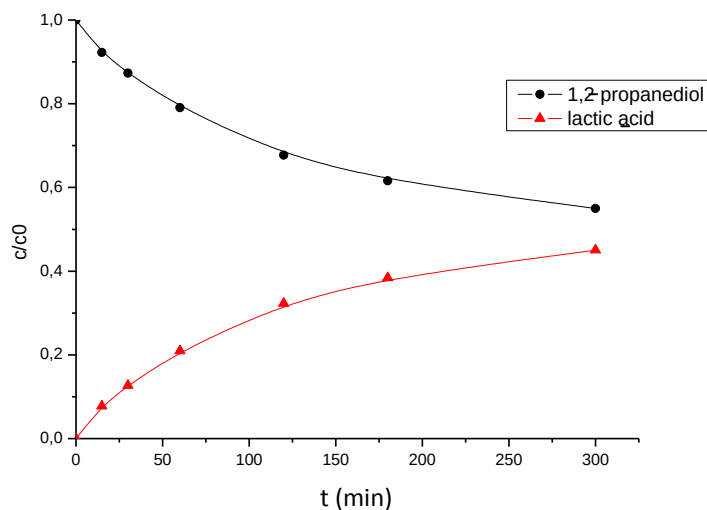


Figure 11-63: Concentration/ time profile for the selective oxidation of 1,2-propanediol. Reaction conditions: catalyst 1.5Au1.5Pd/CeO₂, T=50°C, p=1bar, 1,2-propanediol/Au=1000, NaOH: 1,2-propanediol 1:1, rpm=1000, • 1,2- propanediol, ▲ lactic acid.

1.5Au1.5Pd/TiO₂

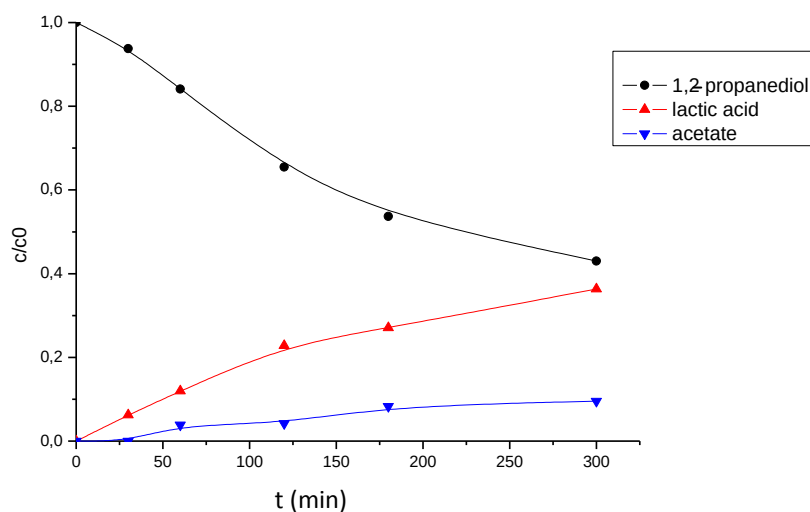


Figure 11-64: Concentration/ time profile for the selective oxidation of 1,2-propanediol. Reaction conditions: catalyst 1.5Au1.5Pd/CeO₂, T=50°C, p=1bar, 1,2-propanediol/Au=1000, NaOH: 1,2-propanediol 1:1, rpm=1000, • 1,2- propanediol, ▲ lactic acid, ▼ acetate.

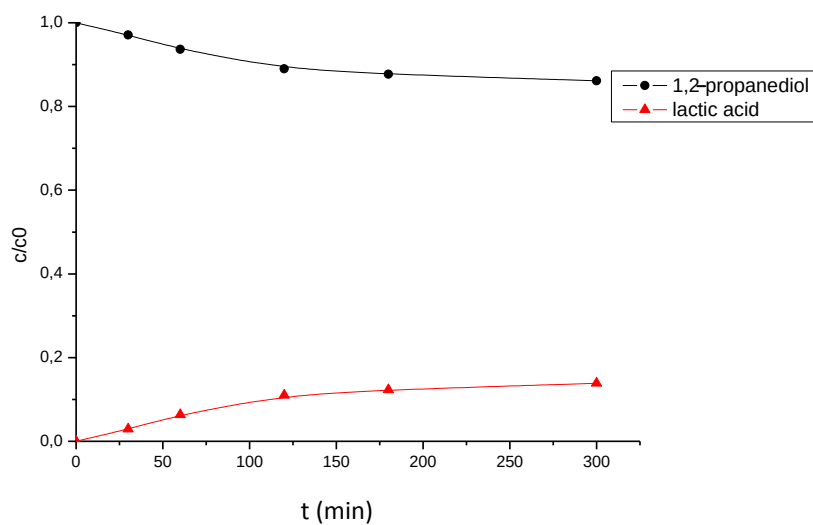
1.5Au/CeO₂

Figure 11-65: : Concentration/ time profile for the selective oxidation of 1,2-propanediol. Reaction conditions: catalyst 1.5Au/CeO₂, T=50°C, p=1bar, 1,2-propanediol/Au=1000, NaOH: 1,2-propanediol 1:1, rpm=1000, • 1,2- propanediol, ▲lactic acid.

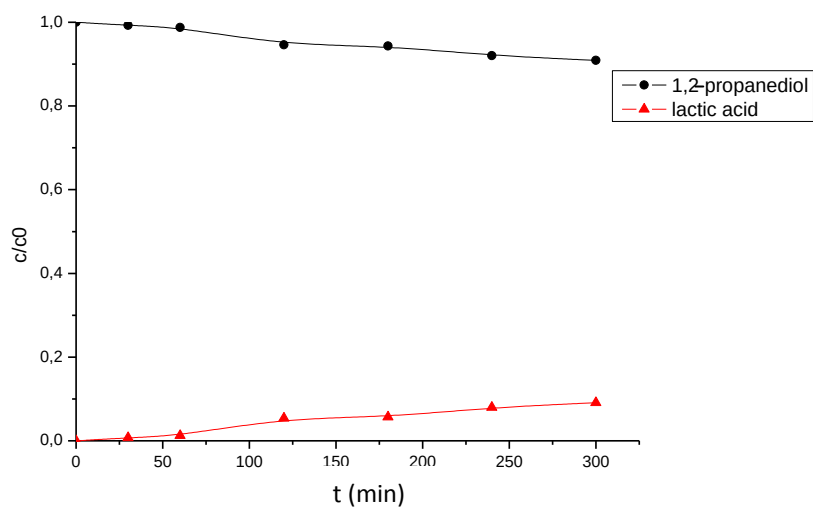
1.5Au/TiO₂

Figure 11-66: Concentration/ time profile for the selective oxidation of 1,2-propanediol. Reaction conditions: catalyst 1.5Au/TiO₂, T=50°C, p=1bar, 1,2-propanediol/Au=1000, NaOH: 1,2-propanediol 1:1, rpm=1000• 1,2- propanediol, ▲lactic acid.

Selective oxidation of glycerol

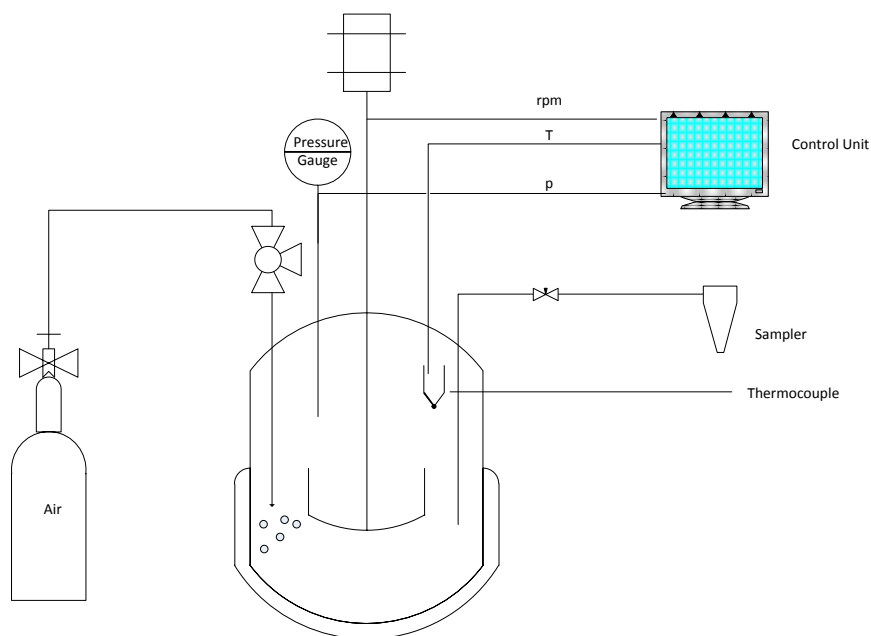


Figure 11-67: Reactor Setup (Parr autoclave) for selective oxidation of glycerol.

1.5Au1.5Pd/C

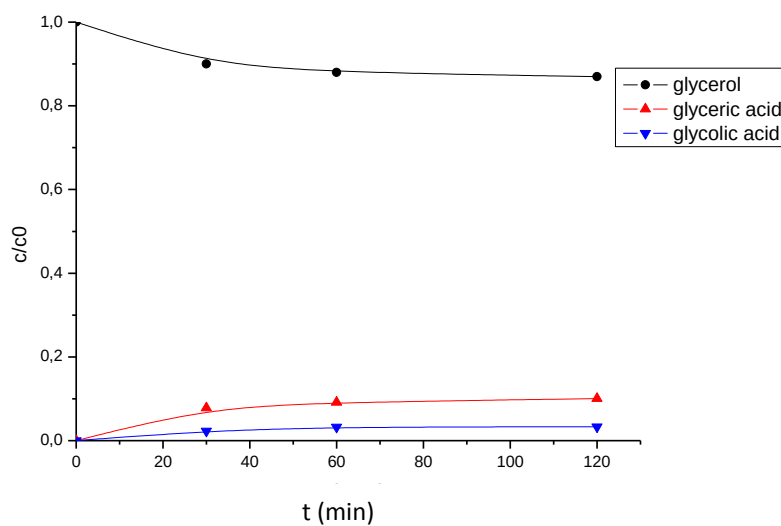


Figure 11-68: Concentration/ time profile for the selective oxidation of glycerol. Reaction conditions: catalyst 1.5Au1.5Pd/C, $T=50^{\circ}\text{C}$, $p=1\text{bar}$, $c_{\text{glycerol}}=0.2\text{M}$, $\text{NaOH:glycerol}=2:1$, $\text{rpm}=1000$, • 1,2 glycerol, ▲ glyceric acid, ▼ glycolic acid.

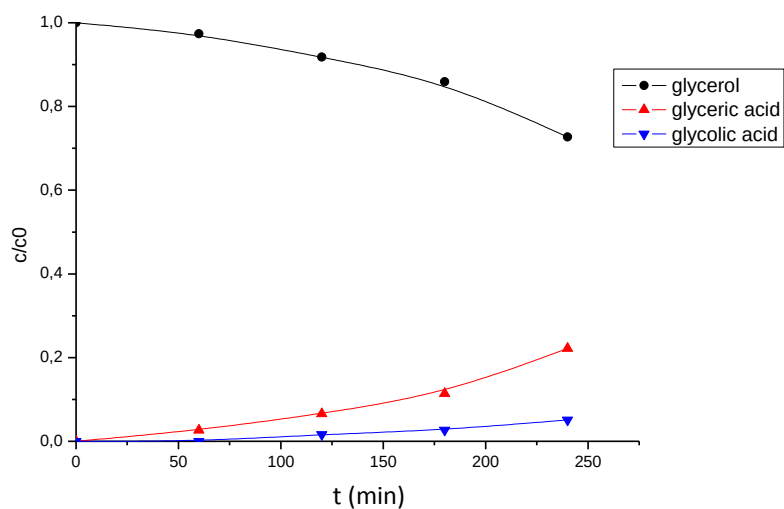
1.5Au1.5Pd/CeO₂

Figure 11-69: Concentration/ time profile for the selective oxidation of glycerol. Reaction conditions: catalyst 1.5Au1.5Pd/CeO₂, T=50°C, p=1bar, $c_{\text{glycerol}} = 0.2\text{M}$, NaOH:glycerol= 2:1, rpm= 1000, • 1,2 glycerol, ▲ glyceric acid, ▼ glycolic acid.

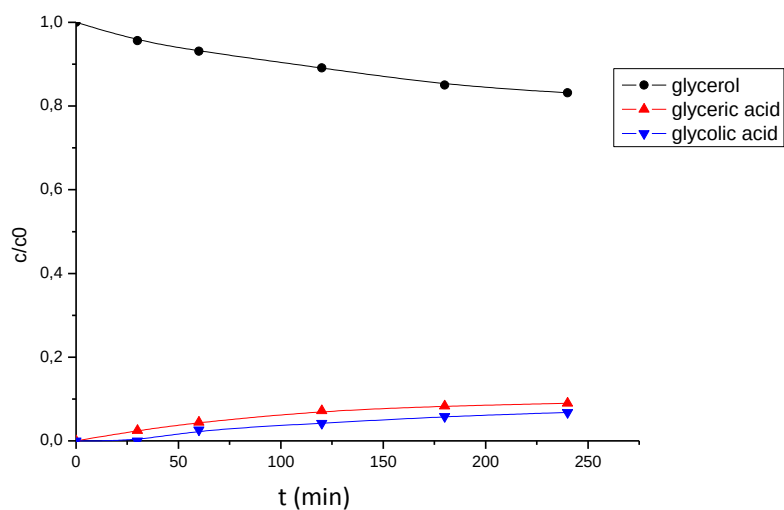
1.5Au/CeO₂

Figure 11-70: Concentration/ time profile for the selective oxidation of glycerol. Reaction conditions: catalyst 1.5Au/CeO₂, T=50°C, p=1bar, $c_{\text{glycerol}} = 0.2\text{M}$, NaOH:glycerol= 2:1, rpm= 1000, • 1,2 glycerol, ▲ glyceric acid, ▼ glycolic acid.

E Moving From Batch to Continuous Processing

TBR Arrhenius Plot

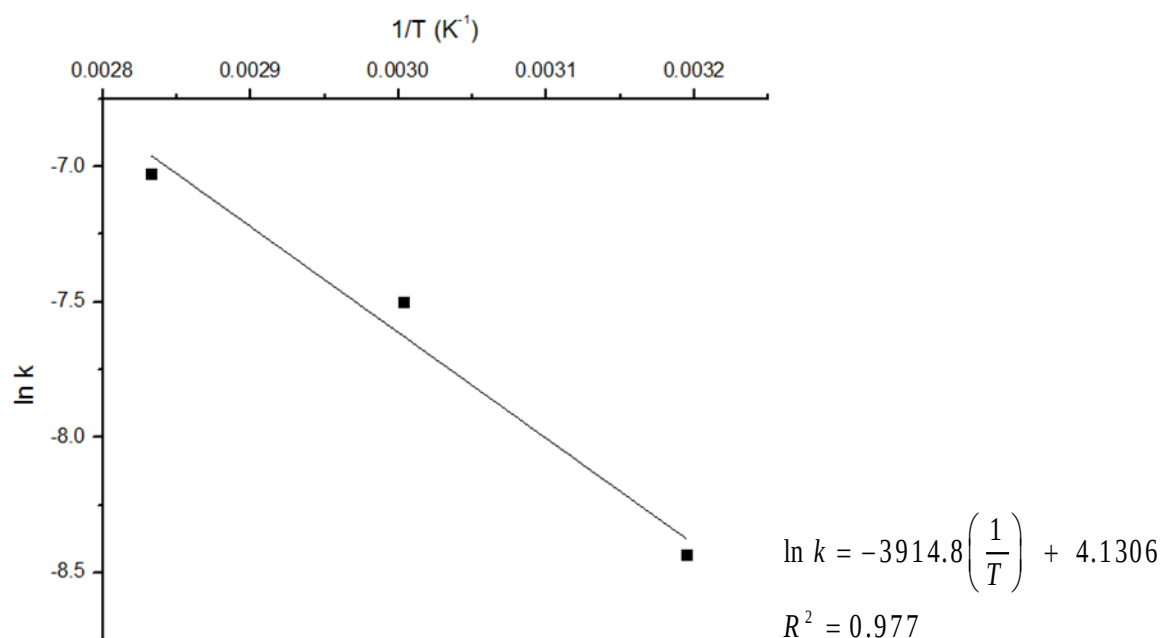


Figure 11-71: Arrhenius plot for selective oxidation of salicyl alcohol in trickle flow reactor.