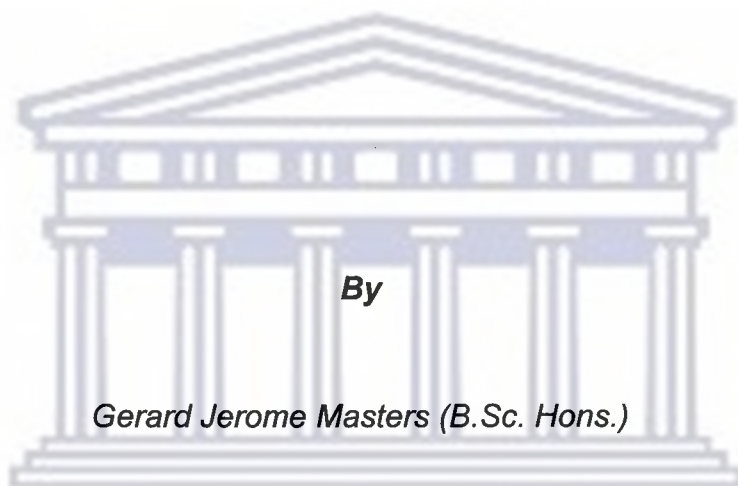


The Oxidation of the Lower Primary Alcohols

In a Catalytic Membrane Reactor



By

Gerard Jerome Masters (B.Sc. Hons.)

UNIVERSITY *of the*
WESTERN CAPE

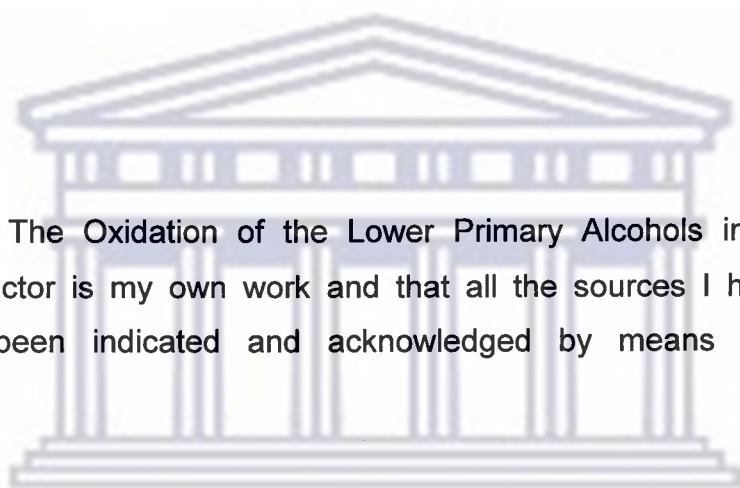
Submitted in fulfillment of the requirements for the degree of
Masters in Chemistry

In the Department of Chemistry, University of the Western Cape

Supervisor : Professor Vladimir M. Linkov

December 2000

"I declare that The Oxidation of the Lower Primary Alcohols in a Catalytic Membrane Reactor is my own work and that all the sources I have used or quoted have been indicated and acknowledged by means of complete references."



UNIVERSITY *of the*
WESTERN CAPE

Signed: _____

Date: _____

ACKNOWLEDGEMENTS

I thank the Lord our God and Father for the opportunities and blessings that He has given me in life.

I take this opportunity to thank everyone that has helped me reach this point in my academic career. I thank my supervisor, Professor Vladimir Linkov, for accepting me into his research program and for providing me with all the resources that I needed to accomplish my tasks. I thank Leslie Petrik for her advice and assistance.

I thank Professor James Darkwa for his assistance and advice with the synthesis of the catalysts and for allowing me to work in his laboratory. I thank post-doctoral fellows Dr. Kim Jong-Soon and Dr. Nagabhusana K.S. for their friendship and encouragement. Special thanks to Professor Shijun Liao for his guidance in helping me understand how heterogeneous catalysts work. I thank post-doctoral fellows Mihaela Iovu-Jahed and Kelin Li for their advice in polymer synthesis.

I thank our colleagues in Belgium especially Professor Pierre Jacobs and Drs. Ivo Vankelecom and Frederik Van Laar from the Catholic University of Leuven and Drs. Roger Leysen, Herman Weyten and Jan Luyten from the Flemish Institute for Technological Research (VITO) for introducing me to the world of catalytic membrane technology. Herman Weyten is thanked for having XPS analysis done on selected catalysts. I am very grateful to the Flemish government and the NRF for funding the bilateral research program.

I thank Timothy Lesch for his help with GC-MS and elemental analyses and Nazeem Jahed for his advice on analytical techniques. A special thanks also goes to Malcolm Mclean for his practical advice and glassblowing services. I also thank Andile Mantyi, Ben de Wet and Carmen Johnson for all the chemicals and consumables that they kindly supplied to me on request.

Acknowledgements

I am extremely grateful to the staff at the mechanical and electronic workshops namely, Shadley, Peter, Magmoed, Vincent and Cedric who were able to make sense of my designs and ideas and to manufacture equipment that not only worked but were better than I had imagined.

I am grateful to Ben Bladergroen for his many probing questions about science and about life. I thank him also for his help in the GC calibrations and reaction studies. I extend my gratitude to all my fellow post-graduate students especially Mmalewane Modibedi, Shadley Mckenzie and Mkhethwa Maluleke for their friendship and camaraderie. A special thanks goes to Angwafor Fru Chi for helping me with some of the drawings and for his assistance in the laboratory. Thanks too to Barbara Rogers and Nicolette Hendricks for their assistance in the laboratory.

I thank all my friends and relatives who encouraged me over the years especially Andre Quimpo, Mark Weber and John Davids and to my brother Damien for his support.

A special thank you goes to my uncle, General David Masters, who bought me my first chemistry set in 1976, before he went into exile to fight for the liberation of our country. I also thank my uncle, Reverend Gerard G. Masters, after whom I am named, for initiating my desire to learn about our world and universe through the interesting toys and books he gave me.

I thank my parents, Jack and Gloria, who set me on my way in life and who have not stopped supporting me in whatever endeavour I pursued. Finally, I thank my wife, Juliet, and children, Brittany and Israel, for their unending support and love and for sacrificing family time by allowing me to spend late nights in the lab.

Summary

The partial oxidation of the lower primary alcohols, namely methanol and ethanol, forms the main thrust of this thesis. The oxidation reactions were performed in a catalytic membrane reactor.

Catalysts that proved to be active in the oxidation of alcohols were sought via a literature search and one of the catalysts that was chosen was a magnesium oxide supported polysilazane-platinum complex (MgO-Si-N-Pt). This catalyst was reported to have high conversion and selectivity in the partial oxidation of primary alcohols. The preparation of MgO-Si-N-Pt was attempted, but the catalyst could not be reproduced. This was due to the fact that silazanes are highly unstable and are easily hydrolysed to form ammonia and silanol and/or siloxane. However, the catalyst what was produced was proposed as being magnesium oxide supported polysilanol-platinum complex (MgO-Si-O-Pt). The characterisation of MgO-Si-O-Pt is supported by the methanol surface probe reaction. The major product of the methanol oxidation reaction was methyl formate, which meant that MgO-Si-O-Pt was a redox type catalyst. A redox catalyst has dual properties i.e. it can be reduced or oxidised. The active sites of MgO-Si-O-Pt were the weakly acidic site Si—OH and the oxidising site O—Pt.

This catalyst, MgO-Si-O-Pt, was supported on a tubular ceramic support. The modified catalyst, called membrane supported magnesium oxide supported polysilanol-platinum complex (+MgO-Si-O-Pt), was highly active in the partial oxidation of methanol and ethanol. In an effort to understand why this catalyst was active despite not being the same as the target catalyst MgO-Si-N-Pt, a series of membrane-supported catalysts were prepared by changing one parameter at a time. The activity of these catalysts was tested in the partial oxidation of methanol and ethanol. Of this series, only the membranes that were modified directly by Pt impregnation were active in the oxidation reactions.

Summary

The membrane reactor was designed from examples of reactors used by researchers in Ukraine and Belgium, and manufactured at the instrument workshop. It consisted of a stainless steel module in which a tubular ceramic supported catalyst was mounted. The reactor set-up was assembled and connected on-line to a gas chromatograph via heated tubing. The reactor system was designed to ensure that it was leak proof in order to produce valid activity calculations.

The physical properties of the supported and unsupported catalysts were determined with respect to surface area, surface morphology, chemical composition and thermal properties. The chemical properties were obtained by temperature-programmed reactions and by the methanol surface probe reaction. Based on the characterisation results, a structure of the synthesised catalyst was suggested. The activity of the membrane-supported catalysts was evaluated in the oxidation of methanol and ethanol with respect to conversion and selectivity.

In methanol oxidation reactions, which were performed at temperatures below 100°C, the selectivity towards methyl formate was rated as the reactor process. Both of the Pt containing catalysts prepared in this study displayed conversion and selectivity results (>90%) that were higher than the results reported in literature. The conversion and selectivity over the catalysts prepared in this study were sensitive to small changes in the reaction temperature, i.e. the conversion and selectivity could be easily controlled by carefully controlling the reaction temperature.

It is suggested that further work be done at higher temperatures and flow rates to determine the effect that it may have on the conversion and selectivity. Preliminary results of reactions run at temperatures of 110°C and higher have revealed a higher conversion with an increase in selectivity towards CO₂. These results suggest that both the catalysts could possibly be used in a direct methanol fuel cell.

TABLE OF CONTENTS

ACKNOWLEDGEMENTS	i
SUMMARY	iii
TABLE OF CONTENTS	v
LIST OF FIGURES	x
LIST OF TABLES	xii
LIST of ABBREVIATIONS	xiv
CHAPTER 1 LITERATURE SURVEY	1
1.1 INTRODUCTION	1
1.2 OXIDATION REACTIONS	2
1.2.1 Oxidation of Alkanes	3
1.2.2 Oxidation of Alcohols	4
1.2.2.1 Oxidation of Methanol	4
1.2.2.2 Oxidation of Ethanol	7
1.3 APPLICATION OF CATALYSTS IN OXIDATION REACTIONS	10
1.3.1 Structural Properties	10
1.3.2 Support types	11
1.3.3 Homogeneous and Heterogeneous catalysts	11
1.3.4 Surface coverage	12
1.4 MEMBRANE TECHNOLOGY	13
1.4.1 Inorganic Membranes	14
1.4.1.1 Ceramic Membranes	15
1.4.1.1.1 Characteristics	15
1.4.1.1.2 Methods of Preparation	15

Table of Contents

1.5	MEMBRANE SUPPORTED CATALYSTS	16
1.5.1	Characteristics	16
1.5.2	Modification procedures	17
1.5.3	Catalyst deactivation	17
1.6	PREPARATION OF CATALYTIC MEMBRANES	19
1.6.1	Techniques used in the preparation of catalytic membranes	19
1.6.2	Modification procedures	19
1.6.2.1	Modification by Sol-Gel Technique	19
1.6.2.2	Modification by ion-exchange	19
1.6.2.3	Modification by grafting	20
1.7	PROPERTIES OF CATALYTIC MEMBRANES	22
1.7.1	Transport mechanisms in porous catalytic membranes	22
1.7.2	Particle size	22
1.8	CATALYTIC MEMBRANE REACTORS (CMR)	23
1.8.1	Catalytic membrane reactor configuration	23
1.8.2	Reactions on porous catalytic membranes	24
1.8.3	Chemisorption	25
1.9	PHYSICAL CHEMISTRY of ALCOHOL OXIDATION	26
1.9.1	Thermodynamics	26
1.9.2	Reaction Kinetics	26
CHAPTER 2	OBJECTIVES OF RESEARCH	28
CHAPTER 3	EXPERIMENTAL METHODS	30
3.1	INTRODUCTION	30
3.2	REAGENTS USED	31
3.3	PREPARATION OF CERAMIC MEMBRANE SUPPORTS	32

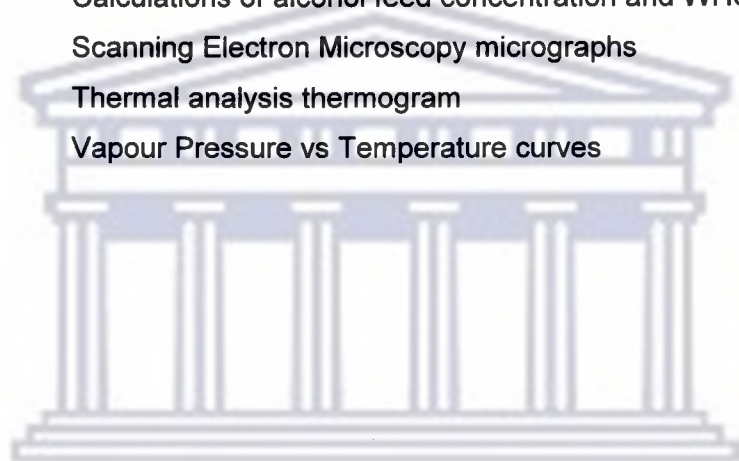
Table of Contents

3.3.1	Preparation of solvents	32
3.3.2	Preparation of magnesium oxide supported platinum-polysilazane complex catalyst (MgO-Si-N-Pt)	32
3.3.2.1	Step 1: Preparation of the unsupported intermediate (MgO-Si-N)	32
3.3.2.2	Step 2: Preparation of unsupported (MgO-Si-N-Pt)	33
3.3.3	Preparation of magnesium oxide modified ceramic membrane	34
3.3.4	Preparation of magnesium oxide supported platinum-polysilazane complex catalyst on ceramic membrane support	34
3.3.4.1	Step 1: Preparation of the supported intermediate (+MgO+Si-N)	34
3.3.4.2	Step 2: Preparation of supported (+MgO-Si-O-Pt)	35
3.3.5	Modification by impregnation with chloroplatinic acid ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$)- Ion exchange method	35
3.4	CHARACTERIZATION	37
3.4.1	X-ray Photoelectron Spectroscopy (XPS)	37
3.4.2	Elemental analysis (CNHS)	37
3.4.3	Energy dispersive X-ray spectroscopy (EDS)	37
3.4.4	Scanning electron microscopy (SEM)	38
3.4.5	Simultaneous thermal analysis	38
3.4.6	Nitrogen adsorption porosimetry	38
3.4.7	Temperature programmed techniques	39
3.4.7.1	Temperature Programmed Reduction (TPR)	39
3.4.7.2	Temperature Programmed Oxidation (TPO)	40
3.4.7.3	Temperature Programmed Desorption (TPD)	40
3.5	CATATALYTIC MEMBRANE REACTOR (CMR) SET-UP	41
3.5.1	Calibration curves	44

CHAPTER 4	CATALYST PREPARATION AND CHARACTERISATION	45
4.1	INTRODUCTION	45
4.2	CATALYST PREPARATION	46
4.2.1	Preparation of magnesium oxide modified ceramic membrane	46
4.2.2	Composition of magnesium oxide supported platinum-polysilazane complex catalyst (MgO-Si-N-Pt)	46
4.2.3	Preparation of magnesium oxide supported platinum-polysilazane complex catalyst on ceramic membrane support	49
4.2.4	Preparation of platinum (Pt) modified membranes by ion-exchange method	50
4.3	CHARACTERISATION	51
4.3.1	XPS results	51
4.3.2	Elemental analysis (CHNS)	52
4.3.3	Pt-weight percentage gain of the modified membranes	52
4.3.4	Energy dispersive X-ray spectroscopy (EDS)	54
4.3.5	Scanning electron microscopy (SEM)	55
4.3.6	Thermal analysis	56
4.3.7	Nitrogen adsorption	58
4.3.9	Temperature programmed techniques	61
4.3.9.1	Temperature programmed reduction (TPR)	61
4.3.9.2	Temperature programmed oxidation (TPO)	62
4.3.9.3	Temperature programmed desorption (TPD)	64
CHAPTER 5	ALCOHOL OXIDATION	65
5.1	INTRODUCTION	65
5.2	CONVERSION AND SELECTIVITY	66
5.2.1	Illustrated example of Conversion and Selectivity	66
5.2.1.1	Conversion	66
5.2.1.2	Selectivity:	68

Table of Contents

5.3	REACTION STUDIES	69
5.2.1	Methanol Oxidation	71
5.2.2	Ethanol Oxidation	79
5.2.3	Comparison of methanol and ethanol oxidations	82
CHAPTER 6	CONCLUSIONS	84
	REFERENCES	87
	APPENDIX	
Appendix A:	Calculations of alcohol feed concentration and WHSV	95
Appendix B:	Scanning Electron Microscopy micrographs	96
Appendix C:	Thermal analysis thermogram	99
Appendix D:	Vapour Pressure vs Temperature curves	100



UNIVERSITY *of the*
WESTERN CAPE

LIST OF FIGURES

The figures in the text are numbered sequentially according to chapter and occurrence.

Chapter 1

- | | | |
|-----|---|----|
| 1.1 | The 5 steps involved in the reaction at the catalyst surface, namely a unimolecular conversion | 12 |
| 1.2 | Zeolite FePcY supported in Polydimethylsiloxane (PDMS) membrane | 14 |
| 1.3 | Comparison of two different methods of preparation of silica supported molybdenum oxide catalysts | 21 |
| 1.4 | Possible flow patterns for CMR on an anisotropic catalytically active membrane | 24 |

Chapter 3

- | | | |
|-----|---|----|
| 3.1 | Product of the first step in the synthesis of (MgO-Si-N-Pt) | 33 |
| 3.2 | Expected structure of Pt-Polysilazane | 33 |
| 3.3 | Reaction set up for the first step in the preparation of platinum-polysilazane complex catalyst | 35 |
| 3.4 | Schematic of the catalytic membrane reactor | 41 |
| 3.5 | Reactor set-up. | 42 |

Chapter 4

- | | | |
|-----|---|----|
| 4.1 | Proposed catalyst structure | 49 |
| 4.2 | Simultaneous TGA and DSC of MgO-Si-O | 57 |
| 4.3 | Simultaneous TGA and DSC of MgO-Si-O-Pt | 58 |
| 4.4 | Graphical representation of increase in surface area with increase in concentration of the platinumic acid solution | 60 |
| 4.5 | Pore size distribution of the prepared catalysts | 61 |
| 4.6 | Graph of temperature programmed oxidation on MgO-Si-O-Pt | 63 |

List of Figures

Chapter 5

5.1	Direction of alcohol/air mixture across the membrane supported catalyst	70
5.2	Conversion and estimated selectivity for oxidation of methanol on Pt 10g/l	73
5.3	Conversion of methanol on the +MgO-Si-O-Pt membrane-supported catalyst	73
5.4	Selectivity towards methyl formate on the +MgO-Si-O-Pt membrane-supported catalyst	76
5.5	The proposed reaction mechanism of the oxidation of methanol	
5.6	Conversion of ethanol on a +MgO-Si-O-Pt catalyst	81
5.7	Selectivity towards acetaldehyde on the +Pt (4g/l) membrane-supported catalyst	80
5.8	Conversion of ethanol on a Blank+Pt(4g/l) catalyst	78
5.9	Selectivity towards acetaldehyde on the +MgO-Si-O-Pt membrane-supported catalyst	82

Appendix

B1	+MgO+Pt(4g/l) (Inner)	96
B2	+MgO+Pt(4g/l) (Outer)	96
B3	+MgO+Pt(4g/l) (Edge)	96
B4	+MgO-Si-O-Pt (Inner surface)	97
B5	+MgO-Si-O-Pt (Outer surface)	97
B6	MgO-Si-O (Intermediate)	98
B7	MgO-Si-O-Pt (Unsupported Catalyst)	98
C1	TGA/DSC of +MgO+Pt(0.1g/l)	99
D1	Vapour pressure vs Temperature curve for methanol	100
D2	Vapour pressure vs Temperature curve for ethanol	100

LIST OF TABLES

The tables in the text are numbered sequentially according to chapter and occurrence.

Chapter 1

1.1	XPS data for Si-N-Pt, Si-N and H_2PtCl_6	8
1.2	Thermodynamic data of the products involved in methanol oxidation (gaseous phase)	26

Chapter 3

3.1	Reagents used in the preparation of the catalysts and in reaction studies	31
3.2	HP5890 GC parameters	43

Chapter 4

4.1	Step by step modification of blank support	48
4.2	Comparison of XPS Data for unsupported MgO-Si-N-Pt complex catalyst	51
4.3	Results of elemental analysis on unsupported catalyst and intermediate	52
4.4	Comparison of the Pt loading on the membranes with respect to immersion time and concentration	53
4.5	Results obtained by Santamaria <i>et. al</i>	53
4.6	Surface elemental composition as determined by EDS	54
4.7	Results of simultaneous thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC)	56
4.8	BET results of the series of prepared catalysts	58
4.9	Results of temperature programmed reduction	62
4.10	Results of temperature programmed oxidation	63
4.11	Results of temperature programmed desorption	64

Chapter 5		
5.1	Sampled results form methanol oxidation	68
5.2	Reaction conditions	71
5.3	Comparison of the conversion and selectivity for the catalytic membranes in methanol oxidation	72
5.4	Oxidation of methanol with various catalysts	76
5.5	Comparison of the conversion and selectivity for the catalytic membranes that were evaluated in ethanol oxidation	79



LIST of ABBREVIATIONS

BET	Brunauer Emmett Teller
BJH	Barret Joyner Halenda
CMR	catalytic membrane reactor
EDS	energy dispersive spectroscopy
EV	electron volt
FID	flame ionisation detector
GC	gas chromatograph
GC-MS	gas chromatograph-mass spectrometer
IUPAC	International Union of Pure and Applied Chemistry
MgO-Si-N	magnesium oxide supported polysilazane
MgO-Si-N-Pt	magnesium oxide supported polysilazane platinum complex
+MgO-Si-O-Pt	Membrane supported polysilanol-platinum (proposed name for catalyst produced)
PI	pressure indicator
SEM	scanning electron microscopy
SV	sampling valve
TC	temperature controller
TPD	temperature programmed desorption
TPO	temperature programmed oxidation
TPR	temperature programmed reduction
WHSV	weight hourly space velocity
XPS	X-ray photoelectron spectroscopy

Chapter 1

Literature Survey

1.1 INTRODUCTION

Methanol and ethanol are important chemical feedstock used in industrial chemistry, since they are the starting materials for the synthesis of various products, including hydrocarbons and mild oxidation products [1, 2]. For instance, methanol can be oxidised to methyl formate, which can be transformed into industrially important products such as N,N-dimethyl formamide or acetic acid [1]. Both methanol and ethanol have also been used as probe reactions, in which they are used to characterise catalysts according to the type of active sites present, namely redox, acidic or basic [3].

The lower primary alcohols are also currently being used in fuel cell research, since the oxidation of alcohols has been proposed as an anode reaction for fuel cells [4]. In the latter case, the important reaction is the complete oxidation of the alcohol to carbon dioxide and water. It is apparent from industrial examples that methanol oxidation can lead to various products by varying the nature of the catalyst and the reaction conditions [1].

Catalytic membranes are a group of catalysts in which the catalyst is impregnated or grafted onto a membrane. The membrane's main purpose is to separate reaction components in order to improve the conversion rate, but it can also be used purely as a support for a catalyst i.e. in which it does not perform the function of separation. Supporting a catalyst on a membrane has a number of advantages over conventional catalytic processes. The membrane thus used allows for the integration of separation and reaction, which leads to advantages such as (i) system simplification (ii) lower

capital costs (iii) yield improvement and (iv) selectivity enhancement [5]. Details regarding the application of catalytic membranes are described in section 1.5.

1.2 OXIDATION REACTIONS

Oxidation of an organic compound is defined as the substitution of a lesser electronegative atom by a more electronegative atom. It could also be defined as addition of oxygen or alternatively it could be defined as the removal of hydrogen (oxidative dehydrogenation). Molecular oxygen can be used for reactions involving the addition of oxygen and is the cheapest oxidising agent. However, several other oxidising agents like MnO_2 , Cl_2 , CrO_3 , HNO_3 and H_2O_2 have been used because of the sensitivity and selectivity needed for a particular oxidation reaction. Molecular oxygen is usually less selective compared to other oxidising agents like Cl_2 or HNO_3 [6].

The oxidation of organic compounds can be classified into two categories namely homolytic and heterolytic oxidation reactions, depending on the nature of the cleavage of the interatomic bonds. Homolytic oxidation reactions are chain reactions, which involve the formation of radicals by homolytic cleavage of interatomic bonds. These reactions occur spontaneously and are commonly known as autoxidations. Generally, homolytic oxidations have low selectivity due to the nature of the intermediate radicals, which isomerise easily, and thus the resulting products are more readily oxidisable than the starting hydrocarbon [6].

Molecular oxygen (O_2) is mainly used in the initiation and propagation stages of the oxidation process. Hydroperoxides are formed which propagate the reaction further. Homolytic gas-phase oxidations are all combustion processes that take place in free gas space without the presence of heterogeneous catalysts. Due to the extreme conditions, only a few simple products are produced in the homogeneous gas phase. Examples of this process is synthesis gas produced by combustion of coal in the presence of water, acetylene by partial combustion of hydrocarbons and the formation of CO_2 by complete combustion of natural gas [6].

In heterolytic oxidation reactions, an active oxygen compound other than molecular oxygen is frequently used to oxidise the starting material via a two-electron transfer

reaction. This reaction is possible in the liquid phase or in the heterogeneous gas phase. Since heterolytic oxidation occurs via defined complexes, it is in principle very selective compared to homolytic oxidation. There are many applications of the heterolytic oxidation reaction.

Heterogeneous and homogeneous catalysed oxidation reactions occur in both homolytic and heterolytic oxidations of organic materials. The most commonly used are heterogeneously catalysed heterolytic oxidation reactions [6].

1.2.1 Oxidation of Alkanes

Alkanes, which are often referred to as paraffins, show little chemical affinity for other molecules and are essentially inert to most reagents that are used in organic chemistry. This is in part due to their low acidity, low basicity and high C—H bond strength [7]. Alkanes do however react with oxygen and oxygen based compounds under specific conditions. For example, the oxidation of methane occurs at high temperatures and pressures. At these elevated temperatures and pressures a number of radicals are formed and they result in multiple or an uncontrolled number of radical reactions [8]. Under these conditions it is difficult to attain high selectivity to the desired product, therefore better results can be obtained by activation under mild conditions. Hence catalytic technology is employed to assist in the partial oxidation of the light paraffins at less stringent conditions.

Significant progress was made after 1986 with catalysts containing MoO_3 and V_2O_5 in the partial oxidation of hydrocarbons [9]. These catalysts were effective when they were either supported or used in bulk form. The introduction of silica based molybdenum and vanadium oxide catalysts gave a major improvement in the yield of formaldehyde from methane [9]. Important parameters in the catalyst system were the type of reactor and the mode in which it was being operated. For instance, Parmaliana *et al.*, used a recirculation flow batch reactor (RFBR), temperature programmed reactor (TPR) and plug flow reactors in continuous flow (CFR) and continuous flow with recycle (CFRR) [9]. The significance of the catalytic membrane reactor is discussed in section 1.6. To convert alkanes to CO_2 and H_2O can be achieved, however controlling the same reaction to give partial oxidation products ranks as one of the most difficult tasks to

accomplish [10]. The reason being that the intermediate is more easily oxidised than the starting alkane. Hence, for better control it means that conversion has to be kept to a minimum by choosing appropriate reaction conditions.

1.2.2 Oxidation of Alcohols

In industry, the oxidation of the lower primary alcohols is mainly achieved under stringent conditions i.e. at high temperatures and pressures. The conditions for the oxidation of alcohols is however less stringent than the conditions for the oxidation of alkanes. Furthermore in alkanes the energy of the primary C—H bonds decreases with increasing chain length. Hence, the C—H bond in methanol would have a higher dissociation energy than the corresponding bond in ethanol. In the presence of O₂, all organic materials are metastable intermediates in the reaction pathway to complete combustion to CO₂ [6]. This is usually a slow process, hence catalysts are used to increase the rate of oxidation of the lower primary alcohols. They also offer the possibility of achieving the oxidations under milder conditions.

Traditionally the oxidation of alcohols is performed in batch form with an unsupported catalyst, which introduces an added drawback due to the problem of separation of the catalyst from the product. The problem is two fold, i.e. there is a loss of catalyst with a simultaneous loss in purity of the product.

In many cases, the effect of the solvent has to be considered as yield and selectivity may be affected. This phenomenon is evident from the work done by Kuno *et al* [11]. They compared the oxidation of higher alcohols using trimethylsilyl chloride modified hydrous zirconium (IV) oxide and unmodified hydrous zirconium (IV) oxide as catalysts in batch reactions [11]. They found that solvents such as toluene and xylene were superior to other solvents, increasing both yield and selectivity to the aldehyde.

1.2.2.1 Oxidation of Methanol

Industrial production of formaldehyde is achieved, based on the selective oxidation of methanol using oxide catalysts such as Fe₂(MoO₄)₃-MoO₃ [12, 13]. However, this iron-

molybdenum catalyst deactivates rapidly due to loss of MoO_3 and reduction of the active $\text{Fe}_2(\text{MoO}_4)_3$ species to the less active FeMoO_4 species. The work by Ivanov *et al.* [12] deals with the preparation of Mn-Mo-O with different Mo/Mn ratios from 1.1 to 1.3 to find a more stable catalyst to replace the iron based oxide catalyst. Comparing the preparative methods of Mn-Mo-O catalysts, Ivanov *et al* found that the catalysts with the highest activity and selectivity were those that were precipitated in the presence of a small excess of MoO_3 . They proposed that the oxidation of methanol on MnMoO_4 occurred in a two-step process [12]. In the first step methanol interacts with Mo(VI) to reduce it to Mo(V)(Mo(IV)). In the second step the reduced molybdenum is oxidised by molecular oxygen from the alcohol-air mixture.

Tatibouët *et al.* [14] considered the effect of catalyst dispersion on the activity of a 12-Molybdosilicic acid supported on silica. They found that the lower the surface coverage the higher the dispersion of the active phase. Previously, they showed that methanol oxidation is sensitive to the dispersion of molybdenum oxide on silica. Silica and alumina, which are used as catalyst supports, are inherently catalytic in the oxidation of methanol. The authors, Cairati and Trifiro [15], attribute the oxidation of methanol to the formation of surface formates, which can be esterified to methyl formate or form CO (see Scheme 1).

A review by Tatibouët [1] considers methanol oxidation as an analytical tool i.e., to act as a surface probe reaction. Methanol oxidation is a highly sensitive process, which allows for the detection of very small variations in the nature of the catalytically active phase. The nature of the catalytic sites are rarely known, however the structure sensitivity of the methanol oxidation reaction allows the identification of different site structures that selectively form a single product. The main advantage of using methanol as a surface probe reaction is that methanol oxidation reveals only the catalytically active part, hence it appears to be particularly adapted to characterise supported catalysts. Furthermore, the characterisation occurs *in situ*, however this advantage has its limitations in that the surface of a catalyst undergoes a continuous fluctuation from an oxidised to a reduced state.

The nature of a catalyst can be examined and chemically characterised via the methanol oxidation reaction [3]. Catalyst sites that are capable of being reduced and oxidised,

namely redox sites, yield formaldehyde and methyl formate. Surface acid sites (Lewis and Brønsted) yield dimethyl ether and surface basic sites yield CO/CO₂ as the major product.

A number of products are involved in the oxidation of methanol in the gaseous phase. The products that are formed depend on the catalyst and the reaction conditions such as reaction temperature, flow rates and partial pressure of reactants. Due to its industrial interest the main product that is cited in the literature is formaldehyde (CH₂O) [12]. Other important products such as dimethyl ether (CH₃OCH₃), methyl formate (HCOOCH₃) and methylal ((CH₃O)₂CH₂) are obtained by varying the reaction conditions. During the methanol oxidation the oxides of carbon (CO₂ and CO) can also be formed. Formic acid is very rarely observed in the product stream, since it is an intermediate in the formation of methyl formate or the carbon oxides.

Oxidation of methanol is considered to have a redox mechanism involving oxidation of the organic molecule and simultaneous reduction of the catalyst. Three elementary steps can describe the reaction [16]:

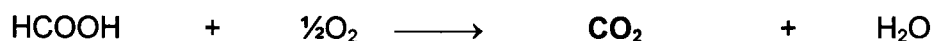
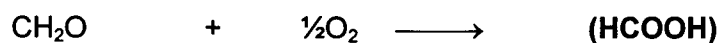
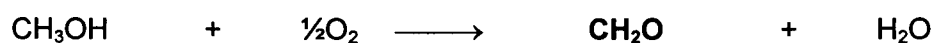
- (i) the binding of the alcohol to some surface site A
- (ii) oxidation and desorption of the bound adsorbate with concurrent loss of oxygen from the catalyst
- (iii) uptake of oxygen by the catalyst at site B with oxygen transport along the surface or through the crystal lattice to replenish the vacancy caused by reaction at site A

A scheme of the reactions that occur in the oxidation of methanol is shown in Scheme 1 [1].

These reactions can be divided into two principal pathways:

- (A) oxidation reactions which require oxygen
- (B) dehydration reactions which do not require oxygen

(A) Reactions which require oxygen - Oxidation Reactions



(B) Reactions which do not require oxygen - Dehydration Reactions



Scheme 1 Reaction scheme of methanol oxidation

In methanol oxidation the rate-determining step was found to be the C—H bond breaking from an adsorbed methoxy group to produce an adsorbed form of formaldehyde. The activation energy was approximately 85 kJ/mol regardless of the catalyst used [1].

1.2.2.2 Oxidation of Ethanol

A number of parameters influence the activity of catalysts in the oxidation of ethanol. Phase transformations of the surface of vanadia/silica system were studied in the oxidation of ethanol by changing variables such as the size of the particles, co-ordination

of vanadium, degree of reduction, and the amount of co-ordinated water. In this study all the reaction conditions were kept nearly identical, only the hydroxyl concentration on the aerosil, used as silica support, was varied [17]. It was found that for high concentrations of surface hydroxyl groups the reaction passes through a non-steady state period, whereas for lower hydroxyl concentrations the reaction exhibits steady state features from the start of the reaction. The latter phenomenon is due to there being no change in the initial surface phase structure of the vanadia during the reaction.

Jiang *et al.* prepared an inorganic polymer-platinum catalyst called magnesium oxide-supported polysilazane-platinum complex (MgO-Si-N-Pt) [18]. This catalyst was used in the oxidation of ethanol and gave a high yield of acetaldehyde at room temperature. It was an improvement on a similar catalyst, previously prepared by the authors, namely silica-supported polysilazane-platinum complex (SiO₂-Si-N-Pt) [19]. They used X-ray photoelectric spectroscopy (XPS) to determine the structure of the catalyst. The XPS data of the catalyst and its intermediate is given in Table 1.1

Table 1.1 XPS data for Si-N-Pt, Si-N and H₂PtCl₆ [18]

XPS Peak	Binding Energy (eV)		
	Si-N-Pt	Si-N	H ₂ PtCl ₆
Pt(4f _{7/2})	72.4	-	75.5
N(1s)	401.9	400.4	-
Si(2p)	104.3	104.4	-
O(1s)	533.4	533.6	-
Cl(2p)	199.2	-	199.4

where:

Si-N-Pt	represents the final catalyst, polysilazane platinum complex
Si-N	represents the intermediate product in preparation of Si-N-Pt
H ₂ PtCl ₆	hexachloroplatinic acid

The binding energy of Si(2p) and O(1s) of Si-N-Pt were similar to that of Si-N and the Cl(2p) binding energy of Si-N-Pt was similar to that of H₂PtCl₆. There was however a difference of 1.5eV in the N(1s) binding energy between Si-N-Pt and Si-N. The difference of Pt(4f_{7/2}) binding energies between Si-N-Pt and H₂PtCl₆ was 3.1eV. These results indicate bonding interaction between the nitrogen atoms and the platinum atom, and can be seen in chapter 3, Figure 3.2.



1.3 APPLICATION OF CATALYSTS IN OXIDATION REACTIONS

Catalysts play an important role in the economy of industrialised societies. The value of catalysts in the whole chemical industry is about 36% and oxidation catalysts, in particular, represent about 11% in value of all the catalysts used in the chemical industry [20]. A catalyst can be defined as “a substance, which by its mere presence alters the velocity of a reaction and may be recovered unaltered in nature or amount at the end of the reaction”. Depending on the reaction type, the ideal catalyst is one that has a high activity and high selectivity for the target molecule and is stable during the reaction. The parameters that are considered when designing a heterogeneous catalyst are: type of active metal (Pd, Pt, Ni, Cu), type of catalyst (supported, powder, skeletal), type of support (active carbon, alumina, silica) and metal loading of the supported catalysts. Other significant parameters to consider are the surface area, dispersion, the size, location of catalyst in the pores and the oxidation state [21]. Furthermore, for industrial applications the catalyst should be regenerable, reproducible, economical, mechanically and thermally stable and possess specific structural properties [22].

1.3.1 Structural Properties

Structural properties of a catalyst play a significant role in a catalytic process. Nikolov *et al.* [23] compared the effect of different preparation conditions on the structure and catalytic activity of Pt/C. They found that the crystal faces as well as the particle size and the partial oxidation of the carbon support, determined the activity of the catalyst [23]. A compound may be either structure-sensitive or structure-insensitive with respect to a certain catalyst. It has been suggested that alcohol oxidation is structure-insensitive over the V_2O_5/SiO_2 supported catalyst whereas ethane oxidation is structure-sensitive on the same catalyst. There is further evidence that ethane is structure sensitive, since its activation energy values change systematically with the concentration of V_2O_5/SiO_2 , whereas the activation energy values of ethanol oxidation does not [24]. Different crystal faces of single crystals have different catalytic activity, for example, the hydrogenation activity for ethylene on the (111) face of a Ni single crystal was twice as large as that on the (110) face, whereas the (100) face is inactive [25].

An uneven surface, as opposed to a smooth surface (e.g. Pt) was found to enhance the catalytic activity [26]. This is analogous to the differences in energy of atoms that are

present in the flat surface compared to those that occur in corners of terraces. The atoms at the distortions have a higher energy, which is used to overcome the activation energy (E_a) in a reaction.

1.3.2 Support types

There are a number of advantages, besides the high surface area, for supporting catalysts on carriers such as carbon or alumina, namely:

(i) facile catalyst recovery (ii) a physical separation of the active sites by dispersion on the support and (iii) because of the large variety of possible supports, a modulation of the chemoselectivity, regioselectivity and shape-selectivity of the reactions catalysed on these supports [27].

Catalysts are generally divided into two groups namely homogeneous and heterogeneous catalysts.

1.3.3 Homogeneous and heterogeneous catalysts

Homogeneous catalysis is initiated by formation of either a reactive intermediate complex or a compound between one of the reactants and the catalyst. In most homogeneous catalysed reactions, the catalysts are co-ordination compounds of transition metals. This trend has been observed in many cases including the carbonylation of methanol to acetic acid involving a rhodium catalyst [28].

Heterogeneous catalytic reactions consist of the following steps:

- (1) transport of the reactant to the catalyst surface
- (2) adsorption of at least one of the reactants on the surface of the catalyst
- (3) reaction of the adsorbed species with the catalyst to yield an intermediate compound
- (4) reaction of the intermediate with another adsorbed or non-adsorbed reactant, resulting in formation of product
- (5) and finally desorption of the product. [29]

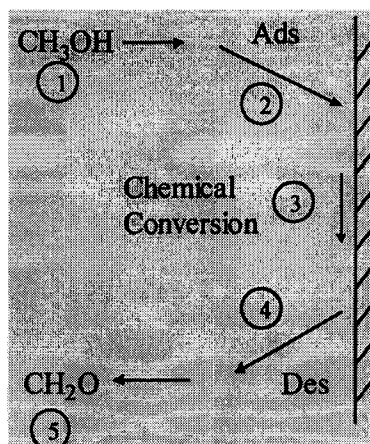


Figure 1.1 The 5 steps involved in the reaction at the catalyst surface, namely a unimolecular conversion of reactant to product where *Ads* denotes adsorption and *Des* denotes desorption

The intermediates can be formed by dissociative chemisorption, by proton or electron transfer, or by bond rearrangement [28].

1.3.4 Surface coverage

Methanol is thought to adsorb molecularly whereas oxygen adsorbs dissociatively onto the surface of a catalyst. The catalyst surface has a higher coverage of oxygen than methanol. This could be confirmed by temperature programmed desorption (TPD) [16].

An important phenomenon in heterogeneous catalysis is termed spillover catalysis and it is often used to explain unexpected experimental results [30]. Spillover catalysis occurs in heterogeneous catalysts that have a multiphase system such as metal islands dispersed on an oxide [31]. In this system for example the molecules adsorb or even react on the metal and then diffuse over onto the oxide where they may react with a different adsorbed species. Lintz *et al.* [30] studied the oxidation of carbon monoxide over platinum-tin (IV) oxide catalysts and concluded that the oxidation is mainly due to the adsorption of oxygen on the oxide surface. The oxygen subsequently migrates to the reaction site, which is located at the border between oxide and noble metal particles [30].

1.4 MEMBRANE TECHNOLOGY

Membrane technology has gained considerable momentum in the recent past due to its many advantages [32,33,34]. A membrane is generally defined as a barrier which is capable of redistributing components in a fluid stream through a driving force such as the difference in pressure, concentration, or electrical potential [35]. When a concentration or electrical potential gradient provides a necessary driving force, this barrier separation process is called dialysis or electro dialysis. Most of the membrane processes are based on an applied pressure difference across the membrane [35].

In nature, membranes in plant and animal cells play a vital role in sustaining life. They perform selective bioseparations, known as permselectivity, by allowing useful nutrients into the cell. A driving force in the form of osmotic pressure achieves this. Similarly, synthetic membranes are used in many technological applications involving separation. They are made of polymers, metals and ceramics [36]. Synthetic membranes have an added advantage in that they allow for reactions to take place at their surface. Numerous workers have exploited the dual nature of the membrane involving both reaction and separation, for a large number of applications. Synthetic membranes can be classified broadly as organic and inorganic membranes, based on the materials used for the manufacture of membranes.

Most organic membranes have a limited pH, temperature and halogen tolerance range [32]. The most important organic polymeric membrane of commercial significance is based upon cellulose acetate and is used for reverse osmosis and ultra filtration. Membranes such as polydimethylsiloxane (PDMS) have been used successfully in the oxidation of organics. Vankelecom *et al.* [37] embedded a catalyst consisting of iron phthalocyanine in zeolite Y (FePcY), in PDMS for the oxidation of cyclohexene at room temperature using tertiary-butyl hydroperoxide as the oxidant (see Figure 1.2). The hydrophobic PDMS membrane served as barrier by separating two immiscible phases, hence, rendering a solvent redundant. The advantage is that this dense membrane removed solvent effects such as dilution of the reactants and prevented fast deactivation of the catalyst by excluding water [37]. A disadvantage of polymeric membranes is their incompatibility with high temperature catalysis. Inorganic membranes on the other hand are known to possess thermal stability and corrosion resistant properties and thus find

use in high temperature catalytic processes but their poor permselectivity restrict their use in many catalytic processes. An example of Polydimethylsiloxane (PDMS) supported zeolite FePcY is shown in Figure 1.2. [37].

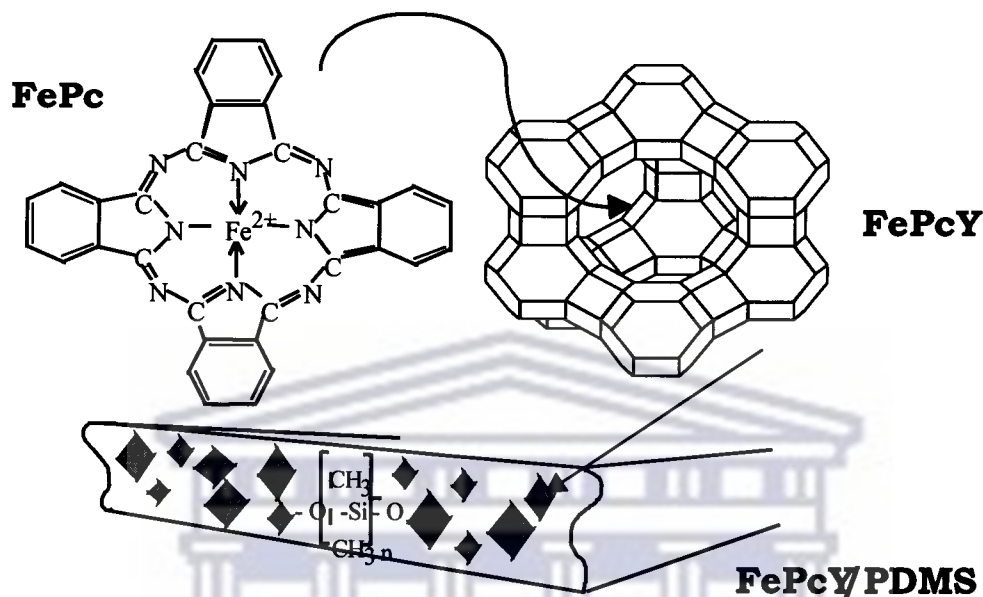


Figure 1.2 Zeolite FePcY supported in Polydimethylsiloxane (PDMS) membrane

1.4.1 Inorganic Membranes

Inorganic membranes can be divided into two main groups namely dense and porous membranes. Dense membranes are made from a number of materials such as palladium, palladium based alloys, platinum and ceramics such as stabilised zirconias. The metal-based membranes allow certain gases (e.g. hydrogen through palladium, oxygen through silver or oxide membranes) to diffuse through their structure [22]. They have high selectivity, but low permeability. In dense membranes, depending upon the solubility of the gas, transport occurs as a result of a concentration gradient. Gas separation also occurs in solid electrolytes, however it depends upon the ionic activity of the membrane material. The permeability is inversely proportional to the thickness of the membrane i.e. the thinner the membrane the higher the permeability [34]. Dense membranes can also be supported on porous substrates. Porous membranes on the other hand are made from glass, alumina, zirconia, titania, silver and stainless steel [22]. Compared to dense membranes, porous membranes have low selectivity, but a high permeability.

1.4.1.1 Ceramic Membranes

1.4.1.1.1 Characteristics

Ceramic membranes have high thermal and chemical stability. This makes them attractive for use in high temperature separations or reactions that occur in an aggressive and corrosive environment [22]. They were initially used in the 1940s in the nuclear industry to separate uranium U^{235} from U^{238} [35]. As the technology grew, ceramic membranes were used in other applications. The ceramic membranes are made of oxides such as silica (SiO_2), alumina (Al_2O_3) and zirconia (ZrO_2), including mixtures of them. A variety of pore sizes can be accurately achieved by milling these oxides to specified particle sizes using a ball mill or using ultrasonic treatment [38].

1.4.1.1.2 Methods of preparation

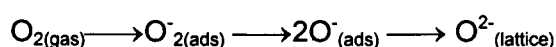
Inorganic membranes are prepared via a number of techniques. The common techniques are extrusion and tape casting. Other techniques, for the production of tortuous pore membranes, include phase separation/leaching, pyrolysis, thin-film deposition and polymerisation. Straight pore membranes are prepared via anodic oxidation and track etching [35]. In the case of slipcasting, pore size varies according to the size of the precursor particles. The moulding essentially involves the preparation of a slip (a water suspension of powdered reagents for ceramic production) that is poured into a gypsum mould. The gypsum absorbs all the water, leaving a green body product. This tubular green body is dried at room temperature, after which it is calcined in a high temperature furnace [38]. According to the requirements of the application, these ceramic tubes can be made to any diameter, length and wall thickness. The tubular form is but one of many forms in which these membranes can be prepared.

1.5 MEMBRANE SUPPORTED CATALYSTS

1.5.1 Characteristics

One of the most important applications of membrane-supported catalysts is in the catalysis of heterogeneous vapour phase reactions. These membranes are used as a catalyst or catalyst support and as a separation medium [39]. In one mode of operation, the permselective characteristic of the membrane is used to simultaneously remove product from the reaction mass as it forms. This can be particularly beneficial to a reversible reaction process by allowing higher per-pass reactor conversions to be achieved as well as simplifying downstream recovery and purification steps [39]. In another mode of operation where parallel or sequential by-product reactions are a problem, the membrane is used to keep bulk reactants separate while allowing the controlled addition of the active reactant to the reaction zone [39]. Therefore, the incorporation of catalysts onto membranes offers the opportunity not only to perform selective catalytic synthesis but also to separate simultaneously reactants and/or products. Catalytic membranes can be divided into two classes, depending on membrane characteristics, namely those membranes that are inherently catalytic, and those membranes onto which a catalyst is grafted or supported.

γ -Al₂O₃ membranes are inherently catalytic and are selective to dimethyl ether in the oxidation of methanol. By modifying the membrane with silver particles the membrane becomes selective to formaldehyde [40]. Furthermore, increasing the silver content increases the selectivity of the membrane to formaldehyde. An interesting phenomenon occurs during the use of a silver metal membrane as catalyst. Silver membranes are selective towards oxygen permeation. Gryasnov *et al.* [41] compared the activity of the oxidation of ethanol by oxygen, which was diffused through the silver membrane to a situation where the oxygen was obtained from the gas phase. They found that acetaldehyde yield was 83% for the former compared to a 56% for the latter under similar conditions [41]. They attributed this enhanced activity to the diffused oxygen being in the form O²⁻_(lattice) as the adsorption of oxygen on silver, in the temperature range 453 to 623°K, occurs by the sequence



In the production of olefins from propane and n-butane over noble metal coated ceramic monoliths, a very simple mechanism was proposed for the observed product distribution. The reactions are initiated by the oxidative dehydrogenation of the alkane by surface oxygen to form a surface alkyl. This adsorbed alkyl on Pt undergoes β -hydrogen and β -alkyl elimination to form the olefin rather than crack to form surface C and H [42].

1.5.2 Modification procedures

In the modification of porous membranes with metal particles, the particles may be deposited in the pores of the membrane if they are small enough to fit in. This has a significant effect on the activity of the metal catalyst. It has been shown for instance that deposited silver metal particles display different properties to, and has a higher catalytic activity, than that of bulk silver [40]. Modification procedures are discussed further in section 1.6.2.

1.5.3 Catalyst deactivation

Deactivation of catalysts occurs due to many processes such as poisoning, which may involve coke deposition, irreversible adsorption, site blockage or loss of active species. In the case of hydrocarbon oxidation the contaminant is coke. In the oxidation of methane, traces of sulphur, which is present in the methane feed stream, poisons the catalyst. The poison acts by blocking the active sites of a catalyst, or in some instances poisons actually modify the surface in a manner that reduces catalytic activity [43]. The deactivation of a catalyst leads to lower conversion rates and hence to lower selectivity. To overcome this problem, removal of any contaminants from the feed before contact with the catalyst may avoid deactivation, as in the case of sulphur removal. In cases where it is impossible to prevent deactivation, such as in the case of coke formation, the catalysts may be regenerated by heat treatment. Catalysts may also be regenerated via reduction with hydrogen or oxidation with oxygen, depending on the nature of the catalyst. For instance, in the case of the silver catalyst, during regeneration of the active species, the oxygen uptake of the bulk metal occurs at slower rates and higher temperatures than when the silver particles are deposited on a porous membrane [40].

Knowledge of the poisons involved in the deactivation of catalysts is invaluable since a manipulation of the poison can be beneficial to the reaction. When a freshly prepared catalyst is introduced into a reactant stream, its selectivity may not be optimal and in

some cases a small amount of “poison” may be added to improve the selectivity by eliminating side reaction [43]. In the oxidation of methanol, certain centres on the catalyst that were responsible for the formation of methyl formate, formaldehyde and CO₂ were destroyed by the addition of poisons such as Na⁺ and Mg²⁺ [15].



1.6 PREPARATION OF CATALYTIC MEMBRANES

1.6.1 Techniques used in the preparation of catalytic membranes

Various methods are employed in supporting a catalyst on a membrane to form a catalytic membrane. One method that has been used extensively and successfully is the sol-gel method. Other methods include chemical vapour deposition (CVD), impregnation by ion exchange and chemical grafting.

1.6.2 Modification procedures

1.6.2.1 Modification by Sol-Gel Technique

The sol-gel technique is used in the preparation and modification of many different membrane types. It has been shown to be an attractive way to produce catalytic membranes. Baron *et al.* [44] prepared a Pd/ γ -Al₂O₃ membrane using sol-gel methods, which displayed a narrow pore size distribution. The palladium was uniformly dispersed in the top layer of the membrane [44]. In the sol-gel process, the noble metal ion-modified boehmite sols were produced by adsorption of the noble metal complexes at the liquid/solid interface of the boehmite sol particles. A thick Pd/ γ -Al₂O₃ membrane could be obtained by a multiple sol-gel process. This catalytic membrane remained intact at elevated temperature.

1.6.2.2 Modification by ion-exchange

Catalytic membranes containing active metals or metal oxides have been produced by impregnation of the support in solutions containing the metal ions [45]. The procedure involves placing or dipping the ceramic support in a solution containing the active metal species, washing with water, drying at ambient temperature and finally heat treatment at elevated temperatures. This could be repeated to give the required percentage of metal loading or thickness.

In the preparation of Pt/ γ -Al₂O₃ by Uzio *et al.* [45], their aim was to study the support effect (compared to the membrane effect) of the modified membrane, the dispersion and morphology of the Pt particles as well as their catalytic surface properties. An ion-exchange method was used. The membrane was an α -Al₂O₃ supported γ -Al₂O₃ layer.

Platinum was only to be deposited in the pores of the γ -Al₂O₃ layer and not in the α -Al₂O₃ layer. During heat treatment oxygen was excluded since the intention was to produce Pt metal and not PtO.

It was found that the depth of Pt loading increased with contact time, which was probably due to the slow diffusion of [PtCl₆]²⁻ from the solution into the porous structure of the membrane [45]. They concluded that further investigation (with respect to contact time, washing, etc.) was required in order to understand the process of ion exchange in the top layer and optimize the loading and dispersion of the Pt catalyst.

1.6.2.3 Modification by grafting

Heterogeneous catalysts have been prepared by anchoring or grafting processes in which stable covalent bonds are formed between the metal complex and the support [46]. Grafting is defined by IUPAC as “deposition involving the formation of a strong (e.g. a covalent) bond between the support and the active element”. “This is achieved through a chemical reaction between functional groups (e.g. hydroxyl groups) on the surface of the support and an appropriately selected inorganic or organometallic compound of the active element”.

Figure 1.3 illustrates the difference in impregnation and grafting methods in the synthesis of molybdenum oxide catalysts [1]. Of these two methods, crystallised MoO₃, was only prepared from the impregnation of the silica support with ammonium heptamolybdate. However, the Mo/SiO₂ was very poorly dispersed. Use of the grafting technique lead to the formation of highly dispersed catalyst.

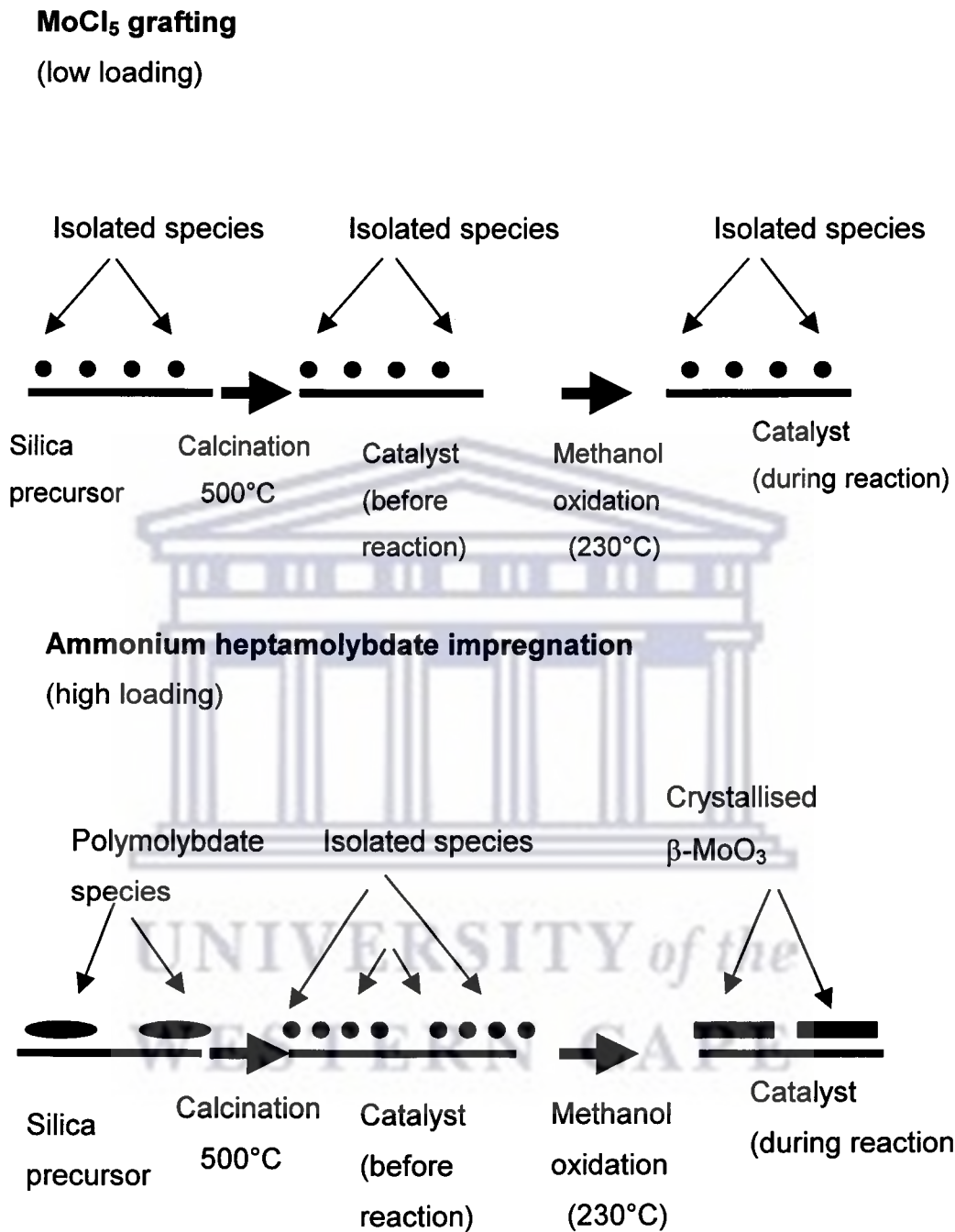


Figure 1.3 A comparison of two different methods of preparation of silica supported molybdenum oxide catalysts.

1.7 PROPERTIES OF CATALYTIC MEMBRANES

1.7.1 Transport mechanisms in porous catalytic membranes

There are six different mechanisms, which may be involved in transport of gases in porous membranes, namely viscous flow (Poiseuille), Knudsen diffusion, surface diffusion, capillary condensation, laminar flow and molecular sieving. For pore sizes greater than 4 nm, Knudsen diffusion is likely to be the dominant transport mechanism at low pressures and elevated temperatures. Gas permeation by Knudsen diffusion varies inversely with the square root of the molecular weight [34]. Knudsen diffusion can limit the selectivity in a reaction/separation system. This problem is overcome by promoting the use of the other modes of transport by surface modifications. Hence, of the six different transport mechanisms that can occur in porous membranes, the mechanism operational at any time is a function of parameters such as pore dimension, temperature, pressure and nature of the membrane and permeating molecules.

A number of these mechanisms can work together in porous membranes making them principally more versatile than dense membranes since they have the capacity to transport more than just oxygen and hydrogen [47]. In their study of mass transfer in composite polymer-zeolite membranes, Baron *et al.* [48] found that the diffusion through the composite membranes could be predicted by using the mass transfer coefficients of pure polymer and pure zeolite and a tortuosity factor, only dependant on the catalyst loading [48].

1.7.2 Particle size

Particle size, especially nanosized particles, has a significant effect on the catalytic activity of the catalytic membrane. The higher activity is a result of the high surface to volume ratio of the particles [49]. In contrast, a study of the effect of particle size on the reactivity of oxygen-adsorbed platinum supported on alumina, revealed that a particle size increase of Pt from 2 to 12 nm resulted in an increase in reactivity of the chemisorbed oxygen [50]. The increase in the activity was due to variations in the strength of the surface platinum-oxygen bond.

1.8 CATALYTIC MEMBRANE REACTORS (CMR)

1.8.1 Catalytic membrane reactor configuration

A review by B. Delmon [20] noted that the selective oxidation of light alkanes in the recent past did not involve spectacular advances in catalytic science, but rather resulted from the use of reactors which had not been used traditionally in catalytic oxidation. There are cases where the type of reactor used is more important than the capability of the catalyst for obtaining high selectivities [20].

The catalytic membrane reactor (CMR) has an advantage over batch reactions in that it is easy to change reaction parameters such as temperature, pressure, flow-rate, reactant concentration, etc. Furthermore, it also allows for the possibility of interchanging the directions of the feed and sweep streams i.e. the feed is directed to the inside of the membrane (axial flow) and a sweep gas is directed to the outside of the membrane (radial flow) or vice versa. The sweep flow could either be concurrent or counter-current to the feed stream. The mode of operation of the CMR as well as the total pressure across the membrane impacts on the selectivity of the reaction [47,51]. In the partial oxidation of methanol on a silver modified membrane, it was found that separating the feed components oxygen and methanol helped to prevent further reaction of the product, formaldehyde [40].

By depositing catalysts on the support surface, or specifically in the pore, their surface area may be effectively increased, enhancing the amount of active surface species available for reaction. This method of immobilising the catalyst on the membrane minimises or eradicates the limitations that are imposed by diffusion on conversion reactions in a packed bed reactor [52]. A membrane prepared in such a manner may be used in a cross flow mode, which is similar to the forced flow mode with the exception being that there may be a very low pressure difference if reactions proceed at atmospheric pressure.

In a study of methanol dehydrogenation, the possible flow patterns that could occur in the catalytic membrane reactor were evaluated and are depicted in Figure 1.4 [47]. The configuration in Figure 1.4(a) led to low residence times which gave the highest

selectivity to formaldehyde and an intermediate value for conversion. The set-up in Figure 1.4(b) led to maximum conversion and minimum selectivity, due to high residence times of the methanol on the catalyst resulting in the formation of side products. The configuration Figure 1.4(c) proved to be the worst as far as conversion is concerned and it gave an intermediate selectivity value. This was thought to be due to the hindrance caused by the diffusional barrier of the support, which the reactants had to pass through in order to reach the catalyst. [47]

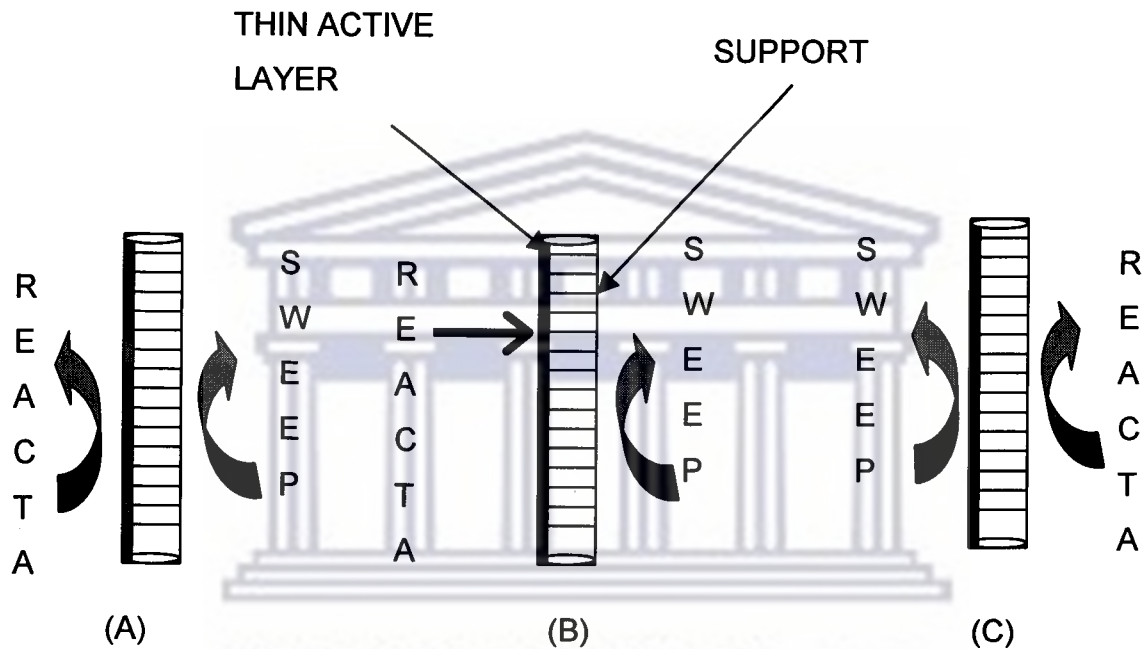


Figure 1.4 Possible flow patterns for CMR on an anisotropic catalytically active membrane: (A) reactant fed at the membrane side; (B) reactant fed forced through the membrane; (C) reactant fed at the support side [47]

1.8.2 Reactions on porous catalytic membranes

Reactions are performed in gas or liquid phase, which either includes or excludes separation. In reactions that do not include separation, the notion of permselectivity is not seriously considered and is at times not relevant [47]. The permselectivity of ceramic membranes is much lower than that of metal-based membranes. However, ceramic membranes are much more permeable and cheaper than metal membranes [47]. In oxidation reactions, higher oxygen fluxes can be obtained on porous ceramic

membrane reactors compared to dense membrane reactors [53]. It was found that a catalyst supported on a porous membrane could be approximately 10 times more active than catalyst pellets, due to the permeation, which provides an enhanced area for the distribution of the catalyst [54].

1.8.3 Chemisorption

Chemisorption is the interaction of gases with solid surfaces when there is a sharing of electrons between the adsorbate molecule and the surface, i.e. when a chemical valency bond is formed. Chemisorption generally occurs on heterogeneous catalysts. It occurs on the active metallic-atom sites on the surface. It is used to determine the density of active sites, also known as the dispersion of the active sites on the surface. Furthermore, it is used to evaluate relative activity of several catalysts in promoting particular chemical reactions. Another application is the determination of catalyst poisoning by impurity deposition. Finally, the degradation of the catalyst with time of use can be established with chemisorption tests [55].

Dispersion information is important in the study of the kinetics of the reaction. The number of active sites gives a relative measure of the activity of a catalyst for different reactions. The dispersion is given as the following ratio:

$$D = N_{\text{Active}} / N_{\text{Total}}$$

Where D is the dispersion, N_{Active} is the number of active metal sites and N_{Total} is the total number of metallic atoms incorporated in the catalyst.

1.9 PHYSICAL CHEMISTRY of ALCOHOL OXIDATION

1.9.1 Thermodynamics

The thermodynamic data related to the possible reaction products of methanol oxidation is shown in Table 1.2 [1]

Table 1.2 Thermodynamic data of the products involved in methanol oxidation (gaseous phase)

Compound	ΔH_f° (298 K) (kJ/mol)	S° (298 K) (J/K.mol)
O ₂	0	205.0
CO	-110.5	197.9
CH ₂ O	-115.9	218.7
CH ₃ OCH ₃	-185.4	266.6
CH ₃ OH	-201.2	237.7
H ₂ O	-214.8	188.7
HCOOCH ₃	-338.9	292.7
HCOOH	-362.8	251.0
(CH ₃ O) ₂ CH ₂	-384.4	335.7
CO ₂	-393.5	213.6

The overall rate of reaction provides significant information about the catalyst surface since it depends on the concentration of the active sites.

1.9.2 Reaction Kinetics

The methanol oxidation can be considered from a kinetic point of view as a series of successive surface reactions occurring from adsorbed intermediates. The Langmuir-Hinshelwood mechanism is widely used to describe the kinetics of surface catalysed

reactions. Under reaction conditions oxygen is adsorbed and desorbed from the surface. This is based on the assumption that the rate of oxygen adsorption is very small. Naumov *et al.* used the thermokinetic method in the study of the kinetics of the complete oxidation of ethanol on a copper–chromium oxide catalyst [56]. The order of the reaction was 0.82 with respect to ethanol and the activation energy was 157 kJ/mol, which is higher than that for platinum catalysts (125.8 kJ/mol). Ling *et al.* considered the catalytic behaviour and electrical conductivity of a LaNiO₃ catalyst in ethanol oxidation and found that in flowing air, the oxidation rate was zero order with respect to oxygen and first order with respect to ethanol [57]. The zero order of oxygen is due to it being in excess. The rate of reaction is given in equation 1.2

$$r = k[\text{O}_2]^0[\text{ethanol}]^1 \quad (1.2)$$

and the resistance is given in equation 1.3

$$R = R_0(1 + \alpha[\text{ethanol}]^\beta) \quad (1.3)$$

Where α and β are temperature dependant constants



UNIVERSITY of the
WESTERN CAPE

Chapter 2

Objectives of Research

The oxidation of the lower primary alcohols occurs at high temperatures and pressures in industrial fine chemical production. Hence, a large proportion of operating costs is incurred by the stringent reaction conditions. The main task of this research was the oxidation of methanol and ethanol under mild conditions using a catalytic membrane reactor (CMR). The application of CMR's have shown that it is possible to enhance conversion and selectivity and to explore unconventional catalytic properties [42]

The objectives of this research were:

1. to prepare active membrane supported catalysts for partial oxidation of alcohols. Suitable catalysts for alcohol oxidation were chosen from literature such as platinum polysilazane polymer complex and platinum oxide. These catalysts were to be synthesised and supported on a tubular ceramic membrane.
2. to use different methods of modifying a ceramic membrane such as ion exchange and chemical grafting.
3. to characterise the membrane-supported catalysts with respect to morphology, surface area, pore size, pore volume and thermal stability.
4. to design and assemble a complete catalytic membrane reactor system in which the alcohol oxidation reactions were to be performed

-
5. to perform the partial oxidation of alcohols under mild conditions with high conversion and selectivity towards methyl formate in methanol oxidation and acetaldehyde in ethanol oxidation
 6. to optimise reaction conditions, by determining the best reactor configuration and experimental parameters



Chapter 3

Experimental Methods

3.1 INTRODUCTION

The porous ceramic membrane supports which were used in this study, had the following chemical composition:

aluminium oxide	Al_2O_3	- 70%
zirconium dioxide	ZrO_2	- 29%
yttrium oxide	Y_2O_3	- 1%

It was essentially a porous yttrium stabilised alumina-zirconia membrane in tubular form. It had an average pore size of $0.21\mu\text{m}$, porosity of about 45% and a surface area of $2.4\text{ m}^2/\text{g}$. The chemical composition of the internal (inner) and external (outer) surfaces are different. The internal surface of the tubular ceramic was rich in zirconium dioxide while the external surface contained more aluminium oxide. This difference in chemical composition corresponded to the fact that the internal surface had a higher density than the external surface. These differences were a result of the method, namely slip-cast moulding, in which the ceramic membranes were made.

The porous ceramic membrane was used as a support for the catalyst, i.e. it was not used as a permselective membrane. The support however did offer the possibility of separating the path of the introduction of the reactants i.e. it could be used for the controlled dosing of one of the reactants as depicted in Figure 1.3.

3.2 REAGENTS USED

The source and purity of reagents that were used in this study are given in Table 3.1.

Table 3.1 Reagents used in the preparation of the catalysts and in reaction studies

Reagents	Supplier	Purity
Acetic acid	Aldrich	99.99+%
Acetaldehyde	Riedel-de Haën	99.5%
Ammonia gas	Afrox	Industrial grade
Ethanol	Aldrich	99.5%
Ethanol	Fluka	Standard for GC
Ethyl acetate	Supelco	Standard for GC
Formaldehyde (in water)	Supelco	Standard for GC
Hexachloroplatinic acid	Next Chimica	99.95%
Magnesium acetate	Merck	99%
Magnesium oxide (light)	Aldrich	99%
Methanol	Merck	99.5%
Methyl formate	Riedel-de Haën	98%
Silicon tetrachloride	Aldrich	99%

UNIVERSITY of the
WESTERN CAPE

3.3 PREPARATION OF CERAMIC MEMBRANE SUPPORTS

The porous, tubular supports were cut to the desired length to fit the stainless steel reactor (102mm). Prior to use the supports were rinsed in deionised water and dried overnight at ambient temperature. The dried membrane supports were subsequently heated in an oven for 1hr at 120°C and were allowed to cool to room temperature before being weighed.

3.3.1 Preparation of solvents

The solvent, hexane, was dried by refluxing it for 48 hrs over sodium wire under a flow of nitrogen and subsequently stored under nitrogen over molecular sieve 3Å. The hexane was degassed with nitrogen for 5 minutes before it was used. Ethanol was dried over Na₂SO₄ by allowing it to stand for a few days. It was essential to dry the solvents since the product of the first step (Figure 2.1) of the synthesis of the platinum polysilazane complex was hygroscopic, i.e. moisture could react with the nitrogen resulting in the release of ammonia.

3.3.2 Preparation of magnesium oxide supported platinum-polysilazane complex catalyst (MgO-Si-N-Pt)

The catalyst, magnesium oxide supported platinum polysilazane polymer complex, was chosen from literature since it had displayed high activity in the partial oxidation of the lower primary alcohols in a conventional batch reaction [18]. This catalyst was to be prepared according to the procedure given by the authors and subsequently supported on a ceramic membrane. The preparation of the platinum-polysilazane complex was done according to the procedure as described by Jiang *et.al.* [18].

3.3.2.1 Step 1: Preparation of the unsupported intermediate (MgO-Si-N)

Hexane 150 ml and 4 g MgO (light), were placed in a 500 ml 3-necked round bottom flask equipped with a stirrer, a gas inlet tube and gas outlet tube. To ensure that the ammonia gas was dry, a moisture trap was inserted between the reaction vessel and the gas cylinder. Silicon tetrachloride 10g was added slowly. The mixture was stirred under

nitrogen for 20 minutes and then ammonia gas was bubbled through the mixture for 10 h until the reaction mixture became alkaline. During the reaction 60 ml of hexane was added slowly as the reaction mixture became viscous.

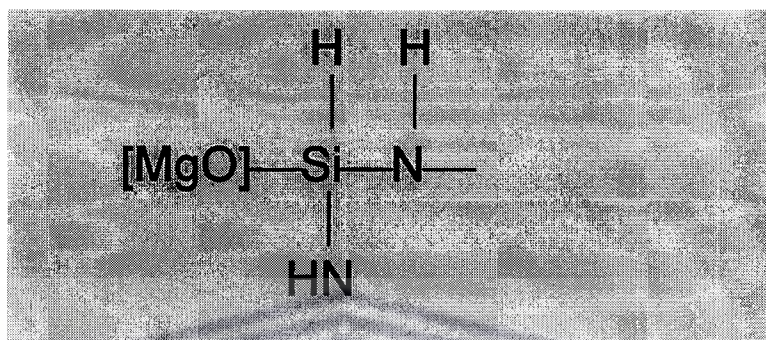


Figure 3.1 (MgO-Si-N) Expected product of the first step in the synthesis of (MgO-Si-N-Pt)

The product was filtered and dried and then it was heated at 450°C for 2 h in a furnace to sublime the by-product. A fine white powder was obtained. The yield was 87.5%.

3.3.2.2 Step 2: Preparation of unsupported (MgO-Si-N-Pt)

Hexachloroplatinic acid (H_2PtCl_6) 0.102 g, was added under nitrogen to 4 g of the intermediate prepared in step 1 and 15 ml of ethanol in a 50 ml 3-neck round bottom flask equipped with a stirrer, a reflux condenser and a gas inlet tube. The mixture was refluxed under a nitrogen atmosphere for 21 h. The white solid powder became black and the pale yellow solution became colourless during the reaction. The product was filtered and dried at 100°C for 2h. The final product was a fine grey powder, similar to that prepared by Jiang *et.al* [18]. The yield was 62.5%.

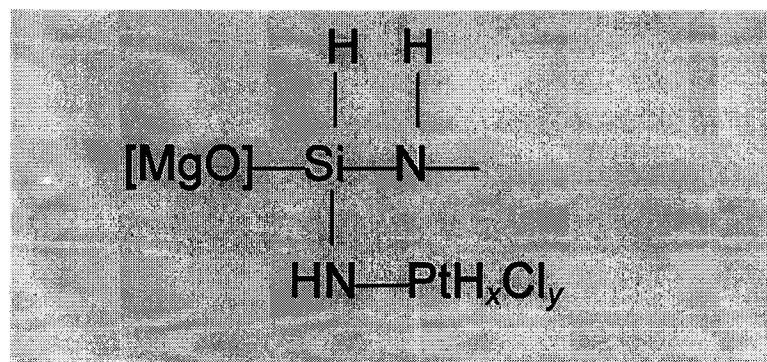


Figure 3.2 Expected structure of Pt-Polysilazane

3.3.3 Preparation of magnesium oxide modified ceramic membrane

The clean pre-weighed membrane supports were placed in a solution of 2M magnesium acetate and allowed to stand overnight and then air-dried at ambient temperature for 24 hrs. The dried supports were heated in a furnace at 800°C for 1 hr. The heating rate was 8.3 °C/min.

3.3.4 Preparation of magnesium oxide supported platinum-polysilazane complex catalyst on ceramic membrane support

3.3.4.1 Step 1: Preparation of the supported intermediate (+MgO-Si-N)

This method is a modification of the procedure in section 3.3.2 since the catalyst could not be successfully reproduced according to the reported procedure (see chapter 4). The ceramic support was modified with magnesium oxide according to the procedure in section 3.3.3. The MgO modified support was placed horizontally in a 1000ml three-necked round bottom flask, which was connected to gas inlet and outlet tubes. A pressure equalising funnel was attached on top as depicted in Figure 3.3. Dry hexane, 300 ml, was added, in a manner that ensured that the tubular support was completely covered by the hexane. Silicon tetrachloride 10g (SiCl_4) was added slowly, with gentle stirring of the hexane, in a nitrogen atmosphere. After stirring for 20 minutes, ammonia gas was introduced into the flask. The reaction proceeded for about 10 hrs during which about 60 ml of hexane was added drop wise from the pressure-equalising funnel, to

prevent the reaction mixture from becoming too viscous. Thereafter, the modified ceramic support was removed from the flask and heated at 500°C in a furnace for 2hrs to sublime the by-product, namely NH₄Cl. The weight gained was 0.42%.

3.3.4.2 Step 2: Preparation of supported (+MgO-Si-N-Pt)

In order to introduce Pt onto the support, the MgO-Si-N modified support that was prepared in step 1, was placed in a tubular glass reaction vessel to which ethanol, 50ml, and 0.102g of hexachloroplatinic acid (H₂PtCl₆) was added. The reaction was refluxed under nitrogen for 21 hrs. The yellow solution turned colourless. The membrane was dried in an oven at 100°C for one hour. The final membrane containing Pt had a light grey colour.

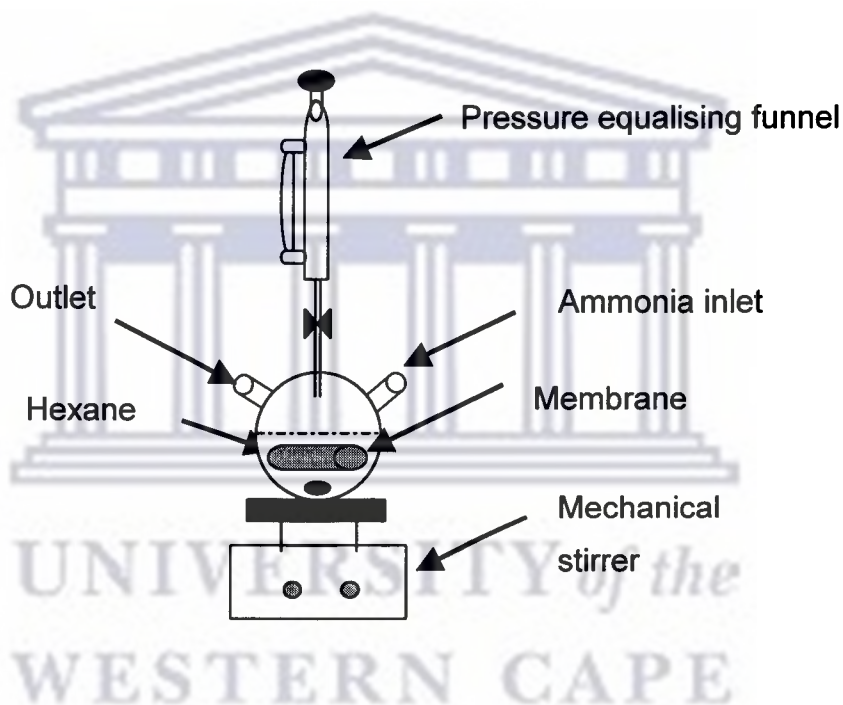


Figure 3.3 Reaction set up for the first step in the preparation of platinum-polysilazane complex catalyst

3.3.5 Modification by impregnation with chloroplatinic acid (H₂PtCl₆ · 6H₂O)- Ion exchange method

Both the blank ceramic membrane and the magnesium oxide-modified membranes were immersed for various times in either 0.02M or 0.05M aqueous solutions of chloroplatinic acid. The chloroplatinic acid solutions had platinum metal concentrations equivalent to

4g/l and 10g/l respectively. A third chloroplatinic acid solution was prepared with a Pt metal concentration of 0.1g/l. The immersion time was varied between 4, 18 and 30 hrs at ambient temperature in all cases. The impregnated membrane supports were air-dried at ambient temperature for 24 hrs. The dried supports were then calcined in a furnace at 350°C for 10 min and at 450°C for 1 hr [14]. The heating rate was 8.3°C/min. The modified membrane supports were allowed to cool to room temperature and subsequently weighed. The weight gained varied according to the length of the immersion time and concentration of the chloroplatinic acid solution (see Table 4.4). The procedure was only performed once i.e. the ceramic supports did not undergo repeated impregnation treatments as was done by Santamaria *et.al.* [58].



3.4 CHARACTERIZATION

3.4.1 X-ray Photoelectron Spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) was performed on a Fisons XPS analyser at the Flemish Institute for Technological Research (VITO). This technique is used to measure the binding energy between the inner core electrons and the nucleus of an atom. The binding energy accurately reflects the chemical environment of an atom.

Conditions

Flood gun	2.4 eV
Resolution	4
Data points	801
Scans, Time	25

3.4.2 Elemental analysis (CNHS)

The fine grey unsupported platinum-polysilazane catalyst was analysed on a NA 1500 Nitrogen Analyser from Carlo Erba Instruments, in order to determine the presence and amount of nitrogen in the catalyst. The analyses were done in duplicate on 0.001g samples of the catalyst.

3.4.3 Energy dispersive X-ray spectroscopy (EDS)

The surface of the blank membrane support was analysed in order to compare the differences in the surface composition after it had been sequentially modified. The EDS attachment to the SEM was a Kevex EDS, and it was used to evaluate the elemental composition of the sample qualitatively and quantitatively. The relative abundance of the elements present in the catalyst is given as mass/weight percentage.

3.4.4 Scanning electron microscopy (SEM)

A Leo S440 analytical scanning electron microscope, University of Cape Town, was used to determine the morphology of the surface of the catalyst samples. The samples were mounted on aluminium stubs and coated with a conductive carbon layer. The operating parameters were as follows:

Accelerating voltage	15 keV
Beam current	2000.0 picoAmps
Tilt angle	0.0°
Resolution	7-9
Working distance	25.0 mm
Take off angle	35.0°
Solid angle *beam current	12.2

3.4.5 Simultaneous thermal analysis

The thermal stability of the catalysts was evaluated on a Rheometric Scientific Simultaneous Thermal Analyser (STA), which was controlled via STA 1500 RSI Orchestrator software. The STA performed both thermogravimetric and differential scanning calorimetric analyses simultaneously. The advantage of using this instrument is that both analyses are carried out at the same time, assuring identical conditions. The samples were evaluated in the temperature range, from ambient to 450°C at a ramp rate of 10°C/min under flowing nitrogen.

3.4.6 Nitrogen adsorption porosimetry

The pore size distribution, pore volume and surface area of the unmodified and modified membranes were evaluated on a nitrogen adsorption porosimeter (Micromeritics ASAP 2100). The samples were accurately weighed and subsequently degassed at 120°C for two hours to remove moisture and then further degassed at 260°C until a zero reading was registered on the vacuum gauge. The analyses were performed at liquid nitrogen temperature (-196°C).

3.4.7 Temperature programmed techniques

Temperature programmed reactions were performed on the AutoChem model 2910 (Micromeritics). Precise thermocouple placement and accurate sample temperature control were critical in analysing the catalysts. The reaction temperature must be correlated with uptake or release of the absorptive gas by the sample.

The catalysts were analysed by temperature-programmed reactions in the following sequence:

1. Temperature programmed reduction
2. Temperature programmed oxidation
3. Temperature programmed desorption

All the catalysts were heated to remove water prior to testing.

3.4.7.1 Temperature Programmed Reduction (TPR)

In temperature-programmed reduction (TPR), a reducible catalyst or catalyst precursor is treated with a flow of reducing gas mixture (normally a few volume % of H₂ in argon) while the temperature is ramped linearly. The rate of reduction is monitored continuously by measuring the H₂ content at the outlet of the reactor using a TCD detector in comparison to a reference gas. The total amount of H₂ adsorbed is used to calculate the degree of reduction and hence the average oxidation state of the reduced solid material. The kinetic parameters of the reduction process may also be determined if the correct model is available.

Conditions

Mass of sample	: 0.5 - 1.0 g
Temperature range	: 25 - 110 / 25 - 450°C
Temperature gradient	: 5 - 10°C
Flow rate	: 50 ml/min
Reductant gas	: 10%H ₂ in Ar

3.4.7.2 Temperature Programmed Oxidation (TPO)

Temperature programmed oxidation can be applied to determine the redox behaviour of catalysts especially when it is applied to cyclic TPR/TPO experiments. It could also be used to determine the temperature at which maximum oxygen consumption occurs.

The catalysts sample was exposed to a flow of 10% O₂/He at a flow rate of 50ml/min and the temperature was ramped from 40°C to 450°C at a rate of 5°C/min.

Conditions

Mass of sample	: 0.5 - 1.0 g
Temperature range	: 25 - 110 / 25 - 450°C
Temperature gradient	: 5 - 10°C
Flow rate	: 50 ml/min
Oxidant gas	: 10.2%O ₂ in He

3.4.7.3 Temperature Programmed Desorption (TPD)

In temperature programmed desorption (TPD) experiments a catalyst is pre-treated and equilibrated with an adsorbing gas or vapour under controlled conditions and then subjected to a linear temperature ramp. It is possible to determine the total amount of gas or vapour that was adsorbed, including the kinetic parameters from the experimental data. This experiment was performed directly sequentially to the TPO and the desorbing oxygen was measured.

Conditions

Mass of sample	: 0.5 - 1.0 g
Temperature range	: 25 - 110 / 25 - 450°C
Temperature gradient	: 5 - 10°C
Flow rate	: 50 ml/min
In a flow of helium	

3.5 CATALYTIC MEMBRANE REACTOR (CMR) SET-UP

The membrane-supported catalyst was mounted in a stainless steel reactor, which thus formed a catalytic membrane reactor (CMR) as depicted in Figure 3.4. The connecting lines, which consisted of 1/8th inch diameter stainless steel tubing, were all connected via swagelock® fittings.

In the CMR set-up, heating tapes were wrapped around all stainless steel tubing leaving the reactor and were controlled by temperature controllers (Gefran 500). The reactor temperature was controlled separately from the tubing. A thermocouple was placed in contact with the external wall of the reactor just beneath the heating tape and was used to control the temperature of the reactor. Another thermocouple (1/16th inch diam.) was positioned half way along the inside of the catalytic support and was used for monitoring the reactor temperature. The sampling valve and the tubing leading into the injector were also thermostatically controlled. In total there were four temperature controllers and one temperature monitor which had the capacity of monitoring three heated areas simultaneously. The temperature of the reaction zone and the lines leading into the GC were monitored by the temperature monitor.

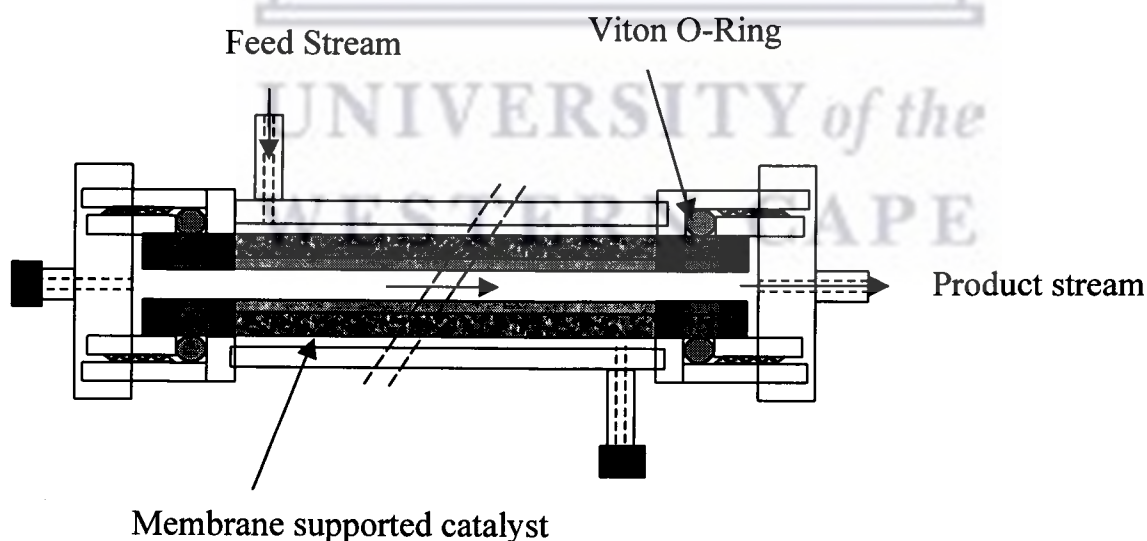


Figure 3.4 Schematic of the catalytic membrane reactor

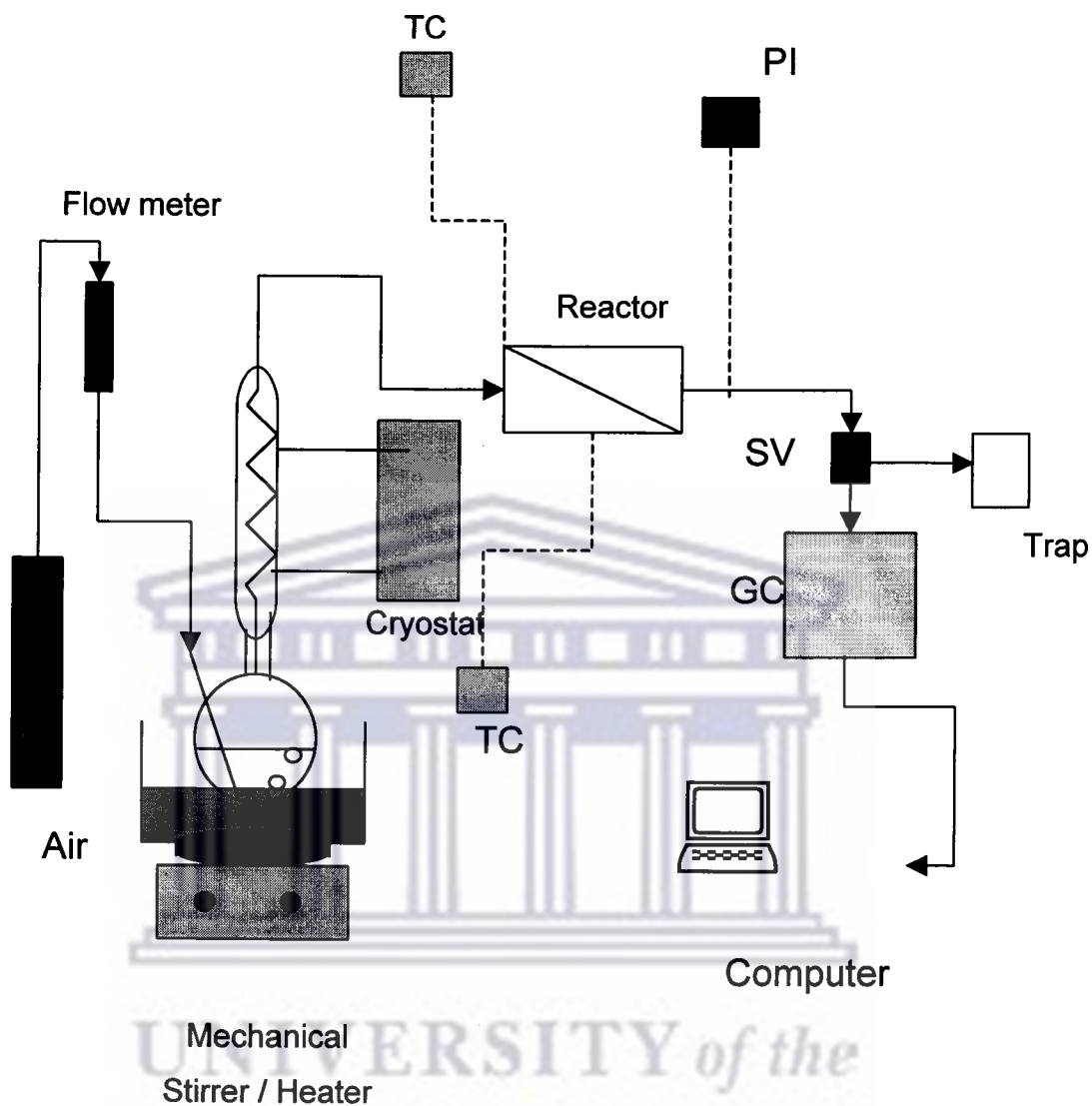


Figure 3.5 Reactor set-up where: (TC)- temperature controllers; (PI)-pressure indicator; (SV) sampling valve and (GC) gas chromatograph

The feed stream consisted of 8% and 4% alcohol in air for methanol and ethanol respectively. The flow rate of the air was 10ml/min, which bubbled through the alcohol in a vaporiser as depicted in Figure 3.4. Hence the air performed a dual role in the reaction i.e. it was the carrier gas as well as the oxidant. The vaporiser or "saturator" consisted of a round bottom flask, which was immersed in a heated oil bath (60-65°C). The round bottom flask had an inlet through which air flowed and bubbled through the

alcohol. Attached to the round bottom flask was a water-cooled condenser. An ice cooled circulating water bath kept the temperature of the water in the condenser relatively constant. The final composition of the feed was calculated from the partial pressure of the alcohol according to the temperature of the circulating water through the condenser. The value of the vapour pressure, at a particular temperature, was read from the curves shown in Appendix D and calculated according to equation (A1) given in Appendix A.

The feed stream entered the reactor on the outer side of the tubular support and flowed through the support in a radial direction, thereby forcing the reactants through the membrane and ensuring maximum contact time with the catalyst. This method gave rise to the highest conversion rate in the work done by Zaspalis *et. al.*[40].

As can be seen in the schematic representation of the reactor set-up Figure 3.4, the gas chromatograph was linked online to the reactor via heated lines and a heated sampling valve. The gas chromatograph used was a Hewlett Packard model HP5890. The column used was a 15m × 0.53mm megabore column from J&W Scientific with liquid phase, GS-Q. A 50µl sampling loop was used for injections, which were electronically controlled by Borwin® software. The Borwin® software was also used for data capturing and integration of the separated peaks. The GC settings and flow rates are shown in Table 3.2

Table 3.2 HP5890 GC parameters

GC Parameter	Setting
Helium Flow rate	30 ml/min
Hydrogen Flow rate	30 ml/min
Air Flow rate	300 ml/min
Column Temperature	100°C
Injector Temperature	180°C
Detector Temperature	200°C

The column gave a good separation of the products and reactants at the isothermal temperature of 100°C.

Confirmation of the products was done on GC-MS, Finnigan MAT GCQ, which was fitted with a Restek column, RTX5MS and had a helium flow-rate of 40 ml/min.

3.5.1 Calibration curves

A calibration curve, representing peak area vs concentration, was produced for each of the major products and for the alcohols. The concentration of the organic substance was a function of the vapour pressure, which in turn was a function of the temperature of the cooling column (Figure 3.5). Different concentrations were achieved by varying the vapour pressure of the reactant or product by controlling the temperature of the water flowing through the condenser. The vapour pressure versus temperature curves was obtained from data in Perry's Chemical Engineers' Handbook [59].

The set up for the production of the calibration curves was identical to the reactor set up in Figure 3.5, except that the reactor was bypassed in this case. Thus the feed flow-rate, the temperature of the tubing and the settings of the GC were the same as the settings for the reaction conditions.

UNIVERSITY *of the*
WESTERN CAPE

Chapter 4

Catalyst Preparation and Characterisation

4.1 INTRODUCTION

Preparation conditions are known to have an effect upon the activity of the catalyst. Ivanov *et al.* prepared Mn-Mo-O catalysts with different Mo/Mn ratios via a precipitation method and studied them in the oxidation of methanol [60]. It was found that samples with the lowest MnO₂ content possess the highest selectivity towards formaldehyde [12]. The activity and selectivity of certain catalytic membranes increases with an increase in the content of the catalyst deposited on the membrane. Zaspalis *et al.* [40] found that an increase in the silver content in the top layer of the membrane caused an increase in selectivity to formaldehyde in the oxidation of methanol. This could be attributed to the increase in surface area of active silver particles.

In a review, Tatibouët compared [1] the catalytic activity of Mo/SiO₂, which was prepared via two different methods namely chemical grafting and impregnation. It was found that the Mo/SiO₂ prepared by the chemical grafting method was selective towards methyl formate while Mo/SiO₂ prepared by impregnation was selective towards formaldehyde. The latter method produced large variations in catalytic behaviour, which possibly indicated a lack of reproducibility with this preparation method.

Hence, it is apparent that when a target molecule is sought, an important parameter in the design of the system is the choice of catalyst and more importantly the method in which it is prepared.

4.2 CATALYST PREPARATION

4.2.1 Preparation of magnesium oxide modified ceramic membrane

In this study the α -Al₂O₃ support was modified with an aqueous solution of magnesium acetate {Mg(O₂CCH₃)₂}. The membranes were placed in a 2M solution of magnesium acetate overnight, dried at ambient temperature for 24h and calcined at 800°C for 2h. The method that was used in this study differs significantly from the method used by Zaspalis [61]. Zaspalis used the “reservoir” method to modify supported γ -Al₂O₃ membranes with magnesia from an aqueous solution of Mg(NO₃)₂·6H₂O and urea. In the reservoir method, the support (α -Al₂O₃) absorbs a larger amount of impregnation solution than the top layer (γ -Al₂O₃). During the drying step, the support supplies the top layer with impregnation solution [61].

4.2.2 Composition of magnesium oxide supported catalyst (MgO-Si-O -Pt)

In the catalyst described by Jiang *et al.* [18], nitrogen played an integral role in the structure and chemistry of the catalyst. From the XPS results in Table 1.1, Jiang *et al.* were able to conclude that there was bonding between the nitrogen atoms and the Pt atom, as depicted in Figure 3.2.

Firstly, an attempt was made to prepare the catalyst according to the procedure (section 3.3.2) given by Jiang *et al.* [18]. The catalyst that was prepared in this study, had the same physical appearance as that reported by the authors, namely, a light grey powder. The catalyst was analysed on the Elemental (C,N,H,O) analyser and the X-ray photoelectric spectroscopy (XPS) analyser. However, analytical results obtained from both these techniques revealed that nitrogen was not present in the catalyst (see Tables 4.2 and 4.3). Hence, the catalyst that was prepared was not the same as that prepared by Jiang *et al.* Silazanes are in general volatile and extremely sensitive to hydrolysis. The hydrolytic reaction of silazanes form ammonia and silanol and/or siloxane [62].

A proposed structure of the catalyst that was prepared is given in Figure 4.1 and it is based on the data obtained from the analytical instruments mentioned above and from

the methanol surface-probe reaction. The proposed catalyst could be called magnesium oxide supported platinum-polysilanol complex (MgO-Si-O-Pt). In the preparation of the catalyst, all possible precautions were taken to prevent the loss of nitrogen, however, all attempts to reproduce the catalyst as described by Jiang *et.al.* [18], were unsuccessful. This could be ascribed to a number of reasons, namely that:

- despite the stringent drying procedures that were performed, the solvent and reactants may not have been completely dry
- the product could have hydrolysed during filtration or calcination after completion of the first part of the synthesis

After several unsuccessful attempts to reproduce the catalyst as described by Jiang *et.al.* [18], a modification of the synthesis procedure was attempted. The catalyst was prepared directly on the membrane support as described in section 3.3.4 and depicted in Figure 3.3. The advantage of this method was that the membrane-supported catalyst was prepared in one step. Hence the subsequent step of supporting the catalyst onto the membrane was unnecessary. This modified method of producing the catalyst did not result in nitrogen being present in the catalyst structure.

This catalyst, MgO-Si-O-Pt, was tested in the catalytic membrane reactor (CMR) system and it displayed high activity in the oxidation of the lower primary alcohols, see section 5.3. To understand why this catalyst was active despite not having the same structure as the target catalyst, the preparation of a series of catalysts was undertaken. In this series, the blank membrane support was modified sequentially, and at each successive step, the activity of the modified support was evaluated in the oxidation of alcohols using the CMR. The catalysts were to be prepared according to the series in Table 4.1

Table 4.1 Step by step modification of blank support

Method Number	Modification
1	Blank Support + MgO
2	Blank Support + MgO + SiCl ₄
3	Blank Support + MgO + SiCl ₄ + H ₂ PtCl _x
4	Blank Support + MgO + H ₂ PtCl _x
5	Blank Support + H ₂ PtCl _x

In method number 2, after modification with SiCl₄, the silica that was deposited on the surface cracked and peeled off in the form of scales. As a result it meant that method number 3 could not be used. Hence, only the modified membranes that were prepared using methods 1, 4 and 5 could be tested for their activity in the oxidation of the alcohols.

There was a high atom % of oxygen present in the catalyst as can be seen in the XPS results in Table 4.2, and EDS results in Table 4.6. Based on the XPS data, the % atom and elemental analysis in Table 4.3, a proposed structure of the actual catalyst morphology is shown in Figure 4.1. Further information to support the proposed structure of the catalyst is found in the products formed in the methanol oxidation reaction. The major product of methanol oxidation reactions on this catalyst was methyl formate (see section 5.3), which according to Arora *et al.* [3] classifies this catalyst as having redox sites. Redox sites are capable of being reduced and oxidised. The proposed catalyst has two active centres, namely a weak acid centre (Si—OH) and an oxidising centre (O—Pt). Initially, formaldehyde is formed at the weak acid site which reacts further with methanol (activated by the Pt site) to form methyl formate (see figure 5.5).

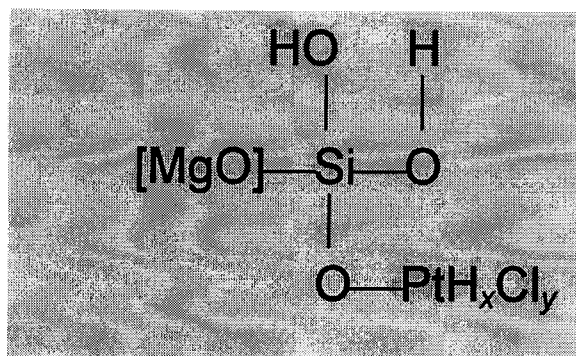


Figure 4.1 Proposed catalyst structure (MgO-Si-O-Pt)

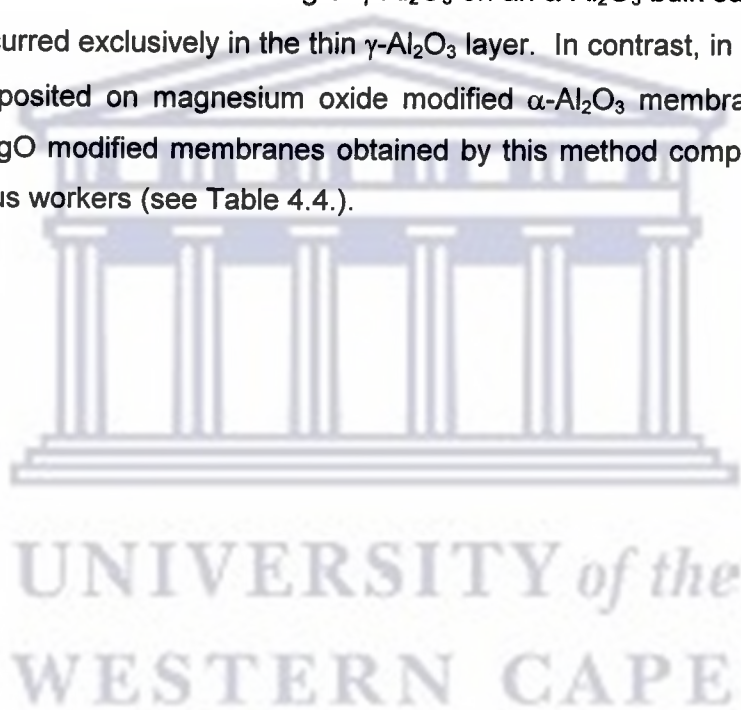
4.2.3 Preparation of magnesium oxide supported platinum-polysilanol complex catalyst on ceramic membrane support

In this procedure, which is described in section 3.3.4, the catalyst was prepared and supported onto a ceramic membrane in a single step and this constituted a modification of the procedure given by Jiang *et al.* [18]. The membrane-supported catalyst had a light grey colour. The catalyst was not uniformly distributed over the surface of the membrane support, since dark patches were randomly dispersed on the surface, as could be seen by SEM (Figures B4 and B5).

Although the ceramic membrane was only used as a support for the catalysts and not as a separator, it played a significant role in the catalytic reactions. Due to its porous structure the reactants and products moved via a tortuous path through the membrane. This increased the contact surface area for the reactants, which may be directly related to an increase in conversion. Furthermore, the ceramic support used in this study contained ZrO_2 (section 3.1), which has been reported to act as a promoter [42]. Hence, the presence of zirconia with alumina may have led to an improvement in the activity, suggesting that a synergy existed between the mixed oxides present in the support and the catalyst. The blank membrane, on its own, was regarded not to be active in the oxidation of the alcohols since it displayed a conversion of less than 1%. This observation supports the suggestion of the existence of a synergy between the mixed oxides and the catalyst.

4.2.4 Preparation of platinum (Pt) modified membranes by ion-exchange method

The ion exchange method was used to prepare the platinum (Pt) modified membranes. The membranes were immersed in different solutions of aqueous chloroplatinic acid, air-dried at ambient temperature, followed by calcination. In this method the membranes were not washed with water to remove excess platinum acid solution. This could have resulted in a higher weight % of Pt loading on the membrane support. Santamaria et al. [58] and Uzio et al. [45] used a similar method. Uzio et al. used a 0.1g/l platinum concentration solution of chloroplatinic acid and Santamaria et al. used a 0.5g/l solution. Both groups used a membrane consisting of γ -Al₂O₃ on an α -Al₂O₃ bulk support. The Pt metal loading occurred exclusively in the thin γ -Al₂O₃ layer. In contrast, in this study, the Pt metal was deposited on magnesium oxide modified α -Al₂O₃ membranes. The Pt loading on the MgO modified membranes obtained by this method compares well with that of the previous workers (see Table 4.4.).



4.3 CHARACTERISATION

The catalysts were characterised in order to establish their physical and chemical properties and to relate this information to their activity in the oxidation of the lower primary alcohols.

4.3.1 XPS results

The XPS data of the unsupported catalyst prepared in this study (MgO-Si-O-Pt) is given in Table 4.2, and it is compared with the data that was obtained by Jiang *et al.* [18].

Comparing the binding energies of the catalyst prepared in this study with that prepared by Jiang *et al.* (Table 4.2), it can be seen that there was a difference of 1.3, 2.4 and 1.7 eV in the binding energies of Pt(4f), Si(2p), and O(1s) respectively. This meant that these atoms were co-ordinated differently in the two catalysts. In this study the XPS analysis was not done on the intermediate product MgO-Si-O. This information would support the proposed catalyst structure (Figure 4.1).

Table 4.2 Comparison of XPS Data for unsupported MgO-Si-O-Pt complex catalyst

XPS peak	Binding Energy (eV)		
	*GM 42	Y.Y Jiang <i>et al.</i>	%Atom
Pt(4f)	70.9	72.4	0.19
C(1s)	284.3	—	14.74
Si(2p)	101.9	104.3	14.22
Mg(2p)	49.5	—	18.38
O(1s)	531.7	533.4	47.84
Cl(2p)	198.3	199.2	5.33
N(1s)	—	401.9	

* Unsupported MgO-Si-O-Pt catalyst

4.3.2. Elemental analysis (CHNS)

The elemental analysis was done in duplicate in order to determine the presence of nitrogen in the catalyst and the results are given in Table 4.3

Table 4.3 Results of elemental analysis on unsupported catalyst and intermediate.

MgO-Si-O (unsupported) intermediate		
Element	atom %	atom %
C	0.14	0.13
H	—	—
N	—	—
S	—	—
MgO-Si-O-Pt (unsupported) catalyst		
Element	atom %	atom %
C	1.83	1.90
H	1.34	1.26
N	—	—
S	—	—

Where:

MgO-Si-O was the product of the first step in the preparation of the magnesium oxide supported platinum polysiloxane complex catalyst.

and

MgO-Si-O-Pt was the final product in the preparation of the magnesium oxide supported platinum polysiloxane complex catalyst.

Nitrogen was not found in either the intermediate or the final catalyst structure, according to the results of elemental analysis, which is given in Table 4.3. There was a small percentage of carbon and hydrogen, which could be due to adsorbed CO₂ and water.

4.3.3. Pt-weight percentage gain of the modified membranes

The effect of immersion time and hexachloroplatinic acid concentration on the Pt-weight % gain of the modified membranes was established (Table 4.4). These membrane-

supported catalysts were impregnated via the ion-exchange method as described in sections 3.3.5 and 4.2.4. The results of the modification by impregnation are given in Table 4.4

Table 4.4 Comparison of the Pt loading on the membranes with respect to immersion time and concentration

Blank or unmodified membrane			
Pt Conc.	0.1g/l	4g/l	10g/l
time	wt%	wt%	wt%
4hr	neg	0.06	0.17
18hr	neg	0.05	0.12

MgO modified membrane			
Pt Conc.	0.1g/l	4g/l	10g/l
time	wt%	wt%	wt%
4hr	0.05	0.23	0.42
18hr	0.16	0.12	0.32

The above results compare well with the work of Santamaria *et al.* who obtained similar results as shown in Table 4.5

Table 4.5 Results obtained by Santamaria *et al.* [58]

Pt Conc.	0.5g/l
ranges	wt%
From	0.016
To	0.45

*%w refers to the percentage change in weight of the membrane after it had been modified with Pt metal

Having compared the weight % of Pt loading on the membranes (Table 4.4), it can be seen that the concentration of the hexachloroplatinic acid solution had an effect on the amount of Pt loading, i.e. the higher the concentration the higher the loading. However, from comparison of the immersion times, it appeared that there was a saturation point that occurred after about 4h and that this time was sufficient to obtain an appreciable Pt loading. Uzio *et al.* [45], found that the platinum loading increased three fold by comparing an immersion period of 4 hrs to that of 1h. Furthermore, in this study,

restriction of the location of the Pt was not aimed at, compared to the membranes prepared by Uzio *et al.*, where the Pt was selectively deposited only in the γ -Al₂O₃ layer of the membrane. Pt was present on both inner and outer surfaces of the ceramic tubular support, which was substantiated by EDS analyses, shown in Table 4.6. It is evident from Table 4.6 that the amount of Pt deposited on the membrane was significantly less than 1% of the total weight of the membrane supported catalyst.

4.3.4 Energy dispersive X-ray spectroscopy (EDS)

The elemental analysis of the surface of the catalysts obtained by energy dispersive X-ray spectroscopy (EDS) is shown in Table 4.6

Table 4.6 Surface elemental composition as determined by EDS

No.	Catalyst		Atomic % of elements present in surface						
			O	Al	Zr	Mg	Si	Pt	Cl
1	Blank	Inner	42.72	39.29	17.99				
		Outer	42.07	39.87	20.11				
2	Blank+Pt(4g/l)		41.56	46.43	12.01			<i>Not detected</i>	
		Outer	41.35	47.14	11.51				
		Edge	46.66	37.73	15.61				
3	Blank+MgO	inner	39.94	46.13	12.38	1.46			
		Outer	42.91	42.18	13.01	1.90			
4	+MgO+Pt(4g/l)		40.83	39.71	19.45				
		Outer	54.13	40.66		1.21	0.60	3.41	
		Edge	35.90	52.89	11.21				
5	+MgO-Si-O-Pt		31.05	15.08	33.74	1.01	2.52	16.60	
		Outer	46.75	18.62	18.26	0.96	2.75	12.66	

Unsupported powdered catalyst

6	MgO-Si-O	40.68			36.76	3.93		17.33
7	MgO-Si-O-Pt	40.68			40.13	5.60	5.17	8.42

The EDS results of the atomic % of the elements present in the support and those elements present as a result of modification show that the values differ from membrane to membrane. This inconsistency revealed that the surface of the membrane support might not have been modified uniformly. EDS of catalyst no.4 revealed that there was no Pt present in the edge, i.e. Pt was only present on the outer surface and it did not penetrate into the bulk of the membrane. Only supported catalyst no. 5 had Pt deposited in both the outer and inner surfaces.

The result of EDS analysis of membrane no.2 did not show the presence of Pt on the membrane, which could have been due to it having a low Pt loading or that only one sample was analysed or that the Pt was unevenly distributed on the support, see Table 4.4. Results of reaction studies on catalyst no. 2, however contradict the EDS results since this catalyst proved to be highly active. Analysis of membrane no.4 gave a loading of Pt which was only located on the outer surface of the membrane, which could be due to a higher MgO loading on the outer surface (as seen in membrane no. 3) than the inner surface of the membrane. Membrane no. 5 which was prepared by chemical grafting gave the highest atomic % of Pt and the Pt was present on both the inner and outer surfaces of the membrane.

A comparison of the EDS results of the unsupported catalyst no. 7 to that of the intermediate product no. 6 reveals that after modification with platinumic acid the oxygen content remains unchanged while the chloride content was reduced in favour of the added Pt.

The activity of the catalysts analysed by EDS was evaluated in a CMR and is discussed in chapter 5.

4.3.5 Scanning electron microscopy (SEM)

The SEM micrographs of the catalysts are shown in Appendix B. This technique was performed in conjunction with energy dispersive X-ray spectroscopy (EDS). The SEM micrograph of the intermediate MgO-Si-O is shown in Figure B6 in which the spherical particles are SiO₂ (5-10 μm diameter) and the rest of the particles are that of the MgO

support. Figure B7 is the micrograph of unsupported MgO-Si-O-Pt catalyst in which it can be seen that the particles formed agglomerates after modification with Pt.

It can be seen in Figures B1 and B2 that most of the Pt loading occurred on the outer surface, in the ion-exchange process of impregnating the membrane with Pt (4g/l), which was confirmed by EDS (membrane no. 4 in Table 4.6). The SEM micrographs of the supported catalyst +MgO-Si-O-Pt (Figures B4 and B5), reveal that the catalyst was not grafted uniformly on the membrane support which can be seen by the light and dark patches of deposited MgO-Si-O-Pt.

4.3.6 Thermal analysis

Thermal analysis was performed on the unsupported catalyst MgO-Si-O-Pt and intermediate MgO-Si-O. Attempts to analyse the membrane-supported catalysts were unsuccessful since the amount of catalyst, on milligram samples of the modified support, was negligible, hence, the results of these analyses were equivalent to the thermal analysis of the blank support ($\alpha\text{-Al}_2\text{O}_3$) (see Figure C1). The weight loss obtained in the case of the unsupported catalyst and its intermediate can be seen in Figures 4.3 and 4.2 respectively.

Table 4.7 Results of simultaneous thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) on the unsupported catalyst and intermediate

Compound	Weight loss %	Heat J/g	Temperature Range °C
MgO-Si-O	12.84	609.23	100 –150
	8.44	81.88	400-500
MgO-Si-O-Pt	6.00	349.19	100-180
	15.49	299.96	280-500

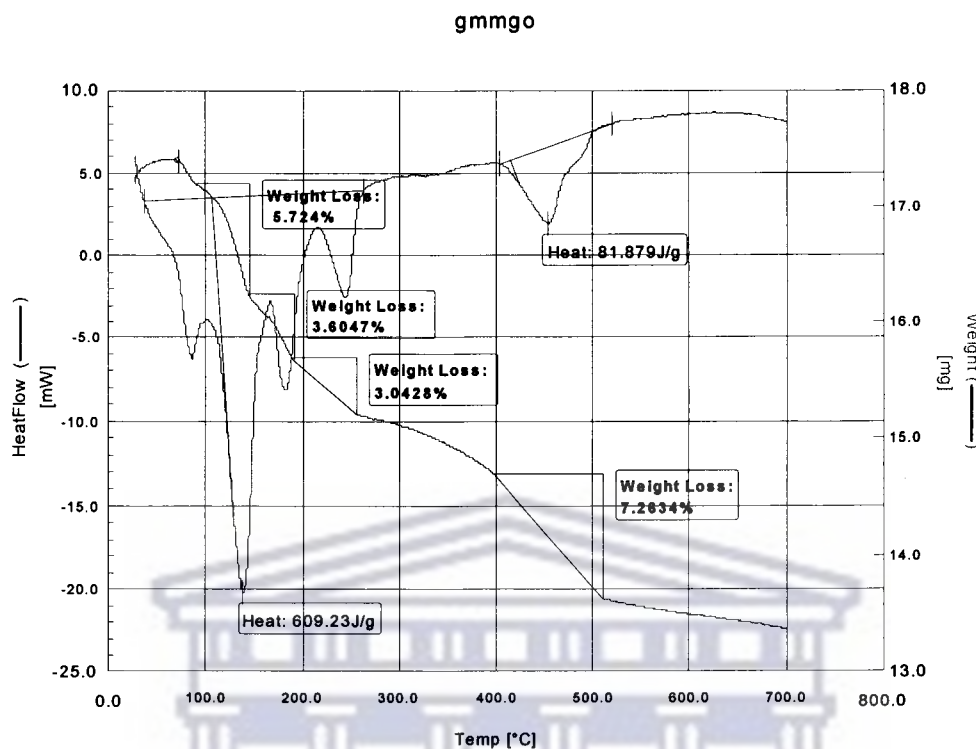


Figure 4.2 Simultaneous TGA and DSC of MgO-Si-O

In Figure 4.2, where the TGA and DSC of MgO-Si-O are shown, there are several endotherms relating to several phase changes or decomposition reactions. The most notable loss was the second weight loss of 5.72% at about 120°C representing the loss of H₂O which is formed from two adjacent OH groups (See Figure 4.1). This high weight loss was accompanied by a high adsorption of heat, which was equivalent to 609.23 J/g. The last peak of the thermogram occurs at temperature between 400 and 500°C and accounted for a % weight loss of 7.26% corresponding to a low heat uptake of 81.88 J/g. The TGA and DSC curves of MgO-Si-O-Pt are given in Figure 4.3 in which the % weight loss, with respect to H₂O (6.5 %), in Figure 4.2. There are fewer endotherms in the thermogram of the catalyst compared to that of the intermediate, which shows that the intermediate is less stable than the final product MgO-Si-O-Pt. This unsupported catalyst MgO-Si-O-Pt decomposed at about 280°C which was visibly evident since the grey catalyst powder turned white.

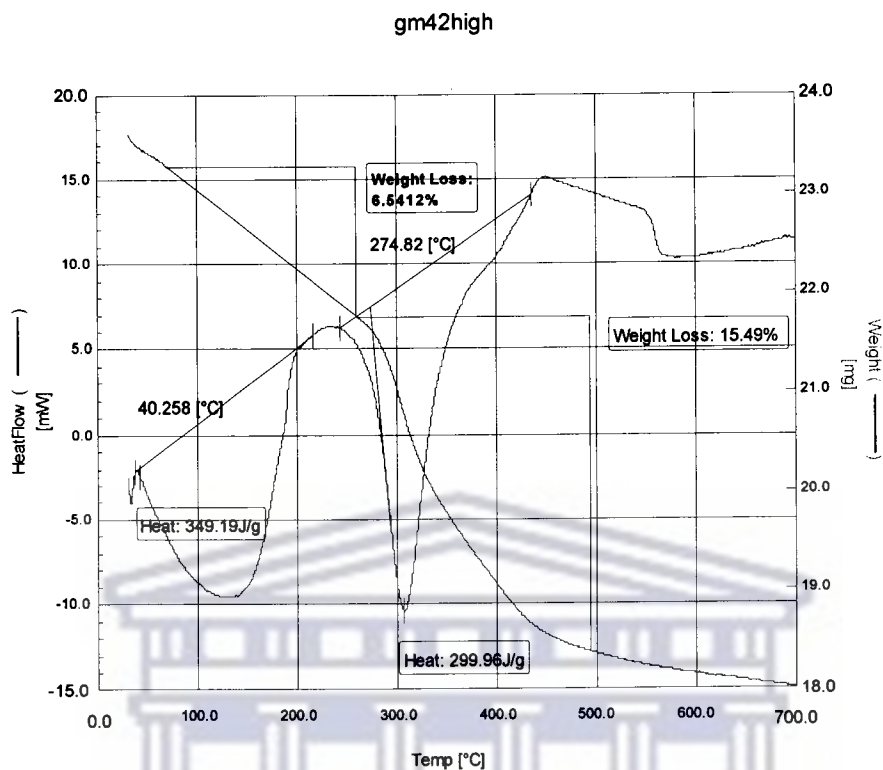


Figure 4.3 Simultaneous TGA and DSC of MgO-Si-O-Pt

A complete comparison and conclusion could not be made between the thermal analyses of the supported and unsupported catalysts due to there being too little catalyst on the support. This catalyst was however stable at the temperatures below 100°C at which the alcohol oxidation reactions occurred.

4.3.7 Nitrogen adsorption

Surface studies play a significant role in the understanding of the catalytic properties of catalysts. The N₂-BET isotherm is the most widely used technique to determine the surface area and the pore size distribution of a porous membrane.

The formula for the BET isotherm is

$$V = \frac{V_m c P}{(P_o - P) \left[1 + \frac{(c - 1)P}{P_o} \right]} \quad (4.1)$$

where c – temperature dependant constant
 P_o – the normal (saturation) vapour pressure
 V – volume of adsorbed gas
 V_m – volume adsorbed to give a monolayer

Table 4.8 BET results of the series of prepared catalysts

Catalyst	BETm ² /g	External Area m ² /g	Micropore Area m ² /g	Micropore Volume cm ³ /g *10 ⁻⁵
Blank	1.92	1.77	0.14	4.9
Blank+Pt(4g/l)	1.81	1.70	0.11	3.5
Blank+MgO	2.21	2.06	0.22	8.3
+MgO+Pt(0.1g/l)	1.80	1.54	0.26	11.1
+MgO+Pt(4g/l)	2.41	2.06	0.35	15.1
+MgO+Pt(10g/l)	2.42	2.03	0.38	16.4
+MgO-Si-O-Pt	8.59	7.23	1.36	58.4

The BET results of all the catalysts that were prepared, including that of the blank support are given in Table 4.8. The blank ceramic membrane contained about 70% α -Al₂O₃, which was responsible for the low surface area observed and this was similar to what Santamaria et al. reported [58]. In the modification of the blank membrane with MgO (Table 4.8), there was a very small change in the surface area. This observation was supported by the low atomic % of Mg as determined by EDS in Table 4.6. There

was however a slight increase in the micropore area and micropore volume due to entrainment of micro particles.

The majority of the pores of the membrane supported platinum catalyst (+MgO+Pt) had a pore diameter in the mesopore range of 40nm (Figure 4.5) which was 10 times larger than the pore diameter (4nm) of the γ -Al₂O₃ layer produced by Uzio et.al. [45]. This was consistent with the nature of the ceramic support membrane used in this study, which contained 70% α -Al₂O₃. Uzio et.al. found that their pore size distributions remained unchanged after Pt deposition, with a maximum at 2.7nm. This was also found to be the case with the modified membranes used in this study. It is important to note that a comparison is being made of the BET isotherms of samples with Pt depositions that resulted from vastly different concentrations of platinum acid solutions, namely 0.1g/l, 4g/l and 10g/l, with respect to platinum metal.

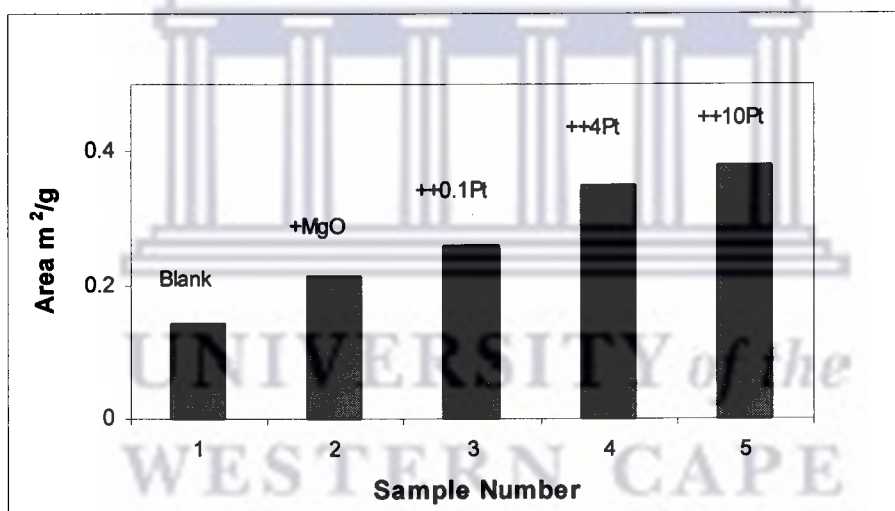


Figure 4.4 Graphical representation of increase in surface area with increase in concentration of the platinum acid solution

Figures 4.4 and 4.5 are graphical representations of the data of Table 4.8 and it can be seen that the increase in surface area was proportional to the increase in concentration of the chloroplatinic acid solution, in the case of the Pt impregnation method (Figure 4.4). The surface area for the membrane supported magnesium oxide supported platinum polysilanol (+MgO-Si-O-Pt) catalyst was however the highest as can be seen in Figure

4.5. This greatly enhanced surface area was due to the high deposition of small Pt particles in the pores of the membrane.

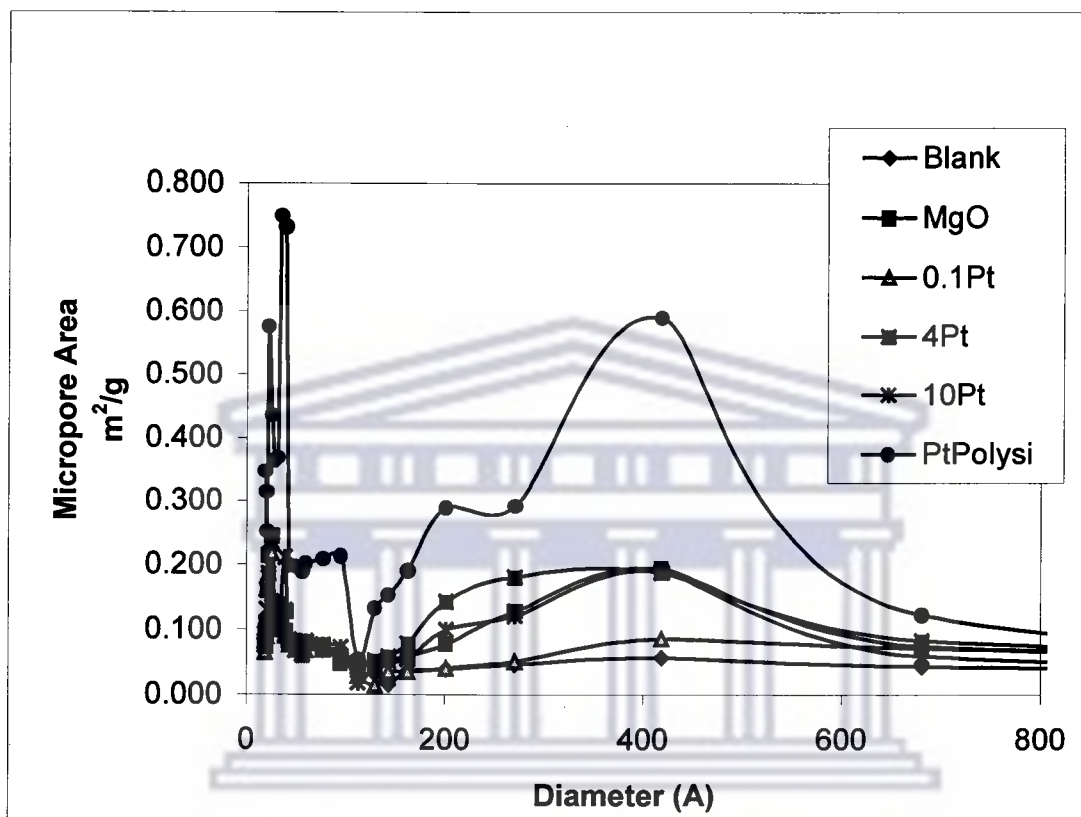


Figure 4.5 Pore size distribution of the prepared catalysts

4.3.9 Temperature programmed techniques

The sequence of analytical procedures and the operational conditions that were chosen for the temperature-programmed reactions were discussed in section 2.5. All the data has been normalised with respect to weight per unit length of the membrane support.

4.3.9.1 Temperature programmed reduction (TPR)

The results of temperature-programmed reduction (TPR) applied to the catalysts are given in Table 4.9. Only the MgO modified membrane was reduced in the temperature

programme used, the rest of the catalysts seemed to be in a reduced state prior to the reduction process, since no uptake of hydrogen was detected. This could mean that the surface of the membrane-supported catalyst contained platinum in a zero oxidation state or that it was not reducible in the temperature range. Catalyst no. 2 had a negligible volume of H₂ adsorbed but it was too low to be taken into account.

Table 4.9 Results of temperature programmed reduction

No.	Catalyst	Temperature at Peak Maximum (°C)	Volume Of H ₂ (ml/g STP)	H ₂ Peak Concentration (%)
1	+MgO	39.5	0.088	0.08
.		42.3	0.035	0.01
2	Blank+Pt(4g/l)	304.0	0.005	0.00
3	+MgO+Pt(4g/l)	_____	_____	_____
4	MgO-Si-O-Pt Unsupported	_____	_____	_____
5	+MgO-Si-O-Pt +Supported	_____	_____	_____

4.3.9.2 Temperature programmed oxidation (TPO)

A temperature programmed oxidation peak is given in Figure 4.6.

The results of temperature-programmed oxidation (TPO) on selected catalysts are given in Table 4.10. These results should be considered in conjunction with the results of TPR in Table 4.9. It can be seen that the catalysts, which were not reduced during TPR, were oxidised during TPO and vice versa.

Oxygen uptake increased from about 50°C and it reached a maximum around 100°C (Figure 4.6) in a flow of 10%O₂/He and ramp rate of 10°C/min. Comparing the O₂ peak concentration of the selected catalysts (Table 4.10), it can be seen that the oxygen uptake of the unsupported (MgO-Si-O-Pt) catalyst was 100 times larger than that of the supported catalyst. This is due to the difference in surface area of the active sites in the fine powder compared to that of the supported catalyst and also to the amount of catalyst present.

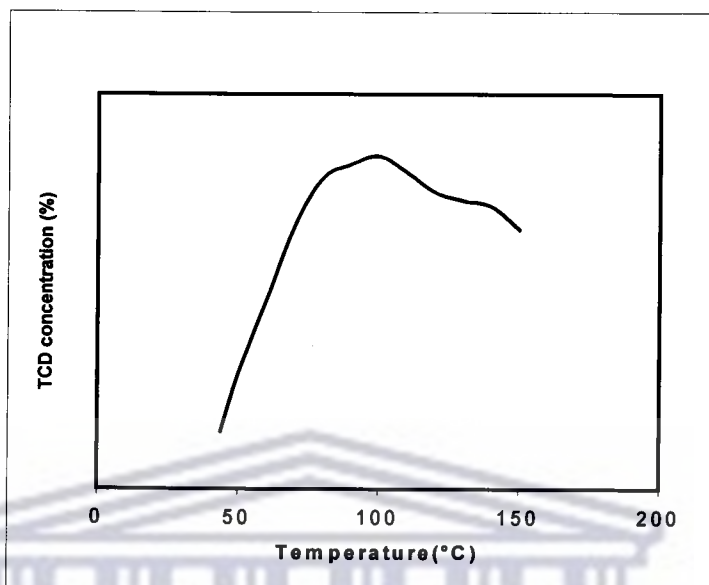


Figure 4.6 Graph of temperature programmed oxidation on MgO-Si-O-Pt

Table 4.10 Results of temperature programmed oxidation

No.	Catalyst	Temperature At Peak Maximum (°C)	Volume Of O ₂ (ml/g STP)	O ₂ Peak Concentration (%)
1	+MgO			
2	MgO+Pt(4g/l)	81.5	11.403	4.35
3	Blank+Pt(4g/l)	75.9	11.202	5.11
4	MgO-Si-O-Pt Unsupported	282.4	14344.54	417.18
5	MgO-Si-O-Pt +Supported	85.7	35.84	7.11

The membranes no.s 2 and 3 in Table 4.10 gave very similar TPO results, even though membrane no. 2 was modified with MgO. From the EDS results in Table 4.6 it is evident

that only a small amount of MgO was deposited on the membrane, hence the two membranes mentioned above may have similar properties. However, when these two membranes were tested for their activity in the oxidation of the lower primary alcohols, membrane no. 2 proved to be inactive whereas membrane no. 3 was highly active. The inactivity of membrane no. 2 could be due to the nature in which the Pt is bound to the MgO, i.e. the Pt may be bound in a manner in which the Pt particles are not accessible for alcohol oxidation.

4.3.9.3 Temperature programmed desorption (TPD)

The results of temperature programmed desorption are given in Table 4.11. Temperature programmed desorption (TPD) was done immediately after TPO. Oxygen was only desorbed from membrane no.1 as shown in Table 4.11.

Table 4.11 Results of temperature programmed desorption

No.	Catalyst	Temperature at Peak Maximum (°C)	Volume O ₂ (ml/g STP)	O ₂ Peak Concentration (%)
1	+MgO	76.4	121.22	9.97
2	Blank+Pt(4g/l)	_____	_____	_____
3	MgO-Si-O-Pt Unsupported	_____	_____	_____
4	MgO-Si-O-Pt +Supported	_____	_____	_____

Comparing the data obtained from TPR, TPO and TPD for the selected catalysts, it can be seen that the MgO modified membrane behaved differently to the other catalyst-supported membranes in each of the experiments. This observation could be due to the basic character of MgO.

Chapter 5

Alcohol Oxidation

5.1 INTRODUCTION

Alcohol oxidation reactions were performed in the catalytic membrane reactor (CMR) which is depicted in Figure 3.4 and described in section 3.4.

Gas chromatography was used to analyse the product stream. The gas chromatograph was equipped with a flame ionisation detector (FID). The FID was chosen because of its sensitivity to organic compounds. The presence of gaseous products such as carbon dioxide was confirmed by GC-MS.

The feed stream for the reactions was a mixture of air and alcohol, which was controlled by the temperature of the water circulating through a condenser in Figure 3.4. The concentration of methanol and ethanol in the feed stream was calculated to be 8% and 4% respectively.

The reaction conditions were kept constant for each alcohol and for each catalyst in order to make significant comparisons of the activity and selectivity of the various catalysts.

5.2 CONVERSION AND SELECTIVITY

The conversion C of the alcohol according to Stoukides *et al.* [63] is defined as:

$$C = \frac{\text{Moles of alcohol consumed}}{\text{Moles of alcohol fed}} \times 100 \quad (5.1)$$

And the selectivity for compound X_i is:

$$X_i = \frac{\text{Moles of } X_i \text{ produced}}{\text{Moles of alcohol consumed}} \times 100 \quad (5.2)$$

and the yield, Y_i , of X_i is $Y_i = C \times X_i$

In the synthesis of methyl formate, two molecules of methanol are consumed to form one molecule of methyl formate so that the selectivity for methyl formate would be given by:

$$X_{MF} = \frac{2 \times \text{Moles of } X_{MF} \text{ produced}}{\text{Moles of alcohol consumed}} \times 100 \quad (5.3)$$

5.2.1 Illustrated example of Conversion and Selectivity

5.2.1.1 Conversion

Using methanol as an example, the reaction equation can be given as:



Where A,B,C and D are possible products

from equation (5.1) the conversion is given as:

$$\text{Conv.} = \frac{(\text{CH}_3\text{OH})_{\text{reacted}}}{(\text{CH}_3\text{OH})_{\text{in}}} \times 100 \quad (5.5)$$

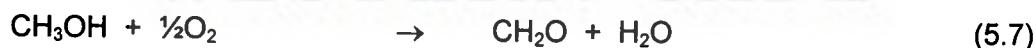
where

$$\text{CH}_3\text{OH}_{\text{reacted}} = \text{CH}_3\text{OH}_{\text{in}} - \text{CH}_3\text{OH}_{\text{out}} \quad (5.6)$$

$\text{CH}_3\text{OH}_{\text{in}}$ was calculated as the product of φ_{in} (the flow-rate of gas entering the reactor) and the concentration of the methanol in the feed stream of the reactor. The unit of $\text{CH}_3\text{OH}_{\text{in}}$ is therefore (mmol/min). The concentration of methanol in the feed was based on the vapor pressure of methanol in a saturated methanol/air mixture and checked quantitatively by GC, by allowing the feed to bypass the reactor before and after the reaction. The results of these measurements gave a very stable methanol feed concentration throughout the reaction.

$\text{CH}_3\text{OH}_{\text{out}}$ was calculated as the product of φ_{out} (the flow-rate of the gas leaving the reactor) and the concentration of the methanol in the product stream of the reactor which was determined by GC.

GC results showed the production of methyl formate which may be formed according to the following balanced equation



Qualitative analysis of GC-MS revealed the presence of CO_2 which could have been produced according to equation (5.10):

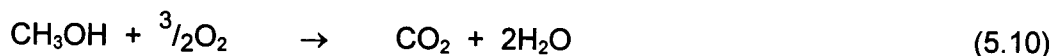


Table 5.1 Sampled results from methanol oxidation

Temp °C	CH ₃ OH _{in} (mmol/min)	CH ₃ OH _{out} (mmol/min)	CH ₃ OH _{reacted} (mmol/min)	Conversion (%)	CHOOCH ₃ produced (mmol/min)
93	2.8	0.4	2.4	86	1.1
108	2.6	0.12	2.5	95	0.6

The maximum amount of CHOOCH₃ that could have been formed from 2.4mmol/min CH₃OH is 1.2mmol/min CHOOCH₃ according to equation (5.9). At a reaction temperature of 93°C a production of 1.1 mmol/min CHOOCH₃ was found. Since CO₂ could not be quantitatively analyzed only an estimated selectivity of 90% for methyl formate can be given at that temperature. The estimated selectivity towards methyl formate at 108°C is significantly lower (about 50%).

When the reaction temperature was returned to 93°C, after the temperature had been constant at 108°C for about 50 minutes, a conversion of (90%) and CHOOCH₃ production of (1.2mmol/min) was obtained which is similar to the results obtained before the temperature was raised.

5.2.1.2 Selectivity:

The selectivity calculation for the above reaction is:

$$\text{Selectivity}_A = A / (A + B + C + D) \quad (5.11)$$

Since the methanol that reacted was converted into products, the following equation can be written:

$$\text{CH}_3\text{OH}_{\text{reacted}} = A + B + C + D \quad (5.12)$$

From equation (5.4), (5.11) and (5.12) it follows that:

$$\text{Selectivity}_A = A / (\text{CH}_3\text{OH}_{in} - \text{CH}_3\text{OH}_{out}) \times 100 \quad (5.13)$$

Note: In the oxidation of ethanol, the major product was acetaldehyde which meant that one mole of ethanol would produce one mole of acetaldehyde. The conversion equation for this reaction would be the same as that of methanol, but the selectivity equation differs by the stoichiometric factor i.e.

$$X_A = \frac{\text{Moles of } X_A \text{ produced}}{\text{Moles of alcohol consumed}} \times 100 \quad (5.14)$$



5.3 REACTION STUDIES

The reaction studies were performed under atmospheric pressure using the reaction conditions shown in Table 5.1. The reactor and the tubing leading to the GC and the automatic sampling valve were all individually thermostatically controlled. As can be seen from Table 5.1, the temperature of the tubing leading to the GC, after the reactor, was set at a higher temperature to prevent possible condensation of the products and reactants. To ensure accurate conversion and selectivity calculations, all the tubing, including the reactor, were leak tested and sealed.

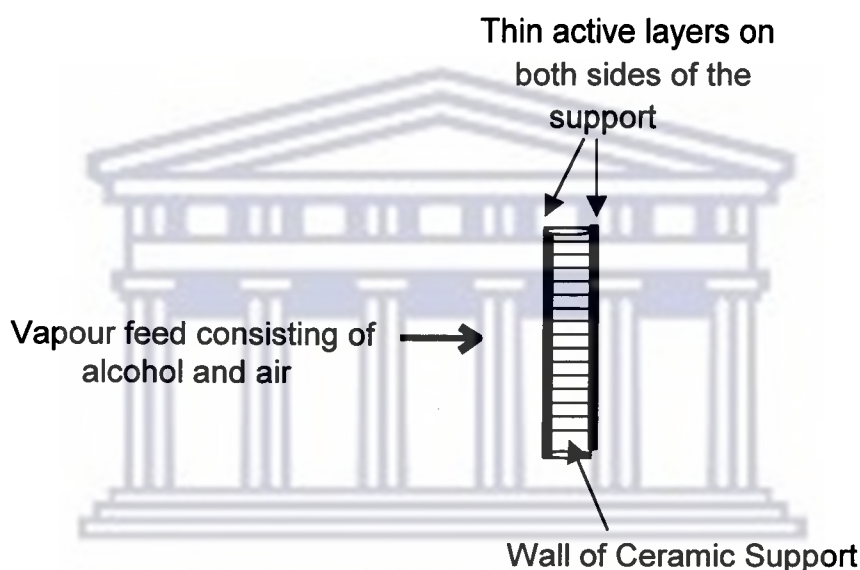


Figure 5.1 Direction of alcohol/air mixture across the membrane supported catalyst

Preliminary studies were done in order to obtain the optimal conditions that would give the highest conversion and selectivity. This was achieved by comparing the effects of different flow rates and different temperatures on the activity of the catalysts. After a number of preliminary runs the best reaction conditions for ethanol and methanol oxidation with respect to conversion and selectivity was found. The common reaction conditions are given in Table 5.1. It was important to ensure that the conditions, at which the reactions were performed for each catalyst, were identical, so that a proper comparison of their activity could be made.

Table 5.2 Reaction conditions

Area	Parameter	Setting
Air	Flow-rate	10 ml/min
Heated bath	Temperature	60°C
Cryostat	Temperature	10 – 13°C
Reactor	Temperature	60 – 100°C
Tubing from reactor	Temperature	120°C
Pressure indicator	Pressure	Atmospheric
Sampling valve	Temperature	120°C

The temperature of the cryostat bath was monitored closely since it controlled the concentration of the alcohol in the feed.

Initial reactions performed on the blank membrane support gave a very low conversion of methanol and ethanol and it was taken as being negligible. The magnesium oxide (Blank+MgO) modified membrane gave a slightly better conversion (about 1%) than the blank membrane support, however it was regarded as negligible due its low conversion.

5.2.1 Methanol Oxidation

The reactions were performed in a catalytic membrane reactor (CMR) as depicted in Figure 2.4. The membrane-supported catalysts were used in methanol and ethanol oxidation reactions. The direction of the methanol/air feed mixture is shown in Figure 5.1 in which the feed enters from the outer side of the membrane and encounters a layer of catalyst on either side of the wall of the membrane. A comparison of conversion and selectivity for methanol over selected catalysts is given in Table 5.3.

Table 5.3 Comparison of the conversion and selectivity for the catalytic membranes that were evaluated in methanol oxidation

Catalyst	Reaction Temp. °C	Conversion %	*Selectivity CHOOCH ₃ %
Blank	90	0	
Blank+Pt (4g/l)	63	0	
	82	92	90
	87	97	60
	94	98	40
	99	99	27
	107	99	12
Blank+MgO	90	0	
+MgO-Pt (4g/l)	98	0	
+MgO-Si-O-Pt	93	91	99
	108	95	50

The concentration of methanol in the feed stream was calculated based on the vapour pressure of methanol, temperature of coolant and the ideal gas law in the ratio methanol:oxygen:nitrogen and found to be 8%:18%:74% respectively. The space velocity (WHSV) was 13 h⁻¹ for methanol. Conversion and selectivity was calculated using equations 5.5 and 5.13. All of the reaction conditions and catalysts that displayed a conversion of methanol had a high selectivity toward methyl formate (see Table 5.3). The catalysts which proved to be active were {Blank+Pt(4g/l)}, {Blank+Pt(10g/l)} and {+MgO-Si-O-Pt}.

The selectivity for methyl formate over catalyst Blank+Pt(4g/l) decreased as the reaction temperature was increased while the conversion increased, suggesting that more CO₂ was formed (see Table 5.3). The +MgO-Si-O-Pt-supported catalyst gave a similar result but was not affected as much by the increase in temperature. The conversion and

selectivity results of methanol oxidation obtained in this study was higher than that which was reported by Ai [64] and the reactions were performed at a lower temperature as shown in Table 5.3.

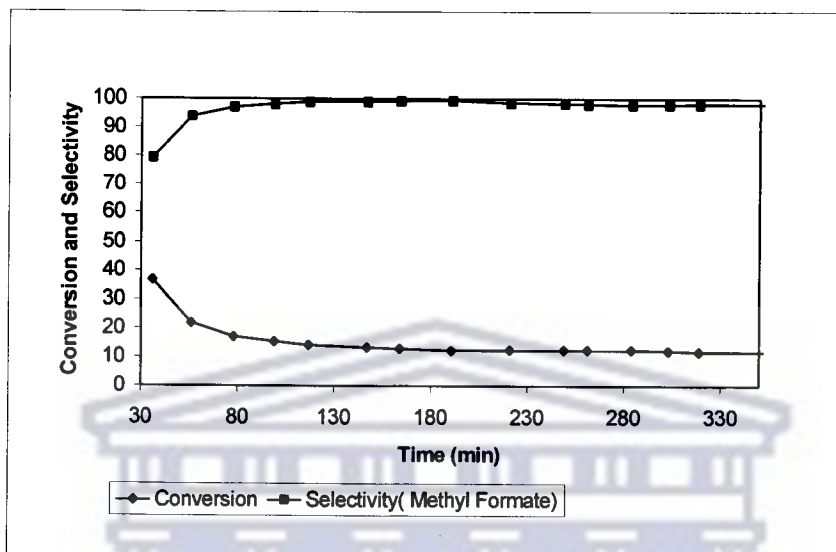


Figure 5.2 Conversion and estimated selectivity for oxidation of methanol on Pt 10g/l

In Figure 5.2 the term estimated selectivity is used as a precautionary measure due to the online GC not having a thermal conductivity detector (TCD) to determine CO_2 gas concentration. This however does not affect the selectivity calculations as long as accurate calculations of conversion are made, including the concentration of the target molecule.

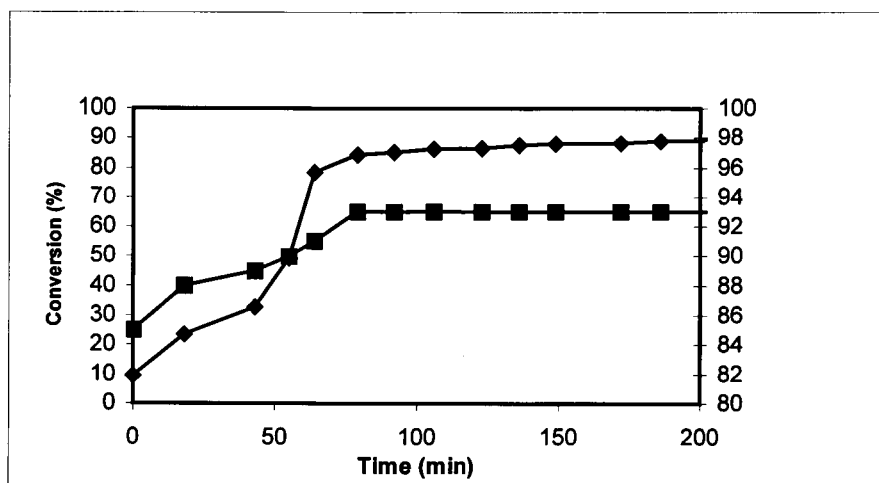


Figure 5.3 Conversion of methanol on the +MgO-Si-O-Pt membrane-supported catalyst

The +MgO-Si-O-Pt membrane-supported catalyst gave the highest conversion (91%) and selectivity (99%) results. At temperatures below 60°C, there was no conversion of methanol, however at temperatures in the region of 90°C there was a sharp increase in the conversion. This catalytic membrane has been used repeatedly without any loss in activity. Hence it was extremely stable under operating conditions. The average time on stream was 6 to 10 hours.

The products that were formed in methanol oxidation reactions, were formaldehyde, methyl formate, carbon dioxide (CO₂) and water.

The membranes were prepared via two methods namely impregnation and chemical grafting. The activity of the catalytic membranes, prepared via the impregnation method, were a function of the Pt loading, i.e. the higher the loading the higher the activity. This was also found to be the case in the work of Santamaria *et al.* [58].

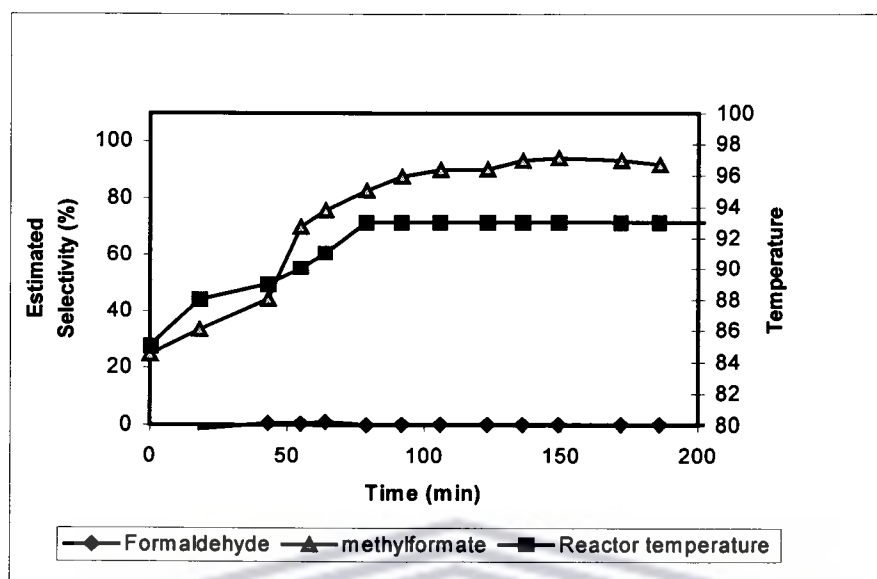


Figure 5.4 Selectivity towards methyl formate on the +MgO-Si-O-Pt membrane-supported catalyst

In this study, methyl formate was the major product in the oxidation of methanol. Formaldehyde, which was expected to be the major product, was merely an intermediate in the reaction process. This phenomenon could be due to the spillover of adsorbed species discussed in section 1.3. There may be a synergy that exists between the oxides and the noble metal particles. Another view is that the methanol is adsorbed in the form of a methoxy group (formed by the reaction of methanol with a silica surface hydroxyl group) [1]. This methoxy group reacts further with the adsorbed formaldehyde to form a hemiacetal intermediate leading to the formation of methyl formate which then desorbs [1].

An alternative mechanism for the formation of methyl formate was given by Ai [64], which states that in the second step, a dimerisation occurred between two formaldehyde molecules to produce methyl formate. The oxidation of methanol and the dimerisation was performed over a $\text{SnO}_2\text{-MoO}_3$ catalyst at a reaction temperature of 160°C . It was concluded that in order for the $\text{SnO}_2\text{-MoO}_3$ catalyst to convert methanol to methyl formate, it had to possess acidic and basic sites. In the first step, formaldehyde was produced on an acidic site and in the second step, dimerisation occurred on a basic site.

This hypothesis was supported by several experiments performed by the author. Some of the results of the work done by Ai [64] in the oxidation of methanol is given in Table 5.4. The reactions in Table 5.4 were performed over 20g of catalyst at a methanol feed flow of 6.3×10^{-2} mol/h which equates to a WHSV of 0.1 h^{-1} .

Comparing the best results of Table 5.4 [64] to the best results of this study in Table 5.3, it can be seen that the oxidation over catalyst +MgO-Si-O-Pt obtained significantly higher conversion and selectivity at a WHSV that was 130 times higher and performed at lower reaction temperature.

Table 5.4 Oxidation of methanol with various catalysts [64]

Catalyst (atom ratio)	Reaction temp. (°C)	CH ₃ OH conv. (%)	Selectivity CH ₃ OOCH (mol%)
V—Mo (9-1)	240	54	7
	250	80	7
Fe—Mo (8-2)	228	71	20
	235	84	17
Fe—Mo (3-7)	300	57	3
Ti—Mo (8-2)	260	24	7
	280	42	4
Ti—Mo (2-8)	220	26	31
	230	37	27
Sn—Mo (7-3)	150	34	92
	160	72	90
Sn—Mo (4-6)	190	33	57
Sn—W (8-2)	275	39	73
Sn—P (9-1)	305	54	25

The oxides present in the catalysts prepared in this study are MgO, Al₂O₃, ZrO₂ and SiO₂. The activity of these metal oxides vary as successful promoters in oxidation reactions. For instance MgO, with very low co-ordination numbers, played an important role in activating the C-H bond in methane oxidation at low temperature [65]. However, in this study, MgO has little or no effect in the activation of the gas phase alcohols as there was no conversion of methanol over the catalysts prepared via the Pt impregnation of membranes previously modified with MgO e.g. +MgO+Pt(4g/l) shown in Table 4.8. Judging from the weight % gained, in Table 4.4, after impregnation with Pt, the +MgO+Pt(4g/l) catalyst had between 2 to 4 times the amount of Pt than the (Blank+Pt(4g/l)) catalyst, however the (Blank+Pt(4g/l)) catalyst was active whereas +MgO+Pt(4g/l) catalyst was not. A reason for this observation could be that the Pt is bonded to the MgO in such a manner that it is not accessible for participation in the oxidation reactions.

Of the supported catalysts studied, aluminium and zirconium oxide were the only common oxides in the two active membrane supported catalysts. Zirconium oxide has been known to act as promoter in catalytic reactions [42]. Hence, a proposed explanation for the high conversion obtained and the observed selectivity towards methyl formate in the oxidation of methanol at a relatively low reaction temperature may be that a synergy existed between the oxides. This synergy could also be present between ZrO₂ and the platinum metal particles. The oxygen may adsorb dissociatively onto the ZrO₂ and then migrate to the molecularly adsorbed methanol, on the platinum surface, to form formaldehyde, which may react further with other adsorbed methanol (in the form of a methoxy group) to form methyl formate. The proposed reaction mechanism is shown in Figure 5.5

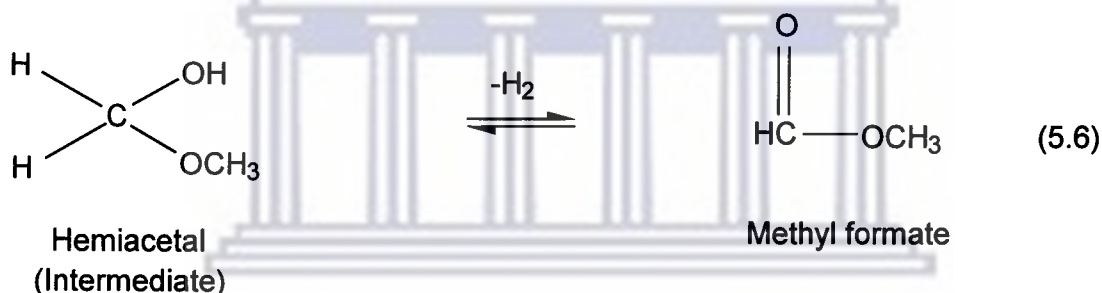
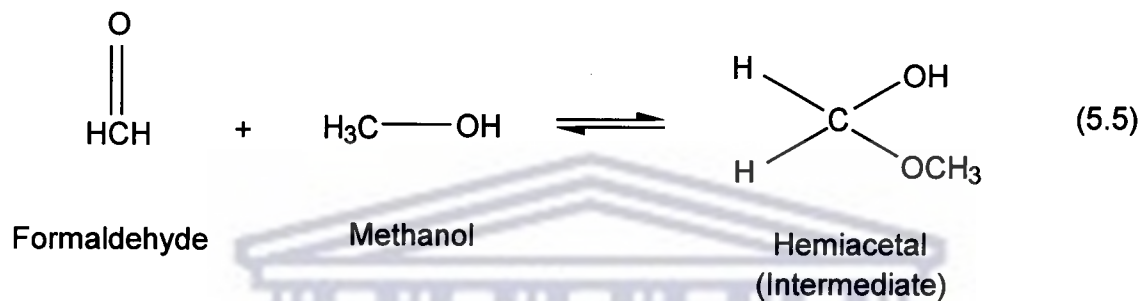
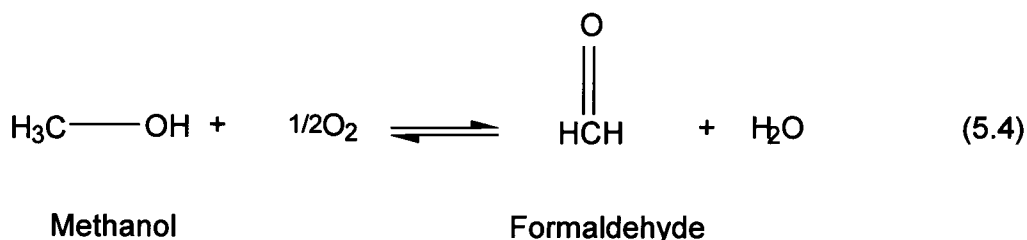


Figure 5.5 The proposed reaction mechanism of the oxidation of methanol

The two active catalysts, +MgO-Si-O-Pt and Blank+Pt(4g/l), displayed a dual function, firstly oxidation occurred to yield formaldehyde and secondly esterification occurred to yield methyl formate. Since formaldehyde and methyl formate were synthesised in the oxidation of methanol, the active sites on the catalysts can be described as being redox in nature according to the explanation given by Arora et.al. [3] in section 1.2.2.1. This bi-functional nature of a catalyst that produces methyl formate was also described by Ai [64].

GC-MS was used to confirm the products of the reaction and it also revealed that polymers of methyl formate were formed in extremely low concentrations such as a dimer of methyl formate.

5.2.2 Ethanol Oxidation

Ethanol oxidation was achieved at a lower temperature when compared to methanol oxidation. The results obtained in studies of ethanol oxidation over the catalysts, +MgO-Si-O-Pt, Blank+Pt(4g/l) etc., listed in Table 4.8, are similar to those obtained for methanol oxidation over the same catalysts. The ethanol feed concentration in the ratio ethanol:oxygen:nitrogen was 4%:19%:77% respectively and a WHSV of 10 h⁻¹.

Table 5.5 Comparison of the conversion and selectivity for ethanol oxidation

Catalyst	Reaction Temp. °C	Conversion %	*Selectivity CH ₃ CHO %
Blank+PtO (4g/l)	72	80	32
	79	81	36
	83	82	41
	87	82	44
+MgO-Si-O-Pt	68	84	36
	75	85	41
	83	86	47

* Estimated value, based on GC-MS and carbon balance

The major product of ethanol oxidation was the aldehyde, namely acetaldehyde and not an ester as was the case for methanol oxidation. The selectivity for acetaldehyde increased as the reaction temperature was increased as can be seen in Table 5.5. More side products were obtained when using these catalysts in the oxidation of ethanol than were obtained in the oxidation of methanol. Hence the catalysts had a lower selectivity towards the preferred product compared to methanol oxidation. Preliminary reactions performed on the unmodified blank membrane and the membrane modified with MgO gave very low conversions of ethanol and were regarded as being negligible. Sampled temperature with the corresponding conversion and selectivities are given in Table 5.5.

The supported catalyst +MgO-Si-O-Pt was more active than the Blank+Pt(4g/l) catalyst since it gave higher conversion and selectivity values at lower reaction temperatures.

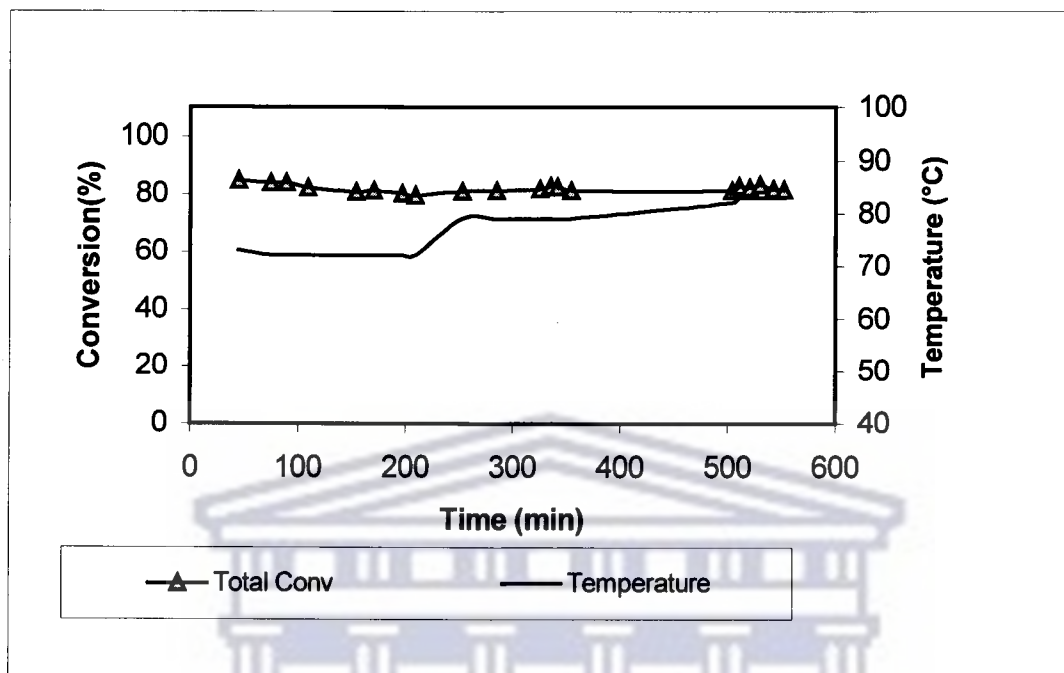


Figure 5.6 Conversion of ethanol on a Blank+Pt(4g/l) catalyst

The conversion of ethanol and selectivity towards acetaldehyde respectively. The selectivity on a Blank+Pt(4g/l) supported catalyst is depicted in Figures 5.6 and 5.7 increased when the reaction temperature was increased which revealed that selectivity was temperature dependent.

UNIVERSITY of the
WESTERN CAPE

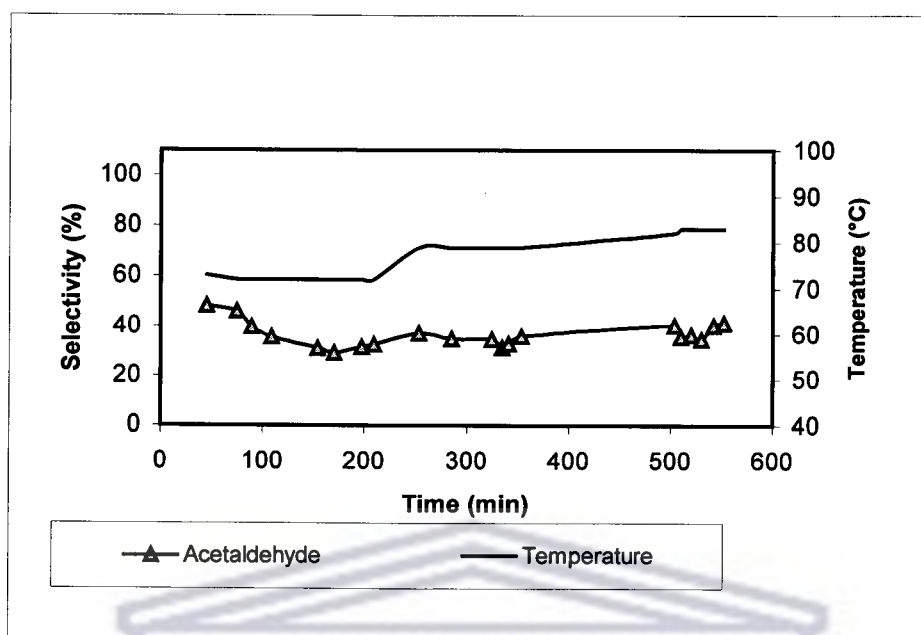


Figure 5.7 Selectivity towards acetaldehyde on the +Pt (4g/l) membrane-supported catalyst

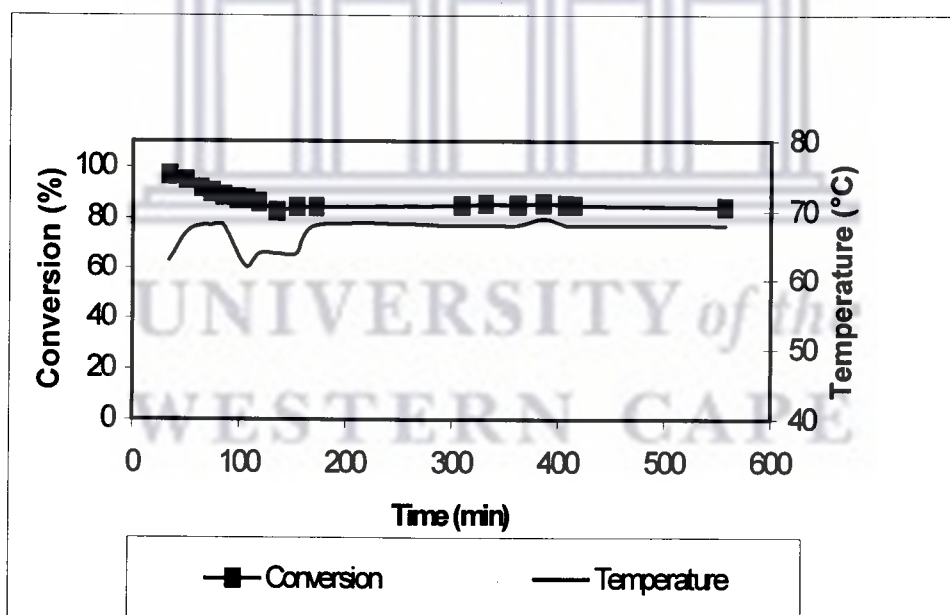


Figure 5.8 Conversion of ethanol on a +MgO-Si-O-Pt catalyst

Figures 5.8 and 5.9 depict the conversion and selectivity of the +MgO-Si-O-Pt catalyst with respect to ethanol oxidation. This catalyst has a marginally higher activity than the

Blank+Pt(4g/l) catalyst which is consistent with the results obtained in methanol oxidation over the same catalysts.

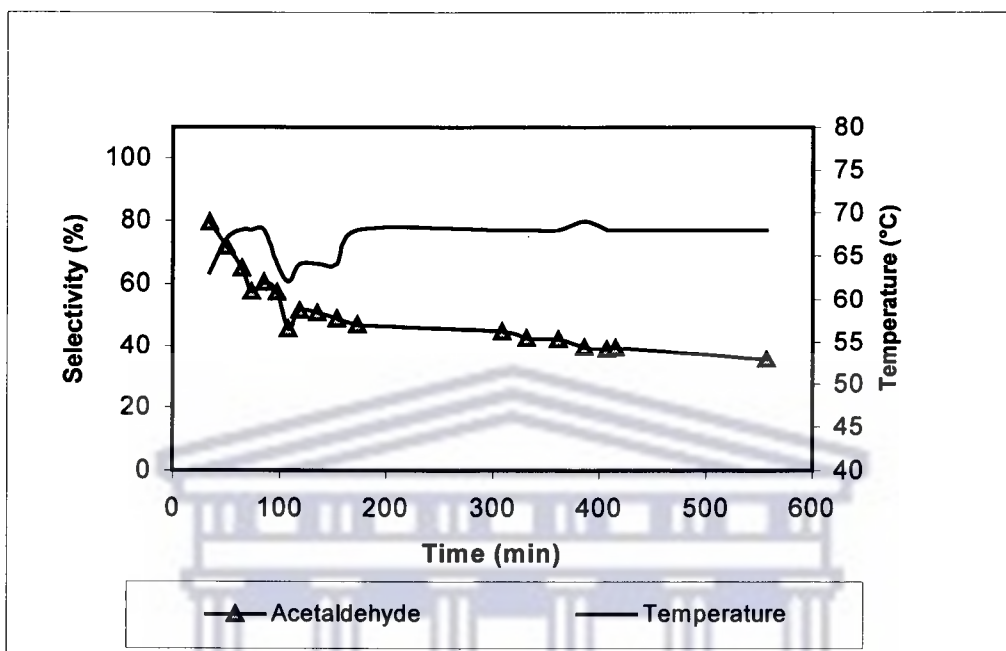


Figure 5.9 Selectivity towards acetaldehyde on the +MgO-Si-O-Pt membrane-supported catalyst

5.2.3 Comparison of methanol and ethanol oxidations

The conversion decreased with an increase in flow rate in both cases, since a higher flow rate reduced the residence time of the alcohol on the catalyst. An increase in temperature up to a certain maximum (approx. 110°C) resulted in an increase in the production of the methyl formate (methanol oxidation) and acetaldehyde (ethanol oxidation). Only a limited increase in temperature (about 10°C to 20°C) was considered, since reaction at higher temperatures could result in:

- decomposition of the catalyst (determined by TGA)
- an increase in the production of CO₂ (determined by GC-MS)
- lower selectivity towards the preferred product

Furthermore, a 10°C to 20°C increase in temperature above 100°C resulted in an increase in conversion with a decrease in selectivity towards the target product. This is

similar to findings by Gomez *et.al.* in the study of the partial oxidation of ethanol on a VMgO catalyst [66].

Of all the catalysts tested, the membrane supported +MgO-Si-O-Pt catalyst gave the best results of conversion and selectivity. This membrane-supported catalyst was stable at higher temperatures and was used repeatedly (more than 6 times) without any sign of deactivation.



Chapter 6

Conclusions

Heterogeneous catalysts have an advantage over conventional unsupported catalysts in that they overcome problems associated with separating the catalyst from the products. This improves product purity and isolation and prevents the loss of catalyst resulting in a cleaner product and process.

In this study catalysts were prepared by ion-exchange method and by grafting techniques. The amount of active catalyst that was deposited on the membrane support was low (<1%) in comparison to the weight of the support, however, due to the porous nature of the membrane, it provided an increased surface area onto which the catalyst could be attached. The amount of catalyst loaded upon the membrane support increased with an increase in the concentration of the impregnation solution. It was found that the membranes that had previously been modified with MgO, had a higher catalyst loading than the blank membranes. Surprisingly, the MgO+Pt(4g/l) catalysts were not active at all in the oxidation of the lower primary alcohols, methanol and ethanol, whereas the Blank+Pt(4g/l) catalyst was highly active under identical reaction conditions.

Reactor design and configuration offered a number of options in which the reaction could be performed as was discussed in section 1.8.1 and shown in Figure 1.4. After a number of preliminary runs, an optimal reaction configuration was obtained in which the feed mixture was introduced into the reactor in radial manner that ensured maximum contact with the catalyst, namely the flow through configuration (Figure 5.1). The optimal flow-rate of the feed stream was 10 ml/min and the reaction temperature was about 93°C for methanol and 87°C for ethanol. The ratio of alcohol/oxygen was about 0.4 and 0.2 and the WHSV was 13 h⁻¹ and 10h⁻¹ for methanol and ethanol respectively.

Changes in the experimental conditions such as feed flow-rate and temperature affected changes in the percentage conversion. The percentage conversion decreased with an increase in flow rate, since a higher flow rate reduced the residence time of the alcohol on the catalyst. A limited increase in temperature, however, increased the percentage conversion to the product. These results are similar to those that Gomez *et al.* [67] observed using VMgO catalyst. A limited increase in temperature (10°C to 20°C) was considered, since a too high temperature could either destroy the catalyst (according to TGA results) or it could promote total oxidation of the alcohol to CO₂ and H₂O.

The catalytic membranes, which proved to be active in the oxidation of the lower primary alcohols, were selective towards methyl formate in methanol oxidation and selective towards acetaldehyde in ethanol oxidation reactions. In methanol oxidation reaction the activity and selectivity was relatively higher than for ethanol oxidation over the same catalysts. The methanol oxidation reaction essentially amounted to a one step esterification process under relatively mild conditions. GC-MS was used to confirm the reaction products and its results also revealed that polymers of methyl formate was present in the product stream of methanol oxidation reactions, albeit at extremely low concentrations.

Of all the catalysts tested, the +MgO-Si-O-Pt membrane supported catalyst proved to be the best in terms of conversion and selectivity. It was stable at higher temperatures and was used repeatedly without any signs of deactivation. The Blank+Pt(4g/l) catalyst was almost as active as the +MgO-Si-O-Pt catalyst, however its advantage was that it was easier to prepare than +MgO-Si-O-Pt. The activity of these catalysts, with respect to methanol oxidation, were compared to the results of previous workers, for instance that of Ai [58] and Busca *et al.*[66], and they were found to be more superior in all aspects, namely conversion (91%), selectivity (99%), WHSV (13h⁻¹) and reaction temperature (93°C).

The conversion and selectivity results were very sensitive to small changes in the reaction temperature. Below 100 °C the oxidation reactions obtained high conversion and selectivity values. Above a reaction temperature of 100°C it appears that the

selectivity for CO₂ increases greatly. This means that the catalyst might have potential for applications in direct methanol fuel cells at temperatures above 100°C.

Future work on this membrane-supported catalytic system should concentrate on chemisorption characterization in order to determine the dispersion of the active metal sites on the support. Ammonia temperature programmed desorption should give further insight into the nature of these sites, i.e. acidic, basic or redox. Reaction studies should be performed at higher flow rates and temperatures in order to determine the stability of the catalysts under these conditions and to determine the selectivity to CO₂ at these parameters.



REFERENCES

1. Tatibouët J.M., "Methanol oxidation as a catalytic surface probe", *Applied Catalysis A: General*, **148**, 1997, 213-252
2. Cao Y., Liu B., Deng J., "Catalytic dehydrogenation of ethanol in Pd-M/r-Al₂O₃ composite membrane reactors", *Applied Catalysis A:General*, **154**, 1997, 129-138
3. Arora N., Deo G., Wachs I.E., Hirt A., "Surface aspects of Bismuth-metal oxide catalysts", *J. Catal.*, **159**, 1996, 1-13
4. Park S-M., Chen N.C., Doddapaneni N., "Electrochemical oxidation of ethanol in aqueous carbonate solutions", *J. Electrochem. Soc.*, **142(1)**, 1995, 40-45
5. Hsieh H.P., *Inorganic membranes for separation and reaction*, Membrane Science and Technology Series, **3**, Elsevier, Amsterdam, The Netherlands 1996, 120
6. Franz G., Sheldon R.A., *Ullman's Encyclopedia of Industrial Chemistry Vol A18*, 261-311
7. Frusteri F., Arena F., Espro C., Mondello N., Parmaliana A., "Partial oxidation of light paraffins on supported superacid catalytic membranes", *Stud. In Surf. Sci. and Catal.*, **119**, 1998, 447-452

8. Baldwin T.R., Burch R., Squire G.D., Tsang S.C., "Influence of homogeneous gas phase reactions on the partial oxidation of methane to methanol and formaldehyde in the presence of oxide catalysts", *Applied Catalysis*, **74**, 1991, 137-152
9. Parmaliana A., Arena F., Frusteri F., Mezzapica A., "High yields in the catalytic partial oxidation of natural gas to formaldehyde: Catalyst development and reactor configuration", *Stud. In Surf. Sci. and Cata.*, **119**, 1998, 551-556
10. Herron N., "The selective partial oxidation of alkanes using zeolite based catalysts: A completely inorganic cytochrome P450 mimic", *New J. Chem.*, **13**, 1989, 761-766
11. Kuno H., Shibagaki M., Takahashi K., Matsushita H., "Oxidation of alcohols to aldehydes and ketones over hydrous zirconium(IV)oxide modified by trimethylsilyl chloride", *Bull. Chem. Soc. Jpn*, **66**, 1993, 1699-1702
12. Ivanov K., Litcheva P., Klissurski, "Mn-Mo-O catalysts for methanol oxidation. II. Oxidation of methanol", *Collection of Czechoslovak chemical communications*, **57**, 1992, 2539-2547
13. Trifiro F., Carbucicchio M., Villa P.L., "Catalytic properties of iron-based mixed oxides in the oxidation of methanol and olefins", *Hyperfine Interactions*, **111**, 1998, 17-22
14. Tatibouet J.M., Che M., Amirouche M., Fournier M., Rocchiccioli-deltcheff C., "Catalytic oxidation of methanol by 12-Molybdosilicic acid supported on Silica: Dispersion Effect", *J. Chem. Soc., Chem. Commun.*, 1988, 1260-1261
15. Trifiro F., Cairati L., "SiO₂ and Al₂O₃ as oxidation catalysts of methanol", *Journal of Catalysis*, **80**, 1983, 25-30

16. Farneth W.E., Ohuchi F., Staley R.H., Chowdhry U., Sleight A.W., "Mechanism of partial oxidation of methanol over MoO₃ as studied by temperature programmed desorption", *J. Phys. Chem.*, **89**, 1985, 2493-2497
17. Richter M., Heise K., Ohlmann G., "Catalytic relevance of phase transformations accompanying the gas phase oxidation of ethanol on silica supported vanadia", *React. Kinet. Catal. Lett.*, **27(1)**, 1985, 115-119
18. He J.G., Shi L., Jiang Y.Y., "Oxidation of isopropanol and ethanol by a magnesium oxide supported polysilazane-platinum complex", *Reactive polymers*, **15**, 1991, 131-134
19. Huang M.Y., Ren C.Y., Jiang Y.Y., "Oxygenation of isopropanol and ethanol catalyzed by a silica-supported polysilazane-platinum complex", *J. Macromol Sci.-Chem.*, **A24(3&4)**, 1987, 269-275
20. Delmon B., Grasselli R.K., Oyama S.T., Gaffney A.M., Lyons J.E., "The future of industrial oxidation catalysis spurred on by fundamental advances", *3rd World Congress on Oxidation Catalysis*, 1997, 43-59
21. Blaser H-U., "Heterogeneous catalysis for fine chemicals production", *Catalysis Today*, **60**, 2000, 161-165
22. Zaspalis V.T., Burggraaf A.J., Bhave R.R., "Inorganic membrane reactors to enhance the productivity of chemical processes", *Inorganic membranes synthesis, characteristics and applications*, Van Nostrand Reinhold, New York, 1991, 177-207
23. Stoyanova A., Naidenov V., Petrov K., Nikolov I., Vitanov T., Budevski E. "Effect of preparation conditions on the structure and catalytic activity of carbon-supported platinum for the electrooxidation of methanol", *Journal of Applied Electrochemistry*, **29**, 1999, 1197-1203

24. Oyama T., Somorjai A., "Effect of structure in selective oxide catalysis: Oxidation reactions of ethanol and ethane on vanadium oxide", *J. Phys. Chem.*, **94**, 1990, 5022-5028
25. Gates B. C., *Catalytic Chemistry*, John Wiley and Sons, New York, 1992, 388
26. Somorjai G.A., *Introduction to surface chemistry and catalysis*, John Wiley & Sons, Inc., 1994, 502
27. Campestrini S., Meunier B., "Olefin epoxidation and alkane hydroxylation catalysed by robust sulfonated manganese and iron porphyrins supported on cationic ion-exchange resins", *Inorg. Chem.*, **31**, 1992, 1999-2006
28. Farkas A., Krabetz R., Mross W.D., *Ullman's Encyclopedia of Industrial Chemistry Vol A5*, 313-367
29. Campbell I. M., *Catalysis at Surfaces*, Chapman and Hall, 1988, 37
30. Grass K., Lintz H.G., "Oxidation of carbon monoxide over platinum-tin(IV) oxide catalysts: an example of spillover catalysts?", *Spillover and Migration of Surface Species on Catalysts*, 1997, 135-142
31. Somorjai G.A., "Introduction to surface chemistry and catalysis", *John Wiley & Sons, Inc.*, 1994, 345
32. Ilias S., Govind R., "Development of high temperature membranes for membrane reactor: An overview", *AIChE Symposium Series*, **85(268)**, 1989, 18-23
33. Ross J.R.H., Xue E., "Catalysis with membranes or catalytic membranes?", *Catalysis Today*, **25**, 1995, 291-301

34. Zaman J., Chakma A., "Review-Inorganic membrane reactors", *Journal of Membrane Science*, **92**, 1994, 1-28
35. Hsieh H.P., "Inorganic membrane reactors", *Catal.Rev.-Sci.Eng.*, **33(1&2)**, 1991, 1-70
36. Chang H.N., Furusaki S., "Membrane Bioreactors: Present and Prospects", *Advances in Biochemical Engineering, Biotechnology*, Managing editor: Fiechter A., **44**, 1991, 27-64
37. Vankelecom I.F.J., Parton R.F., Casselman M.J.A., Uytterhoeven J.B., Jacobs P.A., "Oxidation of cyclohexane using FePcY-Zeozymes occluded in polydimethylsiloxane membranes", *Journal of Catalysis*, **162**, 1996, 1-8
38. Burggraaf A.J., Cot L., "Fundamentals of inorganic membrane science and technology", *Membrane Science and Technology Series*, **4**, Elsevier, 1996, 119-139
39. Armor J.N., "Challenges in membrane catalysis", *Chemtec*, 1992, 557-563
40. Zaspalis V.T., Van Praag W., Keizer K., Van Ommen J.G., Ross J.R.H. Burggraaf A.J., "Reactions of methanol over alumina catalytically active membranes modified by silver", *Applied Catalysis*, **74**, 1991 235-248
41. Gryaznov V.M., Vedernikov V.I., Gul'yanova S.G., "Participation of oxygen, having diffused through a silver membrane catalyst, in heterogeneous oxidation processes", *Kinetics and Catalysis*, **26**, 1986, 129-133
42. Blekkan E.A., Rohr F., Lindvag O.A., Holmen A., "Fischer-Tropsch synthesis over cobalt catalysts supported on zirconia-modified alumina", *Catalysis Today*, **58**, 2000, 247-254
-

43. Somorjai G.A., "Introduction to surface chemistry and catalysis", *John Wiley & Sons, Inc.*, 1994, p451
44. Zhoa H., Xiong G., Baron G.V., "Pore-wall modified metal/ceramic catalytic membranes prepared by the sol-gel method", *Preparation of Catalysts VII*, 1998, 717-724
45. Uzio D., Peureux J., Giroiur-Fendler A., "Platinum/ γ -Al₂O₃ Catalytic membrane: Preparation, morphological and catalytic characterizations", *Applied Catalysis A:General*, **96**, 1993, 83-97
46. Gates B.C., *Stud. Surf. Sci. Catal.*, **29**, 1986, 415-425
47. Saracco G., Specchia V., "Catalytic inorganic membrane reactors: Present experience and future opportunities", *Catal.Rev.-Sci.Eng.*, **36(2)**, 1994, 305-384
48. Langhendries G., Baron G.V., "Mass transfer in composite polymer-zeolyte catalytic membranes", *Journal of Membrane Science*, **141**, 1998, 265-275
49. Shepard D.S., Maschmeyer T., Sankar G., Thomas J.M., Ozkaya D., "Preparation, Characterisation and performance of encapsulated copper-ruthenium bimetallic catalysts derived from molecular cluster carbonyl precursors", *Chem.Europ.J.*, **4(7)**, 1998, 1214-1224
50. Briot P., Auroux A., Jones D., Primet M., "Effect of particle size on the reactivity of oxygen-adsorbed platinum supported on alumina", *Applied Catalysis*, **59**, 1990, 141-152
51. Hargreaves J.S.J., Hutchings G.J., Joyner R.W., "Control of product selectivity in the partial oxidation of methane", *Nature*, **348**, 1990, 428-429

52. Hsieh H.P., *Inorganic membranes for separation and reaction*, Membrane Science and Technology Series, **3**, Elsevier, Amsterdam, The Netherlands 1996, 308-309
53. Gellings P.J., Bouwmeester H.J.M., "Solid state aspects of oxidation catalysis", *Catalysis Today*, **58**, 2000, 1-53
54. Armor J.N., "Catalysis with permselective inorganic membranes", *Applied Catalysis*, **49**, 1989, 1-25
55. Webb P.A., Orr C., *Analytical methods in fine particle technology*, Micromeritics Instrument Corporation, GA, U.S.A., 1997, 219-268
56. Konyukhov V.Y., Chitava V.E., Kuleshova O.P., Naumov V.A., "The kinetics of complete oxidation of ethanol on a copper-chromium oxide catalyst", *Kinetics and Catalysis*, **34(6)**, 1993, 946-948
57. Ling T-R., Chen Z-B., Lee M-D., "Catalytic behaviour and electrical conductivity of LaNiO_3 in ethanol oxidation", *Applied Catalysis A: General*, **136**, 1996, 191-203
58. Pina M.P., Irusta S., Menendez M., Santamaria J., Hughes R., Boag N. "Combustion of volatile organic compounds over platinum-based catalytic membranes", *Ind. Eng. Chem. Res.* **36**, 1997, 4557-4566
59. Perry R.H., Green D., *Perry's Chemical Engineers' Handbook*, McGraw-Hill International Editions, **6 ed**, McGraw-Hill International Editions, 1984, 3-47 – 3-63
60. Ivanov K., Litcheva P., Klissurski, "Mn-Mo-O catalysts for methanol oxidation. I. Preparation and characterisation of the catalysts", *Collection of Czechoslovak chemical communications*, **57**, 1992, 2529-2538
61. Zaspalis V.T., *Catalytically Active Ceramic Membranes, synthesis, properties and reactor applications*, Ph.D. Thesis, Twente University, The Netherlands, 1990

References

62. Moeller T., "Inorganic Syntheses", **vol V**, McGraw-Hill Book Company, New York, 1957, 55-63
63. Eng D., Stoukides M., "Catalytic and electrocatalytic methane oxidation with solid oxide membranes", *Catal. Rev.-Sci. Eng.*, **33(3&4)**, 1991, 375-412
64. Ai M., "The production of methyl formate by the vapour-phase oxidation of methanol", *Journal of Catalysis*, **77**, 1982, 279-288
65. Ito T., Tashiro T., Watanabe T., Toi K., Ikemoto I., "Activation of methane on the MgO surface at low temperatures", *Chemistry Letters, The Chemical Society of Japan*, 1987, 1723-1726
66. Gomez M.F., Arrua L.A., Abello M.C., "Kinetic study of partial oxidation of ethanol over VMgO catalyst", *Ind. Eng. Chem. Res.*, **36**, 1997, 3468-3472
67. Toba M., Niwa S., Shimada H., Mizukami F., "Effect of preparation methods of titania/silicas on their catalytic activities in the oxidation of olefins", *Heterogeneous Catalysis and Fine Chemicals IV*, Blaser H.U., Baiker A. and Prins R. (Editors), 1997, 345-352

UNIVERSITY of the
WESTERN CAPE



APPENDIX A

UNIVERSITY *of the*
WESTERN CAPE

Percentage Concentration of the alcohol in the feed

The partial pressure of the alcohol in the feed was calculated using the vapour pressure tables, by reading off the vapour pressure of the alcohol associated with the temperature of the cooling bath. The ratio of the vapour pressure to atmospheric pressure gives the percentage concentration of the alcohol in the feed.

$$\{P_{VA} / 760\} \times 100 \qquad \qquad \qquad A1$$

where:

P_{VA} - vapour pressure (mmHg) of the alcohol at a specific temperature

Weight hourly space velocity

Weight hourly space velocity is defined as the gram of liquids or gas passed over the unit weight of catalyst per hour

i.e

$$\frac{F}{V_{stp}} \times \frac{FM}{w} = \text{h}^{-1} \qquad \qquad \qquad A2$$

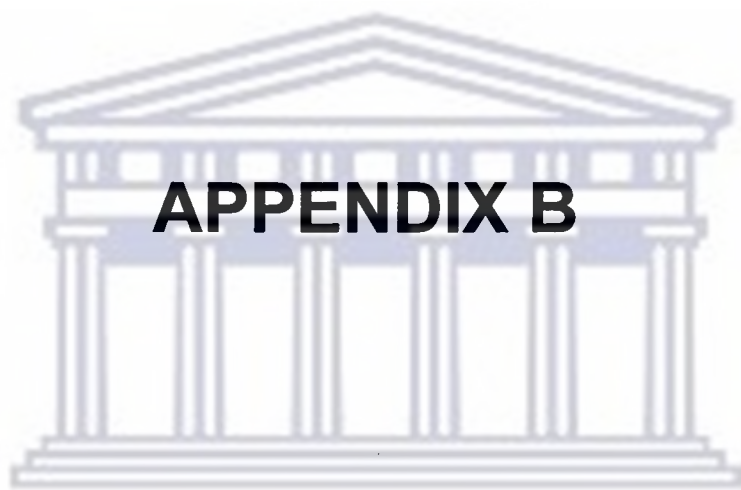
Where:

F - is the flow rate in $L.h^{-1}$

FM - formula mass of the alcohol in $g.mol^{-1}$

w - weight of catalyst in g

V_{stp} - $22.4 L.mol^{-1}$



APPENDIX B

UNIVERSITY *of the*
WESTERN CAPE

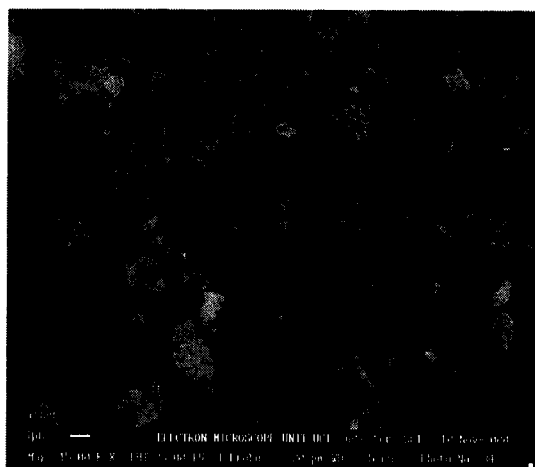


Figure B1 +MgO + Pt (4g/l) (Inner)

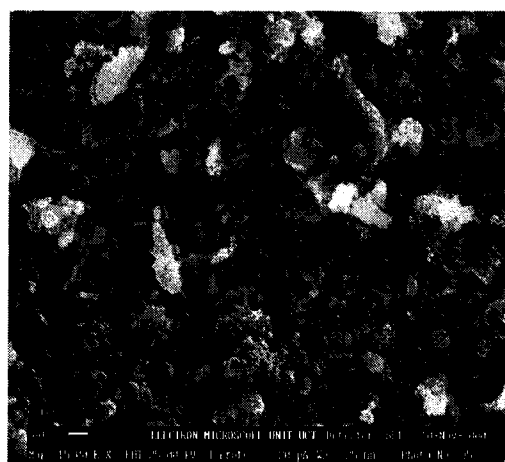


Figure B2 +MgO + Pt (4g/l) (Outer)



Figure B3 +MgO + Pt (4g/l) (Edge)

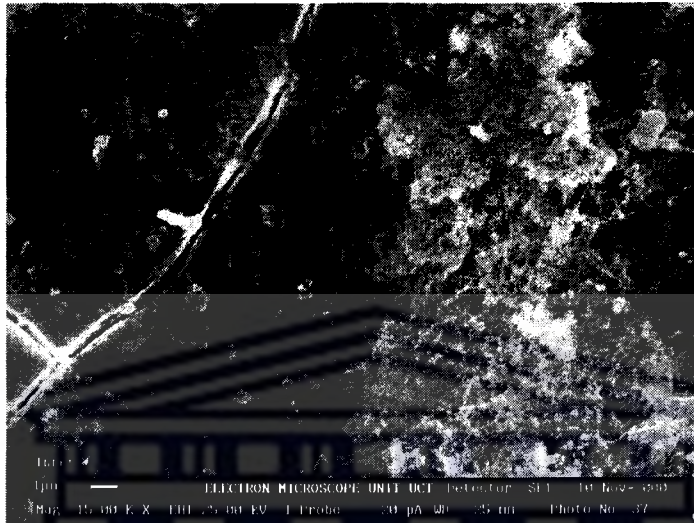


Figure B4 +MgO+PtPolySi (Inner surface)

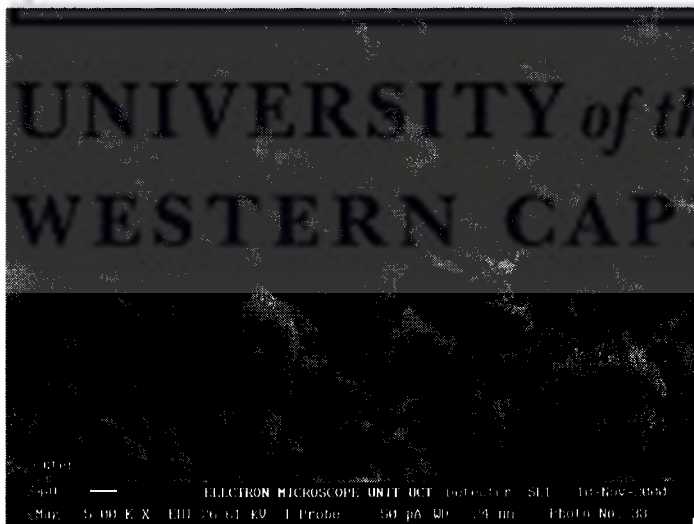


Figure B5 +MgO+PtPolySi (Outer surface)

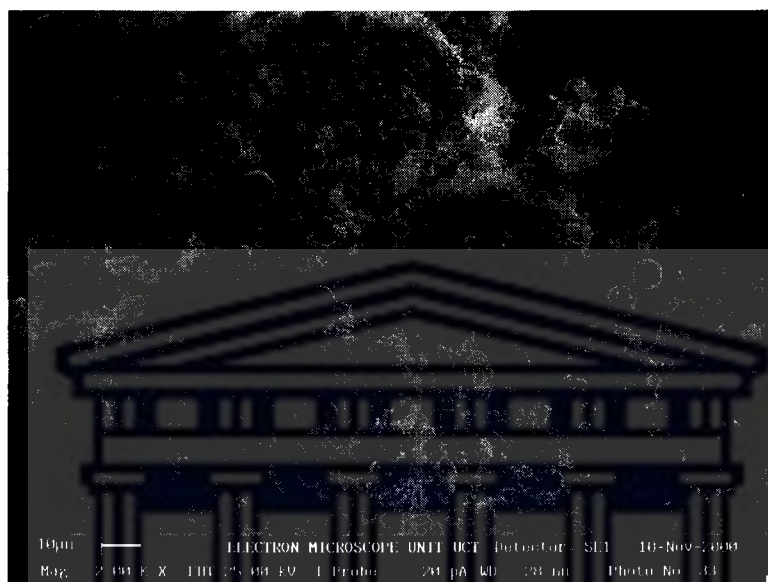


Figure B6 [MgO]-Si-N (Intermediate)

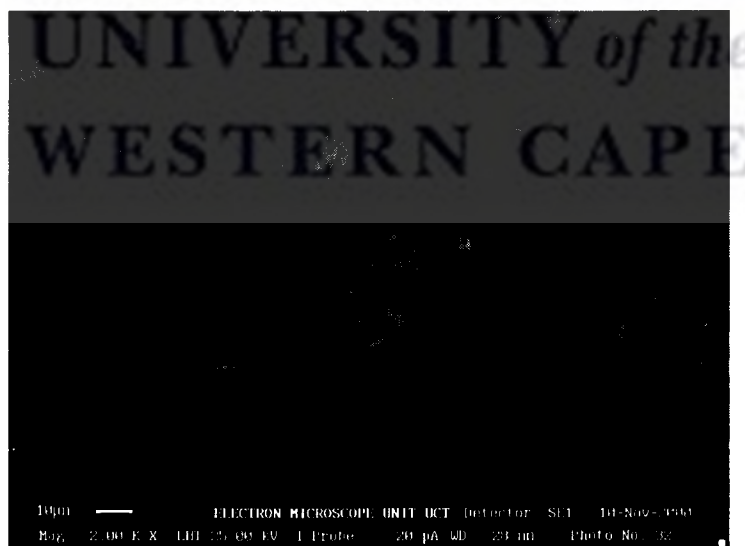


Figure B7 [MgO]-Si-N-Pt (Unsupported Catalyst)



APPENDIX C

UNIVERSITY *of the*
WESTERN CAPE

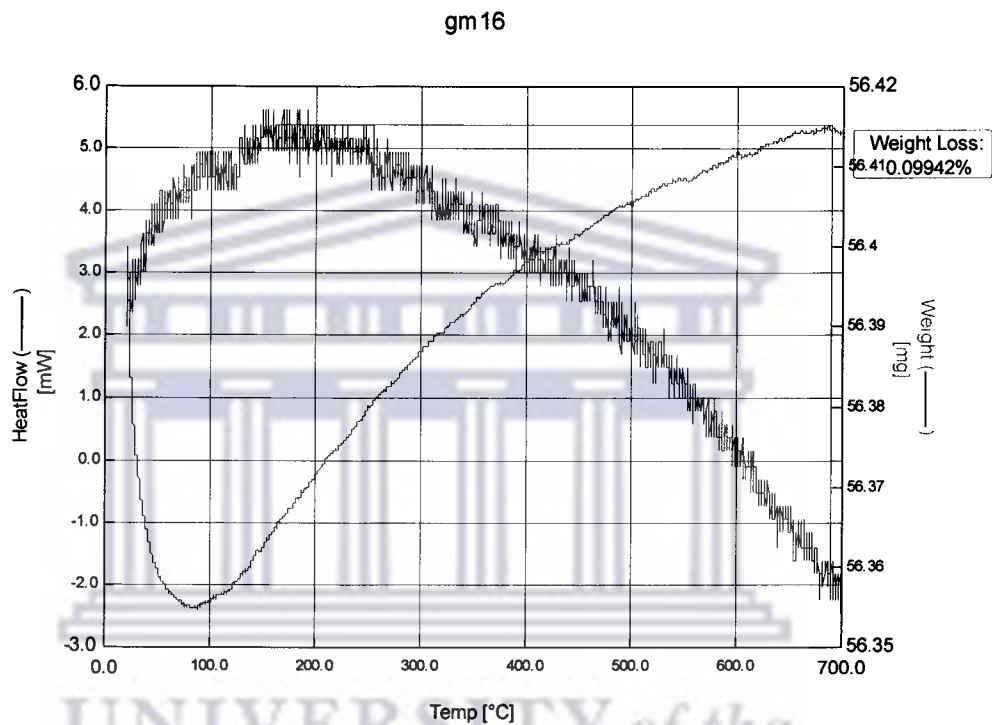


Figure C1 TGA/DSC of MgO+PtO(0.1g/l)

This thermogram closely resembles that of a blank membrane, which is due to the low amount of catalyst on the membrane



APPENDIX D

UNIVERSITY *of the*
WESTERN CAPE

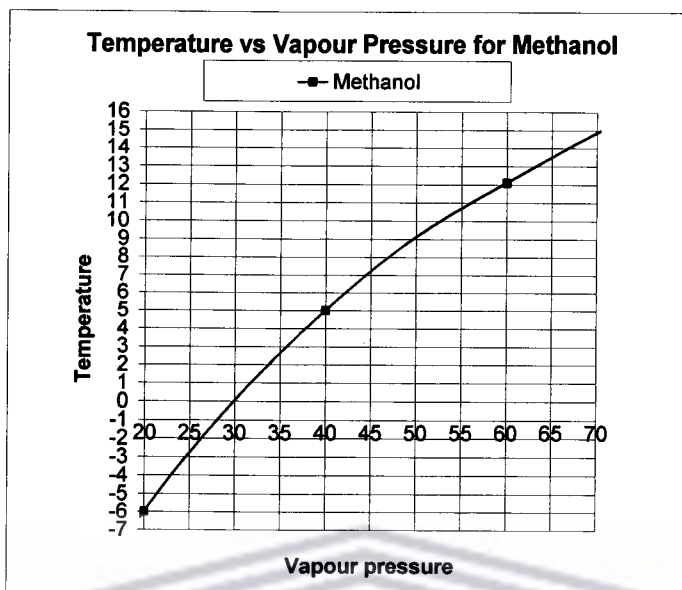


Figure D1 Temperature vs Vapour Pressure graph for methanol (used in calculation of methanol concentration in feed and for the generation of the calibration curves)

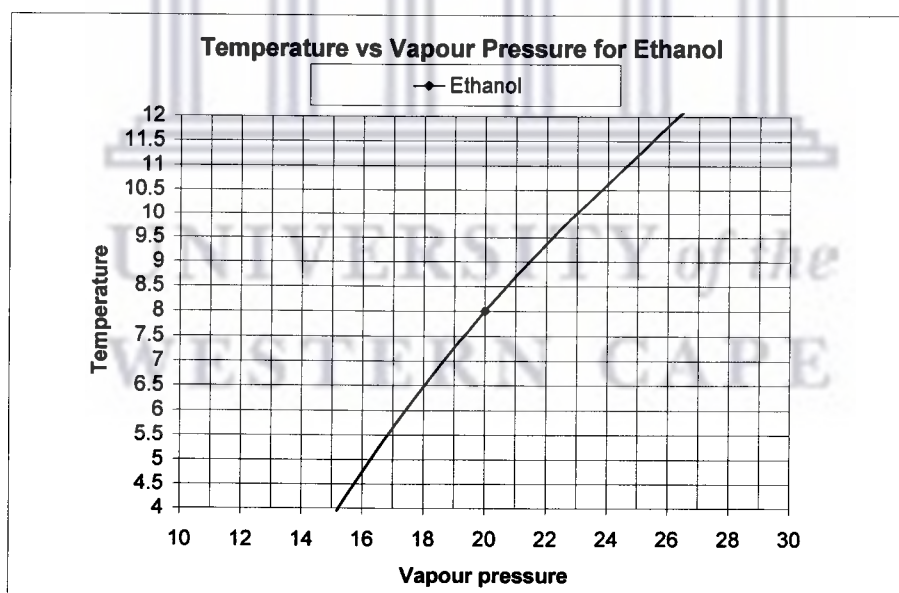


Figure D2 Temperature vs Vapour Pressure graph for ethanol (used in calculation of ethanol concentration in feed and for the generation of the calibration curves)