

# **THE HYDROGENOLYSIS OF GLYCEROL TO LOWER ALCOHOLS**

by

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*This thesis has been prepared according to Format 3 as outlined in the guidelines from the Faculty of Science and Agriculture which states:*

*This is a thesis in which the chapters are written as a set of discrete research papers, with an Overall Introduction and a Final Discussion. These research papers would not be published yet, but at least one paper would have already been submitted for publication. The references are reformatted to a uniform standard.*

Submitted in fulfilment of the academic requirements for the degree of  
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As the candidate's supervisor I have/have not approved this thesis/dissertation for submission.

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## ABSTRACT

Much work has been done towards the hydrogenolysis of glycerol to 1,2-PDO and 1,3-PDO using various heterogeneous systems including Rh, Ru, Pt, PtRu, copper systems and Raney Ni in batch systems. However, routes to lower alcohols, such as 1-propanol and ethanol have been less discussed. From an industry point of view, the production of lower alcohols, such as propanol and ethanol, is very interesting.

Different ruthenium, palladium and platinum catalysts were employed to study the effect of the support on the catalytic performance in batch mode. These catalysts were evaluated for their production of lower alcohols, especially 1-propanol using concentrated glycerol solutions. Among the other solid acids tested in combination with Ru/C, Amberlyst DT gave the most promising results from a 1-PO point of view, achieving a 34.9 mol% glycerol conversion with a selectivity of 38 mol% selectivity to 1-propanol. Despite the low glycerol conversion (1.3 mol%), Pd/C gave a promising 1-PO selectivity (> 85 mol%).

The use of supported Ni catalysts, an inexpensive system, towards the chemical transformation of glycerol to lower alcohols, has appeared less frequently in the literature. The activity of Ni supported catalysts on silica and alumina was studied for the transformation of glycerol to lower alcohols, primarily 1-propanol and ethanol in a fixed bed continuous flow reactor. Several characterisation techniques were performed on the fresh and used catalyst, such as BET, XRD, TPD, TPR, TGA and electron microscopy.

The objective was also to continue the development of a more detailed mechanistic understanding of the formation of lower alcohols from glycerol. In an endeavour to understand the process better, the role of proposed intermediates, 1,2-propanediol, 1,3-propanediol, ethylene glycol and ethanol was investigated, as well as the influence of the hydrogen partial pressure. Under the reaction conditions employed, it was clear that the hydrogenolysis of C-C and C-O bonds of glycerol took place to a lesser extent when compared to dehydrogenation and dehydration which are seen as the dominating initial steps. Ethanol was produced in high selectivities with 1,2-propanediol as feed and 1-propanol was the main product obtained when 1,3-propanediol was used as feed.

## **PREFACE**

All catalytic work was performed at Sasol Technology Research and Development and catalyst characterisation was done the School of Chemistry, University of KwaZulu-Natal, Westville Campus, Durban under the supervision of Prof. H. B. Friedrich.

The studies represent original work by the author and have not otherwise been submitted in any form or degree or diploma to any tertiary institution. Where use has been made of the work by the others authors it is duly acknowledged in the text.

## DECLARATION 1 - PLAGIARISM

I, Esti van Ryneveld, declare that

1. The research reported in this thesis, except where otherwise indicated, is my original research.
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## DECLARATION 2 - PUBLICATIONS

**Publication 1:** Direct hydrogenolysis of highly concentrated glycerol solutions over supported Ru, Pd and Pt catalysts systems. First author: Esti van Ryneveld, Other authors: Abdul B. Mahomed, Pieter S. van Heerden and Holger B. Friedrich. Submitted for publication in Catalysis Letters.

**Publication 2:** A catalytic route to lower alcohols from glycerol using Ni supported catalysts. First author: Esti van Ryneveld, Other authors: Abdul B. Mahomed, Pieter S. van Heerden, Mike J. Green and Holger B. Friedrich. Submitted for publication in Green Chemistry.

**Publication 3:** Mechanistic study for the synthesis of lower alcohols from glycerol using Ni supported catalysts, First author: Esti van Ryneveld, Other authors: Abdul B. Mahomed, Pieter S. van Heerden, Mike J. Green, Cedric Holzapfel and Holger B. Friedrich. Submitted for publication in Applied Catalysis A.

### Contributions by co authors:

Paper 1: co authors acted as research advisors

Paper 2: co authors acted as research advisors

Paper 3: co authors acted as academic / research advisors. Prof Holzapfel made a contribution towards the mechanism in the paper.

Apart from the contributions of people credited in the acknowledgements, I did all the experimental work (construction of reactor as well as data collection / interpretation).

Signed: .....

## **CONFERENCE CONTRIBUTIONS**

Catalysis of Society of South Africa conference 2009, Worcester, Oral Presentation,  
“Catalytic route to ethanol from glycerol using Ni supported catalysts”.

## CONTENTS

This dissertation is written as a series of three technical papers which have been submitted for publication in technical journals. Each paper has its own abstract, introduction, experimental section, results and discussion as well as figures, tables and schemes.

Chapter 1 gives an overall introduction to glycerol hydrogenolysis as well as a discussion on glycerol as a value adding commodity.

Chapter 2 contains the first paper, which discusses direct hydrogenolysis of highly concentrated glycerol solutions over supported Ru, Pd and Pt catalysts systems under batch conditions.

Chapter 3 contains the second paper, which discusses the catalytic route to lower alcohols from glycerol using Ni supported catalysts under fixed bed conditions.

Chapter 4 contains the third paper, which discusses the mechanistic route to lower alcohols from glycerol using Ni supported catalysts.

Chapter 5 gives a final discussion on the summary and conclusions.

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**LIST OF ABBREVIATIONS**

1-PO	1-Propanol
2-PO	2-Propanol
1,2-PDO	1,2-Propanediol
1,3-PDO	1,3-Propanediol
BET	Brunauer, Emmet and Teller
EG	Ethylene glycol
EtOH	Ethanol
GC	Gas Chromatograph
GCMS	Gas Chromatography Mass Spectrometry
GHSV	Gas hour space velocity
Heavies	Aldol condensation products
MeOH	Methanol
LHSV	Liquid hour space velocity
SEM	Scanning Electron Microscopy
TEM	Transmission Electron microscopy
TGA-DSC	Thermo gravimetric analysis – differential scanning calorimetry
TPD	Temperature programmed desorption
TPR	Temperature programmed reduction
XRD	X-ray diffraction

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Lastly, I would like to thank my loving husband, Coert; this journey was difficult at times but thanks to your love, patience and constant support you gave me the strength to complete this chapter of my life.

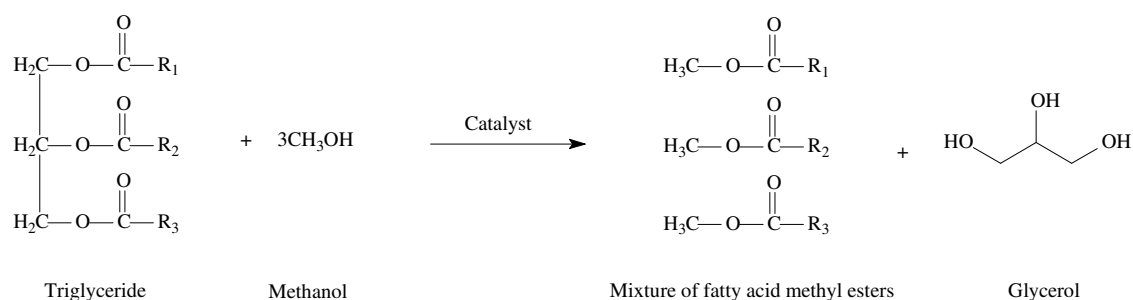
# CHAPTER 1

## GLYCEROL HYDROGENOLYSIS

### 1.1 Introduction

The interest in the catalytic conversion of renewable feedstocks to a range of value added chemical commodities has been increasing. Studies on the hydrogenolysis of polyhydric alcohols have been pursued since 1930. Recently the need has arisen to find new applications for glycerol, a polyhydric alcohol obtained as by-product from the production of biodiesel. One of the routes is to convert glycerol, by reforming, to hydrogen and synthesis gas [1]. Glycerol can also be converted to 1,2-propanediol (1,2-PDO) and 1,3-propanediol (1,3-PDO), which have been produced from petroleum derivatives [2]. In addition, lower alcohols such as methanol, ethanol, 1-propanol (1-PO) and 2-propanol (2-PO) can also be produced from glycerol via consecutive hydrogenation/hydrogenolysis of 1,2-PDO and 1,3-PDO and this route is very appealing to industry [3].

The transesterification of vegetable oil triglycerides with methanol in the manufacture of bio-diesel produces glycerol as a by-product (Scheme 1.1). When triglycerides are reacted with methanol over a basic catalyst, such as NaOH or sodium methoxide, the C<sub>3</sub> molecule separates from the triglyceride as glycerol. The remaining part is three long chain fatty acid molecules (mostly linear) that have reacted with the methanol to form an ester. These methyl esters are referred to as bio-diesel. During triglyceride transesterification, glycerol separates from the oil phase as the reaction proceeds [4].



\* R1 / R2 / R3 = long chain alkyl groups

**Scheme 1.1: Triglyceride transesterification with methanol.**

For every 9 kg of biodiesel produced, about 1 kg of crude glycerol by-product is formed, which contributed towards glycerol's growing importance as a bio-refinery feedstock over the past decade. With the expansion of the biodiesel industry globally, the world is experiencing a large oversupply of glycerol [4]. The oversupply is expected to worsen in the next few years as countries move to implement the directives of the Kyoto protocol, as well as to reduce their dependence on fossil fuels. Therefore, increased biodiesel production results in the accumulation of glycerol which leads to a price decline. The largest producer of biodiesel is the European Union (EU) with 56 % of the world capacity. The EU aims to double the amount of bio-fuels in the fuel pool by 2020 [4]. With glycerol becoming a cheap, large-volume feedstock, using it as a source of organic carbon and as a starting material for chemical transformations, is very appealing.

## 1.2 Glycerol as a value added commodity

The main applications of glycerol include its use in food & beverages, personal care, pharmaceuticals and polymers. It is expected that the major future growth areas will be for chemicals traditionally made from crude oil.

Currently, there is a slow-down in biodiesel production in Germany as a result of the government's removal of subsidies for biodiesel manufacturers. At the same time, other members of the EU are increasing production strongly, especially France [5].

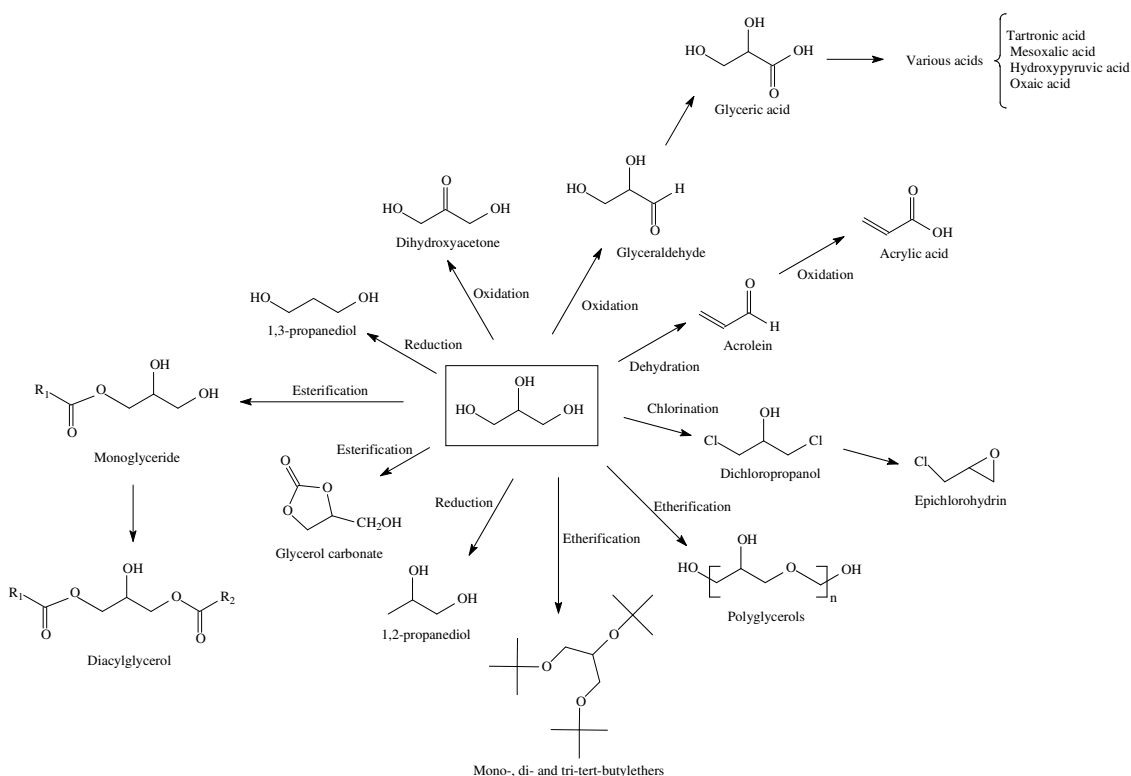
Using the SRI<sup>1</sup> figure for the growth in demand for glycerol of 4.4 % per annum, the global demand in 2010 can be calculated to be about 450 kt. Thus, even with the more conservative estimate of FO Licht<sup>1</sup>, there will still be a large excess of glycerol produced in the world beyond 2010 [4].

Therefore, the development of new applications for glycerol would be welcomed by the entire glycerol industry. From a technical point, glycerol's multifunctional structure can be exploited by several different means. A number of opportunities for glycerol transformation [6] is identified and summarized in Scheme 1.2.

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<sup>1</sup> SRI and FO Licht are both consulting groups which prepare Process Economics Reports for the chemical industry.

A range of possible products can be formed by oxidising glycerol, such as dihydroxyacetone, glyceraldehyde, glyceric acid, hydroxypyruvic acid, mesoxalic acid, oxalic acid and tartronic acid, by using inexpensive oxidising agents such as air, oxygen, hydrogen peroxide or bleach. Dihydroxyacetone is used as a tanning agent in the cosmetic industry. The highly functionalised molecule mesoxalic acid was recently found to show activity as an anti-HIV agent and hydroxypyruvic acid is a flavour component in cheese [6].



**Scheme 1.2: Commodity chemicals derived from glycerol [6].**

The main products arising from the reduction of glycerol are 1,3-propanediol and 1,2-propanediol. 1,3-Propanediol is a speciality chemical which is used in polyester fibres, whereas 1,2-propanediol is used in liquid detergents, antifreeze and cosmetics. An important chemical that can be produced directly by the dehydration of glycerol is acrolein. The most significant application of acrolein is as a herbicide to control the growth of aquatic plants. Acrolein is also an important bulk chemical used as feedstock for acrylic acid production, pharmaceuticals and fibre treatment, amongst other uses [6].

Studies of glycerol halogenation have focussed on the production of 1,3-dichloropropanol, which is an intermediate in the production of epichlorohydrin. Epichlorohydrin is an important raw material for the production of materials such as epoxide resins, synthetic elastomers and sizing agents for the paper making industry [6].

Glycerol ethers include glycerol compounds that were reacted with isobutylene or tert-butanol or glycerol compounds that reacted with further molecules of glycerol to form polyglycerols. The glycerol ethers are excellent oxygen additives for diesel fuel. Polyglycerols are gaining importance in products such as surfactants, lubricants, cosmetics and food additives [6].

The esterification of glycerol with carboxylic acid yielded monoglycerides (MG) as well as diacylglycerol (DAG). MG's are amphiphilic molecules useful as non-ionic surfactants and emulsifiers. They are widely used in bakery products, margarines and dairy products. In the cosmetic industry, they are added as texturing agents for improving the consistency of creams and lotions. Recent studies on DAG's nutritional properties and dietary effects suggested that this component decreased body weight and visceral fat mass. DAG is also naturally present as a minor component of edible fats and oils of various sources [6].

Several companies have recognized the potential of glycerol as a chemical feedstock and have developed processes to exploit this. The two chemicals which are front runners for commercialization are the polyols; 1,2-PDO and ethylene glycol (EG), and epichlorohydrin. A selection of announcements in the chemical press is given Table 1.1.

Therefore, glycerol presents an ideal source for renewable industrial feedstocks, provided that alternative methods for glycerol utilisation that are economically viable can be met.

### **1.3 Hydrogenolysis of glycerol under reductive conditions**

Catalytic hydrogenation refers to the addition of hydrogen to an organic molecule in the presence of a catalyst [7]. If the molecule undergoes cleavage, then the reaction is referred to as hydrogenolysis. These reactions are used to produce a variety of both bulk and fine organic chemicals. In addition, hydrogenation is often used in various purification processes (e.g., selective reduction of trace amounts of acetylene in an ethylene stream or traces of butadiene in a butene stream, and removal of unwanted oxygen, hydrogen or carbon oxides from a variety of

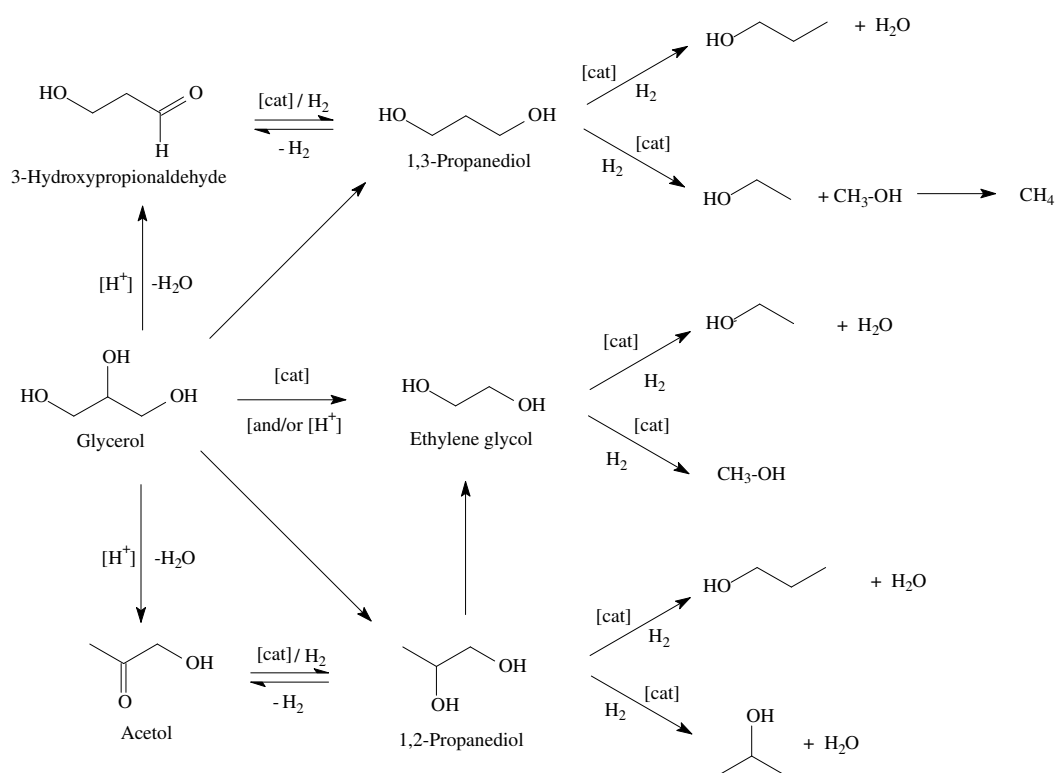
systems). Several catalytic systems are known for the hydrogenolysis of glycerol such as precious metals, copper and nickel systems.

**Table 1.1: Companies utilising glycerol as feedstock [8].**

<b>Company</b>	<b>Announcements made in terms of utilisation of glycerol as feedstock.</b>
Perstorp	Interested in glycerol derivatives, not revealing plans at this stage.
Solvay	10 kt epichlorohydrin plant was built in 2007 in France and is fully optimised. Plans to build a 100 kt plant in Thailand by end of 2011.
DuPont-Tate & Lyle	Completed a 1,3-PDO plant in 2007, no capacity indicated.
Archer Daniels Midlands (ADM)	Built a 100 kt Propylene glycol & Ethylene glycol plant in the USA, completed by end of 2009.
Cargill	Cargill & Ashland to form a joint venture to build a 65 kt PG facility in Frankfurt and manufacturing of the plant started in 2009.  Was considering building a PG plant in the USA by 2008, but process put on hold.
Huntsman	Developed a PG process, product undergoing customer approval trials.
Synergy Chem	A small 27 kt PG plant was built in 2006 in the USA.
Ineos	May build a PG plant to complement their biofuels project in Europe.
Biomethanol Chemie	Built a 100 kt bio-methanol plant using glycerol as feed in Holland (previously Methanor's natural gas based methanol plant).
Dow	Build a 150 kt epichlorohydrin plant in China and is expected to be finished in 2010. Interested in developing glycerol based polyols for PU foams.
BASF	May build a 100 kt PG plant in Europe. Investigating a range of chemicals from glycerol: PG, succinic acid, THF.
Metabolic Explorer	Built a pilot plant in 2007 to make 1,3-propanediol in collaboration with IFP in France. Based on fermentation of glycerol.
Davy Process Technology	Has licensed their vapour phase hydrogenation technology to convert glycerol to PG to Ashland & Cargill.

### 1.3.1 Precious metals (Ru, Rh, Pt and Pd)

The transformation of glycerol in the presence of hydrogen can occur via several pathways as reported in literature (Scheme 1.3). The first, resulting from acid catalysed dehydration, can form 3-hydroxypropionaldehyde (3-HPA) or acetol [3]. Subsequent hydrogenation of 3-HPA and acetol yielded 1,3-PDO and 1,2-PDO respectively. Glycerol can also be transformed directly, via hydrogenolysis, to form 1,2-PDO, 1,3-PDO and ethylene glycol (EG) [9]. The subsequent diols can undergo further hydrogenolysis to form primary alcohols such as 1-propanol (1-PO), ethanol and methanol, as well as secondary alcohols like 2-propanol (2-PO). C<sub>1</sub> products such as methane, CO and CO<sub>2</sub> can form via decomposition reactions or the water gas shift reaction [10].



**Scheme 1.3: Reaction scheme of glycerol hydrogenolysis and degradation reactions [3, 9, 10].**

Tomishige and co-workers [3] reported various carbon supported noble metals (Ru/C, Rh/C, Pt/C and Pd/C) in combination with acids ( $H_2SO_4$ , HCl and Amberlyst 15) as co-catalysts for the hydrogenolysis of glycerol under mild conditions (120 °C and 80 Bar). The conversions over Pt/C and Pd/C were low and the promoting effect of adding Amberlyst was insignificant.

In contrast, the activity of Rh/C was comparable to that of Ru/C and the hydrogenolysis selectivity of Rh/C was higher (63 % versus 26 % 1,2-PDO selectivity). However, the promoting effect of adding Amberlyst to the Ru/C reaction mixture was quite significant, with an increase in conversion from 3.5 % to 12.9 %. On promotion, the hydrogenation activity for the different metals decreased in the order Ru/C >>> Rh/C > Pt/C > Pd/C as shown in Table 1.2.

**Table 1.2: Glycerol hydrogenolysis over metal catalysts and metal + acid catalysts [3].**

Catalyst	Conv. (%)	Selectivity (%)				
		1,2-PDO	1,3-PDO	1-PO	2-PO	Others*
Ru/C	3.5	26.4	4.9	26.7	0.3	41.7
Rh/C	1.9	62.8	6.8	19.3	7.0	4.1
Pt/C	0.3	27.7	0.0	23.5	24.2	24.6
Pd/C	0.2	30.7	0.0	11.3	18.3	39.7
Ru/C + Amberlyst 15	12.9	55.4	4.9	14.1	0.9	24.7
Rh/C + Amberlyst 15	3.0	32.7	9.0	40.4	14.9	3.0
Pt/C + Amberlyst 15	0.3	27.1	0.0	21.5	35.0	16.4
Pd/C + Amberlyst 15	0.2	26.6	0.0	15.8	30.3	27.3
Ru/C + H <sub>2</sub> SO <sub>4</sub>	5.1	56.3	4.0	13.1	7.1	19.5
Rh/C + HCl	0.9	34.0	0.0	21.6	7.8	36.6

Reaction conditions: 20 wt% glycerol solution (20 mL), 80 Bar hydrogen, 120 °C, 10 h, 150 mg catalyst (+300 mg Amberlyst 15).

\* Others = ethylene glycol, methanol, ethanol and methane.

Tomishige and co-workers proposed that the hydrogenolysis of glycerol proceeded via the dehydration of glycerol to either acetol or 3-HPA on the acid catalysts and then, via a consecutive hydrogenation step, propane diols were formed. 1-PO can mainly be formed via 1,3-PDO in glycerol hydrogenolysis over a Ru/C catalyst [3]. Ethanol and methane were formed from the degradation reaction of 1,2-PDO and 1,3-PDO and in addition, ethanol can also be formed during the hydrogenolysis of EG. Methanol is formed via the degradation reaction of EG [3].

In addition, the difference between Amberlyst 15 and Amberlyst 70 in the hydrogenolysis of glycerol to 1,2-propanediol [11] was investigated. Amberlyst 15 and Amberlyst 70 are both highly cross-linked styrene-divinyl benzene copolymer beads with maximum operating temperatures of 130 °C and 190 °C respectively. Ru/C and Amberlyst 15 showed conversions of 8 mol% at 140 °C while Ru/C and Amberlyst 70 showed conversions of 26 mol%.

The promoting effect of different solid acids was also studied [12]. H<sub>2</sub>WO<sub>4</sub> was effective in enhancing the glycerol conversion, while Rh/C and H<sub>2</sub>WO<sub>4</sub> showed higher activity to 1,3-propanediol of 21 mol%. Other zeolites and solid acid catalysts, such as Amberlyst 15, MFI (SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 22, acid amount 0.67 mol/kg), BEA (SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 25, acid amount 0.51 mol/kg), USY (SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 6.3, acid amount 0.70 mol/kg) and SO<sub>4</sub><sup>2-</sup>/ZrO<sub>2</sub>, were also tested and the results are shown in Table 1.3. The highest glycerol conversion was obtained at 180 °C and 80 Bar hydrogen, in the presence of Amberlyst 15 which can be attributed to the higher acid strength of Amberlyst 15.

**Table 1.3: Results of glycerol hydrogenolysis over Ru/C + solid acid catalysts [12].**

Catalyst	Conversion (%)	Selectivity to liquid products (%)				
		1,2-PDO	1,3-PDO	1-PO	2-PO	Others*
Ru/C + SO <sub>4</sub> <sup>2-</sup> /ZrO <sub>2</sub>	8.5	58.9	1.1	0.7	0.1	39.2
Ru/C + BEA	9.8	51.4	2.5	3.4	0.2	42.5
Ru/C + USY	6.7	82.0	0.4	0.9	0.4	16.3
Ru/C + MFI	7.4	44.2	2.6	17.5	0.3	35.4
Ru/C + H <sub>2</sub> WO <sub>4</sub>	5.9	79.4	1.4	1.2	0.2	17.8
Ru/C + Amberlyst 15	15.0	53.4	1.6	5.4	1.0	38.6
Rh/SiO <sub>2</sub> + H <sub>2</sub> WO <sub>4</sub>	1.3	56.7	20.9	10.4	0.7	11.3

Reaction conditions: 20 wt% glycerol solution (20 mL), 80 Bar hydrogen, 180 °C, 10 h, 150 mg catalyst (+300 mg solid acid).

\*Others = ethylene glycol, methanol, ethanol and methane.

A study on the catalytic performance of supported metal catalysts (Rh, Ru, Pt, Pd on active carbon, SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>) during the hydrogenolysis of aqueous glycerol solutions under H<sub>2</sub> showed that Rh/SiO<sub>2</sub> exhibited higher activity and higher selectivity to hydrogenolysis products, such as propanediols and propanols, than Ru/C at 120 °C [13]. With the addition of Amberlyst 15 to

Rh/SiO<sub>2</sub>, the glycerol conversion, as well as selectivity towards 1,2-PDO and 1-propanol, were enhanced. A high selectivity of 42.2 % to 1-propanol was observed, as well as a selectivity of 13 % to 2-propanol (Table 1.4).

**Table 1.4: Results of the glycerol reaction over Rh/SiO<sub>2</sub> and Ru/C catalysts [13].**

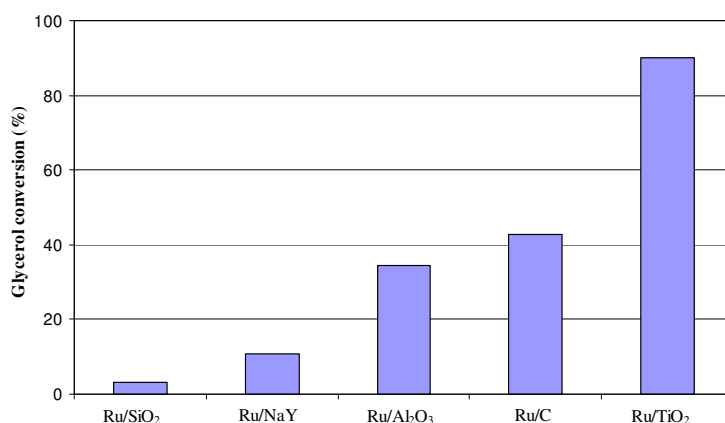
Catalyst	Conversion (%)	Selectivity to liquid products (%)				
		1,2-PDO	1,3-PDO	1-PO	2-PO	Others*
Rh/SiO <sub>2</sub> + Amberlyst 15	14.3	26.0	9.8	42.2	12.9	9.1
Rh/SiO <sub>2</sub>	7.2	38.1	7.9	35.2	12.6	6.1
Ru/C + Amberlyst 15	12.9	55.4	4.9	14.1	0.9	24.7
Ru/C	3.5	26.4	4.9	26.7	0.3	41.7

Reaction conditions: 20 wt% glycerol solution (20 mL), 80 Bar hydrogen, 120 °C, 10 h, 150 mg catalyst (+300 mg Amberlyst 15).

\* Others = ethylene glycol, methanol, ethanol and methane.

It has recently been reported that the addition of Re, Mo and W to Rh/SiO<sub>2</sub> can enhance catalytic activity in glycerol hydrogenolysis [14]. In particular, the formation of 1,3-PDO was enhanced to 20 % by the modification of the catalyst with Re. In addition, the side reactions such as the C-C cleavage were suppressed, as were the propanediol hydrogenolysis reactions. It was also noted that no acetol or 3-HPA was detected in the reaction mixtures and this suggests that the direct hydrogenolysis of glycerol takes place over the Rh-ReO<sub>x</sub>/SiO<sub>2</sub> catalyst.

Feng et al. [15] studied the effect of support and catalyst reduction temperature on the catalytic performance of ruthenium catalysts in the hydrogenolysis of glycerol. Several different ruthenium catalysts were tested which included Ru/SiO<sub>2</sub>, Ru/NaY, Ru/γ-Al<sub>2</sub>O<sub>3</sub>, Ru/C and Ru/TiO<sub>2</sub> at 180 °C and 50 Bar H<sub>2</sub> (Figure 1.1). The TiO<sub>2</sub> supported catalyst exhibited the highest glycerol conversion (90 %), but favoured the production of ethylene glycol (41 %) over 1,2-PDO (20 %), whereas the Ru/SiO<sub>2</sub> showed a high selectivity to 1,2-PDO.



**Figure 1.1: Effect of support on the reaction activity of the glycerol hydrogenolysis [15].**

Reaction conditions: 180 °C, 50 Bar H<sub>2</sub>, 8 h.

Several Ru/Al<sub>2</sub>O<sub>3</sub>, Ru/C and Ru/ZrO<sub>2</sub> catalysts were employed in the hydrogenolysis of glycerol [16] and the effect of Re as an additive was studied on the catalytic performance of these catalysts at 160 °C and 80 Bar hydrogen (Table 1.5). The catalytic performances of the Ru catalysts supported on the three different supports were different. The highest glycerol conversion (29.7 %) and the highest selectivity to 1,2-PDO (50.9 %) were obtained over Ru/C.

**Table 1.5: Glycerol hydrogenolysis results over Ru-based catalysts [16].**

Catalyst	Conv. (%)	Selectivity to liquid products (%)						
		MeOH	EtOH	EG	2-PO	1-PO	1,2-PDO	1,3-PDO
Ru/Al <sub>2</sub> O <sub>3</sub>	18.7	2.0	6.1	29.3	2.2	22.5	34.5	3.4
Ru/ZrO <sub>2</sub>	19.5	0.6	5.8	13.2	3.8	33.0	36.3	7.2
Ru/C	29.7	1.1	6.7	14.4	3.2	22.9	50.9	0.8
Ru/Al <sub>2</sub> O <sub>3</sub> +Re <sub>2</sub> (CO) <sub>10</sub>	53.4	0.4	6.8	7.8	5.1	23.4	50.1	6.4
Ru/ZrO <sub>2</sub> +Re <sub>2</sub> (CO) <sub>10</sub>	27.1	0.2	2.1	4.0	3.8	24.2	53.1	12.6
Ru/C + Re <sub>2</sub> (CO) <sub>10</sub>	59.4	0.2	3.8	1.5	6.3	24.5	56.6	7.2

Reaction conditions: 160 °C, 80 Bar H<sub>2</sub>, 8 h.

However, when Re was added as promoter (using Re(CO)<sub>10</sub> as precursor) the glycerol conversions were enhanced significantly, especially over Ru/C and Ru/Al<sub>2</sub>O<sub>3</sub>. The selectivity to

EG also decreased, which implied that the addition of Re inhibited the degradation reaction of glycerol. A reason for the high activity that these catalytic systems (Ru/C + Re(CO)<sub>10</sub>) show is the uniform depositing of Re particles on the side of the small Ru particles. Because the Ru was highly dispersed on the surface of the active carbon, the addition of the Re species deposited in-situ on the side of Ru particles.

The effect of the metal precursor on Ru-based catalysts on different supports (Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, ZrO<sub>2</sub>) was also evaluated in the glycerol hydrogenolysis reaction at 240 °C and 80 Bar H<sub>2</sub> [17], looking at glycerol conversion and 1,2-PDO selectivity. The Ru/Al<sub>2</sub>O<sub>3</sub> catalyst, prepared with a chloride precursor, showed the highest activity (69 %) but the lowest selectivity to 1,2-PDO (38 %), and this is due to the excessive hydrogenolysis of 1,2-PDO to propanols which is due to the retention of Cl<sup>-</sup> ions on the support. Then, Ru/SiO<sub>2</sub>, prepared with a nitrate precursor, showed the lowest activity (21 %) but with the highest 1,2-PDO selectivity (65 %).

A series of H-β (SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 37), H-ZSM-5 (SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 70), Al<sub>2</sub>O<sub>3</sub>, MgO and hydrotalcite precursor supported Pt catalytic systems was synthesised and tested for the hydrogenolysis of glycerol in a base-free aqueous solution [18]. The hydrotalcite precursor supported Pt catalyst, with a strong alkalinity and highly dispersed Pt particles, showed the best performance for this reaction. A 92 % conversion was achieved with a 93 % selectivity to 1,2-propanediol at low pressures.

D'Hondt et al. [19] reported on the catalytic conversion of glycerol to 1,2-PDO with a non-acidic Pt impregnated NaY zeolite at 230 °C with 20 wt% glycerol solution in the absence of H<sub>2</sub>. During the initial stages of the reaction, glycerol underwent reforming to produce H<sub>2</sub>, CO<sub>2</sub> and CO. The CO<sub>2</sub> dissolved in the reaction medium, generating H<sub>2</sub>CO<sub>3</sub>, which yielded free protons upon dissociation to form H-NaY. This acid zeolite then catalysed the conversion of glycerol into hydroxyacetone and the subsequent hydrogenation on the Pt gave 1,2-PDO.

Gandarias et al. [20] performed glycerol hydrogenolysis reactions to 1,2-PDO on Pt catalysts supported on amorphous silica alumina (Pt/ASA) under mild conditions (220 °C, 45 Bar H<sub>2</sub>). These reactions also took place under N<sub>2</sub> pressure due to hydrogen that is formed during glycerol aqueous phase reforming (APR). No significant APR reactions occurred with Pt/ASA under hydrogen pressure and this shows that hydrogen has an inhibiting effect on the reforming

rate and is caused by the adsorbed hydrogen that blocks the surface sites and decreases the surface concentration of reactive intermediates formed by dehydrogenation reactions.

The hydrogenolysis of glycerol to propanediols was further studied over a Ru/C catalyst using different solid acids as co-catalysts, and the results are summarised in Table 1.6 [21]. Solid acids such as niobia, 12-tungstophosphoric acid (TPA) supported on zirconia, cesium salt of TPA and cesium salt of TPA supported on zirconia were used. The order of glycerol conversion for the solid acids was as follows:  $\text{Nb}_2\text{O}_5 > \text{TPA}/\text{ZrO}_2 > \text{CsTPA} > \text{CsTPA}/\text{ZrO}_2$ . When  $\text{Nb}_2\text{O}_5$  was used as solid acid at 180 °C and 60 Bar  $\text{H}_2$ , the selectivity to 1,2-PDO (61 %) and EG (29 %) was greater than compared to other acids.

**Table 1.6: Effect of solid acid as co-catalyst on the hydrogenolysis of glycerol over Ru/C [21].**

Metal catalyst	Acid catalyst	Conversion	Selectivity (%)		
			1,2-PDO	EG	Others*
Ru/C	$\text{Nb}_2\text{O}_5$	44.6	60.9	29.1	10.0
Ru/C	$\text{TPA}/\text{ZrO}_2$	44.0	64.3	27.0	8.7
Ru/C	CsTPA	21.0	60.2	4.7	35.1
Ru/C	$\text{CsTPA}/\text{ZrO}_2$	25.0	67.0	8.0	25.0

Reaction conditions: 20 wt% glycerol solution (50 mL), 60 Bar hydrogen, 180 °C, 8 h, 3 % metal catalyst weight and 6 % acid catalyst weight.

\* Others = 1,3-PDO, acetol, 2-PO, 1-PO, ethanol and methanol.

Maris and Davis [22] also showed that Ru/C and Pt/C are effective catalysts for glycerol hydrogenolysis, where the selectivities to EG and 1,2-PDO are a function of metal type and solution pH. At 200 °C, 40 Bar and neutral pH, Ru was more active than Pt at converting glycerol to glycols (20 mol% conversion vs 13 mol% conversion). Ru/C favoured the formation of EG (68 %) over 1,2-PDO (32 %), whereas Pt/C favoured the formation of 1,2-PDO (79 %) over EG (17 %). The addition of NaOH enhanced the reactivity of Pt to a greater extent than Ru/C, but lactate formation was significant over both catalysts.

A process was patented [23] to provide a method for the hydrogenation of glycerol, particularly impure glycerol, in the presence of a ruthenium modified catalyst with sulphides to produce 1,2-propanediol and lactic acid. The ruthenium catalyst was supported on activated carbon, typically

between 0.5 % and 7 % by weight, and the preferred sulfates were sodium bisulfates and thiosulfates. The presence of a basic promoter was necessary to achieve high yields of the glycerol conversion and preferred bases were hydroxides of alkali metals or alkaline earth metals. Glycerol solutions between 30 and 40 wt% were used at 240 °C and almost 100 % conversion was achieved with a selectivity of 75.2 % to 1,2-propanediol, 13.4 % to lactic acid and 5 % to ethylene glycol.

Montassier et al. [24] reported an increase in selectivity for propylene glycol from 10 % to 80 % with 1 mole of sulphur per mole of ruthenium. This work was performed at pH 6, which lowered the overall glycerol reaction rate. Several groups have reported two primary effects that sulphur modification of the ruthenium catalyst has on the reaction rate. The first effect is the reduction in the overall reaction rate, as sulphur is a well-known metal catalyst poison. However, in the case of polyol products a second effect occurs: the selectivity for specific products increases.

The results of testing heterogeneous catalysts, including ruthenium, nickel, platinum, copper, Raney nickel, Raney copper, palladium and copper chromite on activated carbon are shown in Table 1.7 [25]. Catalysts like ruthenium and palladium showed selectivities of less than 50 % to propylene glycol, due to the degradation of glycerol, at temperatures above 200 °C and a hydrogen pressure of 13.8 Bar, to form lower alcohols and gases (methane, ethane, propane and carbon dioxide). On the other hand, copper and copper chromite exhibited higher selectivities to propylene glycol with lower formation of degradation products.

Chaminand et al. [9] studied the hydrogenolysis of aqueous solutions of glycerol at 180 °C and 80 Bar hydrogen pressure in the presence of supported metal catalysts to selectively produce 1,2- and 1,3-propanediol. They evaluated different catalysts (Cu, Pd, Rh) on different supports (ZnO, C, Al<sub>2</sub>O<sub>3</sub>) in different solvents (water, sulfolane, dioxane) and additives (H<sub>2</sub>WO<sub>4</sub>) to improve the reaction rate and selectivity to the target molecules. The CuO/ZnO catalyst gave the best activity with 19 mol% glycerol conversion at 80 Bar H<sub>2</sub> and 180 °C. The addition of tungstic acid increased the conversion, particularly with the rhodium catalyst (from 2.5 % to 10 %). In the presence of the palladium catalyst, the 1,2-propanediol was the only diol obtained, while the use of the rhodium catalyst yielded 1,2- and 1,3-propanediol with 52 % and 26 % selectivity respectively.

**Table 1.7: Summary of conversion of glycerol, yield and selectivity to propylene glycol from glycerol over various metal catalysts [25].**

Supplier	Description	Conversion (%)	1,2-PDO yield (%)	Selectivity to 1,2-PDO (%)
Johnson Matthey	5 % Ru/C	43.7	17.5	40.0
Johnson Matthey	5 % Ru/alumina	23.1	13.8	59.7
Degussa	5 % Pd/C	5.0	3.6	72.0
Degussa	5 % Pt/C	34.6	28.6	82.7
PMC Chemicals	10 % Pd/C	8.9	4.3	48.3
PMC Chemicals	20 % Pd/C	11.2	6.4	57.1
Grace Davison	Raney nickel	49.5	26.1	52.7
Grace Davison	Raney copper	48.9	33.8	69.1
Sud Chemie	Copper	53.0	21.1	39.8
Sud Chemie	Copper chromite	54.8	46.6	85.0
Johnson Matthey	Ni/C	39.8	27.3	68.6
Alfa Aesar	Ni/silica-alumina	45.1	29.1	64.5

Reaction conditions: 80 wt% glycerol solution, 200 °C, 14 Bar hydrogen, 24 h.

Aqueous phase hydrogenolysis of glycerol to 1,2-PDO, catalyzed by a mixture of Ru/Al<sub>2</sub>O<sub>3</sub> and Pt/Al<sub>2</sub>O<sub>3</sub>, without externally added hydrogen was reported [10]. The hydrogen necessary for the hydrogenolysis reaction was generated in situ by aqueous phase reforming of glycerol. High conversion of 50 % was obtained with a selectivity of 47 % to 1,2-PDO, compared to runs where hydrogen was added and only a 32 % selectivity to 1,2-PDO was obtained. With the addition of external hydrogen, the conversion of CO and CO<sub>2</sub> to methane and other alkanes increased, due to the increased availability of hydrogen. This affected the 1,2-PDO selectivity compared to in situ hydrogen generation.

The transfer hydrogenolysis of glycerol in the presence of 2-propanol or ethanol at 180 °C, in an inert atmosphere, using a Pd/Fe<sub>2</sub>O<sub>3</sub> catalyst with a 12 wt% solution has been studied [26]. It was found that with the dehydrogenation of the reaction solvent by a supported palladium catalyst, it was possible to transfer a hydrogen molecule from an alcohol (such as 2-propanol or ethanol) to another molecule such as glycerol. Furthermore, the palladium could also be reduced “in situ”

by alcohols at the reaction temperature, avoiding the need for pre-reduction of the catalyst with H<sub>2</sub>.

Pt-Ru bimetallic particles were also evaluated for the hydrogenolysis reactions because bimetallic catalysts can exhibit catalytic activities that exceed those of their monometallic analogues [27]. The physical mixture of Ru/C and Pt/C had initial activity (44 mol% glycerol conversion) comparable to that of the monometallic Ru/C catalyst (40 mol% glycerol conversion), which is expected because Pt/C was significantly less active than Ru/C under neutral conditions at 200 °C and 40 Bar H<sub>2</sub>. Interestingly, the bimetallic PtRu/C catalyst also exhibited similar activity (42 mol% glycerol conversion) to that of the monometallic Ru/C catalyst. The addition of Au/C to the Ru/C decreased the hydrogenolysis activity of Ru/C (25 mol% vs 40 mol% glycerol conversion, respectively). However, modifying the Ru surface with Au gave almost the same glycerol conversion (24 mol%) as the physical mixture of the two monometallic catalysts. The selectivities reported for AuRu/C and Ru/C were also quite similar, both favoured ethylene glycol production (65 % and 68 %, respectively) over propylene glycol production (35 mol% and 32 mol% respectively).

Several Ru-Re bimetallic (Ru-Re/SiO<sub>2</sub>, Ru-Re/ZrO<sub>2</sub>, Ru-Re/TiO<sub>2</sub>, Ru-Re/H-β, Ru-Re/H-ZSM-5) and Ru monometallic catalysts (Ru/SiO<sub>2</sub>, Ru/ZrO<sub>2</sub>, Ru/TiO<sub>2</sub>, Ru/H-β, Ru/H-ZSM-5) were prepared to evaluate their catalytic performances in the hydrogenolysis of glycerol [28]. These catalytic runs were performed in a batch reactor under 80 Bar H<sub>2</sub> at 160 °C for 8 h. The Ru-Re bimetallic catalysts showed much higher activity than the Ru monometallic catalysts, and the Re exhibited a promoting effect on the activity of the catalysts.

Different solvents were studied for the dehydroxylation of glycerol to 1,3-PDO over a Pt/WO<sub>3</sub>/ZrO<sub>2</sub> catalyst [29]. Protic solvents, such as water and ethanol, favoured the formation of 1,3-PDO over aprotic solvents, such as 1,3-dimethyl-2-imidazolidinone (DMI) and sulfolane. Binary solvents, such as DMI-water or DMI-ethanol, showed a synergetic solvent effect on the selectivity for 1,3-PDO.

A process for the catalytic hydrogenolysis of glycerol to propanediols in the presence of a homogenous catalyst was also studied [30]. Typical selectivities obtained were 47 % to 1-propanol, 30 % to 1,3-propanediol and 22 % to 1,2-propanediol. The hydrogenolysis was carried out at moderate reaction conditions, with temperatures in the range of 70–200 °C and

pressure varying between 5–100 Bar  $H_2$ . A  $Pd(OAc)_2$  or  $Pt(acac)$  catalyst was used with ligands (such as 1,2-bis(1,5-cyclooctylenephosphino)ethane (BCPE)) or Lewis acids ( $AlCl_3$ ,  $SnF_3$ ,  $BF_3$ ,  $SnCl_2$ , etc.) or sulphonic acids ( $CF_3SO_3H$ ,  $CH_3SO_3H$ ).

Che [31] also described a process for converting glycerol selectively to propanediols in a homogenous catalytic reaction medium. This invention converts glycerol to lower oxygenated hydrocarbons by reacting glycerol, carbon monoxide and hydrogen ( $CO:H_2$  1:2) in a basic organic solvent with a tungsten catalyst and metal components such as Fe, Co, Ni, Ru, Rh, Pd, Pt or Os at 100–200 °C. Analysis of the reaction mixture indicated selectivities of 44 mol% to 1,3-PDO, 48.5 mol% to 1,2-PDO and 7.5 mol% to 1-propanol. Interestingly the presence of carbon monoxide contributed towards the solubility, stabilisation and activation of the catalyst species. Without the presence of carbon monoxide the conversion of glycerol to propanediols proceeded less efficiently. After completion of the process, the catalyst could be isolated and recycled.

Chen and co-workers [32] investigated the deoxygenation of glycerol in an aqueous medium catalysed by  $Pt/WO_3/ZrO_2$  at temperatures of 110–140 °C under hydrogen pressures of 20-50 Bar in a fixed bed continuous flow reactor. The predominant products that were obtained are 1,3-PDO and 1-propanol and this indicated a high selectivity for the deoxygenation of the secondary hydroxyl group over the primary hydroxyl groups of glycerol. At 130 °C and 40 Bar  $H_2$ , the glycerol conversion reached 61 % with a 36 % selectivity to 1,3-PDO and a 52 % selectivity to 1-propanol with small amounts of 2-propanol and 1,2-PDO.

### 1.3.2 Copper systems

The hydrogenolysis of solvent free glycerol to 1,2-PDO was studied by Huang et al. [33]. Several catalysts were screened and the most effective catalysts ( $Ni/Al_2O_3$  and  $Cu/ZnO/Al_2O_3$ ) were further tested for vapour phase hydrogenolysis in a fixed bed reactor. They found that  $Ni/Al_2O_3$  is not an effective catalyst for the production of 1,2-PDO because of the high selectivity to  $CH_4$  and CO. Over the  $Cu/ZnO/Al_2O_3$  catalyst, glycerol was mainly converted to 1,2-PDO and acetol (Table 1.8). This shows that Cu-based catalysts have poor activity towards C-C bond cleavage. High selectivities of 92 % to 1,2-PDO were achieved with high conversion of glycerol at 190 °C at 6.4 Bar  $H_2$  pressure. Higher pressures favoured 1,2-PDO formation and they found a stoichiometric relationship between 1,2-PDO and acetol.

**Table 1.8: Vapour phase hydrogenolysis of glycerol over Ni/Al<sub>2</sub>O<sub>3</sub> and Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalysts in a fixed bed reactor [33].**

Catalyst	Conversion (%)	Selectivity to products (%)					
		1,2-PDO	EG	Acetol	1-PO	2-PO	Others*
Ni/Al <sub>2</sub> O <sub>3</sub> <sup>a</sup>	92.3	43.6	18.6	13.4	3.2	1.5	19.7
Cu/ZnO/Al <sub>2</sub> O <sub>3</sub> <sup>a</sup>	93.0	65.3	2.5	23.5	1.4	0.6	6.7
Cu/ZnO/Al <sub>2</sub> O <sub>3</sub> <sup>b</sup>	96.2	92.2	0.7	0.8	2.4	0.7	3.2

a) Reaction conditions: WHSV = 0.18h<sup>-1</sup>, 60 wt% glycerol solution, 190 °C, 1 Bar H<sub>2</sub>, H<sub>2</sub>/glycerol = 70:1 (molar ratio).

b) 6.4 Bar H<sub>2</sub>.

\* Others = C<sub>1</sub> gases (CO and CH<sub>4</sub>), ethanol, methanol and unknown products.

Supported Cu-containing bimetallic catalysts were prepared and the effect of different supports, metals, metal loading and impregnation sequences were studied [34]. A synergistic effect was observed between Cu and Ag when supported on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. The addition of Ag resulted in an in situ reduction of CuO and also improved the dispersion of the Cu species on the support. This bimetallic catalyst system can be used directly without a reduction pre-treatment. A glycerol conversion of 27 % was obtained with 96 % selectivity to 1,2-PDO at 200 °C with 15 Bar H<sub>2</sub> pressure in a batch reactor.

The vapour phase reaction of glycerol over copper metal catalysts at ambient hydrogen pressures was also investigated [35]. The 1,2-PDO yield was initially limited at 80 % due to the trade off between dehydration and hydrogenation. Dehydration needs relative high temperatures, whereas hydrogenation is favoured by low temperatures and high hydrogen concentration. A process was developed where glycerol was dehydrated to acetol at 200 °C followed by the subsequent hydrogenation to 1,2-PDO at 120 °C by controlling the thermodynamic equilibrium of the second hydrogenation step. Quantitative glycerol conversions were observed with 96 % selectivity to 1,2-PDO.

Different Cu-supported catalysts were synthesised and compared with a commercial copper chromite catalyst [36]. The Cu/Al<sub>2</sub>O<sub>3</sub> showed a 35 % glycerol conversion with 94 % selectivity to 1,2-PDO whereas the commercial copper chromite showed a 13 % conversion with a 87 % selectivity to 1,2-PDO at 200 °C and 36 Bar H<sub>2</sub>. This result indicated that the support had a strong effect on the performance of the Cu-based catalysts.

A comparative study of the hydrogenolysis of glycerol to 1,2-PDO over a CuO/MgO catalyst, prepared by impregnation and co-precipitation, was published [37]. The CuO/MgO catalyst prepared by co-precipitation showed the best activity with a glycerol conversion of 72 % and a 1,2-PDO selectivity of 98 %. The glycerol conversion was further enhanced to 82 % with the addition of NaOH to the reaction mixture.

The effect that residual sodium has on the performance of the CuO/SiO<sub>2</sub> catalysts in glycerol hydrogenolysis has also been studied [38]. Characterisation showed that residual sodium had a negative effect on the dispersion of the copper and the reducibility of the Cu<sup>2+</sup> species, as well as the absorbance of the reactant molecules. As a consequence of this, the conversion and selectivity decreased with increasing sodium content. On the other hand, the leaching of sodium from the catalyst surface as a base could promote the activity of the catalyst and reduce the deactivation rate of the catalyst. The lowest glycerol conversion (15 %) was obtained with the highest amount of sodium with a 94 % selectivity to 1,2-PDO at 180 °C and 90 Bar H<sub>2</sub>.

The hydrogenolysis of glycerol was investigated over CuO/ZnO catalysts which were prepared by the oxalate gel method and co-precipitation [39]. The CuO/ZnO catalyst prepared by the oxalate gel method exhibited a much higher conversion than the catalyst prepared by the co-precipitation method (46 % compared to 17 %), but similar selectivities of 90 % were seen. The higher activity can be attributed to the higher surface area of the copper. In the presence of water, the copper crystallites of the CuO/ZnO catalyst increased significantly, leading to a decrease in active surface area and a loss of activity.

A method was investigated for the preparation of 1,2-PDO by reaction of 95 wt% glycerol solution under hydrogen pressures varying between 20-100 Bar and temperatures varying between 180-240 °C in an autoclave [40]. The catalyst used for this process comprises of CuO (20-60 wt%), ZnO (30-70 wt%) and MnO (1-10 wt%).

A further process for the preparation of 1,2-propanediol which permits the hydrogenation of the glycerol-containing streams with high selectivity was described by Henkelmann et al. [41]. This process is suitable for the further processing of glycerol streams obtained on industrial scale. The hydrogenation catalyst used comprised at least 35 % by weight of copper, in oxide and/or elemental form, based on the total weight of the catalyst. Copper-containing catalysts of different compositions were tested: 100 % Cu (Raney-Cu) or CuO, ZnO, Al<sub>2</sub>O<sub>3</sub> or CuO, Al<sub>2</sub>O<sub>3</sub>

or Cu, TiO<sub>2</sub> or CuO, MnO<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>. Very high glycerol conversions of between 74 % and 99 % were obtained with selectivities of up to 96 % to 1,2-propanediol at high temperatures (100–320 °C) and pressures (100–325 Bar).

1,2-Propanediol was prepared [42] by the catalytic hydrogenation of glycerol (20 wt% in water) at elevated temperatures (200–250 °C) and pressures (200–325 Bar H<sub>2</sub>). Catalyst systems used consisted of cobalt (CoO), copper (CuO), manganese (MnO<sub>2</sub>) and molybdenum (MoO<sub>3</sub>) with inorganic polyacids or heteropolyacids. The catalyst employed in this process generally contained no catalyst support. The hydrogenation gives selectivities of up to 95 % with 100 % conversions and other products that form are methanol, ethanol, iso-propanol and 1,3-propanediol.

A reactive-separation process was studied, which converts glycerol to propylene glycol through an acetol intermediate, by Suppes and Sutterlin [43]. The glycerol containing stream contained 5 % to 15 % water by weight and the conditions included a temperature range between 150 °C and 250 °C and pressures between 1 to 25 Bar. High glycerol conversions of up to 100 % were obtained with selectivities between 85 % and 95 % to propanediols. The hydrogenation catalyst comprises of 5 wt% to 95 wt% chromium (Cr<sub>2</sub>O<sub>3</sub>) and copper (expressed as CuO).

High surface area nanostructured Cu-Cr catalysts were prepared [44] and evaluated for the hydrogenolysis of glycerol. The reduced Cu-Cr catalysts showed significant catalytic activity and selectivity in glycerol hydrogenolysis. A 51 % glycerol conversion was obtained with a 96 % 1,2-propanediol selectivity under 41.5 Bar H<sub>2</sub> at 210 °C. The Cu-Cr catalysts with low Cu/Cr molar ratio gave high glycerol conversion, which is different from the conventional copper-chromite catalysts.

Selective hydrogenolysis of glycerol to 1,2-PDO was also performed [45] using environmentally friendly hydrotalcite-derived mixed metal oxide catalysts. These mixed metal oxides are inexpensive and non-toxic and their acid-base properties can be tailored to improve the selectivity and conversion of the glycerol hydrogenolysis reaction. The Cu/Zn/Al mixed oxide was the most active catalyst at 48 % conversion with a selectivity of 94 % to 1,2-PDO at 200 °C, 7 Bar and glycerol dilution of 80 %.

### 1.3.3 Nickel systems

Preliminary results on the hydrogenolysis of glycerol with hydrogen using Raney nickel as catalyst were reported [46]. The reactions were done without solvents, but in the presence of a liquid phosphonium salt. When glycerol and Raney nickel were heated to 150 °C for 20 h in a stainless steel autoclave with 10 Bar of hydrogen, the conversion reached 12 % with 93 % selectivity to 1,2-PDO with small amounts of ethanol and CO<sub>2</sub> also formed.

Bloom [47] described a process for the hydrogenolysis of bio-based glycerol feedstock containing a solution of 40 % by weight. A Re-Ni catalyst supported on carbon was used under 80-110 Bar H<sub>2</sub> pressure at 230 °C. Glycerol conversions between 48 % and 96 % were obtained and selectivities between 36 % and 55 % towards 1,2-PDO. In one example they used a Ni/Al<sub>2</sub>O<sub>3</sub> catalyst from Süd-Chemie and obtained a 25 % glycerol conversion with a 72 % selectivity to 1,2-PDO.

A process for the hydrogenolysis of glycerol and other polyols over a Ni/Re catalyst was studied [48]. After 4 h at 230 °C under 82 Bar H<sub>2</sub>, 44 % of 1,2-PDO and 5 % of 1,3-PDO were obtained, together with 13 % of ethylene glycol.

Bullock et al. [49] described a process for the hydrogenolysis of polyols (xylitol, sorbitol or glycerol) to ethylene glycol. In most cases nickel on silica or alumina was used as catalyst and the hydrogen is added in stoichiometric amounts. Solvents that are used must be unreactive and not interfere with the hydrogenolysis reaction, and the polyols must be partly soluble in the solvents. The preferred solvents were monohydric alcohols, such as methanol, or protic solvents such as cyclohexane and a corresponding sodium alkoxide base was added. The reaction temperature varied between 240–315 °C, with elevated pressures between 130–480 Bar H<sub>2</sub> and 40 wt% glycerol solutions were used. High conversions were seen with a 70 % selectivity to 1,2-PDO, 15 % to EG and 11 % of degradation products in MeOH as solvent.

A further process for the conversion of the by-products of the manufacturing of biodiesel, into industrially useful oxygenated products of greater commercial value was demonstrated [50]. A trickle bed reactor was used, in which the glycerol was reacted with hydrogen in the presence of a Ni/W catalyst under refining conditions (550 °C at 110 Bar H<sub>2</sub>) to yield propanediols. A 78 % conversion was obtained with a 100 % selectivity to 1,2-PDO. In some instances small amounts of 1,3-PDO were also detected.

A novel procedure for the preparation of Ni/coconut shell catalyst for glycerol hydrogenolysis was also reported [51]. The preparation involved the carbothermal reduction of the supported nickel nitrate and the reduced sample was further treated with  $\text{KBH}_4$  which contained NaOH. This catalyst gave 63 % conversion after 24 h with a 77 % selectivity to 1,2-PDO at 200 °C and 50 Bar  $\text{H}_2$ . This carbothermal reduction provided the Ni active sites and simultaneously generating oxygen-containing surface groups (OCSG) in the AC support. From these OCSGs, the highly dispersed Ni and acidity was generated which enhanced the activity of the glycerol hydrogenolysis.

### 1.3.4 Other catalytic systems

The simultaneous production of 1,2- and 1,3-PDO from glycerol was investigated by Haas et al. [52]. The first stage is the dehydration of glycerol over a solid catalyst to form acrolein and then the hydration of acrolein takes place under the same conditions to produce the diols. Glycerol is dehydrated in the gas phase at 270 °C over a catalyst such as  $\text{H}_3\text{PO}_4$  on  $\text{Al}_2\text{O}_3$  (zeolites are less suitable) and a 70.5 % yield to acrolein is obtained. For the hydration of acrolein an acidic catalyst (ion exchanger with iminodiacetic active groups) is used either in a homogenous phase or heterogeneous phase at 120 °C. The yield of the 1,3-propanediol relative to the glycerol is 60 % and the yield of the 1,2-propanediol is 10 %.

Iridium nanoparticles on silica were impregnated with rhenium and tested for the direct hydrogenolysis of glycerol to 1,3-PDO in an aqueous medium by Tomishige and co workers [53]. During the initial stages of the reaction, the 1,3-PDO selectivity reached 67 % at low conversions but with time the 1,3-PDO selectivity decreased to 40 % at 81 % conversion. At the same time an increase in 1-propanol selectivity was observed.

Gou et al. [54] investigated the hydrogenolysis of glycerol on the bi-functional catalyst Co/MgO at 200 °C and 20 Bar hydrogen. They proposed that MgO was converted to  $\text{Mg}(\text{OH})_2$  and these basic  $\text{Mg}(\text{OH})_2$  particles provide the active sites for dehydrogenation of glycerol to glyceraldehyde and then the Co particles are responsible for the hydrogenation to 1,2-propanediol, showing a bi-functional mechanism.

#### 1.4 Glycerol hydrogenolysis to lower alcohols (propanol, ethanol and methanol)

As clearly shown in Section 1.3 the hydrogenolysis of glycerol to 1,2-PDO has been extensively studied in recent years, and high conversions and selectivities have been reported. In contrast, the reports on the hydrogenolysis of glycerol or 1,2-PDO to lower alcohols are limited.

Rabello et al. [55] patented a process for the extraction of glycerol from the biodiesel production process and to hydrogenate this glycerol mixture to n-propanol in high conversion (89 %) and selectivities (79.4 %). This propanol was transesterified and added back to the triglyceride pool to reduce the amount of alcohols needed for the biodiesel production. The glycerol was hydrogenated in the presence of a noble metal such as Pd or Pt supported on alumina at 240 °C and 35 Bar H<sub>2</sub> in batch mode for 12 h.

Bullock and co-workers [56] reported on a homogenous Ru catalyst for the hydrogenolysis of 1,2-PDO to propanol. This hydrogenolysis reaction was catalysed at 110 °C in sulfolane and a yield of 54 % was obtained.

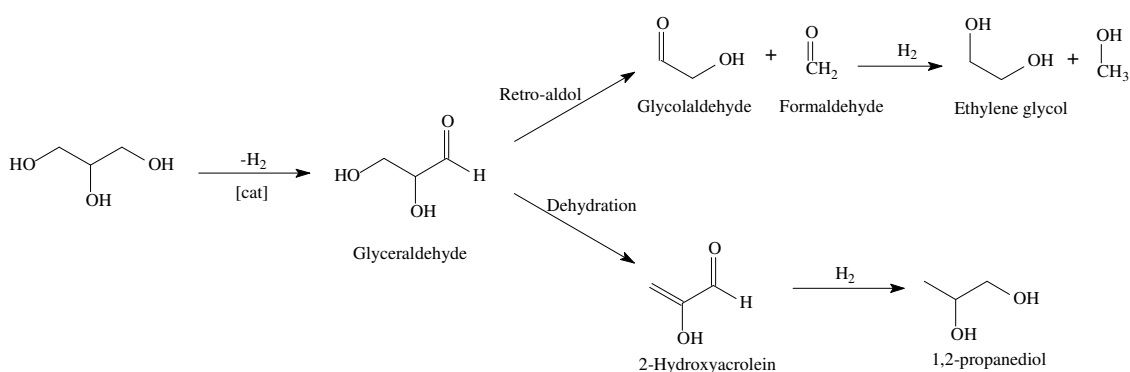
A good selectivity of 42 % to 1-propanol and 13 % to 2-propanol was reported using supported metal catalysts (Rh, Ru, Pt, Pd on active carbon, SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>) during the hydrogenolysis of aqueous glycerol solutions under H<sub>2</sub> in batch mode [13]. The optimised catalytic system gave a glycerol conversion of 14.3 %, 1,2-PDO selectivity of 26 % and decreased formation of degradation products.

A publication by Tomishige and co-workers [57], reported on the development of a heterogeneous catalyst for hydrogenolysis of 1,2-PDO to propanols in batch mode. A Rh/SiO<sub>2</sub> catalyst modified with ReO<sub>x</sub> species exhibited high activity and selectivity in the hydrogenolysis of 1,2-PDO to propanols with low selectivity to degradation products. The optimized Rh-ReO<sub>x</sub>/SiO<sub>2</sub> (Re/Rh = 0.5) catalyst gave high selectivities to 1-PrOH and 2-PrOH (74 % and 19 % respectively) with 87 % conversion after 24 h at 120 °C. Only 1 % degradation products (ethanol, ethane and methane) were seen and 6 % propane. They also proposed that the 1,2-PDO hydrogenolysis proceeded by the hydrogenolysis of the alkoxide species on Re with hydrogen species on the Rh metal surface.

## 1.5 Mechanistic studies on glycerol hydrogenolysis

Several mechanisms have been proposed for the hydrogenolysis of glycerol. The formation of 1,2-PDO from glycerol can occur via several routes as discussed in this section.

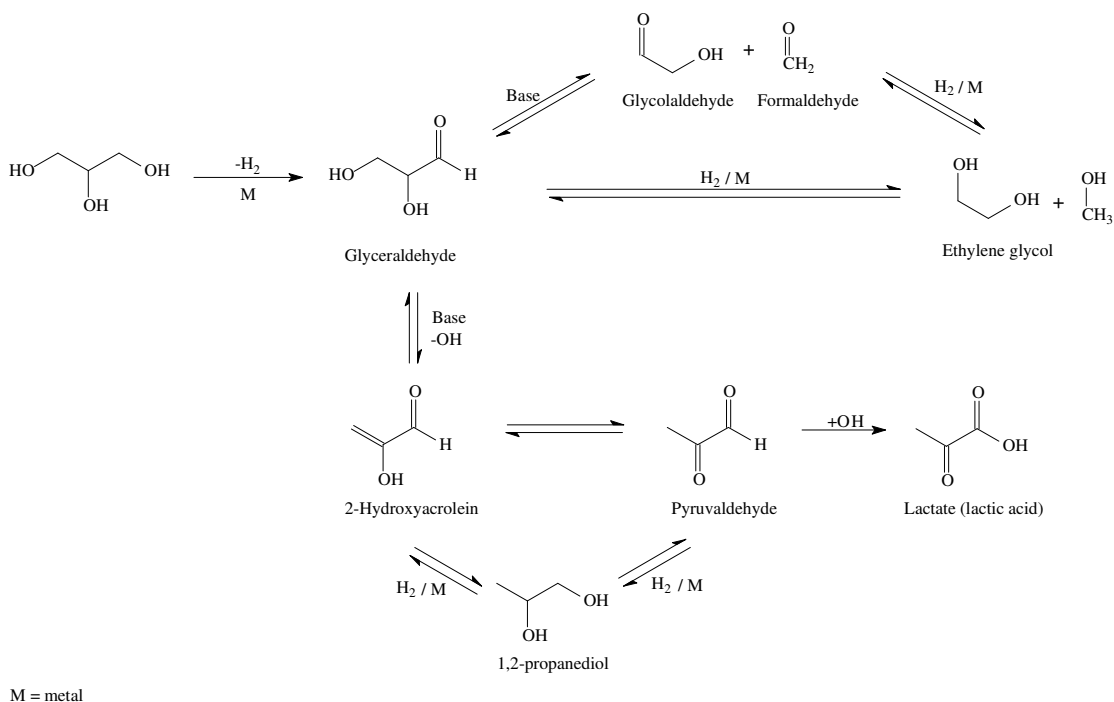
The mechanism proposed by Montassier et al. [24] is shown in Scheme 1.4. Dehydration and retro-aldol reactions of polyols were studied over a bimetallic Cu-Ru catalyst. They have added 1 mole of sulphur per mole of ruthenium at a pH of 6 to lower the glycerol reaction rate. The sulphur modification of the ruthenium catalyst enhances the selectivity for specific polyol products. According to this mechanism, the dehydrogenation of glycerol leads to glyceraldehyde, which is followed by dehydration to 2-hydroxyacrolein and subsequent hydrogenation to 1,2-PDO. Glyceraldehyde can also undergo a retro-aldol reaction to form glycolaldehyde and formaldehyde and subsequent hydrogenation to ethylene glycol and methanol. In this mechanism, the cleavage of C-C bonds occurs through a base-catalysed retro-aldol reaction, whereas the C-O cleavage occurs through a base-catalysed dehydration reaction. The initial dehydrogenation step is believed to occur on the transition metal catalyst.



**Scheme 1.4:** Reaction scheme for the formation of 1,2-PDO as proposed by Montassier [24].

The mechanism proposed by Maris and Davis [22] as illustrated in Scheme 1.5, is based on what Montassier et al. [24] proposed, but was adjusted on the results obtained in their study. In this work, the selectivity and activity of Ru/C and Pt/C were investigated for the hydrogenolysis of glycerol. The effects of NaOH and CaO addition on the reaction rates were used to elucidate the metal-catalysed vs base-catalysed routes in this mechanism. The first step is the dehydrogenation of glycerol to glyceraldehyde on the transition metal catalyst and can be enhanced by the presence of a base. The formation of EG can occur via two routes. Ru is an

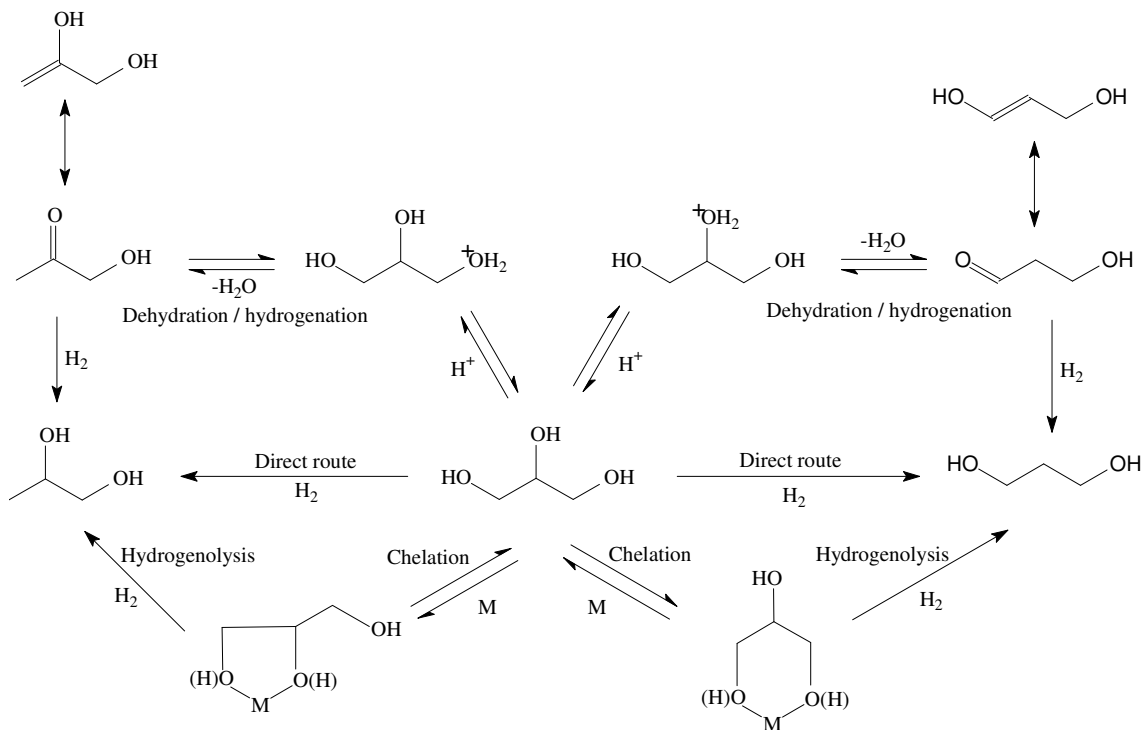
effective C-C bond cleavage catalyst, and therefore glyceraldehyde can be directly hydrogenated to EG and methanol over Ru. Pt, on the other hand, is not effective for C-C bond cleavage and therefore the formation of EG is via a base-catalysed retro-aldol route. The base-catalysed dehydration of glyceraldehyde yields pyruvaldehyde, which forms lactate in the presence of a base. Subsequent hydrogenation of the dehydration intermediates on the metal catalyst gives 1,2-PDO.



**Scheme 1.5: Reaction scheme for the hydrogenolysis of glycerol proposed by Maris and Davis [22].**

Chaminand et al. [9] proposed that diols can form via several routes as shown in Scheme 1.6. In view of their experimental results, they proposed a mechanism to explain the influence of different parameters on the activity and selectivity of the reaction. Parameters that they investigated were the influence of the support on the Ru catalyst as well as the influence of a solvent on the hydrogenolysis of glycerol over the Ru/C catalyst. The presence of an acid favoured the dehydration route via protonation of the hydroxyl groups of glycerol and then the loss of water forms a keto group as intermediate. If a primary OH group is protonated, then acetol will form, which will lead to 1,2-PDO. If the secondary OH group is protonated, then 3-HPA is obtained and this keto group can be easily reduced under the reaction conditions to form

1,3-PDO. The addition of a second metal can chelate glycerol and then, under hydrogenolysis conditions, either 1,2-PDO or 1,3-PDO can form.



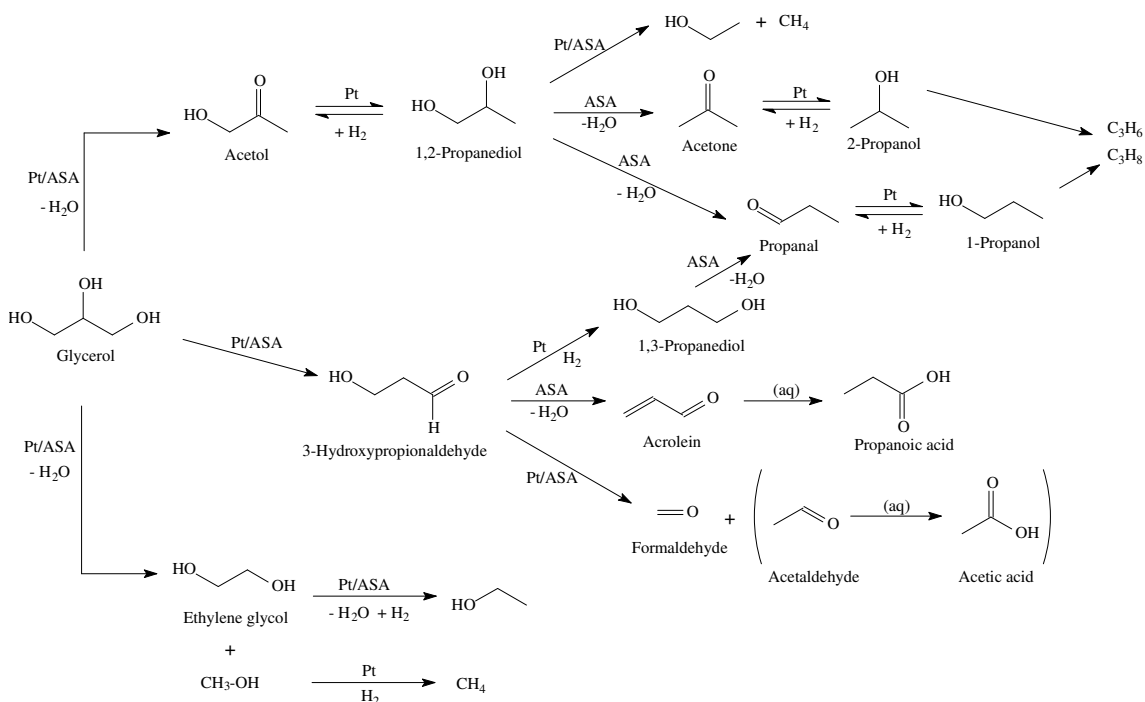
M = metal

**Scheme 1.6: Reaction scheme proposed by Chaminand [9].**

Gandarias et al. studied [20] the role of acid and metal sites of Pt supported amorphous silica alumina (Pt/ASA) in glycerol hydrogenolysis to obtain 1,2-PDO. They also investigated the glycerol hydrogenolysis reactions under  $\text{N}_2$  pressure due to hydrogen available from glycerol aqueous phase reforming. Glycerol is first dehydrated to acetol, which is then hydrogenated to 1,2-PDO. 1,2-PDO is further dehydrated to acetone and propanal; after hydrogenation of these products 1-PO and 2-PO are formed (Scheme 1.7). Glycerol can also be dehydrated to 3-HPA, which is then subsequently hydrogenated to 1,3-PDO. 3-HPA is also readily dehydrated into acrolein. It was suggested that propanoic acid is produced through the oxidation of acrolein in aqueous solutions. 3-HPA is very unstable and was not detected in the reaction mixtures and is instantaneously converted in subsequent reactions.

Next, the route to cracked products was considered. The cracked products detected were EG, methanol, ethanol, acetaldehyde and acetic acid. It was suggested that EG and methanol were

obtained directly from glycerol since these products were not detected in the experiments with 1,2-PDO, 1,3-PDO or acetol as reactants. Furthermore, ethanol can be formed during the hydrogenolysis of EG and methane is formed from the hydrogenation of methanol. It was also proposed that acetaldehyde and formaldehyde were formed from 3-HPA, and that acetaldehyde is oxidised to acetic acid.



**Scheme 1.7: Reaction scheme of glycerol hydrogenolysis and degradation products as proposed by Gandarias et al. [20].**

## 1.6 Conclusions

Glycerol presents an ideal source for renewable industrial feedstocks provided that alternative methods for glycerol utilisation that are economically viable can be met. Recent progress in catalysis makes the conversion of glycerol possible to a host of chemicals, such as 1,2-PDO, 1,3-PDO, EG, acrolein, acrylic acid, glycerol carbonate, epichlorohydrin, glyceric acid, dihydroxyacetone and polyglycerols.

From this overview on glycerol hydrogenolysis, it can be seen that the production of 1,2-PDO from glycerol in batch mode is the main focus area for most research groups. The catalytic systems used for this transformation are precious metals (Ru, Rh, Pt and Pd) with or without

solid acids, and transition metals (Ni, Cu, Co, Mo). From literature, it is evident that glycerol hydrogenolysis involves several consecutive as well as parallel reactions and that the product profile strongly depends on the catalyst, promoters and reaction conditions.

Cu based catalysts were mainly used in fixed bed reactor set-ups and it was found that these catalytic systems are highly active and very selective to the formation of 1,2-PDO. Cu-based catalysts have poor activity towards C-C bond cleavage, whereas Ni catalysts gave high yields towards degradation products.

Several mechanisms have been reported for the hydrogenolysis of glycerol. The formation of 1,2-PDO from glycerol can occur via several routes, such as the dehydrogenation of glycerol to yield glyceraldehyde and then subsequent hydrogenation to yield 1,2-PDO. 1,2-PDO can also form via the protonation of the hydroxyl group of glycerol or the chelation of glycerol. The dehydration of glycerol can also lead to acetol and subsequent hydrogenation give 1,2-PDO. The formation of lower alcohols such as propanol, ethanol and methanol are less discussed in the literature.

## **1.7 Aim of study**

With the expansion of the biodiesel industry globally, the world is experiencing a large oversupply of glycerol. The increased biodiesel production results in the accumulation of glycerol, which leads to a price decline. With glycerol becoming a cheap, large-volume feedstock, using it as a source of organic carbon and as a starting material for chemical transformations is very appealing. Therefore, the need has arisen to find new applications for this glycerol by-product from the production of biodiesel. From an industry point of view, the production of lower alcohols, such as propanol and ethanol, is very interesting. 1-Propanol is produced via the hydrogenation of propanal which is an intermediate product from ethylene hydroformylation [58]. 1-Propanol is primarily used as a solvent in the paint, cosmetic and pharmaceutical industry. Ethanol can be produced from petroleum processes by the direct hydration of ethylene or as a by-product from acetic acid production [59]. Ethanol has two major uses; as a renewable fuel and industrial applications such as solvents. Solvents are used in paints, coatings, adhesive inks and pharmaceuticals. Hence the aims of this study can be summarised as follows:

- A major drawback has been the use of diluted solutions of glycerol for the hydrogenolysis reaction; typically, 10-20 wt % solutions were predominantly used. An additional drawback is the fact that most research efforts to date have focused on the synthesis of 1,2-PDO from glycerol. Very little attention has been given to the production of lower alcohols, especially 1-propanol, a high value commodity chemical. In an effort to overcome the abovementioned drawbacks the focus of this work was the evaluation of supported precious metal catalysts, in combination with and without solid acids, for the hydrogenolysis of highly concentrated glycerol solutions, with the aim to produce lower alcohols, in particular 1-propanol (1-PO).
- Much work has been done towards the hydrogenolysis of glycerol to 1,2-PDO and 1,3-PDO, as well as oxidation of glycerol to glyceric acid or dihydroxyacetone. However, routes to lower alcohols, such as 1-propanol and ethanol have been less discussed. It is known that glycerol can be hydrogenolysed using various heterogeneous systems including Rh, Ru, Pt, PtRu, copper systems and Raney Ni using batch systems. Surprisingly, the use of supported Ni systems as catalysts towards the chemical transformation of glycerol, especially towards the formation of lower alcohols, has appeared less frequently in the literature. The focus was thus the production of lower alcohols, primarily 1-propanol and ethanol, from glycerol using an inexpensive catalyst system, namely Ni supported catalysts, in a continuous flow fixed bed reactor.
- Despite the numerous studies on glycerol hydrogenolysis reported to date, detailed studies giving insight into the reaction mechanism of lower alcohol formation have been limited and inconclusive. EG and 1,3-PDO are shown as possible intermediates to propanol, ethanol and methanol. It was also suspected that 1,2-PDO leads to short chain alcohol formation although little is reported that demonstrates this possibility. The objective of the study is to continue the development of a more detailed mechanistic understanding of the formation of lower alcohols from glycerol. In an endeavour to understand the process better, the role of proposed intermediates, 1,2-PDO, 1,3-PDO, EG and ethanol was investigated, as well as the influence of the hydrogen partial pressure.

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## CHAPTER 2

# DIRECT HYDROGENOLYSIS OF HIGHLY CONCENTRATED GLYCEROL SOLUTIONS OVER SUPPORTED Ru, Pd AND Pt CATALYST SYSTEMS

### Abstract

The focus of this paper is on the evaluation of supported precious metal catalysts, in combination with and without solid acids, for the hydrogenolysis of highly concentrated glycerol solutions, with the aim to produce lower alcohols, in particular 1-propanol (1-PO). Several ruthenium, palladium and platinum metals on different supports with or without the addition of solid acids, such as ionic exchange polymeric resins, Si/Al and H<sub>3</sub>PO<sub>3</sub>/SiO<sub>2</sub>, as co-catalysts were studied. The Ru/C + Amberlyst DT system gave the most promising results from a 1-PO point of view with 38 mol% selectivity at 35 mol% conversion. In addition, GC MS analysis of the products mixtures obtained has set some light on the possible mechanism leading to unwanted condensation products, as well as the composition of these compounds.

Key words: supported precious metal catalysts, solid acids, glycerol, 1-propanol.

### 2.1 Introduction

Glycerol is a recognised renewable feedstock and the ability to use it as a starting material for chemical transformations is very appealing. It is a by-product from the production of biodiesel from vegetable oils. From an industrial perspective a number of potential glycerol value-adding transformations have been reported in literature. The most promising transformations include hydrogenolysis to 1,2-propanediol (1,2-PDO) and 1,3-propanediol (1,3-PDO) [1,2], dehydration to acrolein [3] and reforming into synthesis gas (CO/H<sub>2</sub>) [4]. Other interesting transformations reported are the production of alcohols, such as 1-propanol (1-PO) and 2-propanol (2-PO) [5], and ethylene glycol (EG) [6] from glycerol, albeit yields reported have been disappointingly low.

Tomishige and co-workers [1] reported that various noble metals (Ru/C, Rh/C, Pt/C and Pd/C) and acid catalysts (H<sub>2</sub>SO<sub>4</sub>, HCl and Amberlyst 15) combined, were effective for the hydrogenolysis of glycerol under mild conditions. The promoting effect of adding Amberlyst

15 to the Ru/C reaction mixture was quite significant with an increase in glycerol conversion from 3.5 % to 12.9 %.

Miyazawa et al. [7] also investigated the difference between Amberlyst 15 and Amberlyst 70 in the hydrogenolysis of glycerol to 1,2-PDO. A combination of Ru/C + Amberlyst 70 gave the highest glycerol conversion (26 %) which was related to the heat resistance of the resin. The promoting effect of other solid acids in combination with Ru/C was also studied [8].  $\text{H}_2\text{WO}_4$  was effective in enhancing glycerol conversion, while the Rh/C +  $\text{H}_2\text{WO}_4$  system showed higher activity to 1,3-propanediol. Other zeolites and solid acid catalysts, such as MFI ( $\text{SiO}_2/\text{Al}_2\text{O}_3 = 22$ ), BEA ( $\text{SiO}_2/\text{Al}_2\text{O}_3 = 25$ ), USY ( $\text{SiO}_2/\text{Al}_2\text{O}_3 = 6.3$ ) and  $\text{SO}_4^{2-}/\text{ZrO}_2$ , were also tested. In addition, glycerol hydrogenolysis to propane diols was carried out over Ru/C catalysts using different solid acids, such as niobia, 12-tungstophosphoric acid (TPA) supported on zirconia, cesium salt of TPA and cesium salt of TPA supported on zirconia. The selectivity towards 1,2-PDO and the glycerol conversion varied with the change in the concentration of both the Ru/C and solid acid catalysts [9].

High selectivities of up to 42 % to 1-propanol and 13 % to 2-propanol using supported metal catalysts (Rh, Ru, Pt, Pd on active carbon,  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ) during the hydrogenolysis of aqueous glycerol solutions under  $\text{H}_2$  were also reported [10]. Chaminand et al. [11] evaluated different metals (Cu, Pd, Rh) on different supports ( $\text{ZnO}$ , C,  $\text{Al}_2\text{O}_3$ ) and an additive ( $\text{H}_2\text{WO}_4$ ) to improve the rate of glycerol conversion and selectivity to the target molecules. They found that the combination of Rh/C with  $\text{H}_2\text{WO}_4$  was effective for the hydrogenolysis of glycerol to 1,3-propanediol at a low conversion.

According to Ma et al. [12] the hydrogenolysis of glycerol activity in the presence of Ru/C was higher than that of Ru/ $\text{ZrO}_2$  and Ru/ $\text{Al}_2\text{O}_3$ , presumably due to the smaller particle size of metallic Ru species on the surface of the active carbon. Zheng and co-workers [13] synthesised a series of Pt catalysts supported on H- $\beta$ , H-ZSM-5,  $\text{Al}_2\text{O}_3$ , MgO and hydrotalcite for the hydrogenolysis of glycerol in a base-free aqueous solution. The hydrotalcite supported Pt catalyst showed the best performance with a 92 % glycerol conversion and 93 % selectivity to 1,2-PDO.

In spite of the several research efforts, a major drawback has been the use of diluted solutions of glycerol for this reaction. Typically, 10-20 wt % glycerol solutions were predominantly used,

which will be further diluted by the water from the reaction. Consequently, the average space-time yield of the reaction is reduced, resulting in an increase in energy consumption of the process and in turn a decrease in the profitability of the process. An additional drawback is the fact that most research efforts to date have focused on the synthesis of 1,2-PDO from glycerol. Very little attention has been given to the production of lower alcohols, especially 1-propanol, a high value commodity chemical produced via the hydrogenation of propanal, the intermediate product from ethylene hydroformylation [14]. In an effort to overcome the abovementioned drawbacks the focus of this work was the evaluation of supported precious metal catalysts, in combination with and without solid acids, for the hydrogenolysis of highly concentrated glycerol solutions (60 wt%) , with the aim to produce lower alcohols, in particular 1-propanol (1-PO).

## **2.2 Experimental**

### **2.2.1 Reagents**

The glycerol (98 wt%) was obtained from Sigma Aldrich. The ion exchange resins (IER), i.e. Amberlyst 15, Amberlyst DT, Amberlyst 70 and Amberlyst CH43 (strong IER doped with 0.7 wt% Pd) were purchased from Rohm & Haas (now Dow Corporation). In addition, an in-house prepared IER, Resin-A (Chlorinated Resindion Relite CFS resin) with a temperature stability of 170 °C, was also prepared and tested. The solid phosphoric acid (SPA) and SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst were purchased from Sigma Aldrich. All precious metal supported catalysts were obtained from Johnson Matthey except for Ru/C that was obtained from Sigma Aldrich (Table 2.1).

### **2.2.2 Method of analysis**

The products in the liquid phase were analysed by a gas chromatograph (HP 6890) equipped with a FID. The intermediate column DB 1701 (Agilent 123-0763, length: 60.0 m, diameter: 0.32 mm, film thickness: 1.0 µm) was used for separation, and all intermediate and final product samples were injected under the same conditions. Products were also identified by GC MS (Shimadzu) on a FFAP column (HP 190912-001, length: 50 m, diameter: 0.2 mm, film thickness 0.3 µm).

**Table 2.1: List of supported precious metal catalysts tested for the hydrogenolysis of glycerol.**

Precious metal	Shape	Particle size (mm)
4 % Ru/Al <sub>2</sub> O <sub>3</sub> (doped) <sup>a</sup>	Extrudates	1.5
5 % Ru/C <sup>b</sup>	Powder	-
4 % Ru/Al <sub>2</sub> O <sub>3</sub> <sup>b</sup>	Spheres	1.0
5 % Pd/C <sup>b</sup>	Powder	-
5 % Pd/Al <sub>2</sub> O <sub>3</sub> (doped) <sup>a</sup>	Extrudates	1.5
5 % Pd/Al <sub>2</sub> O <sub>3</sub> <sup>b</sup>	Spheres	1.0
5 % Pd/SiO <sub>2</sub> <sup>b</sup>	Spheres	1.2 - 2.4
5 % Pt/Al <sub>2</sub> O <sub>3</sub> <sup>b</sup>	Spheres	1.0
5 % Pt/SiO <sub>2</sub> <sup>b</sup>	Spheres	1.2 - 2.4
5 % Pt/C <sup>b</sup>	Powder	-

<sup>a</sup> Doped support means a doped alumina to form a modified aluminate structure to change or control the surface properties of the alumina (e.g. remove or modify surface acid / base sites). This is done before the metal addition is done.

<sup>b</sup> The supported precious metal catalysts are impregnated.

For each data point, the selectivity to the different products and the conversion of glycerol were calculated. The conversion of glycerol was calculated as the number of moles of glycerol consumed in the reaction divided by the total moles of glycerol initially present. The selectivity was calculated as the moles of the specific product formed divided by the sum of the moles of all products formed.

### 2.2.3 Catalytic testing

The glycerol solution (156 g, 20 to 100 wt% in water), precious metal catalyst (5 wt% based on the glycerol) with or without a solid acid promoter were introduced into a Parr autoclave (300 mL), and the reaction mixture was heated to the operating temperature (130 to 250 °C) while stirring (1000 rpm). The amount of acid catalyst used was adjusted on the basis of the amount of H<sup>+</sup> (meq/g) relative to Amberlyst 15. The hydrogen pressure was set at the operating pressure (80 Bar), the Danfoss flow meter zeroed and when the reaction temperature was reached; the hydrogen was introduced into the reactor at 80 Bar H<sub>2</sub>.

During the course of the experiment, samples were taken at set intervals and the hydrogen consumption and flow were noted as well. After 24 h no further hydrogen was consumed and the reaction was terminated. The experimental data is estimated to be accurate to  $\pm 1\%$ . The reactions were carried out twice to confirm the reproducibility of the results.

## 2.3 Results and Discussion

### 2.3.1 Effect of glycerol concentration

Since water is generated as by-product during the hydrogenolysis of glycerol, it is always preferable to eliminate water to drive the equilibrium in the forward direction. It is therefore surprising that most studies on precious metals to date use dilute glycerol solutions (10 to 20 wt%), with a single reference reporting a 40 wt% glycerol concentration, the reason being unknown. Suppes and co-workers [2] studied the hydrogenolysis of glycerol in water at concentrations  $> 40\%$  over a copper-chromite catalyst, yielding propylene glycol as major product. According to our knowledge the hydrogenolysis of higher glycerol concentrations ( $> 40\text{ wt}\%$ ) has not been reported for supported precious metal catalysts. In view of this, a known precious metal-solid acid catalyst system, Ru/C + Amberlyst 15, from the work by Tomishige and co-workers [1, 7], was selected and the effect of water to glycerol ratio studied on the selectivity of lower alcohols, in particular 1-propanol. Table 2.2 summarises the results obtained by varying the glycerol concentration between 20 to 100 wt%, while keeping the catalyst to glycerol ratio constant.

**Table 2.2: Effect of initial water content on the hydrogenolysis of glycerol.**

Glycerol Conc. <sup>a</sup> (wt%)	Glycerol Conv. (mol%)	Selectivity (mol%)								Reaction rate <sup>c</sup>
		MeOH	EtOH	2-PO	1-PO	EG	1,2- PDO	1,3- PDO	Others <sup>b</sup>	
20	49.2	0.0	4.3	4.3	10.1	5.9	74.0	1.4	0.0	7.6
40	40.3	0.3	2.9	0.6	11.3	7.9	75.2	1.8	0.0	5.0
60	34.5	0.7	7.3	1.4	15.3	10.1	63.1	2.1	0.0	7.1
80	30.5	0.6	7.9	1.1	21.8	8.1	49.1	2.4	9.1	7.9
100	48.7	0.0	0.2	0.0	6.2	0.0	1.0	0.6	92.0	2.6

<sup>a</sup> Reaction conditions: Ru/C, Amberlyst 15, 130 °C, 80 Bar H<sub>2</sub>, 24 h.

<sup>b</sup> Others = condensation products and unknowns.

<sup>c</sup> g lower alcohols/hour/g metal.

As the glycerol concentration increased from 20 to 80 wt% the glycerol conversion decreased. At the same time the selectivity to 1,2-PDO decreased with a considerable increase in the selectivity to 1-PO and ethanol. When comparing the rate of lower alcohol (MeOH, EtOH, 2-PO and 1-PO) formation, the rate was almost constant (7.1 to 7.9 g lower alcohol/hour/g metal) up to 80 wt% glycerol concentration, except for the outlier at 40 wt%. The overall selectivity towards hydrogenolysis products (including the diols) was high, even at 80 wt % glycerol. Similar trends of decreased glycerol conversions with increasing glycerol concentrations were observed by Tomishige and co-workers [5] over Ru/C, whereas Suppes and co-workers [2] reported an increase in conversion as the water content decreased over a copper-chromite catalyst. At 100 wt% glycerol the conversion increased, but a significant decrease in the selectivity towards lower alcohols and diols (EG, 1,2-PDO and 1,3-PDO) was observed, with a subsequent increase in condensation product formation.

An increase in glycerol conversion was seen as the glycerol concentration was increased from 80 to 100 wt%. According to Le Chatelier's principle if the equilibrium is disturbed by removing a reactant (water in this case), the system will tend to counteract for this change by shifting the equilibrium. This can be a possible reason for the increase in glycerol conversion from 80 wt% to 100 wt% glycerol and also the significant increase in aldol condensation products because the equilibrium is shifted towards these aldol condensation products.

Evidently, the presence of water inhibited condensation product formation. Since a 60 wt% glycerol concentration exhibited a high selectivity towards hydrogenolysis products with no condensation product formation, this concentration was selected for further studies.

### **2.3.2 Catalytic testing of supported precious metal catalysts**

The hydrogenolysis of 60 wt% glycerol was performed over different ruthenium, palladium and platinum metals supported on carbon, Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> to study the effect of the support on the catalytic performance. These experiments were performed without the addition of an acid co-catalyst. The aim was to get some insight into the relationship between the support and the catalytic properties of the metal catalysts at a higher glycerol concentration. Table 2.3 summarises the experimental results for the hydrogenolysis of glycerol using the precious metal catalysts at 180 °C and 80 Bar hydrogen pressure.

The liquid products in the hydrogenolysis of glycerol catalysed by these metal catalysts were 1,2-PDO, 1,3-PDO, EG, acetol, 1-PO, ethanol and methanol. The Ru catalysts were found to be the most active catalysts, affording glycerol conversions as high as 43.3 mol% and 66.7 mol% selectivity towards 1,2-PDO for Ru/C. However, the selectivity to 1,3-PDO (0.2 mol%) over Ru/C was very low and this was consistent with the results reported by Tomishige and co-workers [5]. In addition, a remarkably high selectivity towards EG (23 mol%) was obtained, providing unambiguous evidence that Ru/C is an active catalyst for both the scission of C-O and C-C bonds.

**Table 2.3: Summary of 60 wt% glycerol hydrogenolysis results over precious metal catalysts.**

Catalyst <sup>a</sup>	Glycerol Conv. (mol%)	Selectivity (mol%)							
		MeOH	EtOH	1-PO	Acetol	EG	1,2-PDO	1,3-PDO	Others <sup>b</sup>
5 % Ru/C	43.3	2.7	1.5	0.8	0.5	23.5	66.7	0.2	4.1
4 % Ru/Al <sub>2</sub> O <sub>3</sub> (doped)	38.9	2.6	3.4	6.9	0.7	14.3	38.0	0.3	33.8
4 % Ru/Al <sub>2</sub> O <sub>3</sub>	39.8	2.6	4.1	7.3	0.1	12.4	31.2	0.3	42.0
5 % Pd/C	1.3	0.0	0.0	86.2	0.0	0.0	11.7	2.1	0.0
5 % Pd/Al <sub>2</sub> O <sub>3</sub> (doped)	18.8	1.3	3.9	10.2	0.5	1.9	36.9	1.1	44.2
5 % Pd/Al <sub>2</sub> O <sub>3</sub>	14.0	1.9	5.1	12.3	0.5	1.2	28.5	1.3	49.2
5 % Pd/SiO <sub>2</sub>	1.9	0.0	0.0	10.3	4.6	0.0	33.1	0.0	52.0
5 % Pt/Al <sub>2</sub> O <sub>3</sub>	6.1	0.0	2.6	15.6	1.2	0.0	52.8	1.8	26.0
5 % Pt/SiO <sub>2</sub>	4.0	0.0	2.7	3.9	1.6	0.0	24.2	0.0	67.7
5 % Pt/C	2.4	0.0	0.0	0.0	0.0	0.0	39.5	0.0	60.5

<sup>a</sup> Reaction conditions: 60 wt% glycerol solution, 180 °C, 80 Bar H<sub>2</sub>, 1000 rpm, 24 h.

<sup>b</sup> Others = 2-propanol, condensation products and unknowns.

For the Ru/Al<sub>2</sub>O<sub>3</sub> (doped) and Ru/Al<sub>2</sub>O<sub>3</sub> catalysts, the conversion of glycerol was similar and the main product was 1,2-PDO (39 mol% and 40 mol% selectivity respectively), however, with a high formation of condensation products. Interestingly, a relatively high 1-PO selectivity (6.9 – 7.3 mol%) with subsequent decrease in EG formation was observed, presumably favouring C-O bond scission via a dehydration/hydrogenation mechanistic pathway. The higher selectivities toward condensation products over the Ru/Al<sub>2</sub>O<sub>3</sub> catalyst can possibly be explained by the higher acidity of the Ru/Al<sub>2</sub>O<sub>3</sub> compared to the Ru/Al<sub>2</sub>O<sub>3</sub> (doped) catalyst.

In the case of the Ru catalysts, active carbon is a more suitable support than Al<sub>2</sub>O<sub>3</sub>. It was also noted in previous reports that Ru/C is an effective catalyst for glycerol hydrogenolysis [15]. More EG was observed over Ru supported catalysts than over Pt and Pd supported catalysts. These results suggest that a favourable C-C cleavage pathway exists on Ru that is not available on Pt and Pd systems. These results are further supported by the work of Feng et al. [16] showing that the Ru particle sizes of the catalysts decrease in the order of Ru/SiO<sub>2</sub> > Ru/Al<sub>2</sub>O<sub>3</sub> > Ru/C, which is consistent with their increasing activity. This indicates that the hydrogenolysis of glycerol is more active over small particles. These results are also in good correlation with the results reported by Tomishige and co-workers [17]. The different selectivities of the ruthenium catalysts could be related to the fact that the support material can influence the reaction routes in the presence of the metal catalysts.

All the supported Pd and Pt catalysts exhibited low activity in the glycerol reaction. The Pd and Pt supported catalysts showed significantly lower conversions than the Ru supported catalysts, and this was also observed by Tomishige and co-workers [1] for lower glycerol concentrations. They found the hydrogenation activity to be in the order of Ru/C >>> Rh/C > Pt/C > Pd/C.

The conversions over the Pd supported catalysts varied significantly from 18.8 mol% to 1.3 mol%. As a result of their higher acidity, the Pd/Al<sub>2</sub>O<sub>3</sub> (doped) and Pd/Al<sub>2</sub>O<sub>3</sub> catalysts showed significantly higher conversions than Pd/C and Pd/SiO<sub>2</sub> under the same conditions. The Pd/Al<sub>2</sub>O<sub>3</sub> (doped) gave the highest glycerol conversion of 18.8 mol% with a 37 mol% selectivity to 1,2-PDO. Overall selectivities were found to be similar with perceived higher 1-PO selectivity than seen for the Ru catalysts. A surprisingly high 1-PO selectivity (86.2 mol %) was found for Pd/C, although conversions were very low. Apart from Pd/C, 1,2-PDO was the major monomeric oxygenate reported for all the Pd catalysts. The propensity for hydrogenation is higher for the alumina supported catalyst than silica supported catalyst, as shown by the

higher 1-propanol selectivities found for Pd/Al<sub>2</sub>O<sub>3</sub>. This can be explained by the metal-support interaction where the Pd catalyst supported on Al<sub>2</sub>O<sub>3</sub> is more acidic and therefore influences the C-C bond cleavage as opposed to dehydration. The main degradation products over the alumina supported catalysts are EG, ethanol and methanol.

In general, the Pt catalyst exhibited poor activity, with the more active Pd/Al<sub>2</sub>O<sub>3</sub> only showing 6.1 mol % glycerol conversion versus 39 and 14 mol % conversion for Ru/Al<sub>2</sub>O<sub>3</sub> and Pd/Al<sub>2</sub>O<sub>3</sub>, respectively. 1-PO selectivity was slightly higher and no cracking towards EG was observed. Similar to Pd/C the Pt/C system also showed a very low conversion (2.4 mol%) and very high concentrations of condensation products (61 mol%) were observed.

Ruthenium is known to be more active in glycerol hydrogenolysis than palladium and platinum [1]. Montassier et al. proposed [18] that the cleavage of the C-C bond occurs through a retro-aldol reaction, whereas C-O cleavage occurs through a dehydration reaction. Ruthenium often promotes excessive C-C cleavage resulting in a high selectivity to hydrocarbons, whereas this pathway is not favourable over palladium and platinum. This can be seen from the formation of EG over Ru/C, while no C-C cleavage products were observed over Pd/C and Pt/C.

### 2.3.3 Effect of temperature

The Ru/C catalyst was proven to be very active in glycerol hydrolysis giving the highest conversion, and selectivity to 1,2-PDO, whereas the Pd/C catalyst gave the most promising selectivity to 1-propanol. In this section we decided to focus on these two catalysts and studied the effect of temperature. Table 2.4 showed the temperature dependence of the glycerol hydrogenolysis reaction over Ru/C.

As expected, with an increase in temperature up to 250 °C an increase in glycerol conversion was observed. At 250 °C a quantitative conversion was observed, but the main products were mostly condensation by-products, the result of glycerol/acetol undergoing condensation at these temperatures and under high pressures [see Section 2.3.5]. As the temperature increased up to 200 °C, a slight increase in 1,2-PDO selectivity was observed. Further increase of the reaction temperature to 230 °C resulted in higher glycerol conversion, although the selectivity of 1,2-PDO decreased in favour of condensation product formation. A detailed discussion on the condensation products observed is given in Section 3.5. Based on these results, it was decided to continue all experimental work on 60 wt% glycerol solutions at 180 °C, because at this

concentration and temperature relative high glycerol conversion is obtained with a high selectivity to 1,2-PDO, and low condensation product formation was observed.

**Table 2.4: Effect of higher temperatures on Ru/C hydrogenation.**

Temp <sup>a</sup> (°C)	Glycerol Conv. (mol%)	Selectivity (mol%)								
		MeOH	EtOH	2-PO	1-PO	Acetol	EG	1,2- PDO	1,3- PDO	Others <sup>b</sup>
150	45.1	2.1	4.1	3.5	3.1	0.0	19.7	67.0	0.5	0.0
180	43.3	2.7	1.5	2.3	0.8	0.5	23.5	66.7	0.2	1.8
200	56.6	2.0	1.7	0.5	1.1	4.2	12.0	71.6	0.2	6.7
230	68.9	1.2	1.0	0.0	2.5	6.0	6.6	16.7	0.3	65.7
250	99.8	0.0	0.0	0.0	17.6	1.7	2.0	0.3	0.4	78.0

<sup>a</sup> Reaction conditions: 60 wt% glycerol solution, Ru/C, 80 Bar H<sub>2</sub>, 24 h.

<sup>b</sup> Others = condensation products + unknowns.

Despite the low glycerol conversion seen over Pd/C, the promising selectivity towards 1-PO prompted further investigation of this catalyst and the effect of higher temperature was also evaluated in an attempt to increase the conversion. The hydrogenolysis results of 60 wt% glycerol in the presence of Pd/C over a temperature range of 180 to 250 °C are given in Table 2.5.

**Table 2.5: Effect of higher temperatures on Pd/C hydrogenation.**

Temp <sup>a</sup>	Glycerol Conv. (mol%)	Selectivity (mol%)								
		MeOH	EtOH	2-PO	1-PO	Acetol	EG	1,2- PDO	1,3- PDO	Others <sup>b</sup>
180	1.3	0.0	0.0	0.0	86.2	0.0	0.0	11.7	2.1	0.0
200	4.5	0.0	0.0	0.0	87.7	2.3	0.0	8.9	1.1	0.0
230	20.3	0.4	0.7	0.0	72.6	1.1	0.2	2.2	0.3	22.5
250	38.5	0.1	0.5	0.0	52.8	0.3	1.1	1.9	0.1	43.2

<sup>a</sup> Reaction conditions: 60 wt% glycerol, Pd/C, 80 Bar H<sub>2</sub>, 24 h.

<sup>b</sup> Others = condensation products + unknowns.

With an increase in temperature, an increase in glycerol conversion was observed. The main product that was formed during the reactions over Pd/C was 1-propanol (1-PO), which is in contrast with the results obtained with Ru/C where the main product was 1,2-PDO. At higher temperatures (230 to 250 °C) the amount of condensation products increased considerably, although a promising 1-PO selectivity of 72.6 mol % was still recorded at 230 °C. 1-PO forms via the dehydration of glycerol to acetol or 3-hydroxypropionaldehyde, followed by hydrogenation to yield 1,2-PDO and 1,3-PDO, respectively. Consecutive dehydration and hydrogenation of allyl alcohol results in 1-PO formation (see Figure 2.1, Section 2.3.5).

### 2.3.4 Catalytic testing of Ru/C and Pd/C with solid acid catalysts

Since Ru/C gave the highest conversion and selectivity towards 1,2-PDO, it was decided to screen a series of solid acid catalysts in combination with Ru/C to determine whether promoting the initial dehydration step could improve the selectivity towards 1,2-PDO via initial acetol formation [19]. In a similar fashion, acid catalysed dehydration can promote 1,3-PDO formation via the initial formation of 3-hydroxypropionaldehyde. Based on previous work by Tomishige [1] on a Ru/C and Amberlyst 15 catalyst system, a decision was made to expand this study by including IER's known to have a higher temperature stability. Subsequently, in addition to Amberlyst 15 (1.7 eq/L) with a maximum recommended operating temperature of 130 °C, the chlorinated acidic resins, Amberlyst DT (1.17 eq/L), Amberlyst 70 (0.9 eq/L) and Resin-A (a Chlorinated Resindion Relite CFS resin; 1.9 eq/L) were screened, while solid phosphoric acid (SPA) and  $\text{SiO}_2/\text{Al}_2\text{O}_3$  were also included into the study due to their robustness. The experimental results are summarised in Table 2.6.

Due to its lower temperature stability, the Amberlyst 15 + Ru/C experiment using 60 wt% glycerol was performed at 130 °C and compared to literature results. The addition of Amberlyst 15 to the Ru/C catalyst system gave 34 mol% glycerol conversion with the highest selectivity to 1,2-PDO of 63 mol%. Relatively high selectivities were also seen towards EG (10 mol%), 1-PO (15 mol%) and ethanol (7 mol%). These results compared well to the results published by Tomishige and co-workers [1] for a 20 wt% glycerol solution where the enhancing effect of Amberlyst 15 was evident with a 13 % glycerol conversion (3.5 mol% glycerol conversion without Amberlyst 15).

Among the Ion Exchange Resins (IERs) evaluated, Amberlyst 70 gave the highest glycerol conversion of 56 mol% and with 40 mol% selectivity to 1-PO. The promoting effect of the solid

acid was clear when compared to the experiment at 180 °C in the absence of a resin (56.1 versus 43.3 mol% conversion). Other products that formed during this reaction are ethanol and ethylene glycol and a high amount of condensation products was seen. Surprisingly the runs with other chlorinated resins, Amberlyst DT and Resin-A, gave significantly lower glycerol conversion and did not enhance the rate of hydrogenolysis. The system with Amberlyst DT had a high selectivity to 1-PO (38 mol%) and 1,2-PDO (30 mol%) with a 35 mol% conversion.

**Table 2.6: Experimental results for the hydrogenolysis of glycerol using Ru/C with different solid acids.**

Acid <sup>a</sup>	Glycerol Conv. (mol%)	Selectivity (mol%)								
		MeOH	EtOH	2-PO	1-PO	Acetol	EG	1,2-PDO	1,3-PDO	Others <sup>c</sup>
Amberlyst 15 <sup>b</sup>	34.5	0.7	7.3	1.4	15.3	0.0	10.1	63.1	2.1	0.0
No acid added	43.3	2.7	1.5	2.3	0.8	0.5	23.5	66.7	0.2	1.8
Amberlyst DT	34.9	0.3	2.6	2.3	37.9	0.0	4.5	30.4	4.4	17.5
Amberlyst 70	56.1	0.0	3.1	0.0	39.8	0.3	7.2	0.3	0.3	48.9
Resin-A	29.2	0.8	3.0	0.7	37.3	0.0	4.0	37.3	7.7	9.0
55 % H <sub>3</sub> PO <sub>4</sub> /SiO <sub>2</sub>	58.0	0.4	4.8	1.2	16.1	0.0	6.8	55.3	0.1	15.2
SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> (90/10 Si/Al)	24.0	2.6	4.2	0.0	12.1	2.9	31.9	26.7	0.8	18.7

<sup>a</sup> Reaction conditions: Ru/C, solid acid, 60 wt% glycerol solution, 180 °C, 80 Bar H<sub>2</sub>, 24 h.

<sup>b</sup> Reaction temperature 130 °C.

<sup>c</sup> Others = condensation products and unknowns.

When Ru/C was combined with Resin-A, slightly lower conversions (29 mol%) were observed when compared to Amberlyst DT, but a higher combined selectivity towards 1,2-PDO and 1-PO (74.6 versus 68.3 mol%). Both these catalysts gave significantly less condensation products than observed for Amberlyst 70. Amberlyst DT and Resin-A have a higher acidity than Amberlyst 70 and, although no correlation between the acidity and conversion could be concluded, it seems that dehydration of 1,2-PDO is promoted by higher acidity, subsequently resulting in 1-PO

formation. In contrast, the lower acidity of Amberlyst DT promoted condensation product formation. The higher conversion showed for the Amberlyst 70 + Ru/C system at 180 °C can be explained by possible poisoning of Ru/C with sulfur compounds originating from the thermal decomposition of Amberlyst DT and Resin-A. These two resins have a slightly lower thermal stability than Amberlyst 70. In addition, it is suggested that the presence of Cl<sup>-</sup> ions can decrease the activity of Ru/C because it is absorbed on the Ru surface and can be a poison for the hydrogenolysis catalyst [1].

As a result of their robustness in terms of thermal stability, the Ru/C was next combined with Si/Al and H<sub>3</sub>PO<sub>3</sub>/SiO<sub>2</sub> showing 24 mol% and 58 mol% conversion, respectively, with 1,2-PDO as the predominant product. The system with H<sub>3</sub>PO<sub>3</sub>/SiO<sub>2</sub> exhibited higher glycerol conversion, possibly due to the higher dehydration activity of H<sub>3</sub>PO<sub>3</sub>/SiO<sub>2</sub>. This is also confirmed by the high selectivities obtained to 1,2-PDO over the H<sub>3</sub>PO<sub>3</sub>/SiO<sub>2</sub>. H<sub>3</sub>PO<sub>3</sub>/SiO<sub>2</sub> has Bronsted acid sites, whereas the silica alumina zeolites have Bronsted and Lewis acid sites [20, 21].

From the temperature studies reported in Section 2.3.3, it was evident that higher temperatures result in a significant rate enhancement during the Pd/C catalysed hydrogenolysis of glycerol. Work done by Tomishige and co-workers [1] on the promoting effect of Amberlyst 15 on the Pd/C catalysed hydrogenolysis of glycerol has shown almost no rate enhancement. However, this work was done at 120 °C for a 20 wt% glycerol solution. Therefore it was decided to do some exploratory experiments with Pd/C in the presence of Amberlyst DT at 180 °C with the aim to improve the glycerol conversion. It was also decided to evaluate a recently commercialised bi-functional catalyst by Dow, Amberlyst CH43, which is an IER doped with 0.7 wt% Pd. The results are summarized in Table 2.7.

Two runs with Pd/C + Amberlyst DT were performed at 180 °C for a 20 wt% and 60 wt% glycerol solution respectively, and compared with the experiments without the addition of an acid co-catalyst. In the presence of Amberlyst DT, a significant increase in glycerol conversion was obtained for the 20 wt% (1.0 mol% to 14.9 mol%) as well as the 60 wt% (1.3 mol% to 39.2 mol%) experiments with the 1-PO being the predominant monomeric oxygenate formed in all cases. However, the selectivity to 1-PO dropped to 31 mol% for the 60 wt% run with Amberlyst DT present, with the remainder being mainly glycerol condensation products. Interestingly no methanol, ethanol or ethylene glycol was observed during the above reactions, which shows that no C-C bond cleavage took place.

Amberlyst CH43 (Pd impregnated resin) with higher temperature stability, was also tested. Amberlyst CH43 also gave poor glycerol conversions (< 6 mol%) with a 50 mol% selectivity to 1-propanol and 49 mol% reported as others, again predominantly glycerol condensation products. Two possible reasons for these poor conversions might be the low metal loading on the resin (0.7 %) and decomposition of the resin at the temperature of 180 °C.

**Table 2.7: Experimental results for the hydrogenolysis of glycerol using Pd/C with different solid acids.**

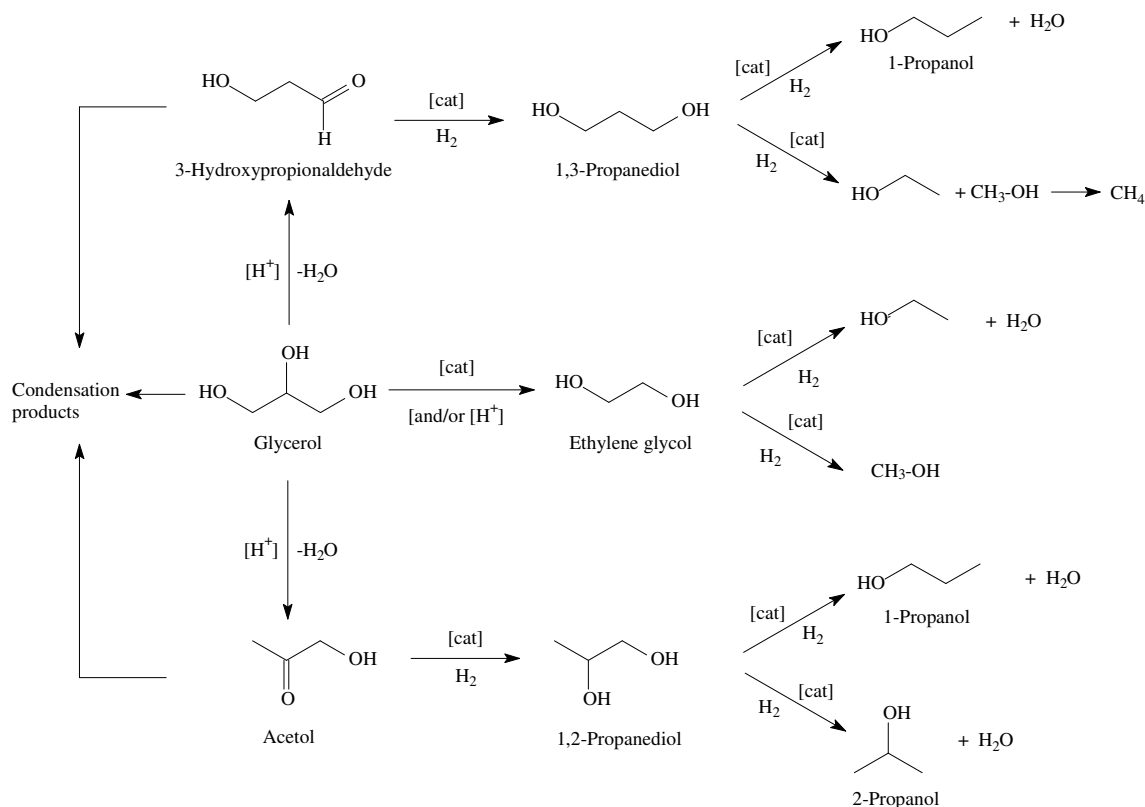
Acid <sup>a</sup>	Glycerol conc. (wt%)	Glycerol Conv. (mol%)	Selectivity (mol%)						
			MeOH	EtOH	2-PO	1-PO	Acetol	1,2-PDO	Others <sup>b</sup>
No acid	20	1.0	0.0	0.0	0.0	86.2	0.0	13.8	0.0
Amberlyst DT	20	14.9	0.0	0.0	0.0	75.4	0.0	0.7	23.9
No Acid	60	1.3	0.0	0.0	0.0	86.2	0.0	11.7	2.1
Amberlyst DT	60	39.2	0.0	0.0	0.4	31.0	0.2	1.2	67.2
Amberlyst CH43	60	5.3	0.0	0.0	0.0	49.6	1.0	0.6	48.8

<sup>a</sup> Reaction conditions: Pd/C, 180 °C, 80 Bar H<sub>2</sub>, 24 h.

<sup>b</sup> Others = ethylene glycol, 1,3-PDO, condensation products and unknowns.

### 2.3.5 Identification of condensation products

Figure 2.1 shows the possible routes to the products obtained in the hydrogenolysis of glycerol [1,22]. The acid catalyses the dehydration of glycerol to either acetol or 3-hydroxypropionaldehyde (3-HPA), followed by subsequent hydrogenation over the supported metal catalyst to give 1,2-PDO and 1,3-PDO, respectively. These diols can undergo a consecutive hydrogenolysis step to form lower alcohols such as 1- and 2-propanol. Another product that can form from the direct hydrogenation of glycerol is ethylene glycol. Ethanol and methane can form via the degradation reaction of 1,2-PDO, and in addition ethanol and methanol can also be formed during the hydrogenolysis of ethylene glycol.



**Figure 2.1: Reaction scheme of glycerol hydrogenolysis and degradation reactions [1,22].**

The formation of heavy condensation products were also observed during most of the experimental runs reported in this paper. Since very little has been reported in literature on the formation and composition of condensation products during the hydrogenolysis of glycerol, GC MS analysis was performed on the above-mentioned reaction mixtures to develop a better understanding of the mechanism leading to the formation of these unwanted products. Table 2.8 represents and summarizes the retention times and qualifier ions for the unknown products observed during a typical hydrogenolysis reaction performed in the presence of Ru/C + acid co-catalyst.

**Table 2.8: Summary of the retention times and qualifier ions for the major unknown products.**

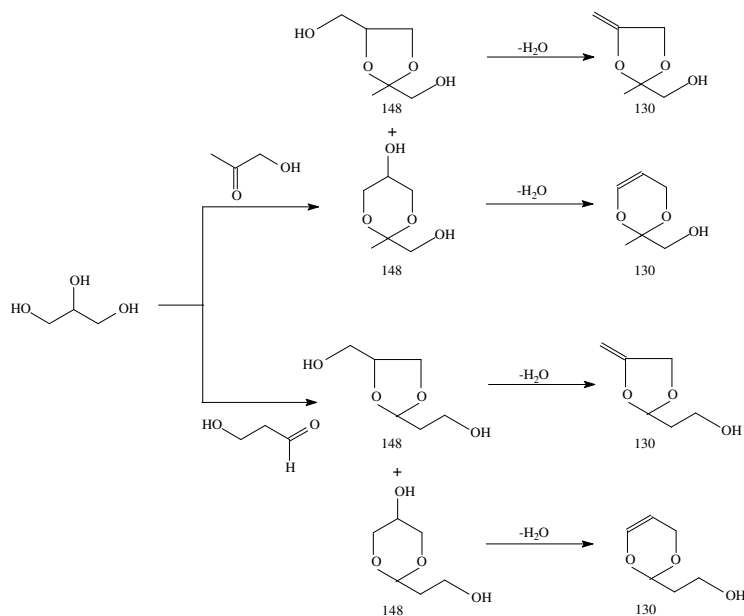
Compound number	Retention time (min) <sup>a</sup>	Qualifier ion <sup>b</sup> ( <i>m/z</i> )
1	17.45	114
2	17.63	114
3	17.99	130
4	18.64	100
5	19.28	112
6	19.35	114
7	19.80	130
8	20.59	130
9	21.43	118
10	23.22	130
11	24.34	132
12	26.84	132

<sup>a</sup> retention times for methanol (4.50), 2-PO (4.84), ethanol (5.03), 1-PO (7.05), acetol (14.40), 1,2-PDO (21.00), EG (21.85) and 1,3-PDO (22.81).

<sup>b</sup> qualifier ion means the molecular weight of the compound that is detected on the GC MS.

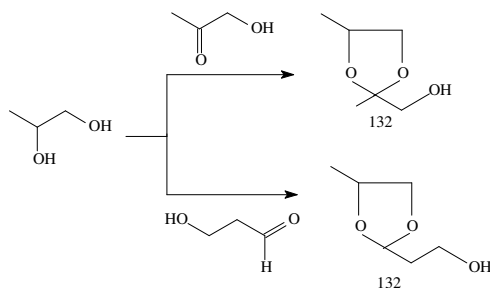
Our investigation focussed on the identification of the unknown peaks that were obtained during the glycerol reactions. The condensation of glycerol with either acetol or 3-HPA to cyclic acetals can form via several routes. The formation of these cyclic acetals by the catalytic condensation of glycerol was reported on by Deutsch et al. [23] and Ruiz et al. [24]. There were four possible isomers that could form during this condensation reaction, each with a molecular weight of 148 and after a loss of water; a compound with a molecular weight of 130 was formed. Subsequent hydrogenation will afford the analogues with a weight of 132 (Scheme 2.1).

All four isomers had the same fragmentation pattern of 103, 57, 43 and 29 and these isomers eluted at 17.99 min, 19.80 min, 20.59 min and 23.22 min, respectively. A mass loss of 27, which can typically be a C<sub>2</sub>H<sub>3</sub> fragment, would give a *m/z* 103. The fragment at *m/z* 57 indicated a mass loss of 73, which can be due to a C<sub>3</sub>H<sub>6</sub>O<sub>2</sub> fragment. The fragmentation pattern of 43 and 29 indicated a general hydrocarbon structure.



**Scheme 2.1: The condensation of glycerol with acetol or 3-HPA to cyclic acetals.**

An alternative pathway towards the formation of two compounds with a molecular weight of 132, which eluted at 24.34 min and 26.84 min, is the condensation of 1,2-PDO with acetol or 3-HPA as shown in Scheme 2.2. These cyclic acetals gave the same fragmentation pattern of 103, 57, 43 and 29, as the compounds discussed above.

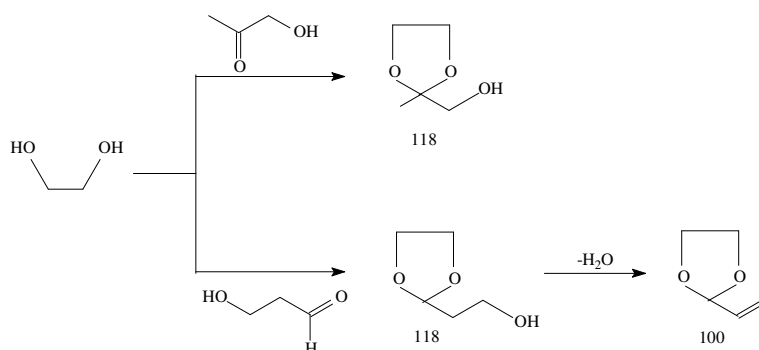


**Scheme 2.2: The condensation of 1,2-PDO with acetol or 3-HPA to cyclic acetals.**

Other dominant qualifier ions observed were  $m/z$  112 and 114 which eluted at 17.45, 17.63, 19.28 and 19.35 min and are believed to be the result of subsequent dehydration/hydrogenation of the  $m/z$  130 and  $m/z$  132 species observed above. The compounds with  $m/z$  114 had the following fragmentation pattern: 71, 55, 43 and 29. A  $m/z$  of 71 indicated a mass loss of 43 which can be attributed to a C<sub>3</sub>H<sub>6</sub> fragment. At the same time a  $m/z$  of 43 was observed, which

indicated the loss of the  $C_3H_4O_2$  fragment. A mass loss of 59 showed the loss of the  $C_3H_4O$  fragment.

In a similar fashion EG undergoes condensation with acetol or 3-HPA to also form cyclic acetals as shown in Scheme 2.3 and this was also reported by Patel et al. [25]. Two compounds with a  $m/z$  100 (18.64 min) and  $m/z$  118 (21.43 min) were observed.



**Scheme 2.3: The condensation of EG with either acetol or 3-HPA.**

The heavy aldol condensation products that can form during glycerol hydrogenolysis have been identified, as have possible routes to these aldol condensation products. This allows proposing a mechanism towards explaining all the possible routes to the different products that can form during glycerol hydrogenolysis.

## 2.4 Conclusion

In this study we have successfully demonstrated the use of highly concentrated glycerol solutions (60 wt %) for the hydrogenolysis reaction. In spite of several research efforts reported in literature, a major drawback has been the use of diluted glycerol solutions for this reaction. These solutions are further diluted by the water formation of the reaction which consequently reduces the average space-time yield of the reaction. This will result in an increase in energy consumption of the process. Even a glycerol solution of 80 wt% was successfully used in this study but at the expense of the formation of unwanted aldol condensation products. If a pure glycerol solution was used, a significant increase in aldol condensation products were observed because the equilibrium is shifted towards the aldol condensation products according to Le Chatelier's principle.

Different ruthenium, palladium and platinum catalysts were employed to study the effect of the support on the catalytic performance. The aim was to get some insight into the relations between the support and the catalytic properties of the metal catalysts and to study the parameters that impact on the average space-time yield of lower alcohols. For this reason different acid ionic exchange polymeric resins, as well as Si/Al and H<sub>3</sub>PO<sub>3</sub>/SiO<sub>2</sub>, have been evaluated as co-catalyst under batch conditions. The highest conversion of glycerol (43.3 mol%) and the selectivity of 1,2-PDO (66.7 mol%) were obtained over the Ru/C catalyst. Despite the low glycerol conversion (1.3 mol%), Pd/C gave a promising 1-PO selectivity (> 85 mol%).

The novelty of this work also includes the solid acids tested, especially the use of chlorinated Amberlyst resin, for the production of 1-PO a high value commodity chemical. The use of the in-house prepared chlorinated resin, in combination of Ru/C, for the glycerol hydrogenolysis reaction was also reported here for the first time. Promising results were obtained with Resin A, with 37 mol% selectivity to 1-PO and a 29 mol% glycerol conversion. Among the other solid acids tested in combination with Ru/C, Amberlyst DT gave the most promising results from a 1-PO point of view, achieving a 34.9 mol% glycerol conversion with a selectivity of 30 mol% to 1,2-propanediol and 38 mol% selectivity to 1-propanol.

The formation of heavy condensation products were also observed during most of the experimental runs reported in this paper. GC MS analysis of the products mixtures obtained has shed some light on the possible mechanism leading to these unwanted compounds, as well as the identity of these molecules.

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## CHAPTER 3

### A CATALYTIC ROUTE TO LOWER ALCOHOLS FROM GLYCEROL USING Ni SUPPORTED CATALYSTS

#### **Abstract**

The activity of Ni supported catalysts on silica and alumina was studied for the transformation of glycerol to lower alcohols, primarily 1-propanol and ethanol. Pressure (40-75 Bar H<sub>2</sub>) had a small effect on glycerol conversion whereas temperature (230-320 °C) had a significant effect on conversion and selectivity. Ni/SiO<sub>2</sub> gave quantitative conversion of glycerol at a lower temperature compared to Ni/Al<sub>2</sub>O<sub>3</sub>. Ni/SiO<sub>2</sub> also gave a higher selectivity to ethanol and propanol (63 %) compared to Ni/Al<sub>2</sub>O<sub>3</sub> (52 %) at a similar conversion. The higher activity of Ni/SiO<sub>2</sub> can be ascribed to its smaller crystallite size ascertained from XRD analysis. The Ni/SiO<sub>2</sub> catalyst also showed improved reducibility compared to Ni/Al<sub>2</sub>O<sub>3</sub>. The used catalyst showed sintering of the Ni which was confirmed by a loss of surface area and an increase in average crystallite size. The route to lower alcohols from glycerol is proposed to occur via 1,2-propanediol. We are therefore proposing a route to convert glycerol into lower alcohols over Ni supported catalysts.

Keywords: 1,2-Propanediol; Ethylene glycol; Propanol; Ethanol.

#### **3.1 Introduction**

The interest in the catalytic conversion of renewable feedstocks to a range of value added chemical commodities has been increasing. Studies on the hydrogenolysis of polyhydric alcohols have been pursued since 1930. Glycerol is an important building block in natural fats and oils [1] and recently the need has arisen to find new applications for this by-product obtained from the production of biodiesel. Glycerol can be converted to hydrogen and synthesis gas by reforming [2], or 1,2-propanediol (1,2-PDO), 1,3-propanediol (1,3-PDO) and ethylene glycol (EG) via hydrogenolysis [3] and also to lower alcohols such as methanol, ethanol, 1- and 2-propanol [4].

Much work has been done towards the hydrogenolysis of glycerol to 1,3- and 1,2-PDO, as well as oxidation of glycerol to glyceric acid or dihydroxyacetone [5]. However, routes to lower

alcohols, such as 1-propanol and ethanol have been less discussed. It is known that glycerol can be hydrogenolysed using various heterogeneous systems including Rh, Ru, Pt, PtRu, copper systems and Raney Ni [6]. Surprisingly, the use of supported Ni systems as catalysts towards the chemical transformation of glycerol, especially towards the formation of lower alcohols, has appeared less frequently in the literature [7-11].

Bloom [7] described a process for the hydrogenolysis of a 40 wt% glycerol feedstock. Several Ni supported catalysts were used, and the major product was 1,2-PDO with a selectivity of up to 72 %. The supports that were used include carbon, silica and alumina.

The hydrogenolysis of polyols (e.g. xylitol, sorbitol or glycerol) to ethylene glycol in the presence of nickel on silica or alumina and hydrogen was described by Bullock et al. [8]. High conversions were observed with a 70 % selectivity to 1,2-PDO and 15 % to ethylene glycol (EG) and 11 % of degradation products.

Huang et al. [9] reported on the hydrogenolysis of solvent free glycerol to 1,2-PDO. Several catalysts were screened and the most effective catalysts (41 wt% Ni/Al<sub>2</sub>O<sub>3</sub> and 32 wt% Cu/ZnO/Al<sub>2</sub>O<sub>3</sub>) were further tested for vapour phase hydrogenolysis in a fixed bed. They found that Ni/Al<sub>2</sub>O<sub>3</sub> is not an effective catalyst for the production of 1,2-PDO because of the high selectivity to CH<sub>4</sub> and CO.

The catalytic hydrogenolysis of glycerol to propanediols using homogeneous Pd and Pt systems was also described by Drent and Jager [10]. Typical selectivities obtained were 47 % to 1-propanol, 31 % to 1,3-PDO and 22 % to 1,2-PDO. The hydrogenolysis was carried out under moderate reaction conditions with temperatures in the range of 140 °C and pressures around 40 Bar H<sub>2</sub>.

Tomishige and co-workers [11] reported a high selectivity of 42 % to 1-propanol and 13 % to 2-propanol using supported metal catalysts (Rh, Ru, Pt, Pd on active carbon, SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>) during the hydrogenolysis of aqueous glycerol solutions under H<sub>2</sub> in a batch reactor.

Thus, much of the work that has been reported focused on the production of 1,2-propanediol from glycerol using Cu supported systems, and at times, Ni catalysts.

The focus of this work was the production of lower alcohols (69 % selectivity), primarily 1-propanol and ethanol, from glycerol using Ni supported catalysts in a continuous flow fixed bed reactor. Biomass is readily converted to biodiesel and glycerol and we are therefore proposing a route to convert biomass into biodiesel and lower alcohols (via glycerol) from the same crop. Lower alcohols are useful chemicals and are mainly used as solvents in industry.

## **3.2 Experimental**

### **3.2.1 Reagents**

The Ni/Al<sub>2</sub>O<sub>3</sub> and Ni/SiO<sub>2</sub> bulk systems were obtained as commercial samples in a partially reduced state from BASF. The average Ni content was between 45–55 wt% for Ni/Al<sub>2</sub>O<sub>3</sub> and Ni/SiO<sub>2</sub> respectively. The glycerol was purchased from Sigma Aldrich and used without further purification. The glycerol feed was prepared as 60 wt% in a water mixture.

### **3.2.2 Catalyst characterisation**

The Brunauer, Emmet and Teller (BET) surface areas were measured by nitrogen physisorption isotherms at -20 °C using the standard multipoint method (eleven points) on a Micrometrics Gemini instrument. Prior to the analysis, samples were degassed in a stream of nitrogen at 200 °C for 24 hours.

Temperature programmed reduction (TPR) and NH<sub>3</sub>-temperature programmed desorption (TPD) experiments were carried out in a Micrometrics 2900 AutoChem II Chemisorption Analyzer. Prior to the reduction in the TPR, the catalyst was pretreated by being heated under a stream of argon (30 mL/min) at 350 °C for 30 min and then cooled down to 80 °C under the same stream of argon. In the reduction experiment, 5 % H<sub>2</sub> in argon was used as a reducing agent at a flow rate of 50 mL/min. Under these reducing conditions, the temperature was ramped up to 950 °C at a rate of 10 °C/min.

In the TPD experiments, the catalysts (ca. 20 mg) were first reduced under 5 % H<sub>2</sub> in argon and thereafter treated with helium for one hour to remove excess hydrogen. A 4 % ammonia in helium gas mixture was then passed (20 mL/min) over the catalyst for 30 min. The excess ammonia was removed by flushing the system with helium (30 mL/min) for 30 min and then adsorbed ammonia was stripped off by the same stream of helium (30 mL/min) and a

temperature ramp of up to 900 °C (at 10 °C/min). The desorption profiles were recorded using a TCD.

Powder X-ray diffraction (XRD) patterns were recorded on a Bruker D8 Advance diffractometer equipped with a graphite monochromator and operated at 40 kV and 40 mA. The source of radiation was Co K $\alpha$ . The 2 $\theta$  covered the range between 10 and 90 degrees at a speed of one degree per minute with a step size of 0.02 degrees and all data were captured by a Sietronics 122D automated microprocessor. The average crystallite size was calculated using the Scherrer equation.

Scanning electron microscopy (SEM) images were obtained using a LEO 1450 Scanning Electron Microscope. Samples for SEM images were coated with gold using a Polaron SC Sputter Coater.

Transmission Electron microscopy (TEM) images were taken on a Jeol JEM 1010 Transmission Electron Microscope operated at a voltage of 100 kV. Samples were prepared by deposition of a small amount of the catalyst between two formvar coated copper grids and the images were captured with the MegaView III Soft Imaging System.

Thermogravimetric analysis – differential scanning calorimetry (TGA-DSC) was performed on the catalysts under a nitrogen atmosphere using a SDT Q 600 TGA-DSC instrument. The temperature was increased from room temperature to 1000 °C at a rate of 20 °C/min.

### **3.2.3 Catalytic testing**

The catalytic reaction of glycerol was performed in a continuous flow fixed bed reactor in down flow mode (See Appendix, Figure B). The reason for the change to a fixed bed reactor is to generate results that are more comparable to industry. The reactor tube was stainless steel with an internal diameter of 20 mm and a length of 250 mm. The catalyst volume was 5 mL (ca. 8.5 g) and mixed with an equal amount of carborandum. The catalyst had a particle size distribution of 300-500  $\mu\text{m}$ . The molar ratio of hydrogen to glycerol solution was 2:1 with a GHSV of 1060  $\text{h}^{-1}$  and a LHSV of 3.0  $\text{h}^{-1}$ . The catalytic reactions were done between 230–320 °C with pressures varying between 40-75 Bar. Prior to the reaction, the catalyst was reduced at 180 °C after which the reactor was commissioned to operating conditions. The liquid products and the

unreacted glycerol were collected in sequential catchpots cooled to 3 °C and -20 °C respectively and the volume of the gaseous components was measured by a wet gas flow meter. The liquid products as well as the gas products were collected at regular intervals, and were analyzed on a GC (HP 6890) equipped with a FID using a DB-1701 column. Another gas sample was injected on a GC equipped with a TCD (Agilent 6850) using a Shincarbon packed column for CH<sub>4</sub> & CO<sub>x</sub> evaluation. Carbon balances were close to 100 % ± 5. The experimental data is estimated to be accurate to ± 1 %. The reactions were carried out twice to confirm the reproducibility of the results.

### 3.3 Results and Discussion

#### 3.3.1 Catalyst characterisation

##### 3.3.1.1 BET surface area

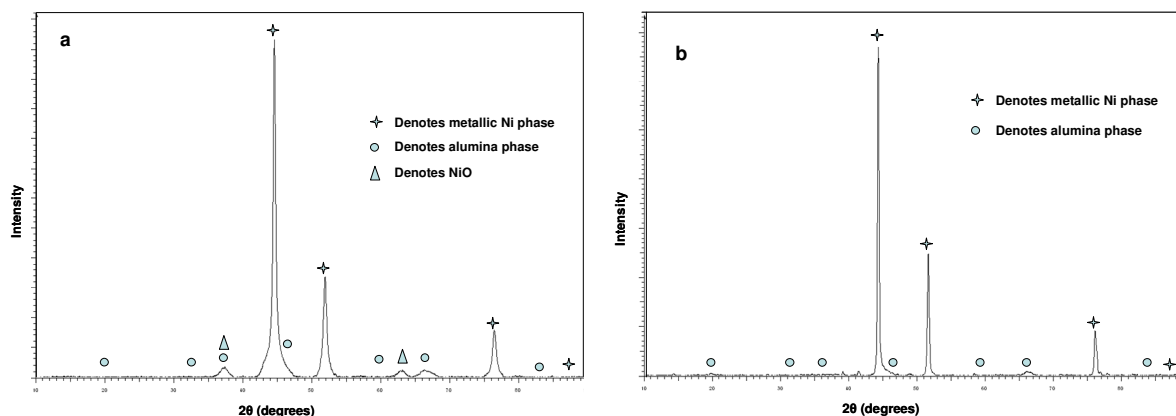
Table 3.1 compiles the BET specific surface area of the fresh and used Ni supported catalysts. Results showed that the surface area for the Ni/Al<sub>2</sub>O<sub>3</sub> was about 15 % higher than Ni/SiO<sub>2</sub>. As observed from the data, there is a significant decrease in surface area between the fresh and used catalysts. This decrease can probably be attributed to the sintering of the Ni particles which is caused by high temperatures and the nature of the liquid phase of the reaction which can result in carbon deposits on the catalyst surface [12].

**Table 3.1: Textural properties of Ni supported catalysts.**

Catalyst	BET Surface area (m <sup>2</sup> /g)	Crystallite size from XRD (nm)	Degree of reducibility (%)
Fresh Ni/Al <sub>2</sub> O <sub>3</sub>	150.5	17.7	51.4
Fresh Ni/SiO <sub>2</sub>	133.4	12.1	78.9
Used Ni/Al <sub>2</sub> O <sub>3</sub>	21.5	31.5	-
Used Ni/SiO <sub>2</sub>	12.9	82.2	-

##### 3.3.1.2 Powder X-ray diffraction

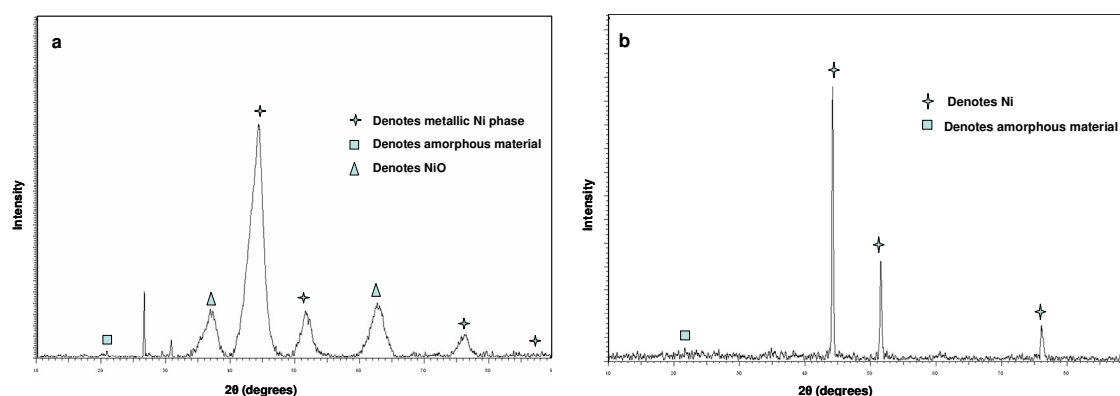
Figure 3.1 illustrates the diffractograms obtained for the fresh Ni/Al<sub>2</sub>O<sub>3</sub> and the used Ni/Al<sub>2</sub>O<sub>3</sub> catalysts. The XRD patterns for the fresh Ni/Al<sub>2</sub>O<sub>3</sub> catalyst shows NiO lines at 2θ = 37.3° (*d* = 2.35), 44.3° (*d* = 2.09) and 62.9° (*d* = 1.45) confirming the presence of “free” nickel oxide [16].



**Figure 3.1: XRD patterns of (a) fresh Ni/Al<sub>2</sub>O<sub>3</sub> catalyst and (b) used Ni/Al<sub>2</sub>O<sub>3</sub> at 320 °C.**

The used Ni/Al<sub>2</sub>O<sub>3</sub> catalyst showed peaks with  $2\theta = 44.5^\circ$  ( $d = 2.03$ ),  $51.8^\circ$  ( $d = 1.76$ ),  $76.3^\circ$  ( $d = 1.25$ ) and  $89.1^\circ$  ( $d = 1.09$ ) which were assigned to the metallic Ni phase, and peaks with  $2\theta = 19.9^\circ$  ( $d = 4.60$ ),  $32.0^\circ$  ( $d = 2.81$ ),  $36.2^\circ$  ( $d = 2.41$ ),  $46.9^\circ$  ( $d = 1.99$ ),  $60.0^\circ$  ( $d = 1.52$ ),  $61.1^\circ$  ( $d = 1.41$ ) and  $83.5^\circ$  ( $d = 1.15$ ) which were assigned to the alumina phase [13].

The XRD patterns of the fresh Ni/SiO<sub>2</sub> and the used Ni/SiO<sub>2</sub> catalysts are shown in Figure 3.2. The broad diffraction peaks can be attributed to the presence of amorphous silica in the catalysts [14] which is seen at  $2\theta = 21.7^\circ$ .



**Figure 3.2: XRD patterns of (a) fresh Ni/SiO<sub>2</sub> catalyst and (b) used Ni/SiO<sub>2</sub> at 320 °C.**

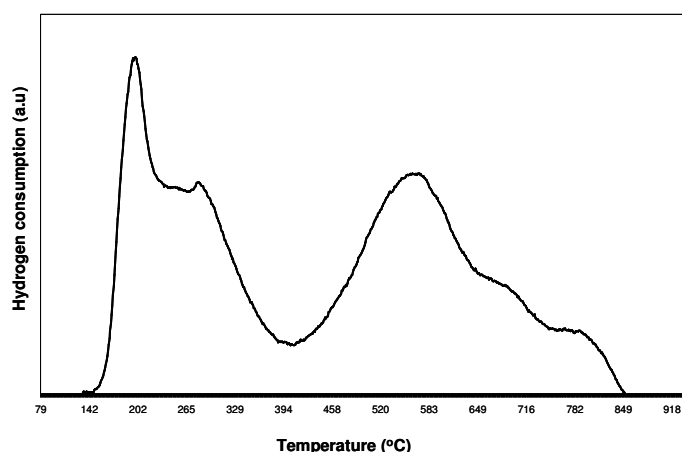
XRD analysis shows that the diffraction lines corresponding to the NiO are slightly more intense on the Ni/Al<sub>2</sub>O<sub>3</sub> than on the Ni/SiO<sub>2</sub>. This indicates the effect of the different support on the size of the Ni crystallites, with Al<sub>2</sub>O<sub>3</sub> favouring better crystallinity and formation of larger Ni crystallites [12,15]. The calculated Ni particle sizes (Sherrer equation), presented in Table

3.1, indeed show that Ni particles supported on Al<sub>2</sub>O<sub>3</sub> were larger than Ni supported on SiO<sub>2</sub> for the fresh catalysts.

The sharpening of the Ni metal peaks in the XRD patterns of the used catalysts suggests improved crystallinity likely due to the sintering of the Ni particles [14].

### 3.3.1.3 Temperature-programmed reduction

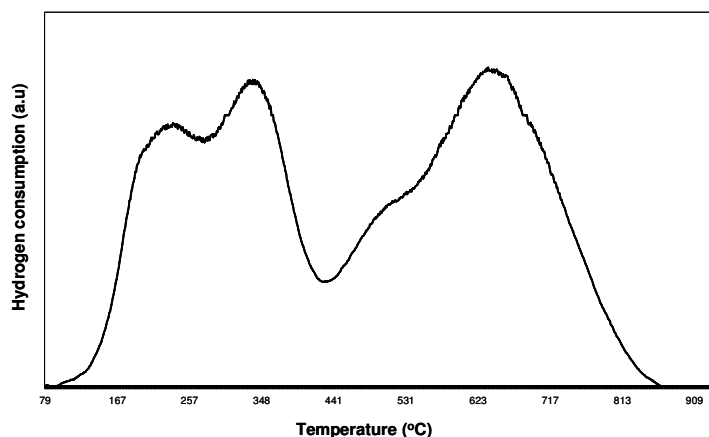
TPR characterisation is often used to analyse catalysts for surface Ni species, reducibility and metal support interaction [20]. Figure 3.3 shows the TPR profile of fresh Ni/Al<sub>2</sub>O<sub>3</sub> and this catalyst exhibited five reduction peaks (198, 280, 570, 700 and 800 °C). Peaks observed at temperatures lower than 400 °C can be attributed to NiO not associated or weakly associated with the support. The reduction peaks at higher temperatures can be associated with the strong interaction of the NiO and the support. Rynkowski et al. [16] reported that the peak at 700 °C is representative of the reduction of nickel that had reacted with the support forming nickel aluminate, NiAl<sub>2</sub>O<sub>4</sub>, and the peak at 800 °C is due to nickel aggregates [17]. Feng et al. [18] also confirmed that the peak at 700 °C is due to the reduction of a NiAl<sub>2</sub>O<sub>4</sub> spinel or strongly interacting NiO-γ-Al<sub>2</sub>O<sub>3</sub> phase.



**Figure 3.3:** TPR profile of fresh Ni/Al<sub>2</sub>O<sub>3</sub>.

Yang et al. [19] studied the effect of Ni loadings on the surface Ni species. They observed, most importantly, that the number of Ni species increased with increased Ni loading. The distinct difference in the number of reduction peaks indicates that the Ni loading has a prominent effect on the Ni species.

Figure 3.4 shows the TPR profile for fresh Ni/SiO<sub>2</sub>. The peak at 240 °C was due to highly dispersed NiO on the support. Mile et al. [20] assigned the peak at 336 °C to the nickel oxide with little or no interaction with the support, the peak at 520 °C showed the “free” nickel oxide and the peak at 645 °C can be associated with a strong metal support interaction.



**Figure 3.4: TPR profile of fresh Ni/SiO<sub>2</sub>.**

#### 3.3.1.4 Temperature-programmed desorption

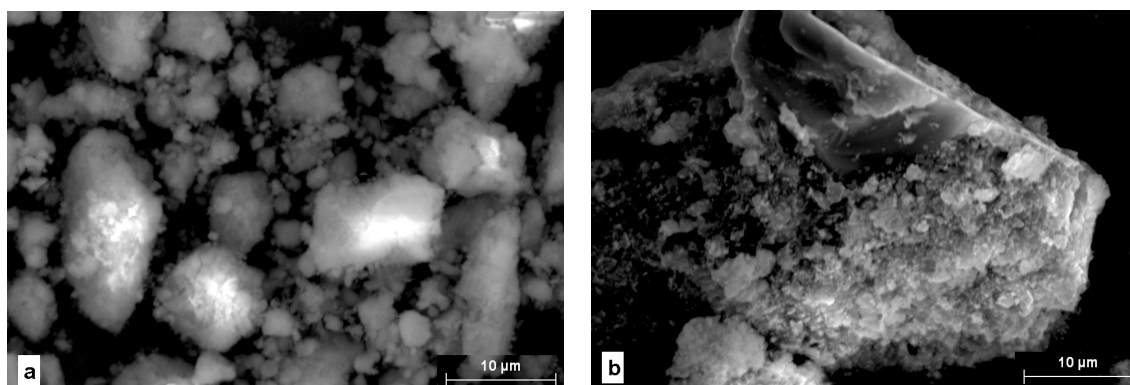
The acidity of the alumina or silica plays an important role in hydrogenolysis. Table 3.2 gives a range of acid sites for the two different systems. The Ni/Al<sub>2</sub>O<sub>3</sub> catalysts showed peaks at 182, 366 and 603 °C whereas, the Ni/SiO<sub>2</sub> catalyst showed peaks at 237, 368 and 662 °C. Pattamakomsan et al. [21] reported that their Al<sub>2</sub>O<sub>3</sub> supported catalyst showed desorption peaks around 170 °C and 340 °C which corresponded to weak and medium acid sites respectively. An additional peak was observed near 600 °C indicating strong acid sites of the Al<sub>2</sub>O<sub>3</sub> support. From Table 3.2 it is clear that the Ni/SiO<sub>2</sub> catalyst had a slightly higher total acidity, but showed a higher distribution of weak acid sites. The Ni/Al<sub>2</sub>O<sub>3</sub> catalyst showed a higher content of strong acid sites.

**Table 3.2: Acidity of the Ni supported catalysts.**

Catalyst	Weak acid sites (mmol NH <sub>3</sub> /g)	Medium acid sites (mmol NH <sub>3</sub> /g)	Strong acid sites (mmol NH <sub>3</sub> /g)	Total acidity (mmol NH <sub>3</sub> /g)
Fresh Ni/Al <sub>2</sub> O <sub>3</sub>	0.085	0.669	1.170	1.924
Fresh Ni/SiO <sub>2</sub>	0.942	0.852	0.381	2.175

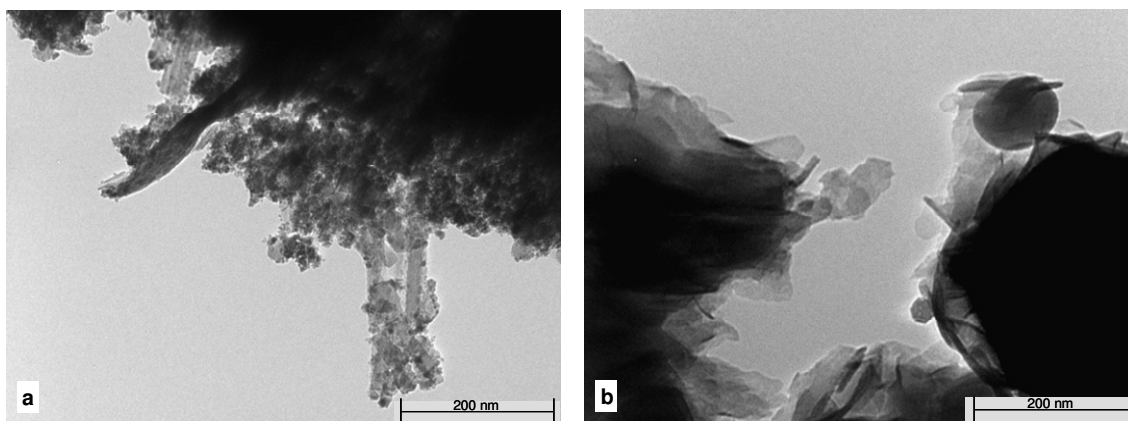
### 3.3.1.5 Electron microscopy

Figure 3.5 presents typical SEM images of the fresh and used Ni/SiO<sub>2</sub> catalysts. The SEM image of the fresh Ni/SiO<sub>2</sub> catalyst showed bright spots on the particles which can be attributed to the Ni crystallites exposed on the surface [22]. The used Ni/SiO<sub>2</sub> catalyst showed large clusters, which can be attributed to sintering, and this was also reflected in the BET measurements.



**Figure 3.5: SEM image of (a) fresh Ni/SiO<sub>2</sub> and (b) used Ni/SiO<sub>2</sub> with glycerol as feed at 320 °C.**

Figure 3.6 shows the TEM images of the fresh Ni/SiO<sub>2</sub> catalyst and the used Ni/SiO<sub>2</sub> catalyst. The fresh Ni/SiO<sub>2</sub> catalyst showed large spherical particles with smaller particles along the edges. The used Ni/SiO<sub>2</sub> catalyst has a thin sheet like appearance with no distinct presence of spherical particles. Evidence of sintering is clearly visible in the TEM image, Figure 3.6 (b).

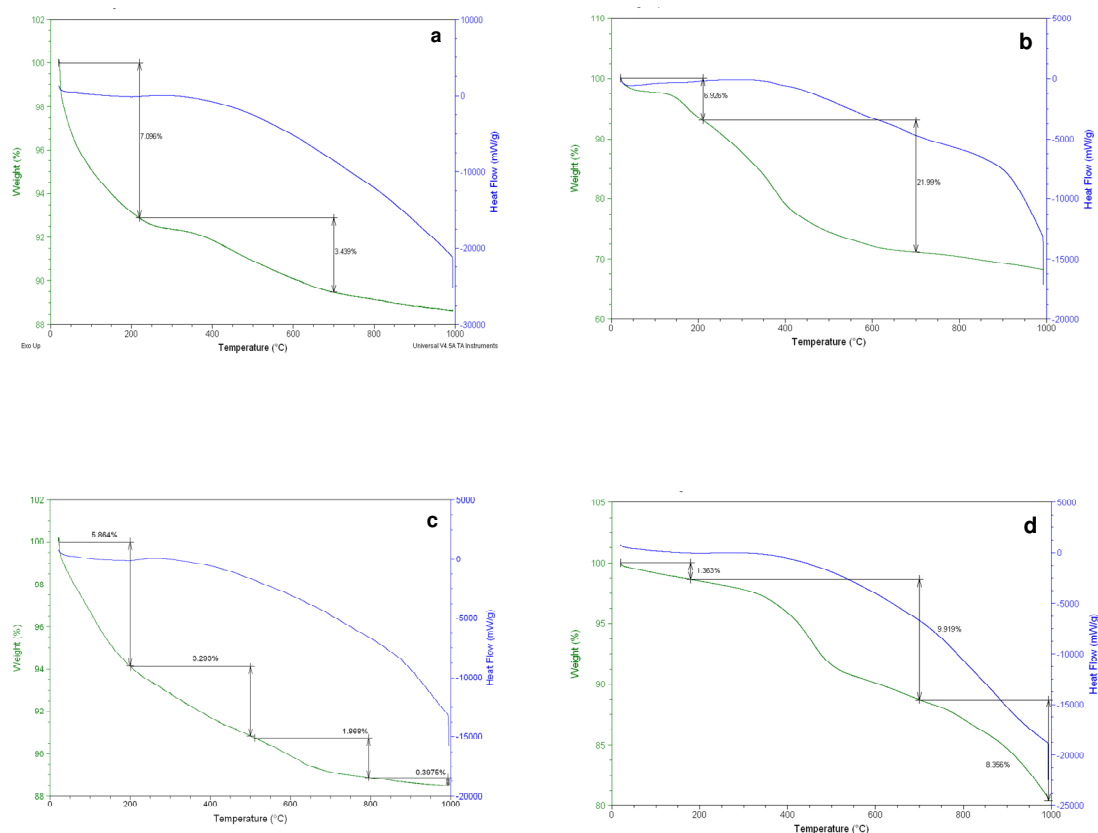


**Figure 3.6:** TEM images of (a) fresh Ni/SiO<sub>2</sub> and (b) used Ni/SiO<sub>2</sub> at 320 °C.

### 3.3.1.6 Thermogravimetric analysis

The thermogravimetric plots for both the fresh Ni/Al<sub>2</sub>O<sub>3</sub> and Ni/SiO<sub>2</sub> catalysts are given in Figure 3.7. The initial weight loss of about 7 % up to 200 °C, for both unreduced catalysts, is attributed to the loss of water. A very slow but constant decrease in weight up to 700 °C was observed for both fresh catalysts and can be attributed to the loss of organic materials from the preparation method [23].

Figure 3.7 also shows the TGA curves for the used Ni/Al<sub>2</sub>O<sub>3</sub> and Ni/SiO<sub>2</sub> catalysts. Again a weight loss was seen up to 200 °C which was attributed to the loss of water. The Ni/Al<sub>2</sub>O<sub>3</sub> catalyst showed a significant weight loss of 21.9 % up to 700 °C. This can be due to the decomposition of by-products which are formed during the catalytic reaction and adsorb on the catalyst. The Ni/SiO<sub>2</sub> catalyst showed a weight loss of 9.9 % up to 700 °C and then a second weight loss of 8.3 % up to 900 °C, which is due to the deposition of carbonaceous material.



**Figure 3.7:** TGA-DSC curve of (a) fresh Ni/Al<sub>2</sub>O<sub>3</sub>, (b) used Ni/Al<sub>2</sub>O<sub>3</sub> at 320 °C, (c) fresh Ni/SiO<sub>2</sub> and (d) used Ni/SiO<sub>2</sub> at 320 °C.

The DSC plots for the fresh Ni/Al<sub>2</sub>O<sub>3</sub> and Ni/SiO<sub>2</sub> catalysts are also shown in Figure 3.7. For the Ni/Al<sub>2</sub>O<sub>3</sub> catalyst, an initial small endothermic peak below 200 °C is attributed to the loss of water, which is supported by the corresponding weight loss in the TGA curve. A second very small endothermic peak at about 300 °C can be due to the loss of more water or due to the loss of organic materials. An endothermic effect was observed for the Ni/SiO<sub>2</sub> catalyst corresponding to the dehydration of silica and water evaporation in the temperature range of 60–400 °C [24].

### 3.3.2 Catalytic testing

#### 3.3.2.1 Effect of pressure on glycerol hydrogenolysis

The extent of hydrogenolysis using a Ni/SiO<sub>2</sub> catalyst, as a function of pressure at constant temperature (230 °C), is shown in Table 3.3. The data showed that pressure does not have a significant influence on the glycerol conversion as similarly observed by Dasari et al. (5-20 Bar) [6], however, a change in the selectivities of the polyols was observed. The selectivity to the

lower alcohols remained essentially unchanged. The products included 1,2-propanediol, acetol, ethylene glycol, ethanol and methane.

**Table 3.3: Effect of pressure on glycerol conversion over a Ni/SiO<sub>2</sub> catalyst at 230 °C.**

Selectivities to different products (C basis)			
	40 Bar H <sub>2</sub>	60 Bar H <sub>2</sub>	75 Bar H <sub>2</sub>
Methane	1.2	3.6	4.8
Methanol	1.3	1.7	2.1
Ethanol	5.5	5.4	4.2
1-Propanol	1.2	0.6	1.1
Acetol	4.5	4.1	1.9
Ethylene glycol	7.3	13.5	15.9
1,2-PDO	77.9	70.6	67.8
Others*	1.1	0.5	2.2
Conversion	14.5	16.2	13.0

\* Others = CO<sub>2</sub>, 1,3-PDO, condensation products, unknowns.

The main product observed during glycerol hydrogenolysis over the Ni/SiO<sub>2</sub> catalyst at the conditions expressed in Table 3.3 was 1,2-PDO. The selectivity to 1,2-PDO decreased with increasing hydrogen pressure from 78 % to 68 %. At low pressures, a selectivity of ≈ 5 % acetol was obtained, which decreased to 2 % as the pressure increased. It is claimed that acetol is the intermediate in the formation of 1,2-PDO using acid catalysts via dehydration and subsequent hydrogenation [4]. The selectivity to 1,2-PDO showed a decrease with increasing pressure to the advantage of EG. The higher EG selectivity is likely due to the degradation of 1,2-PDO to EG [25] at high H<sub>2</sub> pressures. It is also likely, that the higher pressures favour direct hydrogenolysis of glycerol to EG [4]. The increase in methane selectivity also supports this pathway to EG.

### 3.3.2.2 Effect of temperature on glycerol hydrogenolysis

Table 3.4 shows the conversion of glycerol and selectivity to products over the Ni/Al<sub>2</sub>O<sub>3</sub> system as a function of temperature at constant pressure (60 Bar). From the results at 230 °C, 1,2-PDO, acetol and ethanol were observed as the major products.

**Table 3.4: Effect of temperature on glycerol hydrogenolysis over a Ni/Al<sub>2</sub>O<sub>3</sub> catalyst at 60 Bar H<sub>2</sub>.**

Selectivities to different products (C basis)					
	230 °C	250 °C	275 °C	300 °C	320 °C
Methane	2.4	1.7	1.4	1.5	1.8
CO	0.0	0.0	0.2	2.0	3.2
CO <sub>2</sub>	0.3	0.4	0.2	1.2	2.0
Methanol	0.7	0.8	0.8	0.9	2.4
Ethanol	9.0	8.4	10.6	11.4	16.8
Acrolein	0.0	0.4	2.1	8.1	11.9
1-Propanol	0.5	2.4	12.1	24.4	35.3
Acetol	3.2	11.7	22.1	20.4	12.2
Ethylene glycol	3.1	1.0	1.2	1.0	0.4
1,2-Propanediol	79.9	70.2	36.7	12.1	1.8
1,3-Propanediol	0.0	0.3	4.8	6.2	2.2
Others*	0.9	2.7	7.8	10.8	10.0
Conversion	15.9	25.6	39.3	83.7	96.1

\*Others = ethane, propane, acetaldehyde, propenol, 2-propanol, condensation products, unknowns.

The conversion was observed to increase as the temperature increased from 230 °C to 320 °C. At 230 °C, the highest selectivity towards 1,2-PDO of 80 % was achieved with a selectivity of 9 % to ethanol. As the temperature increased, the 1,2-PDO selectivity decreased from 80 % to 2 %, while an increase in ethanol selectivity was observed from 9 % to 17 %. At the same time,

the 1-propanol selectivity was observed to increase to 35 %, as were the selectivities to the dehydration products; acetol and acrolein. The heavier by-products also increased from < 1 % to 9 % as the temperature increased.

The extent of hydrogenolysis using a Ni/SiO<sub>2</sub> catalyst, as a function of temperature at constant pressure (60 Bar H<sub>2</sub>), is shown in Table 3.5. The major products observed at 230 °C included 1,2-PDO, 1-propanol and ethanol.

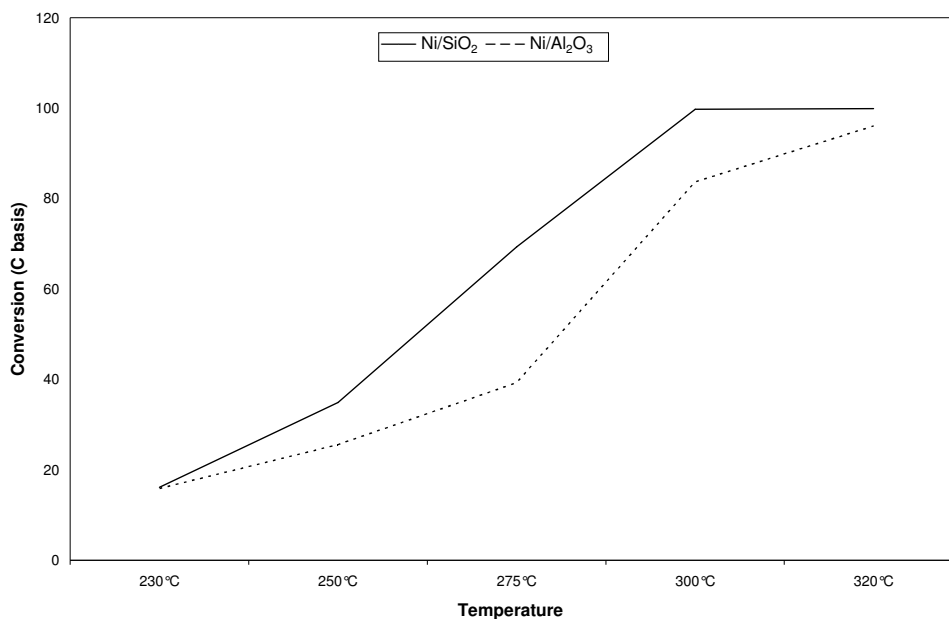
The data showed that temperature again had a significant effect on the glycerol conversion. As the temperature of the reaction increased from 230 °C to 320 °C there was a uniform increase in the glycerol conversion from 16 % to 99 %. The overall selectivity to 1,2-PDO decreased significantly as the temperature was increased to 320 °C, which was accompanied by an increase in the selectivity to ethanol and propanol. A total selectivity of 69 % to lower alcohols was obtained (methanol included). Higher temperatures also produced higher selectivity to gaseous products like methane, ethane, propane and carbon dioxide, as well as heavy constituents. This was also observed by Tomishige and co-workers [26] where at higher reaction temperatures the selectivity to degradation products like ethanol, methanol and methane over SiO<sub>2</sub> supported catalysts increased significantly.

**Table 3.5: Effect of temperature on glycerol hydrogenolysis over a Ni/SiO<sub>2</sub> catalyst at 60 Bar H<sub>2</sub>.**

	Selectivities to different products (C basis)				
	230 °C	250 °C	275 °C	300 °C	320 °C
Methane	3.6	2.8	2.1	2.6	3.0
CO	0.0	0.0	0.9	2.8	4.4
CO <sub>2</sub>	0.3	0.2	0.3	1.0	1.8
Methanol	1.7	1.3	1.5	2.7	5.5
Ethanol	5.4	6.6	12.4	16.9	20.2
Acrolein	0.0	0.0	1.1	2.6	3.9
1-Propanol	0.6	6.3	14.2	36.6	42.8
Acetol	4.1	3.8	12.4	7.7	4.2
Ethylene glycol	13.5	6.6	3.3	0.3	0.5
1,2-Propanediol	70.6	69.1	47.8	19.0	4.6
1,3-Propanediol	0.0	0.3	0.3	0.3	0.6
Others*	0.2	3.0	3.7	7.5	8.5
Conversion	16.2	34.9	69.3	99.8	99.9

\*Others = ethane, propane, acetaldehyde, propenol, 2-propanol, condensation products, unknowns.

A conversion “hysteresis” (Figure 3.8) was observed as temperature was increased from 230 °C to 320 °C, for the different catalysts, in favour of Ni/SiO<sub>2</sub>.



**Figure 3.8: Conversion hysteresis for Ni/SiO<sub>2</sub> and Ni/Al<sub>2</sub>O<sub>3</sub> systems.**

At 300 °C, a quantitative conversion was seen over the Ni/SiO<sub>2</sub>, while a conversion of 83.7 % was observed over the Ni/Al<sub>2</sub>O<sub>3</sub> catalyst.

The higher activity of the Ni/SiO<sub>2</sub> catalyst can be ascribed to a higher density of Ni active sites for reaction. There is also a weaker metal-support interaction and thus improved reducibility when compared to Ni/Al<sub>2</sub>O<sub>3</sub> as suggested by the TPR data.

A possible explanation for the different product selectivities observed for the two systems can be related to metal support interaction [27] and the difference in acidity of the support. The selectivity to 1,2-PDO (80 %) was higher over the alumina supported catalyst than over the silica supported catalyst (71 %) at similar conversion ( $\approx 16$  %). This is likely due to the higher concentration of strong acid sites on the Ni/Al<sub>2</sub>O<sub>3</sub> compared to Ni/SiO<sub>2</sub>, which favoured the dehydration of glycerol to acetol and subsequent hydrogenation of acetol to 1,2-PDO.

A higher EG selectivity (13 %) was observed over the Ni/SiO<sub>2</sub> catalyst than the Ni/Al<sub>2</sub>O<sub>3</sub> catalyst, likely due to the higher propensity for C-C cleavage over the Ni/SiO<sub>2</sub> catalyst. It has been claimed that nickel has a strong ability for breaking C-C bonds, which can lead to shorter

chain products. More available Ni sites for the Ni/SiO<sub>2</sub> catalyst may suggest a reason for the higher EG selectivity for this system.

The selectivity to propanol and ethanol increased with increasing temperature, with a subsequent decrease in EG and 1,2-PDO selectivity. A similar trend was observed by Balaraju et al. [25] over a Ru/C catalyst. They observed that as the glycerol conversion increased, the selectivity to 1,2-PDO decreased and subsequently the selectivity to lower alcohols like ethanol and methanol increased. However, it is generally proposed that the formation of EtOH occurs most likely via 1,3-PDO [4]. The low selectivity to 1,3-PDO observed may suggest that this is not necessarily the dominant pathway to EtOH. It is likely that due to the high concentration of 1,2-PDO present in the product, that this may be the likely intermediate to the propanols as well as EtOH.

As the conversion over the two systems increased, a higher propensity for dehydration was observed for the alumina supported catalyst [28], whilst a higher hydrogenation rate was observed for the Ni/SiO<sub>2</sub> catalyst. This is shown in Table 3.6, which show an increase in dehydration products, such as acrolein and acetol, for the Ni/Al<sub>2</sub>O<sub>3</sub> and alcohols, such as ethanol and propanol, for Ni/SiO<sub>2</sub>.

**Table 3.6: Difference in product selectivities as a function of conversion over Ni/SiO<sub>2</sub> and Ni/Al<sub>2</sub>O<sub>3</sub> systems.**

Product selectivities (C basis)			
Catalyst	Conversion	Alcohols*	Dehydration products**
Ni/Al <sub>2</sub> O <sub>3</sub>	15.9	10.2	3.2
	25.6	11.6	12.1
	39.3	23.5	24.2
	83.7	36.7	28.5
	96.1	54.5	24.1
Ni/SiO <sub>2</sub>	16.2	8.6	0.1
	34.9	14.3	1.1
	69.3	28.1	3.7
	99.8	56.3	7.2
	99.9	68.5	8.5

\* Alcohols = methanol, ethanol and propanol

\*\* Dehydration products = acetol, acrolein and propenol

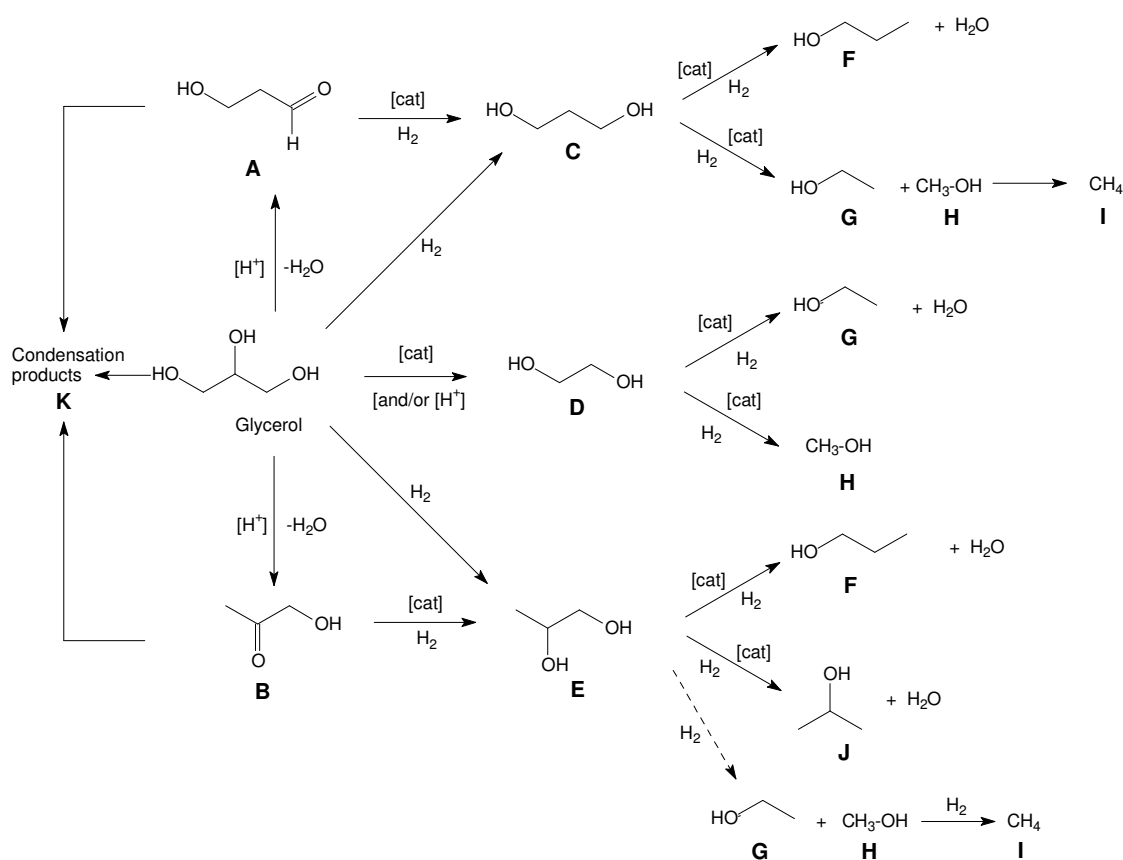
\*\*\* Information from Tables 3.4 and 3.5

The lighter compounds, CH<sub>4</sub>, CO and CO<sub>2</sub> showed a similar selectivity profile for both catalytic systems. The formation of CO and CO<sub>2</sub> is proposed to occur via decarbonylation reactions of aldehydic intermediates coupled to the water gas shift reaction. It is likely that CH<sub>4</sub> forms via direct hydrogenation of CO or MeOH.

However, condensation to give heavier products, which included ethers and aldol type compounds, was more pronounced over the alumina supported catalyst. This can be ascribed to an increased rate of condensation due to the higher acidity of the alumina support.

The possible transformation of glycerol can occur via several pathways as shown in Scheme 3.1 [4,29]. The first, resulting from acid catalysed dehydration, can form 3-hydroxypropionaldehyde (A) and acetol (B), which can be subsequently hydrogenated to 1,3-PDO and 1,2-PDO respectively. Glycerol can also be transformed directly via hydrogenolysis

[3] to form 1,3-PDO (C), EG (D) and 1,2-PDO (E). The subsequent diols can undergo further hydrogenolysis to form primary alcohols such as 1-propanol (F), ethanol (G) and methanol (H), as well as secondary alcohols like isopropanol (J) [4]. C1 products such as methane (I), CO and CO<sub>2</sub> can form via decomposition reactions or the water gas shift reaction [30]. Heavier products can form via condensation reactions of glycerol or the aldehydic intermediates. In addition to the pathways described in Scheme 3.1, we propose that ethanol is also likely to form via 1,2-PDO.



**Scheme 3.1: Reaction scheme showing glycerol transformation [3,4].**

### 3.4 Conclusion

The effect of increasing pressure was observed to have little influence on glycerol conversion. However the selectivity to 1,2-PDO decreased with increasing pressure while EG and CH<sub>4</sub> selectivity was observed to increase. The selectivity to lower alcohols remained essentially unchanged.

Temperature was observed to have a significant effect on the glycerol conversion with Ni/SiO<sub>2</sub> giving a higher conversion than Ni/Al<sub>2</sub>O<sub>3</sub> except at the lowest temperature studied. With respect to selectivity, 1,2-PDO was dominant at low temperature, whilst alcohols such as propanol, ethanol and methanol dominated the product profile at higher temperature. At 320 °C, a quantitative conversion of glycerol was observed with a total selectivity of 69 % to lower alcohols which included 1-propanol, ethanol and methanol. To the best of our knowledge, this is the highest selectivity reported to lower alcohols from glycerol using a continuous flow fixed bed reactor with an inexpensive catalytic system.

The pathway to the lower alcohols is proposed to occur via degradation of the intermediate polyols such as 1,2-PDO, 1,3-PDO and possibly EG.

Comparison of the product selectivity of the two catalysts revealed that the intrinsic properties of the support, such as the acidity of the support and the metal support interaction, had an influence. The higher activity of the Ni/SiO<sub>2</sub> catalyst is due to the weaker metal-support interaction and thus improved reducibility as suggested by TPR data. The Ni/SiO<sub>2</sub> catalyst has a higher propensity for C-C cleavage which is confirmed by the higher selectivity to EG. A higher selectivity to 1,2-PDO was observed over the Ni/Al<sub>2</sub>O<sub>3</sub> catalyst due to a higher concentration of strong acid sites which favoured the dehydration of glycerol to acetol and subsequent hydrogenation to 1,2-PDO.

### **Acknowledgements**

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## CHAPTER 4

# MECHANISTIC STUDY FOR THE SYNTHESIS OF LOWER ALCOHOLS FROM GLYCEROL USING Ni SUPPORTED CATALYSTS

### Abstract

In an effort to understand the hydrogenolysis pathway of glycerol to lower alcohols, the role of the intermediates (1,2-propanediol, 1,3-propanediol, ethylene glycol and ethanol) was investigated. Under the reaction conditions employed in this study, it was clear that the hydrogenolysis of C-C and C-O bonds of glycerol takes place to a lesser extent as compared to dehydrogenation and dehydration which are seen as the dominating initial steps. Ethanol was produced in high selectivities with 1,2-propanediol as feed and 1-propanol was the main product obtained when 1,3-propanediol was used as feed. Ethylene glycol gave methanol and methane as products, whereas ethanol gave methane and CO<sub>2</sub> as major products.

Key words: Glycerol, 1,2-Propanediol; 1,3-propanediol; acetol and ethanol.

### 4.1 Introduction

Interest in the catalytic conversion of renewable feedstocks to chemicals has been increasing over the past decade [1]. The manufacture of bio-diesel produces glycerol as a by-product and consequently glycerol has gained importance as a bio-refinery feedstock. With glycerol becoming a cheap, large-volume feedstock, the ability to use it as a source of organic carbon and as a starting material for chemical transformations is very appealing. The hydrogenolysis of glycerol is usually performed in the presence of hydrogen using various heterogeneous systems including Rh [2], Ru [3, 4, 5], Pt [6], Pd, PtRu [7], Cu systems [8, 9] and Raney Ni [10, 11]. Typical products obtained from the hydrogenolysis reaction are 1,2-propanediol (1,2-PDO), 1,3-propanediol (1,3-PDO), acetol, ethylene glycol (EG), 1-propanol (1-PO) and 2-propanol (2-PO). Subsequently, these catalytic systems can catalyse degradation reactions to yield ethanol, methanol and methane as secondary products [3].

In spite the wealth of information accumulated on glycerol hydrogenolysis, little attention has been given to mechanistic considerations. Tomishige and co-workers [3] proposed that the

hydrogenolysis of glycerol proceeded via the dehydration of glycerol to either acetol or 3-hydroxypropionaldehyde (3-HPA) on acid catalysts and then via a consecutive hydrogenation step over a metal functionality, propane diols were formed. 1-PO and 2-PO can mainly be formed via 1,3-PDO in glycerol hydrogenolysis over a Ru/C catalyst. Ethanol and methane were formed from the degradation reaction of 1,2-PDO and 1,3-PDO and in addition, ethanol can also be formed during the hydrogenolysis of EG. Methanol is formed via the degradation reaction of EG. On the other hand, Montassier et al. [12] proposed the dehydrogenation of glycerol to glyceraldehyde over a metal catalyst, which is followed by the dehydration to 2-hydroxyacrolein and subsequent hydrogenation to 1,2-propylene glycol.

Previous studies by Lahr and Shanks [13] supported the formation of glyceraldehyde as the first intermediate during the hydrogenolysis of glycerol. Subsequently, glyceraldehyde can react through four different pathways: (i) retro-aldol reaction to form glycolaldehyde (EG precursor), (ii) oxidation and subsequent decarboxylation to also form glycol aldehyde, (iii) dehydration to the precursor for 1,2-PDO (2-hydroxypropionaldehyde), or (iv) degradation to unwanted side products. Finally, the respective glycol precursors are hydrogenated by the metal function to the products.

Chaminand et al. [14] proposed that diols can form via several routes. The presence of an acid favoured the dehydration route via protonation of the hydroxyl groups of glycerol and then the loss of water to form a keto group as intermediate. This keto group can easily be reduced under the reaction conditions to form the corresponding diol. The direct conversion to diols is also possible via chelating glycerol in the presence of a metal (e.g. Cu, Pd, Rh supported on ZnO, C, Al<sub>2</sub>O<sub>3</sub>) followed by hydrogenolysis.

In Chapter 4, we reported the highly selective synthesis of lower alcohols, i.e. ethanol and 1-PO, via direct hydrogenolysis of glycerol over Ni-supported catalysts. Despite the numerous studies on glycerol hydrogenolysis reported to date [1-11], detailed studies giving insight into the reaction mechanism of lower alcohol formation have been limited and inconclusive. EG and 1,3-PDO are shown as possible intermediates to propanol, ethanol and methanol [3]. It was also suspected that 1,2-PDO leads to short chain alcohol formation [15] although little is reported that demonstrates this possibility. The objective of the current work is to continue the development of a more detailed mechanistic understanding of the formation of lower alcohols

from glycerol. In particular, the work presented will discuss the role of proposed intermediates, 1,2-PDO, 1,3-PDO, EG and ethanol, as well as the influence of the hydrogen partial pressure.

## **4.2 Experimental**

### **4.2.1 Samples**

The Ni/Al<sub>2</sub>O<sub>3</sub> and Ni/SiO<sub>2</sub> bulk systems were obtained as commercial samples in a partially reduced state from BASF. The Ni content was between 45–55 wt% for Ni/Al<sub>2</sub>O<sub>3</sub> and Ni/SiO<sub>2</sub> respectively. The glycerol, 1,2-PDO and 1,3-PDO, acetol and EG were purchased from Sigma Aldrich and used without further purification. The ethanol was obtained from Merck. The polyol feeds (1,2-PDO, 1,3-PDO and EG) as well as the EtOH were prepared as 60 wt% mixtures in water.

### **4.2.2 Catalytic characterisation**

NH<sub>3</sub>-temperature programmed desorption (TPD) experiments were carried out in a Micrometrics 2900 AutoChem II Chemisorption Analyzer. The catalysts (ca. 20 mg) were first reduced at 350 °C under 5 % H<sub>2</sub> in argon and thereafter treated with helium for one hour to remove excess hydrogen. A 4 % ammonia in helium gas mixture was then passed (20 mL/min) over the catalyst for 30 min. The excess ammonia was removed by flushing the system with helium (30 mL/min) for 30 min. Adsorbed ammonia was then stripped off by the same stream of helium (30 mL/min) and a temperature ramp of up to 900 °C (at 10 °C/min) and the desorption profiles were recorded using a TCD.

### **4.2.3 Catalytic reactions**

The catalytic reaction of diols (1,2-PDO, 1,3-PDO and EG) and EtOH was performed in a continuous flow fixed bed reactor in down flow mode (See Appendix, Figure B). The reactor tube was stainless steel with an internal diameter of 20 mm and a length of 250 mm. The catalyst volume was 5 mL (ca. 8.5 g) and mixed with equal amounts of carborandum. The catalyst had a particle size distribution of 300-500 μm, as specified by catalyst supplier. The molar ratio of hydrogen to diol solution was 2:1 with a GHSV of 1060 h<sup>-1</sup> and a LHSV of 3.0 h<sup>-1</sup>. The catalytic reactions were done at 230 °C and 60 Bar. Partial pressure reduction runs were performed by reducing the H<sub>2</sub> partial pressure but increasing the N<sub>2</sub> partial pressure to maintain the same GHSV and pressure. Prior to the reaction, the catalyst was reduced at 180 °C after which the reactor was commissioned to operating conditions. The liquid products and the

unreacted glycerol were collected in sequential catch pots cooled to 3 °C and -20 °C, respectively and the volume of the gaseous components was measured by a wet gas flow meter. The liquid product, as well as the gas product, were collected at regular intervals, and were analyzed on a GC (HP 6890) equipped with a FID using a DB-1701 column. Another gas sample was injected on a GC equipped with a TCD (Agilent 6850) using a Shincarbon packed column for CH<sub>4</sub> & CO<sub>x</sub> evaluation. Carbon balances were close to 100 % ± 5. The experimental data is estimated to be accurate to ± 1 %. The reactions were carried out twice to confirm the reproducibility of the results.

### 4.3 Results and Discussion

#### 4.3.1 Characterisation

##### 4.3.1.1 Acidity determination

The acidity of the alumina or silica plays an important role in the hydrogenolysis route. As shown in Table 4.1 there were three different acid sites for both catalysts. The Ni/Al<sub>2</sub>O<sub>3</sub> catalysts showed peaks at 182, 366 and 603 °C, whereas the Ni/SiO<sub>2</sub> catalyst showed TPD peaks at 237, 368 and 662 °C. The Al<sub>2</sub>O<sub>3</sub> supported catalyst showed desorption TPD peaks around 170 °C and 340 °C, which corresponded to weak and medium acid sites respectively [16]. An additional peak was observed near 600 °C indicating strong acid sites of the Al<sub>2</sub>O<sub>3</sub> support.

**Table 4.1: Acidity of the Ni supported catalysts.**

Catalyst	Weak acid sites (mmol NH <sub>3</sub> /g)	Medium acid sites (mmol NH <sub>3</sub> /g)	Strong acid sites (mmol NH <sub>3</sub> /g)
Fresh Ni/Al <sub>2</sub> O <sub>3</sub>	0.085	0.669	1.170
Fresh Ni/SiO <sub>2</sub>	0.940	0.852	0.381

Table 4.1 shows that Ni/SiO<sub>2</sub> had a higher distribution of weak acid sites, while Ni/Al<sub>2</sub>O<sub>3</sub> showed a higher content of strong acid sites.

## 4.3.2 Catalytic testing

### 4.3.2.1 The hydrogenolysis of glycerol

The results of the hydrogenolysis of glycerol using Ni/Al<sub>2</sub>O<sub>3</sub> and Ni/SiO<sub>2</sub> catalysts at different temperatures are given in Table 4.2 and Table 4.3. The glycerol conversion and selectivity during hydrogenolysis depended significantly on reaction temperature. As the temperature increased from 230 to 320 °C a uniform increase in conversion from 15.9 to 96.1 % and from 16.2 to 99.9 % is observed over Ni/Al<sub>2</sub>O<sub>3</sub> and Ni/SiO<sub>2</sub>, respectively. It was also observed that the selectivity to the lower alcohols, methanol, ethanol and 1-PO, increased significantly for both systems as the conversion increased, with the Ni/SiO<sub>2</sub> catalyst affording the highest total lower alcohol selectivity of 68.5 % versus 54.5 % for Ni/Al<sub>2</sub>O<sub>3</sub>.

**Table 4.2: Effect of temperature on glycerol hydrogenolysis over a Ni/Al<sub>2</sub>O<sub>3</sub> catalyst at 60 Bar H<sub>2</sub>.**

Selectivities to different products (C basis)					
	230 °C	250 °C	275 °C	300 °C	320 °C
Methane	2.4	1.7	1.4	1.5	1.8
CO	0.0	0.0	0.2	2.0	3.2
CO <sub>2</sub>	0.3	0.4	0.2	1.2	2.0
Methanol	0.7	0.8	0.8	0.9	2.4
Ethanol	9.0	8.4	10.6	11.4	16.8
Acrolein	0.0	0.4	2.1	8.1	11.9
1-Propanol	0.5	2.4	12.1	24.4	35.3
Acetol	3.2	11.7	22.1	20.4	12.2
Ethylene glycol	3.1	1.0	1.2	1.0	0.4
1,2-Propanediol	79.9	70.2	36.7	12.1	1.8
1,3-Propanediol	0.0	0.3	4.8	6.2	2.2
Others*	0.9	2.7	7.8	10.8	10.0
Conversion	15.9	25.6	39.3	83.7	96.1

\*Others = ethane, propane, acetaldehyde, propenol, 2-propanol, condensation products.

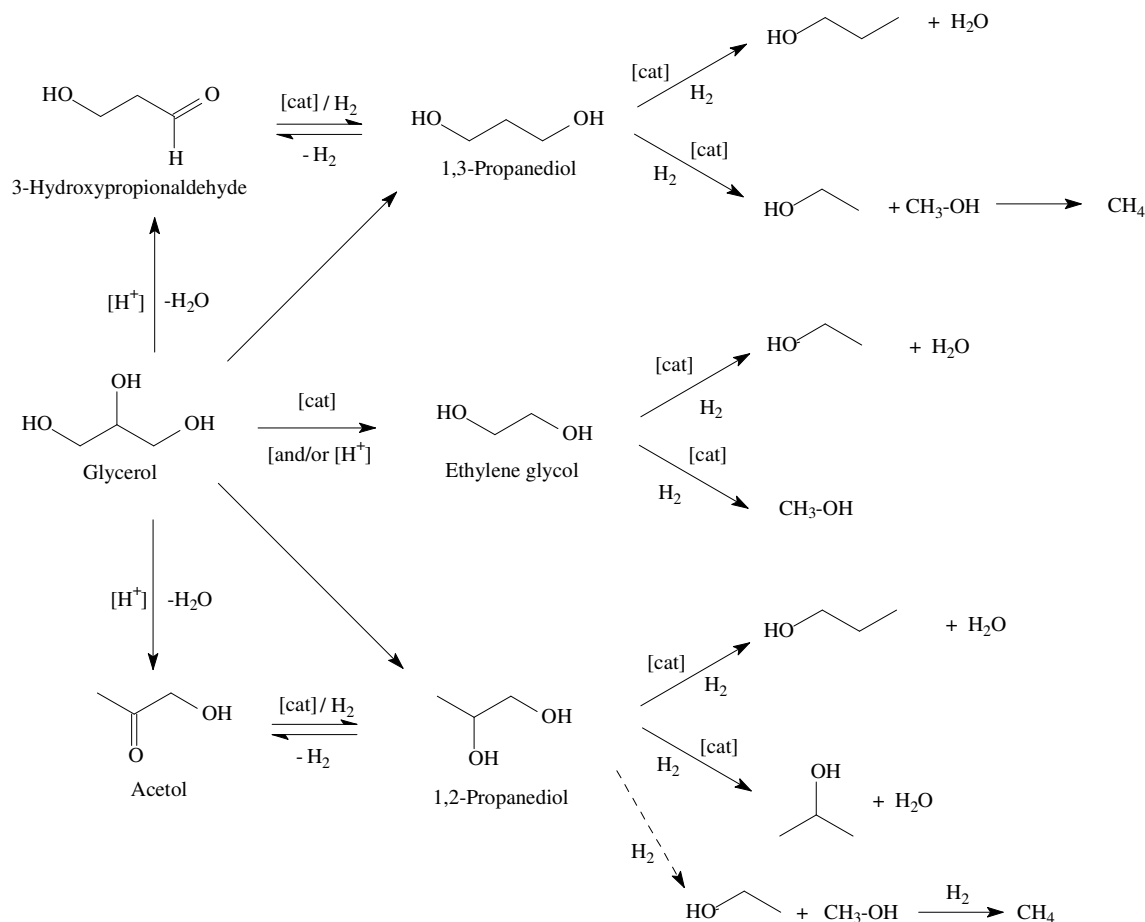
Apart from the lower alcohols, i.e. methanol, ethanol and 1-propanol, the major liquid phase products were 1,2-PDO, 1,3-PDO, acetol and EG. The main carbon containing gas phase products were CO, CO<sub>2</sub> and methane, while the formation of heavier condensation products were also evident.

**Table 4.3: Effect of temperature on glycerol hydrogenolysis over a Ni/SiO<sub>2</sub> catalyst at 60 Bar H<sub>2</sub>.**

Selectivities to different products (C basis)					
	230 °C	250 °C	275 °C	300 °C	320 °C
Methane	3.6	2.8	2.1	2.6	3.0
CO	0.0	0.0	0.9	2.8	4.4
CO <sub>2</sub>	0.3	0.2	0.3	1.0	1.8
Methanol	1.7	1.3	1.5	2.7	5.5
Ethanol	5.4	6.6	12.4	16.9	20.2
Acrolein	0.0	0.0	1.1	2.6	3.9
1-Propanol	0.6	6.3	14.2	36.6	42.8
Acetol	4.1	3.8	12.4	7.7	4.2
Ethylene glycol	13.5	6.6	3.3	0.3	0.5
1,2-Propanediol	70.6	69.1	47.8	19.0	4.6
1,3-Propanediol	0.0	0.3	0.3	0.3	0.6
Others*	0.2	3.0	3.7	7.5	8.5
Conversion	16.2	34.9	69.3	99.8	99.9

\*Others = ethane, propane, acetaldehyde, propenol, 2-propanol, condensation products.

Numerous mechanistic pathways have been proposed for the hydrogenolysis of glycerol to yield 1,2-PDO, 1,3-PDO, acetol and EG. Although 1,2-PDO, 1,3-PDO, acetol and EG are often observed as the major reaction products, the formation of C<sub>1</sub>-C<sub>3</sub> alcohols in low levels have previously been reported by Tomishige and co-workers [3] and Gandarias et al. [17] (Scheme 4.1). However, despite the understanding developed with regards to the conversion of glycerol into diol derivatives, little emphasis was given to pathways leading to lower alcohols.



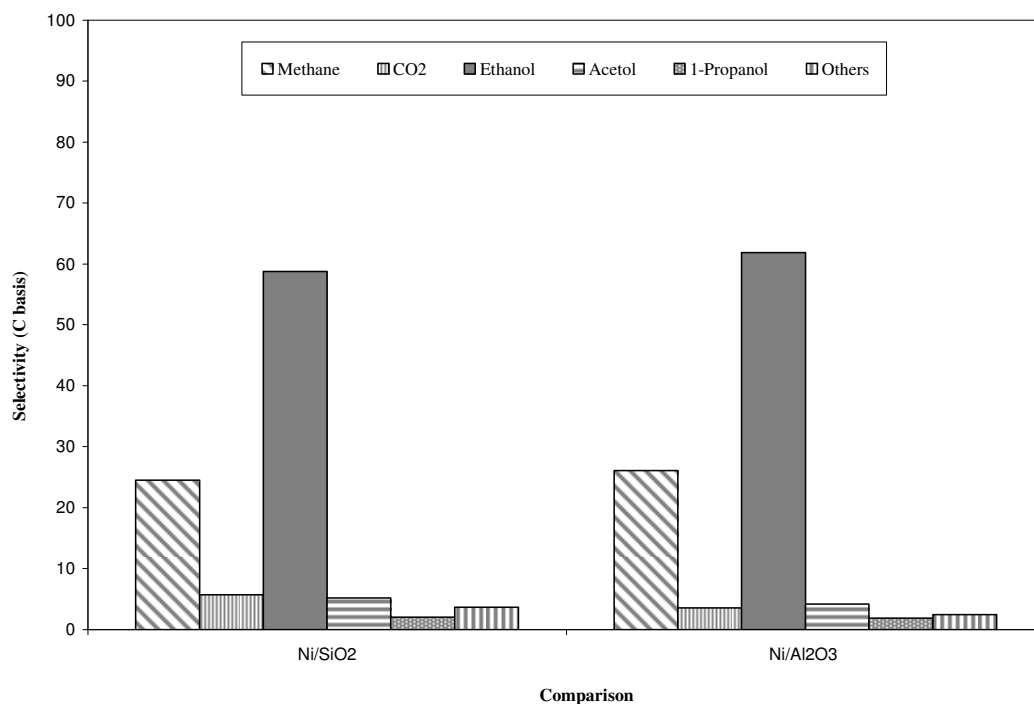
**Scheme 4.1: Reaction scheme showing glycerol to products.**

In an attempt to gain insight into the mechanistic pathways leading to lower alcohols from glycerol over Ni catalysts, the further conversion of the main liquid phase intermediate products, i.e. 1,2-PDO, 1,3-PDO and EG, was studied under reaction conditions favouring the formation of lower alcohols.

#### 4.3.2.2 The hydrogenolysis of 1,2-propanediol (1,2-PDO)

Figure 4.1 shows the comparative data at iso-conversions (23 %) between Ni/SiO<sub>2</sub> and Ni/Al<sub>2</sub>O<sub>3</sub> with 1,2-PDO as feed. From the data it is clear that the reaction of 1,2-PDO in water at 230 °C led significantly to ethanol and methane as products for both systems. The higher selectivity towards ethanol of 62 % was achieved over the Ni/Al<sub>2</sub>O<sub>3</sub> catalyst. Slightly higher methane selectivity was observed over the Ni/Al<sub>2</sub>O<sub>3</sub> catalyst whereas the Ni/SiO<sub>2</sub> gave slightly higher selectivities for CO<sub>2</sub>. Minor quantities of acetol and propanol were also observed. The C<sub>1</sub>-C<sub>3</sub>

oxygenated products were formed directly from 1,2-PDO, while methane and CO<sub>2</sub> are secondary products and must be formed via intermediate species.



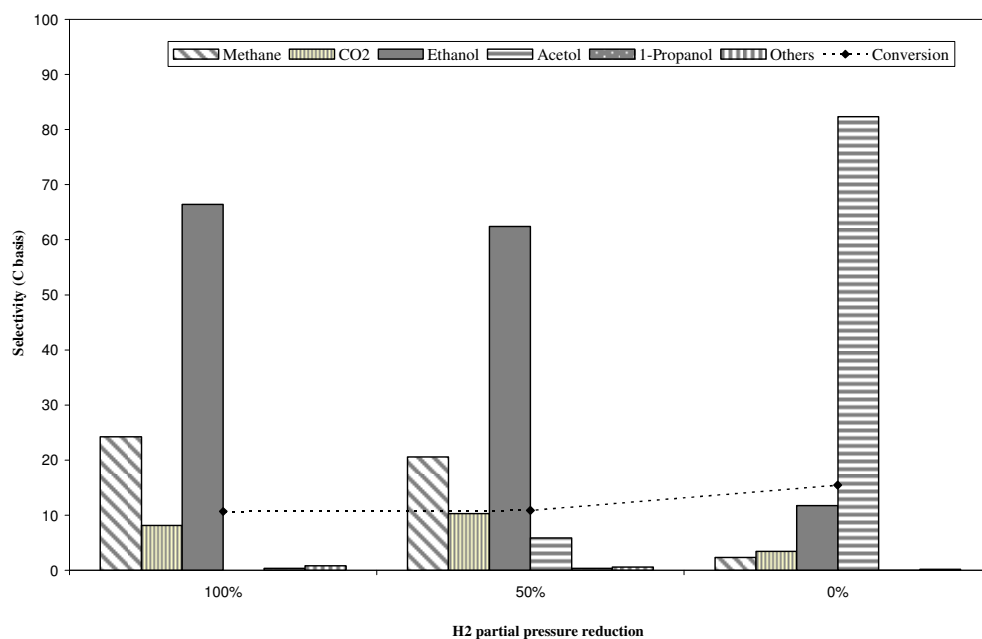
**Figure 4.1: Comparative data between the Ni/SiO<sub>2</sub> catalyst and the Ni/Al<sub>2</sub>O<sub>3</sub> catalyst at 23 % glycerol conversion.**

\*Others = acetaldehyde, ethane, propane, methanol, 1,3-PDO, condensation products and unknowns.

The reaction products suggest that the formation of ethanol and methane occurs via disproportionation of 1,2-PDO. Disproportionation usually occurs in the absence of hydrogen and therefore to understand this pathway better, a set of experiments was done by changing the H<sub>2</sub> partial pressure to see if ethanol is still formed. The GHSV was kept constant at 1060 h<sup>-1</sup> by increasing the N<sub>2</sub> partial pressure when decreasing the hydrogen partial pressure.

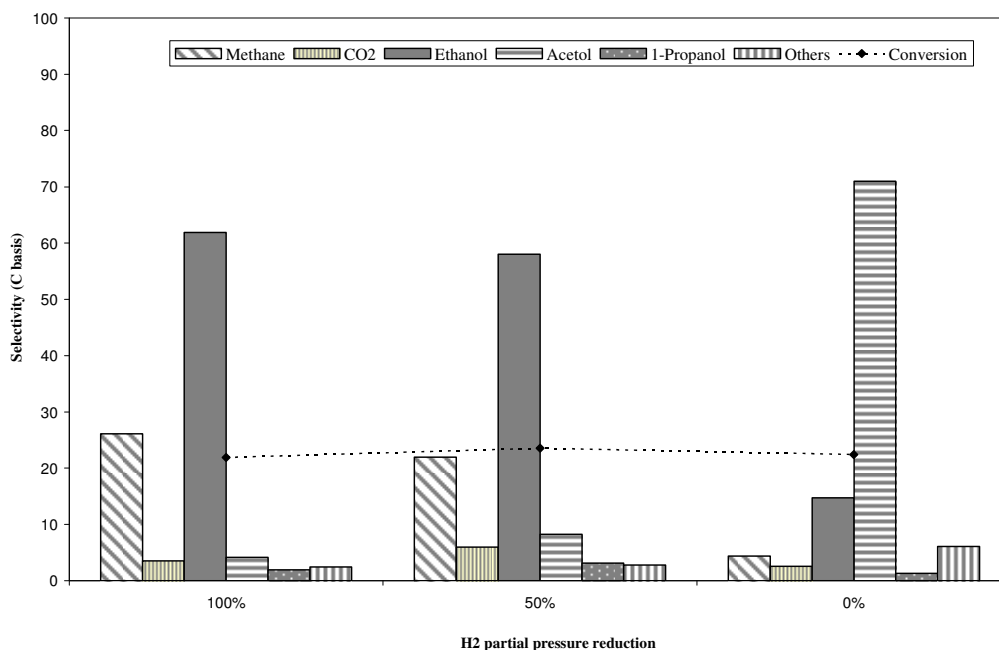
As observed from Figure 4.2, the conversion of 1,2-PDO over Ni/SiO<sub>2</sub> catalyst did not change significantly as the H<sub>2</sub> partial pressure was decreased. However, there was a notable change in the ethanol selectivity when the hydrogen partial pressure was reduced to less than 50 %. At 0 % H<sub>2</sub> partial pressure acetol formed almost exclusively as a result of the dehydrogenation of 1,2-PDO and the selectivity to ethanol was significantly reduced to 16 %. The hydrogen reduction run was repeated with the Ni/Al<sub>2</sub>O<sub>3</sub> catalyst and similar trends were observed (Figure

4.3). However, the decrease in ethanol selectivity was less profound and the formation of higher molecular weight condensation products more eminent. The fact that acetol is the major reaction product shows that the ability of both nickel catalysts to cleave C-C and C-O bonds in the absence of hydrogen is significantly reduced. This is of high importance, as it eliminates a disproportionation mechanism in the absence of hydrogen and indicates that another mechanism plays a role.



**Figure 4.2: Influence of hydrogen partial pressure reduction on the conversion of 1,2-PDO using Ni/SiO<sub>2</sub> (230 °C, 60 Bar H<sub>2</sub>).**

\*Others = acetaldehyde, ethane, propane, methanol, 1,3-PDO, condensation products and unknowns.



**Figure 4.3: Influence of hydrogen partial pressure reduction on the conversion of 1,2-PDO using Ni/Al<sub>2</sub>O<sub>3</sub> (230 °C, 60 Bar H<sub>2</sub>).**

\*Others = acetaldehyde, ethane, propane, methanol, 1,3-PDO, condensation products and unknowns.

In the absence of hydrogen it is believed that the reaction starts with the dehydrogenation of 1,2-PDO and subsequent isomerisation of 2-hydroxypropanal yields acetol as major product. The formation of ethanol as minor product over both nickel catalysts suggests that once 2-hydroxypropanal is formed; bimolecular surface reactions (Tischenko / Cannizzaro [18] type conversions) lead to surface bound 1,2-PDO and 2-hydroxypropanoic acid, which decarboxylates to ethanol and CO<sub>2</sub>.

The introduction of gaseous hydrogen, even at 50 % hydrogen partial pressure, gives high selectivity to ethanol. The methane selectivity decreased as the hydrogen partial pressure was reduced, whereas the CO<sub>2</sub> selectivity increased slightly, up to 50 % H<sub>2</sub> partial pressure reduction. Supported by the work of Chen et al. on the decomposition of ethylene glycol, the overall level of decomposition in the presence of hydrogen suggests that the reaction starts with the dehydrogenation and decarbonylation of 1,2-PDO to form acetaldehyde, CO and H<sub>2</sub>. Subsequent hydrogenation of acetaldehyde yielded ethanol as major product. The adsorption of CO on Ni at > 200 °C is dissociative, resulting in disproportionation to CO<sub>2</sub> and a Ni-C species. The surface carbon species formed from CO is readily hydrogenated to methane [19,20,21].

Although CO<sub>2</sub> formation can also be explained via rapid water gas shift [22], the high methane to CO<sub>2</sub> ratio points to CO dissociation as the faster overall reaction pathway.

#### 4.3.2.3 The hydrogenolysis of ethylene glycol

EG was also reported as one of the liquid products during the hydrogenolysis of glycerol, albeit in significantly lower yields than 1,2-PDO. In order to understand the catalytic chemistry of this simple diol, the conversion of EG was next studied over the Ni catalysts in the presence of hydrogen (Table 4.4). The results in Table 4.4 show that, using both Ni/Al<sub>2</sub>O<sub>3</sub> and Ni/SiO<sub>2</sub> as catalysts, the product selectivity is dominated by methanol and methane with very low selectivity to ethanol. As a result, the combination of dehydration to acetaldehyde with subsequent hydrogenation to ethanol as predominant pathway was discounted. Methanol and methane formation appear to result primarily from the dehydrogenation and decarbonylation of EG to yield formaldehyde and CO as intermediary products, followed by subsequent hydrogenation and disproportionation. However, the fact that a methanol to methane ratio of > 2 was recorded suggests that direct hydrogenolysis of the C-C bond to yield methanol directly should also be considered a valid pathway. Thus, at present, the detailed mechanism for the disproportionation of EG cannot be differentiated.

**Table 4.4: Hydrogenolysis of ethylene glycol under hydrogen using a Ni/Al<sub>2</sub>O<sub>3</sub> and Ni/SiO<sub>2</sub> catalyst (230 °C, 60 Bar).**

	Product selectivities (C basis)	
	Ni/Al <sub>2</sub> O <sub>3</sub>	Ni/SiO <sub>2</sub>
Methane	24.0	21.5
CO <sub>2</sub>	2.6	7.9
Methanol	58.4	60.2
Ethanol	5.6	2.0
1,2-PDO	3.9	8.0
Others	5.5	0.4
Conversion	9.3	11.7

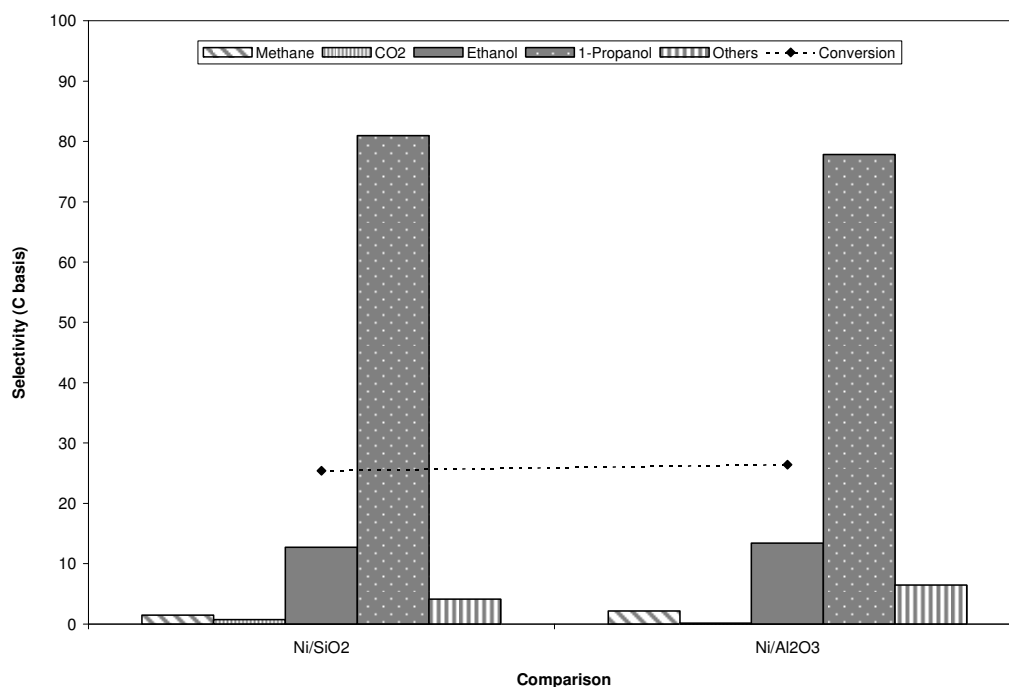
\* Others = ethane, condensation products and unknowns.

Interestingly, 1,2-PDO was observed during the hydrogenolysis of EG over both catalyst systems. The formation of 1,2-PDO from EG can be explained by an aldol reaction to form glyceraldehyde, followed by the loss of water and subsequent hydrogenation to yield 1,2-PDO.

#### **4.3.2.4 The hydrogenolysis of 1,3-propanediol**

During the hydrogenolysis of glycerol (Tables 4.2 and 4.3) 1-propanol was the alcohol produced in highest selectivity at higher temperatures ( $> 275\text{ }^{\circ}\text{C}$ ). Consequently, the low selectivity of 1-propanol observed when using 1,2-PDO as feed suggested that the formation of propanol is likely occurring via 1,3-PDO.

The results of the hydrogenolysis of 1,3-PDO hydrogenolysis over the  $\text{Ni}/\text{Al}_2\text{O}_3$  and  $\text{Ni}/\text{SiO}_2$  catalysts at  $230\text{ }^{\circ}\text{C}$  are presented in Figure 4.4. At similar conversions, both catalysts gave very high selectivities to 1-propanol with the co-production of some ethanol. Other products obtained from these reactions are methane and carbon dioxide, as well as heavier products, the result of cracking and condensation reactions, respectively. 1-Propanol forms via the dehydration reaction of 1,3-PDO with subsequent hydrogenation. The small concentrations of ethanol observed are the result of direct decarbonylation of 1,3-PDO. As discussed previously, CO undergoes disproportionation over Ni to form methane and  $\text{CO}_2$ .



**Figure 4.4: Comparative data between NiAl<sub>2</sub>O<sub>3</sub> and Ni/SiO<sub>2</sub> with 1,3-PDO feed (230 °C, 60 Bar).**

\*Others = ethane, propane, acrolein, methanol, propenol, condensation products and unknowns.

#### 4.3.2.5 Ethanol as feed

In order to explore to what extent the C<sub>1</sub>-C<sub>3</sub> alcohols can undergo consecutive C-C and C-O bond cleavage reactions ethanol was selected as model substrate and studied under the reactions conditions favouring lower alcohol formation from glycerol. Previous studies have demonstrated that disproportionation of ethanol can occur via three reaction pathways, dehydrogenation, decarbonylation, and total decomposition, producing CO, H<sub>2</sub>, CH<sub>4</sub>, C and O [23].

Table 4.5 shows the hydrogenolysis of ethanol using a Ni/SiO<sub>2</sub> catalyst at 230 °C and 60 bar hydrogen pressure. As expected the major products were methane and CO<sub>2</sub>, with small amounts of methanol forming. This result clearly showed that high concentrations of ethanol will disproportionate rapidly under these conditions and provide evidence for another pathway to the formation of methane and CO<sub>2</sub>.

**Table 4.5: Hydrogenolysis of ethanol under hydrogen using a Ni/SiO<sub>2</sub> catalyst (230 °C, 60 Bar).**

Products	Product selectivities (C basis)
Methane	59.4
CO <sub>2</sub>	32.1
Methanol	6.9
Others	1.6
Conversion	28.7

\* Others = acetaldehyde, ethane, condensation products and unknowns.

Although hydrogen partial pressure reduction runs were not performed on ethanol for this study, it was assumed that acetaldehyde would be formed. Rass-Hansen et al. [24] proposed that the steam reforming of ethanol proceeded through two different routes; either by dehydrogenation to acetaldehyde or by dehydration forming ethylene. These intermediate products can then be steam reformed to a mixture of methane, carbon dioxide, carbon monoxide, hydrogen and water.

### 4.3.3 Proposed mechanism

We propose the following detailed mechanism to explain the formation of the lower alcohols, such as 1-propanol, ethanol and methanol (Scheme 4.2). The three primary intermediate products that are formed from glycerol are glyceraldehyde, 3-hydroxypropionaldehyde (3-HPA) and acetol. Glyceraldehyde is formed via dehydrogenation whereas 3-HPA and acetol are formed via the dehydration of the hydroxyl group at the secondary and primary carbon atom.

Glycerol can be dehydrogenated to glyceraldehyde over a metal catalyst. The formation of EG can then occur via direct decarbonylation of glyceraldehyde in the presence of hydrogen yielding CO as by-product. The rate of this reaction appeared to be so fast that glyceraldehyde was not observed in the liquid phase. Alternatively, glyceraldehyde can also undergo retro-aldol condensation to yield glycolaldehyde and formaldehyde, which subsequently gets hydrogenated to yield EG and methanol respectively. This reaction is in equilibrium and can be reversed by the aldol condensation of glycolaldehyde and formaldehyde. The CH<sub>4</sub> and CO<sub>2</sub> observed as

secondary reactions, results from direct CO hydrogenation and the water-gas-shift (WGS) reaction, respectively.

The formation of 1,3-PDO can occur via two routes. Glycerol is dehydrated to form 3-HPA on acid sites, which is then hydrogenated to 1,3-PDO over a metal. 1-Propanol is then formed via dehydration reaction of 1,3-PDO with subsequent hydrogenation. On the other hand, glyceraldehyde can be directly dehydrated and then subsequently hydrogenated to yield 1,3-PDO. Since 3-HPA is more reactive compared to acetol [3,18], it was not observed as an intermediate in the liquid phase. Potentially, 3-HPA can also undergo decarbonylation to give CO and ethanol. Small amounts of ethane were also detected during the hydrogenolysis of 1,3-PDO. 1-Propanol can be dehydrogenated to propanal which is then disproportionated to CO and ethane. The CO is converted to CO<sub>2</sub> via the WGS reaction or hydrogenated to CH<sub>4</sub>. Wawrzetz et al. [18] showed that the conversion of 1-propanol leads to the formation of propanal as primary product over Pt supported on alumina. Ethane and CO<sub>2</sub>, as well as propanoic acid, were formed as secondary products. They excluded direct hydrogenolysis as a pathway to form ethane, but rather suggested that once the propanal is formed, bimolecular surface reactions (Tishchenko / Cannizzaro) lead to surface bound propanol which decarboxylates to ethane and CO<sub>2</sub>. Both pathways are conceivable under the reaction conditions because the Tishchenko reaction is catalysed by acidic sites, whereas the Cannizzaro reaction needs more basic sites.

Acetol, formed by the dehydration of glycerol, was observed in the liquid phase and with rather high selectivities at higher temperatures. Acetol is hydrogenated to give 1,2-PDO, which then dehydrogenates to 2-hydroxypropanal (2-HPA). Subsequently, 2-HPA is decarbonylated to ethanol and CO (yields CO<sub>2</sub> via WGS). Ethanol can be further dehydrogenated to give acetaldehyde and under these conditions the acetaldehyde will disproportionate rapidly to give ultimately CO and methane.

From the mechanism proposed, we conclude that the main route for the formation of 1-propanol is via the hydrogenation of 3-HPA. The formation of ethanol takes place via acetol, whereas methanol is formed via glycolaldehyde.



1-Propanol formed via the dehydration of glycerol to yield 3-HPA and then subsequent hydrogenation gave 1,3-PDO. 1,3-PDO is then dehydrated to yield 1-propanol. Methanol is formed via the dehydrogenation of glycerol to yield glyceraldehyde and via retro-aldol condensation glycolaldehyde and formaldehyde are obtained, which subsequently hydrogenated to yield methanol.

From the hydrogenolysis of EG, methanol and methane were observed as major products, whereas the hydrogenolysis of ethanol gave methane and CO<sub>2</sub> as major products.

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## CHAPTER 5

### SUMMARY AND CONCLUSION

With the expansion of the biodiesel industry globally, the world is experiencing a large oversupply of glycerol. The increased biodiesel production results in the accumulation of glycerol, which leads to a price decline. With glycerol becoming a cheap, large-volume feedstock, using it as a source of organic carbon and as a starting material for chemical transformations is very appealing. Therefore, the need has arisen to find new applications for this glycerol by-product from the production of biodiesel.

Much work has been done towards the hydrogenolysis of glycerol to 1,2-PDO and 1,3-PDO. However, routes to lower alcohols, such as 1-propanol and ethanol have been less discussed. It is known that glycerol can be hydrogenolysed using various heterogeneous systems including Rh, Ru, Pt, PtRu, copper systems and Raney Ni in batch systems. From an industry point of view, the production of lower alcohols, such as propanol and ethanol, is very interesting.

In spite of several research efforts reported in literature, a major drawback has been the use of diluted glycerol solutions for this reaction. These solutions are further diluted by the water formation of the reaction which consequently reduces the average space-time yield of the reaction. This will result in an increase in energy consumption of the process. In this study we have successfully demonstrated the use of highly concentrated glycerol solutions (60 wt %) for the hydrogenolysis reaction.

Different ruthenium, palladium and platinum catalysts were employed to study the effect of the support on the catalytic performance in batch mode. These catalysts were also evaluated for their production of lower alcohols, especially 1-propanol. The highest conversion of glycerol (43.3 mol%) and the selectivity of 1,2-PDO (66.7 mol%) were obtained over the Ru/C catalyst. Despite the low glycerol conversion (1.3 mol%), Pd/C gave a promising 1-PO selectivity (> 85 mol%).

The novelty of the work also includes the solid acids tested, especially the use of chlorinated Amberlyst resin, for the production of 1-PO, a high value commodity chemical. The use of the in-house prepared chlorinated resin, in combination of Ru/C, for the glycerol

hydrogenolysis reaction was also reported here for the first time. Promising results were obtained with Resin A, with 37 mol% selectivity to 1-PO and a 29 mol% glycerol conversion. Among the other solid acids tested in combination with Ru/C, Amberlyst DT gave the most promising results from a 1-PO point of view, achieving a 34.9 mol% glycerol conversion with a selectivity of 30 mol% to 1,2-propanediol and 38 mol% selectivity to 1-propanol.

The use of supported Ni systems, an inexpensive catalytic system, towards the chemical transformation of glycerol, especially towards the formation of lower alcohols, has appeared less frequently in the literature. The activity of Ni supported catalysts on silica and alumina was studied for the transformation of glycerol (also a 60 wt% solution) to lower alcohols, primarily 1-propanol and ethanol in a fixed bed continuous flow reactor. The use of fixed bed reactor instead of a batch reactor, allowed for the results to be more comparable to industry scale.

Pressure had a small effect on glycerol conversion, whereas temperature had a significant effect on conversion and selectivity. Ni/SiO<sub>2</sub> gave higher conversion than Ni/Al<sub>2</sub>O<sub>3</sub> except at the lowest temperature studied. With respect to selectivity, 1,2-PDO was dominant at low temperature, whilst alcohols such as propanol, ethanol and methanol dominated the product profile at higher temperature. At 320 °C, a quantitative conversion of glycerol was observed with a total selectivity of 69 % to lower alcohols, which included 1-propanol, ethanol and methanol. Comparison of the product selectivity of the two catalysts revealed that the intrinsic properties of the support, such as the acidity of the support and the metal support interaction, had an influence.

The higher activity of Ni/SiO<sub>2</sub> can be ascribed to its smaller crystallite size ascertained from XRD analysis. The Ni/SiO<sub>2</sub> catalyst also showed improved reducibility compared to Ni/Al<sub>2</sub>O<sub>3</sub>. The used Ni/SiO<sub>2</sub> catalyst showed sintering of the Ni which was confirmed by a loss of surface area and average crystallite size. The route to lower alcohols from glycerol is proposed to occur via 1,2-propanediol.

Despite the numerous studies on glycerol hydrogenolysis reported to date, detailed studies giving insight into the reaction mechanism of lower alcohol formation have been limited and inconclusive. EG and 1,3-PDO are shown as possible intermediates to propanol, ethanol and methanol. It was also suspected that 1,2-PDO leads to short chain alcohol formation although little is reported that demonstrates this possibility. The objective was to continue the

development of a more detailed mechanistic understanding of the formation of lower alcohols from glycerol. In an endeavour to understand the process better, the role of proposed intermediates, 1,2-PDO, 1,3-PDO, EG and ethanol was investigated, as well as the influence of the hydrogen partial pressure.

From the proposed mechanism, ethanol was the main product forming from 1,2-PDO and it is proposed that 1,2-PDO is the intermediate in the formation of ethanol from glycerol. In the absence of hydrogen, acetol was the main product forming and this suggested a slow route via hydrogen assisted disproportionation. 1-Propanol formed via the dehydration of glycerol to yield 3-HPA and then subsequent hydrogenation gave 1,3-PDO. 1,3-PDO is then dehydrated to yield 1-propanol. Methanol is formed via the dehydrogenation of glycerol to yield glyceraldehyde and via retro-aldol condensation glycolaldehyde and formaldehyde are obtained, which subsequently hydrogenated to yield methanol.

Additional work that might be considered could include finding a suitable temperature where the Ni catalysts are stable for longer periods of time to overcome a potential decrease in conversion with sintering. The addition of a promoter, such as Re, could also be investigated or even the possibility of bimetallic catalytic systems.