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The selective continuous flow synthesis of lower alcohols from polyols – a mechanistic interpretation of the results†

Esti van Ryneveld,[a] Abdul S. Mahomed,[a] Pieter S. van Heerden,[b] Mike J. Green,[c] Cedric Holzapfel[d] and Holger B. Friedrich*[a]

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In an endeavour to understand the hydrogenolysis pathway of glycerol to lower alcohols over Ni on Al_2O_3 and SiO_2 catalysts, the role of the intermediates (1,2-propanediol (1,2-PDO), 1,3-propanediol (1,3-PDO), ethylene glycol (EG) and ethanol) was investigated. Under the reaction conditions employed in this study, it was clear that the hydrogenolysis of the 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 (~67%) with 1,2-propanediol as feed and 1-propanol (1-PO, ~80%) 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_2 as major products.

Introduction

Interest in the catalytic conversion of renewable feedstocks to chemicals has been increasing over the past decade.[1] A number of biomass processes, such as the fermentation of glucose, the hydrogenolysis of sorbitol and the manufacture of biodiesel produce glycerol and consequently glycerol, has gained considerable 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,[3–5] Pt,[6] Pd, PtRu,[7] Cu systems,[8,9] Re[10] and RANEY® Ni.[11,12] 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). Importantly, 1,2-PDO and EG can also be produced from cellulosic biomass.[13–15] Subsequently, these catalytic systems can catalyse degradation reactions to yield ethanol, methanol and methane as secondary products.[3]

Despite the wealth of information accumulated on glycerol hydrogenolysis, little attention was given to mechanistic considerations. Tomishige and co-workers[3] proposed that 1-PO and 2-PO can mainly be formed *via* 1,3-PDO and 1,2-PDO, respectively, in glycerol hydrogenolysis over a Ru/C catalyst. Ethanol and methane are formed from the degradation reaction of 1,2-PDO and 1,3-PDO; 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.*[16] proposed the dehydrogenation of glycerol to glyceraldehyde over a metal catalyst, which is followed by dehydration to 2-hydroxyacrolein and subsequent hydrogenation to 1,2-propylene glycol.

Previous studies by Lahr and Shanks[17] and Auneau *et al.*[18] 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 glycolaldehyde, (iii) dehydration to the precursor to 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.*[19] proposed that diols can form *via* several routes. The presence of an acid favours the dehydration route *via* protonation of the hydroxyl groups of glycerol and then the loss of water to form a ketone compound as the intermediate. This ketone can easily be reduced under the reaction conditions to form the corresponding diol. The direct conversion to diols is also possible *via* chelating

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[a] *University of KwaZulu-Natal, School of Chemistry & Physics, Private Bag X54001, Durban, 4000, South Africa. E-mail: friedric@ukzn.ac.za; Fax: +27 31 260 3091; Tel: +27 31 260 3107*
[b] *Sasol Technology, R&D Division, 1 Klasie Havenga Street, Sasolburg, 1947, South Africa*
[c] *Newcastle University, School of Chemistry, Bedson Building, Newcastle upon Tyne, NE1 7RU, UK*
[d] *University of Johannesburg, Department of Chemistry, Auckland Park, 2006, Johannesburg, South Africa*

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glycerol in the presence of a metal (*e.g.* Cu, Pd, or Rh supported on ZnO, C, or Al_2O_3) followed by hydrogenolysis.

Recently, we reported the highly selective synthesis of lower alcohols, *i.e.* ethanol and 1-PO, *via* direct hydrogenolysis of glycerol over supported Ni catalysts.[20] These two catalyst systems were chosen because they are cheap, non-toxic and readily available. The formation of C_1–C_3 alcohols in low levels has previously been reported by Tomishige and co-workers[3] and Gandarias *et al.*[21] Despite the numerous studies on glycerol hydrogenolysis reported to date,[1–12] detailed studies giving insight into the reaction mechanism of lower alcohol formation have been limited and inconclusive. EG and 1,3-PDO were shown as possible intermediates to propanol, ethanol and methanol.[3,10] It was also suspected that 1,2-PDO leads to short chain alcohol formation[22] and the formation of 1-PO from 1,2-PDO has been reported.[23,24]

The objective of the current work is to contribute towards gaining a more detailed qualitative mechanistic understanding of the formation of lower alcohols from glycerol over Ni on Al_2O_3 and SiO_2 catalysts. In particular, the work presented will discuss the role of proposed intermediates (1,2-PDO, 1,3-PDO, and EG) and ethanol, as well as the influence of the hydrogen partial pressure. As an important result of this study, we also show the highly selective conversion of 1,2-PDO and 1,3-PDO to ethanol and 1-propanol, respectively, thus offering the possibility of producing biodiesel and lower alcohols from the same crop.

Results and discussion

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

Fig. 1 shows the comparative data at iso-conversions (23%) between Ni/SiO_2 and Ni/Al_2O_3 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/SiO_2 catalyst. Slightly higher methane selectivity was observed over the Ni/Al_2O_3 catalyst whereas the Ni/SiO_2 gave slightly higher selectivities for CO_2. Minor quantities of acetol and propanol were also observed. The C_1–C_3 oxygenated products were formed directly from 1,2-PDO, while methane and CO_2 are secondary products and must be formed *via* intermediate species.

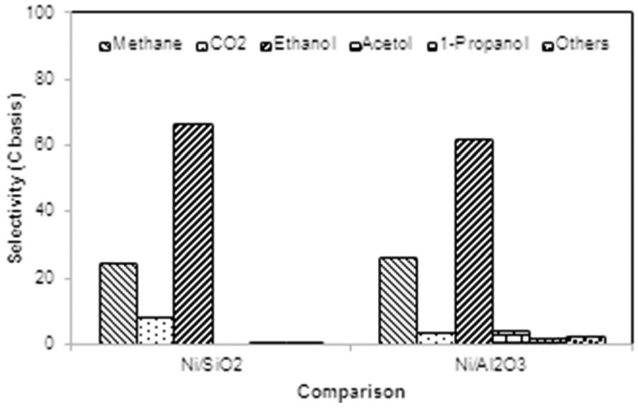


Fig. 1 Comparative data between the Ni/SiO_2 catalyst and the Ni/Al_2O_3 catalyst with 1,2-PDO as feed at 23% conversion (230 °C, 60 bar). Others = acetaldehyde, ethane, propane, methanol, 1,3-PDO, condensation products and unknowns.

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; therefore to understand this pathway better, a set of experiments was done by changing the H_2 partial pressure to see if ethanol is still formed. The GHSV was kept constant at 1060 h^{-1} by increasing the N_2 partial pressure when decreasing the hydrogen partial pressure.

As observed from Fig. 2, the conversion of 1,2-PDO over the Ni/SiO_2 catalyst did not change significantly as the H_2 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_2 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_2O_3 catalyst and similar trends were observed (Fig. 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 considerable importance, as it eliminates a disproportionation mechanism in the absence of hydrogen to a large degree.

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

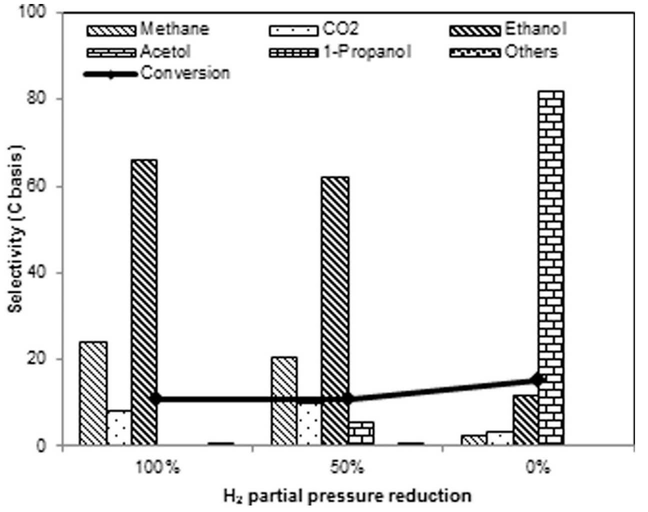


Fig. 2 Influence of the percentage reduction of hydrogen partial pressure on the conversion of 1,2-PDO and selectivity to products using Ni/SiO_2 (230 °C, 60 bar). Others = acetaldehyde, ethane, propane, methanol, 1,3-PDO, condensation products and unknowns.

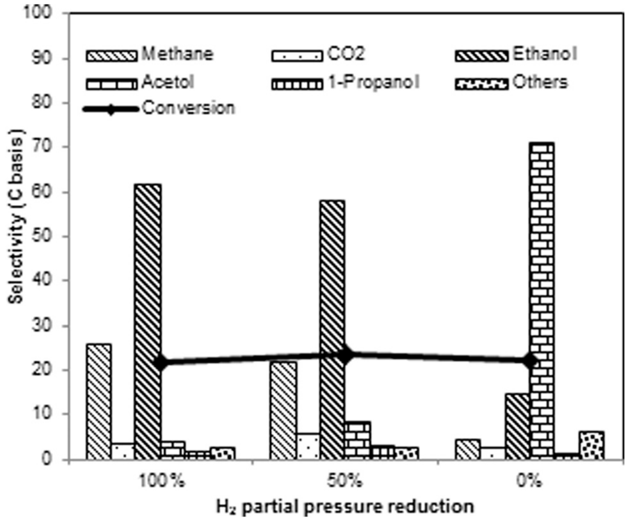


Fig. 3 Influence of the percentage reduction of hydrogen partial pressure on the conversion of 1,2-PDO and selectivity to products using Ni/Al_2O_3 (230 °C, 60 bar). Others = acetaldehyde, ethane, propane, methanol, 1,3-PDO, condensation products and unknowns.

as the major product. The formation of ethanol as a minor product over both nickel catalysts suggests that once 2-hydroxypropanal is formed, bimolecular surface reactions (Tishchenko/Cannizzaro[25] type conversions) lead to surface-bound 1,2-PDO and 2-hydroxypropanoic acid, which decarboxylates to ethanol and CO_2.

The introduction of gaseous hydrogen, even at 50% hydrogen partial pressure, gives high selectivity to ethanol. Indeed, the selectivity to ethanol was essentially quantitative, in terms of the carbon number, at 13% conversion. The methane selectivity decreased as the hydrogen partial pressure was reduced, whereas the CO_2 selectivity increased slightly, up to 50% H_2 partial pressure reduction. Supported by the work of Chen *et al.*[26] 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_2. Subsequent hydrogenation of acetaldehyde yielded ethanol as the major product. The adsorption of CO on Ni at >200 °C is dissociative, resulting in disproportionation to CO_2 and a Ni–C species. The surface carbon species formed from CO is readily hydrogenated to methane.[27–29] Although CO_2 formation can also be explained *via* rapid water gas shift,[30] the high methane to CO_2 ratio points to CO dissociation as the faster overall reaction pathway.

The hydrogenolysis of ethylene glycol (EG)

Table 1 Hydrogenolysis of ethylene glycol in the presence of hydrogen using Ni/Al_2O_3 and Ni/SiO_2 catalysts (230 °C, 60 bar)[a]

	Product selectivities (C basis)	
	Ni/Al_2O_3	Ni/SiO_2
Methane	24.0	21.5
CO_2	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

[a] Others = ethane, condensation products and unknowns.

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 1). The results in Table 1 show that, using both Ni/Al_2O_3 and Ni/SiO_2 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 the predominant pathway was discounted. Methanol and methane formation appears 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.

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.

The effect of hydrogen partial pressure using the Ni/SiO_2 catalyst was also studied. As the H_2 partial pressure was reduced from 100% to 0% the methanol and methane concentration decreased and an increase in acetol, 1,2-PDO and glycerol dimer[31] concentration was seen (Fig. 4).

The hydrogenolysis of 1,3-propanediol

During the hydrogenolysis of glycerol, 1-propanol was the alcohol produced in highest selectivity (25–40%) at higher temperatures (>275 °C) over these supported Ni catalysts.[20] 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 over the Ni/Al_2O_3 and Ni/SiO_2 catalysts at 230 °C are presented in Fig. 5. At similar conversions, both catalysts gave very high selectivities to 1-propanol (>80%) 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 EtOH observed

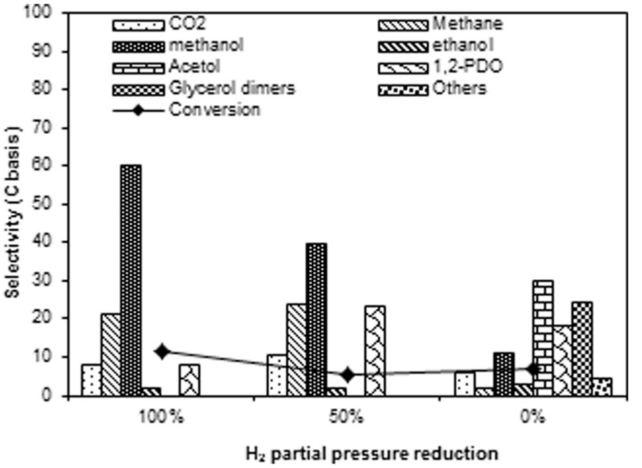


Fig. 4 Influence of the percentage reduction of hydrogen partial pressure on the conversion of EG and selectivity to products using Ni/SiO_2 (230 °C, 60 bar). Others = 2-propanol, 1-propanol, 1,3-PDO, glycerol, ethane, propane, and acetaldehyde.

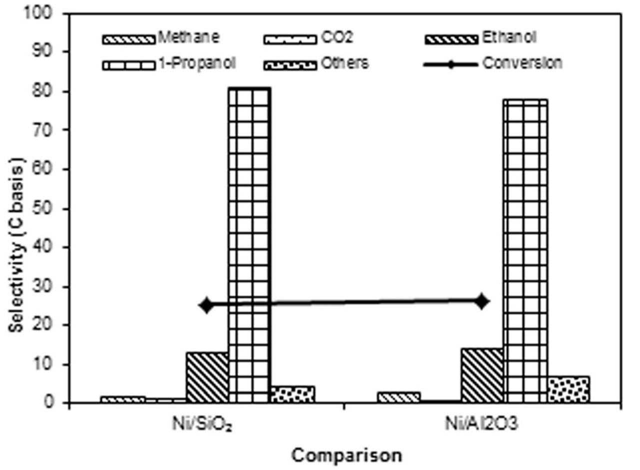


Fig. 5 Comparative data between Ni/Al_2O_3 and Ni/SiO_2 with 1,3-PDO as feed (230 °C, 60 bar). Others = ethane, propane, acrolein, methanol, propenol, condensation products and unknowns.

are the result of direct decarbonylation of 1,3-PDO. As discussed previously, CO undergoes disproportionation over Ni to form methane and CO_2.

The conversion of 1,3-PDO over the Ni/SiO_2 catalyst did not change significantly as the H_2 partial pressure was decreased from 100% to 50% (Fig. 6). The major product formed was 1-propanol with small amounts of ethanol also observed. However, there was a notable change in the 1-propanol selectivity when the hydrogen partial pressure was reduced to 0% and acrolein started to form. At 0% hydrogen partial pressure an increase in conversion was observed. The hydrogen reduction experiment was repeated with the Ni/Al_2O_3 catalyst and similar trends were observed (ESI, Fig. S1†).

Ethanol as feed

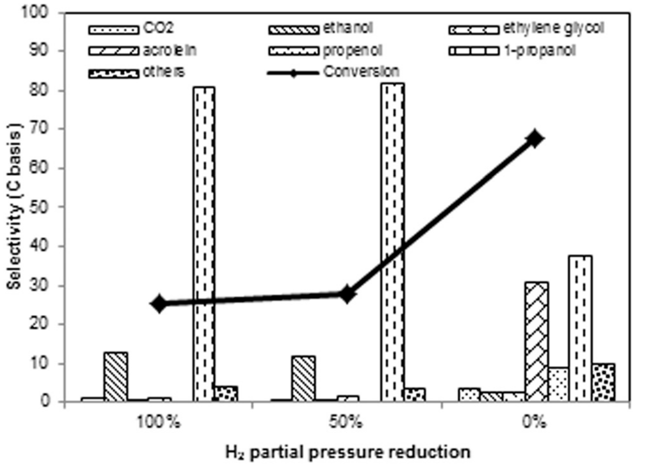


Fig. 6 Influence of the percentage reduction of hydrogen partial pressure on the conversion of 1,3-PDO and selectivity to products using Ni/SiO_2 (230 °C, 60 bar). Others = methanol, acetol, 1,2-PDO, glycerol, glycerol dimers, methane, ethane and propane.

In order to explore to what extent the C_1–C_3 alcohols can undergo consecutive C–C and C–O bond cleavage reactions ethanol was selected as the 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_2, CH_4, C and O.[32]

Table 2 shows the hydrogenolysis of ethanol using a Ni/SiO_2 catalyst at 230 °C and 60 bar hydrogen pressure. As expected the major products were methane and CO_2, with small amounts of methanol formed. This result clearly shows that high concentrations of ethanol will disproportionate rapidly under these conditions and provides evidence for another pathway for the formation of methane and CO_2. Since these results gave the expected product range it was deemed unnecessary to repeat this experiment using the Ni/Al_2O_3 catalyst.

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.*[33] 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.

Table 2 Hydrogenolysis of ethanol in the presence of hydrogen using Ni/SiO_2 catalysts (230 °C, 60 bar)[a]

Products	Product selectivities (C basis)
Methane	59.4
CO_2	32.1
Methanol	6.9
Others	1.6
Conversion	28.7

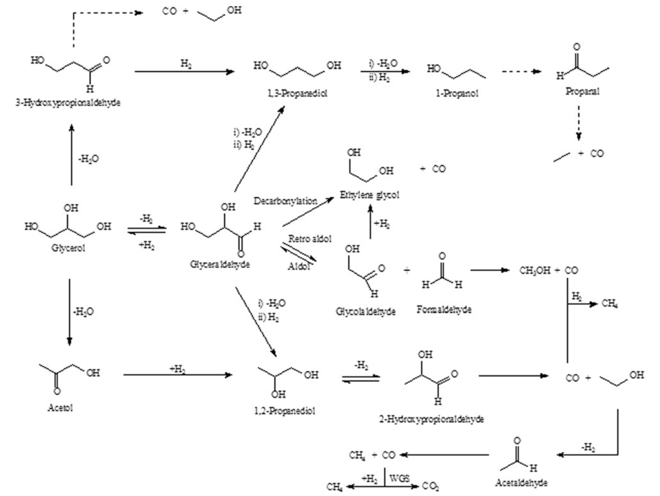
[a] Others = acetaldehyde, ethane, condensation products and unknowns.

Proposed mechanism

In combination with our previously reported results which showed the hydrogenolysis of glycerol over these supported nickel catalysts,[20] the following qualitative mechanism to explain the formation of the lower alcohols, such as 1-propanol, ethanol and methanol, is proposed (Scheme 1). The three primary intermediate products that are formed over the supported Ni catalysts 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 atoms, respectively.

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 a 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 are subsequently 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_4 and CO_2 observed from secondary reactions result from direct CO hydrogenation and the water–gas shift 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,[3,25] 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_2 *via* the water–gas shift (WGS) reaction or hydrogenated to CH_4. Wawrzetz *et al.*[25] showed that the conversion of 1-propanol leads to the formation of propanal as the primary product over Pt supported on alumina. Ethane and CO_2, 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_2. 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.



Scheme 1 Proposed mechanism for the formation of lower alcohols.

Acetol, formed by the dehydration of glycerol, was observed in the liquid phase 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_2 *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.

Conclusions

In an endeavour to obtain a better understanding of the hydrogenolysis of diols and triols, the role of the intermediates in the hydrogenolysis reaction was investigated in the presence and absence of hydrogen.

Under the reaction conditions employed in this study, it was clear that in the case of glycerol the hydrogenolysis of C–C and C–O bonds takes place to a lesser extent, particularly in the earlier stages of the reaction. Dehydrogenation and dehydration are seen as the dominating initial steps.

From our proposed mechanism, ethanol was the dominant product formed from 1,2-PDO and it is proposed that 1,2-PDO is the intermediate in the formation of ethanol from glycerol over the supported Ni catalysts. In the absence of hydrogen, acetol was the main product formed 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, which is subsequently hydrogenated to yield methanol, are obtained.

From the hydrogenolysis of EG, methanol and methane were observed as major products, whereas the hydrogenolysis of ethanol gave methane and CO_2 as major products.

Experimental section

Samples

The Ni/Al_2O_3 and Ni/SiO_2 bulk systems were obtained as pre-reduced commercial samples (Sued-Chemie). The Ni content was between 45–55 wt% for Ni/Al_2O_3 and Ni/SiO_2. 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.

Catalytic reactions

The catalytic reaction of diols (1,2-PDO, 1,3-PDO and EG) and EtOH was performed in a stainless steel (20 mm internal diameter × 250 mm length) continuous flow fixed bed reactor in down flow mode. The catalyst volume was 5 ml (*ca.* 8.5 g) and it was mixed with an equal amount of carborundum. The catalyst had a particle size distribution of 300–500 μm. The molar ratio of hydrogen to diol solution was 2 : 1 with a GHSV of 1060 h^{-1} and a LHSV of 3.0 h^{-1}. The catalytic reactions were done at 230 °C and 60 bar. Partial pressure reduction runs were performed by reducing the H_2 partial pressure but increasing the N_2 partial pressure to maintain the same GHSV and total pressure. Prior to the reaction, the catalyst was reduced at 180 °C for 12 h after which the reactor was commissioned under operating conditions. The liquid products and the unreacted feed were collected in sequential catch pots cooled to 3 °C and −20 °C, respectively, and the volume of the gaseous components was measured using a Ritter drum-type gas flow meter. The liquid and gaseous products were collected at regular intervals and were analyzed using a GC (HP 6890) equipped with a FID and a DB-1701 column. Further, the gas sample was injected on a GC equipped with a TCD (Agilent 6850) using a ShinCarbon packed column for CH_4 & CO_x evaluation. Data was obtained at steady state and carbon balances were 100% ± 5.

Acknowledgements

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