Caprolactam from renewable resources
Teddy, T

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Chapter 1

Introduction
1.1 Biomass as an alternative for fossil resources

The world is highly depending on the use of fossil resources for the production of energy and important products such as polymers, paints and adhesives. It is projected that 630 EJ of fossil resources will be consumed globally in 2030 \[1\]. However, fossil resources are finite and therefore not renewable. Another major point of concern of the fossil resources use is large amounts of emissions in the form of CO$_2$. It is estimated that CO$_2$ emissions have increased from 3 metric million tons of carbon in 1751 to 7985 metric million tons of carbon in 2005 \[2\]. This carbon accumulation in the atmosphere is generally accepted to have a major impact on the global climate.

As a consequence, the development of renewable resources is gaining more and more attention. Biomass is a promising alternative as it is the only renewable resource of fixed carbon, and as such may play an important role for the production of hydrocarbon liquid transportation fuel \[3-8\] and chemicals products \[9-10\].

Many governments actively stimulate the transition from fossil-based economies to bio-based economies. The U.S. Department of Energy predicts that 5% of the total energy demand is met by biopower in 2020 \[11\]. In fact, the share of biomass for energy generation in the U.S. already exceeded 4% in 2009 \[12\]. In the Netherlands, the transition from a fossil-based economy to a bio-based economy is also actively supported by the government. The “Schoon en Zuinig” (Clean and Efficient) policy program for energy and climate was introduced in 2007. One of the goals is a 20% share of renewable energy (including biomass) in the total energy consumption in 2020 \[13\]. In 2010, 4.3% of the primary energy production was from renewable resources of which three-quarters came from biomass \[14\]. In 2011, government and business signed 59 green deals, which consist of concrete projects in the areas of energy saving, renewable energy, sustainable mobility, and sustainable use of raw materials and water \[15\]. This number increased to more than 70 green deals by the end of 2011 \[15\].

1.2 Biomass: definitions, availability and composition

Biomass definitions are available from various sources \[16-17\]. One such definition states that biomass is “any organic matter that is available on a renewable basis, including dedicated energy crops and trees, agricultural food and feed crop residues, aquatic plants, wood and wood residues, animal wastes and other waste materials” \[16\]. UNESCO defined biomass as “the total of organic non-fossil material of biological origin” \[18\], while UNEP says biomass is “the total mass
or amount of living organisms in a particular area or volume" [19]. In this respect, it is clearer to provide examples of well-known biomass sources: woody biomass from tree and grasses, agricultural residues like straw, seed shells and aquatic biomass in the form of micro- and macro-algae.

Biomass is abundantly available and can be used for the production of bioenergy, biofuels and bio-based chemicals [20-28]. The annual global biomass production is estimated to be as large as 170 billion tons, of which 75% consists of carbohydrates [29]. Only 6 billion tons/annum (3.5%) are used by humans, mostly in the food sector (62%), as well as for energy, paper and construction materials (33%), and for the production of clothing and chemicals (5%), see Figure 1.1 for details.

![Figure 1.1 Biomass composition and use](image)

Lignocellulosic biomass typically consists of 40-60% cellulose, 20-40% hemicellulose and 10-25% lignin [30]. Cellulose is a linear polymer of repeating D-glucose units connected by β-glycosidic linkages. Cellulose can be depolymerised into D-glucose, a versatile monomeric sugar for the production of bioethanol and
biobased chemicals such as gluconic acid \(^{[31]}\), citric acid, polylactic acid, and sorbitol \(^{[32]}\).

Hemicellulose is a branched polymer consisting of five-carbon sugars (xylose and arabinose), six-carbon sugars (D-glucose, galactose and mannose), and uronic acids \(^{[30]}\). Hemicellulose has degree of polymerisation (DP) of 70-200 \(^{[33]}\), which is much lower than cellulose.

Lignin is a highly cross-linked macromolecule. It is composed of three phenyl propene monomers, methoxylated to various degrees: (1) \(p\)-coumaryl alcohol, (2) \(p\)-coniferyl alcohol, and (3) \(p\)-sinapyl alcohol.

1.3 Biorefinery concepts

A valuable concept for biomass valorization involves biorefining \(^{[34-36]}\). According to the US National Renewable Energy Laboratory (NREL), a biorefinery is “a facility that integrates biomass conversion processes and equipment to produce fuels, power, and chemicals from biomass” \(^{[37]}\). The basic idea of a biorefinery is to maximise the value of biomass by producing energy and products (chemicals and materials) via integrated processes including co- and by-product valorisation and in- and output optimisation. In a biorefinery, the biomass may be converted to fuels and energy by thermochemical pathways such as pyrolysis and gasification as well as by low temperature conversions such as hydrolysis, fermentation, and chemo-catalytic reactions. Various biorefinery models have been proposed, an example of a “two-platform concept” consisting of a sugar and a syngas platform is shown in Figure 1.2 \(^{[38]}\).

![Figure 1.2 The “two-platform concept” in biorefinery (taken from \(^{[38]}\))](image-url)
However, there are major challenges for the large scale introduction of biorefineries. As biorefineries preferably have to deal with a wide range of biomass inputs, the technology should be flexible in operation. In addition, to gain sufficient economies of scale, large biomass inputs are required, leading to logistic challenges. Currently a number of biorefineries for carbohydrate processing are in operation, examples are the Cargill biorefinery at Blair, Nebraska (US) and the Roquette bio-hub at Lestrem (France).

1.4 From biomass to 5-hydroxymethylfurfural (HMF)

The US Department of Energy (DOE) has issued reports with in depth analyses on important carbohydrate derived building blocks for use as starting material for the synthesis of biobased products and materials [39]. These building blocks are also called biobased platform chemicals. One of these platform chemicals with high application potential is 5-hydroxymethylfurfural (HMF, Scheme 1.1).

![Scheme 1.1](image)

HMF has high potential to serve as a starting material for a range of chemical commodities, such as 2,5-dimethylfuran (DMF) [7], furan-dimethanol (FDM) [40-47], THF-dimethanol (THFDM) [40,43,48-52], esterified products like formioxymethylfurfural (FMF) [53] and acetoxymethylfurfural (AMF) [53], etherified products like methoxymethylfurfural (MMF) [54] and ethoxymethylfurfural (EMF) [54], and 2,5-furandicarboxylic acid (FDCA) [55] (see Scheme 1.2 for details).

The first studies on HMF synthesis appeared in the last decade of the 19th century. In 1944, a landmark paper of Haworth and Jones [56] appeared including a mechanistic proposal. Recently, a number of reviews have been published covering the synthesis and derivatisation of HMF, examples are Newth [57], Feather and Harris [58], Gaset, et al. [59], Faury, et al. [60], Moye [61], Kuster [62], and Cottier and Descotes [63].
HMF is typically prepared by the dehydration of hexoses in water, though organic solvents have been used as well. A wealth of papers reports the synthesis of HMF from D-fructose \cite{48, 64-99}, though other hexoses have also been used. Examples are hexoses other than D-fructose such as D-glucose \cite{65, 75, 81, 83-84, 88, 90, 100-106}, galactose \cite{84, 100}, mannose \cite{84, 100}, and sorbose \cite{82, 100}; disaccharides such as sucrose \cite{53, 65, 82, 100, 107}, cellobiose \cite{65, 100}, palatinose \cite{82}, and turanose \cite{82}, trisaccharides such as raffinose \cite{62} and melezitose \cite{82} and polysaccharide such as starch \cite{65, 108} and inulin \cite{65, 69, 107}, as well as industrial waste streams containing hexoses \cite{79}.

Chemoselectivity is a major issue and byproduct formation occurs to a significant extent (Scheme 1.3). Antal, et al. \cite{67} performed D-fructose decomposition reaction in aqueous solutions and identified four product groups: i) isomerization products (e.g. D-glucose), ii) dehydration products (mainly HMF), iii) fragmentation products (e.g. dihydroxyacetone and glyceraldehyde), and iv) condensation products (humins). Van Dam \cite{109} and Cottier \cite{110} reported the formation of up to 37 products. Subsequent acid-catalysed reactions of HMF lead to levulinic acid, formic acid, and humins.
Haworth and Jones [56] were among the first to report a mechanism for HMF formation from D-fructose. They proposed that HMF is formed by a triple dehydration of D-fructose in the furanose form (path “a” in scheme 1.4). Later, Van Dam [109], Kuster [62], and Antal [67] proposed that hexose dehydration proceeds via two possible pathways: path (a), involving cyclic structures and path (b), involving acyclic intermediates (Scheme 1.4).

Antal [67] proved that HMF is formed through cyclic intermediates (path “a”). This conclusion was based on the following observations: i) fast and more selective formation of HMF from D-fructose and from the fructosyl moiety of sucrose, compared to D-glucose and aldohexoses, ii) fast conversion of 2,5-anhydro-D-mannose, which is the parent aldehyde to the enol intermediate 1, into HMF [57], and iii) the absence of deuterium in HMF when the reaction was performed from D-fructose in D2O. If 3-deoxyglycosulose 2 is present as an intermediate, a carbon-deuterium bond is likely to be formed due to the keto-enol tautomerism and therefore deuterium should be incorporated into HMF [58].

Kuster [62] established five factors that determine the rate of the HMF formation: i) the type of substrate; (ii) the type and the concentration of the catalyst; (iii) time and the temperature of the reaction; (iv) the substrate concentration, which is related to the rate of cross-polymerisation and humin formation; (v) the type of solvent and the stability of HMF at given reaction conditions. These factors will be discussed in more detail in the following sections.
1.4.1 Substrates and substrate concentrations

From a feedstock price perspective, HMF synthesis is preferably carried out with D-glucose instead of D-fructose \[^{[63]}\]. However, HMF synthesis from ketohexoses (such as D-fructose) is much faster and selective than from aldohexoses (such as D-glucose). D-Glucose forms a very stable ring structure in comparison with D-fructose (118 vs 102 kJ/mol activation barriers) \[^{[111]}\] which results in a low degree of enolisation. This reduces HMF yields as enolisation is the rate determining step in the HMF formation \[^{[67]}\]. D-fructose forms difructose dianhydride (Scheme 1.5) in an equilibrium reaction, in which the most reactive groups for cross-polymerisation are internally blocked \[^{[112-114]}\]. On the other hand, D-glucose forms oligosaccharides which still contain reactive reducing groups, leading to cross-polymerisation with intermediates and HMF itself \[^{[62]}\].
Introduction

Scheme 1.5 Difructose dianhydride

A detailed kinetic study on D-glucose \cite{115} and D-fructose \cite{116} decomposition has been performed using H\textsubscript{2}SO\textsubscript{4} as the catalyst. Using D-glucose as the substrate, the kinetic constant for HMF formation is 26 times lower than the subsequent reaction of HMF to levulinic acid, and as such HMF is only present in very low amounts in the reaction mixture \cite{115}. On the other hand, when using D-fructose, the kinetic constant for HMF formation is 3 times higher than the subsequent reaction of HMF conversion to levulinic acid, and as such the intermediate HMF concentration is much higher \cite{116}.

Process economics dictate that high substrate concentrations are preferred. For HMF synthesis from D-glucose/D-fructose, a higher substrate concentration leads to higher levels of cross-polymerisation and humin formation \cite{109, 117}, and as such the selectivity to HMF is lower for higher substrate concentrations. In non-aqueous systems, byproduct formation by oligo- and polymerization reactions is less pronounced. For example, a 70% HMF yield is obtained when using a 50 wt% D-fructose solution in DMSO or polyethyleneglycol \cite{118-120}.

1.4.2 Catalysts for HMF synthesis

Catalysts are of prime importance for HMF synthesis. In the early days, the use of relatively weak Bronsted acids, such as oxalic acid, was very popular \cite{56, 79, 121-123}. Nowadays, more than hundred inorganic and organic compounds have been reported as catalysts for the reaction. Cottier \cite{63} classified the catalysts in five groups (Table 1.1).

Organic acids, including oxalic acid, are still used for the synthesis of HMF. Hu, et al. \cite{124} performed the HMF synthesis from inulin using eutectic mixtures of ionic liquids and organic acids such as choline chloride (ChoCl)/oxalic acid and ChoCl/citric acid. Another example is the use of organic acids in high temperature liquid water \cite{125}. This system was used for D-fructose conversion to HMF using formic acid or acetic acid as the catalyst.

Inorganic acids are also well known as the catalyst for HMF synthesis, particularly sulphuric acid \cite{53, 67, 78-79, 103, 126-128}, hydrochloric acid \cite{65, 73-74, 89, 94}, and phosphoric acid \cite{100, 104}. The highest HMF yield reported using an inorganic acid [126-128].
catalyst was 85%, which was obtained from D-fructose at 170 °C using HCl as a catalyst in a biphasic system consisting of an aqueous phase (water + DMSO) and an organic phase (MIBK + 2-butanol)\[65].

Table 1.1 Catalysts for HMF synthesis

<table>
<thead>
<tr>
<th>Organic acids</th>
<th>Inorganic acids</th>
<th>Salts</th>
<th>Lewis acids</th>
<th>Others</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxalic acid</td>
<td>Phosphoric acid</td>
<td>(NH₄)₂SO₄/SO₃</td>
<td>ZnCl₂</td>
<td>Ion-exchange resins</td>
</tr>
<tr>
<td>Levulinic acid</td>
<td>Sulphuric acid</td>
<td>Pyridine/PO₄³⁻</td>
<td>AlCl₃</td>
<td>Zeolites</td>
</tr>
<tr>
<td>Maleic acid</td>
<td>Hydrochloric acid</td>
<td>Pyridine/HCl</td>
<td>BF₃</td>
<td></td>
</tr>
<tr>
<td>p-TsOH</td>
<td>Hydroiodic acid generated <em>in situ</em></td>
<td>Aluminum salts</td>
<td>Th and Zr ions</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Zirconium phosphate</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ions: Cr, Al, Ti, Ca, In</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>ZrOCl₂</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Vo(SO₄)₂</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>TiO₂</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

HMF synthesis using salts and Lewis acids has been studied in detail \[82-84, 90, 97, 106, 129-143\]. Seri and co-workers \[82\] employed lanthanum chloride and obtained HMF yields of 95% from D-fructose, 61% from sorbose, 93% from sucrose, 36% from palatinose, 25% from turanose, 65% from raffinose, and 24% from melezitose. 91% yield of HMF was obtained starting from D-glucose for a catalyst consisting of [C₄MIM]Cl and chromium chloride in combination with microwave irradiation \[142\]. The use of typical lignocellulosic biomass sources (corn stalk, rice straw, and pine wood) was also explored with this system \[143\] and HMF yields up to 52% could be obtained. Hu and co-workers \[138\] used SnCl₄ in combination with [EMIM]BF₄ and obtained HMF yields of 57% from cellbiose and 47% from starch.

The use of ion-exchange resins for HMF syntheses has also been explored \[76-77, 86, 107, 144-148\]. Morikawa and Nakamura \[146\] reported the use of Diaion® PK-216 and 90% yield of HMF was obtained from D-fructose. The same catalyst was used
by Chheda and Dumesic\cite{107} and 43% HMF yield was obtained from sucrose. The HMF synthesis from inulin using Amberlyst® 15 in combination with ionic liquids ([BMIM]Cl) has been recently reported and 82% yield of HMF was obtained \cite{148}.

### 1.4.3 Reaction conditions

Reaction conditions (e.g. temperature, reaction time in batch and residence time in continuous set-ups) have been assessed in detail. The optimum conditions for the highest HMF yields vary in a broad range and are a function of the substrate, solvent, catalyst, and modes of reactions. For continuous reactions, residence times as low as 0.8 s have been reported \cite{66} while times up to 48 h are also known for batch reactions \cite{94}. Temperatures up to 350 °C have been reported when applying supercritical water \cite{66, 101} but can also be as low as 80 °C \cite{68, 97}. In general, D-fructose is more reactive than D-glucose, leading to shorter reaction times for D-fructose \cite{65}. Kupiainen and co-workers \cite{149} reported a strong effect of temperature on D-glucose decomposition. In the range of 180-220 °C, the reaction time required to achieve 40% conversion significantly decreased from 1 h to 15 min by increasing the temperature by 20 °C. Kinetic studies on D-glucose/D-fructose decomposition to HMF have been reported (Table 1.2).

<table>
<thead>
<tr>
<th>F/G</th>
<th>[C₉]</th>
<th>T (°C)</th>
<th>Time (min)</th>
<th>Acid</th>
<th>Ea (kJ/mol)</th>
<th>Rate constant</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>F</td>
<td>0.25 M</td>
<td>175</td>
<td>2-300</td>
<td>HCOOH (pH = 1-6)</td>
<td>$0.005 + 5 \left[H^+\right] + 1.5 \times 10^8 \left[OH^-\right] + 0.28 \left[WA\right]$ min⁻¹</td>
<td> </td>
<td>150</td>
</tr>
<tr>
<td>F</td>
<td>0.2-1 M</td>
<td>170-220</td>
<td>H₃PO₄ (0.01-0.5 M)</td>
<td>92.1</td>
<td>$0.048 \left(1 + 35 K_w \left[H_3PO_4\right]\right)$</td>
<td> </td>
<td>151</td>
</tr>
<tr>
<td>F</td>
<td>0.5 wt%</td>
<td>210-270</td>
<td>0.5-300 s</td>
<td>HCl (0.0158 M)</td>
<td>$\text{Ea (}k_1\text{)} = 161; \text{Ea (}k_2\text{)} = 132; \text{Ea (}k_3\text{)} = 102$</td>
<td>$k_1 = 4.53 \times 10^{-3} \text{ s}^{-1}; k_2 = 5.12 \times 10^{-4} \text{ s}^{-1}; k_3 = 1.02 \times 10^{-1} \text{ s}^{-1}$</td>
<td>87</td>
</tr>
<tr>
<td>G</td>
<td>5 wt%</td>
<td>170-190</td>
<td>0.5-30</td>
<td>H$_2$SO$_4$ (0.4-1.6 wt%)</td>
<td>138</td>
<td>$0.151 \text{ min}^{-1} (200 \degree \text{C}), 2.32 \text{ min}^{-1} (240 \degree \text{C})$</td>
<td>[152]</td>
</tr>
<tr>
<td>---</td>
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<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>G</td>
<td>0.278-1.112 M</td>
<td>180-260</td>
<td>0.3-60</td>
<td>H$_2$SO$_4$ (0.12-3.8 wt%)</td>
<td>136</td>
<td>$0.171 \text{ min}^{-1} (200 \degree \text{C}), 2.55 \text{ min}^{-1} (240 \degree \text{C})$</td>
<td>[153]</td>
</tr>
<tr>
<td>G</td>
<td>0.4-6 wt%</td>
<td>180-224</td>
<td>0.5-7</td>
<td>H$_2$SO$_4$ (0.5-4 wt%)</td>
<td>128</td>
<td>$0.174 \text{ min}^{-1} (200 \degree \text{C}), 2.22 \text{ min}^{-1} (240 \degree \text{C})$</td>
<td>[154]</td>
</tr>
<tr>
<td>G</td>
<td>0.125 M</td>
<td>180-230</td>
<td>0-40</td>
<td>H$_2$SO$_4$ (pH 1.5-2.2)</td>
<td>139</td>
<td>$(2.132 \times 10^{13} + 2.148 \times 10^{15} \times 10^{-pH}) \exp (-Ea/RT)$</td>
<td>[155]</td>
</tr>
<tr>
<td>G</td>
<td>0.1-1 M</td>
<td>140-200</td>
<td>0-420</td>
<td>H$_2$SO$_4$ (0.05-1 M)</td>
<td>Ea ($k_1$) = 152; Ea ($k_2$) = 165</td>
<td>$k_1 = k_2 = 0.013 \exp[-(Ea/R)(1/T-0.0024)]$</td>
<td>[115]</td>
</tr>
<tr>
<td>G</td>
<td>56 or 112 mM</td>
<td>180-220</td>
<td>0-160</td>
<td>HCOOH (5-20 wt%)</td>
<td>Ea ($k_1$) = 153; Ea ($k_2$) = 110; Ea ($k_3$) = 117</td>
<td>$k = (k_1 + k_{ii}[H^+]) \exp [-Ea/R(1/T-0.002)]$</td>
<td>[149]</td>
</tr>
</tbody>
</table>

$^a$ [WA] = weak acid anions formed during reaction; $^b$ $K_w$ = concentration factor as defined in $^{[151]}$; $^c$ At $T = 180 \degree \text{C}$; $^d$ At $T = 210 \degree \text{C}$, $k_1$ = to HMF, $k_2$ = to 2-furaldehyde, $k_3$ = to humins; $^e$ At 1 wt% acid; $^f$ Reference $T = 140 \degree \text{C}$; $^g$ D-glucose to intermediate ($k_1$), intermediate to HMF ($k_2$) and humins ($k_3$); $^h$ Reference $T = 200 \degree \text{C}$, $k_1$ ($k_i = 0.018$, $k_{ii} = 2.6$), $k_2$ ($k_i = 0.109$, $k_{ii} = 8.6$), $k_3$ ($k_i = 0.058$, $k_{ii} = 2.9$)

### 1.4.4 Solvents

Cottier $^{[63]}$ divided solvents for HMF synthesis into five groups: (1) water with reaction temperature below 200 $\degree \text{C}$; (2) water with reaction temperature over 200 $\degree \text{C}$; (3) non-aqueous solvents; (4) mixed solvents; (5) no solvents. Based on
the recent progress of HMF synthesis, this classification can be expanded into six groups by including ionic liquids as the sixth group.

Water is a green and benign solvent and as such has been used in many studies either below 200 °C [84, 88, 94-95, 106] or above 200 °C [81, 87, 100, 104, 128]. An additional advantage of the use of water is a good solubility of the hexose substrates. The main issue when using water is rehydration reaction of HMF into levulinic acid and formic acid, leading to lower HMF yields. Non-aqueous solvents have been introduced to improve the HMF yields, examples are DMF [156-158], NMP [147], acetonitrile [159], quinoline [160], polyglycol ethers [118, 161], and DMSO, the most promising solvent to date [86, 135-136, 144-145, 162-163]. Issues related to the use of organic solvents are reduced solubility of the substrates and complex separation steps to isolate HMF from the reaction mixture. These problems can be overcome by using mixed solvents in biphasic systems [65, 165]. For example, Dumesic, et al. [65, 73] used a biphasic system consisting of an aqueous phase (water, DMSO) and an organic phase (MIBK, 2-butanol) for the synthesis of HMF. In this case, the HMF formed in the aqueous phase is continuously extracted in the organic phase. Calculations indicate that the work-up session requires 40% less energy compared to a monophase process with DMSO.

A continuous process for HMF synthesis from various carbohydrates (e.g. D-glucose, D-fructose, sucrose, cellulose) in a biphasic system has also been reported [165]. A fixed-bed reactor configuration with a titanium oxide catalyst was used. A solution of the carbohydrate in water was used in combination with an organic solvent such as MIBK or n-butanol. HMF yields up to 35% could be obtained for 2-5 minutes residence time.

Efforts were also made for the HMF synthesis without any solvents. For example, reactions without solvents were performed using pyridinium salts and 70% yield of HMF was obtained [137]. Finally, the use of ionic liquids for HMF synthesis has become a very popular subject and a wealth of papers have been published [83, 90, 97, 138-143, 148, 166], some with conventional heating, others with microwave heating [140-143].

1.5 Biomass for caprolactam synthesis

An unexplored field of catalytic biomass conversions to platform chemicals involves the synthesis of green caprolactam (Scheme 1.6). Caprolactam is an existing bulk chemical with a global demand of 3.9 million tons in 2008 [167]. It is the precursor for nylon-6, a widely used synthetic polymer [168]. More than two-third of the caprolactam is used for the production of fibers for textile, carpet, and industrial yarns, the remainder for engineering plastics and packaging films [169]. In the engineering plastics market, the demand for nylon-6 is growing by about 6% per annum [169].
Caprolactam from Renewable Resources: Catalytic Conversion of 5-Hydroxymethylfurfural into Caprolactone

Scheme 1.6 Caprolactam

DSM is the largest producer of caprolactam in the world, with a market share of 20% and a production capacity of more than 600,000 tons per annum. Other caprolactam producers include Honeywell, Mitsubishi, Bayer, Toray, BASF, Sumitomo/Enichem, and Rhodia. DSM has developed a number of processes, examples are the HPO process (hydroxylamine phosphate oxime) and an improved version (HPO\textsuperscript{plus}), the HSO process (hydroxylamine sulphate oxime), the ALTAM\textsuperscript{TM} process (in collaboration with DuPont and Shell), and the Recycling process (in cooperation with Honeywell). The ALTAM\textsuperscript{TM} process was never implemented due to the rising price of butadiene as starting material, which made this route lose its attraction with respect to the benzene-based routes. The Recycling process ran for a number of years. However, the plant was closed in 2001 since it was not an economic process. In this process, nylon was recovered from nylon carpets and depolymerized to caprolactam.

The conventional process for caprolactam involves three steps (Scheme 1.7): (1) cyclohexanone oxidation to cyclohexanone, (2) cyclohexanone oxime production from the reaction of cyclohexanone with hydroxylamine/ammonia (amnoximation step), and (3) a Beckman rearrangement of the oxime to caprolactam.

Two major concerns of this process are: (i) production of large quantities of undesired ammonium sulphate (4.5 kg per kg of caprolactam produced) and (ii) low selectivity of the cyclohexane oxidation to cyclohexanone at high cyclohexane conversions. To avoid this issue, a 3-8% conversion of cyclohexane per pass is applied to achieve 75-80% selectivity to a mixture of cyclohexanone and cyclohexanol. Improved versions of the conventional process as well as novel caprolactam processes have been developed. Improved versions of the conventional process as well as novel caprolactam processes have been developed.
Table 1.3 Caprolactam processes \[174]\n
<table>
<thead>
<tr>
<th>Process</th>
<th>Feedstock</th>
<th>R</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Classical</td>
<td>Cyclohexane</td>
<td>4.5</td>
<td>1) Plants written off ; 2) Optimised processes possible</td>
<td>1) High (NH₄)₂SO₄ formation ; 2) Low conversion in oxime formation step</td>
</tr>
<tr>
<td>BASF/Inventa</td>
<td>Cyclohexane</td>
<td>1.9</td>
<td>Less (NH₄)₂SO₄ production during oxime formation step</td>
<td>Classical rearrangement step</td>
</tr>
<tr>
<td>HPO</td>
<td>Cyclohexane</td>
<td>1.8</td>
<td>No (NH₄)₂SO₄ production during oxime formation step</td>
<td>Classical rearrangement step</td>
</tr>
<tr>
<td>PNC</td>
<td>Cyclohexane</td>
<td>1.55</td>
<td>One-step reaction to the oxime</td>
<td>High material costs and energy consumption</td>
</tr>
<tr>
<td>SNIA</td>
<td>Toluene</td>
<td>0</td>
<td>1) No (NH₄)₂SO₄ formation; 2) Toluene less expensive than cyclohexane</td>
<td>High fuel costs due to thermal cracking</td>
</tr>
<tr>
<td>H₂O₂ process</td>
<td>Cyclohexane</td>
<td>0</td>
<td>No (NH₄)₂SO₄ formation</td>
<td>Costs of H₂O₂ and zeolite</td>
</tr>
</tbody>
</table>

\(^a\) R = ton of ammonium sulphate produced/ton of caprolactam
In the newer concepts, lower amounts of ammonium sulphate are produced. In case of SNIA and H₂O₂ processes, the formation of this byproduct is completely eliminated. In the BASF/Inventa process, cyclohexanone oxime is formed by the catalytic hydrogenation of nitric oxide in an ammonium hydrogen sulphate solution followed by the reaction with cyclohexanone. In the HPO process, the oxime is formed by the reduction of the phosphoric acid/ammonium nitrate buffer solution with hydrogen followed by the reaction with cyclohexanone. The subsequent step for both processes is the classical Beckmann rearrangement step; therefore the formation of ammonium sulphate is unavoidable. However, the overall production of ammonium sulphate is much less than the classical process (Table 1.2).

The photochemical Nitrosation of Cyclohexane (PNC) was developed by Toray in Japan. In this process, cyclohexanone oxime is produced directly from cyclohexane with UV light (Scheme 1.8). However, this process suffers from high electricity usage, and as such it is only attractive when electricity costs are low.

Scheme 1.8 Photochemical Nitrosation of Cyclohexane (PNC) process

Sumitomo is the first company that produces caprolactam using heterogeneous catalysts (H₂O₂ process, scheme 1.9). This process combines the ammoximation of cyclohexanone using H₂O₂ (originally developed by Enichem [177]) with the vapor phase Beckmann rearrangement of the oxime in the presence of silicalite zeolites [178-180]. The plant produces 60,000 tons/year of caprolactam without the formation of the ammonium sulphate [181]. The drawback of this process is the high costs of the catalyst and hydrogen peroxide.

The SNIA process (Scheme 1.10) uses toluene as the feedstock. The first step involves oxidation of toluene to benzoic acid followed by hydrogenation to cyclohexanoic acid. The latter is converted to caprolactam using nitrosylsulphuric acid in oleum. In this process, the involvement of the oxime intermediate is avoided. In 2003, two plants in Italy (100.000 tons/year) and one plant in the former Soviet Union (80.000 tons/year) were reported to be in operation [175].
Although cyclohexane oxidation to cyclohexanone is mostly used in the caprolactam processes, other routes to cyclohexanone are possible. The DSM process in the Netherlands is based on the palladium-catalysed hydrogenation of phenol to cyclohexanone. The phenol comes from cumene: Benzene is reacted with propene to form cumene; this is reacted with oxygen to form cumyl hydroperoxide. Cumyl hydroperoxide is decomposed to phenol and acetone. The other process that is not based on the cyclohexane oxidation is the Asahi process. In this process, benzene is hydrogenated to cyclohexene. Cyclohexene is hydrated with water to cyclohexanol, which is dehydrogenated to cyclohexanone.

Caprolactam processes have also been developed using butadiene as the feedstock. Examples are a hydro-esterification process (developed by BASF [182-184] and DSM/DuPont [185-187], Scheme 1.11) and a process involving hydrocyanation as the key step (Scheme 1.12). However, these processes have not been implemented because they are more expensive than the benzene-based routes. Butadiene is rather expensive and HCN is also very expensive.
Another interesting development is the use of adiponitrile as the feedstock (Scheme 1.13). This process was developed by BASF (in collaboration with DuPont) and Rhodia (Capucine approach). Adiponitrile is hydrogenated to give a mixture of 6-aminocapronitrile and hexamethylenediamine. 6-aminocapronitrile can be used to produce caprolactam while hexamethylenediamine is a precursor for nylon-6,6 by the reaction with adipic acid. Thus, by well tuning of the process conditions, this process offers the possibility of producing two important precursors of nylon-6 and nylon-6,6. Although this process offers flexibility, it has not been implemented due to higher costs in comparison with the benzene-based routes.
1.6 Thesis outline

As mentioned in the previous section, novel caprolactam processes have been developed using green chemistry and technology principles leading to improved selectivities and less waste product. However, current processes are still based on fossil feedstocks. The objective of the research described in this thesis was to develop a synthetic route for caprolactam starting from a platform chemical from ligno-cellulosic biomass. For this purpose, HMF was selected and the envisaged pathway to caprolactam is given in Scheme 1.14. Characteristics of the proposed route are: i) a high carbon atom efficiency (6 C in HMF, 6 C in caprolactam), ii) the intermediate 1,6-hexanediol (1,6-HD) is already an existing bulk chemical and a precursor for adipic acid, iii) the synthetic step of caprolactone to caprolactam has been operative on commercial scale (though abandoned at the moment) and thus is considered proven technology.

Scheme 1.14 Proposed pathway for the HMF conversion to caprolactam

In Chapter 2, a catalyst screening study on the hydrogenation of HMF to THF-dimethanol (THFDM) is described. This hydrogenation step proved to be essential as in an early stage of the project it was already shown that the direct conversion of HMF to 1,6-HD was not successful. Promising catalysts were selected and process conditions were optimized to obtain high THFDM yields. In addition, a novel catalyst was identified for the synthesis of furan-dimethanol, an intermediate in the hydrogenation reaction of HMF to THFDM.

In Chapter 3, experimental studies on the catalytic ring opening reaction of THFDM to 1,2,6-hexanetriol (1,2,6-HT) are presented. A wide range of catalysts was tested and promising options were identified and further optimized. Byproducts were characterised and a reaction network is proposed to explain the product distributions for the best catalysts.

Chapter 4 reports a screening study on the conversion of 1,2,6-HT to 1,6-hexanediol (1,6-HD) using a hydrodeoxygenation approach. Various monometallic and bimetallic catalysts were studied and the best catalysts were selected and further optimized. A reaction network for various catalysts is proposed.
In *Chapter 5*, the one-pot synthesis of 1,6-HD from THFDM by a hydrodeoxygenation approach using a number of monometallic and bimetallic catalysts is reported. Process optimisation studies, including the addition of various solid acids, were performed for the best catalytic systems. A reaction network is proposed based on intermediates and byproducts observed in the reactions.

An overview of the caprolactam process from HMF is presented in *Chapter 6*. The results of the 1,6-HD conversion to ε-caprolactone are also presented in this chapter.

1.7 References


Introduction


[77] D. Reichert, M. Sarich, F. Merz, EP1958944, **2008**.
[79] K. M. Rapp, EP230250, **1987**.
[86] V. Grushin, N. Herron, G. A. Halliday, WO 03/024947, **2003**.
Caprolactam from Renewable Resources: Catalytic Conversion of 5-Hydroxymethylfurfural into Caprolactone

Introduction


Caprolactam from Renewable Resources: Catalytic Conversion of 5-Hydroxymethylfurfural into Caprolactone

Chapter 2
Catalyst screening studies on the hydrogenation of 5-hydroxymethylfurfural (HMF) to THF- and furan-dimethanol

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Catalyst screening studies on the hydrogenation of 5-hydroxymethylfurfural (HMF) to THF- and furan-dimethanol

Abstract

THF-dimethanol (THFDM) and furan-dimethanol (FDM) are green biobased chemicals with high application potential. We here describe a catalyst screening study on the hydrogenation of 5-hydroxymethylfurfural (HMF), accessible from lignocellulosic biomass, to THFDM and FDM. Nickel catalysts were shown to be the most promising for both products. THFDM was obtained in 99% yield with a Raney nickel catalyst (100 °C, 90 bar hydrogen, 14 h, 0.13 M HMF, ethanol, 10 wt-% catalyst intake). In addition, synergic effects were observed for certain catalyst combinations (e.g. copper chromite with Pd/C or Ru/C) giving higher yields of THFDM than with the individual catalysts. A statistical model was developed for Raney Ni to correlate the THFDM yield with relevant reaction conditions like temperature (75-250°C), batch time (4-14 h) and hydrogen pressure (50-90 bar). FDM was obtained in high yields (> 99%) using a supported Ni catalyst (NiCu/ZrO₂, 150 °C, 80 bar, 5 h, 10 wt-% catalyst, ethanol).
2.1 Introduction

Biomass is a very attractive resource for the sustainable production of fuels and chemicals in future bio-based societies \[1^{1-16}\]. A wide range of bio-based chemicals from lignocellulosic biomass sources have been proposed and ranked by Werpy et al. \[17\]. HMF is considered a very promising platform chemical \[18\]. However, the commercial applications of HMF and products derived thereof are still limited due to the high cost of HMF production, mainly associated with low product selectivities and difficult product separation procedures. Another major reason for the high price of HMF is the high cost of the raw material D-fructose. D-fructose is prepared by an enzymatic isomerization from D-glucose. However, since D-glucose and D-fructose are very similar in free energy content, the equilibrium ratio is 45:55. Separation of this mixture is done using large-scale Simulated Moving Bed (SMB). The challenge is to be able to make HMF directly from lignocellulose. In the last decade, significant progress has been made and improved catalysts and solvents have been identified for the high yield synthesis of HMF \[19-21\].

A number of interesting HMF derivatives with high application potential have been identified. Examples include formioxymethylfurfural (FMF) and acetoxyethylfurfural (AMEF) by esterification with organic acids \[22\], methoxymethylfurfural (MMF) and ethoxymethylfurfural (EMF) by etherification with alcohols \[23\], hydrogenation products like dimethylfuran (DMF) \[24\], and oxidation products like 2,5-furandicarboxylic acid (FDCA) \[25\] (Figure 2.1). Avantium has opened a pilot plant for the production of a polyester based on FDCA and ethylene glycol. This polyester is touted as a replacement of PET, the raw material of soft drink bottles.

Two other well-known examples of products from the HMF hydrogenation platform are THF-dimethanol (THFDM) and furan-dimethanol (FDM, Figure 2.1). Both are symmetrical diols with potential applications in, among others, fine chemicals \[26-29\] and polyester synthesis \[29-31\]. In addition, THFDM may also serve as a starting material for the synthesis of 1,6-hexanediol and caprolactam \[32\].

Catalytic hydrogenation studies for THFDM from HMF have been reported (Table 2.1). A wide range of reaction temperatures, hydrogen pressures (40-280 °C, 5-415 bar) and solvents are used. Good THFDM yields (> 90 mol%) were reported for typical Ni catalysts (Raney Ni, Ni on kieselguhr) and Ru/C. Recently, the group of Dumesic \[33\] reported the use of Ru/CoOx, Ru/Mg-Zr and Ru/γ-alumina (130 °C and 30 bar) in a biphasic system of 1-butanol/water to obtain 87-91% yield of THFDM.
Catalyst screening studies on the hydrogenation of 5-hydroxymethylfurfural (HMF) to THF- and furan-dimethanol

Figure 2.1. HMF conversion platform

Table 2.1. Overview of catalysts for the hydrogenation of HMF to THFDM

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>P (bar)</th>
<th>T (°C)</th>
<th>Solvent</th>
<th>Y_THFDM</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raney Ni</td>
<td>75-140</td>
<td>130-160</td>
<td>Diethyl ether</td>
<td>90</td>
<td>[34]</td>
</tr>
<tr>
<td>CuCr</td>
<td>20-415</td>
<td>150-175</td>
<td>various</td>
<td>n.a.</td>
<td>[35]</td>
</tr>
<tr>
<td>CuCr &amp; Pd/C</td>
<td>380</td>
<td>280</td>
<td>cyclohexane</td>
<td>n.a.</td>
<td>[35]</td>
</tr>
<tr>
<td>Ni/kieselguhr</td>
<td>70-345</td>
<td>&gt;100</td>
<td>water</td>
<td>various</td>
<td>[36]</td>
</tr>
<tr>
<td>Raney Ni</td>
<td>70</td>
<td>140</td>
<td>water</td>
<td>90</td>
<td>[37]</td>
</tr>
<tr>
<td>Ru/C</td>
<td>70</td>
<td>140</td>
<td>water</td>
<td>92</td>
<td>[37]</td>
</tr>
<tr>
<td>Ni/kieselguhr (G-69B,Sud-Chemie)</td>
<td>105</td>
<td>200</td>
<td>ethanol</td>
<td>quantitative</td>
<td>[26]</td>
</tr>
<tr>
<td>Co/SiO₂</td>
<td>35</td>
<td>120</td>
<td>water</td>
<td>80</td>
<td>[38]</td>
</tr>
<tr>
<td>Ni/SiO₂</td>
<td>35</td>
<td>70</td>
<td>water</td>
<td>55</td>
<td>[38]</td>
</tr>
<tr>
<td>Raney Ni</td>
<td>5</td>
<td>60</td>
<td>methanol</td>
<td>quantitative</td>
<td>[39]</td>
</tr>
<tr>
<td>Ni-Pd/SiO₂</td>
<td>80</td>
<td>40</td>
<td>water</td>
<td>95</td>
<td>[40]</td>
</tr>
<tr>
<td>Ru/support a</td>
<td>30</td>
<td>130</td>
<td>1-butanol/water</td>
<td>87-91</td>
<td>[33]</td>
</tr>
</tbody>
</table>

*a* support = CeOₓ, Mg-Zr, or γ-alumina
Stoichiometric \(^{[28, 41-43]}\) and catalytic procedures have been reported for FDM synthesis from HMF. In this case, the objective is to selectively hydrogenate the aldehyde group of HMF without C-C double bond hydrogenation leading to THFDM. An overview of catalytic procedures is given in Table 2.2. Typical reaction temperatures are between 40 and 150 °C, and pressures between 20-345 bar. Commonly, polar solvents like ethanol and water are applied, likely related to the good solubility of HMF in these solvents. Best results were obtained with Cu-based catalysts. FDM can also be produced using microorganisms such as Saccharomyces cerevisiae \(^{[44]}\).

### Table 2.2. Overview of catalysts for the hydrogenation of HMF to FDM

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>P (bar)</th>
<th>T (°C)</th>
<th>Solvent</th>
<th>(Y_{FDM})</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuCr</td>
<td>345</td>
<td>150</td>
<td>ethanol</td>
<td>quantitative</td>
<td>[35]</td>
</tr>
<tr>
<td>CuCr</td>
<td>20</td>
<td>150</td>
<td>dimethoxyethane</td>
<td>quantitative</td>
<td>[35]</td>
</tr>
<tr>
<td>CuCr, Pt/C, or PtO(_2)</td>
<td>70</td>
<td>140</td>
<td>water</td>
<td>100</td>
<td>[37]</td>
</tr>
<tr>
<td>Raney cobalt</td>
<td>35</td>
<td>60</td>
<td>water</td>
<td>97</td>
<td>[38]</td>
</tr>
<tr>
<td>Pt/Al(_2)O(_3)</td>
<td>35</td>
<td>60</td>
<td>water</td>
<td>92</td>
<td>[38]</td>
</tr>
<tr>
<td>Ru/support (^{a})</td>
<td>30</td>
<td>130</td>
<td>1-butanol/water</td>
<td>75-93</td>
<td>[33]</td>
</tr>
<tr>
<td>Ir or Ru complex</td>
<td>n.a. (^{b})</td>
<td>40</td>
<td>THF</td>
<td>99</td>
<td>[45]</td>
</tr>
</tbody>
</table>

\(^{a}\) support = CeO\(_x\), Mg-Zr, or \(\gamma\)-alumina; \(^{b}\) not applicable

However, systematic catalyst screening studies using a set of well-defined process conditions to allow for a proper comparison of catalysts are absent for both the hydrogenation of HMF to THFDM and FDM. We report here a systematic catalyst screening study for both reactions at well-defined conditions. The best catalysts have been identified and process conditions have been optimized using design of experiment techniques with the objective to achieve high product yields of either THFDM or FDM. A reaction pathway for the hydrogenation of HMF is proposed based on product compositions.
Catalyst screening studies on the hydrogenation of 5-hydroxymethylfurfural (HMF) to THF- and furan-dimethanol

2.2 Materials and methods

2.2.1 Materials

HMF (>99%) was purchased from Aldrich. FDM (98%) was purchased from Interchim (France) and THFDM (97%) was purchased from Advanced Technology & Industrial (Hong Kong). Ethanol (≥ 99.9%) was purchased from Merck, methanol (99.8%) and isopropanol (99.7%) were purchased from LabScan. Copper chromite catalysts were obtained from BASF (Cu-1985P) and purchased from Aldrich (product number: 209325) and Acros (product number: 19782). The copper zinc PRICAT CZ/A P catalyst was obtained from Johnson Matthey. Ni-Cu/ZrO₂ (Ni 29.4 wt-%, Cu 11.2 wt-%) was obtained from the Boreskov Institute of Catalysis (Russia). 50 wt-% Ni/Al₂O₃ catalyst was purchased from Acros. The G-69B catalyst (nickel on kieselguhr with zirconia as promoter) was obtained from Sud-Chemie. Raney nickel, Pd/C (10 wt-%), Pt/C (5 wt-%), Ru/C (5 wt-%), and Ru/Al₂O₃ (5 wt-%) were purchased from Aldrich. Ru/TiO₂ (5 wt-%) was purchased from Degussa. Ru/C (0.5 wt-% and 5 wt-%) were obtained from Johnson Matthey. HCl (37%) was purchased from Aldrich. Hydrogen (> 99.9999%) and nitrogen (technical grade, > 98%) were purchased from Hoek Loos.

2.2.2 Methods

2.2.2.1 Reactor set-ups

The catalytic hydrogenation reactions were performed in two different set-ups. The first consists of a 100 mL batch autoclave (Parr, maximum 350 °C and 350 bar) equipped with an overhead stirrer and a four-bladed impeller. The second consists of a 250 mL batch autoclave (Parr, maximum 350 °C and 200 bar) where reactions were carried out in 8 ml glass vials (capped with a septum and pierced with a small needle) placed in the autoclave (maximum 7 vials). Stirring was performed using a Teflon stirring bar placed in the reactor vial.

2.2.2.2 Representative example for the hydrogenation of HMF in the 100 ml batch autoclave

HMF (500 mg, 4 mmol), catalyst (50 mg), and ethanol (30 mL) were placed in a stainless steel batch reactor (Parr) equipped with an overhead stirrer. The reactor was flushed three times with nitrogen and subsequently with hydrogen. Subsequently, the reactor was pressurized with hydrogen to 90 bar, and the reaction mixture was heated to 200 °C under stirring (1000 rpm). The reaction was
carried out for 14 h. After cooling to ambient temperature, the reaction product was filtered over a PTFE membrane to remove the catalyst and the filtrate was analysed. Most reactions and analyses were performed in duplicate.

2.2.2.3 Representative example for the hydrogenation of HMF in a glass vial inserted in the 250 ml batch autoclave

HMF (100 mg, 0.8 mmol), catalyst (10 mg), ethanol (2 mL) and a Teflon stirring bar were added to a glass vial (8 mL) capped with a septum. The vial was subsequently pierced with a small needle and placed in a stainless-steel autoclave. The lid of the autoclave was closed and stirring was started at 1000 rpm. After three times pressurizing, first two times with nitrogen and then with hydrogen, the actual reaction was performed at 80 bar, 100 °C, and 5 h reaction time. The autoclave was then cooled to ambient temperature and the pressure was released. Reaction mixtures were filtered over a PTFE membrane to remove the catalyst and the filtrates were analysed. Most reactions and analyses were performed in duplicate.

2.2.2.4 Preparative reaction of HMF to THFDM

HMF (3 g, 24 mmol), Raney nickel (300 mg), and ethanol (45 mL) were placed in a stainless steel batch reactor (Parr) equipped with an overhead stirrer. The reactor was flushed three times with nitrogen and subsequently with hydrogen. The reactor was pressurized to 90 bar with hydrogen, and the reaction mixture was heated to 100 °C under stirring (1000 rpm). The reaction was carried out for 14 h. After cooling to ambient temperature, the reaction product was filtered over a PTFE membrane to remove the catalyst. The solvent was removed by evaporation (100 mbar, 60 °C) to give THFDM as a pale yellow liquid in 93% isolated yield. The GC retention time was similar to that of an authentic sample.

\[ ^{1}H-NMR \ (200 \text{ MHz, } D_{2}O) \ \delta \ 1.59 \ (m, 2H), \ 1.9 \ (m, 2H), \ 3.52 \ (t, J = 12 \text{ Hz}, 4H), \ 4.04 \ (m, 2H) \text{ ppm.} \]

\[ ^{13}C-NMR \ (50 \text{ MHz, } D_{2}O) \ (\text{major isomer}): \delta \ 26.5, \ 63.8, \ 79.9 \text{ ppm;} \]

\[ (\text{minor isomer}) \ 26.9, \ 63.4, \ 79.5 \text{ ppm.} \]

Elemental analysis, calculated: C 54.5%, H 9.1%. Found: C 53.9%, H 9.3%.

2.2.2.5 Product analysis

Gas chromatography using a CP-WAX57CB column (25 m length, 0.2 mm internal diameter, and 0.25 μm film thickness) and a flame ionization detector (GC-FID) was used for liquid product analysis. The injector and detector temperature
were set at 250 °C. The oven temperature was kept at 40 °C for 5 minutes then heated up to 180 °C with a heating rate of 5 °C/min and subsequently to 230 °C with a heating rate of 10 °C/min and kept at this temperature for 15 minutes. A split ratio of 50 was used. Helium was used as the carrier gas with a flow rate of 1.1 ml/min. Toluene was used as an internal standard and the response factor of each compound was determined using pure components. The identification of the compounds was done by spiking with authentic samples and by GC-MS analyses.

GC-MS analyses were performed on a Hewlett-Packard 5890 gas chromatograph equipped with a quadrupole Hewlett-Packard 6890 MSD selective detector and a sol-gel capillary column (30-m, 0.25-mm internal diameter, 0.25-μm film). The injector temperature was set at 250 °C. The oven temperature was kept at 40 °C for 5 minutes, then increased to 250 °C at a heating rate of 3 °C/min, and then held at 250 °C for 10 minutes.

Elemental analyses were performed using a EuroVector EA3400 Series CHNS-O analyser with acetonilide as reference. All analyses were carried out twice and the average value is reported. Oxygen content was determined by difference.

The 1H-NMR spectra were measured on a 200 MHz NMR spectrometer (Varian). D2O (Sigma-Aldrich) was used as the solvent. The chemical shifts are denoted in δ-units (ppm) and the residual protons in the solvent (D2O, δ = 4.8 ppm) were used as the reference. The NMR field for 13C-NMR spectra was 50 MHz.

### 2.2.2.6 Statistical evaluation of the design of experiments

The effects of the process conditions (temperature T, pressure P, and reaction time t) on the yield of THFDM were studied and analysed. The experimental data were modeled using an expression given in Equation 2.1.

\[
y = \beta_0 + \sum_{i=1}^{3} \beta_i x_i + \sum_{i=1}^{3} \beta_{ii} x_i^2 + \sum_{i=1}^{3} \sum_{j=1}^{3} \beta_{ij} x_i x_j
\]

(eq 2.1)

Mathcad® and Design-Expert® software were used to calculate the regression coefficients (\(\beta_i\), \(\beta_{ii}\), and \(\beta_{ij}\)) and the intercept (\(\beta_0\)). A t-test was performed to determine the statistical significance of the individual terms and the non-significant terms were deleted from the model.

### 2.2.2.7 Definitions

The conversion of HMF (X_{HMF}) was calculated using the following equation:
Caprolactam from Renewable Resources: Catalytic Conversion of 5-Hydroxymethylfurfural into Caprolactone

\[ X_{\text{HMF}} = \left(1 - \frac{C_{\text{HMF}}}{C_{\text{HMF,0}}} \right) \times 100\% \]  
(eq 2.2)

where \( C_{\text{HMF}} \) is the concentration of HMF after a certain reaction time and \( C_{\text{HMF,0}} \) is the initial concentration of HMF.

The yield (\( Y_i \)) and selectivity (\( S_i \)) of a product \( i \) were calculated using the following equations:

\[ Y_i = \frac{C_i}{C_{\text{HMF,0}}} \times 100\% \]  
(eq 2.3)

\[ S_i = \frac{C_i}{C_{\text{HMF,0}} - C_{\text{HMF}}} \times 100\% \]  
(eq 2.4)

where \( C_i \) is the concentration of products after a certain reaction time.

2.3 Results and discussion

2.3.1 Catalyst screening

A wide variety of catalysts were tested for the hydrogenation of HMF to THFDM and FDM, including noble metal (Ru, Pd) catalysts on various supports, Ni catalysts (Ni on kieselguhr and Raney Ni) and Cu-based catalysts (CuCr and CuZn). The screening study was performed in a batch set-up at 100 °C and 80 bar hydrogen pressure for 5 h in ethanol with a catalyst intake of 10 wt.-%. The results are provided in Table 2.3. Both the HMF conversion and the chemo-selectivity are a strong function of the catalyst type.

The HMF conversion ranges from 8 to essentially quantitative. The best catalyst for THFDM synthesis appears Raney nickel, with a 83% yield at 100% HMF conversion, in line with literature data (Table 2.1). For FDM, Ru/Al\(_2\)O\(_3\) gives the highest yield (67%) at 97% HMF conversion. Although not very active at these conditions (8% HMF conversion), NiCu on zirconia gives 100% selectivity to FDM and as such is of interest to test at more severe reaction conditions (vide infra).

Of interest is the observation of a synergic effect for combinations of copper chromite and Pd/C. The THFDM yield is 52% when using the combination, compared to 0% for CuCr and 23% for Pd/C. On the basis of this finding, other noble metal and copper-based catalyst combinations were tested as well and the
results are presented in Table 2.4. Best results were obtained using Ru/C in combination with CuCr, leading to 59% THFDM yield.

Table 2.3. Catalyst screening studies on HMF hydrogenation

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>( X_{\text{HMF}} )</th>
<th>( Y_{\text{THFDM}} )</th>
<th>( Y_{\text{FDM}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiCu/ZrO(_2)</td>
<td>8</td>
<td>0</td>
<td>8</td>
</tr>
<tr>
<td>Ni/Al(_2)O(_3)</td>
<td>15</td>
<td>0</td>
<td>4</td>
</tr>
<tr>
<td>RaNi</td>
<td>100</td>
<td>83</td>
<td>0</td>
</tr>
<tr>
<td>Ni on kieselguhr (G-69B)</td>
<td>61</td>
<td>0</td>
<td>29</td>
</tr>
<tr>
<td>CuCr</td>
<td>99</td>
<td>0</td>
<td>49</td>
</tr>
<tr>
<td>CuCr-Pd/C</td>
<td>100</td>
<td>52</td>
<td>0</td>
</tr>
<tr>
<td>CuZn</td>
<td>99</td>
<td>0</td>
<td>48</td>
</tr>
<tr>
<td>Ru/Al(_2)O(_3)</td>
<td>97</td>
<td>0</td>
<td>67</td>
</tr>
<tr>
<td>Ru/TiO(_2)</td>
<td>91</td>
<td>0</td>
<td>50</td>
</tr>
<tr>
<td>Ru/C</td>
<td>100</td>
<td>33</td>
<td>0</td>
</tr>
<tr>
<td>Pd/C</td>
<td>100</td>
<td>23</td>
<td>0</td>
</tr>
<tr>
<td>Pt/C</td>
<td>71</td>
<td>0</td>
<td>50</td>
</tr>
</tbody>
</table>

\(^a\) T = 100 °C, P \( \text{H}_2 \) = 80 bar, \( t = 5 \) h, cat. intake = 10 wt-\%, solvent = ethanol

Table 2.4. Combined catalysts for HMF hydrogenation to THFDM

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>( X_{\text{HMF}} )</th>
<th>( Y_{\text{THFDM}} )</th>
<th>( Y_{\text{FDM}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd/C + CuCr</td>
<td>100</td>
<td>52</td>
<td>0</td>
</tr>
<tr>
<td>Ru/C + CuCr</td>
<td>100</td>
<td>59</td>
<td>0</td>
</tr>
<tr>
<td>Pd/C + CuZn</td>
<td>100</td>
<td>46</td>
<td>12</td>
</tr>
</tbody>
</table>

\(^a\) T = 100 °C, P \( \text{H}_2 \) = 80 bar, \( t = 5 \) h, cat. intake = 10 wt-\%, solvent = ethanol

The synergic effect may be explained by assuming that copper chromite (or copper-based catalysts in general) are active and reasonably selective for the hydrogenation of the aldehyde group of HMF to form FDM, whereas the noble
metal catalysts are more active for the hydrogenation of the furan ring to THFDM than for aldehyde reduction (eq 2.5). Apparently, rapid hydrogenation of the aldehyde moiety leads to less by-product formation, presumably due to the high reactivity of this group in oligomerisation/decarbonylation reactions.

![Reaction Scheme](image)

(\text{eq 2.5})

In the next phase of the research, several catalysts were selected for screening studies at higher temperatures and longer reaction times to allow for a catalyst comparison at 100\% HMF conversion. The experiments were performed at 200 °C and 90 bar of hydrogen pressure in ethanol and the results are provided in Table 2.5.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>(Y_{\text{THFDM}})</th>
<th>(Y_{\text{FDM}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru/C (ALD) 5%</td>
<td>30</td>
<td>0</td>
</tr>
<tr>
<td>Ru/C (JM) 5%</td>
<td>46</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Ru/C 0.5%</td>
<td>12</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Pd/C 10%</td>
<td>38</td>
<td>0</td>
</tr>
<tr>
<td>Ni on kieselguhr (G-69B, Sud)</td>
<td>55</td>
<td>1</td>
</tr>
<tr>
<td>Ra-Ni</td>
<td>79</td>
<td>0</td>
</tr>
<tr>
<td>CuCr (ALD)</td>
<td>9</td>
<td>0</td>
</tr>
<tr>
<td>CuCr (AC)</td>
<td>11</td>
<td>0</td>
</tr>
<tr>
<td>CuCr-Pd/C</td>
<td>62</td>
<td>0</td>
</tr>
</tbody>
</table>

\text{Table 2.5. Catalyst screening of HMF hydrogenation at 200°C}^{a,b}

\(T = 200 \, ^\circ C, \ P_{H_2} = 90 \, \text{bar}, \ t = 14 \, \text{h}, \ \text{cat. intake} = 10 \, \text{wt-%}, \ \text{solvent} = \text{ethanol}; \ X_{\text{HMF}} = 100\%, \ \text{note: ALD = Aldrich, JM = Johnson Matthey, Sud = Sud-Chemie, AC = Acros}^{6}\)
Quantitative HMF conversions were obtained for all catalysts at this condition. As expected, the yield of FDM is negligible due to subsequent hydrogenation of the C-C bond at more severe conditions. The highest yield of the THFDM (80%) was obtained with Raney nickel catalysts. Thus, nickel-based catalysts seem to be the most potential catalysts for this reaction, which is also supported by the result for the Ni on kieselguhr (G-69B). This finding is in line with literature data [26, 34, 36-37]. Ru/C and Pd/C catalysts gave a THFDM yield of only 46% and 38%, respectively, which for Ru/C catalyst is close to literature value (50%) [33]. The THFDM yield when using copper chromite catalysts was very low due to the formation of ring-opening products such as 1,2,6-hexanetriol (29-34%). At these conditions, synergic effects were also observed. For instance, a mixture of copper chromite and Pd/C catalysts gave a 62% yield of THFDM compared to 9-11% for copper chromite and 38% for Pd/C only.

2.3.2 Effect of process conditions on THFDM synthesis

An optimization study on the synthesis of THFDM from HMF using design of experiments was performed with the Raney Ni catalyst, the best catalyst in the screening study (vide supra). The effects of hydrogen pressure (50-90 bar), reaction temperature (75-250 °C) and reaction time (4-14 h) on the hydrogenation reaction were evaluated and the results are provided in Table 2.6. All experiments were carried out in a well stirred 100 mL batch autoclave and each entry in Table 2.6 represents one experiment. An initial HMF concentration of 0.13 M, ethanol as the solvent and a fixed catalyst intake of 10 wt-% was used.

The effect of process conditions on THFDM yield was modeled using non-linear multivariable regression. The experimental data are best described with a quadratic model excluding three statistically non-significant terms (P, T.P, and T.t). The yield of THFDM as a function of process conditions is presented in eq. 2.6, the values for β are given in Table 2.7.

\[
Y_{\text{THFDM}} = \beta_0 + \beta_1 T + \beta_3 t + \beta_{11} T^2 + \beta_{22} P^2 + \beta_{33} t^2 + \beta_{23} P.t
\]  
(eq 2.6)

The results of the analysis of variance (ANOVA) are presented in Table 2.8. The very low P-value indicates that the model is statistically significant. The \( R^2 \), \( R^2_{\text{adjusted}} \), and \( R^2_{\text{press}} \) values for the model are 0.976, 0.956, and 0.872, respectively. The value of the \( R^2_{\text{adjusted}} \) is close to the value of \( R^2 \), indicating that all significant variables are included in the model. The \( R^2_{\text{press}} \) value (0.872) indicates that the model is a good predictor for the THFDM yields within the range of the process conditions. Thus, the model describes the experimental data well, which is also supported by a parity plot of the experimental and model yield of THFDM (Figure 2.2).
### Table 2.6. Effect of process conditions on the hydrogenation of HMF to THFDM $^a$

<table>
<thead>
<tr>
<th>#</th>
<th>T (°C)</th>
<th>P (bar)</th>
<th>t (h)</th>
<th>$Y_{\text{THFDM}}$ (mol%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>200</td>
<td>90</td>
<td>14</td>
<td>80</td>
</tr>
<tr>
<td>2</td>
<td>75</td>
<td>90</td>
<td>14</td>
<td>91</td>
</tr>
<tr>
<td>3</td>
<td>100</td>
<td>90</td>
<td>14</td>
<td>99</td>
</tr>
<tr>
<td>4</td>
<td>150</td>
<td>90</td>
<td>14</td>
<td>88</td>
</tr>
<tr>
<td>5</td>
<td>250</td>
<td>90</td>
<td>14</td>
<td>50</td>
</tr>
<tr>
<td>6</td>
<td>200</td>
<td>50</td>
<td>14</td>
<td>71</td>
</tr>
<tr>
<td>7</td>
<td>200</td>
<td>70</td>
<td>14</td>
<td>77</td>
</tr>
<tr>
<td>8</td>
<td>100</td>
<td>80</td>
<td>5</td>
<td>83</td>
</tr>
<tr>
<td>9</td>
<td>100</td>
<td>90</td>
<td>4</td>
<td>65</td>
</tr>
<tr>
<td>10</td>
<td>100</td>
<td>90</td>
<td>6</td>
<td>79</td>
</tr>
<tr>
<td>11</td>
<td>100</td>
<td>90</td>
<td>9</td>
<td>95</td>
</tr>
<tr>
<td>12</td>
<td>100</td>
<td>50</td>
<td>14</td>
<td>85</td>
</tr>
</tbody>
</table>

$^a X_{\text{HMF}} = 100\%$ except for entry 9 (99%)

### Table 2.7. Model coefficient values

<table>
<thead>
<tr>
<th>Coefficient</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\beta_0$</td>
<td>61.909</td>
</tr>
<tr>
<td>$\beta_1$</td>
<td>0.549</td>
</tr>
<tr>
<td>$\beta_3$</td>
<td>4.089</td>
</tr>
<tr>
<td>$\beta_{11}$</td>
<td>-0.002403</td>
</tr>
<tr>
<td>$\beta_{22}$</td>
<td>-0.009025</td>
</tr>
<tr>
<td>$\beta_{33}$</td>
<td>-0.585</td>
</tr>
<tr>
<td>$\beta_{23}$</td>
<td>0.105</td>
</tr>
</tbody>
</table>
Catalyst screening studies on the hydrogenation of 5-hydroxymethylfurfural (HMF) to THF- and furan-dimethanol

Table 2.8. Analysis of variance for the model

<table>
<thead>
<tr>
<th></th>
<th>SS</th>
<th>DF</th>
<th>MS</th>
<th>F</th>
<th>P-value</th>
<th>R² values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model</td>
<td>1.971 x 10³</td>
<td>6</td>
<td>328.542</td>
<td>40.231</td>
<td>1.375 x 10⁻¹</td>
<td>0.976</td>
</tr>
<tr>
<td>Error</td>
<td>48.998</td>
<td>6</td>
<td>8.166</td>
<td></td>
<td></td>
<td>0.956</td>
</tr>
<tr>
<td>Total</td>
<td>2.02 x 10³</td>
<td>12</td>
<td></td>
<td></td>
<td></td>
<td>0.872</td>
</tr>
</tbody>
</table>

Figure 2.2. Experimental and model predictions for the THFDM yield

Within the experimental window, the hydrogen pressure has a very limited effect on the $Y_{THFDM}$, indicative for saturation kinetics (first order at low hydrogen pressure, zero order at higher pressures). The effects of temperature and reaction time on the THFDM are given in Figure 2.3. Clearly, the $Y_{THFDM}$ is a strong function of both variables and an optimum is observed for both temperature and reaction time. This optimum is close to the experiment performed at 100 °C, 90 bar pressure and 14 h reaction time, leading to 99% THFDM yield. Thus, near quantitative THFDM yields are possible by proper selection of the reaction conditions.
Caprolactam from Renewable Resources: Catalytic Conversion of 5-Hydroxymethylfurfural into Caprolactone

Figure 2.3. 3D contour plot of the THFDM yield as a function of reaction temperature (T) and time (t) at a constant pressure of 70 bar

As is evident from Figure 2.3, the batch time has a significant effect on the $Y_{\text{THFDM}}$. At low temperatures, the $Y_{\text{THFDM}}$ increases with time and reaches a constant level. At higher temperatures, a clear optimum is observed and lower yields are attainable at prolonged reaction times.

To gain further insights in the $Y_{\text{THFDM}}$ versus reaction time, additional hydrogenation reactions were performed in a 100 mL batch autoclave at 100 °C and 90 bar hydrogen pressure (ethanol, initial HMF concentration of 0.13 M, 10 wt-% of Raney nickel, periodic sampling). The results are provided in Figure 2.4. It is clear that FDM is the intermediate product which is further converted to THFDM. After 9 h batch time, all FDM has reacted and is quantitatively converted to THFDM.
Catalyst screening studies on the hydrogenation of 5-hydroxymethylfurfural (HMF) to THF- and furan-dimethanol

Figure 2.4. Concentration versus time profile for the HMF hydrogenation using Raney nickel catalysts (100 °C, 90 bar hydrogen, ethanol)

At elevated temperatures, the \( Y_{THFDM} \) shows an optimum and at prolonged reaction times, the yield drops (Figure 2.3). This is due to subsequent reactions of THFDM at more severe reaction conditions. This was experimentally verified by performing reactions at 150, 200 and 250°C, see Figure 2.5 for details. At 150 °C and above, the yield of THFDM is reduced due to the formation of by-products such as 1,2,6-hexanetriol (1,2,6-HT), THF-methanol (THFM) and some unknowns. As a consequence, the yield of THFDM at 250 °C is only 50% compared to 99% at 100 °C.

A reaction network for the hydrogenation of HMF using the Raney Ni catalyst in line with the experimental findings and supported by the statistical modeling is provided in Figure 2.6. It involves the initial hydrogenation of the aldehyde function of HMF to FDM, followed by hydrogenation of the C-C bonds to THFDM. At elevated temperatures and reaction times, THFDM may be converted to 1,2,6-HT by a ring opening reaction. This reaction has been reported for Rh-Re/SiO\(_2\) catalysts \([32]\). 1,2,6-HT may also be formed directly from FDM via a ring-opening to form a conjugated ketone-diene followed by hydrogenation \([33]\). THFM formation under the prevailing reaction conditions is known for Ru/C and Raney nickel \([46]\) and likely involves dehydrogenation of THFDM to the corresponding aldehyde followed by decarbonylation to THFM.
Figure 2.5. Product distributions of the HMF hydrogenation reactions using Raney nickel catalysts at different temperatures (P H₂ = 90 bar, t = 14 h, initial HMF concentration of 0.13 M, ethanol, cat. = 10 wt-%, X_HMF = 100%)

Figure 2.6. Reaction network for HMF hydrogenation using Raney-Ni

**Preparative synthesis of THFDM**

The highest yield of THFDM (99%) within the experimental design window was obtained at 100 °C and 90 bar pressure (14 h, initial HMF concentration of
0.13 M, ethanol, cat. = 10 wt-%, see Table 2.6). A preparative hydrogenation was carried out at these conditions and after reaction THFDM was isolated as a pale yellow liquid in 93% isolated yield. Both $^1$H- and $^{13}$C-NMR confirm the formation of THFDM. The NMR data clearly show the presence of the two isomers of THFDM (cis-trans, see Scheme 2.1). The cis- configuration predominates (42:1), which is much higher than reported in the literature (19:1)\textsuperscript{[39]}. 

![cis- THFDM](image1.png) ![trans- THFDM](image2.png)

Scheme 2.1 cis- and trans-THFDM

### 2.3.3 Optimisation studies on the hydrogenation of HMF to FDM

Supported nickel catalysts (Ni/Al$_2$O$_3$ and NiCu/ZrO$_2$) and Ru/Al$_2$O$_3$ were shown to be promising catalysts for the synthesis of FDM (\textit{vide supra}). At standard conditions (100 °C, 80 bar, 5 h, 10 wt-% cat., ethanol), the highest yield of FDM was 67 mol% (Ru/Al$_2$O$_3$). The effect of temperature on the Y$_{FDM}$ was determined for these promising catalysts, see Table 2.9 for details.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>T (°C)</th>
<th>X$_{HMF}$</th>
<th>Y$_{FDM}$</th>
<th>Y$_{THFDM}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiCu/ZrO$_2$</td>
<td>100</td>
<td>8</td>
<td>8</td>
<td>0</td>
</tr>
<tr>
<td>NiCu/ZrO$_2$</td>
<td>150</td>
<td>&gt;99</td>
<td>&gt;99</td>
<td>0</td>
</tr>
<tr>
<td>Ni/Al$_2$O$_3$</td>
<td>100</td>
<td>15</td>
<td>4</td>
<td>0</td>
</tr>
<tr>
<td>Ni/Al$_2$O$_3$</td>
<td>150</td>
<td>59</td>
<td>43</td>
<td>4</td>
</tr>
<tr>
<td>Ru/Al$_2$O$_3$</td>
<td>100</td>
<td>97</td>
<td>67</td>
<td>0</td>
</tr>
<tr>
<td>Ru/Al$_2$O$_3$</td>
<td>150</td>
<td>94</td>
<td>94</td>
<td>0</td>
</tr>
<tr>
<td>Ru/Al$_2$O$_3$ $^b$</td>
<td>100</td>
<td>94</td>
<td>30</td>
<td>39</td>
</tr>
</tbody>
</table>

$^a$ P H$_2$ = 80 bar, t = 5 h, cat. intake = 10 wt-%, solvent = ethanol, $^b$ 25 wt-% cat. was used
Best results were obtained using the NiCu on zirconia and the Ru on alumina catalysts and nearly quantitative FDM yields are achievable with these catalysts at 150 °C. The use of NiCu/ZrO₂ catalyst is an absolute novelty of this paper and may be an attractive alternative for the use of more expensive Ru-based catalysts.

2.4 Conclusions

Systematic catalyst screening studies and process optimization studies on the catalytic hydrogenations of HMF to THFDM and the intermediate FDM have been performed. Ni catalysts were shown to be the most promising catalyst, leading to > 99 mol% yield for THFDM (Raney-Ni, 100 °C, 90 bar, 14 h, ethanol) and FDM (Ni-Cu/ZrO₂, 150 °C, 80 bar, 5 h, ethanol). The latter result is unprecedented and further process studies in dedicated continuous set-ups to assess catalyst stability are in progress.

2.5 Acknowledgement

We would like to thank ACTS-ASPECT for providing a grant to this research (ASPECT Project 053.62.017), Rudy Parton, Rob Meier (DSM), Peter Witte, Peter Berben (BASF), Annemarie Beers (Norit), Jean Paul Lange (Shell), and Bart Zwijnenburg (Johnson Matthey) for helpful discussions, Francesco Picchioni for the discussion over statistical modeling, and Boreskov Institute of Catalysis for providing Ni-Cu/ZrO₂ catalyst.

2.6 References

Catalyst screening studies on the hydrogenation of 5-hydroxymethylfurfural (HMF) to THF- and furan-dimethanol

Caprolactam from Renewable Resources: Catalytic Conversion of 5-Hydroxymethylfurfural into Caprolactone


Chapter 3
Catalyst studies on the ring opening of tetrahydrofuran-dimethanol to 1,2,6-hexanetriol

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- Submitted to Catalysis Today

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Abstract

The metal catalysed hydrogenolysis of the biomass-derived THF-dimethanol to 1,2,6-hexanetriol using heterogeneous catalysts was investigated. Bimetallic Rh-Re catalysts (4 wt% Rh and a Re/Rh (mol. ratio of 0.5)) on a silica support gave the best performance and 1,2,6-hexanetriol was obtained in 85% selectivity at 31% conversion (120 °C, 80 bar, 4 h). The product distribution at prolonged reaction times shows the formation of diols and mono-alcohols, indicating that the 1,2,6-hexanetriol is prone to subsequent hydrodeoxygenation reactions. Different silica supports were investigated and best results were obtained with an amorphous silica featuring an intermediate surface areas and an average mesopore size of about 6 nm. TPR and XPS surface analysis support the presence of mixed Rh and Re particles. The redox Re⁰/Reⁿ⁺ surface ratio correlates with the product yield in a volcano type dependency. Both gas phase as well as Rh₂₀₀Re₁OH cluster DFT calculations support an acid-metal bifunctional mechanism.
3.1 Introduction

The increasing demand for energy together with declining petroleum resources will require the use of new sources for fuels and chemicals. Biomass is considered one of the foreseeable sustainable sources of biofuels and biobased chemicals and materials [1]. Particularly, lignocellulosic biomass is a potential source of various important bio-based chemicals such as levulinic acid or 5-hydroxymethylfurfural (HMF, 1). HMF is a very versatile platform chemical and may be converted to a wide range of derivatives [2]. An example is THF-dimethanol (2), which is accessible by catalytic hydrogenation reactions (eq 3.1) [3-10].

\[
\begin{array}{c}
\text{O} \\
\text{OH} \\
\text{cat.} \\
\text{H}_2 \\
\text{O} \\
\text{OH}
\end{array}
\quad \text{1} \quad \xrightarrow{\text{cat.} \ H_2} \quad \begin{array}{c}
\text{O} \\
\text{OH} \\
\text{cat.} \\
\text{H}_2 \\
\text{O} \\
\text{OH}
\end{array}
\quad \text{2}
\]

(eq 3.1)

We have recently reported studies on the development of catalytic methodology for 1,6-hexanediol (4) from HMF (eq 3.2) [11]. The sequence of reactions to 4 involves the conversion of HMF to the corresponding diol 2, followed by ring-opening to 1,2,6-hexanetriol 3. Though these studies focused on optimization of 1,6-hexanediol synthesis from 1, the intermediate triol 3 is also an interesting example of a polyol. Polyols [12,13] are used in a wide range of applications such as a moisturizing agent in the pharmaceutical and cosmetics industry, as a carrier solvent in the ink and paint industries, and as a reactive component in synthetic resins like polyurethanes.

\[
\begin{array}{c}
\text{O} \\
\text{OH} \\
\text{cat.} \\
\text{H}_2 \\
\text{O} \\
\text{OH} \\
\text{cat.} \\
\text{H}_2 \\
\text{OH} \\
\text{OH} \\
\text{2} \\
\text{THPM}
\end{array}
\quad \xrightarrow{\text{cat.} \ H_2} \quad \begin{array}{c}
\text{O} \\
\text{OH} \\
\text{cat.} \\
\text{H}_2 \\
\text{O} \\
\text{OH}
\end{array}
\quad \xrightarrow{\text{cat.} \ H_2} \quad \begin{array}{c}
\text{O} \\
\text{OH} \\
\text{cat.} \\
\text{H}_2 \\
\text{O} \\
\text{OH}
\end{array}
\quad \xrightarrow{\text{cat.} \ H_2} \quad \begin{array}{c}
\text{O} \\
\text{OH} \\
\text{cat.} \\
\text{H}_2 \\
\text{O} \\
\text{OH}
\end{array}
\quad \text{4}
\]

(eq 3.2)

Synthetic routes for 3 have been reported. An example is the catalytic dihydroxylation of 5-hexen-1-ol [14] (6) using formic acid and hydrogen peroxide (55 °C, 6 h) giving 3 in 84% yield (eq 3.3).
Catalytic ring opening reactions of substituted tetrahydrofuranics have been studied. Generally, harsh reaction conditions are required and the synthesis suffers from limited yields. For instance, Utne et al.\textsuperscript{[15]} reported the ring-opening reaction of 2 over copper chromite catalyst to give 4 in 50\% yield (300 °C and 380 bar). In subsequent studies starting with 1\textsuperscript{[4]}, 3 was obtained in 43\% yield using a copper chromite catalyst (175 °C, 365 bar, 12 h).

The use of supported bimetallic catalysts is gaining high interest at the moment for catalytic reactions in general\textsuperscript{[16]} and hydro(deoxy)genation reactions in particular\textsuperscript{[17]}. The properties of the catalysts can be modified by proper selection of the metals allowing control over the electronic and structural interactions between the two metals\textsuperscript{[18]}. The choice of the catalyst support is also very important and has shown to have a profound effect on activity and performance of the catalysts. Particularly, the use of bimetallic catalysts supported on high surface area supports (e.g. silica) has become very attractive due to the better performance in various relevant chemical catalytic reactions than the individual metals\textsuperscript{[19-33]}.

Relevant to this work, is the research carried out by the group of Tomishige on the use of bimetallic Rh-ReO\textsubscript{x}/SiO\textsubscript{2} catalysts for the ring opening reaction of THF-methanol 7 to 1,5-pentanediol 8 (eq 3.4)\textsuperscript{[34,35]}. Compared to the corresponding monometallic counterparts, a very high selectivity to 1,5-pentanediol (94\%) was obtained. More interestingly, the reaction was performed at mild conditions; 120 °C and 80 bar. Bimetallic Rh-MoO\textsubscript{x}/SiO\textsubscript{2} catalysts were also reported to be active for the same reaction\textsuperscript{[36-37]} as well as the hydrogenation of HMF over Ni-Pd/SiO\textsubscript{2} to THF-dimethanol\textsuperscript{[38]} and tetrahydropyran-2-methanol on Rh-ReO\textsubscript{x}/C to 1,6-hexanediol\textsuperscript{[39]}. Recently, Dumesic et al. reported on the use of related bimetallic Rh-ReO\textsubscript{x} catalysts on carbon supports for the hydrogenolysis of C-O bonds in a range of cyclic ethers and polyols\textsuperscript{[40]}. Catalyst performance was compared with that of the individual monometallic catalysts and major improvements were observed, rationalized by synergic effects between the two metals. The presence of a \(-\text{CH}_2\text{OH}\) group α to the ether C-O bond has a markedly positive effect on the rate of the reaction.
There is increasing evidence that the actual catalyst is a bifunctional catalyst containing partly oxidized Re species with acidic Re-OH groups and fully reduced Rh metals. On a mechanistic level, two models have been proposed. Tomishige's group\textsuperscript{[41]} suggested that the reaction proceeds via the initial reaction of 7 with the Re-OH group to form the alkoxide and water. In the next step, hydrogenolysis of the Re alkoxide species with adsorbed H on the Rh metal surface occurs and 1,5-pentanediol is formed. On the other hand, Dumesic-Neurock\textsuperscript{[40]} proposed a mechanism involving an initial protonation of absorbed 7 by the Re-OH group and the formation of a stabilized oxocarbenium ion species, followed by hydrogenation to 1,5-pentanediol. DFT calculations confirm that the hydroxyl groups on rhenium atoms associated with rhodium are acidic.

Herein, we present a comprehensive study on the conversion of the THF-dimethanol 2 to the triol 3 using bimetallic catalysts under mild conditions (eq 3.5).

The objective is to obtain 3 at a high selectivity and not necessarily at high conversion of 2. The reason is that 3 is expected to find applications in the bulk-chemical industry, where product selectivity is by far more important than substrate conversion. For instance, for the production of ethylene-oxide from ethylene, the conversion per pass in the reactor is about 10-20\% to achieve high ethylene-oxide selectivities. The effect of various inorganic supports, different metals, catalyst compositions, and process conditions on the reaction performance is thoroughly investigated. The results are supported by DFT calculations.

3.2 Materials and methods

3.2.1 Materials

Compound 2 (> 98\% purity) was produced by the hydrogenation of 1 according to a procedure described previously\textsuperscript{[11]}. 1 (>99\%) was purchased from
Caprolactam from Renewable Resources: Catalytic Conversion of
5-Hydroxymethylfurfural into Caprolactone

Aldrich, 3 (> 97%) was obtained from Acros, and 1-propanol (> 99%) was purchased from Merck Chemicals.

Rhodium chloride hydrate (Rh 38-40 wt%), rhodium(III) nitrate hydrate (~36 wt% rhodium basis), ammonium perrhenate (> 99%), and perrhenic acid solution (65-70 wt% in H$_2$O, 99.99%) were obtained from Aldrich. Tetraammineplatinum(II) nitrate (99%) and tetraamminepalladium(II) nitrate solution (5.0 wt% as Pd) were purchased from Strem Chemicals. Ammonium molybdate tetrahydrate (MoO$_3$ 81-83 wt%), chromium(III) nitrate nonahydrate (99%), and manganese(II) nitrate tetrahydrate (> 97%) were acquired from Aldrich. Tin chloride dihydrate (> 98%) was bought from Riedel-de Haén. Ammonium tungsten oxide (> 99.99%) was purchased from Alfa Aesar. CARiACT G-6 3 micron and G-6 5 micron silica were kindly supplied by Fuji Silysia, HDK® T40 silica was provided by Johnson Matthey, a mesostructured silica (abbreviated SS815) was prepared by surfactant assisted sol-gel chemistry according to the method reported elsewhere [42], and two other types of silica (product number: 637238 and 637246) were acquired from Aldrich. γ-Al$_2$O$_3$ (product number: 044658) and CeO$_2$ (REacton® 99.9%) were purchased from Alfa Aesar. TiO$_2$ (product number: 14021), SiO$_2$-Al$_2$O$_3$ (grade 135), Nb$_2$O$_5$ (99.99%), sulfated zirconium(IV) hydroxide (product number: 464341), and activated carbon (product number: 484164) were purchased from Aldrich. Hydrogen gas (> 99.9999%) was purchased from Hoek Loos.

3.2.2 Methods

3.2.2.1 General procedure for preparation of the bimetallic Rh-ReO$_x$ catalysts

All catalyst preparations were carried out in air. An aqueous solution of rhodium(III) chloride hydrate (176 mg, 0.8 mmol) in water (5 mL) was added to the silica (2 g, Fuji CARiACT G-6 3 micron; BET surface area 529 m$^2$g$^{-1}$ and pore volume 0.617 cm$^3$g$^{-1}$) and stirred for 2 h at room temperature. After drying at 383 K for 13-14 h, the solid was added to an aqueous solution of ammonium perrhenate(VII) (113 mg, 0.4 mmol) in water (5 mL) and stirred for 2 h, followed by drying at 383 K for 13-14 h. Calcination in air at 773 K for 3 h gave a catalyst containing 4 wt% of Rh and a Re/Rh molar ratio of 0.5. A similar procedure was used for the preparation of other Rh-based bimetallic catalysts, except for Rh-ReO$_x$/C, where the calcination step was omitted.

Rh-ReO$_x$/SiO$_2$ catalysts with different rhodium loadings and Re/Rh molar ratio were also prepared. A combination of rhodium(III) chloride hydrate and ammonium perrhenate(VII) of (a) 171 mg (0.8 mmol) and 29 mg (0.1 mmol), (b) 183 mg (0.9 mmol) and 235 mg (0.9 mmol), (c) 41 mg (0.2 mmol) and 27 mg (0.1 mmol), and (d) 302 mg (1.4 mmol) and 193 mg (0.7 mmol) was used to prepare
catalysts with (a) 4 wt% Rh and Re/Rh of 0.13, (b) 4 wt% Rh and Re/Rh of 1, (c) 1 wt% Rh and Re/Rh of 0.5, and (d) 6.5 wt% Rh and Re/Rh of 0.5.

Monometallic Rh/SiO\(_2\) (4 wt%) and Re/SiO\(_2\) (4 wt%) catalysts were also produced using 169 mg (0.8 mmol) of rhodium(III) chloride hydrate and 120 mg (0.4 mmol) of ammonium perrhenate(VII), respectively. Additional types of precursors of Rh and Re were also investigated. A combination of (a) 176 mg (0.8 mmol) of rhodium(III) chloride hydrate and 163 mg perrhenic(VII) acid solution (0.4 mmol perrhenic acid) and (b) 243 mg (0.8 mmol) of rhodium(III) nitrate hydrate and 106 mg (0.4 mmol) of ammonium perrhenate(VII) was used to produce Rh-ReO\(_x\)/SiO\(_2\) catalysts with 4 wt% Rh and Re/Rh molar ratio of 0.5. For some Rh-ReO\(_x\)/SiO\(_2\) catalysts (as stated in the text), the silica was precalcined at 773 K for 3 h prior to the impregnation.

Catalysts with various metal combinations were prepared as well. Rhodium(III) chloride hydrate was combined with: (a) chromium(III) nitrate nonahydrate (164 mg, 0.4 mmol), (b) manganese(II) nitrate tetrahydrate (103 mg, 0.4 mmol), (c) tin(II) chloride dihydrate (94 mg, 0.4 mmol), (d) ammonium molybdate tetrahydrate (131 mg, 0.1 mmol), and (e) ammonium tungsten oxide (30 mg, 0.1 mmol) to produce the corresponding bimetallic catalysts. Non-Rh bimetallic catalysts were prepared from (a) tetra-ammine platinum(II) nitrate (169 mg, 0.4 mmol) and ammonium perrhenate(VII) (58 mg, 0.2 mmol) and (b) tetra-ammine palladium(II) nitrate solution (1.7 g) and ammonium perrhenate(VII) (109 mg, 0.4 mmol) providing Pt-ReO\(_x\)/SiO\(_2\) and Pd-ReO\(_x\)/SiO\(_2\) catalysts, respectively.

3.2.2.2 General procedure for the reaction of 2 to 3

2 (100 mg, 0.76 mmol), the Rh-ReO\(_x\)/SiO\(_2\) catalyst (25 mg), water (2 mL) and a Teflon stirring bar were added to an 8 mL glass vial capped with a septum. The septum was pierced with a small needle. The vial was placed in a stainless-steel autoclave, the autoclave was closed and the stirring was started at 1000 rpm. After three times pressurizing with first nitrogen and then hydrogen, the autoclave was pressurized with hydrogen to 10 bar and the temperature was raised to 120 °C. After 1 h, the pressure was raised to 80 bar and the reaction was continued for 4 h. Then, the autoclave was allowed to cool to ambient temperature and the pressure was released. The reactor content was filtered over a PTFE membrane to remove the catalyst and the filtrate was subjected to GC analysis.

Adjustments were made for some experiments (when stated in the text): (1) 1-propanol as the solvent, (2) temperature of 80 and 180 °C, (3) reaction time of 20 h, (4) catalyst intake of 10 wt%, and (5) no pre reduction step for 1 h at 10 bar hydrogen pressure.
3.2.2.3 Characterization of the catalyst and supports

The metal particle size was determined by TEM analysis. The samples were ground and the resulting fine powder was mixed with isopropanol. One drop was dispersed onto a carbon TEM-grid and left to dry for 15 minutes. Microstructural characterization was carried out using a Jeol 2010F Transmission Electron Microscope (TEM). The TEM micrographs were recorded with a Gatan digital camera with Digital Micrograph. The X-rays were recorded by a Bruker 5000 series of liquid N$_2$-free XFlash® Silicon Drift Detectors (SDD) and ESPRIT software to provide quantitative energy dispersive microanalysis. Metal particle size was determined using Gatan Digital Micrograph software.

The density of OH groups was determined by a method reported by Blin and Carteret $^{[43]}$ using thermogravimetric analysis (TGA). The TGA patterns were recorded using a Mettler-Toledo analyser (TGA/SDTA851e) using fused alumina crucibles and a flow of synthetic dry air of 100 ml/min (STP). The temperature was increased from 30 to 900 °C at 5 °C/min with a plateau of 1 h at 130 °C. Blank curve subtraction using an empty crucible was performed.

Textural analysis of the fresh and spent catalysts was carried out by N$_2$ physisorption analyses at -196 °C on a Micromeritics ASAP 2420 analyser. Prior to the measurements all samples were degassed under vacuum at 200 °C for 10 h for the fresh materials. The surface area was calculated by the BET method $^{[44]}$ in the relative pressure range of 0.06-0.25 ($S_{BET}$). The single point total pore volume ($V_T$) was estimated from the amount adsorbed at a relative pressure of 0.98 in the desorption branch. The pore size distribution was derived from the BJH model $^{[45]}$. Micropore volume ($V_\mu$) was derived from the t-plot method $^{[46]}$.

Temperature-programmed reduction (TPR) with H$_2$ was carried out in a Micromeritics Autochem II instrument, using a mixture of 5 vol% H$_2$ in Ar to reduce the samples by mixing high purity H$_2$ and Ar. Silver oxide (99.999%) was used for calibration. The sample was not dried before analysis as the gas at the reactor outlet was passed through a cold trap consisting of acetone–dry ice; this removes both the physisorbed water as well as the water produced during the reduction before entering the thermal conductivity detector.

X-ray photoelectron spectroscopy (XPS) was used to study the chemical composition and the oxidation state of the elements on the catalyst surface. The XPS instrument, a VG Escalab 200 R spectrometer with a MgK$\alpha$ X-ray source ($h\nu = 1253.6$ eV; $1$ eV = $1.602\times10^{-19}$ J), was equipped with a pre-treatment chamber with controlled atmosphere and temperature in which the catalyst samples could be treated under various conditions.
3.2.2.4 DFT Calculations

Gradient-corrected density functional theory (DFT) calculations were used to determine the gas phase carbenium ion reaction energies as well as reaction energies and activation barriers over Rh$_{200}$Re$_1$OH clusters which are comprised of 200 Rh atoms, 1 Re atom and 1 OH group. The gas phase energies were carried out using DFT calculations implemented in DMol3 [47,48]. Numerical basis sets of double numerical quality (DNP) with d-type polarization functions were used for wave functions with the cutoff of 3.5 Å. The Perdew-Wang 91 [49] (PW91) form of generalized gradient approximation (GGA) was used to model the correlation and exchange energies and gradient corrections. The electronic density was converged to within 1 x 10$^{-5}$ au. The energy in each geometry optimization cycle was converged to within 2 x 10$^{-5}$ Hartree with the maximum displacement of 4 x10$^{-3}$ Å and the maximum force of 3x10$^{-3}$ Hartree/Å.

The gas-phase reaction energies for formation of carbenium ion for ring structures were calculated as:

\[ \text{ROR} + \text{H}^+ \rightarrow \text{RORH}^+ \]

where ROR and RORH$^+$ refer to the initial ring structure and the ring-opened carbenium ion.

The calculations on the Rh$_{200}$Re$_1$OH clusters were carried out using periodic plane wave DFT calculations implemented in the Vienna Ab Initio Simulation Program (VASP) [50-52]. The PW91 form of the GGA was used to determine gradient corrections to the exchange and correlation energies. Wave functions were constructed by expanding a series of plane waves within a cutoff energy of 400 eV. Vanderbilt ultrasoft pseudopotentials [53] were used to model the interactions between the core and valence electrons. The electronic energies were converged to within 1x 10$^{-4}$ eV and forces on each atom were optimized to within 0.05 eVÅ$^{-1}$. The calculations on Rh$_{200}$Re$_1$ clusters were carried out in a 30.44 Å cubic unit cell to ensure a sufficient vacuum region to separate clusters in neighboring cell and all cluster atoms were allowed to relax in energy calculations and transition state searches. Transition state searches were performed using the dimer method [54] with the initial guesses for the transition state structure and the reaction trajectory obtained through the nudged elastic band method [55].

3.2.2.5 Product analyses

The products were analysed by gas chromatography using a CP-WAX57CB column (25 m length, 0.2 mm internal diameter, and 0.25 μm film thickness) and a flame ionization detector (GC-FID). The injector and the detector temperature were set at 250 °C. The oven temperature was kept at 40 °C for 5 minutes then heated up to 180 °C with a heating rate of 5 °C/min and to 230 °C
Caprolactam from Renewable Resources: Catalytic Conversion of 5-Hydroxymethylfurfural into Caprolactone

with a heating rate of 10 °C/min and kept at this temperature for 15 minutes. A split ratio of 50 was used. Helium was used as the carrier gas with a flow rate of 1.1 ml/min. Toluene was used as an internal standard.

Gas chromatography coupled with mass-spectrometry detection (GC-MS) was performed on a Hewlett-Packard 5890 instrument equipped with a quadrupole Hewlett-Packard 6890 MSD selective detector and a 30-m × 0.25-mm internal diameter × 0.25-μm-film sol-gel capillary column. The injector temperature was set at 250 °C. The oven temperature was kept at 40 °C for 5 minutes, then increased to 250 °C at a heating rate of 3 °C/min, and then held at 250 °C for 10 minutes.

3.2.2.6 Definitions

The conversion of the starting material \( X_i \) was calculated using the following equation:

\[
X_i = \left(1 - \frac{C_i}{C_{i,0}}\right) \times 100\%
\]  
(eq 3.6)

where \( C_i \) is the concentration of starting material 1 or 2 after a certain reaction time and \( C_{i,0} \) is the initial concentration.

The yield \( Y_j \) and selectivity \( S_j \) of the different reaction products were calculated as:

\[
Y_j = \frac{C_j}{C_{i,0}} \times 100\%
\]  
(eq 3.7)

\[
S_j = \frac{C_j}{C_{i,0} - C_i} \times 100\%
\]  
(eq 3.8)

where \( C_j \) is the concentration of a product after a certain reaction time.

3.3 Results and discussion

3.3.1 Effect of support on catalytic performance of bimetallic Rh-Re catalyst

Rh-Re catalysts using various supports (SiO\(_2\), γ-Al\(_2\)O\(_3\), CeO\(_2\), TiO\(_2\), Nb\(_2\)O\(_5\), sulphated ZrO\(_2\), SiO\(_2\)-Al\(_2\)O\(_3\), and carbon) were prepared and their performance for
Catalyst studies on the ring opening of tetrahydrofuran-dimethanol to 1,2,6-hexanetriol

the reaction of 2 to 3 in terms of catalyst activity and selectivity was evaluated (120 °C, P₁ = 10 bar, t₁ = 1 h, P₂ = 80 bar, t₂ = 4 h, 25 wt% catalyst, water). The results are shown in Table 3.1. At the prevailing conditions, the conversion of 2 was between 0 and 31 %. The main product was the desired triol 3, byproducts were 1,6- and 1,5-hexanediol (vide infra), produced by subsequent hydrodeoxygenation reactions of already formed 3. Apparently, the ring opening of the tetrahydrofuran-dimethanol is very selective and byproducts are solely formed by consecutive reactions of the primary product.

Silica based catalysts gave the best results (entry 1-2). The use of other oxidic supports such as CeO₂, γ-Al₂O₃, and TiO₂ also gave active catalysts (entry 3-5); though the activity was lower than for the best silica based catalyst. Comparison of selectivities is hampered by the fact that the conversions for all catalysts are not equal. Of interest though, are the high selectivities for niobia and titania (> 94%). The carbon based and sulphated zirconia based catalysts are both inactive. Dumesic reported that the Rh-ReOₓ catalyst on a carbon support is active for the ringopening of 7 to 1,5-pentanediol (eq. 3.4). Here, the catalyst was reduced with hydrogen at 723 K and passivated with 2% O₂ in He at 298 K. This activation step was not applied for the carbon based catalyst used in this study and is likely the reason for the poor performance. It can be concluded that the Fuji G-6 3 SiO₂ support gives the most active catalyst, though some other supports offer opportunities for further optimization (TiO₂ and Nb₂O₅).

Table 3.1. Hydrogenolysis of 2 to 3 using Rh-ReOₓ on various supports.¹

<table>
<thead>
<tr>
<th>Entry</th>
<th>Supports</th>
<th>%-conv.</th>
<th>%-sel. to 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>SiO₂</td>
<td>14</td>
<td>85</td>
</tr>
<tr>
<td>2</td>
<td>SiO₂</td>
<td>31</td>
<td>84</td>
</tr>
<tr>
<td>3</td>
<td>CeO₂</td>
<td>10</td>
<td>21</td>
</tr>
<tr>
<td>4</td>
<td>γ-Al₂O₃</td>
<td>4</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>TiO₂</td>
<td>11</td>
<td>94</td>
</tr>
<tr>
<td>6</td>
<td>Carbon</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>7</td>
<td>Nb₂O₅</td>
<td>17</td>
<td>95</td>
</tr>
<tr>
<td>8</td>
<td>Sulphated ZrO₂</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>9</td>
<td>SiO₂- Al₂O₃</td>
<td>9</td>
<td>71</td>
</tr>
</tbody>
</table>

¹ T = 120 °C, P₁ = 10 bar, t₁ = 1 h, P₂ = 80 bar, t₂ = 4 h, catalyst = 25 wt%, solvent = water; purity of 2 was 98%, catalysts contained 4 wt% Rh with a Rh-Re molar ratio of 0.5, b Wacker HDK® T40; c Fuji G6-3; d purity of 2 was 99%.
3.3.2 Bimetallic catalysts: effect of metal combinations

The effect of other metal combinations than Rh and Re on the conversion and selectivity of 2 to 3 was investigated. The principal hydrogenating metal (Rh, Pt, and Pd) was combined with different oxidic promoters (Re, Mo, W, Cr, Mn, and Sn) using the G6-3 Fuji silica support (120 °C, 80 bar, 4 h). The results are presented in Table 3.2.

Table 3.2. Hydrogenolysis of 2 to 3 using various metal combinations.\(^\text{a}\)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Metal 1</th>
<th>Metal 2</th>
<th>%-conv.</th>
<th>%-sel. to 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Rh</td>
<td>Re</td>
<td>31</td>
<td>84</td>
</tr>
<tr>
<td>2</td>
<td>Pd</td>
<td>Re</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>Pt</td>
<td>Re</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>Rh</td>
<td>Cr</td>
<td>3</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>Rh</td>
<td>Mn</td>
<td>5</td>
<td>0</td>
</tr>
<tr>
<td>6</td>
<td>Rh</td>
<td>Sn</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>7 (^\text{b})</td>
<td>Rh</td>
<td>Mo</td>
<td>11</td>
<td>76</td>
</tr>
<tr>
<td>8 (^\text{b})</td>
<td>Rh</td>
<td>W</td>
<td>10</td>
<td>77</td>
</tr>
<tr>
<td>9 (^\text{b})</td>
<td>Rh</td>
<td>Re</td>
<td>7</td>
<td>89</td>
</tr>
</tbody>
</table>

\(^{a}\) T = 120 °C, P\(_1\) = 10 bar, t\(_1\) = 1 h, P\(_2\) = 80 bar, t\(_2\) = 4 h, catalyst = 25 wt\%, solvent = water, Metal 1 = 4 wt\%, Metal 2/Metal 1 = 0.5 mol/mol; \(^{b}\) Mo/Rh = 0.91 mol/mol, W/Rh = 0.13 mol/mol, Re/Rh = 0.13 mol/mol.

The first experiments were conducted using either Rh, Pd, or Pt in combination with Re. Noticeable differences were observed regarding catalyst activity and the Rh-ReO\(_x\)/SiO\(_2\) catalyst is by far the most active catalyst. Apparently, Pd and Pt metals do not show a synergetic effect in combination with Re, though both are active hydrogenation catalysts. Possible reasons may be the choice of the metal precursors or the formation of high amounts of monometallic particles instead of bimetallic alloys.

Rh-promoted catalysts using other oxophilic metals like Cr, Mn, Sn, Mo or W were prepared and tested (Table 3.2). The activity of all combinations (0-11% conversion) is by far lower than for the Rh-Re catalyst (31% conversion).
Promotion with Sn even leads to an inactive catalyst. Only Mo and W provide a relatively high selectivity to 3 (entry 7 and 8). Koso et al. [37] and Dumesic et al. [40] also reported Mo in combination with Rh as an active catalyst for the hydrogenolysis of cyclic ethers.

The effect of the different Rh and Re precursors was also explored. A Rh-Re on silica catalyst using Rh nitrate as the precursor was prepared, and gave 24% conversion of 2 and 85% selectivity to 3. The catalyst prepared from Rh chloride (entry 1 in Table 3.2) is slightly more active, implying that the metal catalyst precursor also plays a role regarding activity, an observation made for various heterogeneous catalysts [56].

### 3.3.3 Effect of the silica support: structure-performance relations

In section 3.1 it was shown that silica supports provide the most active bimetallic Rh-ReOₓ catalysts for the hydrogenolysis reaction of 2 to 3. In this section, the performance of six Rh-ReOₓ catalysts with different types of silica is described to determine the impact of the silica characteristics (structure and texture) on catalytic performance. The Rh content of the catalysts studied was fixed at 4 wt% with a Re/Rh mol ratio of 0.5. The results of the catalytic screening experiments are provided in Table 3.3 and plotted in Figure 3.1 for comparison.

<table>
<thead>
<tr>
<th>Silica</th>
<th>%-conv.</th>
<th>%-sel. to 3</th>
<th>%-yield of 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>SS-815</td>
<td>15</td>
<td>73</td>
<td>11</td>
</tr>
<tr>
<td>G6-5</td>
<td>14</td>
<td>74</td>
<td>10</td>
</tr>
<tr>
<td>G6-3</td>
<td>31</td>
<td>84</td>
<td>26</td>
</tr>
<tr>
<td>HDK-T40</td>
<td>14</td>
<td>85</td>
<td>12</td>
</tr>
<tr>
<td>ALD 5-15</td>
<td>9</td>
<td>64</td>
<td>6</td>
</tr>
<tr>
<td>ALD 10-20</td>
<td>10</td>
<td>68</td>
<td>7</td>
</tr>
</tbody>
</table>

Table 3.3. Hydrogenolysis of 2 using Rh-ReOₓ with various silica supports.

*Rh = 4 wt%, Re/Rh = 0.5 (mol/mol), T = 120 °C, P₁ = 10 bar, t₁ = 1 h, P₂ = 80 bar, t₂ = 4 h, catalyst = 25 wt%, solvent = water*
Caprolactam from Renewable Resources: Catalytic Conversion of 5-Hydroxymethylfurfural into Caprolactone

Figure 3.1. Conversion of 2, selectivity and yield of 3 as a function of silica type for Rh-ReOₓ/SiO₂ having 4 wt% Rh and Re/Rh=0.5. Reaction conditions are given in Table 3.3.

The Fuji G6-3 is by far the most active catalyst and the conversion (31%) is double of that of the second best catalyst (SS-815, 15% conversion). Selectivities for 3 ranged between 64 and 85%. As mentioned earlier, comparison of selectivities at different conversion levels provides limited information and as such no meaningful conclusions can be drawn regarding selectivity.

To determine the relevant parameters that determine catalyst activity for the various silica based bimetallic Rh-Re catalysts, both the supports and catalysts were characterized by various physico-chemical techniques. This included textural analysis, XRD, OH density, metal particle size, oxidation state, surface compositions by XPS, and interaction between Rh-Re by TPR.

3.3.3.1 Structural and textural properties of the bare silica supports

Relevant data for the various silica supports are compiled in Table 3.4. Most silicas have an amorphous structure, the only exception is SS-815, which is ordered. BET areas range from 370-610 m²/g for the amorphous silicas to 876 m²/g for the ordered SS-815. Average pore sizes range from 3.0 to 9.4 nm. The best catalyst support, G6-3, is amorphous, has an average pore size of 5.7 nm, a BET surface area of 604 m²/g, and an OH density of 4.2 nm⁻². The use of ordered silicas (such as SS-815), thereby having higher surface areas, is not beneficial in terms of conversion. This is a remarkable insight as those silicas require elaborated synthesis protocols and are normally more expensive than precipitated amorphous silicas.
The micropore volume was analysed using the \textit{t-plot} method. The results are provided in Table 3.5. In general, the samples are purely mesoporous except for ALD 5-15 and ALD 10-20, where a 25\% of micropore volume is present. This high percentage of micropores, compared to the other silicas, resulted in the worst results: lowest conversion, selectivity and yield of 3. This may be (partly) due to steric effects. Since substrate 2 is relatively bulky, the presence of micropores in the catalyst support is expected to lead to lower activity. Additionally, the presence of micropores can affect metal incorporation by capillary forces; having the metals mainly located within the less accessible micropores. This can impose a mass transfer barrier, explaining the lower conversion as well.

Table 3.5. Total pore and micropore volumes of the bare silicas.\textsuperscript{a}

<table>
<thead>
<tr>
<th>Silica</th>
<th>$V_T$ (cm$^3$/g)</th>
<th>$V_\mu$ (cm$^3$/g) \textsuperscript{b}</th>
<th>Micropore volume fraction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SS-815</td>
<td>0.67</td>
<td>b.d.l.</td>
<td>b.d.l.</td>
</tr>
<tr>
<td>G6-5</td>
<td>0.87</td>
<td>b.d.l.</td>
<td>b.d.l.</td>
</tr>
<tr>
<td>G6-3</td>
<td>0.86</td>
<td>b.d.l.</td>
<td>b.d.l.</td>
</tr>
<tr>
<td>HDK-T40</td>
<td>0.86</td>
<td>0.01</td>
<td>1</td>
</tr>
<tr>
<td>ALD 5-15</td>
<td>0.61</td>
<td>0.15</td>
<td>25</td>
</tr>
<tr>
<td>ALD 10-20</td>
<td>0.59</td>
<td>0.15</td>
<td>25</td>
</tr>
</tbody>
</table>

\textsuperscript{a} b.d.l. = below the detection limit; \textsuperscript{b} determined by the \textit{t-plot} method.
The hydroxyl concentration is considered an important property of the silica surface \[ ^{57,58} \]. This quantity was calculated based on a simplified method reported by Blin and Carteret after complete removal of physisorbed water \[ ^{43} \]. The results are given in Table 3.4. A plot of catalyst performance versus the OH density is given in Figure 3.2 and a clear dependency is absent.

![Figure 3.2. Yield of 3 as a function of OH density.](image)

We have attempted to relate catalyst performance with textural properties, BET area, and pore volume by statistical analyses of the data. However, clear relations with the reaction performance were absent. Thus, it can be concluded that the silica support plays a major role and determines catalyst performance to a great extent. However, clear relations between catalyst performance and relevant properties of the support could not be established. As such, it appears that the size and composition of the Rh-ReO\(_x\) metal cluster, which is expected to be a function of the silica support properties, are of more importance. Therefore, the loaded metal catalysts were analysed using TPR, XRD and XPS and the results are provided in the following section.
3.3.3.2 Rh-Re interactions and metal oxidation states as a function of silica support type

The reduction temperature profiles of the various Rh-ReO$_x$/SiO$_2$ catalysts were determined (Figure 3.3). The TPR profiles of the bimetallic catalysts for various silica supports, as shown in Figure 3.3, are comprised of either a single or two reduction steps. Considerable differences are observed for the various catalysts and the main reduction step is between 72 and 90 °C.

![Figure 3.3. TPR profiles for the Rh-ReO$_x$/SiO$_2$ catalysts (4 wt% Rh and Re/Rh=0.5): 1) ALD 10-20; 2) ALD 5-15; 3) HDK-T40; 4) G6-3; 5) G6-5 and 6) SS-815.](image)

The lower temperature peak likely involves the reduction of Rh(III) to a lower valence, while the higher temperature peak can be attributed to Rh in interaction with Re (Figure 3.3). Dumesic et al. [40] reported a broad peak, likely consisting of a number of individual peaks at a maximum of about 150 °C for Rh-
ReOₓ on carbon. Koso reported a single reduction temperature peak of Rh-ReOₓ (Re/Rh = 0.5) at 97 °C [33], which is close to the values provided here. The reduction temperatures for Rh/SiO₂ and Re/SiO₂ are 77°C and >500 °C respectively [33,59]. Thus, Rh in interaction with Re enhances the reducibility of the latter, at expense of its own reducibility and suggests the formation of metal alloys. This is confirmed by XPS (see HTCAT-5 in Figure 3.6 and Table 3.9); where the amount of Re(0) was quantified as 70%. Thus, it can be concluded that interactions between Rh and Re are present in all catalysts, in line with literature data on supported bimetallic Rh-ReOₓ catalysts.

Table 3.6. Temperatures of the main reduction step and metal particle size (TEM) for the Rh-ReOₓ/SiO₂ catalysts (4 wt% Rh and Re/Rh=0.5).

<table>
<thead>
<tr>
<th>Silica</th>
<th>Main reduction temperature (°C)</th>
<th>Average metal particle size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SS-815</td>
<td>72</td>
<td>2.3</td>
</tr>
<tr>
<td>G6-5</td>
<td>85</td>
<td>2.7</td>
</tr>
<tr>
<td>G6-3</td>
<td>90</td>
<td>2.9</td>
</tr>
<tr>
<td>HDK-T40</td>
<td>80</td>
<td>2.7</td>
</tr>
<tr>
<td>ALD 5-15</td>
<td>78</td>
<td>2.0</td>
</tr>
<tr>
<td>ALD 10-20</td>
<td>80</td>
<td>1.1</td>
</tr>
</tbody>
</table>

The metal particle size was determined by direct visualization of the catalysts by TEM. Figure 3.4 gives an example of the TEM images of the Rh-ReOₓ/Fuji G6-3 silica catalyst, where the darker spots are assigned to metal particles containing Rh and Re. TEM-EDX confirmed the presence of Rh, Re, Si, and O. The Re/Rh atomic ratio was calculated to be 0.46 on average (0.5 theoretical).

The metal particle size of all the Rh-ReOₓ/SiO₂ catalysts was determined, see Table 3.6 for details. The average particle size is between 1 and 3 nm, which is in line with data from Dumesic and co-workers [40] for an Rh-ReOₓ/C catalysts, where an average metal particle size of 2.1 nm was reported. Koso reported a slightly higher average particle size of 3.5 nm for a Rh-ReOₓ catalyst on silica (Re/Rh = 0.5) [34]. Figure 3.5 represents the conversion of 2 and the yield of 3 as a function of the average metal particle size. No maximum was found; the yield progressively increases with the particle size. Thus, the metal particle size has an
clear effect on catalyst performance and attempted synthesis of Rh-ReO\textsubscript{x} catalysts with a particle size exceeding 3 nm are of interest to identify the optimum particle size for the reaction.

Figure 3.4. TEM images of the Rh-ReO\textsubscript{x}/Fuji G6-3 SiO\textsubscript{2} catalyst (4 wt% Rh, Re/Rh = 0.5).
3.3.4 Optimization of the metal composition for the Rh-ReO\(_x\)/SiO\(_2\) catalyst

From the study above with various silica supports, it was concluded that Rh-Re in combination with a Fuji G6-3 silica support yields the best performance. We carried out further analysis and optimization of different catalyst compositions by varying the Rh loading and the Re/Rh molar ratio for the Fuji G6-3 silica support. The results are presented in Table 3.7. Catalytic activity is a strong function of the catalyst composition. To get a better understanding, XPS surface analysis with in-situ reduction was performed and the results are shown in Figure 3.6 and Table 3.8.

Rh(III) was fully reduced to Rh(0) in all formulations (Figure 3.6, left), whereas Re(VII) was partially reduced under the pretreatment conditions (pre-reduced in H\(_2\) at 120 °C for 1 h) as can be seen from Figure 3.6, right. As mentioned earlier, the reduction of Re normally takes place at 400-600 °C \[33,59\]. Thus, this finding indicates the presence of Rh-Re interactions after the pretreatment. These results are also in line with the TPR results, indicating the interaction between bulk Rh and Re particle in the Rh-ReO\(_x\)/SiO\(_2\) catalysts, as well as with literature data on (related) catalysts \[33,40\].

Figure 3.5. Yield of 3 and conversion of 2 as a function of metal size.
Catalyst studies on the ring opening of tetrahydrofuran-dimethanol to 1,2,6-hexanetriol

Table 3.7. Effect of catalyst composition for Rh-Re in combination with Fuji G6-3 silica support on the hydrogenolysis of 2 to 3. a

<table>
<thead>
<tr>
<th>Samples</th>
<th>Rh (wt%)</th>
<th>Re/Rh molar ratio</th>
<th>%-conv.</th>
<th>%-sel. to 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>HTCAT-1</td>
<td>4</td>
<td>1</td>
<td>17</td>
<td>89</td>
</tr>
<tr>
<td>HTCAT-2</td>
<td>1</td>
<td>0.5</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>HTCAT-3</td>
<td>6.5</td>
<td>0.5</td>
<td>21</td>
<td>88</td>
</tr>
<tr>
<td>HTCAT-4</td>
<td>4</td>
<td>0.13</td>
<td>7</td>
<td>89</td>
</tr>
<tr>
<td>HTCAT-5</td>
<td>4</td>
<td>0.5</td>
<td>31</td>
<td>84</td>
</tr>
</tbody>
</table>

a T = 120 °C, P₁ = 10 bar, t₁ = 1 h, P₂ = 80 bar, t₂ = 4 h, catalyst = 25 wt%, solvent = water

The binding energies of Rh3d₅/₂ in all reduced catalysts at 307.0-307.1 eV are attributed to Rh⁰ [60]. However, the Re precursor is only partial reduced, because the Re4f profile can be decomposed into two doublets whose Re4f₇/₂ components appear at ca. 40.3 and 43.5-44.7 eV, indicating the existence of Re⁰ and Re⁵⁺ species, respectively [61]. Because the doublets are rather broad, the presence of Re³⁺ should also be considered. Thus, the average Re valence is between Re³⁺ and Re⁵⁺. This value is slightly higher than the average valence reported by Koso et al. [62], Reⁿ⁺ (n=2–3) for Rh-ReOₓ on silica.

The redox Re⁰/Re⁵⁺ surface ratio was calculated after deconvolution of the two Re4f doublets (see dashed area in Figure 3.6, right). Figure 3.7 correlates the conversion and selectivity to 3 with this surface ratio and shows a volcano type dependency. The highest conversion was obtained at a ratio of 2.4 while both lower (ca. 1.0) or higher (ca. 3.0) ratios gave lower conversions. This observation is likely the result of two opposing effects: close interaction between Rh-Re is advantageous and favored by a high amount of Re⁰ but the actual catalyst involves a ReOₓ (Re⁵⁺) species.
Caprolactam from Renewable Resources: Catalytic Conversion of 5-Hydroxymethylfurfural into Caprolactone

Figure 3.6. XPS surface analysis of the electronic Rh 3d and Re 4f core levels of the catalysts made on Fuji G6-3 silica support after *in-situ* pre-reduction at 120 °C in H₂.
Table 3.8. Binding energies (eV) and surface atomic ratios of in-situ reduced catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Si2p</th>
<th>Rh3d_{3/2}</th>
<th>Re4f_{7/2}</th>
<th>Rh/Si</th>
<th>Re/Si</th>
<th>Rh/(Rh+Re)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HTCAT-1</td>
<td>103.4</td>
<td>307.1</td>
<td>40.3 (75), 43.9 (25)</td>
<td>0.0028</td>
<td>0.0043</td>
<td>0.394</td>
</tr>
<tr>
<td>HTCAT-2</td>
<td>103.4</td>
<td>307.1</td>
<td>40.3 (48), 44.7 (52)</td>
<td>0.0008</td>
<td>0.0010</td>
<td>0.444</td>
</tr>
<tr>
<td>HTCAT-3</td>
<td>103.4</td>
<td>307.0</td>
<td>40.2 (75), 43.8 (25)</td>
<td>0.0055</td>
<td>0.0046</td>
<td>0.545</td>
</tr>
<tr>
<td>HTCAT-4</td>
<td>103.4</td>
<td>307.0</td>
<td>40.3 (49), 43.8 (51)</td>
<td>0.0038</td>
<td>0.0029</td>
<td>0.567</td>
</tr>
<tr>
<td>HTCAT-5</td>
<td>103.4</td>
<td>307.0</td>
<td>40.3 (71), 43.5 (29)</td>
<td>0.0022</td>
<td>0.0038</td>
<td>0.367</td>
</tr>
<tr>
<td>Rh/SiO₂</td>
<td>103.4</td>
<td>307.0</td>
<td>-</td>
<td>0.0020</td>
<td>-</td>
<td>1.0</td>
</tr>
</tbody>
</table>

*Composition is given in Table 3.7; *b in parenthesis peak percentages.

Figure 3.7. Conversion of 2 as a function of Re⁰/Re⁵⁺ surface ratio.

3.3.5 DFT calculations

All data provided above in combination with literature data support the hypothesis that the Rh-Re catalyst on supports are bifunctional catalysts with acidic Re-OH groups and reduced Rh metals. Close interaction between Rh and Re is a prerequisite for optimal performance. In this section, we further investigate by DFT
calculations whether the bifunctional mechanism can explain the high selectivity for the reaction of THF-dimethanol to triol 3.

The acid-metal bifunctional site model proposed by Chia et al.\textsuperscript{[40]} for the hydrogenolysis of 7 and other oxygenates, suggests that hydrogenolysis proceeds by an acid catalyzed activation of the C-O bond at sites that stabilize carbenium ion formation followed by the subsequent hydrogenation of unsaturated surface intermediate at a neighbouring Rh site. Such model was used herein to examine the ring opening of THF-dimethanol. The previous DFT indicate that the high activity and selectivity of the ring opening and C-OH hydrogenolysis on Rh-ReO\textsubscript{x} catalysts is the result of a concerted ring opening-hydride transfer process forming a stable oxocarbenium ion intermediate in the presence of β-hydroxyl group\textsuperscript{[40]}.

Similar calculations for both the gas phase carbenium ion intermediates as well as Rh\textsubscript{200}Re\textsubscript{1}OH surface intermediates for the ring opening of THF-dimethanol which contains one extra –CH\textsubscript{2}OH substitute than 7 were carried out herein. The results for both the gas phase calculations and over Rh\textsubscript{200}Re\textsubscript{1}OH are reported in Fig. 3.8 A and B, respectively. The reaction energy for the formation of the gas-phase oxocarbenium ion from THF-dimethanol was calculated to be -862 kJ/mol (Fig. 3.8 A), which is slightly lower than that for 7 (-852 kJ/mol), indicating that the extra –CH\textsubscript{2}OH in THF-dimethanol does not significantly influence the acid-catalyzed ring opening.

More rigorous DFT calculations for the ring opening of THF-dimethanol were conducted on the Rh\textsubscript{200}Re\textsubscript{1}OH “cluster model” as shown in Fig. 3.8 B. The transition state structure that is shown for THF-dimethanol is very similar to that reported previously for 7; in that ring opening proceeds directly with a hydrogen transfer step. The presence of water molecules helps to stabilize the transition state via hydrogen bonding. The activation energy to carry this out on the Rh\textsubscript{200}Re\textsubscript{1}OH cluster in water was calculated to be 90 kJ/mol, which is also in a very good agreement with the barrier calculated previously for 7 (88 kJ/mol). This also agrees with the similar gas phase oxocarbenium ion formation energies for THF-dimethanol and 7.

The Rh\textsubscript{200}Re\textsubscript{1}OH and gas phase carbenium ion results both show that the extra –CH\textsubscript{2}OH group removed from the active C-O bond in THF-dimethanol does not influence its acid-catalyzed ring opening. As such, the mechanism and kinetics for the hydrogenolysis and ring opening of THF-dimethanol over Rh-ReO\textsubscript{x} based catalysts should be similar to that for 7 reported by Chia et al.\textsuperscript{[40]}, involving hydride transfer and oxocarbenium formation, Fig. 3.9.
Catalyst studies on the ring opening of tetrahydrofuran-dimethanol to 1,2,6-hexanetriol

Figure 3.8 A) DFT-calculated gas-phase reaction energies for the formation of the oxocarbenium ion intermediate (from 7 and THF-dimethanol); B) for the concerted ring opening-hydride transfer of 7 and THF-dimethanol at the acid site on the Rh$_{200}$Re$_{1}$OH cluster model.
3.3.6 Optimization studies on the best leads

The catalytic experiments presented in sections 3.3.3 indicate that both Rh-ReO$_x$/Fuji G6-3 SiO$_2$ and Rh-ReO$_x$/Wacker HDK$^\text{®}$ T40 SiO$_2$ are the most promising catalysts for the hydrogenolysis of 2 to 3 (Table 3.1). As a next step, the effect of important process variables like catalyst pre-reduction, temperature, and reaction time was investigated in more detail.

The effect of the reduction pretreatment was investigated by comparing catalyst performance for three different reactions conditions: (1) complete reaction including 1 h catalyst reduction, (2) a reaction without catalyst reduction, (3) a 1 h reduction pretreatment only. The results are provided in Table 3.9.

Table 3.9. Effect of the reduction pretreatment on the hydrogenolysis of 2 to 3 with Rh-ReO$_x$/Fuji G6-3 SiO$_2$ (HTCAT-5)$^a$.

<table>
<thead>
<tr>
<th>Conditions</th>
<th>%-conv.</th>
<th>%-sel. to 3</th>
<th>%-sel. to 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 h (10 bar) + 4 h (80 bar)</td>
<td>31</td>
<td>84</td>
<td>3</td>
</tr>
<tr>
<td>5 h (80 bar)</td>
<td>8</td>
<td>91</td>
<td>0</td>
</tr>
<tr>
<td>1 h (10 bar)</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

$^a$ $T = 120 \, ^\circ\text{C}$, catalyst = 25 wt%, solvent = water
The results indicate that the reduction pretreatment step is very important. When the reaction was performed without this step, the conversion dropped from 31 to 8%. On the other hand, it is also evident that no reaction occurs when only a reductive pretreatment is performed. Thus, the reduction at mild conditions is necessary to activate the catalyst. The XPS surface analysis with in-situ reduction showed that Rh was fully reduced whereas Re was partially reduced after the pretreatment condition described above. These results clearly show that the Rh-Re interactions, which are important for the catalytic activity, are only formed under mild hydrogenation conditions. Similar observations about the significant influence of the activation step have been pointed out by Dumesic, et al.\[40\].

Results with Rh-ReO_x/Fuji G6-3 SiO_2 and Rh-ReO_x/Wacker HDK-T40 SiO_2 at a range of reaction conditions are presented in Table 3.10. The first five entries are the results for the Fuji G6-3 silica based catalysts. Increasing the temperature from 120 to 180 °C or applying longer reaction times (20 instead of 4 h) led to a lower selectivity to 3. At those reaction conditions, 3 was further converted into 4 and 1,5-hexanediol (9). In addition, the reaction at 180 °C produced another byproduct 1,2-hexanediol (10). The reaction at 180 °C was also performed at a longer reaction time (20 h); a different effect compared to that at 120 °C was observed. The conversion was very high, however the selectivity to 3 and 4 dropped quite significantly. Interestingly, 1-hexanol (11) was detected under this reaction condition.

<table>
<thead>
<tr>
<th>Entry</th>
<th>T (°C)</th>
<th>t_2 (h)</th>
<th>Support</th>
<th>%-conv.</th>
<th>%-sel. to 3</th>
<th>%-sel. to 4</th>
<th>%-sel. to 9</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>120</td>
<td>4</td>
<td>G6-3</td>
<td>31</td>
<td>84</td>
<td>3</td>
<td>5</td>
</tr>
<tr>
<td>2</td>
<td>120</td>
<td>20</td>
<td>G6-3</td>
<td>53</td>
<td>76</td>
<td>10</td>
<td>9</td>
</tr>
<tr>
<td>3</td>
<td>180</td>
<td>4</td>
<td>G6-3</td>
<td>46</td>
<td>50</td>
<td>27</td>
<td>16</td>
</tr>
<tr>
<td>4</td>
<td>180</td>
<td>20</td>
<td>G6-3</td>
<td>88</td>
<td>34</td>
<td>18</td>
<td>15</td>
</tr>
<tr>
<td>5</td>
<td>80</td>
<td>20</td>
<td>G6-3</td>
<td>11</td>
<td>92</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>6</td>
<td>120</td>
<td>4</td>
<td>HDK-T40</td>
<td>55</td>
<td>77</td>
<td>15</td>
<td>5</td>
</tr>
<tr>
<td>7</td>
<td>120</td>
<td>20</td>
<td>HDK-T40</td>
<td>81</td>
<td>61</td>
<td>28</td>
<td>10</td>
</tr>
<tr>
<td>8</td>
<td>180</td>
<td>4</td>
<td>HDK-T40</td>
<td>83</td>
<td>54</td>
<td>30</td>
<td>15</td>
</tr>
</tbody>
</table>

\[^a\] P_1 = 10 bar, t_1 = 1 h, P_2 = 80 bar, catalyst = 25 wt%, solvent = water, Re/Rh = 0.5; \[^b\] G6-3 = 4 wt% Rh, HDK-T40 = 6.5 wt% Rh

From these results, it is obvious that 3 and 4 are the intermediate products, and are further converted to diols and mono-alcohols, the exact amount depending on the reaction conditions. If the aim is a highly selective synthesis of 3, high
temperatures should be avoided. Connected to this, the reaction at 80 °C for 20 h was performed. As expected, a very high selectivity to 3 (92%) was obtained though the conversion was low (11%). Thus, temperatures between 80 and 120 °C likely render an optimal selectivity of 3.

Figure 3.10 shows the conversion-selectivity relations using Rh-ReO\textsubscript{x}/Fuji G6-3 SiO\textsubscript{2} catalysts. The selectivity to 3 decreases at higher conversion levels, which is due to the subsequent reactions of 3 to other products (Figure 3.10). The highest selectivity to 3 (reaction at 80 °C) was obtained at the lowest conversion. On the other hand, the temperature of 180 °C gave the lowest selectivity to 3 though the conversion was very high.

![Figure 3.10](image)

**Figure 3.10.** Conversion-selectivity relation of the reaction of 2 to 3 using Rh-ReO\textsubscript{x}/Fuji G6-3 SiO\textsubscript{2} catalysts (HTCAT-5) under various reaction conditions as indicated in the graph.

Reactions with the Rh-ReO\textsubscript{x} catalysts supported on Wacker HDK-T40 SiO\textsubscript{2} were also performed (entries 6-8 in Table 3.10). In this case, a higher Rh content (6.5 wt%) was used. The effects of the reaction time and temperature were similar with those using Fuji G6-3 silica.
Based on the reaction product distribution, a reaction pathway for the hydrogenolysis of 2 using Rh-ReOₓ/SiO₂ catalysts is proposed, which is represented in Figure 3.11. The ring-opening hydrogenolysis of 2 leads to the selective production of 3. 3 is not inert under these conditions as 4 and 9 (major compounds) and 10 (minor compound) are formed by subsequent hydrodeoxygenation reactions. 11 was also detected in the reaction at 180 °C and 20 h and is likely formed from 10. This is consistent with the results reported by Chia et al. [40] who showed increased reactivity and selectivity for the activation of the secondary OH groups of 1,2 diols as a result of the increased stabilization of the carbenium ion intermediates by -CH₂OH groups at an α position.

\[ \text{Figure 3.11. Reaction pathway of the hydrogenolysis of 2 using Rh-ReO}_x/\text{SiO}_2 \text{ catalysts.} \]

### 3.4 Conclusions

Bimetallic heterogeneous catalysts on inorganic supports have been explored for the ring-opening hydrogenolysis of THF-dimethanol to 1,2,6-hexanetriol. Based on performance and catalyst characterization data, the reaction is best performed with a Rh-Re combination on a mesoporous silica support (G6-3 silica, ~6 nm average pore size) at an optimal composition of 4 wt% Rh and a molar Re/Rh ratio of 0.5. The reduction temperature profiles and XPS surface data indicate the formation of Rh-Re alloys with average particle sizes between 1.0-2.9 nm, the actual value being a strong function of the silica support. A clear relation between catalyst performance and average catalyst particle size was observed and the largest particle sizes in the range have the highest activity. As such, the development of Rh-ReOₓ catalysts with larger metal cluster sizes warrants further investigations. TPR and XPS surface analysis also evidenced the existence of close Rh and Re interactions. The Re⁰/Re⁵⁺ surface ratio correlates well with the conversion and shows a volcano dependency. Both gas phase as well as
Rh$_{200}$Re$_3$OH cluster DFT calculations support an acid-metal bifunctional mechanism for the hydrogenolysis of THF-dimethanol.

The most selective ring-opening reaction of THF-dimethanol to 1,2,6-hexanetriol (92% selectivity to 1,2,6-hexanetriol at 11% conversion) was obtained with a Rh-ReO$_x$/G6-3 silica at 80 °C, 80 bar, and a reaction time of 20 h. Thus, a highly selective ring-opening reaction for the synthesis of green 1,2,6-hexanetriol from the biomass-derived THF-dimethanol has been developed.

### 3.5 Acknowledgements

We would like to acknowledge ACTS-ASPECT for financial support to this research (ASPECT Project 053.62.017). Dr. Rudy Parton, Dr. Rob Meier (DSM), Dr. Peter Witte, Dr. Peter Berben (BASF), Dr. Annemarie Beers (Norit), Dr. Jean-Paul Lange (Shell) and Dr. Bart Zwijnenburg (Johnson Matthey) of the industrial steering committee are acknowledged for helpful discussions as well as Prof. Bob Davis (University of Virginia) for a stimulating discussion about their recent work during the NCCC-XIII conference in Noordwijkerhout (The Netherlands).

### 3.6 References

Catalyst studies on the ring opening of tetrahydrofuran-dimethanol to 1,2,6-hexanetriol


Caprolactam from Renewable Resources: Catalytic Conversion of 5-Hydroxymethylfurfural into Caprolactone


Material Studio, V. 4.0; Accelrys, Inc.: San Diego, CA, 2010.


Catalyst studies on the ring opening of tetrahydrofuran-dimethanol to 1,2,6-hexanetriol

Chapter 4
From 5-Hydroxymethylfurfural (HMF) to Polymer Precursors: Catalyst Screening Studies on the Conversion of 1,2,6-hexanetriol to 1,6-hexanediol


Abstract

1,6-hexanediol (1) is an important polymer precursor for the polyester industry. In this paper, exploratory catalyst screening studies on the synthesis of 1 from 1,2,6-hexanetriol (2) are described via two different routes. The latter is available by a two-step procedure from 5-hydroxymethylfurfural (HMF, 3), a promising bio-based platform chemical. In the first approach, the direct catalytic hydrodeoxygenation of 2 to 1 with heterogeneous catalysts and molecular hydrogen was explored. Best results were obtained using a Rh–ReOx/SiO2 catalyst in water (180 °C, 80 bar H2, 20 h reaction time), leading to full conversion of 2 and 73 % selectivity to 1, the main byproduct being 1,5-hexanediol (4). In a second approach, 2 was first converted to tetrahydropyran-2-methanol (2-THPM, 5) in quantitative yield using triflic acid as catalyst (125 °C, 30 min). Various catalysts were explored for the subsequent ring opening/hydrodeoxygenation of 5 to 1 using a hydrogenation protocol and the best results were obtained with a Rh–ReOx/SiO2 catalyst, viz. 96 % selectivity to 1 at 26 % conversion (120 °C, 80 bar H2, 20 h).
4.1 Introduction

1,6-hexanediol (1) is an important chemical for use in the production of high performance polyesters, polyurethane resins, and adhesives [1]. In 2000, the worldwide production volume of 1 was about 33,000 ton/year [2]. The major route to 1 involves the hydrogenation of adipic acid or its esters (e.g., dimethyl adipate) using heterogeneous catalysts based on carbon supported Ru-Pt-Sn [3-5], Cu-Cr-Ba oxide [6], Sn-modified Raney Ru [7], various copper-based catalysts [8-9], CuO/ZnO/Al₂O₃ [10-14], and RuSn/Al₂O₃ [15-16] (Equation 4.1).

\[
\begin{array}{c}
\text{adipic acid or} \\
methyl adipate \\
H_2 \\
cat. \\
\text{1}
\end{array}
\]  
(eq 4.1)

Our interest in this field concerns the synthesis of green 1,6-hexanediol from renewable resources. We have recently shown the proof of principle for the reaction of hydroxymethylfurfural HMF (3) to 1 via THF-dimethanol (THFDM) and 1,2,6-hexanetriol (2) as the intermediates (Eq. 4.2) [17].

\[
\begin{array}{c}
\text{3} \\
H_2 \\
cat. \\
\text{THFDM} \\
\text{2} \\
H_2 \\
cat. \\
\text{1}
\end{array}
\]  
(eq 4.2)

HMF is considered to be a promising bio-based platform chemical and is regarded as a “sleeping giant” in the field of intermediate chemicals from renewable resources [18]. It is accessible by acid-catalyzed dehydration of the C6-sugars (e.g., D-glucose, D-fructose, and D-mannose) present in lignocellulosic biomass. HMF derivatives like dimethylfuran [19-21] and its ethers such as methoxymethylfurfural and ethoxymethylfurfural [22] have potential as fuel additives, whereas 2,5-furandicarboxylic acid (FDCA) [23-31], and tetrahydrofuran-dimethanol (THFDM) may serve as building blocks in advanced polymers [32-38].

Here we report catalytic screening studies on the synthesis of the diol 1 from triol 2. The reaction involves the selective removal of a secondary alcohol in the presence of two primary alcohols. A well-known approach involves catalytic
hydrodeoxygenation using heterogeneous catalysts and, in most cases, molecular hydrogen. Examples for structurally related alcohols like 1,2-propanediol (6), 1,2-butanediol (7), 1,2-pentanediol (8), and 1,2-hexanediol (9) are provided in Table 4.1.

Table 4.1. Overview of catalytic reactions involving selective removal of secondary alcohol group in the presence of primary alcohol groups

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Catalyst</th>
<th>T (°C)</th>
<th>P H₂ (bar)</th>
<th>t (h)</th>
<th>%-conv.</th>
<th>%-selectivity</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>Pt/WO₃/ZrO₂</td>
<td>140</td>
<td>40</td>
<td>24</td>
<td>91</td>
<td>90</td>
<td>[39]</td>
</tr>
<tr>
<td>6</td>
<td>Rh/SiO₂ a</td>
<td>120</td>
<td>80</td>
<td>10</td>
<td>18</td>
<td>57</td>
<td>[40]</td>
</tr>
<tr>
<td>6</td>
<td>Rh/SiO₂</td>
<td>120</td>
<td>80</td>
<td>10</td>
<td>10</td>
<td>67</td>
<td>[40]</td>
</tr>
<tr>
<td>6</td>
<td>Rh-ReOₓ/SiO₂</td>
<td>120</td>
<td>80</td>
<td>24</td>
<td>87</td>
<td>74</td>
<td>[41]</td>
</tr>
<tr>
<td>6</td>
<td>Ir-ReOₓ/SiO₂ b</td>
<td>120</td>
<td>80</td>
<td>24</td>
<td>72</td>
<td>85</td>
<td>[42]</td>
</tr>
<tr>
<td>6</td>
<td>CeO₂ c</td>
<td>375</td>
<td>-</td>
<td>n.a.</td>
<td>11</td>
<td>23</td>
<td>[43]</td>
</tr>
<tr>
<td>7</td>
<td>Rh-ReOₓ/C</td>
<td>120</td>
<td>34</td>
<td>4</td>
<td>15</td>
<td>78</td>
<td>[44]</td>
</tr>
<tr>
<td>7</td>
<td>CeO₂ c</td>
<td>375</td>
<td>-</td>
<td>n.a.</td>
<td>16</td>
<td>17</td>
<td>[43]</td>
</tr>
<tr>
<td>8</td>
<td>Rh-ReOₓ/C</td>
<td>120</td>
<td>34</td>
<td>4</td>
<td>9</td>
<td>88</td>
<td>[44]</td>
</tr>
<tr>
<td>9</td>
<td>Rh-ReOₓ/C</td>
<td>120</td>
<td>34</td>
<td>4</td>
<td>12</td>
<td>80</td>
<td>[44]</td>
</tr>
<tr>
<td>9</td>
<td>Rh-ReOₓ/C</td>
<td>120</td>
<td>34</td>
<td>4</td>
<td>12</td>
<td>80</td>
<td>[44]</td>
</tr>
<tr>
<td>9</td>
<td>Rh-ReOₓ/SiO₂</td>
<td>100</td>
<td>80</td>
<td>24</td>
<td>76</td>
<td>73</td>
<td>[45]</td>
</tr>
</tbody>
</table>

a with Amberlyst-15; b with sulfuric acid; c no solvent

Bimetallic catalysts based on Rh-Re, Ir-Re, and Pt-W have shown to be very promising catalysts and selectivities between 73 and 90% are reported. In some cases soluble acids (e.g. sulfuric acid) were added to improve catalytic conversions. There are also reports on the use of homogeneous ruthenium catalysts in combination with triflic acid (HOTf) and sulfolane as the solvent for the selective removal of secondary alcohol in the presence of a primary alcohol. For example, Schlaf et al. [51] reported the production of 1-propanol from 6 using \{[Cp*Ru(CO)²(µ-H)]²⁺OTf\} (52 bar H₂, 110 °C, 30 h) and obtained 92% conversion with 54% selectivity to 1-propanol. Better results were obtained using \{cis-Ru(6,6'-Cl₂-bipy)₂(OH₂)₂(CF₃SO₃)₂\} (48 bar H₂, 125 °C, 48 h), giving 63% yield of 1-propanol.

While preparing this manuscript, Dumesic et al. [44] reported hydrodeoxygenation reaction of various diols and triols using bimetallic Rh-ReOₓ catalysts on carbon supports. When using 2 as the substrate, 1 was obtained in 99.9% at 8% conversion (120 °C, 34 bar, 4 h). Prolonged reaction times (14 h)
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resulted in improved conversions (59%), though, the selectivity to 1 was reduced considerably (62%).

In this paper, a screening study on the conversion of 1,2,6-hexanetriol to 1,6 hexanediol using a hydrodeoxygenation approach is reported. Emphasis is on the use of bimetallic Rh-Re complexes on different supports, though monometallic catalysts have been tested as well, and the results will be compared.

4.2 Materials and methods

4.2.1 Materials

1 (97%) and tetrahydrofuran-2-methanol 5 (98%) were purchased from Aldrich. 2 (> 97%) was purchased from Acros. 1-propanol (> 99%) was purchased from Merck Chemicals. Sulfolane (99%) was purchased from Aldrich. Triflic acid (99%), para-toluenesulfonic acid monohydrate (> 98.5%), aluminum chloride hexahydrate (> 99%), copper triflate (98%), and potassium carbonate (99%) were purchased from Aldrich.

Copper chromite catalysts were kindly supplied by BASF (Cu-1985P) and Sud-Chemie (T-4419), as well as purchased from Aldrich (product number: 209325). Copper zinc PRICAT CZ/A P and PRICAT CZ/B P catalysts were kindly supplied by Johnson Matthey. Copper zinc T-2130 was kindly supplied by Sud-Chemie. Ru/C (5% w/w), Ru/Al₂O₃ (5% w/w), Pt/C (5% w/w), Rh/C (5% w/w), Rh/Al₂O₃ (5% w/w), Pd/C (5% w/w), and Pd/Al₂O₃ (5% w/w) were purchased from Aldrich. RuCl₃ was purchased from Strem. Ru/TiO₂ (5% w/w) was purchased from Degussa and a supported nickel catalyst G-69B was kindly supplied by Sud-Chemie. RhCl₃·nH₂O (Rh 38-40%), ammonium perrhenate (> 99%), ammonium molybdate tetrahydrate (MoO₃ 81-83%) were purchased from Aldrich while tinchloride dihydrate (> 98%) was purchased from Riedel-de Haën. Ammonium tungsten oxide (> 99.99%) was purchased from Alfa Aesar. CARiACT G-6 3 micron silica was donated by Fuji Silysia, TiO₂ (product number: 14021), SiO₂-Al₂O₃ (grade 135), and activated carbon (product number: 484164) were purchased from Aldrich. γ-Al₂O₃ (product number: 044658) was purchased from Alfa Aesar. Hydrogen gas (> 99.9999%) was purchased from Hoek Loos.
4.2.2 Methods

4.2.2.1 General procedure for the preparation of the bimetallic Rh-ReOₓ catalysts

All catalyst preparations were carried out in air. An aqueous solution of RhCl₃.nH₂O (176 mg, 0.8 mmol) in water (5 mL) was added to silica (2 g, Fuji CARiACT G-6 3 micron; BET surface area 529 m²g⁻¹ and pore volume 0.617 cm³g⁻¹) and stirred for 2 h at room temperature. After drying at 383 K for 13-14 h, the solid was added to an aqueous solution of ammonium perrhenate (113 mg, 0.4 mmol) in water (5 mL) and stirred for 2 h, followed by drying at 383 K for 13-14 h. Calcination in air at 773 K for 3 h gave the catalyst containing 4 wt% of Rh and a Re/Rh molar ratio of 0.5.

The same procedure was used for the preparation of other Rh-based bimetallic catalysts, except for Rh-ReOₓ/C, where the calcination step was omitted. Ammonium molybdate tetrahydrate (131 mg, 0.1 mmol), ammonium tungsten oxide (30 mg, 0.1 mmol), and tin chloride dihydrate (94 mg, 0.4 mmol) were used for preparing the Rh-MoOₓ/SiO₂, Rh-WOₓ/SiO₂, and Rh-SnOₓ/SiO₂ catalysts.

4.2.2.2 Reaction procedure for the catalyst screening study of 2 to 1 in 1-propanol

2 (100 mg, 0.75 mmol), catalyst (10 mg), 1-propanol (2 mL), and a Teflon stirring bar were added to an 8 mL glass vial capped with a septum, which was punctured with a short needle. The vial was placed in a stainless-steel autoclave, the autoclave was closed and stirring was started at 1000 rpm. After three times pressurizing with first nitrogen and then hydrogen, the autoclave was pressurized with hydrogen to 10 bar and the temperature was raised to 180 °C. After 1 h, the pressure was raised to 80 bar and the reaction was continued for 3 h. Then, the autoclave was allowed to cool to ambient temperature and the pressure was released. The reactor content was filtered to remove the catalyst and the filtrate was subjected to GC analysis.

4.2.2.3 Reaction of 2 to 1 using CuCr catalysts at an elevated temperature

2 (500 mg, 4 mmol) dissolved in 1-propanol (30 mL) and a CuCr catalyst (100 mg) were added to a 100 mL stainless steel autoclave (Parr). The reactor was flushed three times with nitrogen and subsequently with hydrogen. After flushing, the reactor was pressurized to 100 bar, and the reaction mixture was stirred (1000 rpm) and heated to 260 °C for 6 h. Then, the autoclave was allowed to cool to ambient temperature and the pressure was released. Product mixtures were filtered to remove the catalyst and the filtrate was subjected to GC analysis.
4.2.2.4 General reaction procedure for the reaction of 2 to 1 in water

2 (100 mg, 0.75 mmol), the Rh-ReO$_x$/SiO$_2$ catalyst (10 mg), water (2 mL), and a Teflon stirring bar were added to an 8 mL glass vial capped with a septum, which was pierced by a short needle. The vial was placed in a stainless-steel autoclave, the autoclave was closed and stirring was started at 1000 rpm. After three times pressurizing with first nitrogen and then hydrogen, the autoclave was pressurized with hydrogen to 10 bar and the temperature was raised to 180 °C. After 1 h, the pressure was raised to 80 bar and the reaction was continued for 3 h. Then, the autoclave was allowed to cool to ambient temperature and the pressure was released. The reactor content was filtered to remove the catalyst and the filtrate was subjected to GC analysis.

4.2.2.5 Cyclization of 2 to 5

In a 100 mL three-neck round bottom flask, 2 (3.354 g, 25 mmol) was dissolved in sulfolane (25 mL). Then, triflic acid (13.3 µL, 0.15 mmol) was added and the reaction mixture was heated to 125 °C for 30 minutes. The reaction mixture was cooled and analysed using GC-FID, GC-MS, and $^1$H- and $^{13}$C-NMR.

4.2.2.6 General procedure for the reaction of 5 to 1 in water

The procedure described here is for the Rh-ReO$_x$/SiO$_2$ catalyst. The same procedure was used for all other catalysts. 5 (100 mg, 0.9 mmol), the Rh-ReO$_x$/SiO$_2$ catalyst (10 mg), water (2 mL), and a Teflon stirring bar were added to a glass vial and the hydrogenation was performed as described above for the hydrogenolysis of 2, except that the content was stirred for 3.5 h at 80 bar instead of 3 h. Product mixtures were filtered to remove the catalyst and the filtrate was subjected to GC analysis.

4.2.2.7 Product analyses

Gas chromatography using a CP-WAX57CB column (25 m length, 0.2 mm internal diameter, and 0.25 µm film thickness) and a flame ionization detector (GC-FID) was used for product identification and quantification. The injector and the detector temperature were set at 250 °C. The oven temperature was kept at 40 °C for 5 minutes then heated up to 180 °C with a heating rate of 5 °C/min and to 230 °C with a heating rate of 10 °C/min and kept at this temperature for 15 minutes. A split ratio of 50 was used. Helium was used as the carrier gas with a flow rate of 1.1 ml/min. Toluene was used as an internal standard for the GC analysis.
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4.3 Results and discussion

4.3.1 One-step conversion of 2 to 1

4.3.1.1 Exploratory catalyst screening studies

A wide range of catalysts were screened for the catalytic hydrodeoxygenation of 2 to 1 in 1-propanol as the solvent (180 °C, 3 h, 80 bar) including CuCr (three types), CuZn (three types), Ru-based catalysts (Ru/C, Ru/TiO₂, Ru/Al₂O₃), Rh-based catalysts (Rh-ReOₓ/SiO₂, Rh/C, Rh/Al₂O₃, Rh/SiO₂), Pd-based catalysts (Pd/Al₂O₃, Pd/C), Pt/C, and Ni/kieselguhr (promoted with zirconium). Most of the catalysts were not active at this reaction condition, the only exceptions being Ru/C and the bimetallic Rh-ReOₓ on silica. Activity though, was very low and the conversion of 2 was less than 10% (5% for Rh-ReOₓ/SiO₂ and 8% for Ru/C) with a selectivity to 1 of 57% for Rh-ReOₓ/SiO₂ and 56% for Ru/C. The byproduct for the reaction with Rh-ReOₓ/SiO₂ catalyst was the undesired 1,5-hexanediol 4 (Eq. 4.3), byproducts for the reaction with Ru/C were not identified. It is clear that both Ru/C and Rh-ReOₓ/SiO₂ showed similar performance.

The screening studies revealed that CuCr catalyst were not active under the prevailing reaction conditions. This is remarkable as Utne and co-workers reported the use of copper chromite catalyst for the direct conversion of THFDM to 1, most likely also involving 2 as an intermediate. However, reaction conditions used by Utne (300 °C and 380 bar) to obtain 40-50% yield of 1 were far more severe than used here [53]. Thus, additional experiments were performed with CuCr (BASF) at elevated temperatures and pressures (260 °C, 100 bar, 6 h, 1-propanol) using 2 as the substrate. At these conditions, the catalyst is indeed active and 93% conversion of 2 was achieved. The selectivity to 1, though, was relatively low.
90

(46%), giving a yield of 43%, in the same range as observed by Utne under more severe conditions. Byproducts were the diol 4 (25%), tetrahydropyran-2-methanol (5, 11%), 1-hexanol (10, 10%), and 1,5-pentanediol (11, 8%) (Eq. 4.4).

![Chemical structure](eq 4.4)

**4.3.1.2 Detailed studies using bimetallic Rh-Re catalysts**

Further investigations aimed to increase the yield of 1,6-hexanediol were performed using bimetallic Rh-Re catalysts on various supports in water as solvent (Table 4.2).

<table>
<thead>
<tr>
<th>Cat. system</th>
<th>%-conv.</th>
<th>%-sel. to 1</th>
<th>%-sel. to 4</th>
<th>%-sel. to others</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rh-ReOₓ/SiO₂ &lt;sup&gt;b&lt;/sup&gt;</td>
<td>5</td>
<td>57</td>
<td>28</td>
<td>15</td>
</tr>
<tr>
<td>Rh-ReOₓ/SiO₂</td>
<td>17</td>
<td>73</td>
<td>27</td>
<td>0</td>
</tr>
<tr>
<td>Rh-ReOₓ/SiO₂ + γ-Al₂O₃</td>
<td>22</td>
<td>69</td>
<td>24</td>
<td>7</td>
</tr>
<tr>
<td>Rh-ReOₓ/SiO₂·Al₂O₃</td>
<td>7</td>
<td>66</td>
<td>19</td>
<td>15</td>
</tr>
<tr>
<td>Rh-ReOₓ/SiO₂·Al₂O₃&lt;sup&gt;c&lt;/sup&gt;</td>
<td>20</td>
<td>76</td>
<td>18</td>
<td>6</td>
</tr>
<tr>
<td>Rh-ReOₓ/γ-Al₂O₃</td>
<td>3</td>
<td>38</td>
<td>22</td>
<td>40</td>
</tr>
<tr>
<td>Rh-ReOₓ/SiO₂ + K₂CO₃</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td>K₂CO₃</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>100</td>
</tr>
</tbody>
</table>

<sup>a</sup> T = 180 °C, P₁ = 10 bar, t₁ = 1 h, P₂ = 80 bar, t₂ = 3 h, catalyst = 10 wt%, solvent = water;  <sup>b</sup> solvent = 1-propanol;  <sup>c</sup> t₂ = 20 h

The conversion and selectivity to 1 were considerably higher in water than in 1-propanol, the solvent in the screening study. These differences in catalytic performances may be due to competitive adsorption of the solvent (1-propanol)
and the substrate on the ReO\textsubscript{x} clusters. Tomishige et al. \cite{54} proposed a mechanism for the reaction of THF-alcohol to 1,5-pentanediol using Rh-Re catalysts. It involves coordination of the OH group of the substrate to Re and subsequent hydrogenolysis of the C-O bond by the neighboring Rh centre. Thus, it is possible that water is bound more weakly to Re than 1-propanol, leading to enhanced reaction rates.

The possible positive effects of enhanced acidity on catalyst performance, as observed in the literature (Table 4.1), was probed by investigating the use of more acidic supports, either by using bimetallic Rh-Re catalyst on \(\gamma\)-alumina and mixed silica-alumina supports or the addition of \(\gamma\)-alumina to a bimetallic Rh-Re catalyst on silica. The use of Rh-Re catalyst on alumina for alcohol deoxygenation studies has to the best of our knowledge not been reported before.

Reactions using Rh-Re on silica in combination with alumina (without Rh-Re), led to slightly higher conversions than for the reaction in the absence of alumina (22 vs. 17\%), though the selectivity to 1 was slightly reduced (69\% vs. 73\%). Thus, it seems that catalyst activity is positively affected by the addition of alumina.

Reactions at standard conditions with a Rh-Re catalyst on a mixed silica-alumina support led to considerably lower conversions compared to the silica only catalyst (7 vs. 17\%). Further prolongation of the reaction time to 20 h led to 20\% conversion with 76\% selectivity to 1. The selectivity at this conversion level is similar to that of the silica only catalyst. Thus, the use of mixed alumina-silica supports leads to a considerable reduction in catalyst activity, though the selectivity is comparable with that of silica at similar conversion levels. Apparently, silica is essential for high catalyst activity.

The use of a bimetallic Rh-Re catalyst on \(\gamma\)-alumina led to low catalyst activities (3\% conversion vs. 17\% for silica), in line with the results for the mixed silica-alumina catalyst. Thus, the use of alumina instead of silica or partial substitution of silica by alumina has a negative effect on catalyst performance.

Experiments with the standard Rh-Re catalyst on silica in the presence of K\textsubscript{2}CO\textsubscript{3} gave a negligible conversion at standard conditions, an indication that bases have a negative effect on the reaction rates. Similar observations were reported by Dumesic and co-workers \cite{44} for the conversion of 5 using Rh-ReO\textsubscript{x} catalysts on carbon in the presence of 0.1 M NaOH (120 °C, 34 bar H\textsubscript{2}, 4 h).

The effects of the process conditions (temperature, reaction time) on the hydrogenation of 2 were investigated using the Rh-Re on silica catalyst (Table 4.3). Temperature has a profound effect on catalyst activity and conversions of 2 increased from 9\% to near quantitative conversion at 180°C for reaction times of 20-24 h. The almost constant selectivity to 1 at the different conversion levels (67-73\%) is remarkable. It suggests that the activation energy for the desired reaction to 1 is rather similar to that of the undesired reaction to 4.
Table 4.3. Effect of process conditions on reaction of 2 to 1 using a Rh-ReOx/SiO2 catalyst

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>t2 (h)</th>
<th>%-conv.</th>
<th>%-sel. to 1</th>
<th>%-sel. to 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>120</td>
<td>24</td>
<td>9</td>
<td>67</td>
<td>19</td>
</tr>
<tr>
<td>150</td>
<td>20</td>
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<td>3</td>
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<td>27</td>
</tr>
<tr>
<td>180</td>
<td>20</td>
<td>100</td>
<td>73</td>
<td>28</td>
</tr>
</tbody>
</table>

* * P1 = 10 bar, t1 = 1 h, P2 = 80 bar, catalyst = 10 wt%, solvent = water

4.3.2 Two-step synthetic approach via tetrahydroxyran-2-methanol

Experiments on the conversion of 2 using CuCr catalysts in 1-propanol at elevated pressures and temperatures (vide supra) resulted in the formation of tetrahydroxyran-2-methanol 5 as a side product (Eq. 4.4). This compound may be considered as an intermediate in the reaction sequence, as it is formed by an intramolecular etherification of 2, and a ring opening reaction could either lead to diol 1 or 9 (Eq. 4.5). This observation triggered us to perform additional catalytic hydrogenation experiments using 5 as the starting material.

\[
\begin{align*}
\text{HO} & \quad \text{OH} \\
\text{HO} & \quad \text{HO} \\
\text{HO} & \quad \text{HO} \\
\text{2} & \quad \text{O} \\
& \quad \text{OH} \\
\end{align*}
\]

\[
\begin{align*}
\text{HO} & \quad \text{OH} \\
\text{OH} & \quad \text{OH} \\
\text{HO} & \quad \text{OH} \\
\text{5} & \quad \text{OH} \\
& \quad \text{OH} \\
\end{align*}
\]

\[
\begin{align*}
\text{HO} & \quad \text{OH} \\
\text{OH} & \quad \text{OH} \\
\text{HO} & \quad \text{OH} \\
\text{1} & \quad \text{O} \\
& \quad \text{OH} \\
\end{align*}
\]

\[
\begin{align*}
\text{HO} & \quad \text{OH} \\
\text{OH} & \quad \text{OH} \\
\text{HO} & \quad \text{OH} \\
\text{9} & \quad \text{OH} \\
& \quad \text{OH} \\
\end{align*}
\]

(eq 4.5)

Synthetic methodology for the synthesis of 5 has been reported, examples are the oxidative cyclization reaction of 5-hexen-1-ol [55-57] using TS-1 (60 °C, 6 h) [55-56] or a PNIPAAm-PW12O403- complex (60 °C, 6 h) [57] to give 90% and 70% yield of 5, respectively. The synthesis of 5 from 2 [58] using BuSnCl3 as the catalyst (230 °C, 3 h) has also been explored and 5 was obtained in 60% yield.

An improved synthetic procedure was developed by us involving the acid catalysed ring-closure of 2 by triflic acid in sulfolane at 125 °C. After 30 min, conversion was quantitative and 5 was the sole product (GC and GC-MS), indicating that it is a very viable alternative for the synthetic methodology using n-butyltin trichloride.
A wide range of catalysts was screened for the catalytic hydrogenolysis reaction of pyran 5 to 1 using hydrogen gas (180 °C, 80 bar, 3.5 h, water as solvent). Ru-based catalysts (Ru/C, Ru/Al₂O₃), Pd-based catalysts (Pd/C, Pd/Al₂O₃), Cu-based catalysts (CuCr, CuZn), Rh-based catalysts (Rh/C, Rh/SiO₂, Rh/Al₂O₃), Pt/C, and Ni/kieselguhr (promoted with zirconium) were not active at the prevailing reaction conditions. More promising results were obtained with bimetallic Rh-based catalysts on various supports (Table 4.4).

Four catalysts (Rh-ReOₓ/SiO₂, Rh-ReOₓ/TiO₂, Rh-ReOₓ/SiO₂-Al₂O₃, Rh-MoOₓ/SiO₂) gave up to 5-12% conversion with 100% selectivity to 1. The activity is a function of the support type and best results were obtained with titania. Surprisingly, the Rh-ReOₓ on carbon catalyst is inactive, an observation not in line with literature data [44-45]. Tomishige [45] reported 36% conversion with 97% selectivity to 1 (100 °C, 80 bar, 24 h) whilst Dumesic [44] obtained 27% conversion with 97% selectivity to 1 (120 °C, 34 bar, 4 h) using carbon supported catalysts. A possible explanation is the use of different catalyst preparation protocol. We did not perform a calcination step after catalyst synthesis to avoid partial destruction of the C support.

Replacement of Re in the bimetallic Rh-Re catalysts with other metals only lead to an active catalyst in case of Mo. W and Sn promoted Rh-catalysts were not active.

Table 4.4. Results for catalyst screening study on the conversion of pyran 5 to diol 1

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>%-conv.</th>
<th>%-sel. to 1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rh-ReOₓ/SiO₂</td>
<td>8</td>
<td>100</td>
</tr>
<tr>
<td>Rh-ReOₓ/TiO₂</td>
<td>12</td>
<td>100</td>
</tr>
<tr>
<td>Rh-ReOₓ/Al₂O₃</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Rh-ReOₓ/C</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Rh-ReOₓ/SiO₂-Al₂O₃</td>
<td>5</td>
<td>100</td>
</tr>
<tr>
<td>Rh-MoOₓ/SiO₂</td>
<td>9</td>
<td>100</td>
</tr>
<tr>
<td>Rh-WOₓ/SiO₂</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Rh-SnOₓ/SiO₂</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

² T = 180 °C, P₁ = 10 bar, t₁ = 1 h, P₂ = 80 bar, t₂ = 3.5 h, catalyst = 10 wt%, water; ² Mo to Rh molar ratio of 0.91; ² W to Rh molar ratio of 0.13
Further improvements in catalytic performance were explored by variation of the Rh content of the catalyst at a fixed Rh-Re ratio and the results are provided in Table 4.5. Higher Rh content (6.5 wt%) led to higher conversions but the selectivity to \( \mathbf{1} \) decreased from 100% to 71%. Also a reaction using this catalyst was performed with a higher catalyst intake (20 wt%) on substrate. Essential quantitative conversion was obtained (96%), however the selectivity to \( \mathbf{1} \) was only 55%, the main byproduct being 1,2-hexandiol (9).

Table 4.5. Conversion of pyran \( \mathbf{5} \) to diol \( \mathbf{1} \) using Rh-ReO\(_x\)/SiO\(_2\) catalysts with various Rh contents and catalyst intakes

<table>
<thead>
<tr>
<th>Conditions</th>
<th>%-conv.</th>
<th>%-sel. to ( \mathbf{1} )</th>
<th>%-sel. to 9</th>
</tr>
</thead>
<tbody>
<tr>
<td>4 wt% Rh, 10 wt% cat.</td>
<td>8</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td>6.5 wt% Rh, 10 wt% cat.</td>
<td>62</td>
<td>71</td>
<td>0</td>
</tr>
<tr>
<td>6.5 wt% Rh, 20 wt% cat.</td>
<td>96</td>
<td>55</td>
<td>35</td>
</tr>
</tbody>
</table>

The effect of reaction conditions and particularly reaction time and temperature on catalyst performance of the Rh-Re/silica catalyst was determined (Table 4.6). A low conversion, though with 100% selectivity to \( \mathbf{1} \) was obtained at 120 °C. Prolonged reaction times (20 h) at this temperature gave 26% conversion with 96% selectivity to \( \mathbf{1} \). At elevated temperatures (180 °C) and 20 h reaction time, 86% conversion was obtained, though the selectivity to \( \mathbf{1} \) dropped to 46%. Thus, the most promising result was obtained at 120 °C and 20 h reaction time leading to a high selectivity to \( \mathbf{1} \) (96%) at a reasonable conversion (26%).

Table 4.6. Reaction of \( \mathbf{5} \) to \( \mathbf{1} \) using Rh-ReO\(_x\)/SiO\(_2\) at different reaction conditions

<table>
<thead>
<tr>
<th>( T ) (°C)</th>
<th>( t_2 ) (h)</th>
<th>%-conv.</th>
<th>%-sel. to ( \mathbf{1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>180</td>
<td>3.5</td>
<td>62</td>
<td>71</td>
</tr>
<tr>
<td>120</td>
<td>3.5</td>
<td>7</td>
<td>100</td>
</tr>
<tr>
<td>120</td>
<td>20</td>
<td>26</td>
<td>96</td>
</tr>
<tr>
<td>180</td>
<td>20</td>
<td>86</td>
<td>46</td>
</tr>
</tbody>
</table>

\( ^a \) \( P_1 = 10 \) bar, \( t_1 = 1 \) h, \( P_2 = 80 \) bar, catalyst = 10 wt%, solvent = water
4.4 Conclusions

The catalytic synthesis of 1,6-hexanediol from 1,2,6-hexanetriol using a hydrodeoxygenation approach with heterogeneous catalysts has been explored. Various catalysts have been tested and Rh-ReO$_x$/SiO$_2$ catalysts were found to be the best. Two approaches were explored, a one pot approach and a two-step approach using tetrahydropyran-2-methanol 5 as the intermediate, see Eq. 4.6 for details.

![One-step approach diagram](image1)

The one-step approach gave a maximum yield of 1 of 73% at full conversion of 2. The first step in the two step approach was achieved in essentially quantitative yields. For the second step, the ring opening of 5 to diol 1, the Rh-Re catalyst showed excellent selectivity (96%), though at a relatively low conversion level (26%). Thus, when aiming for an overall high selectivity, as preferred for bulk-chemical processes with elaborate recycle streams, the two step approach seems preferred.

4.5 Acknowledgement

We would like to thank ACTS-ASPECT for providing a grant to perform this research (ASPECT Project 053.62.017), and Rudy Parton, Rob Meier (DSM), Peter Witte, Peter Berben (BASF), Annemarie Beers (Norit), Jean Paul Lange (Shell), and Bart Zwijnenburg (Johnson Matthey) for stimulating discussions and supply of the catalysts.
4.6 References

From 5-Hydroxymethylfurfural (HMF) to Polymer Precursors: Catalyst Screening Studies on the Conversion of 1,2,6-hexanetriol to 1,6-hexanediol

Caprolactam from Renewable Resources: Catalytic Conversion of 5-Hydroxymethylfurfural into Caprolactone

Chapter 5

1,6-Hexanediol from Renewable Resources: Catalytic Ring Opening and Hydro(deoxy)genation of Tetrahydrofuran-dimethanol (THF-dimethanol) using Bimetallic Rh-Re Catalysts in Combination with Solid Acid Catalysts

- Submitted to Catalysis Science & Technology

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Abstract

1,6-hexanediol is an important bulk commodity monomer for the polyester and polyurethane industry. In this chapter, a catalyst screening study on the one-pot synthesis of 1,6-hexanediol from THF-dimethanol (THFDM), a biomass-derived compound, by a hydrodeoxygenation approach using a range of monometallic (Ru/C, Rh/C, Pt/C, and Raney Ni), bimetallic Cu (CuCr, CuZn), and Rh/Re-based catalysts is reported. Best results were obtained using the Rh-Re catalyst on a SiO₂ carrier in combination with a solid acid catalyst in the form of Nafion® SAC-13. Full conversion of THFDM and 86% selectivity to 1,6-hexanediol was obtained at mild reaction conditions (120-150 °C, 80 bar, water). The main byproduct was 1,5-hexanediol. A reaction network based on intermediates (a.o. 1,2,6-hexametriol) and byproduct formation is proposed.
5.1 Introduction

1,6-Hexanediol (1,6-HD) is an important commodity monomer for the synthesis of polyesters and polyurethanes. The estimated global production in 2007 was about 70000 ton/year [1]. 1,6-Hexanediol is commonly produced by the hydrogenation of adipic acid or its esters (e.g. methyl adipate) using heterogeneous catalysts [2-15].

There is a clear incentive to develop efficient catalytic pathways for the production of important monomers in the polymer industry using renewable starting materials. In this respect, carbohydrates like cellulose, starch and hemicellulose have high potential. The US Department of Energy (DOE) has issued reports with in depth analyses on important carbohydrate derived building blocks for use as starting material for the synthesis of biobased products and materials [16]. One of the building blocks with high application potential is 5-hydroxymethylfurural (HMF). HMF is accessible in high yield from D-fructose by various catalytic conversions [17-20].

Our interest involves the use of HMF for the synthesis of polymer precursors and particularly 1,6-hexanediol, caprolactone, and caprolactam [21]. For 1,6-hexanediol synthesis from HMF, a reaction scheme involving a sequence of hydrogenation/hydrodeoxygenation reactions was anticipated (Eq. 5.1).

\[
\begin{align*}
\text{HMF} & \xrightarrow{\text{cat, } H_2} \text{THF-dimethanol} \\
\text{THF-dimethanol} & \xrightarrow{\text{cat, } H_2} \text{1,6-HD}
\end{align*}
\]

(eq 5.1)

The direct synthesis of 1,6-hexanediol from HMF has been studied by Utne, et al. [22]. A 30% yield of 1,6-hexanediol was obtained when the reaction was performed at severe conditions (380 bar, 280 °C, 11 h) in methanol using hydrogen as the reductant and a mixture of Pd/C and copper chromite as the catalyst. Better results were obtained by Utne when starting with the intermediate THF-dimethanol (THFDM) [23]. When using copper chromite catalysts in combination with molecular hydrogen, 50% yield of 1,6-hexanediol was reported, though details are lacking in the patent. The main drawback is the extreme conditions (300 °C and 380 bar pressure).

Of relevance for this research are recent reports on the catalytic ring opening of substituted tetrahydrofurans like tetrahydrofurfurylalcohol (THF-alcohol) into 1,5-pentanediol (Eq. 5.2)
Active catalysts for this reaction are CuCr \cite{24-25}, bimetallic Rh-Re \cite{26}, and Rh-Mo systems \cite{27}. The CuCr catalysts perform best at elevated pressures and temperatures and a reaction at 250-300 °C, 230-240 bar, and 9 h reaction time gave 1,5-pentanediol (1,5-PD) in a 40-47% yield \cite{24}. A continuous process at 275 °C and 300 bar was also reported giving 1,5-PD in about 30% yield \cite{25}. The bimetallic Rh-Re \cite{26} and Rh-Mo \cite{27} catalysts perform at milder conditions and 1,5-PD selectivities up to 94% at 57% conversion could be obtained at 120 °C and 80 bar pressure.

An alternative approach to 1,5-PD was proposed by Schniepp and Geller \cite{28}. THF-alcohol was converted to the dihydropyran at 375 °C using alumina, followed by the hydrolysis to $\delta$-hydroxyvaleraldehyde and a subsequent hydrogenation to 1,5-pentanediol at 150 °C and 140 bar (Eq. 5.3). An overall 70% yield of 1,5-PD from THF-alcohol was obtained.

In this paper, we report a catalyst screening study on the synthesis of 1,6-hexanediol from THFDM using monometallic (noble-) metal catalysts and bimetallic Cu- and Rh-based catalyst. The latter was used either as such or in combination with solid acid catalysts. The best catalytic systems were selected for further optimization studies to determine the optimum process conditions for the highest 1,6-hexanediol yields. A reaction network is proposed based in intermediates and byproducts observed in the various reactions.
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5.2 Materials and methods

5.2.1 Materials

Tetrahydrofuran-dimethanol (THFDM) was obtained by the hydrogenation of 5-hydroxymethylfurfural (HMF) according to a procedure described in the literature \(^{21, 29}\). HMF (> 99%), 1,6-hexanediol (97%), and tetrahydropyran-2-methanol (98%) were purchased from Aldrich. 1,2,6-hexanetriol (> 97%) was purchased from Acros, 1-propanol (> 99%) was from Merck Chemicals.

Copper chromite catalysts were obtained from BASF (Cu-1190P, Cu-1890P, and Cu-1985P), Sud-Chemie (G-22/2), and purchased from Aldrich (product number: 209325). Copper zinc PRICAT CZ/A P and PRICAT CZ/B P catalysts were obtained from Johnson Matthey, the copper zinc T-2130 was from Sud-Chemie. Ru/C (5% w/w), Pt/C (5% w/w), and Rh/C (5% w/w) were purchased from Aldrich, Raney nickel (product number: 39592) was from Acros.

Rhodium chloride hydrate (Rh 38-40%) and ammonium perrhenate (> 99%) were purchased from Aldrich. SiO\(_2\) (Wacker HDK\(^{®}\) T40) was obtained from Johnson Matthey and TiO\(_2\) (product number: 14021) was from Aldrich. Sulfonated carbon (prepared in house), ammonium–BEA (Zeolyst CP-814E, Si/Al = 11.1), ammonium–MFI (Alsi Penta SM-27, Si/Al = 12.5 and Alsi Penta SM-55, Si/Al = 21.1), Nafion\(^{®}\) SAC-13 and sulfated zirconia (Aldrich), Amberlyst\(^{TM}\) 16wet (Rohm\&Haas), and Smopex\(^{®}\)-101 (Johnson Matthey) were used as solid acids. Hydrogen gas (> 99.9999%) was purchased from Hoek Loos.

5.2.2 Methods

5.2.2.1 Standard procedure for Rh-ReO\(_x\)/SiO\(_2\) catalyst preparation

A solution of RhCl\(_3\) (302 mg, 1.4 mmol) in water (10 mL) was added to silica (2 g, Wacker HDK\(^{®}\) T40; BET surface area 328 m\(^2\)g\(^{-1}\) and pore volume 0.742 cm\(^3\)g\(^{-1}\)) and stirred for 2 h at room temperature. After drying at 383 K for 13-14 h, this material was added to a solution of NH\(_4\)ReO\(_4\) (193 mg, 0.7 mmol) in water (10 mL) and stirred for 2 h, followed by drying at 383 K for 13-14 h. Calcination in air at 773 K for 3 h gave the catalyst with 6.5 wt% of Rh and a Re/Rh molar ratio of 0.5.
5.2.2.2 Representative example for the catalytic hydrodeoxygenation of THFDM using bimetallic Cu and various monometallic catalysts (Ru/C, Rh/C, Pt/C, Raney Ni)

THFDM (500 mg, 3.8 mmol), catalyst (100 mg), and 1-propanol (30 mL) were placed in a stainless steel batch reactor (Parr) equipped with an overhead stirrer. The reactor was flushed three times with nitrogen and subsequently with hydrogen. The reactor was pressurized to 100 bar with hydrogen, and the reaction mixture was heated to 260 °C under stirring (1000 rpm). The reaction was carried out for 6 h. After cooling to ambient temperature, a gas sample was collected in a gasbag (SKC Tedlar 3 L sample bag) and analysed. Liquid product mixtures were filtered over a PTFE membrane to remove the catalyst and the filtrate was analysed. Most reactions (e.g. reaction with CuCr catalyst) and analyses were performed in duplicate.

5.2.2.3 Representative example for the catalytic hydrodeoxygenation of THFDM using Rh/Re-based catalysts

THFDM (100 mg, 0.8 mmol), Rh-ReOx/SiO2 catalyst (25 mg), solid acid catalyst (15 mg), water (2 mL), and a Teflon stirring bar were added to a glass vial (8 mL) capped with a septum. The vial was subsequently pierced with a small needle and placed in a stainless-steel autoclave. The lid of the autoclave was closed and stirring was started at 1000 rpm. After three times pressurizing, first two times with nitrogen and then hydrogen, the autoclave was pressurized to 10 bar and the temperature was raised to 120 °C. After 1 h, the pressure was raised to 80 bar and the reaction was continued for 20 h. Then, the autoclave was cooled to ambient temperature and the pressure was released. Reaction mixtures were filtered over a PTFE membrane to remove the catalyst and the filtrate was analysed. Most reactions and analyses were performed in duplicate.

5.2.2.4 Liquid product analysis

Gas chromatography technique using a CP-WAX57CB column (25 m length, 0.2 mm internal diameter, and 0.25 μm film thickness) and a flame ionization detector (GC-FID) was used for the liquid product analysis. Temperature for the injector and the detector was set at 250 °C. The oven temperature was kept at 40 °C for 5 minutes then heated up to 180 °C with a heating rate of 5 °C/min and to 230 °C with a heating rate of 10 °C/min and kept at this temperature for 15 minutes. A split ratio of 50 was used. Helium was used as the carrier gas with a flow rate of 1.1 ml/min. Toluene was used as an internal standard and a response
factor of each compound was determined. The identification of the compounds was done by spiking with authentic samples and by GC-MS analyses.

GC-MS analyses were performed on a Hewlett-Packard 5890 gas chromatograph equipped with a quadrupole Hewlett-Packard 6890 MSD selective detector and a 30-m × 0.25-mm internal diameter × 0.25-μm-film sol-gel capillary column. The injector temperature was set at 250 °C. The oven temperature was kept at 40 °C for 5 minutes, then increased to 250 °C at a heating rate of 3 °C/min, and then held at 250 °C for 10 minutes.

5.2.2.5 Gas product analysis

GC-TCD analysis was performed using a Hewlett Packard 5890 Series II GC equipped with a Porablot Q Al₂O₃/Na₂SO₄ column and a Molecular Sieve (5A) column. The injector temperature was set at 150 °C and the detector temperature was at 90 °C. The oven temperature was kept at 40 °C for 2 minutes then heated up to 90 °C with a heating rate of 20 °C/min and kept at this temperature for 2 minutes. The column was flushed for 30 seconds with gas sample before starting the measurement. A reference gas containing hydrogen, carbon monoxide, carbon dioxide, methane, ethylene, ethane, propylene, and propane with a known composition was used for identification and quantification.

5.2.2.6 Definitions

The conversion of THFDM (X_{THFDM}) was calculated using the following equation:

\[
X_{THFDM} = \left(1 - \frac{C_{THFDM}}{C_{THFDM,0}}\right) \times 100\% \quad \text{(eq 5.4)}
\]

where \(C_{THFDM}\) is the concentration of THFDM after a certain reaction time and \(C_{THFDM,0}\) is the initial concentration of THFDM.

The yield \((Y_i)\) and selectivity \((S_i)\) of the products \(i\) were calculated using the following equations:

\[
Y_i = \frac{C_i}{C_{THFDM,0}} \times 100\% \quad \text{(eq 5.5)}
\]

\[
S_i = \frac{C_i}{C_{THFDM,0} - C_{THFDM}} \times 100\% \quad \text{(eq 5.6)}
\]

where \(C_i\) is the concentration of products after a certain reaction time.
5.3 Results and discussion

5.3.1 Exploratory catalytic experiments on the conversion of HMF to 1,6-HD

The direct synthesis of 1,6-hexanediol (1,6-HD) from HMF was attempted using two catalyst systems, CuCr (Aldrich) in combination with Pd/C, a system explored by Utne \[22\] and by using bimetallic Rh-ReO\(_x\)/SiO\(_2\) catalysts, all with molecular hydrogen as the hydrogen donor. With CuCr in combination with Pd/C, quantitative HMF conversion was obtained after 14.5 h reaction time in methanol. The main product was THF-dimethanol (30 mol% yield), whereas the yield of the desired 1,6-HD was only 4 mol%. Other identified byproducts (GC-MS) were 1,2,6-hexanetriol (1 mol%), 1-hexanol (1 mol%), 1,5-pentanediol (1 mol%), and cyclohexanediol (8 mol%). Apparently, the reaction is not very selective. The use of CuCr or Pd/C alone gave lower 1,6-HD yields, indicating synergic effects of Pd/C and CuCr. The formation of 1,5-pentanediol is indicative for carbon loss, for instance by decarbonylation of the aldehyde group, or –CH\(_2\)OH loss from the intermediate THFDM (vide infra).

The application of the Rh-ReO\(_x\)/SiO\(_2\) catalyst (120 °C, water, 10 bar H\(_2\) for 1 h, followed by 17 h at 80 bar) led to a dramatic change in the chemo-selectivity. The main product was 1-hydroxyhexane-2,5-dione (HHD) which was obtained with 81% selectivity (at 100% HMF conversion), whereas 1,6-HD was obtained in only 7% yield (Eq. 5.7).

The formation of HHD from HMF has been reported before when performing the hydrogenation of HMF in acidic conditions (water, oxalic acid, 100-140 °C, 30-70 bar, Ru/C or Pt/C, 60-70% yield) \[30\]. A mechanism for the formation of HHD has been proposed and involves the initial hydrogenation of the aldehyde bond, followed by an acid catalyzed rearrangement of the intermediate furan-dimethanol to HHD \[31\].

\[
\begin{align*}
\text{HMF} + 2 \text{H}_2 & \rightarrow \text{HHD} \\
\text{(eq 5.7)}
\end{align*}
\]
Thus, it may be concluded that the direct synthesis of 1,6-HD from HMF using catalytic hydrodeoxygenation chemistry shows a low selectivity to 1,6-HD and leads to a mixture of compounds (CuCr/Pd on C), or the formation of mainly a dione (Rh-ReOₓ/SiO₂). Though not the major objective of this paper, the Rh-Re catalyst is thus an excellent catalyst for the synthesis of HHD, which yields exceeding those reported in the literature (81% versus 70%) and without the need of an external acid.

5.3.2 Catalytic hydro-(deoxy)genation of THF-dimethanol to 1,6-HD

Based on the results described above, it was anticipated that possible side reactions involving the aldehyde and C-C double bonds of HMF could be suppressed by using THF-dimethanol (THFDM) instead of HMF as the starting material for catalytic hydro-(deoxy)genation studies (Eq. 5.8). THFDM is accessible in high yields by a catalytic hydrogenation reaction of HMF. \(^{22, 29-30, 32-36}\) We used Ra-Ni for this hydrogenation and obtained a virtual quantitative yield of THFDM.

\[
\text{THF-dimethanol} + 2\text{H}_2 \rightarrow \text{1,6-HD} + \text{H}_2\text{O}
\]  
(eq 5.8)

Three catalyst systems were explored for the conversion of THFDM to 1,6-HD: monometallic catalysts (Ru/C, Rh/C, Pt/C, and Raney Ni), bimetallic Cu-based catalysts, and bimetallic Rh-based catalysts. The results obtained with the various catalytic systems will be provided separately in the following sections.

5.3.2.1 Studies on the conversion of THFDM to 1,6-HD using monometallic catalysts

The Ru/C, Rh/C, Pt/C, and Raney Ni catalysts were tested at 260 °C, 100 bar of hydrogen, a catalyst intake of 20 wt% and 1-propanol as the solvent. The THFDM conversion was highest for Raney Ni (90%), followed by Ru/C (24%) and, Pt/C (8%), whereas Rh/C was not active at the prevailing conditions (Table 5.1). Complex reaction mixtures were obtained (Table 5.1), in which the desired 1,6-HD could not be detected.
Table 5.1. Overview of catalyst screening results for catalytic hydrodeoxygenation of THFDM

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>$X_{\text{THFDM}}$ (mol%)</th>
<th>$S_{1,6\text{-HD}}$ (mol%)</th>
<th>$S_{1,5\text{-HD}}$ (mol%)</th>
<th>$S_{1,2,6\text{-HT}}$ (mol%)</th>
<th>$S_{1,2\text{-PD}}$ (mol%)</th>
<th>$S_{1,5\text{-PD}}$ (mol%)</th>
<th>$S_{\text{THFM}}$ (mol%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt/C</td>
<td>8</td>
<td>-</td>
<td>5</td>
<td>6</td>
<td>14</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Ru/C</td>
<td>24</td>
<td>-</td>
<td>-</td>
<td>3</td>
<td>-</td>
<td>16</td>
<td>35</td>
</tr>
<tr>
<td>Rh/C</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>RaNi</td>
<td>90</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>2</td>
<td>17</td>
</tr>
<tr>
<td>CuZn 1</td>
<td>26</td>
<td>7</td>
<td>4</td>
<td>-</td>
<td>21</td>
<td>-</td>
<td>25</td>
</tr>
<tr>
<td>CuZn 2</td>
<td>71</td>
<td>3</td>
<td>3</td>
<td>-</td>
<td>3</td>
<td>-</td>
<td>40</td>
</tr>
<tr>
<td>CuZn 3</td>
<td>78</td>
<td>3</td>
<td>3</td>
<td>1</td>
<td>1</td>
<td>-</td>
<td>50</td>
</tr>
<tr>
<td>CuCr</td>
<td>70</td>
<td>25</td>
<td>16</td>
<td>-</td>
<td>5</td>
<td>-</td>
<td>11</td>
</tr>
</tbody>
</table>

$^a$ T = 260 °C, P $H_2$ = 100 bar, t = 6 h, cat. intake = 20 wt%, solvent = 1-propanol

The main product of the reaction with Raney Ni and Ru/C was THF-methanol (THFM, 35 mol% for Ru/C, 17 mol% for Raney Ni, Eq. 5.9), besides smaller amounts of 1,2-pentanediol (1,2-PD). In addition, significant amounts of gas phase compounds were formed, viz. methane, ethane and CO$_2$ (Table 5.2). Apparently under these conditions, C-C bond cleavage reactions occur and the THF-dimethanol is converted to lower molecular weight components. The presence of 1,2-PD suggests that the initial step involves catalytic cleavage of THF-dimethanol to THF-methanol followed by catalytic ringopening to 1,2-PD.

\[
\text{THF-dimethanol} \xrightarrow{\text{catalytic hydrodeoxygenation}} \text{THF-methanol} + \text{1,2-pentanediol} + \text{CH}_4 + \text{C}_2\text{H}_6 + \text{CO}_2
\] (eq 5.9)

The catalytic removal of a -CH$_2$OH group from a furan ring has been reported [37]. For instance, THF-methanol is converted to tetrahydrofuran (THF) with a copper nickel catalyst using a hydrogenation protocol (250 °C) in yields up to 88%. A mechanism was proposed and involves dehydrogenation of THF-methanol to the corresponding aldehyde followed by decarbonylation to THF.
1,6-Hexanediol from Renewable Resources: Catalytic Ring Opening and Hydro(deoxy)genation of Tetrahydrofuran-dimethanol (THF-dimethanol) using Bimetallic Rh-Re Catalysts in Combination with Solid Acid Catalysts

Table 5.2. Gas phase composition for the hydrodeoxygenation of THFDM with Ru/C and Raney Ni

<table>
<thead>
<tr>
<th>Component (%)-% (mol)</th>
<th>Ru/C</th>
<th>Raney Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen</td>
<td>66</td>
<td>34</td>
</tr>
<tr>
<td>Methane</td>
<td>20</td>
<td>35</td>
</tr>
<tr>
<td>Ethane</td>
<td>14</td>
<td>26</td>
</tr>
<tr>
<td>Propane</td>
<td>&lt;1</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Carbon monoxide</td>
<td>&lt;1</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>&lt;1</td>
<td>4</td>
</tr>
</tbody>
</table>

5.3.2.2 Studies on the reaction of THFDM to 1,6-HD using bimetallic Cu-based catalysts

Two types of bimetallic Cu catalysts were tested: CuZn catalysts from different suppliers (CuZn 1: PRICAT CZ/A P, CuZn 2: PRICAT CZ/B P, CuZn 3: T-2130) and a CuCr catalyst (Cu-1985P). Reactions were performed at 260 °C, 100 bar hydrogen, a catalyst intake of 20 wt% in 1-propanol as the solvent and the results are shown in Table 5.1. The THFDM conversion varied from 26 to 78% for the CuZn catalysts, with CuZn-3 being the most active. Activity of the CuCr catalyst was in the range for the most active CuZn catalysts (70% conversion). The selectivity for the desired 1,6-HD was best for the CuCr catalyst (25%), and less than 7% for the others. Main byproducts were 1,5-hexanediol (1,5-HD), 1,2,6-hexanetriol (1,2,6-HT) and a C5 alcohol, 1,5-pentanediol (1,5-PD).

The product composition indicates the occurrence of a complex reaction network involving a number of intermediates, see Scheme 5.1 for details.

The first step involves the catalytic ring opening of THFDM to 1,2,6-HT (C6 pathway). In parallel, one of the CH2OH groups of THFDM is catalytically removed to form THFM, which is subsequently ringopened to form 1,5- or 1,2-PD (C5 pathway). Subsequent hydrodeoxygenation reactions of 1,2,6-HT lead to removal of alcohol groups and the formation of C6-diols (1,6-HD, 1,5-HD, and 1,2-HD). Thus, a good catalyst should i. be capable to convert THFDM selectively to 1,2,6-HT and not to the C5 precursor THFM and ii. have a high chemoselectivity for the subsequent hydrodeoxygenation of 1,2,6-HT to 1,6-HD in the C6 alcohol pathway. CuZn catalyst are not suitable and mainly the C5 pathway is followed leading to the formation of THFM and 1,5-PD. CuCr in this respect is more promising, with a higher preference for the C6 pathway, though some C5 pathway products are formed.
The use of CuCr catalysts for the formation of 1,6-HD was further explored by performing experiments with five CuCr catalysts with different compositions (Table 5.3). Conditions were similar as for the initial screening study using Cu-1985P. Liquid samples were taken periodically from the reaction mixture and the composition was analysed.

The best selectivity to 1,6-HD at highest conversion of THFDM, about 40% at 40% conversion, was obtained with the two catalysts with the highest amount of Cu$_2$Cr$_2$O$_5$ spinels (Cu-1890P and Cu-1190P). Close similarities in catalyst performance for these two catalysts also suggests that the addition of BaCrO$_4$ as in Cu-1190P does not have a major effect. In contrast, the addition of MnO$_2$, as in Cu-1985P resulted in a lower 1,6-HD selectivity at similar conversion levels, indicating a negative effect on catalyst performance.

Main byproducts were 1,2,6-HT and 1,5-HD, indicating that the C6-pathway is dominant (Scheme 5.1). Upon use of Cu1985-P, some 1-hexanol was formed as well (max. 10%), suggesting that subsequent hydrodeoxygenation of 1,5- and 1,6-HD may also occur.
Table 5.3. Overview of results for the catalytic hydrodeoxygenation of THFDM with various CuCr catalysts

<table>
<thead>
<tr>
<th></th>
<th>ALDRICH</th>
<th>G-22/2</th>
<th>Cu-1985P</th>
<th>Cu-1890P</th>
<th>Cu-1190P</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S_{1,6}$-HD, max (mol%)</td>
<td>32</td>
<td>29</td>
<td>22</td>
<td>41</td>
<td>39</td>
</tr>
<tr>
<td>$X_{THFDM}$ (mol%) $^b$</td>
<td>11</td>
<td>14</td>
<td>44</td>
<td>41</td>
<td>42</td>
</tr>
<tr>
<td>Time (h) $^c$</td>
<td>2</td>
<td>2</td>
<td>5</td>
<td>6</td>
<td>6</td>
</tr>
</tbody>
</table>

$\text{Cu}_2\text{Cr}_2\text{O}_5$ - - 60-75 75 63
CuO 41.5 47 20-35 25 22
MnO$_2$ - - 1-10 - -
Cr (6+) - - 0-1 0-0-3 -
CrO 47 - - - -
Cr$_2$O$_3$ - 34 - - -
BaO 9,3 6 - - -
BaCrO$_4$ - - - - 15

$^a$ conditions: $T = 260 \degree C$, $P H_2 = 100$ bar, solvent = 1-propanol, catalyst intake = 20 wt% ; $^b$ at max $S_{1,6}$-HD ; $^c$ for max $S_{1,6}$-HD

5.3.2.3 Catalytic conversions of THFDM to 1,6-HD using bimetallic Rh-Re catalysts

5.3.2.3.1 Screening studies with bimetallic Rh-Re catalysts on silica

The use of bimetallic Rh-Re catalyst for the conversion of THFDM to 1,6-HD was explored in water at 120 °C, 80 bar pressure and 4 h reaction time. In the initial stage a silica catalyst support was used (Wacker HDK® T40 silica) and the catalyst was prepared by a wet impregnation technique using rhodium chloride and ammonium perrhenate as the catalyst precursors. A THFDM conversion of 46% was obtained with 14% selectivity to 1,6-HD and, interestingly, a high (82%) selectivity to 1,2,6-HT. C5 products were not detected, and clearly indicates that the C6 pathway is preferred. In this respect, the Rh-ReO$_x$/SiO$_2$ catalyst differs from the bimetallic Cu catalysts described above and as such it is more promising.

Further attempts to improve the 1,6-HD yield involved the addition of acids, with the incentive to improve the rate for the reaction of 1,2,6-HT to the C6 diols. Initial experiments were performed using soluble acids (e.g. para-toluene sulfonic acid)
Conversion of THFDM was incomplete for most reactions, except for that using Nafion® SAC-13 after prolonged reaction times. In most cases, the activity of the Rh-Re catalyst is lowered upon the addition of the solid acid catalyst, see Table 5.4 for details. A possible explanation is adsorption of the THFDM and intermediates to the solid acid catalysts, effectively lowering the concentration in the liquid and on the Rh-Re-silica catalyst, leading to lower reaction rates. The most pronounced exception is Nafion® SAC-13, where the THFDM conversion increased to 57% after 4 h reaction time compared to 46% for the reaction in the absence of the solid catalyst.

The main products were 1,2,6-HT, 1,6-HD, and 1,5-HD, all from the C6 pathway (Scheme 5.1). C5 alcohols were not detected. The highest selectivity to
1,6-Hexanediol from Renewable Resources: Catalytic Ring Opening and Hydro(deoxy)genation of Tetrahydrofuran-dimethanol (THF-dimethanol) using Bimetallic Rh-Re Catalysts in Combination with Solid Acid Catalysts

1,6-HD was also found for the most active catalyst in the series (Nafion® SAC-13, 86%), giving an overall yield to 1,6-HD of 86%. This is considerably higher than for the bimetallic Cu-based catalyst described in the previous section. So far, it is not clear why Nafion is the best catalyst in the series, though may be related to the high acidity in combination with high surface area/hydrophobicity.

The product distribution is in line with the mechanistic pathway depicted in Scheme 5.1, involving 1,2,6-HT as the intermediate that is subsequently converted to either 1,5-HD or 1,6-HD at prolonged reaction times. Apparently, the removal of the secondary alcohol from 1,2,6-HT is favored, leading to a high selectivity for 1,6-HD. 1,2-HD is not present in the reaction mixture, which would require the selective removal of the primary OH group at the C-6 position. Thus, the 1,2 diols appear to be more reactive than the 1,6-diol. This is in line with the literature data and has led to the hypothesis of a cooperative reaction mechanism for the bimetallic Rh/Re catalysts. It assumes that one OH group is adsorbed on the Re center whereas the adjacent O-X group (X = H or R) is bound to a Rh center and subsequently hydrogenolyzed [38]. In case of 1,2,6-HT, the two OH groups at the 1 and 2 position will be adsorbed preferentially, leading to either 1,5-HD or 1,6-HD and not to 1,2-HD.

Recently, Dumesic et al [39] disclosed experimental and theoretical calculations based on the density functional theory (DFT) for the hydrogenolysis of secondary C-O bonds of a broad range of cyclic ethers and polyols using a ReOx-promoted Rh/C catalyst. Based on the results, a bifunctional catalyst is hypothesised that facilitates selective hydrogenolysis of C-O bonds by acid-catalyzed ring-opening and dehydration reactions coupled with metal-catalyzed hydrogenation. DFT calculations suggest that hydroxyl groups on rhenium atoms associated with rhodium are acidic, due to the strong binding of oxygen atoms by rhenium, and these groups are likely responsible for proton donation.

In Figure 5.1, the selectivity versus the conversion for 1,6-HD for all acid catalyzed reactions shown in Table 5.4 is represented. All data points clearly follow the same trend, indicating that all solid acid catalyst have a similar effect on the various reactions in the proposed reaction network and do not catalyze secondary reactions. Reaction with the Nafion® SAC-13 alone did not give any conversion, indicating that the combination of the hydrogenation and dehydration catalysts is essential.
Caprolactam from Renewable Resources: Catalytic Conversion of 5-Hydroxymethylfurfural into Caprolactone

Figure 5.1. Conversion-selectivity relations for the reaction of THFDM to 1,6-hexanediol using Rh-ReO$_x$/SiO$_2$ and various solid acids

5.3.2.3.2 Effect of process conditions on catalyst performance for the Rh-Re on silica/ Nafion$^\text{®}$ SAC-13 system

A number of experiments were performed with the combined Rh-Re on silica/ Nafion$^\text{®}$ SAC-13 system at different reaction times to gain insights in product selectivities versus time (120 °C, 80 bar, water). The effect of reaction time on the concentration profiles is given in Figure 5.2. THFDM is completely converted within 20 h reaction time, 1,2,6-HT is a clear intermediate, whereas 1,6-HD and 1,5-HD are the main products. The profiles in Figure 5.2 were modeled using a simple kinetic scheme (Scheme 5.2), assuming first order reactions for all reactions involved and a constant hydrogen pressure (Eq. 5.10 - 5.13).

\[
\frac{dC_{\text{THFDM}}}{dt} = -k_1C_{\text{THFDM}}
\]  
(eq 5.10)

\[
\frac{dC_{1,2,6HT}}{dt} = k_1C_{\text{THFDM}} - k_2C_{1,2,6HT} - k_3C_{1,2,6HT}
\]  
(eq 5.11)
The experimental data points and model line predictions are provided in Figure 5.2. An acceptable fit was obtained for reaction times less than 15 h. The values for the kinetic constants were \( k_1 = 0.20 \pm 0.05 \) h\(^{-1}\), \( k_2 = 0.10 \pm 0.03 \) h\(^{-1}\), and \( k_3 = 0.015 \pm 0.01 \) h\(^{-1}\) indicating that the reaction of 1,2,6-HT to 1,6-HD is about 7 times faster than that for the undesired reaction to 1,5-HD.

For reaction times > 15 h, the kinetic model shows larger deviations. The actual 1,2,6-HT concentration is much lower and the 1,6-HD concentration is much higher than anticipated by the model. It is possible that the THFDM plays a role and that the reaction rates increase at higher THFDM conversions due to preferential adsorption of THFDM to active sides. Further detailed kinetic studies at a wide range of reaction conditions will be required to unequivocally prove whether this assumption is correct, though are beyond the scope of this exploratory catalyst screening study.
Figure 5.2. Experimental and modeled concentration-time profiles for the reaction of THFDM with hydrogen using Rh-ReOₓ/SiO₂ in combination with Nafion® SAC-13

5.3.2.3.3 Screening studies with Rh-Re on a TiO₂ support in combination with various solid acid catalysts

Support effects on the bimetallic Rh-Re catalyst were explored by performing experiments with Rh-Re on titania in combination with a number of solid acid catalysts. The results are presented in Table 5.5. Activity of the TiO₂ based catalyst is lower than Rh-ReOₓ/SiO₂, irrespective of which solid acid catalyst was used.
Table 5.5. Results for the conversion of TFDM as a function of support of the bimetallic Rh-Re catalyst in combination with solid acid catalyst a

<table>
<thead>
<tr>
<th>Solid acid</th>
<th>Support</th>
<th>(X_{\text{THFDM}}) (mol%)</th>
<th>(S_{1,6\text{-HD}}) (mol%)</th>
<th>(S_{1,5\text{-HD}}) (mol%)</th>
<th>(S_{1,2,6\text{-HT}}) (mol%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfonated C</td>
<td>SiO(_2)</td>
<td>65</td>
<td>26</td>
<td>4</td>
<td>70</td>
</tr>
<tr>
<td>Sulfonated C</td>
<td>TiO(_2)</td>
<td>24</td>
<td>10</td>
<td>3</td>
<td>87</td>
</tr>
<tr>
<td>SM-55</td>
<td>SiO(_2)</td>
<td>92</td>
<td>61</td>
<td>12</td>
<td>27</td>
</tr>
<tr>
<td>SM-55</td>
<td>TiO(_2)</td>
<td>54</td>
<td>11</td>
<td>3</td>
<td>86</td>
</tr>
<tr>
<td>Nafion SAC-13</td>
<td>SiO(_2)</td>
<td>100</td>
<td>86</td>
<td>14</td>
<td>0</td>
</tr>
<tr>
<td>Nafion SAC-13</td>
<td>TiO(_2)</td>
<td>72</td>
<td>30</td>
<td>7</td>
<td>63</td>
</tr>
</tbody>
</table>

a \(T = 120^\circ\text{C}, P_1 = 10\text{ bar}, t_1 = 1\text{ h}, P_2 = 80\text{ bar}, t_2 = 20\text{ h},\) catalyst = Rh-ReO\(_x\)/SiO\(_2\) 25 wt\%, acid = 15 wt\%, solvent = water

5.4 Conclusions

The one-pot synthesis of 1,6-hexanediol from THFDM using a hydrodeoxyxygenation protocol with various types of heterogeneous catalysts has been explored. Best results were obtained using a Rh-ReO\(_x\)/SiO\(_2\) catalyst in combination with a solid acid catalyst in the form of Nafion\(^{\circledR}\) SAC-13, giving 1,6-HD in 86% yield at quantitative THFDM conversion. Reaction profiles combined with kinetic modeling studies indicate that reaction sequence involves 1,2,6-HT as the intermediate, which is converted mainly to 1,6-HD. The chemo-selectivity of the Rh-ReO\(_x\)/SiO\(_2\) catalyst is unique among the catalysts tested in this study as it does not lead to the formation of C5 products like 1,2-PD and 1,5-PD. The latter are most likely formed from THF-methanol, formed by dehydrogenation/decarbonylation of THFDM.

5.5 Acknowledgement

We would like to thank ACTS-ASPECT for providing a grant to this research (ASPECT Project 053.62.017), and Rudy Parton, Rob Meier (DSM), Peter Witte, Peter Berben (BASF), Annemarie Beers (Norit), Jean Paul Lange (Shell), and Bart Zwijnenburg (Johnson Matthey) for helpful discussions.
5.6 References


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Chapter 6

Caprolactam from Renewable Resources: Catalytic Conversion of 5-Hydroxymethylfurfural into Caprolactone


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6.1 Overview

Lignocellulosic biomass is a very promising feedstock for the production of biobased chemicals [1-8]. The C6-sugars (for example D-glucose, D-fructose, and D-mannose) in lignocellulosic biomass are interesting precursors for a broad range of chemicals with high application potential. Apart from fermentation to bioethanol [9] and reforming to CO/H2 [10], the direct conversion of these sugars to useful platform chemicals is highly attractive [11]. Examples of such chemicals are levulinic acid [11] and 5-hydroxymethylfurfural (HMF) [12]. HMF can be prepared in high yield from D-fructose [13] although research is underway to convert D-glucose or even cellulose directly into HMF [14]. It can be converted into a range of derivatives with potential applications as a biofuel (furanics) and as building blocks for the polymer and solvent industry [15].

Herein, we present our work on the conversion of HMF into caprolactam, the monomer for nylon-6, a widely used synthetic polymer with an annual production of about 4 million tons [16]. The proposed reaction for the conversion of HMF into caprolactone, via 1,6-hexanediol (1,6-HD) is shown in Scheme 6.1. The conversion of caprolactone into caprolactam by the reaction with ammonia is well established and has already been used on a production scale [17]. A major breakthrough, needed in this research is the conversion of HMF to 1,6-hexanediol. For the feasibility of a bulk chemical process, it is absolutely essential that all conversions proceed with a selectivity in excess of 90%, preferable even higher. High conversion is desirable, but not a prerequisite, and indeed many bulk processes, in particular oxidations, are run at very low conversions to maintain a high selectivity.

Scheme 6.1. Synthetic routes for the conversion of HMF into caprolactam
Four different routes were explored involving catalytic hydrogenation and hydrodeoxygenation reactions with various homogeneous and heterogeneous catalysts: 1) the direct hydrogenation of HMF to 1,6-HD, 2) a two-step sequence via 2,5-THF-dimethanol (THFDM), 3) a three-step synthesis via THFDM and 1,2,6-hexanetriol (1,2,6-HT), and 4) a four-step synthesis via THFDM, 1,2,6-HT and tetrahydro-2H-pyran-2-ylmethanol (2-THPM). The last step in the sequence, namely the catalytic conversion of diols into lactones is a known reaction \[18\] but the conversion of 1,6-HD into caprolactone (5) rarely proceeds with high selectivity \[19\]. Probably the best method in terms of yield and selectivity is the oxidation with 30% \(\text{H}_2\text{O}_2\) using heteropolyacids as catalyst which was reported twice and gave caprolactone in 70% and 98% yields, respectively \[19d,f\]. However, the use of \(\text{H}_2\text{O}_2\) may be too expensive for a bulk caprolactam process. Herein, we report a version based on an Oppenauer oxidation that has never been used before on this substrate \[18c\].

The one-step hydrogenation reaction of HMF to 1,6-HD was performed under severe conditions (270 °C, 150 bar) with hydrogen as the reductant and a mixture of copper chromite and Pd/C (1 : 0.6) as the catalyst following a synthetic procedure reported by Utne and co-workers \[20\]. After 16 h reaction time, the HMF conversion was 100 % and a mixture of products was obtained. The main product was THFDM; the desired product 1,6-HD was present in less than 4 % yield. Use of just CuCr or Pd/C led to worse results. Rather worrying was that also some C\(_5\) products, such as 1,5-pentanediol, were found. A possible pathway towards C\(_5\) compounds is via decarbonylation of the aldehyde group. For this reason, it was deemed wiser to first hydrogenate HMF to THFDM under milder conditions and then hydrogenate this compound in a second step to 1,6-HD.

The catalytic hydrogenation of HMF to THFDM has been reported \[21-27\] using supported metal catalysts. A catalyst screening study was performed using a variety of catalysts and Raney-Ni (10 wt% catalyst intake, 100 °C, 90 bar hydrogen, 14 h) gave essentially quantitative yields of THFDM (cis/trans = 98:2). Good selectivities to the intermediate furan-dimethanol were also obtained using bimetallic Ni-Cu catalysts on zirconia and Ru on alumina, catalysts that have not been tested to date for this reaction.

Hydrogenolytic ring opening of THFDM to 1,6-HD using a range of catalysts (various types of CuCr and CuZn catalysts, Pt/C, Ru/C, NiCu/ZrO\(_2\), Raney-Ni) was explored in a batch autoclave setup at 260°C, 100 bar pressure in 1-propanol as the solvent. The emphasis was on copper-containing catalysts, as Utne and co-workers reported a maximum 1,6-HD yield of 50% using a CuCr catalyst, although extreme conditions were applied (380 bar, 300 °C) \[26\]. The best results in our screening study were obtained using a CuCr catalyst consisting of 75% Cu\(_2\)Cr\(_2\)O\(_5\) and 25% CuO, giving a maximum selectivity to 1,6-HD of 41% at 41% THFDM conversion. Thus, although the hydrogenolytic opening of
tetrahydrofuranyl ring of THFDM is possible the selectivity is still too low for further scale-up.

Recently, the Tomishige group reported the hydrogenolytic ring-opening reaction of tetrahydrofuran-2-yl-methanol using Rh-Re/SiO₂ catalyst under mild conditions (120 °C and 80 bar hydrogen) to give 94% selectivity to 1,5-pentanediol at 57% conversion (Scheme 6.2)\(^{[28]}\).

\[
\begin{align*}
\text{Rh-Re/SiO₂} & \quad \text{H₂} \\
\text{H₂O} & \quad \text{HO-} \quad \text{OH}
\end{align*}
\]


A similar reaction using THFDM as the substrate could be envisaged to lead to the formation of 1,2,6-HT. In a subsequent step, a selective hydrogenolysis of the secondary alcohol group could lead to 1,6-HD. In the event, the hydrogenation of THFDM was carried out using a Rh-Re catalyst on a silica support (6.5 wt% Rh, 6 wt% Re). The reactions were carried out in water at temperatures between 80 and 180 °C. The initial pressure was 10 bar (1 h), and subsequently the pressure was increased to 80 bar for reaction times between 4 and 20 h (Table 6.1). The highest selectivity to 1,2,6-HT was 97%, and was obtained at 21% THFDM conversion (Table 6.1, entry 4). Higher temperatures and longer reaction times led to increased THFDM conversions, although the selectivity to 1,2,6-HT dropped. Byproducts are 1,6-HD and 1,5-hexanediol (1,5-HD). This indicates that the diols are likely formed from 1,2,6-HT in a consecutive reaction pathway (Scheme 6.3).

Further reduction to 1-hexanol was not observed under the prevailing reaction conditions. The presence of the diols indicates that subsequent dehydroxylation of 1,2,6-HT is possible using the supported Rh-Re catalysts. In a next step, the hydrogenation of 1,2,6-HT was attempted with a variety of catalysts, including CuCr, CuZn, Pd, Ru, Rh and the Rh-Re/SiO₂ catalyst, leading to mixtures of 1,6-HD and 1,5-HD (Scheme 7.3). The highest selectivity to 1,6-HD (73%) was obtained using the latter catalyst at 17% 1,2,6-HT conversion. The remainder is 1,5-HD. To date, we have not been able to suppress the formation of 1,5-HD by variation of process conditions.
Table 6.1. The ring opening reaction of THFDM to 1,2,6-HT using Rh-Re/SiO$_2$ catalysts $^{[a]}$

<table>
<thead>
<tr>
<th>Entry</th>
<th>$T$ ($^\circ$C)</th>
<th>$t$ (h)</th>
<th>THFDM conv. (%)</th>
<th>Selectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>120</td>
<td>4</td>
<td>55</td>
<td>77 15 5</td>
</tr>
<tr>
<td>2</td>
<td>120</td>
<td>20</td>
<td>81</td>
<td>61 28 10</td>
</tr>
<tr>
<td>3</td>
<td>180</td>
<td>4</td>
<td>83</td>
<td>54 30 15</td>
</tr>
<tr>
<td>4</td>
<td>80</td>
<td>20</td>
<td>21</td>
<td>97 0 0</td>
</tr>
</tbody>
</table>

$^{[a]}$ Rh content 6.5 wt%, Re content 6 wt%, $P_1$ 10 bar, $P_2$ 80 bar, $t_1$ 1 h, catalyst intake 25 wt%, 5 wt% THFDM in water

Scheme 6.3. Reaction of 1,2,6-HT to produce 1,6-HD and 1,5-HD

In an attempt to increase the selectivity to 1,6-HD, we added Brønsted acids to the hydrogenation reaction of 1,2,6-HT with the objective to selectively dehydrate the alcohol at the 2-position. Surprisingly this led to the formation of tetrahydro-2H-pyran-2-ylmethanol (2-THPM) in very high yields (Scheme 6.4).

Indeed, treatment of 1,2,6-HT with 0.6 mol% of trifluoromethanesulfonic acid in sulfolane at 125 $^\circ$C for 0.5 h gave full conversion into 2-THPM in a very clean reaction. In view of the structural similarity between 2-THPM and 2-tetrahydrofuran-2-yl-methanol, we decided to subject the former to another hydrogenolysis reaction using the same Rh-Re/SiO$_2$ catalyst. After 1 h at 10 bar and 3.5 h at 80 bar and 180 $^\circ$C, 2-THPM conversion was 17% and 1,6-HD was obtained with 100% selectivity. This result finally gives us access to a high
selectivity route from HMF to 1,6-HD involving THFDM, 1,2,6-HT and 2-THPM as the intermediate products. A remaining drawback of this process to 1,6-HD is the number of steps. However, as both the hydrogenations of THFDM and of 2-THPM use the same catalysts and conditions, an obvious next step was to try to combine the two hydrogenations and the ring-closure to 2-THPM in a single process. In Table 6.2 we show the results of hydrogenating THFDM using the Rh-Re/SiO$_2$ catalyst in the presence of various solid acid catalysts. Full conversion was obtained after 20 h with Nafion SAC-13; with a very promising selectivity to 1,6-HD of 86% (Table 6.2, entry 9). Other solid acids showed similar activities but led to slightly lower selectivities.

Scheme 6.4. 1,6-HD production from 1,2,6-HT via 2-THPM. Conditions: a) TFSA, sulfolane, 125 °C, 30 min; b) Rh-Re/SiO$_2$, water, H$_2$ 80 bar, 180 °C, 4.5 h.
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Table 6.2 One-pot conversion of THFDM to 1,6-HD

<table>
<thead>
<tr>
<th>Entry</th>
<th>Acid catalyst</th>
<th>t (h)</th>
<th>% conv.</th>
<th>% selectivity</th>
</tr>
</thead>
<tbody>
<tr>
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*Sulfonated carbon (Sulf-C) was prepared by heating glucose at 400 °C for 15h under N₂, followed by sulfonation with conc. H₂SO₄ during 15h. Zeolite 1 is SM-27, Zeolite 2 is SM-55 (2 types of ZSM-5 silica from Alsi Penta) [30]; Zeolite 3 is CP-814E from Zeolyst (a type of beta zeolite) [30].

Application of the Rh-Re/SiO₂-catalysed hydrogenation directly on HMF led to an unexpected result. Using 10 mol% of the catalyst at 120 °C on an aqueous solution of HMF at 10 bar for 1 h, followed by 17 h at 80 bar led to full conversion and formation of 1,6-HD with only 7% selectivity; furthermore, 1-hydroxyhexane-2,5-dione (HHD) was formed with 81% selectivity (Scheme 6.5). Formation of this product from HMF has been reported before during a hydrogenation under acidic conditions [21].
Caprolactam from Renewable Resources: Catalytic Conversion of 5-Hydroxymethylfurfural into Caprolactone

Scheme 6.5. Reaction of HMF using Rh-Re/SiO$_2$. Conditions: 120 °C, 80 bar.

Next, we turned our attention to the conversion of 1,6-HD into caprolactone. This is essentially a one-pot two-step process in which the diol is first converted into the monoaldehyde, which cyclizes spontaneously to the lactol, which is again dehydrogenated to the lactone. We were attracted by the method developed by Murahashi and co-workers, which is basically an Oppenauer oxidation using acetone as oxidant and a homogeneous Ru catalyst (H$_2$Ru(PPh$_3$)$_3$)\[^{18c}\] . They did report the formation of lactones from α,ω-diols, but the oxidation of 1,6-HD was not reported. In initial tests, we found that homogeneous ruthenium catalysts indeed outperformed a number of other catalysts based on iridium or titanium. Screening of ligands led us to the finding that the catalyst made in situ from [Ru(cymene)Cl$_2$]$_2$ and 1,1'-bis(diphenylphosphino)ferrocene (DPPF) gave the best results. Thus, a solution of 1,6-HD in MIBK (methyl isobutylketone) was treated with this catalyst (1 mol%) at reflux temperature for 30 min. to give a virtually quantitative yield of caprolactone (Scheme 6.6). The use of MIBK instead of acetone allows much higher reaction temperatures (b.p. MIBK 117 °C) and thus faster rates. The only shortcoming of the method is the formation of stoichiometric amounts of the reduction product of MIBK, 4-methyl-2-pentanol. In an industrial setting this would need to be catalytically dehydrogenated back to MIBK, thus adding an extra step. A direct dehydrogenation of 1,6-HD to caprolactone without the use of an oxidant would be much preferred, but to date selectivities are too low.

Scheme 6.6. Caprolactone production from 1,6-HD

In conclusion, we have identified a pathway that allows the conversion of HMF, which can be obtained from renewable resources like D-fructose, into caprolactone with a very good overall selectivity. Using the one-pot conversion of THFDM into 1,6-HD, we can now convert HMF into caprolactam in only four steps,
whereas the current caprolactam process needs six steps from benzene and ammonia. Furthermore, the current cyclohexane to cyclohexanone oxidation proceeds with very low conversion.

Note: While preparing this manuscript we became aware of a paper of the Tomishige group describing the catalytic hydrogenation of tetrahydro-2H-pyran-2-ylmethanol using their Rh-Re catalyst [29].

6.2 Experimental Section

Preparation of the Rh-Re/SiO₂ catalyst: An aqueous solution of RhCl₃ (302 mg, 1.4 mmol) in water (10 mL) was added to silica (2 g, Wacker HDK T40; BET surface area 328 m²g⁻¹ and pore volume 0.742 cm³g⁻¹) and stirred for 2 h at room temperature. After drying at 383 K for 13-14 h, this material was stirred with an aqueous solution of NH₄ReO₄ (193 mg, 0.7 mmol) in water (10 mL) for 2 h, followed by drying at 383 K for 13-14 h. Calcination in air at 773 K for 3 h gave a material with 6.5 wt% Rh and 6 wt% Re.

Hydrogenation of HMF to THFDM: HMF (500 mg, 4 mmol) dissolved in ethanol (30 mL) and Raney nickel catalyst (50 mg) were added to a 100 mL stainless steel autoclave (Parr). The reactor was flushed three times with nitrogen and subsequently with hydrogen. After flushing, the reactor was pressurized to 90 bar, and the reaction mixture was stirred and heated to 100 °C for 14 h. GC analysis showed 100% conversion and 99% selectivity to THFDM.

Hydrogenation of THFDM to 1,2,6-HT: THFDM (100 mg, 0.8 mmol), Rh-Re/SiO₂ catalyst (25 mg), water (2 mL), and a Teflon stirring bar were added to a 8 mL glass vial capped with a septum. The vial was then pierced with a small needle and placed in a stainless-steel autoclave. The lid of the autoclave was closed and stirring was started at 1000 rpm. After three times pressurizing with first nitrogen and then hydrogen, the autoclave was pressurized to 10 bar and the temperature was raised to 80 °C. After 1 h, the pressure was raised to 80 bar and the reactions were continued for 20 h. The autoclave was allowed to cool to ambient temperature and the pressure was released. GC analysis showed 21% conversion and 97% selectivity to 1,2,6-HT.

Cyclisation of 1,2,6-HT to 2-THPM: In a 100 mL three-neck round bottom flask, 1,2,6-hexanetriol (3.354 g, 25 mmol) was dissolved in sulfolane (25 mL). Trifluoromethanesulfonic acid (13.3 µL, 0.15 mmol) was then added. The reaction mixture was heated to 125 °C for 30 min. GC shows full conversion with 2-THPM as the only product.

Hydrogenation of 2-THPM to 1,6-HD: 2-THPM (100 mg, 0.9 mmol), the Rh-Re/SiO₂ catalyst (10 mg), water (2 mL), and a Teflon stirring bar were added to a glass vial and hydrogenation was effected as described above for the hydrogenation of THFDM, except at a temperature of 180°C. After 4.5 h, GC analysis showed 17% conversion and 100% selectivity to 1,6-HD.

One-pot hydrogenation of THFDM to 1,6-HD: The same procedure was used as described above for the hydrogenation of THFDM to 1,2,6-HT, but with an additional 15 mg of acid catalyst added (see Table 7.2).
1,6-HD to caprolactone: In a two-necked round-bottom flask with a condenser under an inert atmosphere, [Ru(Cymene)Cl$_2$]$_2$ (0.02 mmol) and DPPF (0.022 mmol) were suspended in MIBK (5 mL) at room temperature. 1,6-HD (1.0 mmol), K$_2$CO$_3$ (0.2 mmol) and MIBK (25 mL) were then added, and the mixture was refluxed for 0.5 h. GC analysis showed 100% conversion of 1,6-HD with complete selectivity to caprolactone.

In all cases, samples were isolated by distillation or column chromatography and further analysed by NMR and MS.

6.3 Acknowledgements

We would like to thank ACTS-ASPECT for providing a grant to this research (ASPECT Project 053.62.017), and Rudy Parton, Rob Meier (DSM), Peter Witte, Peter Berben (BASF), Annemarie Beers (Norit), Jean Paul Lange (Shell), and Bart Zwijnenburg (Johnson Matthey) for helpful discussions.

6.4 References


Caprolactam from Renewable Resources: Catalytic Conversion of 5-Hydroxymethylfurfural into Caprolactone


Summary

High dependencies on non-renewable fossil resources for the production of energy, transportation fuels and chemicals will cause major issues in the near future. As such, the development of renewable resources as alternatives for fossil resources is high on the global agenda. Biomass is a promising alternative as it is the only renewable resource of fixed carbon, and as such may play an important role for the production of hydrocarbon liquid transportation fuels and chemical products.

C6-sugars in lignocellulosic biomass are interesting precursors for a broad range of chemicals with high application potential. An example is 5-hydroxymethylfurfural (HMF). It can be prepared in high yields from D-fructose, and potentially also from other cheaper resources (D-glucose). In this thesis, experimental studies on the conversion of HMF into caprolactam, the monomer for nylon-6, a widely used synthetic polymer, are described. The proposed pathway is given in Scheme 1. It involves two catalytic hydrogenation steps followed by a dehydrogenation and an amination step. The last step (caprolactone to caprolactam) was operated already on commercial scale (though abandoned at the moment) and is considered proven technology.

Scheme 1. Proposed synthetic route for the HMF conversion to caprolactam
A major breakthrough in this research involved the development of catalytic technology for the conversion of HMF to 1,6-hexanediol (1,6-HD). Four different routes were explored involving catalytic hydrogenation and hydrodeoxygenation reactions with various homogeneous and heterogeneous catalysts: i) The direct hydrogenation of HMF to 1,6-HD; ii) a two-step sequence via 2,5-THF-dimethanol (THFDM); iii) a three-step synthesis via THFDM and 1,2,6-hexanetriol (1,2,6-HT); and iv) a four-step synthesis via THFDM, 1,2,6-HT, and tetrahydro-2H-pyran-2-ylmethanol (2-THPM), see Scheme 2 for details.

![Scheme 2. Catalytic routes for the conversion of HMF to 1,6-hexanediol (1,6-HD)](image)

The direct conversion of HMF to 1,6-HD by catalytic hydrogenation methodology proved not successful. However, the use of tetrahydrofuran-dimethanol (THFDM), attainable by the catalytic hydrogenation of HMF, gave better results. A catalyst screening study on the hydrogenation of HMF to THFDM is described in Chapter 2. Promising catalysts were identified and process conditions were optimized to obtain high THFDM yields. Best results (99% THFDM yield)
were obtained with a Raney nickel catalyst at 100 °C. A statistical model was developed for this catalyst to correlate the THFDM yield with relevant reaction conditions like temperature (75-250°C), batch time (4-14 h) and hydrogen pressure (50-90 bar). The intermediate product furan-dimethanol was obtained in high yields (> 99%) using a NiCu/ZrO₂ catalyst at 150 °C.

Chapter 3 describes experimental studies on the catalytic ring opening reaction of THFDM to 1,2,6-HT. A wide range of heterogeneous catalysts were tested and bimetallic Rh-Re catalysts on silica supports were identified as the best option. Further investigations on the silica properties, metal composition, and process conditions were performed. The optimal catalyst composition contained 4 wt% Rh and a Re/Rh mol ratio of 0.5. Best results were obtained at 80 °C, giving 92% selectivity to 1,2,6-HT at 11% THFDM conversion. A reaction network is proposed based on the products observed in the course of the reaction.

The results of the catalytic hydrodeoxygenation of 1,2,6-HT to 1,6-HD are presented in Chapter 4. Various catalysts were screened and Rh-ReOₓ/SiO₂ catalysts were found to give the best results. Two approaches were explored, a one-step and a two-step approach involving 2-THPM as the intermediate. The one-step approach led to a maximum of 73% selectivity to 1,6-HD at full conversion. An overall selectivity of 96% at 26% conversion could be obtained in a two-step approach employing trifilic acid in the first step (125 °C) and a catalytic hydrogenation using a Rh-ReOₓ/SiO₂ catalyst in the second step (120 °C, 80 bar).

In Chapter 5, the one-pot synthesis of 1,6-HD from THFDM by a hydrodeoxygenation approach using a range of monometallic, bimetallic Cu and Rh-Re-based catalysts is reported. The best catalytic systems were selected for further optimization studies, including the addition of various solid acids. Excellent results were obtained using a combination of a Rh-ReOₓ/SiO₂ catalyst and Nafion® SAC-13 as the solid acid catalyst, giving 1,6-HD in 86% yield (120 °C, 80 bar). Reaction profiles combined with kinetic modeling studies indicate that reaction
sequence involves 1,2,6-HT as the intermediate, which is converted mainly to 1,6-HD.

Finally, an overview of all findings is presented in Chapter 6, including some additional research on the conversion of 1,6-HD to caprolactone using homogeneous catalysts.
Samenvatting

De sterke afhankelijkheid van niet hernieuwbare fossiele bronnen voor de productie van energie, transport brandstoffen en chemicaliën zal in de nabije toekomst voor grote problemen zorgen. Dit heeft een grote stimulans gegeven aan de ontwikkeling van hernieuwbare bronnen als alternatief voor de fossiele bronnen. Biomassa is een veelbelovend alternatief gezien het feit dat het de enige hernieuwbare koolstof bron is, en als zodanig kan het een belangrijke rol gaan spelen in de productie van transport brandstoffen en chemische producten.

C6-suikers in lignocellulolische biomassa zijn interessante start materialen voor groene chemicaliën met grote toepassingsmogelijkheden. Een bekend voorbeeld is 5-hydroxymethylfurfural (HMF). Het kan gemaakt worden uit D-fructose en, gezien recente ontwikkelingen, mogelijk ook uit goedkopere suikers als D-glucose. In deze dissertatie zijn experimentele studies beschreven naar de omzetting van HMF naar caprolactam, de uitgangsstof voor nylon 6, een veelgebruikt synthetisch polymeer. De voorgestelde route is weergegeven in Schema 1 en bestaat uit twee katalytische hydrogenatie stappen gevolgd door een de-hydrogenatie en een aminering stap. De laatste stap (caprolacton naar caprolactam) is reeds op grote schaal industrieel uitgevoerd en is daarom beschouwd als bewezen technologie.
Caprolactam from Renewable Resources: Catalytic Conversion of 5-Hydroxymethylfurfural into Caprolactone

Schema 1. Voorgestelde synthetische route voor de conversie van HMF naar caprolactam

Een grote uitdaging voor dit onderzoek betrof de ontwikkeling van katalytische routes voor de omzetting van HMF naar 1,6-hexanediol (1,6-HD). Vier verschillende routes zijn onderzocht: i) de directe hydrogenatie van HMF naar 1,6-HD; ii) een twee-stap route via 2,5-THF-dimethanol (THFDM); iii) een drie-stap synthese via THFDM en 1,2,6-hexanetriol (1,2,6-HT); en iv) een vier-stap synthese via THFDM, 1,2,6-HT, en tetrahydro-2H-pyran-2-ylmethanol (2-THPM), zie Schema 2 voor details.

Schema 2. Katalytische routes voor de conversie van HMF naar 1,6-hexanediol (1,6-HD)
De directe conversie van HMF naar 1,6-HD met katalytische hydrogenatie methodologie bleek niet succesvol. Echter, het gebruik van tetrahydrofuran-dimethanol (THFD) als startmateriaal, verkrijgbaar door een katalytische hydrogenatie van HMF, gaf betere resultaten. Een studie naar mogelijke katalysatoren voor de hydrogenatie van HMF naar THFD is beschreven in Hoofdstuk 2. Veelbelovende katalysatoren zijn geïdentificeerd en proces condities zijn geoptimaliseerd om THFD in hoge opbrengsten te verkrijgen. De beste resultaten (99% THFD opbrengst) zijn behaald met een Raney nikkel katalysator bij 100 °C. Voor deze katalysator is een statistisch model ontwikkeld om de THFD opbrengst te correleren aan relevante reactie condities zoals temperatuur (75-250 °C), reactietijd (4-14 h) en waterstof druk (50-90 bar). Het intermediaire furan-dimethanol was in hoge opbrengsten (>99%) te synthetiseren met een NiCu/ZrO₂ katalysator bij 150 °C.

Hoofdstuk 3 beschrijft experimentele studies naar de katalytische ring opening reactie van THFD naar 1,2,6-HT. Een brede scala aan heterogene katalysatoren is getest en bimetalische Rh-Re katalysatoren op silica gaven de beste resultaten. De optimale katalysator bevat 4 wt% Rh en een Re/Rh mol ratio van 0.5. De beste resultaten zijn behaald bij 80 °C, waar 92% selectiviteit naar 1,2,6-HT bij 11% THFD conversie werd gevonden.

De resultaten van de katalytische hydrodeoxygenatie van 1,2,6-HT naar 1,6 HD worden gepresenteerd in Hoofdstuk 4. Verschillende heterogene katalysatoren zijn getest en Rh-ReOₓ/SiO₂ katalysatoren gaven de beste resultaten. Er zijn twee routes bestudeerd, een één-stap en een twee-stap route, waarbij in de laatste 2-THPM als intermediair wordt gebruikt. Bij de één-stap methode is de maximale selectiviteit naar 1,6-HD 73% bij volledige omzetting van 1,2,6-HT. Bij de twee-stap methode kon een 1,6-HD selectiviteit van 96% bij 26% 1,2,6-HT omzetting behaald worden, gebruikmakend van trifluoromethaansulphonzuur in de eerste stap (125 °C) en een katalytische
hydrogenatie met een Rh-ReO\textsubscript{x}/SiO\textsubscript{2} katalysator in de tweede stap (120 C, 80 bar).

In Hoofdstuk 5 wordt een één-pot synthese van 1,6-HD vanuit THFDM door middel van een katalytische hydrodeoxygenatie reactie beschreven. Zeer goede resultaten, 86% opbrengst aan 1,6-HD, zijn behaald met een combinatie van een Rh-ReO\textsubscript{x}/SiO\textsubscript{2} katalysator en Nafion\textsuperscript{®} SAC-13 als de vaste zure katalysator (120 °C, 80 bar). Experimentele reactie profielen gecombineerd met kinetiek modellering geven aan dat 1,2,6-HT als intermediair wordt gevormd, die vervolgens voornamelijk naar 1,6-HD wordt omgezet.

In Hoofdstuk 6 wordt een overzicht gegeven van alle vindingen. Tevens worden de resultaten van additioneel onderzoek aan de omzetting van 1,6-HD naar caprolacton met behulp van homogene katalysatoren gepresenteerd.
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List of Publications

Patent
1. a) J. G. de Vries, **Teddy**, P. H. Phua, I. V. Melián-Cabrera, H. J. Heeres, Preparation of caprolactone, caprolactam, 2,5-tetrahydrofuran dimethanol, 1,6-hexanediol or 1,2,6-hexanetriol from 5-hydroxymethyl-2-furfuraldehyde, WO2011/149339, 2011.
   b) J. G. de Vries, **Teddy**, Preparation of caprolactone, caprolactam, 2,5-tetrahydrofuran dimethanol, 1,6-hexanediol or 1,2,6-hexanetriol from 5-hydroxymethyl-2-furfuraldehyde, EP2390247, 2011.

Peer-reviewed journal


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