Biobased chemicals from lignin
Kloekhorst, Arjan

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Chapter 5

Catalytic hydrotreatment of dimeric model compounds using Ru/C

Part of this chapter was presented as a poster at:

ABSTRACT
The catalytic hydrotreatment of dimeric lignin model compounds representing different lignin linkages (guaiacylglycerol-β-guaiacyl ether (β-O-4), 4-benzyloxy-3-methoxybenzaldehyde (α-O-4), and 2,2′-biphenol (5-5)) was performed with supported Ru on C as the catalyst with n-dodecane as the solvent (250 °C, for 4-5 h, 100 bar of H₂). The composition of the reaction mixture versus batch time for the individual model components were analysed using GC-MS-FID and GCxGC-FID and rationalized by a reaction network. Ether linkages were found to be easily cleaved at the reaction conditions performed, while the 5-5 bond in 2,2′-biphenol was not affected. Ru/C shows a high activity for hydrogenation of aromatic rings and saturated ring structures are found to a large extent. A unique feature of the Ru catalyst is the possibility to cleave sp³-sp³ C-C bonds as is evident from the ring opening of cyclohexyl units and the hydrogenolysis of CH₂-CH₃ bonds.

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5.1 INTRODUCTION

Increased environmental concerns combined with the impending depletion of fossil resources has led to an increase in research on renewable resources for energy, transportation fuels and chemicals. An attractive alternative is lignocellulosic biomass [1-4]. Lignin, the major biopolymer in lignocellulosic biomass, is a potential source for bulk chemicals with aromatic rings like alkylphenolics and aromatics. From a chemical perspective, lignin is an amorphous polyphenolic thermoset which is made in the plant/tree by radical coupling of mainly three aromatic monomers, namely, coniferyl, sinapyl, and p-coumaryl alcohols [5]. A highly complex three-dimensional polymer is formed with different types of linkages between the aromatic nuclei. Of these, the β-O-4, α-O-4, β-5, and 5-5 are the most common.

An interesting valorization technique for lignin involves catalytic hydrotreatment using molecular hydrogen in combination with supported metal catalysts [6, 7]. Early examples of catalysts for the catalytic hydrotreatment of lignin are supported sulphided NiMo/CoMo’s on alumina [8-12]. Typical reaction conditions are around 300 to 450 °C with pressures up to 200 bar H₂. These relatively extreme conditions are required to depolymerise the lignin into a low molecular weight oil as shown by earlier work from Meier et al., and Oasmaa et al. [13, 14]. However, product selectivity is a major issue. In all cases, catalytic hydrotreatments of lignin leads to a complex reaction mixture with various component classes (catechols, alkylphenolics, alcohols, alkanes). In addition, the products are not solely monomeric compounds but also contain a large proportion of oligomers (GPC). Thus, there is a great incentive to develop active catalyst with a high selectivity to monomeric compounds like alkylphenolics and aromatics, existing bulk chemicals with a value between 800 and 1200 euro/ton. As a result, model studies with primarily monomeric lignin compounds have been performed in great detail [6]. However, catalytic hydrotreatment model studies with dimeric lignin model compounds have been investigated in by far less detail. These studies are of interest to probe the reactivity of the various linkages in the lignin structure and to steer the reactivity to the formation of monomeric compounds. An overview of literature studies on the catalytic hydrotreatment of dimeric lignin compounds using supported metal catalysts is given in Table 5.1. The table is divided into two sections, one for non-noble metal catalysts like NiMo and CoMo and a second part for noble metal catalysts (Pd, Pt, Ru, Pd).

The reactions are typically carried out in batch set-ups with temperatures between 200 and 450 °C and hydrogen pressures between 20 and 138 bar. Reactions in apolar solvents (alkanes) as well as the other extreme regarding polarity (water) have been reported. In some cases, the reactions were carried out in neat model compound without dilution. Early research on dimeric model compounds was performed with supported NiMo and CoMo catalysts [6,7]. Krishnamurty et al. explored the catalytic
Table 5.1. Literature overview on the catalytic hydrotreatment of dimeric lignin model compounds using supported metal catalysts.

<table>
<thead>
<tr>
<th>Catalyst Support</th>
<th>Reaction conditions</th>
<th>Solvent</th>
<th>Model Compound</th>
<th>Products</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>T (°C) P (bar) t (h)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Non-noble</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NiMo Al₂O₃</td>
<td>287-376 68-138 2</td>
<td>n-Dodecane</td>
<td>Dibenzofuran, 2-phenyl phenol, 2-cyclohexyl phenol</td>
<td>Cyclic dimers, biphenyl, phenol, cyclohexane</td>
<td>[15]</td>
</tr>
<tr>
<td>CoMo Al₂O₃</td>
<td>300-330 69 7.4-8.25</td>
<td>n-Hexadecane</td>
<td>2,2'-Biphenol</td>
<td>Biphenyl, cyclohexylbenzene, dibenzofuran, 2-phenylphenol</td>
<td>[16]</td>
</tr>
<tr>
<td>CoMo Al₂O₃</td>
<td>280-320 69 4.9-5.3</td>
<td>n-Hexadecane</td>
<td>Phenylether</td>
<td>Benzene, cyclohexane, phenol</td>
<td>[16]</td>
</tr>
<tr>
<td>NiMo Al₂O₃</td>
<td>350-390 70 0-20 h⁻¹ LHSV</td>
<td>C₈ paraffin mixture</td>
<td>Dibenzofuran</td>
<td>Cyclohexylbenzene, dicyclohexyl, biphenyl, monocyclic structures, benzene</td>
<td>[17]</td>
</tr>
<tr>
<td>Thermal</td>
<td>390-450 98 0.83</td>
<td>-</td>
<td>Dimeric compounds</td>
<td>Benzene, monophenols, dimers</td>
<td>[18]</td>
</tr>
<tr>
<td>Fe₂O₃, NiMo, MoO₃ Al₂O₃, TiO₂</td>
<td>390-450 98 0.83</td>
<td>-</td>
<td>Dimeric compounds</td>
<td>Benzene, monophenols, dimers</td>
<td>[18]</td>
</tr>
<tr>
<td>CoMo Al₂O₃ (S)</td>
<td>300 50 4</td>
<td>n-Dodecane</td>
<td>(β-O-4),(5-5) dimeric</td>
<td>Phenolic, aromatics,</td>
<td>[19]</td>
</tr>
<tr>
<td>Noble</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pd C</td>
<td>250 40 0.5-2 H₂O</td>
<td>5-5 dimer</td>
<td>Intact structure</td>
<td></td>
<td>[20]</td>
</tr>
<tr>
<td>Pd C</td>
<td>250 40 0.5-2 H₂O</td>
<td>α-0-4 dimer</td>
<td>Three C₇-C₉ hydrocarbons</td>
<td></td>
<td>[20]</td>
</tr>
<tr>
<td>Pt C</td>
<td>200 20 2 H₂O, H₃PO₄/H₂O</td>
<td>Phenol, guaiacol, dimeric compounds</td>
<td>Cyclic alkanes, aromatics, phenolics</td>
<td></td>
<td>[21]</td>
</tr>
</tbody>
</table>
hydrotreatment of dibenzofuran (DBF) with a sulphided NiMo/γ-Al₂O₃ catalyst (343-376 °C, 68.9-138 bar, 2 h, catalyst intake 1.75-2.5 wt%), see Scheme 5.1. [15].

Scheme 5.1. Reaction network for the HDO of dibenzofuran [15].

Main products were biphenyl and cyclohexyl benzene, and indication that the C-O bond is more easily cleaved than the C-C bond. In addition, phenyl hexanol was observed, which also suggests that C-C bonds are cleaved by the action of the catalyst (Scheme 5.1). However, the formation of phenyl-hexanol is doubted in a later study by LaVopa et al. [17].

Lavopa et al. also investigated the catalytic hydrotreatment of DBF in a continuous setup with a sulfided NiMo/Al₂O₃ catalyst in a C₁₆ paraffin mixture as solvent [17]. The reaction was performed at a LHSV of 0-20 h⁻¹ reactant at 350-390 °C at a hydrogen pressure of 70 bar. Main components were similar to those reported by Krishnamurthy et al. [15] with the main difference that a higher amount of monomeric compounds viz, (methyl)cyclohexane, (methyl)cyclopentane, cyclohexene and benzene (~70 % on initial DBF) were reported.

The use of 2,2'-biphenol and phenylether as model components was explored by Petrocelli et al. [16]. The reactions were performed with an sulphided CoMo/γ-Al₂O₃ (69 bar hydrogen, at 7.4-8.25 h and 300-330 °C for 2,2'-biphenol and 4.9-5.3 h and 280-320 °C for phenyl ether) with n-hexadecane as solvent and 4 wt% of catalyst on reactant intake, see Scheme 5.2.

Scheme 5.2. Reaction pathway of the hydrodeoxygenation of (a) 2,2'-biphenol and (b) phenyl ether [16].
Products of phenyl ether were benzene, cyclohexane, and phenol, indicative for complete cleavage of the ether bond and the formation of monomers. In contrast, the products from 2,2'-biphenol were mainly dimers and some phenol and benzene. Thus, cleavage of the 5-5 linkage at these conditions is more difficult than for the ether bond.

The cleavage of ether and carbon-carbon linkages was investigated by Koyoma using benzylphenylether, 4-hydroxydiphenylether, diphenylether, 4-hydroxydiphenylmethane, diphenylmethane, dibenzyl, biphenyl, and 2-hydroxy-biphenyl [18]. Multiple catalysts (Fe$_2$O$_3$-S, Fe$_2$O$_3$/Al$_2$O$_3$-S, NiMo/Al$_2$O$_3$, MoO$_3$/TiO$_2$-S) and model compounds in the absence of a solvent were used (340-450 °C for 50 min with 98 bar of hydrogen).

Most of the carbon-carbon linkages in the dimeric compounds were not converted, even at very high reaction temperatures (450 °C). The only exception is dibenzyl which formed benzene (83 % GC area) at these conditions. Apparently, the cleavage of linkages between two sp$^3$ C-C bonds (DB) is more facile than for sp$^2$ C-C bonds (BP) and
mixed sp²-sp³ C-C bonds (DPM). The presence of –OH substituents on the aromatic rings also affect the level of monomer formation. Highest levels of carbon-carbon cleavage was observed for the Mo based catalysts (NiMo and MoO₃/TiO₂-S). For comparison, the reactions were also performed in the absence of a catalyst (thermal). Monomer (phenol and benzene) yields of up to 70 % were obtained for the dimeric model compounds with ether linkages at reaction temperature exceeding 390 °C. However, substantial repolymerisation occurred leading to the formation of higher oligomers (e.g. dimers).

A recent article from Jongerius et al. reports the reactivity of dimeric lignin model compounds with ether and carbon-carbon bond linkages (Scheme 5.3) [19].

![Scheme 5.3. Conversion and selectivity (mol%) for a) 1-hydroxy-1-(4-hydroxy-3-methoxyphenyl)-2-(2,6-dimethoxyphenoxy)ethane (β-O-4) and b) 2,2′-biphenol (5-5) with an sulphided CoMo/Al₂O₃ catalyst (300 °C, 50 bar H₂, 4 h) [19].](image)

Reactions were performed in n-dodecane (300 °C, 4 h, 50 bar H₂) with a sulphided CoMo/Al₂O₃ catalyst (10 wt% on reactant intake). The ether linkage (β-O-4) in 1-hydroxy-1-(4-hydroxy-3-methoxyphenyl)-2-(2,6-dimethoxyphenoxy)ethane (top (a) in Scheme 5.3) was completely converted after reaction (¹H-NMR) and 33 mol% of monomeric compounds like, phenol, methylphenolics and methoxyphenolics, were formed. The 5-5 linkage in 2,2′-biphenol was very persistent and cleavage was not observed after 4 h reaction time.

Recently, studies on the catalytic hydrotreatment of dimeric lignin model compounds have been reported using noble metal catalysts. Yan et al. investigated the catalytic hydrotreatment of lignin model compounds with an α-O-4 and 5-5 linkage using Pd/C as the catalyst and acidified water (5 wt% H₃PO₄) as the solvent (40 bar H₂, 250 °C, 0.5 h) [20]. The α-O-4 linkage was quantitatively cleaved and monomeric compounds were formed (three C₇-C₉ hydrocarbons and methanol), see Scheme 5.4 for details.
CATALYTIC HYDROTREATMENT OF DIMERIC MODEL COMPOUNDS USING RU/C

Scheme 5.4. Catalytic hydrotreatment of 5-5 and α-O-4 dimers using Pd/C [20].

The 5-5 linkage remained intact during the catalytic hydrotreatment, but methoxy and hydroxyl groups were hydrodeoxygenated.

The activity of Pt/C for the cleaving of ether and carbon-carbon bonds in dimeric compounds was investigated by Güvenatam et al. [21]. The reactions were performed in water in the presence and absence of a Brønsted acid (H₂PO₄) at 200 °C with an initial intake of 20 bar H₂ for 4 h. The ether linkage was easily cleaved while the 5-5 linkage remained intact (Scheme 5.5). The catalyst showed a high activity for the hydrogenation of aromatic compounds to saturated cyclic ring structures.

Scheme 5.5. Catalytic hydrotreatment of biphenylether with Pt/C catalyst (4 h, acidic condition, 200 °C, water, 20 bar H₂ [21].

We here report a study on the catalytic hydrotreatment of dimeric lignin model using Ru/C as the catalyst. Ru/C is reported to be an effective catalyst for the depolymerization of lignin towards monomeric lignin compounds, as shown by Pepper et al. [22, 23]. This was supported by recent research on the hydrotreatment of pyrolytic lignin (400 °C, 100 bar H₂, 4 h) with Ru/C [24]. Recent experiments with monomeric lignin model compounds like guaiacol, phenol, and anisole showed that Ru/C is an active hydrodeoxygenation catalyst, though hydrogenation of the aromatic ring to saturated cyclic structures occurs to a significant extent [21, 25-28].

The dimeric lignin compounds used in the study contain the three most relevant linkages namely, guaiacylglycerol-β-guaiacyl ether (β-O-4), 4-benzyloxy-3-methoxybenzaldehyde (α-O-4), and 2,2'-biphenol (5-5), see Figure 5.2 for details.
The reactions with the dimeric model compounds were performed in a batch reactor with \( n \)-dodecane as the solvent at 250 °C at 100 bar with a reaction time of 4.5 to 5.5 h. Major components were identified in the liquid phase and quantified with GCxGC-FID and GC-MS-FID. \( n \)-Dodecane was selected as the solvent because of its high boiling point and apolar nature. As such it represents the rather apolar products formed upon the catalytic hydrotreatment reaction and is representative for the actual lignin hydrotreatments.

5.2 MATERIALS AND METHODS

5.2.1 Chemicals
Ruthenium on carbon (5 wt% Ru, powder), 4-benzyloxy-3-methoxybenzaldehyde (98 %), 2,2'-biphenol (99 %), di-\( n \)-butylether (≥99,5 %), tetrahydrofuran (99.99 %), bicyclohexyl (99 %), and \( n \)-dodecane (99.9 %) were obtained from Sigma Aldrich. Guaiacylglycerol-\( \beta \)-guaiacyl ether (>99 %) was obtained from TCI Europe. All chemicals and catalyst were used as received. Hydrogen (> 99.999 %) and nitrogen gas (> 99.999 %) were obtained from Hoekloos.

5.2.2 Catalytic hydrotreatment reactions
The catalytic hydrotreatment experiments of the model compounds were performed in a 100 ml batch autoclave (Parr) equipped with a dip tube and a sample collection system. The autoclave has a maximum operation temperature of 350 °C and pressure of 350 bar. The reactor is surrounded by a metal block containing electrical heating elements and channels allowing the flow of cooling water. The reactor content was stirred mechanically using a Rushton type turbine with a gas induced impeller at 1200 RPM to avoid G-L mass transfer limitations. Temperature and pressure were monitored and logged on a PC.

Before reaction, the catalyst was activated with hydrogen. For this purpose, the reactor was charged with 5 wt% of Ru/C (based on reactant intake) and 30-35 g of \( n \)-dodecane. After closing the reactor 20 bar of hydrogen was added at room temperature, afterwards the reactor was heated till 250 °C and kept there for 2 h. After cooling and venting the gasses, the reactor was loaded with 5 g of 2,2'-biphenol or 4-benzyloxy-3-methoxybenzaldehyde. Intake for guaiacylglycerol-\( \beta \)-guaiacylether
was only 1 g due to limited availability. Subsequently, the reactor was closed and leak tested by pressurizing to 100 bar hydrogen. After this leak test, the reactor was flushed three times with hydrogen and pressurized to 10 bar of hydrogen at room temperature, and subsequently stirring (1200 RPM) and heating was started to the intended reaction temperature with a rate of about 20 °C min⁻¹. When the reaction temperature was reached the hydrogen pressure was increased to 100 bar pressure and the reaction time is set to t = 0. In the first hour, liquid samples were taken every 15 min and after 1 hour reaction time, liquid samples were taken on an hourly basis. A typical reaction time lasted between 4.5 and 5.5 h. After reaction, the reactor was cooled to room temperature.

5.3 LIQUID ANALYSES

Before GC-MS-FID and GCxGC-FID analyses, the organic samples were diluted with tetrahydrofuran (THF) and a 1000 ppm di-n-butylether (DBE) was added as an internal standard.

GC-MS-FID analyses were performed on a Hewlett Packard 5890 series II plus with a Quadrupole Hewlett Packard 5972 MSD and a FID. The GC is equipped with a Restek RTX-1701 capillary column (60 x 0.25 mm i.d. and 0.25 μm film thickness) and the product after the column is split in a 1:1 ratio and sent to an MS and FID detector. The injector temperature was set at 280 °C. The oven temperature was kept at 40 °C for 4 minutes then heated up to 250 °C at a rate of 3 °C min⁻¹.

GCxGC-FID analysis were performed on organic samples with a trace GCxGC from Interscience equipped with a cryogenic trap system and two columns: a 30 m x 0.25 mm i.d. and 0.25 μm film of RTX-1701 capillary column connected by a meltfit to a 120 cm x 0.15 mm i.d. and 0.15 μm film Rxi-5Sil MS column. An FID detector was applied. A dual jet modulator was applied using carbon dioxide to trap the samples. Helium was used as the carrier gas (continues flow 0.8 ml min⁻¹). The injector temperature and FID temperature were set at 280 °C. The oven temperature was kept at 40 °C for 5 minutes then heated up to 250 °C at a rate of 3 °C min⁻¹. The pressure was set at 70 kPa at 40 °C. The modulation time was 6 seconds.
5.4 RESULTS AND DISCUSSION

The reactions with the dimeric model compounds were performed in a batch reactor with \( n \)-dodecane as the solvent at 250 °C at 100 bar with a reaction time of 4.5 to 5.5 h. In all cases, Ru/C was used as the catalysts. The results for the individual model components will be discussed in detail in the following sections.

5.4.1 Catalytic hydrotreatment of 4-benzyloxy-3-methoxybenzaldehyde (1)

The product distribution versus the batch time for the reaction of 1 is given in Table 5.1 and Scheme 5.6. Full conversion of the reactant was found after 1 h reaction time. The main products after reaction were fully saturated compounds without remaining C-C double bonds, viz. a single dimer, 4-cyclohexyl-methoxy-3-methoxy-1-methylcyclohexane 4 and four monomers viz., 4-methylcyclohexanol (cis and trans) 7, methylocyclohexane 8, 4-methyl-cyclohexanol 9, and cyclohexanol 10. Thus cleavage of the ether bond of the dimeric reactant occurs to a significant extent (90 %) but is not quantitative. In addition, hydrogenation of aromatic C-C double bonds is facile with Ru/C leading to a high extent of cyclic saturated structures.

![Scheme 5.6](image)

Table 5.1. Product distribution for the conversion of 4-benzyloxy-3-methoxybenzaldehyde 1.*

<table>
<thead>
<tr>
<th>Time (h)</th>
<th>Conv. 1 (%)</th>
<th>2 (%)</th>
<th>3 (%)</th>
<th>4 (%)</th>
<th>5 (%)</th>
<th>6 (%)</th>
<th>7 (%)</th>
<th>8 (%)</th>
<th>9 (%)</th>
<th>10 (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.3</td>
<td>43</td>
<td>24.7</td>
<td>0.0</td>
<td>0.0</td>
<td>0.2</td>
<td>0.6</td>
<td>0.0</td>
<td>0.1</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>0.6</td>
<td>72</td>
<td>42.7</td>
<td>0.2</td>
<td>0.0</td>
<td>1.0</td>
<td>1.5</td>
<td>0.0</td>
<td>0.3</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>1.1</td>
<td>98</td>
<td>6.1</td>
<td>8.5</td>
<td>0.2</td>
<td>4.1</td>
<td>9.6</td>
<td>20.1</td>
<td>4.5</td>
<td>4.5</td>
<td></td>
</tr>
<tr>
<td>2.6</td>
<td>100</td>
<td>0.0</td>
<td>5.2</td>
<td>6.2</td>
<td>0.0</td>
<td>0.0</td>
<td>23.2</td>
<td>28.5</td>
<td>12.6</td>
<td>8.8</td>
</tr>
<tr>
<td>4.6</td>
<td>100</td>
<td>0.0</td>
<td>0.0</td>
<td>10.1</td>
<td>0.0</td>
<td>19.2</td>
<td>29.7</td>
<td>16.2</td>
<td>15.7</td>
<td></td>
</tr>
</tbody>
</table>

*) Reaction with 5 g reactant in 30 gr of \( n \)-dodecane: 250 °C, 100 bar H\(_2\), 4 h, with 5 wt% of Ru/C on reactant (yields in wt% on compound intake), †) Maximum yield of individual compounds are displayed in bold.
On the basis of the product composition versus batch time, a reaction network is proposed and given in Scheme 5.6. The main intermediate is the dimeric 4-benzyloxy-3-methoxy-1-methylbenzene 2, formed in 43% yield after 0.6 h by hydrodeoxygenation of the aldehyde group of substrate 1. This initial high reactivity of the aldehyde group is a known feature of the Ru/C catalyst [25, 29].

Scheme 5.6. Proposed reaction network for the catalytic hydrotreatment of (1) using a Ru/C catalyst.

Subsequently, 2 is converted by at least two parallel reactions pathways. The first involves cleavage of the ether bond by hydrogenolysis and the formation of 2-methoxy-4-methylphenol 5 and toluene 6. In parallel, hydrogenation of aromatic C-C double bonds occurs, ultimately leading to 4. Both hydrogenolysis of the ether bond in 4 and the subsequent hydrogenation of 5 and 6 lead to the fully saturated monomeric compounds 7 and 8. In the final stage, considerable demethoxylation takes place and 4-methylcyclohexanol is formed 9.

Thus, it appears that both hydrogenolysis of the ether linkage as well as hydrogenation of C-C double bonds are the main reactions occurring with the Ru/C catalyst. C-C double bond hydrogenation is faster at the prevailing reaction conditions than ether hydrogenolysis as full conversion of the ether linkage (and the concomitant formation of monomers) is not observed. Demethoxylation appears less favorable and occurs only at a significant extent at the end of the reaction.
5.4.2 Catalytic hydrotreatment of guaiacylglycerol-β-guaiacylether (a)

The product distribution versus the batch time for the reaction of guaiacylglycerol-β-guaiacylether (a) is given in Table 5.2 and Scheme 5.7. Unfortunately, it proved not possible to quantify the amounts of the substrate by GC, thus conversion data cannot be provided. In addition, ring saturated dimers arising from a were also not detected. This may either indicate that the ether linkage in a is easily cleaved with Ru/C to form monomeric compounds or that these are also not GC-detectable. Suitable model components could not be obtained to verify the suitability for GC analyses. This aspect seriously hampers the discussion on the rate of dimer conversion to monomers and the reactivity of the ether bond.

The main products after reaction were two monomeric compounds, e (9.2 wt%) and h (26.8 wt%). The formation of the former is surprising as it contains an ethyl substituent instead of the expected n-propyl group. This indicates that hydrogenolyses of a CH2-CH3 group is possible with Ru/C, likely with the concomitant formation of methane.

Table 5.2. Production composition for the catalytic hydrotreatment of guaiacylglycerol-β-guaiacylether (a).*

<table>
<thead>
<tr>
<th>Time (h)</th>
<th>Conv. a (%)</th>
<th>b</th>
<th>c</th>
<th>d</th>
<th>e</th>
<th>f</th>
<th>g</th>
<th>h</th>
<th>Yield (wt%)†</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25 n.d.</td>
<td>14.8</td>
<td>9.5</td>
<td>5.1</td>
<td>0.7</td>
<td>0.0</td>
<td>0.0</td>
<td>1.8</td>
<td>0.0</td>
<td></td>
</tr>
<tr>
<td>1 n.d.</td>
<td><strong>27.7</strong></td>
<td><strong>16.1</strong></td>
<td><strong>10.1</strong></td>
<td>2.7</td>
<td>0.0</td>
<td>0.0</td>
<td>4.6</td>
<td>0.0</td>
<td></td>
</tr>
<tr>
<td>2.5 n.d.</td>
<td>21.4</td>
<td>9.5</td>
<td>10.0</td>
<td>7.7</td>
<td>3.6</td>
<td>0.6</td>
<td>17.9</td>
<td>1.2</td>
<td></td>
</tr>
<tr>
<td>5.5 n.d.</td>
<td>10.5</td>
<td>2.7</td>
<td>7.2</td>
<td><strong>9.2</strong></td>
<td><strong>9.6</strong></td>
<td><strong>2.8</strong></td>
<td><strong>26.8</strong></td>
<td>5.0</td>
<td></td>
</tr>
</tbody>
</table>

*) Reaction with 1 g reactant in 35 g of n-dodecane: 250 °C, 100 bar H2, 5 h with 5 wt% of Ru/C on reactant (yields in wt% on compound intake), †) Maximum yields of individual compounds are given in bold.
Scheme 5.7. Proposed reaction pathway for the catalytic hydrotreatment of (a) using Ru/C.

Based on the product distribution versus time, a reaction network is proposed and given in Scheme 5.7. Main intermediates are dihydroconiferyl alcohol b, 2-methoxyphenol c, and 2-methoxy-4-propylphenol d. Dihydroconiferyl alcohol is also detected in reaction mixtures after the catalytic hydrotreatment of lignin with Ru/C at low temperatures and is formed by hydrogenolysis of the ether bond followed by water elimination/hydrogenation (hydrodeoxygenation) of the alcohol at the α-position [22, 23]. Further hydrodeoxygenation of the alcohol group at the γ-position gives 2-methoxy-4-propylphenol d. This compound may react in two parallel reaction pathways to 2-methoxy-4-ethylcyclohexanol f, viz. i) demethylation followed by hydrogenation of the C-C double bonds or ii) hydrogenation of the aromatic C-C double bonds and subsequently demethylation.

On the basis of the product distribution, we can conclude that C-C double bond hydrogenation occurs to a lesser extent than for model the compound 4-benzyloxy-3-methoxybenzaldehyde 1. Unfortunately, a proper comparison is difficult as i) it proved not possible to identify and quantify the dimeric reactant and possible dimeric products by GC and ii) the intake of reactant for both reactions were different.
5.4.3 Catalytic hydrotreatment of 2,2'-biphenol (I)

The product distribution versus the batch time for the catalytic hydrotreatment reaction of I is given in Table 5.3 and Scheme 5.8. After 4 h, only 20 % of the reactant is converted to monomeric compounds, which indicates that hydrogenolyses of the C-C bond is difficult. The main products formed after the reactions were three ring saturated dimers (2-cyclohexylphenol II, 2-hydroxy-bicyclohexyl III, and bicyclohexyl IV) and a single monomer (n-pentylcyclohexane V). This indicates that hydrogenation of the C-C double bonds occurs to a significant extent. In addition, it appears that OH removal takes place after the hydrogenation of the aromatic C-C double bonds and that direct cleavage of the sp$^2$-C-OH bond does not occur.

![Reaction scheme](image)

Table 5.3. Product composition for the catalytic hydrotreatment of 2,2'-biphenol (I) with Ru/C.*

<table>
<thead>
<tr>
<th>Time (h)</th>
<th>Conv. I (%)</th>
<th>II</th>
<th>III</th>
<th>IV</th>
<th>V</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>31.8</td>
<td>3.5</td>
<td>12.6</td>
<td>1.0</td>
<td>0.2</td>
</tr>
<tr>
<td>0.75</td>
<td>61.6</td>
<td><strong>13.4</strong></td>
<td>36.1</td>
<td>8.9</td>
<td>0.8</td>
</tr>
<tr>
<td>1</td>
<td>83.3</td>
<td>3.3</td>
<td><strong>51.4</strong></td>
<td>18.2</td>
<td>2.2</td>
</tr>
<tr>
<td>2</td>
<td>99.6</td>
<td>0.0</td>
<td>49.9</td>
<td>35.1</td>
<td>9.8</td>
</tr>
<tr>
<td>4</td>
<td>100</td>
<td>0.0</td>
<td>7.9</td>
<td><strong>71.8</strong></td>
<td>12.2</td>
</tr>
</tbody>
</table>

*) Reaction with 5 gr reactant in 30 gr of n-dodecane: 250 °C, 100 bar H$_2$, 4 h with 5 wt% of Ru/C on reactant, †) Maximum yields of individual components are given in bold.

Formation of monomer V reveals that cleavage of C-C bonds is possible with Ru/C (as in the case of model compound a). Further proof of ring opening was explored by performing a catalytic hydrotreatment reaction with IV at 250 °C with 100 bar H$_2$ for 4 h, see Table 5.4 for details. The reaction was performed in the absence of n-dodecane, so that the formation of ring-opened alkanes can be traced back solely to the reactant.
Table 5.4. Production composition for the catalytic hydrotreatment of bicyclohexyl (IV).*

<table>
<thead>
<tr>
<th>Time (h)</th>
<th>Conv. IV (%)</th>
<th>V Yield (wt%)†</th>
<th>VI Yield (wt%)†</th>
<th>VII Yield (wt%)†</th>
<th>VIII Yield (wt%)†</th>
<th>IX Yield (wt%)†</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>8.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>1.5</td>
<td>15.7</td>
<td>0.1</td>
<td>1.1</td>
<td>0.6</td>
<td>1.6</td>
<td>0.3</td>
</tr>
<tr>
<td>3</td>
<td>24.4</td>
<td>0.3</td>
<td>2.9</td>
<td>1.5</td>
<td>4.0</td>
<td>0.7</td>
</tr>
<tr>
<td>5</td>
<td>35.7</td>
<td>0.6</td>
<td>4.8</td>
<td>2.5</td>
<td>6.7</td>
<td>1.7</td>
</tr>
</tbody>
</table>

*) Reaction with 30 g compound without solvent (250 °C, 100 bar H₂, 4 h with 5 wt% of Ru/C on reactant, †) Maximum yields of individual compounds are given in bold.

After 4 h reaction time, about 35 % of IV was converted to ring opened products, indicative that cleavage of C-C bonds is feasible with Ru/C though at a relatively low reaction rate. The main products were 5 monomeric compounds with 11 and 12 carbon atoms; n-pentylcyclohexane V, (1-methylpentyl)-cyclohexane VI, (1-ethylbutyl)-cyclohexane VII, hexylcyclohexane VIII, and (1-methylpropyl)-cyclohexane IX. The C12 products are formed by cleavage of the C-C bond in cyclohexyl rings by hydrogenolysis, the C11 products likely by a subsequent hydrogenolysis of CH₂-CH₃ groups and the formation of methane. In line with these finding is the presence of methane in the gasphase after reaction. Remarkably, cleavage of the C-C linkage between the cyclohexyl groups was not observed. This reactivity pattern suggests that hydrogenolysis of C-C bonds with primary carbons is more facile than for more substituted carbon atoms.

On the basis of the product composition versus batch time for I, supported by individual reactions with intermediate (IV) a reaction network is proposed and given in Scheme 5.8.
Scheme 5.8. Proposed reaction pathway for the catalytic hydrotreatment of (I) using Ru/C.

The formation of alkanes (e.g. cyclic alkanes with a hydrocarbon side chain) is also reported for the catalytic hydrotreatment of Alcell lignin with Ru/C at 400 °C for 4 h with 100 bar H₂ initial hydrogen intake, see Chapter 2, Table 2.4 and 2.5. Based on the findings reported here, these are likely formed by C-C scissions of a bicyclohexyl unit (IV), formed by hydrogenation of aromatic rings linked by a 5-5 bond.

5.5 CONCLUSION

A model compound study was performed on the catalytic hydrotreatment of three dimeric lignin compounds with Ru/C as the catalyst. It appears that ether bond cleavage is very facile, whereas hydrogenolyses of the substituted C-C bond linkage in 2,2-biphenol is not possible under the given reaction conditions. Ru/C shows a high activity for hydrogenation of aromatic rings and saturated ring structures are found to a large extent. Hydrodeoxygenation reactions like the removal of -OH and -OMe groups are often occurring in a later stage. A unique feature of the Ru catalyst is the possibility to cleave sp³-sp³ C-C bonds. This reactivity is evident from the ring opening reactions of cyclohexyl groups and the conversion of n-propyl substituents to ethyl substituents.
ACKNOWLEDGMENT

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REFERENCES


