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Green Chemistry

Catalytic cleavage of lignin β-O-4 link mimics using copper on alumina and magnesia–alumina†

Zea Strassberger, Albert H. Alberts, Manuel J. Louwerse, Stefania Tanase* and Gadi Rothenberg*

Copper on γ-alumina and mixed magnesia–alumina, Cu/MgO–Al₂O₃, catalyse the hydrodeoxygenation (HDO) of β-O-4 lignin-type dimers, giving valuable aromatics. The typical selectivity to phenol is as high as 20%. By changing the support’s acidity we can modify the dispersion of copper. Interestingly, more HDO occurs with larger copper agglomerates than with finely dispersed particles. The presence of copper also increases the selectivity of the HDO cleavage. Three different pathways are hypothesized for the reaction on the catalyst surface. Thus, copper activates ketones more and especially more selective towards cleavage than their corresponding alcohols. DFT calculations of bond dissociation energies correlate well with this experimental observation. Excitingly, ethylbenzene is formed in proportional amounts to phenol, showing that these catalysts can reduce the oxygen content of lignin-type product streams. Considering its low price and ready availability, we conclude that copper on alumina is a promising alternative catalyst for lignin depolymerization.

Introduction

Woody biomass holds the key for reducing our dependency on fossil carbon sources. The majority of nonfood-derived biomass is lignocellulose, a giant matrix of hemicellulose, cellulose and lignin. Currently, two approaches are used for converting this into liquid fuels and bulk chemicals: acid-catalyzed treatment and high-temperature pyrolysis/gasification. But both of these routes share the same problem: the breaking down of the valuable functional groups in lignin and cellulose. Since 2000, several methods have been published regarding transforming cellulose to more valuable chemicals such as glucose, sorbitol and HMF. However, there is still no viable process for converting lignin into chemicals, even though some industrial sectors produce massive amounts of lignin as a by-product. The pulp and paper industry, for example, produced in 2008 over 40 million tons of lignin, 95% of which was simply burned to generate energy.

Burning lignin is wasteful, because it is the most abundant natural resource of aromatic compounds. Fig. 1 shows a typical lignin fragment. Phenylpropane monomers have been identified as the major units of typical lignin (it is a random biopolymer), linked together through C–O bonds of α- and β-arylalkyl ethers. The β-O-4 linkages (highlighted dashed frames in Fig. 1) account for roughly 50% of all the linkages in lignin. Cleaving them selectively would give smaller fragments, while preserving the aromatic groups.

Fig. 1 A typical lignin fragment (lignin is a random biopolymer) showing four β-O-4 linkages highlighted by dashed rectangles.
Our aim, thus, is finding a selective catalytic alternative for converting lignin into high-value aromatics. The challenge is not so much in depolymerising lignin, but rather in finding a catalyst that will selectively cleave the β-O-4 linkages while preserving the aromaticity. Here we will show that Cu/γ-Al₂O₃ can do this job.

Results and discussion

To start with, we selected appropriate β-O-4 linkage analogues. These must be similar enough to the real lignin so that the results are relevant, yet still simple enough for carrying out meaningful experiments on laboratory scale. While previous research focused on small monomers and alcohol–ether-type dimers, we opted for ketone–ether dimers, which are also important products of lignin depolymerisation. These were synthesized following the procedure of Britt et al. (eqn (1) and (2)).

\[
\begin{align*}
\text{Ph} & \quad \text{Br} \quad \text{OH} \\
+ & \quad \text{KOH} \\
\text{DMF} & \quad 16h, 25^\circ C \\
\text{Ph} & \quad \text{O} \\
\text{Ph} & \quad \text{O} \\
\text{isolated yield of 86% 1} \\
\text{Ph} & \quad \text{O} \\
\text{Ph} & \quad \text{O} \\
\text{isolated yield of 73% 2}
\end{align*}
\]

(1)

(2)

For catalysts, we focused on copper and copper oxides supported on γ-Al₂O₃ and MgO–Al₂O₃. Apart from their economic and environmental advantages over heavy/noble metals, copper catalysts were also reported for hydro-deoxygenation reactions. Allegrini et al. showed the potential of reductive deoxygenation using copper on different supports, where aromatic ketones were fully deoxygenated to their methylene analogues. More recently, Sittisa et al. reported that surface copper interacts preferentially with carbonyl groups rather than with aromatic rings. This was explained in terms of the preferred adsorption mode on Cu, n°(O)-carbonyl, and the relatively weak interaction of copper with carbon–carbon double bonds. Therefore, we reasoned that copper sites might help to retain the aromaticity of our products.

As supports, we used the acidic/basic combination of magnesia–alumina, details of which are published elsewhere, and pure γ-alumina. We thus synthesised CuO/γ-Al₂O₃ and CuO/MgO–Al₂O₃.

The X-ray diffraction patterns of Cu/γ-Al₂O₃ and CuO/γ-Al₂O₃ show broad peaks for the alumina, indicating small crystallites. However, the copper peaks are very sharp, so the clusters are rather large (Fig. 2). These reflect the formation and agglomeration of crystalline Cu and CuO. Conversely, the XRD patterns of Cu/MgO–Al₂O₃ reveal much more dispersed copper particles, showing broad Cu(0) and CuO peaks. Note that Feng et al. reported that the presence of MgO can lead to a wider dispersion of the metal on the surface of the support.

Using TPR data (see Fig. 3) to approximate the reduced metal content by measuring the hydrogen consumption, we calculated that there was 10.6 wt% of copper on the alumina and 10.4 wt% of copper on the mixed support, magnesia–alumina. Nonetheless, comparing the two graphs shows two main differences: the peak shape and the temperature of reduction. For alumina we can identify two distinguished peaks and a temperature of reduction ranging from 230 to 250 °C. This corresponds to the reduction of Cu(II). The first peak is assigned to CuO clusters, whilst the second one is due to dispersed CuO particles on the γ-Al₂O₃ surface.

In the case of Cu/MgO–Al₂O₃, the XRD pattern showed finely dispersed copper particles but the reduction temperature was higher than for CuO/γ-Al₂O₃ (see Fig. 3). This indicates a stronger interaction between copper oxide and the MgO–Al₂O₃ support, making the CuO particles less accessible.
acetate was stirred under 25 bar of H₂ at 150 °C in a stainless steel autoclave with 2 wt% catalyst without prior reduction of the catalyst (see the detailed procedure in the Experimental section). To also investigate the role of Cu[0], the catalyst was pre-reduced in H₂ for 2 h at 300 °C (the reduction temperature was selected from TPR experiments, see Fig. 3). Reaction progress was monitored by GC. Note that obtaining a quantitative mass balance in HDO reactions is particularly difficult. 16 Here we succeeded in quantifying typically 85–95% with careful calibration and rigorous low-temperature quenching of the reaction mixture.

The main products were monoaromatics, (see Tables 2 and 3) plus typically 3–18% of oligomers. When using the ketone 1, we also observed a significant amount of reduction to the alcohol 2. Using Cu/γ-Al₂O₃ and Cu/MgO-Al₂O₃ gives phenol and ethylbenzene as the main monoaromatic products. This indicates that the cleavage occurs mostly at the C–O-aryl bond (pathway B) and that HDO is the main reaction route. Introducing basic sites on the support hinders HDO (the selectivity to ethylbenzene drops considerably; see for example the last two entries in Tables 2 and 3).

![Fig. 3](Image 303x579 to 342x629) Temperature programmed reduction (TPR) plots for CuO/γ-Al₂O₃ (gray line) and CuO/MgO-Al₂O₃ (black line) using hydrogen as a reducing agent.

Interestingly, the alcohol 2 is less reactive than its ketone analogue. Other studies on several β-O-4 models reported a reduction of the bond dissociation energy (BDE) for oxidized species compared to their alcohol analogues. 35,36 We calculated BDEs with DFT for our reactants as well, showing that indeed the ether bond is weaker in the ketone than in the alcohol (Table 1). As BDEs only explain thermal non-catalytic cleavage, we also studied the cleavage of protonated molecules (the cleavage is catalysed by alumina, the activity of which is usually explained by its acidity). However, these calculations were severely hindered by reorganisation of bonds, and therefore no numbers are reported here. Nevertheless, we do observe that both for the ketone and the alcohol the ether bond (pathway B) is activated by protonation of the ether. In the case of the alcohol, though, an immediate reorganisation occurs resulting in oligomerisation rather than cleavage. This fits strikingly well with the oligomerisation observed experimentally.

A side effect increasing the difference in reactivity between the alcohol and ketone may be the three-dimensional shape of the molecules. Modelling the ketone and the corresponding alcohol in the gas phase, we see that the ketone is planar, which allows both oxygens to adsorb simultaneously. The alcohol, however, is twisted (see Fig. 4) making adsorption more difficult. Constraining the alcohol into a planar shape costs 12 kJ mol⁻¹.

Nichols et al. 37 reported the oxidation of the alcohol dimer 2 to the ketone dimer 1 via a well-known Ru-dehydrogenative equilibrium. Under our conditions (substrate 2 and 25 bar of hydrogen pressure), this equilibrium is not observed, as neither dimer 1 nor acetophenone 4 were detected by GC analysis. To rule out the influence of the thermal cleavage in the absence of hydrogen, we ran a series of control experiments with argon pressure. These reactions gave less than 5% conversion. The main products were high-molecular-weight oligomers, with no oxidation of dimer 2 to dimer 1. Thus, at 150 °C an external hydrogen source is required to cleave the β-O-4 linkage via hydrodeoxygenation.

A series of blank experiments starting from 1, both in the absence of any catalyst and with only the oxide support (but

<table>
<thead>
<tr>
<th>Reactant</th>
<th>Pathway</th>
<th>BDE</th>
</tr>
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<tr>
<td>A</td>
<td>265</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>253</td>
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</tr>
<tr>
<td>A</td>
<td>284</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>201</td>
<td></td>
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</table>

Table 1 Bond dissociation energies (BDEs) of 1 and 2 for pathways A and B. Energies are given in kJ mol⁻¹.
no copper), showed no traces of the alcohol 2. This affirms that the reduction of 1 to 2 requires the copper active site.

For both 1 and 2, we envisage a two-step process. To illustrate this hypothesis, we propose the following mechanism for dimer 1 (Scheme 1). Alumina-catalysed hydrogenolysis of the dimer's C–O(aryl) bond (pathway B) occurs first, giving acetophenone and phenol. This is followed by copper-catalysed hydrodeoxygenation of the carbonyl group to the

![Scheme 1 Reaction pathways for the β-O-4 cleavage of dimer 1.](image)

Table 2 Product distribution for the conversion of 2-phenoxy-1-phenylethanone 1

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Reactant</th>
<th>Conv. %</th>
<th>Mass balance %</th>
<th>2</th>
<th>3</th>
<th>Yield%</th>
</tr>
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<tr>
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<td>88.1</td>
<td>45.2</td>
<td>17.3</td>
<td>1.8</td>
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<tr>
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<td>0.1</td>
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<td>87.5</td>
<td>34.4</td>
<td>10.2</td>
<td>1.6</td>
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</table>

Cu/MgO–Al2O3

Yields determined by GC analysis (chlorobenzene is the external standard).

<table>
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<tr>
<th>Catalyst</th>
<th>Reactant</th>
<th>Conv. %</th>
<th>Mass balance %</th>
<th>3</th>
<th>Yield%</th>
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<td>&lt;1</td>
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<tr>
<td>γ-Al2O3</td>
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<td>89.5</td>
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<td>MgO–Al2O3</td>
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<td>CuO/γ-Al2O3</td>
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<td>93.0</td>
<td>21.7</td>
<td>0.1</td>
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<tr>
<td>Cu/MgO–Al2O3</td>
<td></td>
<td>47.0</td>
<td>95.0</td>
<td>24.7</td>
<td>0.1</td>
</tr>
</tbody>
</table>

Yields determined by GC analysis (chlorobenzene is the external standard). Standard reaction conditions: 0.120 mg reactant 1 in 10 mL EtOAc; 25 bar H2; 150 °C; 21 h, 2 wt% catalyst (amount of copper relative to 1) and with a minimal TON of 48–50. Catalyst was used without prior reduction and no inert conditions during reaction process. Standard reaction conditions: 0.120 mg reactant 2 in 10 mL EtOAc; 25 bar H2; 150 °C; 21 h, 2 wt% catalyst (amount of copper relative to 2) and with a minimal TON of 42–48. Prior to the experiments, all catalysts were reduced at 300 °C under a flow of H2 for 2 h, the solvent was purged for 2 h with N2 and autoclaves were purged thrice.

**Table 3 Product distribution for the conversion of 2-phenoxy-1-phenylethanol 2**

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Reactant</th>
<th>Conv. %</th>
<th>Mass balance %</th>
<th>Yield%</th>
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<td>25.7</td>
<td>89.5</td>
<td>2.5</td>
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<tr>
<td>MgO–Al2O3</td>
<td></td>
<td>23.4</td>
<td>94.8</td>
<td>5.0</td>
</tr>
<tr>
<td>CuO/γ-Al2O3</td>
<td></td>
<td>16.8</td>
<td>95.6</td>
<td>3.6</td>
</tr>
<tr>
<td>CuO/MgO–Al2O3</td>
<td></td>
<td>20.6</td>
<td>87.5</td>
<td>10.9</td>
</tr>
<tr>
<td>Cu/γ-Al2O3</td>
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<td>52.5</td>
<td>93.0</td>
<td>21.7</td>
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<tr>
<td>Cu/MgO–Al2O3</td>
<td></td>
<td>47.0</td>
<td>95.0</td>
<td>24.7</td>
</tr>
</tbody>
</table>

Yields determined by GC analysis (chlorobenzene is the external standard). Standard reaction conditions: 0.120 mg reactant 2 in 10 mL EtOAc; 25 bar H2; 150 °C; 21 h, 2 wt% catalyst (amount of copper relative to 2) and with a minimal TON of 8–10. Catalyst was used without prior reduction and no inert conditions during reaction process. Standard reaction conditions: 0.120 mg reactant 2 in 10 mL EtOAc; 25 bar H2; 150 °C; 21 h, 2 wt% catalyst (amount of copper relative to 2) and with a minimal TON of 23–26. Prior to the experiments, all catalysts were reduced at 300 °C under a flow of H2 for 2 h, the solvent was purged for 2 h with N2 and autoclaves were purged thrice.

![Fig. 4 DFT-optimised 3D structures of the ketone 1 (top left) and the alcohol 2 (top right) and a possible approach of these to the catalyst surface (bottom).](image)
Copper particles supported on γ-alumina catalyse the scission of lignin-type β-O-4 linkages under HDO conditions, yielding phenol and ethylbenzene in substantial amounts. Using magnesium-alumina as the support increases the dispersion of copper, yet lowers the selectivity towards HDO. For industrial applications, the catalyst price/performance ratio is the key criterion, and the main challenge in this case is catalyst stability. Working with real lignin depolymerisation feeds means dealing with sulphur in the feedstock, as well as rapid deactivation by coke formation and potential poisoning by water. Importantly, our supported copper catalysts are cheap and readily available. As such, they open a practical route for decreasing the oxygenated content of lignin depolymerisation streams while keeping the aromatic rings intact, a key hurdle for efficient biomass conversion.

Experimental section

Materials, instrumentation and computational methods

Unless otherwise noted, all chemicals were purchased from commercial sources and used as received. The MgO–Al2O3 was a gift sample from Eurosupport.

X-Ray diffraction (XRD) patterns were obtained with a MiniFlex II diffractometer using Ni-filtered CuKα radiation. The X-ray tube was operated at 30 kV and 15 mA. Temperature programmed reduction (TPR) was carried out using hydrogen on an instrument equipped with a thermal conductivity detector (TCD). The H2-TPR studies were carried out for all catalysts. Samples of ca. 100 mg were loaded into a quartz U-tube reactor and were pre-treated in N2 (40 ml min−1) at 473 K for 30 min. After cooling to ambient temperature, the gas stream was switched to 5% H2/N2 flowing at 40 ml min−1. The samples were heated at 10 K min−1 to 1000 K, during which the hydrogen consumption was determined quantitatively by TCD. Surface area measurements were performed by the BET method using N2 at 77 K on a Thermo Scientific Surfer instrument. The samples were dried in a vacuum (1 × 10−3 mbar) for 3 h at 200 °C prior to the measurement.

DFT calculations were performed with the ADF package,43 using the pRPE functional and a DZP basis set. Calculations were done on isolated molecules. BDEs were calculated by comparing the energies of the starting molecules and the isolated radicals formed. For the protonated species, linear transits were performed, slowly breaking the bonds instead of comparing only the end energy. In this manner, the calculations allow for the possibility of oligomerisation.

Gas chromatography analyses were run on an Interscience GC-8000 gas chromatograph with 14% cyanopropylphenyl and 86% dimethyl polysiloxane capillary column (Rtx-1701, 30 m; 25 mm ID; 1 μm df). Samples were diluted in 1 ml MeOH. GC conditions: isotherm at 50 °C (2 min); ramp at 2 °C min−1 to 70 °C; ramp at 70 °C min−1 to 140 °C; ramp at 10 °C min−1 to 280 °C; isotherm at 260 °C (2 min). Products were identified by comparing their retention times to those of authentic samples.
Procedure for catalyst synthesis

Example: 10 wt% CuO/γ-Al2O3. 1.0 g of γ-Al2O3 was added to a sol. of Cu(NO3)2·6H2O (0.38 g, 1.6 mmol) in 20 ml water and stirred for 2 h at 25 °C. The liquid was evaporated overnight on an oil bath at 60 °C, yielding a light green powder. This was dried at 120 °C for 24 h and then calcined in air at 500 °C (2 °C min⁻¹) for 4 h. The analogous 10 wt% CuO/MgO–Al2O3 was prepared as above starting from 1.0 g of MgO–Al2O3. BET analysis data of all catalysts are given in the ESI.

Procedure for synthesising 2-phenoxyl-1-phenylethanol 1

This is a modification of a previously published procedure.21,45 Bromoacetophenone (9.0 g, 45 mmol) and phenol (5.0 g, 53 mmol) were dissolved in 200 ml DMF, mixed with KOH (3.0 g, 53 mmol) and stirred overnight at room temperature. The product was then extracted with H2O and Et2O, dried over Na2SO4 and recrystallized from ethanol (yellowish powder, 86 mol% pure product yield based on bromoacetophenone). 1H NMR (DMSO) δ 5.58 (s, 2H), 6.93–6.98 (m, 3H), 7.27–7.31 (m, 2H), 7.56–7.60 (m, 2H), 7.68–7.72 (m, 1H), 8.02–8.04 (m, 2H), see ESI.†

Procedure for synthesising 2-phenoxyl-1-phenylethanol 2

This is a modification of a previously published procedure.21,45 A solution of 2-phenoxyl-1-phenylethanol 1 (2.5 g, 11 mmol) in methanol (100 ml) was treated with small portions of sodium borohydride (5.5 mmol) and stirred for 2 h. A saturated solution of ammonium sulfate (200 ml) followed by CHCl3 (200 ml) was added to the reaction mixture. The organic layer was separated, washed with water (2 × 100 ml), dried and recrystallized from ethanol (fine white needles, 73 mol% pure compound yield based on 1). 1H NMR (DMSO) δ 4.01–4.02 (m, 2H), 4.90–4.94 (m, 1H), 5.63–5.64 (d, 1H), 6.90–6.94 (m, 3H), 7.25–7.47 (m, 7H), see ESI.†

Procedure for catalytic hydrodeoxygenation (HDO)

Experiments were carried out in a six-parallel stainless steel 75 ml autoclave. In a typical experiment without an inert atmosphere and without pre-reducing the catalysts (results in Tables 2 and 3), 2 wt% of catalyst (copper weight relative to starting material) was added to a solution of 2-phenoxyl-1-phenylethanol 1 (0.120 g, 0.56 mmol) in 10 ml of EtOAc. The autoclave was pressurized with 25 bar H2 and heated to 150 °C for 21 h. Then, the reactors were cooled down to room temperature using an ice bath. Liquid samples were analysed by GC using chlorobenzene as an external standard.

The reactors were cooled down to room temperature using an ice bath. Liquid samples were analysed by GC using chlorobenzene as an external standard.

Procedure for recycling and leaching tests

Recycling and leaching tests were carried out in a six-parallel stainless steel 75 ml autoclave.

For the recycling test, 2 wt% of catalyst (copper weight relative to starting material using 10 wt% CuO/γ-Al2O3 was added to a solution of 2-phenoxyl-1-phenylethanol 1 (0.240 g, 1.12 mmol) in 20 ml of EtOAc. The autoclave was pressurized with 25 bar H2 and heated to 150 °C for 21 h. Then, the reactors were cooled down to room temperature using an ice bath. The catalyst was filtered out and placed in a desiccator overnight. The recycled catalyst was then reused for an extra 21 h reaction using 2-phenoxyl-1-phenylethanol 1 (0.120 g, 0.56 mmol) in 10 ml of EtOAc with 2 wt% of catalyst (copper weight relative to starting material). Liquid samples were analysed by GC using chlorobenzene as an external standard.

For the leaching test, the autoclave was pressurized with 25 bar H2 and heated to 150 °C for 3 h. Then, the reactors were cooled down to room temperature using an ice bath. The catalyst was filtered out and the reaction mixture (without catalyst) was charged again with 25 bar H2 and heated to 150 °C for 20 h. Liquid samples were analysed by GC using chlorobenzene as an external standard.

Acknowledgements

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Notes and references

42 http://www.eurosupport.nl/