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Hydrogen Transfer from Supercritical Methanol over a Solid Base Catalyst: A Model for Lignin Depolymerization

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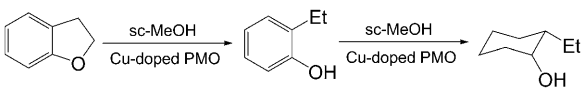
Lignins are heterogeneous macromolecules which constitute nearly 30% of woody biomass and have high potential value as precursors of aromatics and alkane derivatives for liquid fuels.[1,2] Given the increasing interest in non-food, renewable, biomass feedstocks, the transformation of lignins to more tractable monomers or oligomers is a very attractive goal. However, chemical methods for such conversions of lignocellulose materials have been very elusive. Characteristic lignin units are methoxylated and hydroxylated 4-propylphenols coupled as ethers and occasionally cross-linked with carbon–carbon bonds.[2] Possible strategies for chemical disassembly include hydrolysis or hydrogenolysis of ether linkages,[3–7] and oxidative C–C bond cleavage in analogy to degradation by white rot fungus.[8,9] The advantage of hydrogenolysis is the increased fuel value from adding H_2 equivalents, which in principle may be obtained by reforming biomass-derived alcohols such as glycerol or cellulose. Here we describe the catalytic transfer of H_2 equivalents from methanol to the lignin model compound dihydrobenzofuran (DHBF) under supercritical (sc) conditions leading to ether hydrogenolysis and to aromatic ring hydrogenation [Eq. (1)].



(1)

The present study was stimulated by the report[10,11] that a stoichiometric excess of KOH promotes the degradation of lignins and various models in methanol at 300 °C, which is above the supercritical temperature (239.6 °C).[12] We repeated this experiment with the lignin model DHBF (220 mg), KOH (200 mg), and MeOH (3 mL) in a sealed microreactor for 2 h. The substrate was converted into 2-ethylphenol (22%), methylated 2-ethylphenols (63%), and phenol (11%) as determined by GC-MS analysis with an internal standard. Notably, these products result from hydrogenolysis of the DHBF ether linkage rather than base-catalyzed hydrolysis, since no 2-(hydroxyethyl)phenol was found. In addition, a white solid (78 mg) and a quantity of gas (45 mL) were formed. The solid, apparently K_2CO_3, released gas upon acidification and showed a ^{13}C NMR signal characteristic of carbonate ion. GC analysis showed the gas to be approximately 96% H_2 and the remainder to be CO_2.

The KOH-promoted process consumes the base, thus it is not truly catalytic, so the present study was initiated to develop a solid catalyst that might similarly promote the transfer of hydrogen from alcohols to aromatic ethers. Porous metal oxides (PMOs) obtained by calcining metal-ion-doped Mg-Al hydrotalcite-like (HTC) precursors with molar ratios Mg/[Al+dopant(1)] or [Mg+dopant(2)]/Al of about 3 exhibit the properties of strong solid bases.[13–15] For examples, Ga-doped PMOs are reversible CO_2 adsorbents,[13] and Fe-doped Mg-Al PMOs are base catalysts for the transesterification of seed oil to biodiesel fuel.[14] In this context, several HTC-derived PMOs doped with transition metal ions (see Experimental Section) were surveyed to identify promising catalysts for the transformations of DHBF. A key advantage of DHBF as a lignin model is that the carbon frameworks remain intact, making the hydrogenolysis and hydrogenation products easier to track. In each case, the PMO (100 mg), MeOH (3 mL), and DHBF (50 mg) were added to a 10 mL stainless steel bomb (see Supporting Information). This microreactor was sealed and heated at 300 °C for 1–4 h, then the reactions were quenched by rapid cooling under cold water. The reactors were opened, and the liquid products were analyzed by GC-MS. When a Cu-doped PMO was used, the principal product was 2-ethylcyclohexanol, the result of phenolic ether hydrogenolysis and of aryl group hydrogenation. Upon opening, the reactors were pressurized even at room temperature owing to gas formation. Of several PMOs surveyed, those doped with copper (Cu10 and Cu20)[1] exhibited the most promising reactivities, and subsequent studies focused on these. The Ni10 and Mn10 PMOs displayed moderate activity toward ring hydrogenation; however, Fe10 PMO showed minimal activity. Co10 and the PMO prepared from undoped MgAl HTC showed none.

Initially, the Cu-doped PMOs were green; after reaction they were reddish. X-ray photoelectron spectroscopy (XPS) studies show that the color change was accompanied by reduction of Cu^{II} to Cu^{I} and/or Cu^{0}. The PMOs were recovered by centrifugation and reused and showed a moderately decreased reactivity.

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[1] The label indicates the dopant (metal) and its mole percentage of the +2 or +3 ions for which substitution is intended in the salts used in the HTC preparation described in the Supporting Information.

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Recalcination of the recovered catalysts regenerated the green catalyst with activity equivalent to that of the original material.

Figure 1 summarizes the time course of two key reaction products, 2-ethylphenol and 2-ethylcyclohexanol, as monitored by GC-MS experiments for the reaction of DHBF in methanol at

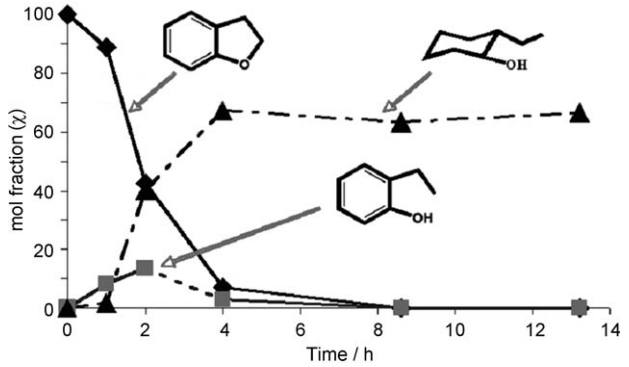
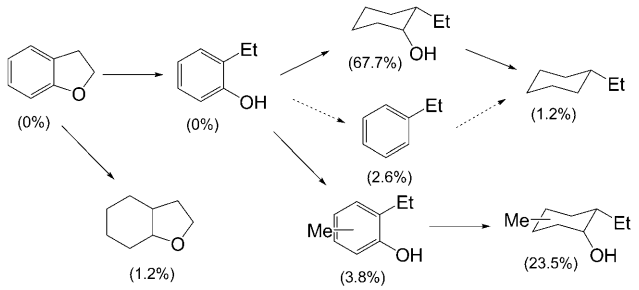


Figure 1. Primary products as a function of time for the conversion of 2,3-dihydrobenzofuran (100 mg, 0.84 mmol) catalyzed by Cu20-PMO (100 mg) in MeOH (3.0 mL) at 300 °C. Each point represents a separate experiment carried out in microreactors for the specified time period.

300 °C using Cu20-PMO. After 1 h, 2-ethylphenol is the most prominent product and represents about 90% of the DHBF consumed. The concentration of this species peaks at around 2 h, then declines, while the concentration of the aryl ring hydrogenation product 2-ethylcyclohexanol increases, consistent with relatively fast hydrogenolysis of the ether linkage to give a phenol, followed by slower hydrogenation of the aromatic ring [Eq. (1)].

At longer reaction times, 2-ethylcyclohexanol represents about 68% of the DHBF consumed. The remaining products were largely methylethylcyclohexanols (≈24%), but small amounts of methylethylphenols, ethylbenzene, ethylcyclohexane, and octahydrobenzofuran were identified by GC-MS. Scheme 1 shows the product distribution after 13 h and likely sequences by which these might be formed. The methylated products apparently result from alkylation of DHBF or phenolic intermediates.

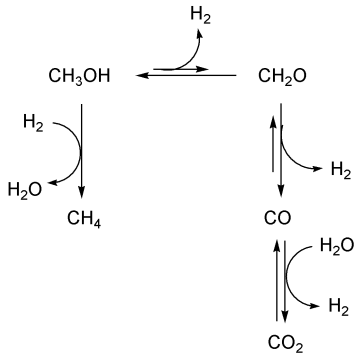
Other substrates tested include 2-ethylphenol, which underwent conversion (91%) into ethylcyclohexanol (63%) and



Scheme 1. Products from the Cu20-PMO-catalyzed reaction of 2,3-dihydrobenzofuran with methanol at 300 °C. The yields after 13 h reaction are indicated in parentheses.

methylethylcyclohexanols (17%) plus methylethylphenol (11%) after 4 h with the Cu20-PMO catalyst in MeOH at 300 °C. The analogous reaction in CD_3OD was significantly slower with only 46% conversion. Diphenyl ether was converted into cyclohexanols and methylcyclohexanols (83% after 4 h) with Cu20-PMO.

Supported copper materials are known to be catalysts for alcohol reformation[15] and for hydrogenation,[4] so a likely scenario involves the catalyzed formation of dihydrogen from methanol ($CH_3OH \rightleftharpoons CO + 2H_2$) followed by substrate hydrogenolysis and/or hydrogenation. This premise gains support from the observed formation of gas during a catalytic run. The gases were captured by opening the microreactor in a high-quality latex balloon, and their total volume (≈360 mL) was determined using the Archimedes principle. A sample was withdrawn using a gas-tight syringe and analyzed using GC-TCD. The major component was H_2 (74%), and the minor components were CO (15%), CO_2 (10%), and CH_4 (1%). A control reaction with catalyst but no added substrate gave a similar mixture, while no gas formed in the absence of catalyst. Thus, the build-up of gas must be due to methanol dehydrogenation and subsequent small-molecule processes like those illustrated in Scheme 2.[15–17]



Scheme 2. Possible reactions leading to the catalyzed disproportionation of methanol.

Figure 2 summarizes the effect of catalyst and substrate loadings on the rates of DHBF reactions in sc-MeOH catalyzed by Cu20-PMO. The number of H_2 equivalents used to form the products was the figure of merit and corresponds to the moles of phenols, plus five times the moles of cyclohexanes, plus four times the moles of cyclohexanols in the product mix. Thus, in a typical 4 h run with $\chi_{DHBF} = 3.15\%$ and using 100 mg Cu20-PMO (0.21 mmol Cu), 5.2 mmol H_2 was transferred with a turnover frequency (TOF) of 5.7 h^{-1}. The rate of H_2 equivalents transferred increased approximately linearly as the catalyst loading was varied from 20 mg to 100 mg, thus the TOF is nearly invariant under these conditions.

Figure 2 also shows the effect of varying the substrate loading while holding the amount of catalyst constant. The rate of H_2 transfer increased at low substrate loadings but became saturated at higher substrate concentrations with a TOF of about 7 h^{-1} for a 100 mg sample of Cu20-PMO. The reaction is

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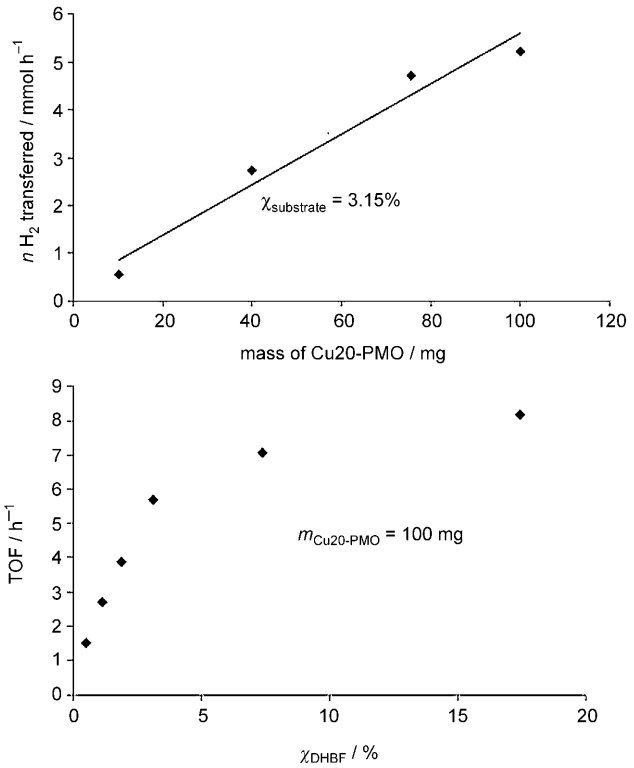

Figure 2. Top: Number of H_2 equivalents transferred per hour in a typical 4 h run with DHBF (45 mg) in MeOH at 300 °C as a function of catalyst (Cu20-PMO) loading. Bottom: Turnover frequency for Cu in Cu20-PMO (100 mg) during a 4 h run in MeOH at 300 °C as function of DHBF loading.

strongly temperature dependent. No activity was seen below 240 °C, which coincidentally is close to the supercritical temperature. An Eyring plot of the catalytic activity over 240–300 °C was linear and gave an activation enthalpy of 240 kJ mol^{-1}.

In summary, we have demonstrated that porous metal oxides prepared by calcining Cu-doped hydrotalcites are effective, reusable heterogeneous catalysts for hydrogenolysis and hydrogenation of lignin model compounds. The hydrogen equivalents are produced from the methanol solvent, which serves as a relatively inexpensive in situ liquid syngas precursor. This transfer hydrogenolysis/hydrogenation approach to lignin disassembly using a robust, non-precious-metal catalyst in a single reactor has several advantages over multicatalyst/serial-reactor systems. For example, this method eliminates the need for separating intermediate products, an important benefit for scale-up. While the current system is not optimal, it should be possible to modify and optimize conditions. In this context, ongoing studies are directed toward suppressing methane formation and toward accelerating pathways leading to ether hydrogenolysis and/or aryl hydrogenation. The goal is to improve the selectivity of the desired substrate transformations, including the conversion of lignins into higher-value products. These results also support the strategy of catalytic in situ hydrogen transfer from biomass-derived alcohols such as cellulose itself to hydrogenolize and hydrogenate the closely associated biopolymer lignin.

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Keywords: copper · heterogeneous catalysis · hydrogen transfer · lignin · supercritical fluids

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