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Copper-Based Catalysts for Efficient Valorization of Cellulose

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The combination of diminishing fossil fuel resources and an increasing energy demand has increased the focus on the possible transformations of renewable feedstocks. Biomass is a promising alternative source of carbon for implementing a potentially fossil-free chemical industry. When employed in fuel production, biomass reduces the carbon dioxide footprint of combustion. This has led to an increased use of biofuels such as biodiesel and bioethanol in recent years; however, their production is based on food crops, which induces competition between food and fuel production. This challenge can be remedied by using lignocellulose as feedstock.[1–3] Lignocellulose consists of cellulose, hemicellulose, and lignin, with cellulose as the major constituent in amounts of up to 50%. Therefore, efficient chemical transformations of cellulose into platform chemicals will play a potentially crucial role in the transition to biorefinery schemes.

Acid treatment of cellulose depolymerizes this abundant biopolymer to glucose, and depending on the reaction conditions dehydration to products such as 5-hydroxymethylfurfural (HMF) occurs.[3,4] Combining hydrolysis with hydrogenation enables the direct transformation of cellulose into highly valuable intermediates such as C_6 sugar alcohols and short-chain alcohols. The first studies on hydrolytic hydrogenation were performed in the 1960s by Sharkov, using noble-metal catalysts together with diluted mineral acids.[5] Recently, Fukuoka et al. reported the aqueous-phase conversion of cellulose over Pt/Al_2O_3 at 190 °C within 24 h, reaching up to 30% yield of hexitols.[6] In addition, Lu et al. demonstrated the hydrolytic hydrogenation of cellulose over Ru clusters at higher temperature in significantly shorter times, reaching yields of C_6 polyols of up to 40%.[7] Previously, we investigated the conversion of cellulose by combining diluted mineral acids and noble-metal catalysts, such as Ru, Pt, and Pd, supported on activated carbon. Interestingly, rather different product distributions were observed over these catalysts: C_5–C_6 polyols were the main products in the case of Ru, while Pd and Pt yielded short-chain alcohols and gaseous products.[8] Optimization of the reaction conditions and acid-to-metal ratio allowed the selective formation of C_6 sugar alcohols,[9] or up to 80% yields of C_4–C_6 sugar alcohols at only 160 °C.[8]

Nevertheless, when considering large-scale applications the high costs and limited availability of noble metals encourages the development of noble-metal-free catalysts. Recently, Zhang et al. presented first studies on cellulose degradation over nickel-promoted tungsten carbide, yielding up to 75% ethylene glycol.[10] However, the recyclability of the catalysts remained challenging. Simple Cu-based catalysts present a promising alternative, as they are known for their high activity toward hydrodeoxygenation of C–O bonds and have already reached high activity in the hydrogenolysis of glycerol.[11] Moreover, Gallezot et al. investigated Cu-based catalysts in the hydrogenolysis of sugar alcohols such as sorbitol with 63% selectivity to deoxyhexitols.[12] Interestingly, in a recent study a Cu-doped porous metal oxide was utilized to transform wood biomass into liquid and gaseous products.[13] Liquefaction occurred in supercritical methanol at temperatures above 300 °C and pressures of 160–220 bar, resulting in a mixture of various aliphatic alcohols and CO_2. In contrast, we present herein the controlled hydrolytic hydrogenation of cellulose over Cu-based catalysts into C_1–C_3 compounds that are already utilized in today's chemical industry, including methanol, ethylene glycol (EG), 1,2- and 1,3-propanediol (PD), as well as glycerol.

First investigations concentrated on $CuO/ZnO/Al_2O_3$, a catalyst usually utilized in industrial methanol synthesis.[14] At a reaction temperature of 245 °C, using water as solvent, C–C and C–O bond cleavage was facilitated, resulting in C_1–C_3 compounds as main products. In line, reactions at this temperature over Ru- and Pt/Al_2O_3 delivered significant amounts of the described C_1–C_3 compounds. Interestingly, a comparable product distribution could be reached by applying simple Cu-based materials, allowing direct conversion of cellulose (Figure 1a and Supporting Information Table S1). These results could be further optimized by increasing the metal content of the catalyst, reaching overall yields of liquid-phase products of up to 95%, with 67.4% C_1–C_3 compounds of which 15.4% 1,2-PD and 27.1% methanol, respectively (Figure 1b). In addition, the high reaction temperature initiates not only the formation of C_1–C_3 compounds but also dehydroxylation to products such as 1,2,6-hexanetriol (1,2,6-HT) or 1,2-butanediol (1,2-BD; Supporting Information Table S2). Interestingly, these results can be transferred to spruce as feedstock, achieving 87.6% conversion and 38.6% yield emphasizing EG and 1,2-PD as main products (Supporting Information Table S3). Based on these results $CuO/ZnO/Al_2O_3$ catalysts can be classified as promising alternatives for supported-noble-metal catalysts in the direct transformation of cellulose.

From an industrial and environmental point of view, catalyst recyclability is of major importance considering continuous production processes. To facilitate recycling experiments, cellobiose was used as substrate in a first step (Supporting Information Figure S1). The investigated Cu-based catalyst could be

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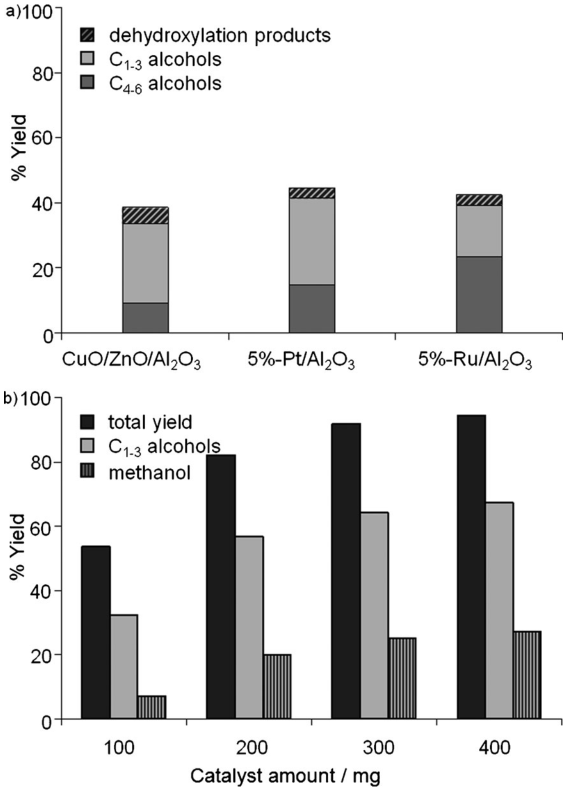

Figure 1. Catalytic activity of $CuO/ZnO/Al_2O_3$ in the transformation of cellulose to sugar alcohols, a) in comparison with supported noble metal catalysts and b) utilizing different amounts of catalyst. Reaction conditions: 245 °C, 50 bar H_2 (25 °C), 10 mL H_2O, 0.5 g cellulose.

successfully recycled for at least 4 runs, while elemental analysis of the reaction solution indicated the absence of Cu leaching. Surprisingly, recycling tests with cellulose as substrate indicated deactivation of the catalysts (Supporting Information Figure S2, Table S3), but again no evidence for Cu leaching was found. Thermogravimetric analysis (TGA) showed weight loss of the catalyst after recycling at around 300 °C, and extraction with DMSO after intense washing of the catalyst with water and MS analysis of the solution revealed oligomeric species (Supporting Information Figures S3 and S4). These results can be attributed to adsorption of polymeric species on the catalyst surface, inducing deactivation and explaining the observed formation of HMF upon recycling caused by coverage of the active metal sites with carbon deposits (Supporting Information Table S4). Future studies will focus on methods to circumvent deactivation or implement regeneration strategies.

To set the baseline for a knowledge-driven optimization of catalyst and reaction system, the influence of reaction conditions as well as catalyst composition was investigated. Temperature variations clearly illustrated that a minimum temperature of 245 °C is required to achieve significant conversion of cellulose, most probably due to the high activation energy of cellulose hydrolysis (Supporting Information Table S2). Increasing the hydrogen pressure from 20 to 50 and up to 80 bar caused no increase in conversion and only a slight increase of the amount of formed polyols, indicating a minor impact of gas–liquid transfer and hydrogen concentration in the reaction solution for hydrogen pressures above 30 bar. However, such high pressures place high demands on technical implementation. Consequently, further experiments were carried out at 30 bar H_2 pressure, which proved sufficient to achieve efficient transformation of cellulose (Supporting Information, Figure S5).

Based on the findings described above achieved with commercial $CuO/ZnO/Al_2O_3$, a set of Cu-based catalysts was synthesized and subsequently tested in the transformation of cellulose to allow first insight into the influence of catalyst composition on activity and selectivity (Table 1). $CuO/ZnO/Al_2O_3$ and $CuO/NiO/Al_2O_3$ catalysts were prepared by co-precipitation at pH 5–6.5 and 35–70 °C.[14] The catalysts are denoted as $CuO/ZnO/Al_2O_3$-cp-*x*, where *x* represents the precipitation temperature. Depending on the synthesis conditions the metal content as well as specific surface area of the materials varied. Energy-dispersive X-ray (EDX) analysis revealed a low zinc content (<1 %) for $CuO/ZnO/Al_2O_3$-cp-35 prepared at 35 °C and pH 5 ($63\ m^2g^{-1}$), whereas a zinc content of up to 12 wt % was observed for materials prepared at neutral or only slightly acidic pH values and 70 °C ($CuO/ZnO/Al_2O_3$-cp-70, $40\ m^2g^{-1}$). Interestingly, in catalysis experiments both materials exhibited results comparable to the commercial system ($98\ m^2g^{-1}$; entry 1). Consequently, the presence of zinc is not necessary to achieve significant activity in the transformation of cellulose. Likewise, the presence of zinc does not seem to have a major effect on product distribution. This conclusion is further emphasized by the comparable activities and product distributions for CuO/Al_2O_3-cp-35 and $CuO/NiO/Al_2O_3$-cp-35 (entries 4 and 5).

Interestingly, the preparation procedure of the catalyst did have a clear effect on activity and selectivity. Cu/Al_2O_3 and Cu/C catalysts were prepared by impregnation using copper nitrate as a precursor. CuO/Al_2O_3, irrespective of the synthesis method, as well as Cu/C achieved comparable results with regard to the conversion of cellulose, but the yield of liquid-phase products changed significantly. While CuO/Al_2O_3 prepared via precipitation or Cu/Al_2O_3 based on high-surface-area alumina (Table 1, entries 5 and 8; 116 and $157\ m^2g^{-1}$) gave yields of liquid-phase products of 79.4 and 65.9 %, respectively, a Cu/Al_2O_3 catalyst based on impregnation of a commercial support only reached a yield of 24 % (entry 7; $<5\ m^2g^{-1}$) indicating further C–C and C–O cleavage to gaseous products such as CO_2.[8] This result points towards a positive effect of a high specific surface area for Al_2O_3-based catalysts. In contrast, Cu/C (entry 6) only reached a yield of 22.7 % liquid-phase products; a result that is currently difficult to rationalize but may be related to the use of activated carbon as support.

With regard to the overall product distribution, little methanol and 1,2-PD were formed over catalysts prepared via impregnation (Table 1, entries 6–10), while catalysts prepared via precipitation, such as commercial $CuO/ZnO/Al_2O_3$, deliver yields of liquid-phase products of up to 95 %, with 14.7 % 1,2-PD and 22 % methanol (entry 1). Mechanistic investigations concerning the hydrogenolysis of sorbitol suggest a 1,5-cleavage via a retro-aldol reaction to release methanol.[11] Hence, different acid–base properties of the catalyst may play an important role, and will be the focus of future studies. Moreover, some commercial Cu-based catalysts, such as Raney copper,

Table 1. Hydrogenolysis of cellulose over different Cu-based Catalysts

Entry	Catalyst	Conv.[a] [%]	Total yield[b] [%]	Individual yields[c] [%]											
				sorbitol	sorbitan	isosorbide	xylitol	anhydroxylitol	erythritol	glycerol	EG	1,3-PD	1,2-PD	MeOH	1,2-BD, 1,2,6-HT
Precipitation catalysts															
1	$CuO/ZnO/Al_2O_3$[d]	100	95.1	5.1	1.2	10.3	1.0	2.1	1.3	7.7	13.6	5.2	14.7	22.2	10.1
2	$CuO/ZnO/Al_2O_3$-cp-35	100	76.9	3.5	0.6	11.5	1.1	1.4	1.1	6.8	10.9	3.6	11.4	15.4	9.3
3	$CuO/ZnO/Al_2O_3$-cp-70	100	58.8	8.9	1.4	4.5	0.6	0.8	1.2	3.9	11.0	1.3	13.3	2.8	8.6
4	$CuO/NiO/Al_2O_3$-cp-35	100	63.9	2.5	0.5	5.9	1.2	0.0	0.5	2.7	14.2	3.0	14.3	10.4	8.4
5	CuO/Al_2O_3-cp-35	100	79.4	2.9	0.5	8.8	0.4	0.0	0.8	4.5	13.3	4.6	13.2	20.6	9.4
Supported catalysts															
6	25 % Cu/C	92.8	22.7	0.8	1.7	0.3	1.0	5.6	3.4	2.3	3.9	0.0	0.2	1.4	1.8
7	25 %-Cu/Al_2O_3[e]	100	24.0	2.7	0.8	0.0	0.7	0.0	0.6	0.5	9.4	0.0	4.7	2.9	1.4
8	25 %-Cu/Al_2O_3[f]	91.0	65.9	17.7	0.0	7.6	5.8	0.0	1.8	5.0	6.2	0.0	9.6	5.1	6.8
9	5 %-Cu/Al_2O_3[g]	91.6	37.8	0.8	2.0	0.5	0.8	0.0	0.6	2.7	9.3	4.1	9.2	3.3	4.2
Full catalysts															
10	Raney copper	96.0	77.2	6.5	0.0	11.2	1.9	0.0	1.3	8.1	9.9	0.0	15.8	14.0	8.3
11	copper chromite	98.0	46.7	7.1	0.0	3.7	2.0	0.0	0.4	2.7	6.0	0.0	13.2	5.4	6.0
12	Cu_2O	96.6	26.3	3.8	1.1	0.0	1.5	0.0	0.7	2.0	4.9	0.0	3.4	7.3	0.9
13	CuO	96.8	48.1	5.3	0.5	1.8	1.1	0.0	0.8	3.3	6.0	0.0	11.4	11.7	5.8

[a] Based on the recovered amount of cellulose. [b] Based on the yields of compounds 1–13. [c] Neither glucose nor its dehydration products were formed. [d] Commercial catalyst (ICI). [e] Commercial alumina. [f] Alumina was prepared by hard templating. [g] Alumina was synthetized by sol–gel technique.

copper chromite, and copper oxides that exhibited promising results for glycerol hydrogenolysis, were investigated for the direct transformation of cellulose. Surprisingly, all materials allowed almost complete conversion of cellulose while without catalyst only 64.4 % was reached (Supporting Information Table S4). Raney copper reached a yield of liquid-phase products of up to 77 %, with up to 48 % of C_1–C_3 compounds (14 % methanol), and even for pure CuO 48 % overall yield including 32.3 % of C_1–C_3 compounds with 11.7 % methanol could be achieved (entries 10 and 13).

XPS measurements were performed to investigate the nature of the active copper species (Supporting Information Figures S6 and S7). The Cu 2p spectra of commercial $CuO/ZnO/Al_2O_3$ were characteristic for copper in the 2+ oxidation state. The main peak of the catalyst after reaction was an overlap of two copper species: Cu^{2+}, with a binding energy value of 933.9 eV, and a lower oxidation state with a peak at 931.5 eV that can be assigned to either Cu^0 or Cu^+. Usually, Cu^+ and Cu^0 can be distinguished by their Auger peaks, but in this case the copper Auger peak overlaps with the zinc Auger lines. For the impregnated and reduced Cu on Al_2O_3, the main photo peak at 931.5 eV and the Auger peak at 918.1 eV can be clearly assigned to Cu^0. The reduction of Cu^{II} under the employed reaction conditions is further emphasized by the rose color of the catalyst after reaction. Therefore, we suggest that Cu^0 acts as active species under reaction conditions. In line, experiments with Raney copper and Cu/Al_2O_3 fully reduced to Cu^0 before reaction (Table 1, entries 8 and 10) allowed an efficient transformation of cellulose, further emphasizing the role of Cu^0 in the reaction. However, further investigations to clarify the nature of the catalytically active sites under the employed reaction conditions are certainly necessary.

In conclusion, we show that noble-metal-free catalysts based on copper allow an efficient transformation of cellulose into ethylene glycol, 1,2-PD, and methanol as main products. Additionally, variation of the catalyst composition and reaction parameters indicates a significant impact of preparation method and support material on activity and selectivity of the catalyst. Cu^0 seems to be essential for a high catalytic activity, but the presence of Cu^I can hardly be excluded. Future investigations will focus on rationalization of the Cu oxidation state and acid–base properties of the catalysts, as well as possibilities to enhance catalyst selectivity and recyclability.

Experimental Section

Experimental and catalyst preparation procedures are described in the Supporting Information.

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Keywords: biomass · copper · heterogeneous catalysis · hydrogenolysis · methanol

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