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The role of metallic copper in the selective hydrodeoxygenation of glycerol to 1,2-propanediol over Cu/ZrO$_2$

Thomas Gabrysch[a], Baoxiang Peng*[a,b], Sorin Bunea[a], Gerald Dyker[c] and Martin Muhler*[a,b]

A series of Cu/ZrO$_2$ catalysts with nominal CuO loadings of 5, 10, 18 and 31 wt.% was synthesized by co-precipitation, characterized and applied in the hydrodeoxygenation of glycerol under mild reaction conditions (200 °C, 25 bar H$_2$). These catalysts were highly selective for the cleavage of C-O bonds while preserving C-C bonds leading to 95% selectivity to 1,2-propanediol. The conversion of glycerol was observed to be linearly correlated with the specific copper surface area derived from N$_2$O frontal chromatography. The reaction was found to occur through the dehydration of glycerol to acetol followed by its hydrogenation to 1,2-propanediol. Metallic copper was identified as the active site for both reactions suggesting the acid ZrO$_2$ sites to be blocked by water. Reusability studies showed that the catalyst was relatively stable and the conversion decreased by only 18% after three cycles.

Introduction

Due to the gradual depletion of fossil resources, numerous efforts have been made to develop sustainable processes converting renewable feedstocks into value-added products.[1,2] In the biodiesel process, glycerol (1,2,3-propanetriol) is obtained as by-product with approximately 10 wt.% of the total biorefinery products.[3,4] The sharp increase of the biodiesel production during the last decades resulted in a considerable overproduction of glycerol,[5] exceeding the global demands by far and causing a strong decrease of the market price.[6] The high availability, low cost, non-toxicity and high functionality turn glycerol into a versatile platform chemical for the production of value added biomass-derived products.[7-9]

Recently, many studies focused on the catalytic transformation of glycerol, such as esterification,[10-12] etherification,[13] hydrogenolysis/hydrodeoxygenation,[14-16] dehydration and reforming,[17] of which the hydrodeoxygenation (HDO) to 1,2-propanediol (1,2-PDO) is one of the most attractive valorization approaches. 1,2-PDO is widely used in the production of unsaturated polyester resins and polyurethanes and has direct applications as humectant in foods, cosmetics and pharmaceuticals. The challenging aspect of glycerol HDO to 1,2-PDO is the selective cleavage of the primary C-O bond while preserving the C-C bonds as well as suppressing the formation of overhydrogenolysis products to increase the selectivity to 1,2-PDO. Catalysts applied for the HDO are usually based on noble metals (Pt, Ru, Rh) or transition metals (Cu, Ni, Co). It is found that noble metals offer a higher activity for hydrogenolysis reactions, but the selectivity towards 1,2-PDO is considerably lower because of the parallel activation of C-C bond hydrogenolysis. On the contrary, transition metal-based catalysts are less active, but offer higher selectivity for the HDO of the primary hydroxyl group.[18]

Multiple HDO reaction mechanisms are reported in literature including a three-step dehydrogenation-dehydration-hydrogenation,[19,20] a two-step dehydration-hydrogenation,[3,21] and a direct HDO mechanism over ReO$_x$-modified Ir catalysts.[22,23] The reaction is strongly affected by the type of catalyst used and the applied reaction conditions. It is widely accepted that the dehydration step of glycerol proceeds on the Brønsted or Lewis acid-base sites of the support, while the metallic sites are solely required for the consecutive hydrogenation to 1,2-PDO.[24,25] Moreover, mechanistic studies have shown that the addition of acidic catalysts like zeolites,[26] Nb$_2$O$_5$[27] and Amberlyst ion exchange resins[28-30] as well as alkaline additives[31] such as NaOH and KOH significantly increase glycerol conversion, indicating a strong influence of the acid-base properties on the dehydration step.

ZrO$_2$ is frequently used as support due to its high mechanical and thermal stability,[32] high specific surface area,[32] suitable acid-base[33] as well as redox properties.[34] For example, Cu nanoparticles supported on ZrO$_2$ are applied in methanol synthesis,[35] in the hydrogenation of ethyl acetate[36] and in the isomerization of *n*-butane.[37] The Lewis acid-base properties of ZrO$_2$ originate from alternating unsaturated Zr^{4+} and O^{2-} pairs at the surface, while Brønsted acidity is due to surface OH groups. The influence of the bifunctional properties of Cu/ZrO$_2$ due to the presence of metallic Cu^0 and acidic Zr-OH groups on the kinetics of the hydrogenation of ethyl acetate in the gas phase was investigated in detail by Schittkowski et al.[36]

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Here, the HDO of glycerol and the conversion of the intermediates were systematically studied over a series of Cu/ZrO_2 with different CuO loadings to elucidate the reaction mechanism of the polyol transformation in the aqueous phase involving C-O and C-C bond cleavage.

Results and Discussion

Catalyst Characterization

Table 1. Physicochemical properties of the co-precipitated CuO/ZrO_2 catalysts.

CuO loading [wt.%]	Surface area [m² g^{-1}]	Cu surface area [m² g^{-1}]	Degree of reduction [%]
0	140	0.0	-
5	158	2.9	n.d.*
10	157	3.9	95
18	144	4.2	96
31	142	5.7	98

* n.d. = not determined

The specific surface areas of the co-precipitated CuO/ZrO_2 catalysts determined by N_2 physisorption, the Cu surface areas determined by N_2O reactive frontal chromatography (RFC) and the degrees of reduction derived from the temperature-programmed reduction (TPR) in H_2 are summarized in Table 1. The specific surface areas are found to be in the range from 140 to 158 m² g^{-1}, which decrease slightly with increasing CuO loading from 5 wt.% to 31 wt.%. For CuO loadings higher than 5 wt.%, the degree of reduction is close to 100%. The specific Cu surface areas increase with increasing CuO loading, but do not show a linear correlation, which is probably due to the agglomeration of Cu nanoparticles especially at higher CuO loading. The highest Cu surface area is found to be 5.7 m² g^{-1} for 31 wt.% CuO/ZrO_2. These Cu surface areas are low, suggesting that the Cu is in the form of nanoparticles embedded in the ZrO_2 support.[36]

The X-ray diffraction (XRD) patterns of the calcined CuO/ZrO_2 samples with CuO loadings of 5, 10, 18 and 31 wt.% as well as the Cu-free ZrO_2 support are shown in Figure 1. Pure ZrO_2 crystallized in the tetragonal structure, indicated by the characteristic reflections at 30.2°, 35.5°, 50.3° and 60.2° 2θ. The reflections observed for 5 wt.% CuO/ZrO_2 also indicate the presence of tetragonal ZrO_2. A further increase of the CuO loading up to 31 wt.% leads to strong structural changes: the presence of CuO prevented the crystallization of ZrO_2 resulting in an essentially X-ray amorphous state. For the 31 wt.% CuO/ZrO_2 two additional reflections at 35.6° and 38.9° 2θ are observed, indicating the formation of a second CuO species on the ZrO_2 support.[36]

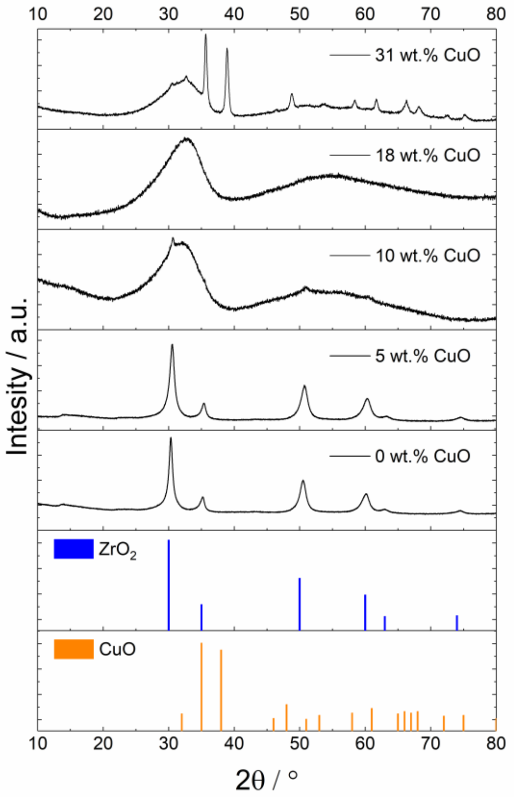


Figure 1. XRD patterns of pure ZrO_2 and the CuO/ZrO_2 samples. All samples were synthesized by co-precipitation at pH 10.5 and calcined at 490 °C for 3 h in 20% O_2 in N_2.

The TPR profiles of the calcined samples are shown in Figure 2. For pure ZrO_2 no reduction peak was observed, whereas the TPR profiles of the 10 wt.% and 18 wt.% CuO/ZrO_2 samples show one symmetric reduction peak at 130 °C due to the reduction of Cu^{2+} to metallic Cu^0. Two reduction peaks were observed for 31 wt.% CuO/ZrO_2 at temperatures around 127 °C and 144 °C, indicating a less homogeneous dispersion of the Cu nanoparticles. Based on the low Cu surface areas in spite of the high CuO loading and the structural change of ZrO_2 from tetragonal ZrO_2 to an amorphous state with increasing CuO loading, it can be concluded that most Cu nanoparticles are embedded homogeneously in the ZrO_2 support.

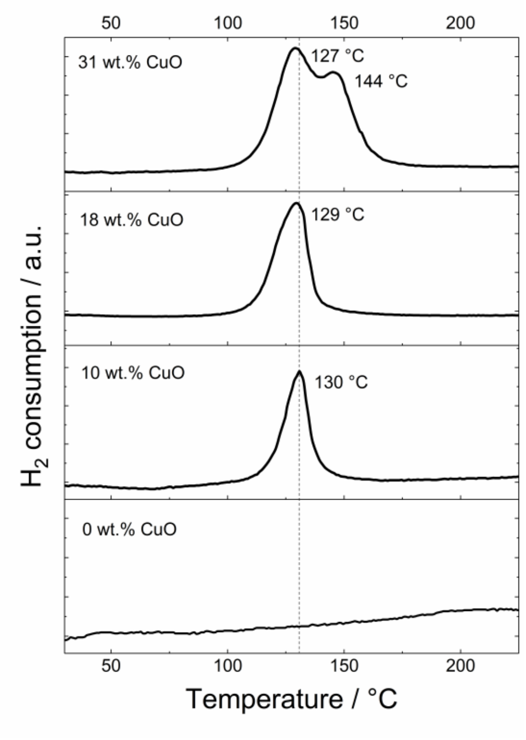


Figure 2. TPR profiles of calcined pure ZrO_2 and the CuO/ZrO_2 samples.

Influence of the CuO loading on the catalytic properties

The Cu/ZrO_2 samples with nominal CuO loadings of 5, 10, 18 and 31 wt.% were applied in the liquid-phase hydrodeoxygenation of glycerol using aqueous 4 wt.% glycerol solutions at 200 °C under 25 bar H_2 pressure for 8 h (Table 2). Prior to the catalytic tests, all catalysts were pre-reduced in the autoclave at 200 °C and 20 bar H_2 pressure for 10 h in the absence of solvent and reaction solution. The identified liquid products were 1,2-PDO, ethylene glycol, acetol as well as trace amounts of methanol and 2-propanol. Interestingly, 1,3-propanediol was not detected, suggesting a higher reactivity of the primary than the secondary hydroxyl group. According to the ab initio calculations (B3LYP-6-31G*) an intermediary propen-1,2-diol is thermodynamically favored by about 30 kJ mol^{-1} due to its intramolecular hydrogen bond compared with the isomeric propen-1,3-diol. Thus, a detailed mechanistic interpretation has to consider a concerted E2 elimination,[38] which is typical for the dehydration of primary alcohols, as well as glycidol as an alternative dehydration product, which can be hydrogenated to 1,2-PDO, too.[39]

Pure ZrO_2 led to less than 0.3% conversion without the formation of 1,2-PDO and acetol, indicating that Cu-free ZrO_2 can neither catalyze the hydrodeoxygenation of glycerol to 1,2-PDO nor the dehydration of glycerol to acetol under the applied aqueous-phase conditions presumably due to the coverage of the acidic sites by water. This phenomenon was also observed by Engelhardt et al.,[40] who studied the influence of water on molybdenum carbide catalysts applied in the HDO of phenol and concluded that at increased pressures, water molecules preferentially bind to the surface of the catalyst, thus blocking the active sites for the adsorption of reactants.

The conversion of glycerol depends strongly on the CuO loading of the catalysts (Figure S1). Up to 10 wt.% CuO loading conversion increased almost linearly to 25%, yielding 1,2-PDO as main product with a selectivity of about 95%. Although the nominal CuO loading was further increased by a factor of 3 to 31 wt.%, the conversion only slightly increased from 25% to 35%, while the selectivity to 1,2-PDO remained almost constant. The main by-product was ethylene glycol, probably originating from the overhydrogenolysis of 1,2-PDO or from the direct cleavage of the C-C bond through direct hydrogenolysis of glycerol. For the catalysts with higher CuO loadings the selectivity to ethylene glycol slightly increased from 2.1% to 4.7%. The highest conversion of 35% was achieved with the 31 wt.% CuO/ZrO_2 catalyst, which is only 4% higher in comparison to 18 wt.% CuO/ZrO_2. 18 wt.% CuO/ZrO_2 was identified as an optimum catalyst with appropriate CuO loading and activity and was chosen for further mechanistic studies. In contrast, the catalytic activity was found to be correlated linearly with the specific Cu surface areas (Figure 3), indicating that metallic Cu is the active site for the HDO of glycerol.

Table 2. Glycerol HDO over Cu/ZrO_2 catalysts with varying CuO loading.[a]

CuO loading [wt.%]	Conversion [%]	Selectivity [%]				
		1,2-PDO	Ethylene glycol	Acetol	2-PrOH[b]	MeOH[b]
0	<0.3	-	-	-	-	-
5	14.7	95.2	2.1	1.6	-	1.1
10	25.0	95.2	3.0	1.2	0.3	1.0
18	31.3	94.5	3.5	0.8	0.3	1.0
31	35.0	93.3	4.7	0.9	0.3	0.8

[a] Reaction conditions: 4 wt.% aqueous glycerol solution (20 mL); T = 200 °C; $p(H_2)$ = 25 bar, 400 mg catalyst; 8 h reaction time; 750 rpm stirring speed; all catalysts pre-reduced at 200 °C for 10 h.

[b] 2-PrOH: 2-propanol; MeOH: methanol

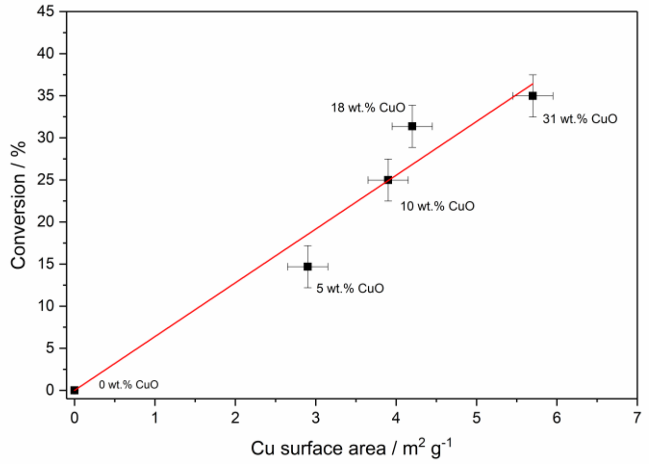


Figure 3. Correlation of the degrees of glycerol conversion with the specific Cu surface areas.

Reaction pathway of glycerol HDO to 1,2-PDO

To explore the reaction pathways of glycerol HDO, the kinetics was investigated with 5 wt.% CuO/ZrO_2 catalyst under identical reaction conditions (Figure 4). Conversion increased linearly to 15% as the reaction time increased to 8 h, indicating that the catalytic HDO of glycerol is a zero-order reaction. The selectivity of 1,2-PDO and ethylene glycol remained almost constant at 95% and 2.5%, respectively. More interestingly, the selectivity of acetol gradually decreased from 5% at 2% glycerol conversion to 1.6% with the progress of reaction, indicating that acetol originating from the dehydration of glycerol is the main intermediate and primary product during 1,2-PDO production. To prove this conjecture, the reaction was performed with the pre-reduced 18 wt.% CuO/ZrO_2 catalyst under inert N_2 atmosphere at 200 °C for 8 h. As expected, acetol was obtained as the main product reaching 79% selectivity at 18% glycerol conversion. 1,2-PDO and ethylene glycol were found as by-products with selectivities of 12% and 8%, respectively. In addition, the intermediate acetol was further converted over Cu/ZrO_2 under identical conditions in a separate experiment (Figure 5a). The result showed that acetol was almost exclusively converted into 1,2-PDO within only 1 h, attaining 98% yield at 98.5% conversion. Thus, the HDO of glycerol proceeds via the slow dehydration of glycerol to acetol as rate-determining step followed by the fast hydrogenation of acetol to 1,2-PDO. The amount of 1.4% unconverted acetol, which is consistent with the low acetol concentration after 8 h during glycerol conversion (Figure 4), is presumably due to the equilibrium between acetol and 1,2-PDO at high H_2 pressure. Other by-products produced by consecutive overhydrogenolysis reactions were identified as methanol (0.1%), ethanol (0.2%), 1-propanol (0.15%) and 2-propanol (0.25%).

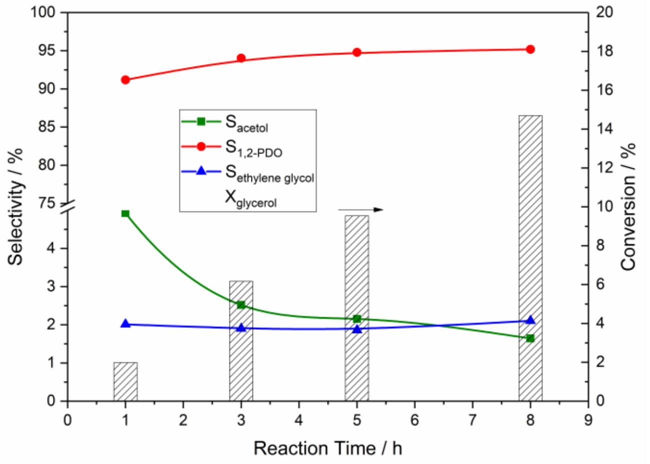


Figure 4. Glycerol conversion and liquid product selectivity in the HDO of glycerol as a function of time. Reaction conditions: 20 mL of 4 wt.% aqueous glycerol solution, 400 mg 5 wt.% CuO/ZrO_2, 200 °C, 25 bar H_2 pressure and 750 rpm stirring speed.

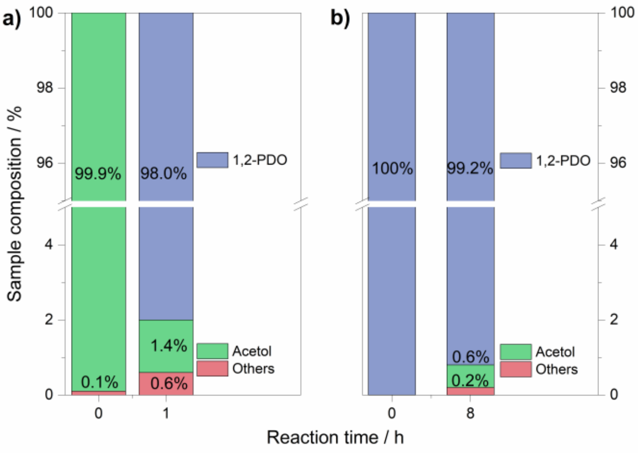
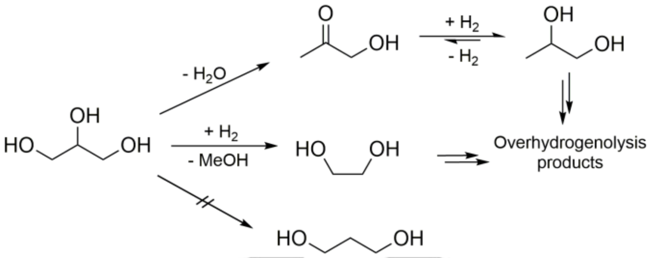


Figure 5. Product distributions of the reactions using acetol (a) and 1,2-PDO (b) as the reactant. Reaction conditions: 20 mL of 4 wt.% aqueous reactant solutions, 400 mg of 18 wt.% CuO catalyst (pre-reduced), 200 °C, 25 bar H_2 pressure and 750 rpm stirring speed.

It is generally accepted that over metal-supported catalysts dehydration occurs on the acidic support (e.g., Al_2O_3, ZrO_2), and hydrogenation is catalyzed by the metal (e.g., Pt, Cu).[16] In the present work, the hydrogenation step occurs on metallic Cu; while the active site for the rate-determining dehydration step is still unclear. Therefore, pure metallic Cu derived from the reduction of commercial CuO (Sigma Aldrich, nanopowder < 50 nm) at 225 °C and 20 bar H_2 for 10 h was applied in the glycerol dehydration under inert N_2 atmosphere. The corresponding XRD patterns of the commercial CuO before and after reduction (Figure S2) indicate the complete reduction of Cu^{2+} to metallic Cu^0 prior to reaction. The TPR profile of pure CuO shows one reduction peak at 181 °C (Figure S3), which is about 40 °C higher than all the supported catalysts (Figure 2), suggesting that ZrO_2 can efficiently increase the reducibility of CuO. The catalytic results showed that glycerol was converted into acetol with 100% selectivity during the whole reaction time yielding 6.5% conversion after 8 h (Figure S4). In comparison, 205 mg CuO nanoparticles were used vs. 400 mg of 18 wt.% CuO/ZrO_2. This observation suggests that pure metallic Cu is an efficient and active catalyst for the dehydration of glycerol. This conjecture is consistent with literature reports that pure metallic Cu catalyzes the dehydration of glycerol to acetol in the gas phase under inert conditions, attaining a yield of 64% acetol at 250 °C.[24] Cu-catalyzed dehydration was proposed to proceed via the formation of Cu alkoxide species.[24] In the liquid phase the dehydration of glycerol to acetol was also reported using metallic Cu foil under ambient N_2 atmosphere, leading to 45% selectivity of acetol at a very low conversion of less than 1% due to the extremely low surface area.[41]

Combined with the observation that pure ZrO_2 cannot catalyze the dehydration of glycerol presumably due to the blockage of acid sites by water in the aqueous phase, it can be concluded that metallic Cu is not only the active species for the hydrogenation, but also the active site for the dehydration of glycerol to acetol, resulting in a linear correlation of the conversion of glycerol with the specific Cu surface area (Figure 3). ZrO_2 probably acts mainly as support and increases the dispersion of Cu through embedding the Cu nanoparticles efficiently in its porous structure. Furthermore, the bifunctional nature of Cu/ZrO_2 in the gas-phase hydrogenation of ethyl acetate[36] and the dominant role of metallic Cu in the hydrodeoxygenation of glycerol under the present liquid-phase conditions point to the important role of water as inhibiting adsorbate in the aqueous-phase reaction.

The reactivity of 1,2-PDO was also investigated to determine its stability and possible overhydrogenolysis reaction products under the present reaction conditions (Figure 5b). The use of 1,2-PDO as reactant resulted in a tiny conversion of 0.80% after 8 h reaction time yielding trace amounts of acetol (0.6%), 1-propanol (0.16%) and methanol (0.04%). Since 1,2-PDO is very stable under the chosen reaction conditions, we can conclude that ethylene glycol is not the overhydrogenolysis product of 1,2-PDO, suggesting that it originates from the direct hydrogenolysis of glycerol. As the primary and main product of 1,2-PDO conversion, acetol is mainly formed through the dehydrogenation of 1,2-PDO catalyzed by metallic Cu, being limited by the employed high H_2 pressure. This observation of the different catalytic behavior of Cu/ZrO_2 in the dehydration of glycerol to acetol and in the dehydrogenation of 1,2-PDO to acetol is consistent with literature reports on Raney Cu and Cu/Al_2O_3.[24]



Scheme 1. Reaction pathways of the hydrodeoxygenation of glycerol over Cu/ZrO_2 catalysts.

The identified reaction pathways of the glycerol hydrodeoxygenation and hydrogenolysis reactions are shown in Scheme 1. The high selectivity to 1,2-PDO is mainly determined by the stability of the product 1,2-PDO, the selective scission of C-O over C-C bonds, and the selective dehydration of the primary hydroxyl group instead of the secondary hydroxyl group. First, using 1,2-PDO as reactant demonstrated the high stability of 1,2-PDO, avoiding undesired further degradation products. Second, the dominant selectivity of 1,2-PDO compared with ethylene glycol (95% vs. < 5%) suggests the selective cleavage of C-O over C-C bonds, which can be attributed to the relatively weak ability of Cu^0 to catalyze hydrogenolysis as well as the stronger C-C bond strength of glycerol compared with that of the C-O bond (Table S1, i.e., 347 vs. 335 $kJ\,mol^{-1}$). Third, the absence of 1,3-propanediol in the formed products and the identification of acetol as the primary and dominant intermediate indicate that the selective dehydration of the terminal hydroxyl group to acetol is favored over the secondary hydroxyl group dehydration to 3-hydroxypropanal. This conjecture cannot be explained by the C-O bond strengths of primary and secondary OH groups (Table S1, i.e., 333.0 vs. 335.6 $kJ\,mol^{-1}$), which are quite similar, but points to the different reactivities of these two OH groups. Our previous study showed that the overall reaction rates of C3 alcohols over Pt/Al_2O_3 decrease in the sequence 1,3 propanediol ≈ glycerol > 1,2-propanediol ≈ 1-propanol, indicating that the primary OH group is much more reactive for dehydration than the secondary OH group.[42] Furthermore, the ability of Cu/ZrO_2 to catalyze dehydration is dramatically decreased due to the blockage of acidic Zr-OH sites by water in the aqueous phase, leading to the elimination of the terminal OH group rather than the more difficult secondary OH group elimination.

Catalyst stability

Owing to the superior performance of the Cu/ZrO_2 catalyst for the HDO of glycerol, the stability of the catalytic performance was also investigated (Figure 6). During the recycling test, the mass loss of the catalyst after each cycle was approximately 27 mg (8%) in average. The reusability results showed that the catalyst lost around 18% of its activity after 3 cycles, indicating the catalyst was rather stable for the HDO of glycerol. Additionally, the selectivity was not affected by catalyst recycling. The reaction solutions after the first and third cycle were analyzed by AAS to determine if Cu leaching into the solution

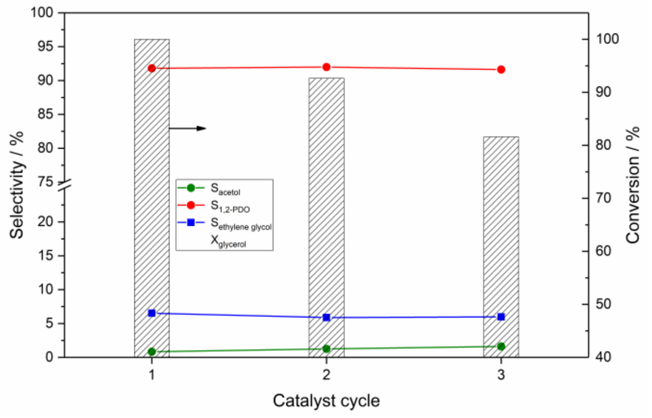


Figure 6. Reusability of Cu/ZrO_2 in the hydrodeoxygenation of glycerol. The compensation of the catalyst mass loss is taken into account in the relative conversion calculation. Reaction conditions: 20 mL of 4 wt.% aqueous glycerol solution, 400 mg of 18 wt.% CuO/ZrO_2 (pre-reduced), 25 bar H_2 pressure, 750 rpm stirring speed and 8 h reaction time.

had occurred. Only 0.74% (20 ppm) and 0.54% (15 ppm) of the total Cu was found to be leached into the solution after the first and third cycle, respectively. This low degree of Cu leaching points to an efficient stabilization of the metallic Cu nanoparticles in the ZrO_2 support under the applied reaction conditions. The XRD patterns (Figure S5) of the freshly reduced catalyst and the catalyst after three cycles reveal structural changes of metallic Cu from small particle sizes to larger agglomerates. This agglomeration of metallic Cu could lead to the decrease of the specific Cu surface area and thus cause the deactivation of the catalyst. A similar deactivation mechanism was also reported by Vasiliadou et. al. for HDO of glycerol with Cu/SiO_2.[43]

Conclusions

A series of co-precipitated Cu/ZrO_2 catalysts was synthesized and applied in the aqueous-phase hydrodeoxygenation of glycerol (4 wt.% in water) at 200 °C and 25 bar H_2 pressure. The catalysts exhibited high activity and selectivity of about 95% for the terminal C-O bond cleavage to 1,2-propanediol while preserving the C-C bonds, in this way avoiding the formation of by-products. The HDO of glycerol was found to proceed via a two-step dehydration-hydrogenation reaction pathway forming acetol as dehydration intermediate, which is further hydrogenated to 1,2-propanediol. As major by-product ethylene glycol was produced from the direct C-C hydrogenolysis of glycerol with a selectivity of less than 5%. Glycerol conversion was linearly correlated with the specific Cu surface area of the catalysts. In addition, using pure metallic Cu revealed the dominant role of metallic Cu in the dehydration of glycerol to acetol. The acidic Zr-OH sites did not contribute to the catalytic activity presumably due to blockage by abundant water under the employed aqueous-phase reaction conditions. Studies of the catalyst reusability showed that the catalyst was relatively stable with only a slight decrease of the catalytic activity after three reaction cycles.

Experimental Section

Catalyst preparation

Precursors of the Cu/ZrO_2 catalysts were prepared by co-precipitation method. Calculated amounts of copper nitrate (Sigma Aldrich, 99.999%) and zirconium oxynitrate (Sigma Aldrich, 99.0%) were dissolved in 100 mL deionized water (HPLC purity) and precipitated at a constant pH value of 10.5 using a 25 wt.% sodium hydroxide solution as precipitating agent. The resulting precipitates were filtered and washed with deionized water until the filtrate was free of nitrates. After drying at 105 °C overnight, the precursors were calcined at 490 °C for 3 h in synthetic air (20% O_2/N_2), and a series of CuO/ZrO_2 catalysts with nominal CuO loadings of 5, 10, 18 and 31 wt.% was obtained.

Characterization

Temperature-programmed reduction (TPR) measurements were carried out in a flow set-up using 5 vol.% H_2 in Ar at a flow rate of 84 mL min^{-1}. For each experiment 100 mg of catalyst in a sieve fraction of 250 µm to 355 µm were loaded in a stainless-steel U-tube reactor. The samples were heated up to 240 °C with a heating rate of 1 °C min^{-1}. The H_2 concentration in the exhaust gas was measured by a thermal conductivity detector.

N_2O reactive frontal chromatography (N_2O-RFC) measurements were carried out after the TPR measurements with a flow rate of 1% N_2O in He at room temperature. The exhaust gas stream was analysed with an Advance Optima AO2020 continuous gas analyser (ABB).

X-Ray powder diffraction (XRD) patterns were recorded with an PANalytical theta-theta powder diffractometer equipped with a Cu Kα radiation source in a 2θ range of 10° to 80°. Qualitative phase analysis was carried out using HighScore Plus V.3.0 software and ICDD powder diffraction database.

For the N_2 physisorption measurements (BET and BJH) 200 mg of the calcined catalysts in a sieve fraction of 250 µm to 355 µm were used in a BELSORP-max device. Prior to the measurements, the catalysts were heated to 200 °C for 2 h under vacuum to remove residual water. The measurements were carried out at -196 °C with a relative pressure (p/p_0) in the range of 0 to 1. The specific surface area, average pore volume and average pore diameters were calculated from the obtained isotherms.

Atomic absorption spectroscopy (AAS) of the liquid reaction solutions were carried out using a VARIAN AA 300 spectrometer equipped with a flame ionization system to determine the Cu leaching.

Catalytic tests

The catalytic performance of the Cu/ZrO_2 catalysts was tested in a Parr 5050 stainless-steel autoclave reactor (100 mL). Prior to the catalytic test, the catalyst was pre-reduced in the reactor in the absence of liquid reaction solution in order to form metallic Cu active sites. For each test 400 mg catalyst was loaded in the reactor. Subsequently, the reactor was flushed with H_2 (99.999%) to remove ambient air and pressurized and subsequently heated to 200 °C at 20 bar for 10 h to reduce the catalysts. After cooling and depressurization, 20 g of 4 wt.% aqueous glycerol solution was loaded through a sampling tube (without opening the reactor) to minimize the exposition of the reduced catalyst to air. After flushing the reactor with H_2 again, the reaction was performed at 200 °C, 25 bar H_2 partial pressure at a stirring speed of 750 rpm for 8 h. During reaction liquid samples of 1.5 mL were taken out after 1, 3, 5 and 8 h. The samples were filtered using membrane filters and analyzed by gas chromatography.

Prior to the catalytic test under inert nitrogen gas atmosphere, the catalyst was pre-reduced in the reactor in the absence of the reaction solution, according to the method described above. After cooling and depressurization, 20 g of 4 wt.% aqueous glycerol solution was loaded through a sampling tube (without opening the reactor) to minimize the exposition of the reduced catalyst to ambient air. After flushing the reactor several times with N_2, the reactor was pressurized with N_2 to 12 bar and heated to 200 °C. The reaction was run for 8 h at a stirring speed of 750 rpm. During reaction 1.5 mL liquid samples were taken out after 1, 3, 5 and 8 h. The samples were filtered using membrane filters and analyzed by gas chromatography.

For catalytic reusability tests, the HDO reaction was performed without sampling during the reaction and the catalyst was recycled after 8 h from the reaction solution by centrifugation, washing with deionized water and freeze-drying overnight. The mass loss of the catalyst after each cycle was approximately 8%. After each cycle the catalyst was pre-reduced prior to the reaction in the absence of any solvent or solution and subsequently reused for the HDO of glycerol.

Analysis of liquid-phase products

Liquid-phase reaction products were analysed by an Agilent 7820A gas chromatography equipped with a capillary column (ZB-WAXplus, 30 m × 0.32 µm × 0.25 µm) and a flame ionization detector (FID). The GC was calibrated using external standard calibration resulting in relative standard deviations (RSD%) of 2-4% depending on the compound. The conversion of glycerol as well as the selectivity and yield were calculated based on liquid products using the following equations:

$$\text{Conversion of glycerol [\%]} = \frac{\text{moles of glcerol reacted}}{\text{moles of initial glycerol}} \cdot 100$$

$$\text{Selectivity [\%]} = \frac{\nu_i \cdot \text{moles of specific product}}{\text{moles of glycerol reacted}} \cdot 100$$

where v_i is the stoichiometric factor, 1 for glycerol, acetol, 1,2-PDO and propanols, 2/3 for ethylene glycol and ethanol and 1/3 for methanol.

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Keywords: Hydrodeoxygenation of glycerol • 1,2-propanediol • Cu/ZrO_2 • metallic copper

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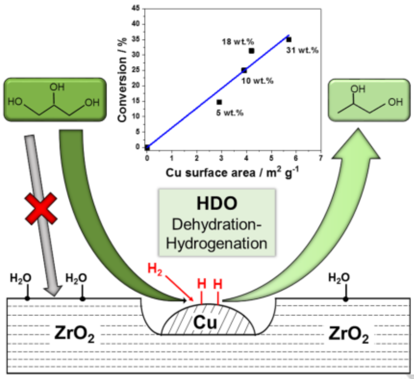
FULL PAPER

Cu - Commonly underrated: Cu/ZrO_2 catalysts exhibit high selectivity for the hydrodeoxygenation of glycerol to 1,2-propanediol under mild reaction conditions. Metallic Cu is identified as the active site for the sequential dehydration - hydrogenation reaction steps.



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The role of metallic copper in the selective hydrodeoxygenation of glycerol to 1,2-propanediol over Cu/ZrO_2