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# Cu/C-catalyzed hydrogenolysis of sorbitol to glycols-on the influence of particle size and base

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Abstract: Herein, a series of Cu catalysts supported on activated carbon with increasing particle size was tested for the conversion of sorbitol to glycols including 1,2-propanediol and ethylene glycol in the presence of Ca(OH)<sub>2</sub>. Activity measurements reveal a distinct correlation between TOF and particle size, which increases until 14 nm (N<sub>2</sub>O chemisorption based) after which a plateau is reached. However, variation of the particle size has no apparent effect on the selectivity for  $C_3/C_3$  and  $C_2/C_4$  cleavage. In contrast, variation of the Ca(OH)<sub>2</sub> equivalent has a profound impact on selectivity. The ratio of  $C_3/(C_2+C_4)$  products reaches an optimum at 0.45 eq. of Ca(OH)<sub>2</sub>. Notably, the time course of the reaction demonstrates that the byproducts lactic acid and glycerol are in-situ converted to the desired product 1,2-propanediol, contributing to the unprecedented combined glycol selectivity of 84.5% at 513 K, 5 MPa  $H_2$  and 0.3 eq. of Ca(OH)<sub>2</sub>. Furthermore, recycling tests reveal a rapid deactivation which is attributed to the aggregation of Cu observed in TEM.

#### Introduction

Biomass is a cheap and abundant carbon source, which is playing an increasingly important role in the utilization of alternative resources.<sup>[1]</sup> Among the various biomass-based platform chemicals, sorbitol, which can be obtained from the hydrogenation of glucose, has attracted considerable attention.<sup>[2]</sup> The hydrogenolysis of sorbitol under alkaline conditions results in the formation of glycerol (GLY),[3] lactic acid (LA),[4] 1,2propanediol (1,2-PDO),<sup>[5]</sup> ethylene glycol (EG)<sup>[6]</sup> as well as a minor amount glycolic acid (GA)<sup>[7]</sup> (Scheme 1). It is generally accepted that the major reaction pathways under these conditions are dehydrogenation of the polyol, base-catalyzed retro-aldolization to form  $C_2$  and  $C_3$  products and rehydrogenation. The resulting products have been widely applied in industry for renewable plastics, paints, antifreeze, cosmetics and pharmaceuticals.<sup>[8]</sup>

The employed catalyst systems for polyol hydrogenolysis can be divided into noble metal based (e.g. Ru, Pd, Pt, Rh) and nonnoble metal based (e.g. Ni, Cu, W). Guo et al. observed excellent performance for Ru supported on carbon nanotubes (CNTs) in the conversion of sorbitol.<sup>[9]</sup> Full conversion and 60% selectivity to glycols was obtained over the WO<sub>x</sub>-promoted Ru/CNTs catalyst in the presence of Ca(OH)<sub>2</sub> at 478 K. A kinetic study by our group on sorbitol and xylitol hydrogenolysis under neutral/acidic conditions, revealed that Ru/C also catalyzes

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Scheme 1. Metal-catalyzed hydrogenolysis of sorbitol under basic conditions to short chain polyols and acids.

decarbonylation and deoxygenation, leading to degradation and formation of gaseous products.<sup>[10]</sup> Banu et al. investigated the conversion of sorbitol over Ru-, Pt- and Ni-NaY catalysts in the presence of base.<sup>[11]</sup> Ni-NaY showed the best results with over 60% conversion and 70% selectivity to glycols. Ni/Al<sub>2</sub>O<sub>3</sub> was investigated by Ye et al..<sup>[12]</sup> It was found that the addition of Ce significantly improved the activity. However, also here the formation of considerable amounts of gaseous products (e.g. CH<sub>4</sub> and CO<sub>2</sub>) is a disadvantage. Therefore, strong hydrogenolysis of C-C and C-O bonds and poor hydrothermal stability make Ni an unsuitable alternative.<sup>[13]</sup>

Montassier et al. first investigated the conversion of polyols (i.e. sorbitol, xylitol, erythritol and glycerol) over a series of carbon supported catalysts.<sup>[14]</sup> Ru, Ni, Rh and Ir catalyzed both C-C and C-O cleavage leading to the formation of methane, whereas over Cu mainly C-O cleavage was favored. This suggests that Cu possesses a high potential to obtain glycols with high selectivity. Recently, Jin et al. developed a multi-functional Cu/CaO-Al<sub>2</sub>O<sub>3</sub> catalyst over which the combined selectivity to 1,2-PDO and EG reached 61.5% with full sorbitol conversion at 503 K after 6h.<sup>[15]</sup> A synergistic two-phase mechanism, where the CaCuAIO phase presents the active site for dehydrogenation and retro aldolization, and spinel CuAl<sub>2</sub>O<sub>4</sub> species catalyze hydrogenation, was proposed. Ca2+ was considered as crucial for the cleavage of C-C bonds to smaller products (e.g. 1,2-PDO, LA and EG). However, the deeper understanding of the respective roles of Cu and Ca<sup>2+</sup> on the reaction is still missing. Furthermore, the low intrinsic activity (TOF) of Cu/CaO-Al<sub>2</sub>O<sub>3</sub> is a considerable disadvantage as compared to noble metal catalysts. Huang et al. revealed that the activity of Cu catalyst in the conversion of xylitol to glycols is dependent on particle size.<sup>[16]</sup> But contrary results regarding the optimum particle size of Cu supported on SiO<sub>2</sub> were proposed in different papers.<sup>[17]</sup> Therefore, more and straightforward techniques should be used to better determine the particle size. In addition, the highest selectivity to glycols in former papers is low (61.5%). Thus, a study on improving the activity of Cu catalyst meanwhile accelerating the selectivity to glycols is highly important.

Here we present a study concerning the influence of Cu particle size and equivalents of  $Ca(OH)_2$  on the activity and selectivity of the hydrogenolysis of sorbitol to glycols including 1,2-PDO and EG. Other than SiO<sub>2</sub> used as support in former papers, activated carbon due to its low strong metal-support interactions (SMSI) with metal is employed to support Cu in this work.<sup>[18]</sup> The effects of metal loading, reaction conditions, equivalence of Ca(OH)<sub>2</sub> and recycling are investigated.

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Table 1. Physical properties of Cu catalysts with different loadings.							
Catalyst	BET area <sup>[a]</sup> (m²/g)	Pore volume <sup>[a]</sup> (cm <sup>3</sup> /g)	Dispersion <sup>[b]</sup> (%)	Cu area <sup>[b]</sup> (m²/g)	Particle size (N₂O) <sup>[b]</sup> (nm)	Particle size (XRD) <sup>[c]</sup> (nm)	Particle size (TEM) <sup>[d]</sup> (nm)
С	1803	0.89	-	-	-		
5%Cu/C	1698	0.84	17.1	115.9	5.8	4.9	3.8 (1.2) <sup>[e]</sup>
10%Cu/C	1606	0.79	13.5	91.5	7.4	8.0	n.d.
15%Cu/C	1288	0.64	11.5	78.1	8.7	9.3	9.5 (3.0)
25%Cu/C	1112	0.54	7.1	48.3	14.0	18.3	16.4 (5.4)
40%Cu/C	742	0.38	4.2	28.6	23.7	26.0	25.0 (4.7)

[a] Measured by BET. [b] Measured by N₂O Chemisorption. [c] Calculated from XRD. [d] Calculated from TEM. [e] Standard deviation.

#### **Results and Discussion**

A series of Cu/C catalysts with different loadings (i.e. 5 - 40 w.t %) was prepared using wet impregnation. The results of N<sub>2</sub> physisorption, N<sub>2</sub>O-chemisorption (CS) and XRD of the reduced catalysts are summarized in Table 1. Notably, with increasing loading the BET area decreases from 1803 m<sup>2</sup>/g for activated carbon to 742 m<sup>2</sup>/g for 40 w.t % Cu/C (see Figure S1 for isotherms). At the same time, the pore volume decreases from 0.89 to 0.38 cm<sup>3</sup>/g. The significant decrease of both BET surface area and pore volume with increasing metal loading suggests an incremental filling of the micropores by Cu. N<sub>2</sub>O-CS is a wellknown method for the evaluation of the dispersion of Cu catalysts. In short, first the  $Cu(NO_3)_2$  loaded materials are reduced using H<sub>2</sub>. The resulting accessible Cu<sup>0</sup> surface is oxidized to Cu<sub>2</sub>O by N<sub>2</sub>O, which in the final step is reduced back to Cu<sup>0</sup>, giving the total accessible surface. Based on the obtained data the dispersion, specific Cu<sup>0</sup> surface and crystallite size are calculated (Table 1).<sup>[19]</sup>

The data confirm that with increasing loading the dispersion decreases from 17.1% to 4.2%, the specific Cu surface area declines from 115.9 to 28.6 m<sup>2</sup>/g and the particle size increases from an average of 5.8 nm to 23.7 nm. Thus a clear trend is observed between loading and mean particle size. This is further confirmed by XRD and TEM analysis of the reduced catalysts. XRD patterns of the reduced catalysts are shown in Figure S2. Metallic Cu exhibits diffraction peaks at  $2\theta = 43.3^{\circ}$  (Cu(111)), 50.4° (Cu(200)) and 74.1° (Cu(220)). Characteristic reflexes of Cu(I) are missing, confirming that Cu has been fully reduced by H<sub>2</sub> after 4 h at 623 K. The Cu(111) reflex was used to determine the particle size using the Debye-Scherrer equation (Table 1). The data emphasize that the particle size increases with increasing loading from 4.9 nm for 5 w.t % to 26 nm for 40 w.t % is in well agreement with data obtained by chemisorption. Also TEM analysis of the reduced catalysts confirms a clear trend between the loading and the particle size. Representative TEM images and Cu particle distributions are illustrated in Figure 1. As can be seen, the particle size distribution migrates to higher ranges with increasing loading. Moreover, the presented data of particle sizes determined by three different methods are in line with each other. The minor discrepancy indicates that the results of particle size are highly reliable.



Figure 1. Particle distributions of Cu catalysts and corresponding electron microscopy images. Cu<sub>n</sub>: Cu average particle size.  $\sigma_n$ : standard deviation of Cu<sub>n</sub>. The scale in TEM is equal to 100 nm.

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Table 2. Performance of Cu catalysts in the conversion of sorbitol. [a]								
Catalyst	Conversion (%)	Selectivity						0 //0 +0 >
		1.2-PDO	EG	GLY	LA	GA	Others <sup>[c]</sup>	C3/(C2+C4)
С	_ [b]	-	-	-	-		-	· ·
5%Cu/C	17.2	39.3	10.4	10.2	23.4	11.2	5.3	2.7
10%Cu/C	30.8	39.1	12.3	14.4	21.9	7.0	5.2	3.1
15%Cu/C	35.9	36.3	12.2	18.9	19.4	6.1	7.2	3.0
25%Cu/C	42.3	34.4	12.3	25.0	16.3	6.3	7.5	3.2
40%Cu/C	20.6	41.0	10.5	3.1	26.5	8.9	10.2	2.5

[a] Conditions: 20 mL H<sub>2</sub>O, 0.66 g sorbitol, 10 mg Cu, 0.2g Ca(OH)<sub>2</sub>, 433 K, 2 h, 5 MPa H<sub>2</sub>, 750 rpm. [b] No conversion. [c] Including C<sub>4</sub>-C<sub>6</sub> hexitols, pentitols, triols, diols and trace amount of C<sub>1</sub> chemicals.



Figure 2. High resolution TEM image of 25%Cu/C.

A high resolution TEM of 25%Cu/C is presented in Figure 2. Large particles with extended lattice planes are observed. The distance between the observed lattice fringes is 2.08 Å, which corresponds to the (111) interplanar spacing of metallic Cu crystals. The hydrogenolysis of sorbitol was performed in the presence of Ca(OH)<sub>2</sub> at 433 K for 2 h under 5 MPa H<sub>2</sub>. The amount of Cu in the reaction was kept constant. Due to the microporous nature of activated carbon, it is assumed that the Cu particles are located mainly on the external surface. As a result the effect of intra-particle mass transfer on the reaction pressure does not change significantly during the reaction. The influence of initial H<sub>2</sub> pressure on conversion and products distribution is shown in Figure S3 and shows no significant influence within a range of 3 to 7 MPa. Therefore we propose

that mass transfer limitation due to gas diffusion can also be neglected. Table 2 summarizes the obtained results. Activated carbon was also tested and gave no conversion, confirming it is inert in the reaction. 5%Cu/C enabled 17.2% conversion with 39.3% selectivity to 1,2-PDO, 10.4% to EG, 10.2% to GLY, 23.4% to LA and 11.2% to GA. With increasing Cu loading, the conversion increases to an optimum of 42.3% over 25%Cu/C followed by a decrease to 20.6% over 40%Cu/C. The ratio between  $C_3$  and  $(C_2+C_4)$  products  $(C_3/(C_2+C_4))$  remains roughly constant, indicating that the particle size has little effect on the selectivity of the reaction. However, there is significant variation in the production of 1,2-PDO, LA and GLY. The combined selectivity of 1,2-PDO and LA decreases from 62.7% over 5%Cu/C to 50.7% over 25%Cu/C, whereas the selectivity to GLY increases from 10.2% to 25.0%. This suggests that a stronger hydrogenation catalyst favors the production of GLY while the total production of C<sub>3</sub> products remains constant.

In order to identify the role of the Cu particle size on sorbitol conversion, the turnover frequency (TOF) was determined in relation to the average Cu particle size obtained by N<sub>2</sub>O CS (Figure 3). The reported TOF is based on the accessible copper surface and represents the TOF per hour/Cu atom. The data reveals a clear trend. Increasing the particle size from 5.8 nm to 14 nm leads to a significant increase of the TOF from 10.4 to 54.8 h<sup>-1</sup>. From 14 nm onwards the TOF remains constant. The observed activity of nanoparticles can be the result of several factors such as strong metal support interactions (SMSI), cooperative effects at the metal-support interface and the proportions of different active surface sites.<sup>[18a, 20]</sup> Given the low SMSI of carbon supports, we consider that the size-dependent dehydrogenation performance of Cu is due to the changes of the Cu surface rather than the interaction with carbon.<sup>[18c]</sup> In any case the apparent TOF is the average of various different TOFs due to crystallographic features such as Miller-index planes, steps, kinks, edges, corners and their respective proportions in the accessible surface.<sup>[21]</sup> It is considered that with increasing particle size the proportion of the more stable Cu(111) surface grows. In line with this the above results suggest that this is also the catalytically most active surface. Furthermore, the data



Figure 3. TOF of sorbitol conversion as a function of Cu average particle size. (Conditions: TOF determined at < 35% conv., 1-2 h, 433 K, 5 MPa H<sub>2</sub>, 750 rpm. (Particle size determined by N<sub>2</sub>O CS)).

confirm that beyond 14 nm the specific surface activity of Cu is independent on particle size. This suggests that for larger particles the proportion of densely packed surfaces, e.g. Cu(111), is high regardless of particle size. Thus, since the specific surface area decreases with increasing particle size it can be postulated that 14 nm is the ideal particle size in case of the Cu-catalyzed hydrogenolysis of sorbitol.

Nevertheless, the hydrogenolysis of polyols is the result of a synergy between Cu-catalyzed dehydrogenation and Ca(OH)2promoted isomerization and retro aldolization. Therefore, not only reaction temperature and time but also the equivalence of Ca(OH)<sub>2</sub> was investigated. The influence of temperature on the products distribution was studied using 4h reaction in the temperature range 433-513 K (Figure S4). In all cases sorbitol was fully converted at the end of the reaction. The combined selectivity to glycols (EG and 1,2-PDO) increases with higher temperature. Notably, the selectivity towards acids (i.e. LA and GA) significantly decreases at higher temperature. Thus, the data emphasize that higher reaction temperature favours the production of the desired glycols. The evolution of the product distribution over reaction time was monitored at 513 K (Figure 4). Time zero was set at the time when the reactor first reached the reaction temperature. During the heating phase (approx. 30 min) sorbitol was already fully converted. The selectivity to 1,2-PDO increases while those of LA and GLY decrease, suggesting that GLY and LA are converted to 1,2-PDO during the reaction. In contrast, EG and 1,2-butanediol (1,2-BDO) remain constant. At 24h, full conversion and a selectivity to glycols (EG and 1,2-PDO) of up to 84.5% was achieved. To the best of our knowledge, this is the highest selectivity reported for EG and 1,2-PDO so far.<sup>[15]</sup> The conversion of GLY to 1,2-PDO over Cu catalysts is well known, whereas the conversion of LA to 1,2-PDO over Cu has rarely been reported.<sup>[8, 22]</sup> A reaction performed with LA, under otherwise similar conditions, gave 20% conv. with 1,2-PDO as the sole product. This is the first report on the conversion of lactic acid over Cu under aqueous reaction conditions. Therefore, it is proposed that the unprecedented selectivity to glycols is the result of an in-situ conversion of the side products LA and GLY to the desired 1,2-PDO.

The impact of  $Ca(OH)_2$  as a promoter on the product distribution was identified by varying the amount added in the reaction. Here,



Figure 4. Products evolution over 25%Cu/C. (Conditions: 0.18 M sorbitol, 0.08 g Cu, 0.2g Ca(OH)<sub>2</sub>, 20 ml H<sub>2</sub>O, 513 K, 5 MPa H<sub>2</sub>, 750rpm, full conversion.)

particularly the  $C_3/(C_2+C_4)$  ratio provides insight into the cleavage position of the retro-aldol reaction and the identity of the preceding carbohydrate intermediate.<sup>[22b, 23]</sup> For example, retro-aldol cleavage of an aldose yields one C2 and one C4 fragment, whereas cleavage of a 2-ketose yields two C3 fragments (Scheme 2). Figure 5 shows the product distribution and the carbon-based ratio of C3 products (i.e., 1.2-PDO, LA and GLY) and C<sub>2</sub>+C<sub>4</sub> products (i.e., EG, GA, BDOs and BTO) as a function of Ca(OH)<sub>2</sub> equivalents w.r.t. sorbitol. The  $C_3/(C_2+C_4)$ ratio increases from 1.9 at 0.15 eq. Ca(OH)<sub>2</sub> to a plateau of approx. 6 at 0.45 eq. This suggests that with increasing amount of Ca(OH)<sub>2</sub>, the relative amount of ketose in the reaction increases leading to higher amount of C<sub>3</sub> products. In principle, metal-catalyzed dehydrogenation of hexitols can yield 1-aldose, 2-ketose and 3-ketose intermediates. Dehydrogenation at the 1pos. is generally more facile than at the 2-pos. due to a lower activation barrier.<sup>[15]</sup> It is proposed that the increasing  $C_3/(C_2+C_4)$ ratio with increasing amount of Ca(OH)<sub>2</sub> is the result of base-



**Scheme 2.** Conversion pathways of hexitols. The main pathway to produce 1.2-PDO is highlighted in red.



**Figure 5.** Product distribution and selectivity ratio of C<sub>3</sub> and C<sub>2</sub>+C<sub>4</sub> products versus the amount of Ca(OH)<sub>2</sub>. (C<sub>3</sub> products include 1,2-PDO, GLY and LA and C<sub>2</sub>+C<sub>4</sub> products include GA, EG, Butanediols). Reaction conditions: 0.18 M sorbitol, 0.08 g Cu (25%Cu/C), 20 ml H<sub>2</sub>O, 4 h, 513 K, 5 MPa H<sub>2</sub>, 750 rpm, full conversion.

catalyzed isomerization (i.e. via the Lobry-de-Bruyn-van-Ekenstein reaction).<sup>[24]</sup> Due to the low production of C<sub>1</sub> and/or C<sub>5</sub> chemicals, the route involving the formation of 3-ketose appears not to be preferred. Besides this, the selectivity for LA formation also increases, partly at the expense of 1,2-PDO. It should be noted that the employed amount of Ca(OH)<sub>2</sub> exceeds solubility in all cases, thus all reactions are performed in saturated Ca(OH)<sub>2</sub> solution with a fraction of solid Ca(OH)<sub>2</sub>.<sup>[25]</sup>

In fact, the amount of  $Ca(OH)_2$  is sufficient (i.e., even when taking the formation of lactic acid into account) to remain saturated throughout the whole experiment. Given the strong dependence of the product distribution on the total amount of  $Ca(OH)_2$ , this suggests that the solid fraction also participates in the reaction. Compared to the invariant selectivity ratio observed for the Cu particle size data, these results reveal that the total amount of  $Ca(OH)_2$  plays a much more important role on the product distribution.

The stability of the 25%Cu/C catalyst was tested in 5 subsequent runs at 513 K, 5 MPa. The obtained results are shown in Figure 6. The data reveal that both the conversion of sorbitol and the selectivity to glycols decrease significantly. Moreover, the selectivity to LA increases at the expense of 1,2-PDO. These results indicate that the hydrogenation activity of



**Figure 6.** Conversion and products distribution of catalyst recycling experiments. Reaction conditions: 0.18 M sorbitol, 0.08 g Cu (25%Cu/C), 20 ml H<sub>2</sub>O, 4 h, 513 K, 5 MPa H<sub>2</sub>, 750 rpm, full conversion.

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**Figure 7.** Particle distributions of used and recalcined Cu catalysts and corresponding electron microscopy images. Cu<sub>n</sub>: Cu average particle size.  $\sigma_n$ : standard deviation of Cu<sub>n</sub>. The scale in TEM is equal to 100 nm. Used represents 5-time used catalyst. Recalcined catalyst is obtained from calcination of 5-time used catalysts.

Cu steadily decreases over the runs. ICP-OES analysis of the filtered solutions reveals that leaching (< 0.05%) is negligible in each run (Table S1). A TEM image and particle size distribution of the catalyst 5 times used is displayed in Figure 7. Cu particles with increasing size w.r.t the pristine catalyst are observed. Moreover the average particle size has shifted from 16.5 to 42.6 nm and now also significant amounts of particles large than 60 nm are observed. Therefore, the deactivation of Cu catalyst is attributed to sintering during the hydrothermal reaction.

Liu et al. reported that aggregated Cu particles supported on SiO<sub>2</sub> can be redispersed by a thermal treatment (re-calcination) with recovery of the catalytic activity.<sup>[17]</sup> In line with this we have attempted reactivation of the aggregated catalyst by first washing with diluted H<sub>3</sub>PO<sub>4</sub> soln., followed by calcination under N<sub>2</sub> at 823 K and reduction under H<sub>2</sub> at 623K. XRD patterns in recalcined catalyst (Figure S2) show no peaks other than Cu confirming the removal of all Ca salts. A TEM image of the treated catalyst (Figure 6) shows no improvement in the particle size distribution and also the activity was not recovered. Presumably the poor stabilization of atomic copper on active carbon prevents a redispersion at high temperature.

#### Conclusions

Cu catalysts supported on activated carbon with different particle sizes were thoroughly investigated by XRD, N<sub>2</sub>O chemisorption and TEM. All methods confirm a clear trend that particle size is increased with higher loading. Moreover, the results of particle size determined by different methods are in line with each other. Cu catalysts with different particle size were used for the conversion of sorbitol to produce glycols in the presence of Ca(OH)<sub>2</sub>. The TOF reveals a distinct relation between the intrinsic activity and particle size. It is proposed that Cu particle size dependence is attributed to the fraction of Cu(111) lattice plane of the accessible surface. However, Cu particle size has no significant effect on the ratio of C<sub>3</sub>/(C<sub>2</sub>+C<sub>4</sub>) products which is controlled by the eq. Ca(OH)<sub>2</sub>. The ratio of C<sub>3</sub>/(C<sub>2</sub>+C<sub>4</sub>) increases

from 1.9 at 0.15 eq. Ca(OH)<sub>2</sub> to a plateau of approx. 6 at 0.45 eq. Therefore, the respective roles of Cu and Ca(OH)<sub>2</sub> on sorbitol conversion to glycols are identified: (1) conversion of sorbitol is controlled by the Cu particle size while (2) the selectivity to  $C_3/(C_2+C_4)$  products is affected by the equivalence of Ca(OH)<sub>2</sub>. Notably, the time course indicates in-situ conversion of the side product lactic acid to 1,2-PDO, leading to full conversion and an unprecedented selectivity of 84.5% to glycols (EG and 1,2-PDO) at 513 K, 5 MPa H<sub>2</sub> and 0.3 eq. Ca(OH)<sub>2</sub>. Recycling tests show that the Cu/C-catalyst was deactivated due to the aggregation of particles verified by TEM.

Thus it is demonstrated that Cu/C is a promising catalyst for sorbitol hydrogenolysis that can achieve excellent selectivity to glycols. Nevertheless, high temperatures and high amounts of base are needed and the propensity for copper to sinter is still a challenge that needs to be addressed. Therefore it would be of importance to design new catalysts that prevent the aggregation of Cu nanoparticles.

#### **Experimental Section**

All chemicals were used as received. Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O ( $\ge$  98%), Ca(OH)<sub>2</sub> (98%), 1,2-propanediol (99%) ethylene glycol (99.8%) glycolic acid (99%), 1,2-butanediol (98%), 1,2,3-butanetriol, 1,2,4-butanetriol ( $\ge$  90%), and sorbitol ( $\ge$  98%) were obtained from Sigma Aldrich. Xylitol (100%) and glycerol (100%) were obtained from SUPELCO. Activated carbon supra was obtained from ACROS Organics. Lactic acid (90%) was obtained from Fluka.

Copper catalysts supported on activated carbon with different loadings were prepared via a wetness impregnation method. The required amounts of  $Cu(NO_3)_2$ ·3H<sub>2</sub>O was dissolved into deionized water (DI, 10 mL) with stirring for 1 h in a flask followed by addition of activated carbon (1 g). The resulting slurry was stirred at around 500 rpm for at least 2 h at room temperature in order to obtain a well-dispersed suspension. The slurry was dried using a rotary evaporator (323 K, 7 kPa, 160 rpm) and resulting materials were additionally dried in a drying oven at 353 K for overnight. The catalysts were stored under Ar atmosphere before activity tests.

Brunauer–Emmett–Teller (BET) Measurement. The textual properties of the samples were determined by N<sub>2</sub> adsorption at 77 K using QUADRASORB SI automated surface area and pore size analyzer. Samples were prepared in vacuum at 473 K for overnight. The pore-size distribution was estimated by the Barrett-Joyner-Halenda (BJH) method from the desorption branches of the adsorption isotherms. Surface areas were calculated using the BET method.

X-ray diffraction (XRD). The wide-angle XRD patterns were recorded on a Bruker D8 Advance X-ray diffractometer using nickel-filtered Cu Kα radiation ( $\lambda = 0.15406$  nm) with a scanning angle (20) range of 20–80°, a scanning speed of 4°/min with a voltage of 40 kV, and a current of 20 mA. The crystallite sizes (d) of Cu in the samples were calculated by the Scherrer equation (Eq. 1):

 $d = \frac{k\lambda}{\beta cos\theta}$ (Eq. 1)

Where k is the Debye–Scherrer constant (0.90),  $\theta$  is the diffraction angle and  $\beta$  is the full width at half maximum. The average crystallite size of Cu<sup>0</sup> was estimated from Cu(111) (2 $\theta$  = 43.3°).

Transmission electron microscopy (TEM). Images were obtained using a Philips TECNAI G2 F20 system electron microscope at 100 kV equipped with a field emission gun. The sample powder was dispersed in ethanol

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by ultrasonication. Drops of the suspension were applied onto a nickle grid-supported transparent carbon foil and dried in air. The particle size was determined by software ImageJ.

Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES). ICP-OES was performed on an ICP Spectroflame D by spectro.

 $N_2O$  Chemisorption (N\_2O CS). The specific Cu surface areas, dispersion and crystallite size were measured by  $N_2O$  chemisorption on a ChemBET Pulsar TPR/TPD automated chemisorption analyzer.  $^{[19a-c]}$  The  $N_2O$  chemisorption process consists of three sequential steps:

$CuO + H_2 \rightarrow Cu^0 + H_2O$	H <sub>2</sub> consumption= A1	(Eq. 2)
$2Cu^0 + N_2O \rightarrow Cu_2O + N_2$		(Eq. 3)
$Cu_2O + H_2 \rightarrow 2Cu^0 + H_2O$	$H_2$ consumption= A2	(Eq. 4)

First, CuO is reduced to Cu<sup>0</sup> (Eq. 2). In this step, 5 vol.% H<sub>2</sub> in Ar (100 mL/min) was used as a reducing agent (H<sub>2</sub> consumption A1), and the temperature raised from r.t. to 623 K (10 K/min). Then Cu<sup>0</sup> is oxidized to Cu<sub>2</sub>O by N<sub>2</sub>O (Eq. 3). This step was initiated after the reduced catalyst was cooled to 333 K in He (100 mL/min) and purged with He for 30 min. Then, pure N<sub>2</sub>O (100 mL/min) was introduced to the catalyst at 333 K for 1 h. Subsequently, the catalyst was purged with He (100 mL/min) for 1 h to remove the residual N<sub>2</sub>O. Eq. 4 represents the reduction of Cu<sub>2</sub>O surface species. In this step, 5 vol.% H<sub>2</sub>/Ar (100 mL/min) was used as the reducing agent (H<sub>2</sub> consumption A2) and the temperature raised from 333 K to 623 K with a heating rate of 10 K/min. The dispersion (D) of Cu was calculated using Eq. 5: [<sup>19d]</sup>

$$D = \frac{2A2}{41} \times 100\%$$
 (Eq. 5)

Specific area of metallic copper was calculated from the amount of H<sub>2</sub> consumption (A2) with 1.4 × 10<sup>19</sup> copper atoms/m<sup>2</sup>. The accessible surface area (S<sub>cu</sub>) and particle size of Cu (*d*) were calculated using Eq. 6 and Eq. 7: <sup>[19d]</sup>

$$S = \frac{2 \cdot A2 \cdot N_{av}}{A1 \cdot M_{Cu} \cdot 1.4 \times 10^{19}} \approx \frac{1353 \, A2}{A1} = 676.5 \, D \tag{Eq. 6}$$

$$l = \frac{6}{S \cdot \rho_{Cu}} \approx \frac{1}{D}$$
 (Eq. 7)

With  $N_{av} = 6.02 \times 10^{23}$  (mol<sup>-1</sup>),  $M_{Cu} = 63.546$  (g/mol),  $\rho_{Cu} = 8.92$  (g/cm<sup>3</sup>).

Hydrogenolysis of sorbitol was carried out in a 50 mL autoclave with Teflon insert. In a typical run, aqueous sorbitol solution (20 g, 5 w.t%),  $Ca(OH)_2$  (0.2 g) and Cu catalyst were charged into the autoclave. The reactor was purged five times and pressurized to 5 MPa with H<sub>2</sub>. The sealed autoclave was heated to 513 K with 750 rpm stirring. Samples were taken periodically.

The gas-phase was collected using a gasbag and analyzed by GC performed on a Agilent HP 6890 instrument with a Shin Carbon ST micropacked GC column (308-373 K, TCD, He). Liquid-phase products were analyzed by HPLC performed on a Shimadzu system (Rezex ROA Organic Acid H<sup>+</sup> (8%) column by Phenomenex, eluent: 0.05 M H<sub>2</sub>SO<sub>4</sub>). The sorbitol conversion (Eq. 8) and selectivity (Eq. 9) were calculated on the basis of carbon. The TOF was calculated using (Eq. 10).

$$Conversion = \frac{mole \ of \ reactant \ consumed}{mole \ of \ reactant \ charged} \times 100\%$$
 (Eq. 8)

$$Selectivity = \frac{mole of product \times C \ atoms in product}{mole of reactant \ consumed \times C \ atoms in reactant} \times 100\%$$
 (Eq. 9)

$$OF(h^{-1}) = \frac{\text{mole of reactant consumed}}{\text{mole of surface copper atoms } \times \text{time}(h)} \times 100\%$$
(Eq. 10)

Т

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Keywords: Sorbitol • 1,2-propanediol • ethylene glycol • copper particle • Ca(OH)<sub>2</sub> • hydrogenolysis

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### **Entry for the Table of Contents**

## FULL PAPER

Sorbitol conversion to glycols is a synergistic reaction catalyzed by Cu and Ca(OH)<sub>2</sub>. The activity of Cu depends on particle size with a maximum TOF reached at 14 nm. Regarding the decreased specific surface area for bigger particle, the catalyst with 14 nm Cu particle diameter shows highest activity. However, particle size does not influence the ratio of  $C_3/(C_2+C_4)$  products which is controlled by the equivalence of Ca(OH)<sub>2</sub> charged.



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Copper-catalysed hydrogenolysis of sorbitol to glycols-on the influence of particle size and base

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