

Hydrogenolysis of glycerol over a highly active CuO/ZnO catalyst prepared by an oxalate gel method: influence of solvent and reaction temperature on catalyst deactivation

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The hydrogenolysis of glycerol was performed in an autoclave at temperatures between 190 and 225 °C and at a H₂ pressure of 5 MPa over a CuO/ZnO catalyst prepared by an oxalate gel (OG) method. Compared to a CuO/ZnO catalyst prepared by coprecipitation, much higher conversions of glycerol and space–time yields up to 9.8 g_{propylene glycol} g_{Cu}⁻¹ h⁻¹ are achieved with CuO/ZnO-OG, whereas both catalysts produced propylene glycol with selectivities of about 90%. Additionally, the influence of the temperature and the solvent was examined. Compared to a conversion of glycerol of only 5% in an aqueous glycerol solution, the use of 1,2-butanediol as a solvent leads to a high conversion of 55%. Moreover, experiments were carried out in pure glycerol and from transmission electron microscopy images of fresh and spent catalysts, it was obvious that the morphology of the catalyst changed during the reaction. By X-ray diffraction and N₂O chemisorption, it was proved that a tremendous loss of copper surface area occurred during the hydrogenolysis of glycerol. Taking together the influence of the solvent on the conversion of glycerol and the results of the catalyst characterization, it can be concluded that water, as an unavoidable by-product of the reaction, is responsible for a strong deactivation of the catalyst.

1. Introduction

As a byproduct of biodiesel production, glycerol is a highly-functionalized platform chemical available in large amounts and, thus, at low costs. Therefore, the development of new catalytic processes to convert glycerol to value-added products, *e. g.* dihydroxyacetone or hydrogen,¹ is the subject of an increasing number of investigations. One of the promising approaches is the hydrogenolysis of glycerol, leading to 1,2-propanediol (propylene glycol). Propylene glycol has a wide range of practical applications, like its use as a heat transfer fluid or its polymerisation to polyesters and polyurethanes. Supported Pt, Rh, Co, Ru and Cu catalysts are used for the hydrogenolysis of glycerol at temperatures between 170 and 220 °C under elevated hydrogen pressures and in dilute aqueous solutions of glycerol.^{2–8} Several attempts were made to enhance glycerol conversion by the addition of solid acids like ion-exchange resins^{9,10} or zeolites and sulfated zirconia¹¹ to supported noble metal catalysts, suggesting that the hydrogenolysis of glycerol occurs in two steps. Initially, glycerol is dehydrated to acetol over acid sites followed by hydrogenation over metal catalysts. Indeed, acetol was detected by several groups,⁶ particularly when the hydrogenolysis of glycerol is carried out in the vapour phase and, thus, under rather low hydrogen pressures.^{12,13}

Among the different noble metal catalysts, Cu catalysts turned out to combine high selectivities for propylene glycol with satisfying conversion levels of glycerol.^{5,6,14–17}

However, the reaction times needed to achieve high glycerol conversions are rather long. Additionally, Cu catalysts suffer from deactivation in the hydrogenolysis of glycerol. It is observed in the literature that a strong decrease in glycerol conversion occurs if a Cu/Zn/Al catalyst is used in a second run, regardless of whether the spent catalyst was dried or calcinated before it was reused.¹⁷ Moreover, Montassier *et al.* reported the deactivation of Cu/C because of the sintering of copper particles in the hydrogenolysis of glycerol in a tube reactor.¹⁵

Besides the preparation of copper catalysts by precipitation,^{5,14,17} different preparation methods like the template preparation of Cu–Cr catalysts¹⁸ and the precipitation–gel method for a Cu/SiO₂ catalyst¹⁹ have been applied. However, the Cu/ZnO catalysts used in the hydrogenolysis of glycerol have usually been prepared by precipitation and the effect of the Cu/ZnO catalyst synthesis procedure was not investigated, although the properties of Cu/ZnO catalysts, and, thus, their performance in the methanol synthesis from CO and H₂, have been shown to be strongly dependent on the preparation method.^{20–22} Here, we report the preparation of a copper catalyst by an oxalate gel method, its characterization and its use in the hydrogenolysis of glycerol. Additionally, the deactivation of the catalyst was examined with regard to the reaction temperature and the generation of water as a by-product of the hydrogenolysis of glycerol.

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2. Experimental

2.1 Preparation of the catalysts

The preparation of the CuO/ZnO catalyst was carried out by an oxalate gel coprecipitation method.²³ Cu(NO₃)₂·2.5H₂O (4.87 g, 20.9 mmol) and Zn(NO₃)₂·6 H₂O (12.2 g, 41 mmol) were dissolved in 65 ml ethanol. Then, oxalic acid (6.68 g, 74.3 mmol) in 40 ml ethanol was added to form a light blue precipitate. After one hour, the precipitate was separated by filtration, washed with 500 ml deionised water and finally dried overnight at 70 °C. Afterwards, the precipitate was calcined at 150, 200 and 300 °C for one hour at each temperature, followed by a final step at 360 °C for four hours. Hereafter, this catalyst will be referred to as the CuO/ZnO-OG catalyst.

As a reference, a CuO/ZnO catalyst was prepared by coprecipitation. Copper acetate (3.8 g, 20.9 mmol) and Zn(NO₃)₂·6H₂O (12.2 g, 41 mmol) were dissolved in 300 ml deionised water. Precipitation was achieved by the dropwise addition of 140 ml of a 1 M NaOH solution at 80 °C. The precipitate was aged for 2 h at a constant pH value of 9 at the same temperature. Finally, the precipitate was separated by filtration, washed with one litre of deionised water and dried overnight at 70 °C. The calcination of this catalyst was the same as that for the CuO/ZnO-OG catalyst. This catalyst will be referred to as the CuO/ZnO-CP catalyst. The copper oxide content of both catalysts was 33 wt%.

2.2 Catalyst characterisation

Copper surface areas were determined by N₂O chemisorption followed by temperature-programmed reduction (TPR) of the formed Cu₂O species in a stream of H₂ (Cu₂O-TPR). All these treatments of the catalyst were carried out by means of a TPDR 1100 device (Porotec). Before the analysis, *in situ* pre-reduction of the catalysts in a stream of 4.95% H₂ in Ar (20 ml min⁻¹), at a heating rate of 10 °C min⁻¹, to a temperature of 330 °C was performed. This temperature was held for 60 min. The catalyst was cooled down in a stream of He in order to oxidize Cu to Cu₂O with 1% N₂O in He (10 ml min⁻¹) at 20 °C. Finally, Cu₂O-TPR was carried out in 4.95% H₂ in Ar (20 ml min⁻¹) at a heating rate of 10 °C min⁻¹, to a temperature of 330 °C. From the amount of H₂ needed to completely reduce Cu₂O, the specific copper surface area, the dispersion and the mean particle diameter were calculated.

Additionally, the morphology of the catalysts was examined by transmission electron microscopy (HRTEM JEOL, JEM 3010, 300 kV). Powder X-ray diffraction (XRD) patterns of the catalysts were recorded using Co K α 1 radiation ($\lambda = 1.78896 \text{ \AA}$).

2.3 Hydrogenolysis of glycerol

In a standard experiment, 140 mL pure glycerol and 3 g catalyst were loaded into a stainless steel reactor (Parr). The reactor was pressurized with hydrogen to a pressure of 5 MPa and heated to a temperature of 200 °C. The samples were taken at desired time intervals and analyzed with a Hewlett-Packard 6890 gas chromatograph equipped with a DB-WAX GC column and a flame ionization detector. The selectivity of the products was calculated on a carbon basis.

In order to investigate the role of water (section 3.4) in the deactivation of the catalyst, 1,2-butanediol was used as a solvent. Glycerol and the reaction products, including several alcohols, have to be dissolved easily in the solvent making the use of an alcohol desirable. Furthermore, no C₁ to C₃ components were chosen as solvent due to their possible formation during the hydrogenolysis of glycerol. Therefore, this C₄ polyol was used as the solvent.

3. Results and discussion

3.1 Preparation method of the catalyst

Initially, the CuO/ZnO catalysts prepared by the two different preparation methods were tested in the hydrogenolysis of glycerol. According to Table 1, no differences between the two catalysts in terms of the selectivities are observed. Both CuO/ZnO-OG and CuO/ZnO-CP catalysts exhibited high selectivities towards propylene glycol of 90 and 87%, respectively. Moreover, the selectivities towards undesired side products like ethylene glycol and acetol were low. Concerning the activity of the two catalysts, a much higher conversion of glycerol was achieved in the case of the CuO/ZnO-OG catalyst compared to CuO/ZnO-CP. Using the CuO/ZnO-OG catalyst, a conversion of 46% is achieved, whereas the conversion at the CuO/ZnO-CP catalyst is only 17%. With the CuO/ZnO-OG catalyst, the space–time yield amounts to 9.8 g_{propylene glycol} g_{Cu}⁻¹ h⁻¹. Compared to other copper-based catalysts like Cu/SiO₂¹⁹ and CuO/ZnO, prepared by coprecipitation,¹⁴ which produce propylene glycol with space–time yields of 3.2 and 0.8 g_{propylene glycol} g_{Cu}⁻¹ h⁻¹, respectively, the CuO/ZnO-OG catalyst is extremely active. Therefore, the CuO/ZnO-OG catalyst was chosen for further investigations.

In order to determine the reason for the different conversions of glycerol, N₂O chemisorption was carried out with both catalysts which were reduced in 4.95% H₂ in Ar at 330 °C (heating rate = 10 °C min⁻¹) for 60 min prior to N₂O chemisorption. The resulting copper surface areas, dispersions and mean copper particle diameters are listed in Table 2. The copper surface area of the CuO/ZnO-CP catalyst amounts to 16.8 m² g⁻¹, and

Table 1 Hydrogenolysis of glycerol over the CuO/ZnO-OG and CuO/ZnO-CP catalysts, both with a copper oxide content of 33 wt%

Catalyst	Conversion (%)	Selectivity(%)			
		Propylene glycol	Ethylene glycol	Acetol	Others ^b
CuO/ZnO-OG ^a	46	90	1	1	8
CuO/ZnO-CP ^a	17	87	0	1	12

^a Reaction conditions: 140 mL pure glycerol, 3 g catalyst, 5 MPa H₂, 200 °C, 7 h. ^b Unidentified side products.

Table 2 Comparison of the structural properties of the CuO/ZnO-OG and CuO/ZnO-CP catalysts determined by N₂O chemisorption

Catalyst	$S_{\text{Cu}}^a / \text{m}^2 \text{g}^{-1}$	$D^b / \%$	$d_{\text{Cu}}^c / \text{nm}$
CuO/ZnO-OG	30.1	16.8	6.3
CuO/ZnO-CP	16.7	9.1	12.1

^a Copper surface area. ^b Dispersion. ^c Mean copper particle size.

the mean copper particle diameter is 12.1 nm. Agrell *et al.*²⁴ prepared a CuO/ZnO catalyst by coprecipitation of an aqueous Zn(NO₃)₂ and Cu(NO₃)₂ solution and obtained a catalyst with a copper surface area of 21.5 m² g⁻¹. Taking into account the higher copper oxide loading of 39 wt% in the study of Agrell compared to 33 wt% of the CuO/ZnO-CP catalyst, the results are in good agreement. In comparison, the copper surface area of the CuO/ZnO-OG catalyst is twice as high, which indicates the reason for the improved activity of this catalyst compared to the CuO/ZnO-CP catalyst.

3.2 Recycling of the catalyst

The CuO/ZnO-OG catalyst was recovered and used in a second experiment under the same reaction conditions. However, a glycerol conversion of just 10% was achieved, although the high selectivity for propylene glycol was preserved (97%). In order to examine the reason for the loss of activity, the catalyst was recovered after the first experiment and analysed by XRD and N₂O chemisorption. The XRD pattern of the spent catalyst, along with the pattern of the fresh catalyst, is shown in Fig. 1.

The fresh CuO/ZnO-OG catalyst contained merely CuO and ZnO crystallites. After the hydrogenolysis of glycerol at 200 °C and at a hydrogen pressure of 5 MPa, the CuO phase was completely reduced to metallic copper. The crystallite sizes of the CuO, Cu and ZnO were calculated using the Scherrer equation. The resulting crystallite sizes, together with the copper surface areas and copper particle sizes obtained from N₂O chemisorption, are listed in Table 3. Before the reaction, the mean diameters of the CuO and ZnO crystallites were determined to be 15 and 10 nm, respectively. After the reaction, the mean crystallite diameters obtained from XRD of both the Cu and ZnO crystallites were calculated to be 40 nm. Therefore, a strong increase in the copper crystallite size during the reaction was observed, leading to a decrease in the active surface area and, thus, to a loss of activity. These results were confirmed by N₂O chemisorption as the copper surface area decreases during the reaction from 30.1 m² g⁻¹ to 5.3 m² g⁻¹. Moreover, a strong increase in the ZnO crystallite size is also observed. A loss of activity may occur as well because of the agglomeration of the ZnO crystallites, as glycerol may be dehydrated to acetol and glycidol at the ZnO surface.⁵ The loss of active copper surface area is also known for methanol synthesis. Muhler *et al.*²⁵ reported the growth of copper particles in a Cu/ZnO methanol catalyst with increasing time on stream.

To further investigate the deactivation of the CuO/ZnO-OG catalyst, TEM images of the catalyst were recorded before and after the reaction (Fig. 2). From the TEM images, a change in morphology is clearly observed. Before the catalyst was used in the hydrogenolysis of glycerol, almost spherical particles with

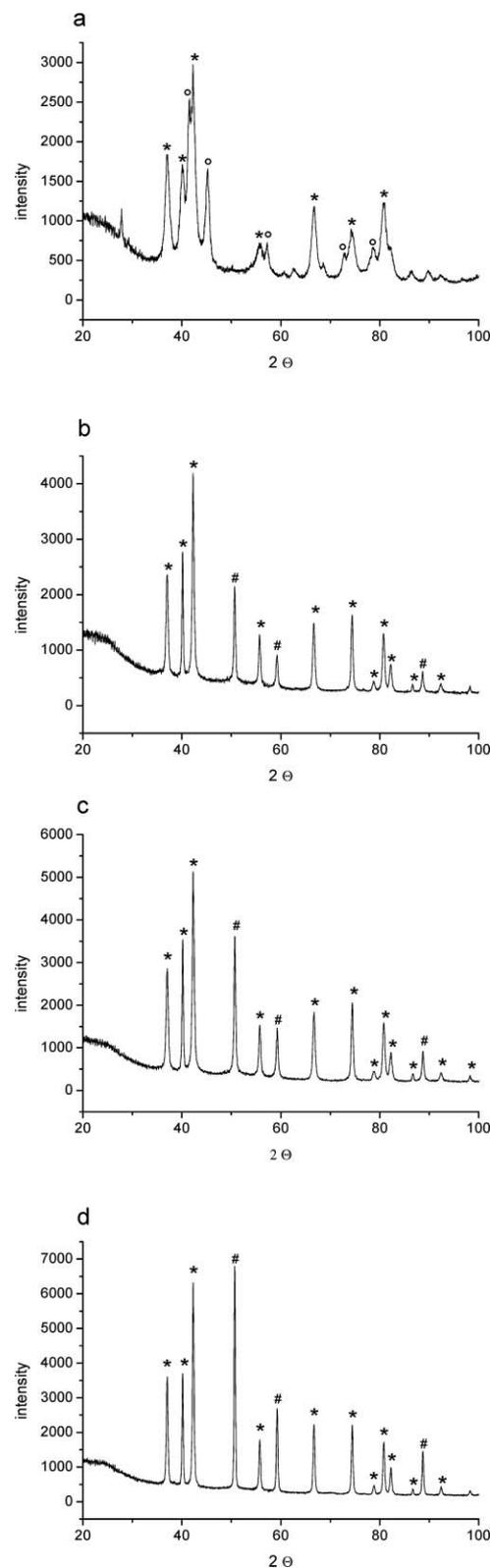


Fig. 1 XRD patterns of the CuO/ZnO-OG catalyst before (a) and after (b) use in the hydrogenolysis of pure glycerol or of glycerol with 1,2-butanediol (c) or water (d) as a solvent. Reaction conditions: 140 mL pure glycerol (b) or 140 mL 50 wt% glycerol in 1,2-butanediol (c) or water (d), 3 g catalyst, 5 MPa H₂, 200 °C, 7 h. * ZnO, ○ CuO, # Cu.

Table 3 Comparison of the structural properties of fresh and spent CuO/ZnO-OG catalysts

Catalyst	$d_{\text{CuO}}^d/\text{nm}$	$d_{\text{ZnO}}^d/\text{nm}$	$d_{\text{Cu}}^e/\text{nm}$	$S_{\text{Cu}}^e/\text{m}^2 \text{g}^{-1}$	$d_{\text{Cu}}^e/\text{nm}$
Fresh CuO/ZnO-OG	15	10	—	30.1	6.3
Spent Cu/ZnO OG ^a	—	40	40	5.3	38.2
Spent Cu/ZnO OG ^b	—	40	40	4.2	47.5
Spent Cu/ZnO OG ^c	—	40	80	2.7	75.6

^a Reaction conditions: 140 ml pure glycerol, 3 g catalyst, 5 MPa H₂, 200 °C, 7 h. ^b Reaction conditions: 140 ml 50 wt% glycerol in 1,2-butanediol, 3 g catalyst, 5 MPa H₂, 200 °C, 7 h. ^c Reaction conditions: 140 ml 50 wt% glycerol in water, 3 g catalyst, 5 MPa H₂, 200 °C, 7 h. ^d Mean CuO, Cu and ZnO crystallite sizes determined by XRD. ^e Copper surface area and mean copper particle size determined by N₂O chemisorption.

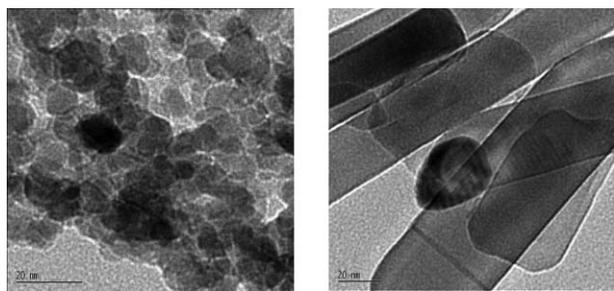


Fig. 2 TEM images of the CuO/ZnO-OG catalyst before (left) and after (right) use in the hydrogenolysis of glycerol. Reaction conditions: 140 ml pure glycerol, 3 g catalyst, 5 MPa H₂, 200 °C, 7 h.

a mean diameter of about 10 nm are visible, while after the reaction, the catalyst consists of rod-shaped particles with a considerably larger size.

3.4 The effect of the solvent

Montassier *et al.* proved that the size of copper particles in a Cu/C catalyst increased if the catalyst is stirred in water at elevated temperatures.¹⁵ As no water is loaded into the reactor at the beginning of the reaction, the deactivation of the CuO/ZnO-OG catalyst might be due to formation of water as an unavoidable by-product during the hydrogenolysis of glycerol. Because of this, the deactivation of the catalyst should occur much faster if the hydrogenolysis of glycerol is carried out with an aqueous glycerol solution.

Therefore, a 50 wt% aqueous solution of glycerol was loaded into the reactor. As a reference, the same experiment was repeated but now with a solution of glycerol in 1,2-butanediol. The results of these experiments are shown in Table 4. It is obvious that the conversion of glycerol is strongly affected by the choice of solvent. Compared to a conversion of glycerol of only 5% in an aqueous glycerol solution after 7 h, the use of 1,2-butanediol as a solvent leads to a higher conversion of 55%.

Table 4 Effect of the solvent on the conversion of glycerol and the selectivities towards propylene glycol, ethylene glycol and acetol of the CuO/ZnO-OG catalyst

Solvent	Conversion ^a (%)	Selectivity (%)			
		Propylene glycol	Ethylene glycol	Acetol	Others ^b
1,2-Butanediol	55	86	1	1	12
Water	5	87	9	2	2

^a Reaction conditions: 140 ml 50 wt% glycerol dissolved in 1,2-butanediol or water, 3 g catalyst, 5 MPa H₂, 200 °C, 7 h. ^b Unidentified side products.

In order to determine the reason for the poor conversion of an aqueous solution of glycerol compared to 1,2-butanediol, the catalysts were recovered after the reaction and characterised by XRD and N₂O chemisorption. The XRD patterns of the two recovered catalysts are shown in Fig. 1. From the XRD patterns, the CuO, Cu and ZnO crystallite sizes were calculated and are shown in Table 3, together with the copper surface areas determined after the reaction. Before the catalyst CuO/ZnO-OG was used in the hydrogenolysis of glycerol, the mean crystallite size of the CuO and ZnO crystallites was determined to be 15 and 10 nm, respectively (Table 3). Regarding the ZnO crystallite size, a strong increase ($d = 40$ nm) is observed, which is not affected by the choice of solvent (Table 3). However, the calculated size of the Cu crystallites after the reaction strongly depends on the solvent. In comparison to 1,2-butanediol as a solvent, the size of the Cu crystallites is, in the case of water, twice the size. This increase in the copper particle size can be confirmed by N₂O chemisorption as the copper surface is also influenced by the choice of solvent. The copper surface area strongly decreased in the case of water as a solvent, from 30.1 m² g⁻¹ before to 2.7 m² g⁻¹ after the reaction, while in the case of 1,2-butanediol the copper surface area diminished to 4.2 m² g⁻¹.

3.5 Reaction temperature

As well as the solvent, the reaction temperature might also play an important role in the deactivation process of the Cu/ZnO-OG catalyst. Thus, the hydrogenolysis of glycerol was performed in the temperature range between 190 and 225 °C. The effect of the reaction temperature on the conversion of glycerol and the selectivity for propylene glycol are shown in Fig. 3. While there was no significant influence of the reaction temperature on the selectivity for propylene glycol ($S = 84$ – 92%), the conversion of glycerol was strongly affected when raising the temperature. However, there is no consistent dependence of the conversion on the reaction temperature as would be expected according to Arrhenius behaviour: the conversion first strongly increases

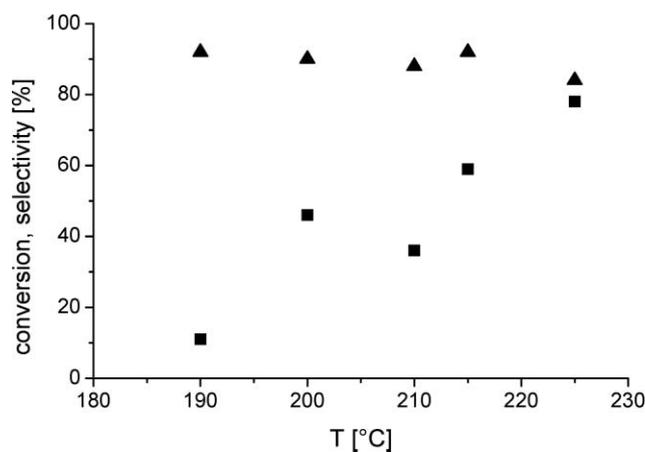


Fig. 3 Dependence of the conversion (▲) and the selectivity for propylene glycol (■) on the reaction temperature. Reaction conditions: 140 ml glycerol, 3 g CuO/ZnO-OG catalyst, 5 MPa H₂, 7 h.

with an increase in temperature from 190 to 200 °C, but then, if the temperature is further increased to 210 °C, the conversion decreases. Raising the temperature further to 215 °C, and finally, to 225 °C then gives the expected increase in conversion again. The reason for this relationship between the reaction temperature and the conversion during glycerol hydrogenolysis may be an interference between the acceleration of the reaction rate due to elevated temperatures and the stronger deactivation of the catalyst at higher reaction temperatures. Furthermore, an interplay between the temperature dependence of the adsorption constants determining the individual adsorption enthalpy of one or more reactants and the temperature dependence of the rate constant dictating the activation energy may cause the observed decrease in conversion with rising temperature. According to the copper surface areas determined by N₂O chemisorption for the CuO/ZnO-OG catalyst after being used in the hydrogenolysis of glycerol at different temperatures (Fig. 4), the temperature seems to influence the growth of the copper particles. It is expected that the decrease in the copper surface area correlates with the amount of water produced during the reaction. However, at a reaction temperature of 210 °C, the

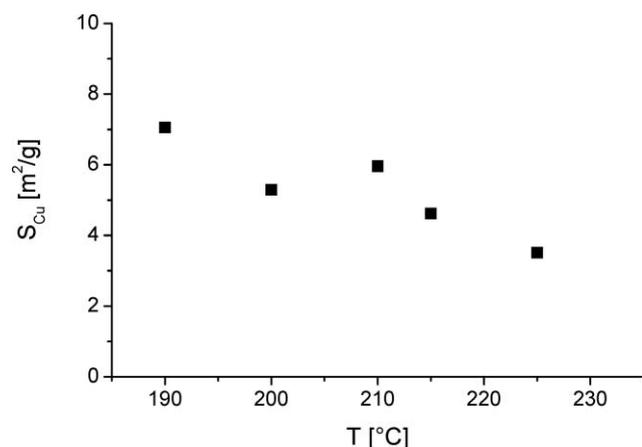


Fig. 4 Copper surface areas determined by N₂O chemisorption of the CuO/ZnO-OG catalyst after the reaction at temperatures between 190 and 225 °C. Reaction conditions: 140 ml glycerol, 3 g CuO/ZnO-OG catalyst, 5 MPa H₂, 7 h.

glycerol conversion, which proved to be reproducible with a standard deviation of $\pm 3\%$, is only 36% compared to 46% at 200 °C, suggesting that less water is formed at a reaction temperature of 210 °C. From that, an increase of the copper surface area can be assumed and Fig. 4 shows that this is indeed the case ($6.0 \text{ m}^2 \text{ g}^{-1}$ vs. $5.2 \text{ m}^2 \text{ g}^{-1}$). Therefore, it is worth mentioning that by an increase of reaction temperature from 200 to 210 °C, the conversion of glycerol decreased (Fig. 3) although the copper surface area increased (Fig. 4). Thus, the decrease in glycerol conversion between 200 to 210 °C cannot be attributed to a growth of copper particles. Keeping in mind that the product distribution remained unchanged during the course of glycerol hydrogenolysis between 190 and 225 °C (1,2-propanediol is always produced with high selectivity, Fig. 3), a change of the reaction mechanism should be ruled out, and the unusual behavior is likely to be due to a difference in the temperature dependence of the rate constant and the reactants' adsorption constants.

4. Conclusions

A CuO/ZnO catalyst prepared by an oxalate gel method was proven to be highly active in the hydrogenolysis of glycerol compared to a CuO/ZnO catalyst prepared by the standard coprecipitation method. The higher activity can be attributed to the copper surface area, which was as high as $30.1 \text{ m}^2 \text{ g}^{-1}$ in the case of the CuO/ZnO-OG catalyst, whereas the copper surface area of the CuO/ZnO-CP catalyst amounted to only $16.7 \text{ m}^2 \text{ g}^{-1}$. With both catalysts, a selectivity for propylene glycol of about 90% is achieved.

In the presence of water, the size of the copper crystallites of the CuO/ZnO catalyst increases tremendously, leading to a decrease in active surface area and, thus, to a loss of activity. Even if no water is loaded into the reactor, the water formed during the hydrogenolysis of glycerol causes the deactivation of the catalyst. Increasing the reaction temperature has no significant influence on the loss of active surface area and cannot, therefore, be the reason for the deactivation of the catalyst.

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References

- 1 A. Brandner, K. Lehnert, A. Bienholz, M. Lucas and P. Claus, *Top. Catal.*, 2009, **52**, 278–287.
- 2 E. Maris and R. Davis, *J. Catal.*, 2007, **249**, 328–337.
- 3 D. Lahr and B. Shanks, *J. Catal.*, 2005, **232**, 386–394.
- 4 I. Furikado, T. Miyazawa, S. Koso, A. Shima, K. Kunimori and K. Tomishige, *Green Chem.*, 2007, **9**, 582–588.
- 5 S. Wang and H. Liu, *Catal. Lett.*, 2007, **117**, 62–67.
- 6 M. Dasari, P. Kiatsimkul, W. Sutterlin and G. Suppes, *Appl. Catal., A*, 2005, **281**, 225–231.
- 7 Q. Liu, X. Guo, Y. Li and W. Shen, *J. Phys. Chem. C*, 2009, **113**, 3436–3441.
- 8 M. Balaraju, V. Rekha, P. S. Sai Prasad, B. L. A. Prabhavathi Devi, R. B. N. Prasad and N. Lingaiah, *Appl. Catal., A*, 2009, **354**, 82–87.
- 9 T. Miyazawa, S. Koso, K. Kunimori and K. Tomishige, *Appl. Catal., A*, 2007, **329**, 30–35.
- 10 T. Miyazawa, S. Koso, K. Kunimori and K. Tomishige, *Appl. Catal., A*, 2007, **318**, 244–251.

- 11 Y. Kusunoki, T. Miyazawa, K. Kunimori and K. Tomoshige, *Catal. Commun.*, 2005, **6**, 645–649.
- 12 L. Huang, Y. Zhu, H. Zheng, Y. Li and Z. Zheng, *J. Chem. Technol. Biotechnol.*, 2008, **83**, 1670–1675.
- 13 C. Chiu, A. Tekeci, W. Sutterlin, J. Ronco and G. Suppes, *AIChE J.*, 2008, **54**, 2456–2463.
- 14 M. Balaraju, V. Rekha, P. S. Sai Prasad, R. B. N. Prasad and N. Lingaiah, *Catal. Lett.*, 2008, **126**, 119–124.
- 15 C. Montassier, J. Dumas, P. Granger and J. Barbier, *Appl. Catal., A*, 1995, **121**, 231–244.
- 16 J. Chaminand, L. Djakovitch, P. Gallezot, P. Marion, C. Pinel and C. Rosier, *Green Chem.*, 2004, **6**, 359–361.
- 17 L. Meher, R. Gopinath, S. Naik and A. Dalai, *Ind. Eng. Chem. Res.*, 2009, **48**(4), 1840–1846.
- 18 C. Liang, Z. Ma, L. Ding and J. Qiu, *Catal. Lett.*, 2009, **130**, 169–176.
- 19 Z. Huang, F. Cui, H. Kang, J. Chen, X. Zhang and C. Xia, *Chem. Mater.*, 2008, **20**(15), 5090–5099.
- 20 M. Kurtz, n Bauer, C. Büscher, H. Wilmer, O. Hinrichsen, R. Becker, S. Rabe, K. Merz, M. Driess, R. Fischer and M. Muhler, *Catal. Lett.*, 2004, **92**, 49–52.
- 21 Y. Guo, W. Meyer-Zaika, M. Muhler, S. Vukojević and M. Epple, *Eur. J. Inorg. Chem.*, 2006, 4774–4781.
- 22 T. Shishido, Y. Yamamoto, H. Morioka, K. Takaki and K. Takehira, *Appl. Catal., A*, 2004, **263**, 249–253.
- 23 Q. Sun, Y.-L. Zhang, H.-Y. Chen, J.-F. Deng, D. Wu and S.-Y. Chen, *J. Catal.*, 1997, **167**, 92–105.
- 24 J. Agrell, M. Boutonnet, I. Melián-Cabrera and J. Fierro, *Appl. Catal., A*, 2003, **253**, 201–211.
- 25 M. C. Carroll, B. Skrotzki, M. Kurtz, M. Muhler and G. Eggeler, *Scr. Mater.*, 2003, **49**, 527–532.