

PAPER

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7, 5614Selective glycerol oxidation over ordered
mesoporous copper aluminum oxide catalysts†Stefan Schünemann, Ferdi Schüth and Harun Tüysüz *

Glycerol is a major by-product of the biodiesel production and is therefore produced in high quantities. While currently there are limited possible applications for this highly functionalized molecule, glycerol can be a cheap and abundant feedstock for value-added products that are accessible by selective oxidation. Usually, the selective oxidation of glycerol utilizes expensive noble metal catalysts, such as Au, Pt, and Pd. Here we report the selective oxidation of glycerol in basic media, using ordered mesoporous Cu–Al₂O₃ catalysts with various Cu loadings prepared by a facile soft-templating method. The materials were characterized in detail by nitrogen physisorption, vis-NIR spectroscopy, EDX, low- and wide-angle XRD, XPS, and TEM. Subsequently the reaction conditions for glycerol oxidation were optimized. The catalytic oxidation of glycerol yields C₃ products, such as glyceric acid and tartronic acid, and also C₂ and C₁ products, such as glycolic acid, oxalic acid, and formic acid. Moreover, the role of the solvent on the catalytic reaction was investigated, and the addition of various co-solvents to the aqueous reaction mixture was found to increase the initial reaction rate up to a factor of three. The trends of the initial reaction rates correlate well with the polarity of the water/co-solvent mixtures. The prepared Cu–Al₂O₃ catalysts are a more cost-efficient and environmentally viable alternative to the reported noble metal catalysts.

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Introduction

There have been many scientific and political efforts in the last decade to reduce the emission of greenhouse gases in order to slow down anthropological climate change and to preserve the progressively depleting fossil fuel reserves. In this context, biomass derived fuels that are used as additives to conventional fossil fuels have gained great importance.^{1–6} As a result, between 2008 and 2015 the worldwide production of biodiesel increased from 1.6 to 3.2 million m³ per year and this is predicted to further increase in the future.⁷ The raw materials for biodiesel are various vegetable oils derived *e.g.* from rapeseed, palm, and sunflowers. The biodiesel production from these feedstocks involves the homogeneous base catalyzed transesterification of triglyceride with methanol or ethanol to form fatty acid methyl esters or fatty acid ethyl esters, respectively.^{8–10} As an unavoidable side product of this

process, approximately 10 wt% of glycerol is produced.⁵ Despite the fact that glycerol – containing three hydroxyl groups – is a highly functionalized molecule, only a few commercial applications have been developed so far.¹

The large supply of glycerol from biodiesel production and the lack of utilization of this molecule, together with its high functionalization, offer profitable possibilities for upgrading reactions. In this context, selective oxidation reactions are of particular interest as this reaction opens pathways to produce a variety of value-added products.¹¹ Such products include glyceric, glycolic, tartronic, oxalic, and formic acids, which are used, for example, as pharmaceuticals, cosmetics, and intermediates in the chemical industry.¹¹ Also, the catalytic formation of formic acid from biomass recently has attracted attention for energy conversion related applications.^{12–14} Active catalysts for this reaction most often are composed of supported noble metal nanoparticles, such as Au,^{15–21} Pd,^{15–17,22,23} Pt,^{15–17,24–29} Ag,³⁰ and alloys^{17,31–33} thereof, which were frequently demonstrated to catalyze selective glycerol oxidation in neutral and basic media. Furthermore, noble metal/Cu alloys are also reported as active catalysts for the selective oxidation of glycerol.^{34–36} Despite the variety of possible noble metal catalysts, more abundant and cost-efficient catalysts are highly desirable. An attractive alternative to noble metals in selective oxidation reactions is copper, which was demonstrated to be active for the selective oxidation of various alcohols and polyols.^{37–41} However, there

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† Electronic supplementary information (ESI) available: Nitrogen physisorption isotherms and textural parameters of prepared catalysts; Cu 2p XPS spectrum of 5-Cu; glycerol conversions at varying temperatures, oxygen pressures and NaOH : glycerol molar ratios; glycerol conversion after adding additional NaOH during the reaction; selectivity–time profiles in water/ethanol mixtures; selectivities and carbon mass balances at approximate isoconversions; recyclability of the catalyst.; calculations of conversion, selectivity, carbon mass balance, and the initial reaction rate. See DOI: 10.1039/c7cy01451a



are only few reports on selective oxidation of glycerol in basic media with non-noble metal catalysts, such as with the toxic and carcinogenic cobalt,^{42–44} layered double hydroxide supported transition metals,^{45–47} or using hydrogen peroxide instead of molecular oxygen as an oxidizing agent.^{48,49}

Key factors for the fabrication of efficient supported catalysts are firstly a high dispersion of the active component on the support material; secondly, high surface areas of the support; and thirdly, large porosity to allow efficient diffusion of reactants to the active centers. A particularly intriguing support for Cu based catalysts is γ -Al₂O₃, in which Cu cations are atomically dispersed by occupying the tetrahedral and octahedral sites of Al₂O₃.⁵⁰ In this context, ordered mesoporous Cu- γ -Al₂O₃ is of special interest for catalytic applications due to the fine dispersion of copper in the γ -Al₂O₃ matrix and its high surface area.⁵¹

High concentrations of glycerol typically lead to highly viscous liquids, and therefore liquid phase catalytic reactions involving glycerol are usually carried out with relatively low concentrations between 0.05 M and 0.3 M in order to avoid mass transport limitations in the solvent. The solvent of choice is typically water. However, various studies indicate that the solvent has a strong influence on the catalytic activity in various heterogeneously catalyzed alcohol oxidations^{39,52,53} and other reactions^{54–58} with vastly altered activities and selectivities. Solvents can influence the activity and selectivity of a reaction, for example, by changing the solvent shell around the reactants to allow facilitated catalyst/solvent interactions,⁵⁸ by varying the diffusion and adsorption properties of reactants within the catalyst pores^{39,52,53,59} by facilitating cation solvation, resulting in less competition between the solvent and reactant for the base,⁶⁰ and solvent induced changes of the pK_a.^{61,62}

We synthesized ordered mesoporous Cu-Al₂O₃ catalysts for the selective oxidation of glycerol with Cu loadings between 0 and 20 wt% using a facile soft-templating approach. After detailed characterization comprising N₂ physisorption, small-angle X-ray diffraction (XRD), wide-angle XRD, energy dispersive X-ray (EDX) spectroscopy, transmission electron microscopy (TEM), and vis-NIR spectroscopy, the catalysts were used for the selective oxidation of glycerol in the aqueous phase. The reaction conditions were optimized and various co-solvents (methanol, ethanol, 1-propanol, and *tert*-butanol) were added to the aqueous reaction medium with volumetric concentrations of 5, 20, 35, and 50%. The catalytic performance of the material was significantly enhanced by the addition of a co-solvent due to the reduced polarity which facilitates the interaction between the polar glycerol molecule and the catalyst's surface, with the exception of methanol.

Experimental

Catalyst preparation

All chemicals and reagents were purchased from Sigma-Aldrich and were used without further purification. The Cu-

Al₂O₃ catalysts were synthesized by a modified protocol from the literature.⁶³ Briefly, 4.5 g of Pluronic P123 and 7.5 mL of a 65% HNO₃ were added to 100 mL of ethanol. After stirring for 4 h, the appropriate quantities of aluminum isopropoxide and copper(II) nitrate were added under vigorous stirring. The total amount of the metal was kept constant at 10 mmol. The mixture was stirred at room temperature until a clear solution was obtained. Subsequently, the solution was placed in an oven at 60 °C to undergo slow solvent evaporation for 24 h. Calcination was performed by slowly increasing the temperature (1 °C min⁻¹ ramping rate) to 400 °C and holding this temperature for 4 h, following a ramping rate of 10 °C min⁻¹ to 900 °C and holding this temperature for 1 h. The samples were labeled with the general form x-Cu, with x being the Cu content in wt%. For comparison, a surfactant-free sample containing 5 wt% Cu was prepared by using the same method without using the soft-template P123 (named 5-Cu-sf for surfactant-free). Additionally, a commercial Al₂O₃ material (Aluminum oxide C from Degussa) was impregnated with an aqueous Cu(NO₃)₂ solution to give a copper content of 5 wt% (5-Cu-Comm). After drying at 60 °C, the sample was calcined under the same conditions as the other samples.

Catalyst characterization

Nitrogen physisorption isotherms were measured at liquid nitrogen temperature with a NOVA 3200e. All samples were degassed at 300 °C for 19 h prior to the measurement. The surface area was determined using the multi-point BET method at relative pressures from 0.06 to 0.2. The pore size distribution was determined with the BJH-algorithm from the desorption isotherm. The total pore volume was determined at a relative pressure of 0.97. TEM-micrographs were recorded with a Hitachi H-7100 electron microscope with an acceleration voltage of 100 kV. SEM images were taken with a Hitachi S-5500 under the following conditions: accelerating voltage: 30 kV, working distance: 100 μ m, and emission current: 11 000 nA. EDX data were taken with a Thermo Scientific NORAN System 7 X-ray Microanalysis System with an UltraDry EDS detector. Wide-angle and small-angle XRD patterns collected at room temperature were recorded with a STOE θ/θ diffractometer in Bragg-Brentano geometry (Cu K $_{\alpha 1/2}$ radiation). The measured patterns were evaluated qualitatively by comparison with entries from the ICDD-PDF-2 powder pattern database. DR vis-NIR spectra of powdered samples were recorded from 1800 nm to 500 nm with a Varian Cary 5G UV-vis-NIR spectrophotometer equipped with a Harrick praying-mantis sample holder. MgO NPs from Sigma Aldrich were used to record the baseline.

Glycerol oxidation

Glycerol oxidation was carried out in a sealed stainless-steel autoclave under typical reaction conditions reported in the literature.⁶⁴ In a typical experiment, the glass inlay of the autoclave was loaded with 15 mL of a 0.05 M aqueous glycerol solution with a NaOH concentration of 0.2 M, 30 mg of



Small angle XRD further confirms a loss of ordering in the pore structure when the Cu content is increased above 10 wt% (Fig. 1a). The incorporation of Cu into the Al_2O_3 matrix also influences the crystallinity of the catalysts.⁵¹ The wide angle XRD pattern of the copper free 0-Cu shows very broad reflections at positions that can be assigned to the γ -phase of Al_2O_3 (Fig. 1b). As the Cu content increases, the reflections become narrower, which indicates larger primary crystallites. Also, at a Cu content of 20 wt%, the positions of the reflections shift to lower angles and thus become more related to the CuAl_2O_4 spinel structure (Fig. 1b). As a result of the absence of a structure directing agent during the synthesis, 5-Cu-sf consists of much larger primary crystallites compared to 5-Cu, indicated by sharper reflections in the XRD patterns (Fig. 1b). Furthermore, the XRD patterns do not show additional reflections from Cu species like CuO, even for very high Cu loadings of 20 wt%.

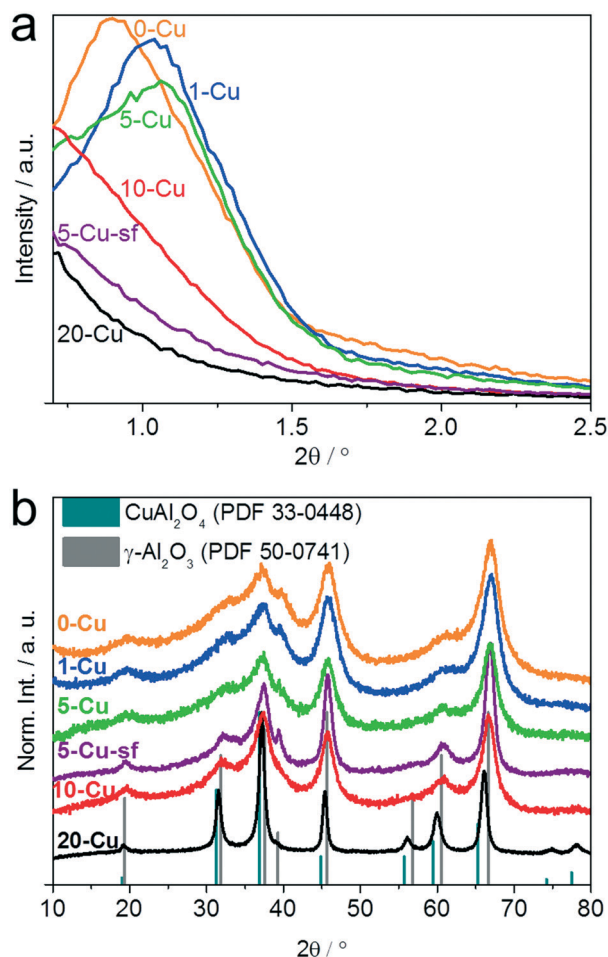


Fig. 1 Small angle (a) and wide angle (b) XRD patterns of copper aluminum oxide with various copper amounts – 0-Cu, 1-Cu, 5-Cu, 5-Cu-sf, 10-Cu, and 20-Cu.

The ordered pore structure and fine Cu dispersion through the structure were further studied by transmission electron microscopy (Fig. 2a) and EDX maps of 5-Cu (Fig. 2b–e). The micrograph in Fig. 2a shows a well-ordered and parallel aligned tubular mesopore structure, which is typical for the hexagonally ordered mesoporous materials like SBA-15. The EDX maps of oxygen (Fig. 2c), aluminum (Fig. 2d), and copper (Fig. 2e) of the particle shown in Fig. 2b show that copper is uniformly dispersed throughout the particle. Conclusively, the varied lattice parameters upon Cu incorporation (as depicted by the shifted XRD reflection peaks), the absence of XRD signals from other Cu species, the electron microscopy images, and the EDX maps strongly suggest that Cu is fully incorporated into the structure of Al_2O_3 .

The structure of $\gamma\text{-Al}_2\text{O}_3$ is under debate in the literature; however, most studies suggest a cubic defect spinel structure comprising a densely packed array of O^{2-} anions in which Al^{3+} randomly occupies some of the octahedral (O_h) and tetrahedral (T_d) sites.^{66–68} Cu^{2+} cations can occupy the remaining voids in the O_h and T_d sites of the closely packed O^{2-} array.

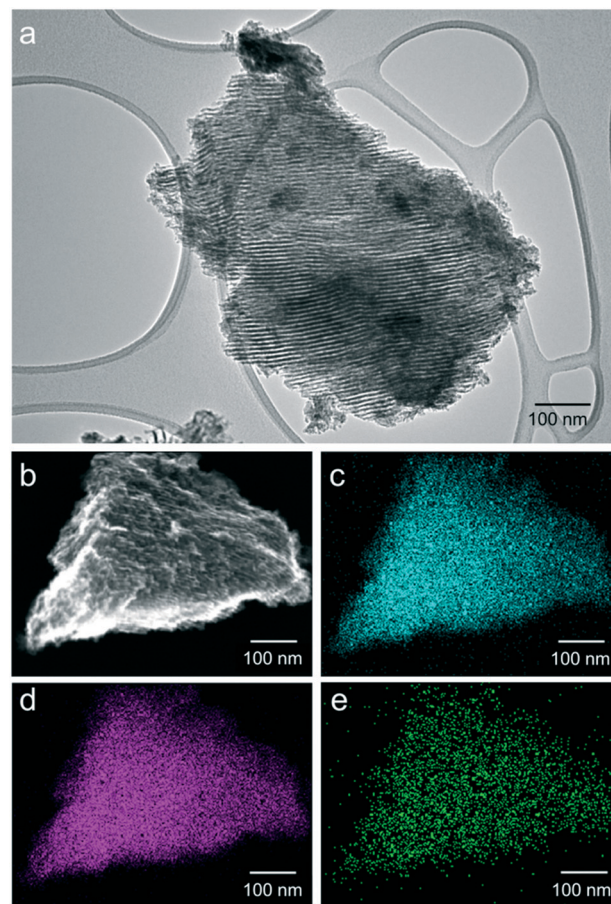


Fig. 2 Transmission electron micrograph of 5-Cu (a). Scanning electron microscopy image (b) and element mapping of oxygen (c), aluminum (d), and copper (e) of 5-Cu.

The possibility for Cu^{2+} to occupy the void sites in the O^{2-} lattice results in the high dispersion of Cu^{2+} within $\gamma\text{-Al}_2\text{O}_3$. The d–d transition energies of Cu^{2+} with a d^9 electron configuration are different for octahedrally and tetrahedrally coordinated Cu^{2+} cations and can be qualitatively probed by vis-NIR spectroscopy.⁶⁶ Octahedrally coordinated Cu^{2+} absorbs at approximately 720 nm, whereas tetrahedrally coordinated Cu^{2+} absorbs photons with wavelengths of approximately 1500 nm.⁶⁶ The Kubelka–Munk transformation of the diffuse reflectance vis-NIR spectrum for 0-Cu does not show any peaks (Fig. 3). At a very low Cu content of 1 wt%, only the minor peak at the wavelength of 720 nm is observed. The samples 5-Cu, 5-Cu-sf, 10-Cu, and 20-Cu show pronounced absorption bands at approximately 720 nm, which can be assigned to d–d transitions of octahedrally coordinated Cu^{2+} cations. In addition to that, 20-Cu and, to a lesser extent, 10-Cu also show pronounced absorption bands at approximately 1500 nm, which belong to d–d transitions of tetrahedrally coordinated Cu^{2+} cations. Thus, the vis-NIR spectra suggest that at Cu contents exceeding 10 wt%, Cu^{2+} begins to occupy tetrahedral sites, which are commonly considered to be less active for many redox reactions.^{50,66,69}

Additionally, XPS measurements of 5-Cu show pronounced satellite peaks of the Cu $2p_{3/2}$ and $2p_{1/2}$ signals at binding



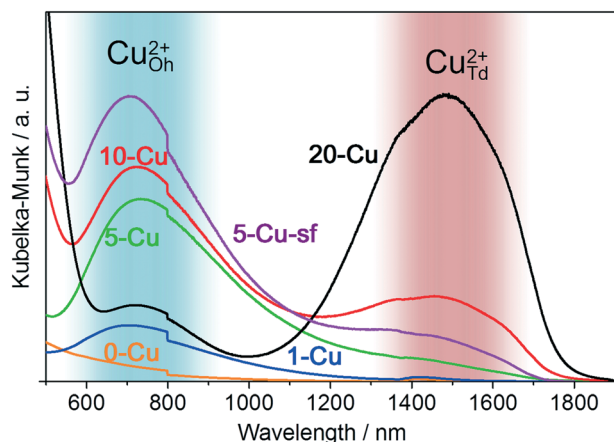


Fig. 3 Kubelka-Munk transformation of the diffuse reflectance vis-NIR spectra of 0-Cu, 1-Cu, 5-Cu, 5-Cu-sf, 10-Cu, and 20-Cu.

energies of 943 eV and 963 eV, respectively, which indicate the presence of Cu^{2+} in the sample (Fig. S3†). Since all catalysts were prepared without a reduction step, no metallic Cu was observed from XPS measurements in the samples. Conclusively, the physical characterization of the prepared catalysts reveals that the incorporation of Cu into the Al_2O_3 matrix has a detrimental effect on important physical properties of a solid catalyst, such as the surface area and pore size distribution. Additionally, the vis-NIR spectra show that at Cu contents exceeding 10 wt%, Cu begins to occupy the tetrahedral voids, which are considered to be less catalytically active sites for redox reactions. The results therefore suggest the existence of an optimal Cu content between 5 and 10 wt%.

Catalytic activity toward selective glycerol oxidation

After the characterization of the materials, the first catalytic experiments were performed under conditions typical for

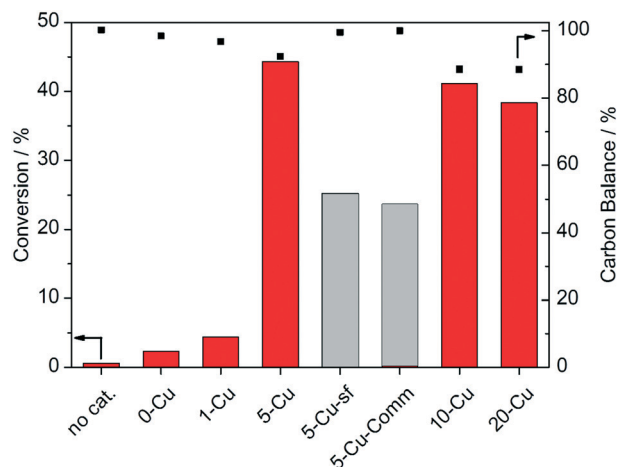


Fig. 4 Glycerol conversions and carbon balances of the prepared catalysts with various copper amounts (wt%). Reaction conditions: 30 mg of catalyst, 15 mL of 0.05 M aq. glycerol solution, 4:1 NaOH: glycerol, 90 °C, 10 bar oxygen, 3 h.

glycerol oxidation, namely with 30 mg of the prepared catalysts in 15 mL of a 0.05 M glycerol solution in 0.2 M NaOH at 90 °C and 10 bar oxygen pressure for 3 h (Fig. 4). All reported results from catalytic experiments are mean values from repeated measurements. The deviations between individual measurements were below 5% in each case. Without a catalyst, no considerable conversion of glycerol was observed after 3 h. However, recently it was reported that sodium hydroxide itself can act as a catalyst for the selective oxidation of glycerol.⁷⁰ Thus, the catalytic reaction without the presence of a heterogeneous catalyst was performed for 16 h as well, which resulted in a minor glycerol conversion of 3%, which is well within the error range of the HPLC analysis. 0-Cu and 1-Cu only show very low conversions of 2 and 4%, respectively. When the Cu content is further increased to 5 wt%, the glycerol conversion drastically increases to 44%. Further increasing the Cu content to 10 and 20 wt%, respectively, leads to decreasing catalytic activities. This can be attributed to both the incorporation of Cu^{2+} into the catalytically less active tetrahedrally coordinated sites of Al_2O_3 , as shown by the vis-NIR spectra (Fig. 2), and the reduced surface areas and the absence of an ordered pore structure in 10-Cu and 20-Cu.

The glycerol conversion of 5-Cu-sf, which was synthesized without P123 as a structure directing agent, and that of 5-Cu-Comm, which was synthesized from a commercial Al_2O_3 source, are two times lower than that of 5-Cu, which demonstrates the superior catalytic properties of the ordered mesoporous structure. The lower activities of these non-ordered samples may result from the lower BET surface areas of 5-Cu-sf (30 m² g⁻¹) and 5-Cu-Comm (80 m² g⁻¹) compared to 5-Cu (145 m² g⁻¹) and the absence of mesoporosity that may cause diffusion and mass transportation limitations in these materials. In summary, the observed trends of the catalytic activity seem to be affected by mainly three factors which are the surface area, the total Cu^{2+} concentration and the ratio between tetrahedrally and octahedrally coordinated Cu^{2+} . These initial catalytic experiments confirm the superior catalytic activity of 5-Cu as a result of the beneficial coordination of Cu^{2+} into the octahedrally coordinated sites and its superior textural properties indicated by the high surface area. Therefore, all further experiments were performed with the 5-Cu catalyst.

As a next step, different reaction conditions were screened to optimize the reaction conditions. Fig. S4a† shows the glycerol conversion after 3 h at different temperatures. As expected, higher temperatures lead to increased reaction rates, which caused a steady increase in the glycerol conversion from 10 to 44% as the reaction temperature is increased from 60 to 90 °C (Fig. S4a†). The influence of oxygen pressure on the glycerol conversion was examined to exclude operation conditions in which the oxygen concentration in the liquid phase, or oxygen mass transfer, could limit the glycerol conversion. Glycerol oxidation experiments with 5-Cu were performed at different oxygen pressures up to 15 bar and no change in conversion above 10 bar was observed (Fig. S4b†), which shows that, at oxygen pressures above 10 bar, the



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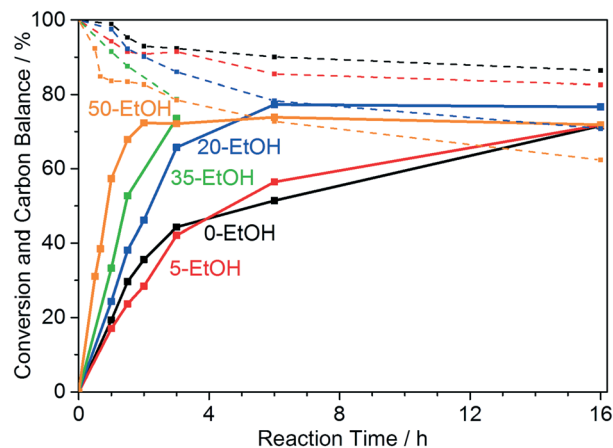


Fig. 7 Glycerol conversions (solid lines) and carbon balances (dotted lines) of 5-Cu in water (0-EtOH), 5 vol% EtOH (5-EtOH), 20 vol% EtOH (20-EtOH), and 50 vol% EtOH (50-EtOH). Reaction conditions: 30 mg catalyst, 15 mL 0.05 M glycerol solution, 4 : 1 NaOH : glycerol, 90 °C, 10 bar oxygen.

mixture, and consequently to a reduced activity of the catalyst. Measurements show that the pH of 50-EtOH dropped from the initial value of 12.3 to 9.3 and 8.9 after a reaction of time of 3 and 16 h, respectively. As mentioned before (Fig. S4c†), low pH values mitigate the catalytic activity.

Glycerol is produced in large scale from bio oil transesterification with ethanol or methanol.⁸⁻¹⁰ Consequently, the crude glycerol stream contains large amounts of either methanol or ethanol. Thus, the beneficial effect of EtOH as a co-solvent is the most relevant and interesting observation and was studied in more detail in the following.

The selectivity profiles of the reaction performed in water (Fig. 5) and that of the reactions performed in various water/ethanol mixtures (Fig. 8) show very similar trends. In the initial phase of the reaction, until a conversion of approximately 36% is reached, the selectivities towards glyceric, glycolic, tartronic, and formic acid increase for each water/ethanol mixture (Fig. 8). At this point, the selectivities at iso-conversions of 36% towards all observed reaction products are almost identical in each water/ethanol mixture (Table S2†). From this point, until the final conversion of approximately 75% is reached, the selectivities towards higher oxidized C₂ and C₁ products (formic and oxalic acid) increase at the expense of glyceric and glycolic acid, the selectivities of which decrease during this phase of the reaction. After the final conversion of 75% is reached, the selectivities of the oxidation products (with the exception of formic acid) remain constant and these products do not undergo further oxidation. Solely the selectivity towards formic acid decreases, which indicates that formic acid undergoes further oxidation

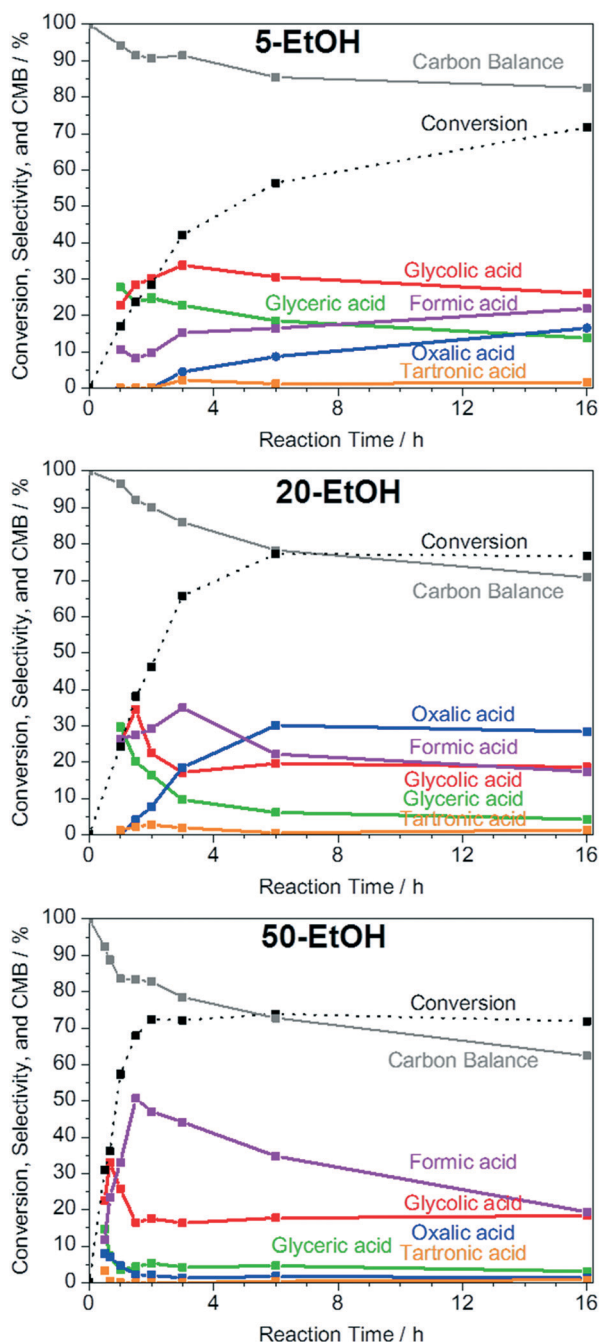


Fig. 8 Selectivity over time for 0-EtOH, 5-EtOH, 20-EtOH, and 50-EtOH as indicated in the figures. Reaction conditions: 30 mg 5-Cu, 15 mL 0.05 M aq. glycerol solution, 4 : 1 NaOH : glycerol, 90 °C, 10 bar oxygen, 750 rpm stirring speed.

to CO₂, which leads to a significant drop of the carbon mass balance. CO₂ forms carbonate species in the basic reaction medium, which cannot be detected *via* HPLC. Furthermore, it should be noted that, at comparable conversions (below the equilibrium conversion), the carbon mass balances in each water/EtOH mixture are almost identical to the carbon mass balance in water (Fig. 7, Table S2†), which rules out consecutive reactions with the glycerol oxidation products and EtOH.

The highest selectivities are observed at a conversion of approximately 35% in each water/ethanol mixture. Table S2† summarizes the selectivities in each water/ethanol mixture which are almost identical in each case. In 50-ethanol, a lower selectivity towards glyceric acid is observed. This can be explained by the short reaction time (40 minutes), which leads to a significant effect of the initial heat-up phase of 10 minutes on the product selectivities. Thus, it is reasonable to assume that the co-solvent does not influence the reaction mechanism itself, but rather increases the reaction kinetics. The same trend is also observed for the other water/co-solvent mixtures studied (Fig. S10†).

Post-reaction characterization of the spent catalyst was carried out by XRD analysis after a reaction time of 3 h in all 50 vol% water/co-solvent mixtures. The X-ray patterns show no significant change of the catalyst's crystal structure in each case. Furthermore, the Cu content of the spent catalyst after 3 h of glycerol oxidation in 50 vol% ethanol of 5.2% is identical to the initial Cu concentration, which indicates that the solvent mixture does not influence the catalyst's structure, as it was also observed for the reaction performed in water (Fig. S7†).

Conclusions

In conclusion, we prepared ordered mesoporous Cu-Al₂O₃ catalysts with various Cu loadings *via* a facile soft-templating method and employed them for the liquid phase oxidation of glycerol in basic media. The catalyst is a cost efficient and environmentally more viable alternative to the reported glycerol oxidation catalysts based on noble metals. Comparison between the templated Cu-Al₂O₃ and its non-templated counterpart shows the superior catalytic activity of the templated material in glycerol oxidation. The oxidation of glycerol yields C₃ products, such as glyceric acid and tartronic acid, and also C₂ and C₁ products, such as glycolic acid, oxalic acid, and formic acid. The addition of ethanol, 1-propanol, and *tert*-butanol as co-solvents results in strongly improved reaction kinetics. The initial reaction rate can be increased threefold from 4.8 mmol g⁻¹ h⁻¹ in water to 14.2 mmol g⁻¹ h⁻¹ when a mixture of 50 vol% ethanol in water is used as solvent. The observed initial reaction rates in the water/co-solvent mixtures correlate well with the solvent polarity determined from the solvatochromic shift of the dye betaine 30 (*E*_T(30)). The results strongly suggest that the reduced solvent polarity by the addition of alcohols to the aqueous reaction solution is the reason for the increased catalytic activities. However, further investigations are required and will be conducted by our group in order to shed light on the role of the solvent on the catalytic performance for glycerol oxidation.

Conflicts of interest

There are no conflicts to declare.

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