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The kinetics of glycerol hydrodeoxygenation to 1,2-propanediol over Cu/ZrO$_2$ in the aqueous phase

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Graphical abstract
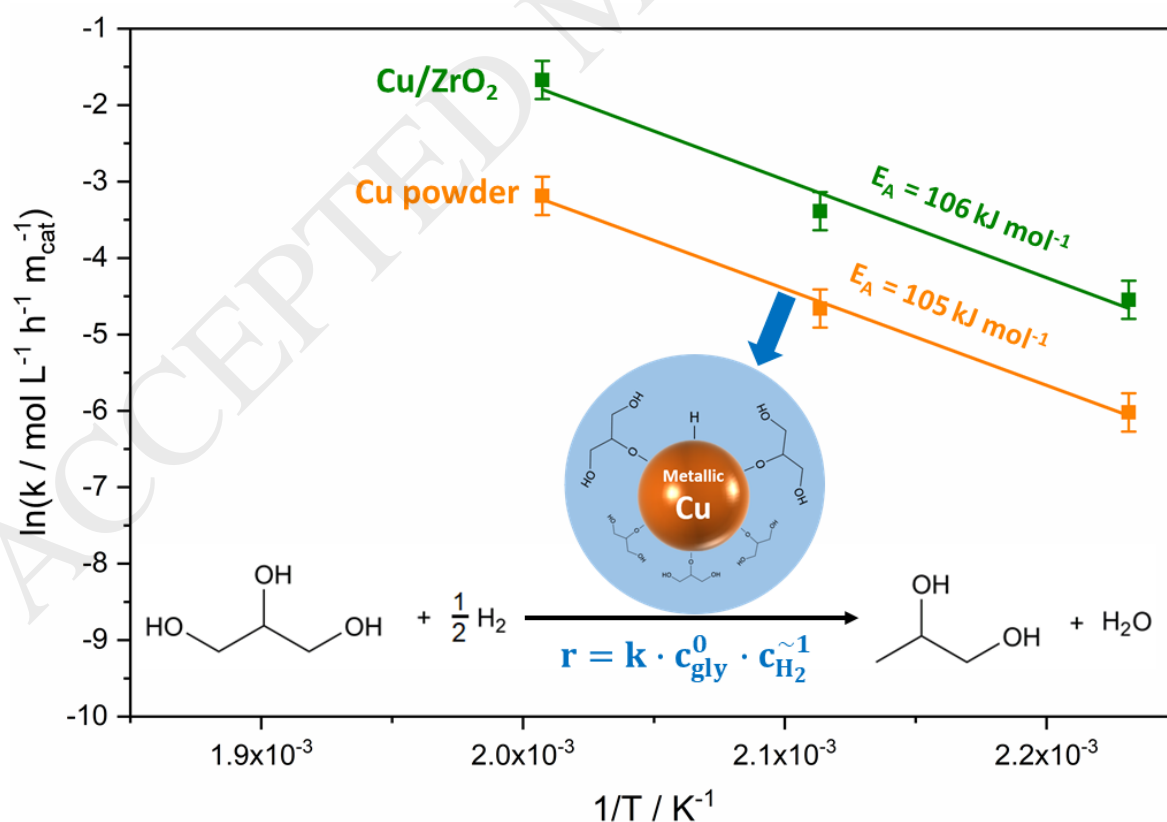
Highlights

- The kinetics of glycerol hydrodeoxygenation to 1,2-propanediol over Cu/ZrO_2 has been systematically studied.
- The kinetic study yielded a zero-order dependence on glycerol concentration and a first-order dependence on H_2 concentration
- H_2 removes adsorbed atomic oxygen originating from water dissociation
- The similar apparent activation energies for the hydrodeoxygenation over Cu/ZrO_2 and Cu powder further identify the active sites as fully adsorbate-covered metallic Cu.

Abstract

The kinetics of glycerol hydrodeoxygenation to 1,2-propanediol via the selective cleavage of the primary C-O bond was systematically studied in the aqueous phase over a co-precipitated Cu/ZrO_2 catalyst. Unsupported pure metallic Cu was used as reference catalyst. Batch experiments were performed in an autoclave by varying the reaction temperature (175 – 225 °C), H_2 partial pressure (25 – 35 bar) and initial glycerol concentration (2 – 8 wt%). The Cu/ZrO_2 catalyst was found to be highly selective to 1,2-propanediol (up to 95%), and ethylene glycol was obtained as major by-product from parallel C–C bond hydrogenolysis. The apparent activation energies amounting to 106 and 105 kJ mol^{-1} for Cu/ZrO_2 and pure metallic Cu, respectively, of the hydrodeoxygenation pathway provide further evidence for metallic Cu acting as the active site. Kinetic analysis of the rate of glycerol consumption yielded a zero-order dependence on the concentration of glycerol suggesting an essentially almost full coverage of adsorbed glycerol as most strongly bound organic adsorbate. In contrast, a first-order dependence on hydrogen concentration was observed. Hydrogen is assumed to be not only required for the fast hydrogenation of the intermediate acetol, but also for the removal of adsorbed atomic oxygen originating from water dissociation to create empty sites for dissociative glycerol adsorption. Thus, the active Cu sites are assumed to be fully adsorbate-covered under reaction conditions.

Keywords: hydrogenolysis; ethylene glycol; metallic copper; kinetic study

1. Introduction

In recent years increasing bio-diesel production resulted in an excess production of glycerol, which is the main by-product of this process.[1-3] The further utilization of biomass-based aqueous glycerol solutions to value-added products such as ethers,[4,5] esters,[6-8] propanediols[9-11] and acrolein[12-14] is of great interest to increase the economic efficiency and environmental sustainability of bio-refineries. A promising utilization route is the selective hydrodeoxygenation (HDO) of glycerol to 1,2-propanediol (1,2 PDO). HDO requires the selective cleavage of a terminal C-O bond while preserving C-C bonds, whereas hydrogenolysis refers in particular to the cleavage of C-C bonds. Most previous studies mainly focused on developing suitable HDO catalysts such as supported noble (e.g., Pt, Ru)[15-17] and less active, but selective non-noble (e.g., Cu, Ni, Co)[18-20] metals and characterising their relevant properties such as acidity, surface areas and metal dispersion.[21-23] Among these two classes of catalysts, Cu-based catalysts were found to be optimum, combining high selectivity to 1,2-PDO and moderate activity.[24-26] Owing to the mechanistic complexity of HDO, the number of studies focussing on reaction kinetics is rather low.

A kinetic analysis of glycerol HDO over Cu:Zn:Cr:Zr mixed metal oxide catalysts was conducted by Sharma et al.[27] using high initial glycerol concentrations up to 100%. The addition of Zn and Zr to the catalyst matrix significantly increased glycerol conversion and the selectivity to 1,2-PDO, which was ascribed to enhanced bifunctionality. Assuming a Langmuir-Hinshelwood-Hougen-Watson reaction mechanism following the dehydration-hydrogenation pathway, pseudo-first order kinetics for glycerol consumption and an activation energy of 132 kJ mol^{-1} were derived for the HDO route.

Vasiliadou et al.[28,29] studied the reaction kinetics of glycerol HDO over a 18 wt% Cu/SiO$_2$ catalyst. Two parallel routes leading to the formation of 1,2-PDO (95% selectivity) and 1,3-PDO (main by-product) were considered, and the kinetic parameters were derived assuming a power-law kinetic model. A reaction order of 0.17 was found for the overall glycerol consumption, and a reaction order of 1.06 was derived considering the H$_2$ concentration in the liquid phase. The activation energies for the 1,2-PDO and 1,3-PDO routes were found to be 94.3 and 135.3 kJ mol^{-1}, respectively. However, this work was performed using 1-butanol as solvent. The consideration of possible solvent effects is an important factor for liquid-phase reactions, and water is usually preferred to any organic solvents. Bienholz et al.[30] reported that glycerol conversion increased from 5% to 55% over a Cu/ZnO catalyst when water was replaced by 1,2-butanediol as solvent. N$_2$O reactive frontal chromatography measurements using the catalyst before and after reaction revealed that the use of 1,2-butanediol led to a lower decrease of the Cu surface area due to inhibited growth of the Cu particles. Wang et

al.[31] studied solvent effects with a Cu/ZnO catalyst using water, methanol and ethanol. It was found that solvents with low surface tension such as methanol and ethanol tend to inhibit the agglomeration of Cu particles, thus resulting in higher degrees of Cu dispersion and higher glycerol conversion, while highly polar solvents such as water tend to increase the product selectivity to 1,2-PDO.

In our previous study, HDO of glycerol over Cu/ZrO$_2$ in the aqueous phase was found to proceed via a two-step dehydration-hydrogenation reaction pathway, yielding 1,2-PDO as main product with a high selectivity of 95% at 31% conversion under moderate reaction conditions (200 °C, 25 bar H$_2$, 8 h reaction time).[32] A linear dependence of glycerol conversion on the specific Cu surface area was observed. Thus, metallic Cu was identified as the active site for both dehydration and hydrogenation, whereas the acidic sites of the ZrO$_2$ support had no detectable effect on the catalytic activity under the applied aqueous reaction conditions.

The aim of the present work is to investigate glycerol HDO kinetics under aqueous conditions in the presence of an active, highly selective and rather stable Cu/ZrO$_2$ catalyst. In contrast to other kinetic studies claiming acid sites of the support to catalyse dehydration followed by hydrogenation on metallic sites, here a kinetic study over Cu-based catalysts is reported, which provides no evidence for bifunctionality. The reaction kinetics of glycerol HDO was first studied over Cu/ZrO$_2$ with 18 wt% CuO nominal loading by varying the reaction temperature (175 – 225 °C), H$_2$ partial pressure (25 - 35 bar) as well as the initial glycerol concentration (2 – 8 wt%). Unsupported pure metallic Cu, derived from the reduction of commercial CuO nanopowder, was used as reference catalyst in comparison to the Cu/ZrO$_2$ catalyst to prove the dominant role of metallic Cu in the HDO of glycerol kinetically.

2. Experimental

2.1. Materials

The Cu/ZrO$_2$ catalyst was prepared using copper nitrate (Cu(NO$_3$)$_2$ · 3 H$_2$O, Sigma Aldrich, 99.999%), zirconium oxynitrate (ZrO(NO$_3$)$_2$ · 3 H$_2$O, Sigma Aldrich, 99.0%) and sodium hydroxide (NaOH, VWR Chemicals, 98.5-100.5%). Glycerol (VWR Chemicals, 99.5%), 1,2-propenediol (Fluka, 99.5%), ethylene glycol (Alfa Aesar, 99%), hydroxyacetone (Alfa Aesar, 95%) and methanol (Fischer Chemicals, 99.8%) were used for experiments and GC calibration. CuO powder (Sigma Aldrich, < 50 nm) was used as reference catalyst precursor.

2.2. Catalyst preparation

The 18 wt% CuO/ZrO_2 precursor was prepared by co-precipitation at room temperature.[32] Copper nitrate and zirconium oxynitrate were dissolved in 100 mL deionized water (HPLC purity). 25 wt% aqueous solution of sodium hydroxide was used as precipitating agent. The pH value of the solution was maintained constant at 10.5 during precipitation in an autotitrator. After precipitation the suspension was aged for 15 min at room temperature under continuously stirring. The obtained precipitate was filtered and washed several times with deionized water until the filtrate was free of nitrate. After drying at 105 °C overnight, the precursor was calcined at 490 °C for 3 h in synthetic air (20% O_2/N_2) and ground to particle sizes < 25 μm.

2.3. Kinetic experiments

The kinetic experiments were carried out in a Parr 5050 stainless-steel autoclave reactor (100 mL) equipped with temperature controller, mechanical stirrer and sampling tube for taking liquid products. Prior to each experiment, CuO/ZrO_2 and CuO nanopowder were pre-reduced in the reactor in the absence of the aqueous glycerol solution. For each reaction 400 mg of CuO/ZrO_2 or a defined amount of CuO was loaded in the reactor. Subsequently, the reactor was pressurized and purged several times with H_2 (99.999%) to remove ambient air. The pre-reduction was carried out at 200 °C and 20 bar H_2 pressure for 10 h to reduce CuO/ZrO_2 and CuO powder to metallic Cu. After cooling and depressurization, 20 mL of 4 wt% aqueous glycerol solution was dosed into the autoclave through the sampling tube without opening the reactor to minimize the exposure of the reduced catalyst to ambient air. After flushing the reactor several times with H_2 again, the reactor was pressurized with H_2. For each temperature variation experiment the total pressure in the reactor was kept constant at 40 bar. The reaction was performed in the temperature range from 175 to 225 °C, using 2 to 8 wt% initial glycerol concentration and 25 to 35 bar H_2 pressure for 8 h with a stirring speed of 750 rpm. During reaction liquid samples of approximately 1.5 mL were taken from the reactor after 1, 3, 5 and 8 h. The liquid samples were filtered using membrane filters to remove residual catalyst particles and analysed by gas chromatography (GC).

2.4. Quantitative analysis of liquid products

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

$$Conversion\ of\ glycerol\ [\%] = \frac{moles\ of\ converted\ glycerol}{moles\ of\ initial\ glycerol} \cdot 100 \qquad (1)$$

$$Selectivity\ [\%] = \frac{v_i \cdot moles\ of\ specific\ product}{moles\ of\ converted\ glycerol} \cdot 100 \qquad (2)$$

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

The turnover frequency (TOF) for the HDO pathway was calculated as moles of produced 1,2-PDO per moles of surface metallic Cu atoms after 8 h (Equation 3). An average number of 1.47×10^{19} atoms per m^2 Cu surface area was used.[33]

$$TOF\ [h^{-1}] = \frac{moles\ of\ produced\ 1,2-PDO}{moles\ of\ surface\ Cu\ atoms \cdot 8\ h} \qquad (3)$$

3. Results and discussion

The HDO of glycerol to 1,2-PDO over Cu/ZrO_2 proceeds via a two-step dehydration-hydrogenation reaction pathway forming acetol as dehydration intermediate, which is further hydrogenated to 1,2-PDO with approximately 95% selectivity.[32] The parallel direct C-C bonds hydrogenolysis leading to ethylene glycol and methanol is the main side reaction with about 5% selectivity. The formation of 1,3-PDO resulting from HDO of the secondary C-O bond has not been observed. Further degradation products such as propanols and ethanol resulting from overhydrogenolysis are present only in trace amounts (<2% selectivity). Therefore, only the formation of 1,2-PDO and ethylene glycol are considered in the following. The simplified reaction scheme for the hydrodeoxygenation and hydrogenolysis of glycerol is shown in Scheme 1, where k is the overall rate constant of glycerol consumption, k_1 is the rate constant of HDO and k_2 is the rate constant of hydrogenolysis.

In order to assess the impact of reaction parameters like glycerol concentration, hydrogen pressure and reaction temperature on glycerol HDO as well as to obtain reliable kinetic data, the external

mass transfer limitation has to be excluded. Control experiments were carried out by varying the stirring speed using 500, 750, and 1000 rpm to investigate the influence of film mass transfer between the bulk liquid phase and the catalyst surface. It was observed that there is no further increase of the initial reaction rate at 750 and 1000 rpm, suggesting the absence of external mass transfer resistance on the overall reaction rate. This is consistent with reports in literature.[29] Therefore, a stirring speed of 750 rpm was chosen for further detailed kinetic study.

3.1 Effect of the initial glycerol concentration

The impact of glycerol concentration on the hydrodeoxygenation kinetics over Cu/ZrO_2 was investigated by varying the initial glycerol concentration between 2 and 8 wt% with 400 mg of catalyst at 200 °C and 25 bar H_2 pressure after 8 h. As shown in Figure 1, glycerol conversion after 8 h decreased from 73.1% to 20.4% with increasing initial glycerol concentration. The roughly inverse relation between the achieved degrees of conversion and the initial glycerol concentration points to zero-order kinetics with respect to glycerol. Interestingly, the selectivities to 1,2-PDO, ethylene glycol and acetol were hardly affected by the initial glycerol concentration and remained rather constant during reaction. 1,2-PDO was found as main product with a selectivity between 91.0% and 94.8%. Ethylene glycol originating from the parallel hydrogenolysis of C-C bonds was found as main by-product with a selectivity varying between 7.2% and 4.3%. The selectivity to acetol showed a slight increase with increasing glycerol concentration but remained below 1% for each concentration variation experiment, indicating that the hydrogenation of acetol to 1,2-PDO is a fast consecutive reaction. It has been previously reported that a 4 wt% aqueous acetol was almost completely hydrogenated to 1,2-PDO (97% yield) in less than 1 h.[32]

Furthermore, the rate of glycerol conversion was studied by taking liquid samples after 1, 3, 5 and 8 h. The concentration of glycerol was found to decrease linearly as a function of reaction time (Figure 2), suggesting that glycerol HDO does not depend on the applied initial glycerol concentration indicating zero-order kinetics. Correspondingly, the slopes are almost the same. A reaction order of zero in glycerol is consistent with some literature reports,[28,34] however, first-order kinetics has been also reported.[35-37] The glycerol reaction order mainly depends on the employed catalysts, reaction conditions and H_2 supply (external or *in situ* production by aqueous phase reforming). It has to be mentioned that the derived zero-order dependence is not due to the lower H_2 concentration in solution compared with the glycerol concentration, as the dehydration is the rate-determining step

and the concentration of dissolved H_2 is steadily in excess relating to the concentration of acetol.[32] Instead, it suggests that the metallic Cu sites are almost fully covered by adsorbed glycerol.[29,34]

Based on the assumption of a Langmuir-Hinshelwood mechanism for glycerol HDO, power-law kinetics can be applied to the overall glycerol consumption and the formation of the two main products 1,2-PDO and ethylene glycol. Equation 4 is the specific reaction rate for glycerol consumption:

$$r = -\frac{dc_{gly}}{dt} = k \cdot c_{gly}{}^{n1} \cdot p_{H_2}{}^{n2} \tag{4}$$

where r, k, c_{gly}, p_{H_2}, n1 and n2 are reaction rate, rate constant, glycerol concentration, H_2 pressure, reaction order for glycerol and H_2, respectively. Since a zero-order reaction for glycerol conversion $(n1 = 0)$ was derived from the concentration variation experiments, the reaction rate depends exclusively on the H_2 partial pressure. Consequently, Equation 4 can be simplified to

$$r = -\frac{dc_{gly}}{dt} = k \cdot p_{H_2}{}^{n2} \tag{5}$$

As the amount of gaseous H_2 is in 7-8 fold excess to the stoichiometric demand (i.e., 64 mmol H_2 vs 8.7 mmol glycerol), the pressure of H_2 inside the reactor can be considered constant. Thus, the rate of glycerol conversion depends exclusively on the rate constant. The averaged reaction rate of the overall glycerol consumption at 200 °C and 25 bar H_2 pressure for three different initial glycerol concentrations (Figure 2) is derived as

$$r = -\frac{dc_{gly}}{dt} = k = 4.74 \cdot 10^{-2} \pm 1.9 \cdot 10^{-3} \, mol \cdot L^{-1} \cdot h^{-1} \cdot g_{cat}{}^{-1} \tag{6}$$

with respect to the mass of the catalyst applied in the kinetic measurements.

3.2 Effect of the hydrogen pressure

Hydrogen pressure variation experiments were carried out in a pressure range of 25 to 35 bar H_2 with an increment of 5 bar at 200 °C for 8 h with 400 mg catalyst precursor and 4 wt% glycerol aqueous solution. The H_2 concentrations in water at 200 °C were estimated to amount to 0.024, 0.034 and 0.047 mol L^{-1} at 25, 30 and 35 bar H_2 partial pressure, respectively.[38] The impact of the H_2 pressure variation on the rate of glycerol HDO is shown in Figure 3. The H_2 pressure predominantly affects the conversion of glycerol. When increasing the H_2 pressure from 25 to 35 bar, glycerol conversion after 8 h almost doubled from 31.4% to 57.2%. The selectivity to acetol decreased from 1.0% to 0.4%,

which is caused by the equilibrium shift from acetol to 1,2-PDO at higher H_2 pressure. It is worth mentioning that the H_2 pressure has marginal impacts on the selectivity to the main products 1,2-PDO and ethylene glycol. The selectivity to 1,2-PDO slightly decreased by 1.1%, while the selectivity to ethylene glycol increased by 2.2% with increasing H_2 pressure. This observation indicates that the direct C-C bond hydrogenolysis leading to ethylene glycol is slightly favoured at higher H_2 pressure. Furthermore, only methanol and 2-propanol were detected as mono-alcoholic by-products originating from overhydrogenolysis of products and intermediates. These by-products are produced in very low amounts with approximately 1% selectivity (not shown in detail), suggesting that the readsorption of the primary HDO products 1,2-PDO and ethylene glycol on the active sites is unlikely to occur.[32]

Liquid-phase hydrogenation reactions using external H_2 supply usually require high H_2 pressure, because the conversion of reactants is limited by the solubility of H_2 in the liquid phase. When the H_2 pressure is used in the rate expressions Equations 4 and 5, it has to be assumed that the absorption and diffusion of H_2 into the aqueous phase is fast establishing gas-liquid equilibrium. The importance of using H_2 concentration instead of H_2 partial pressure for liquid-phase hydrogenation has been emphasized by the Boudart group.[39] Therefore, the H_2 concentration in the aqueous phase instead of the H_2 partial pressure in the reactor is used for the reaction rate calculation in the present study, and Equation 5 can be expressed as

$$r = -\frac{dc_{gly}}{dt} = k \cdot c_{H_2}{}^{n2} \tag{7}$$

In contrast to the glycerol concentration variation experiments, the variation of the H_2 pressure does not indicate a reaction order of zero with respect to H_2 (Figure 4). Instead, the log-log plot of glycerol conversion vs. H_2 concentration in the aqueous phase results in a reaction order of 1.0 for H_2. This result leads to the question of the origin of the positive effect of the H_2 concentration on the rate of glycerol conversion. The dehydration of glycerol to acetol and water was identified as the rate-determining step, whereas the subsequent hydrogenation of the intermediate acetol to 1,2-propanediol was observed to be a fast reaction. Thus, the surface dehydration of glycerol to acetol is the slowest step among dissociative glycerol adsorption, dehydration, acetol hydrogenation and product desorption. Furthermore, the metallic Cu surface sites are assumed to be covered mostly by adsorbed glycerol, presumably as glycerolate, and marginally by hydrogen atoms resulting in the observed zero-order dependence on glycerol concentration. The adsorption of glycerol presumably does not affect H_2 adsorption. It has to be mentioned that water is subcritical under the

present reaction conditions, resulting in high levels of H$^+$ and OH$^-$, which are beneficial for the dehydration of glycerol to acetol.[40]

It has to be considered that the reaction occurs in the aqueous phase, and that also H$_2$O can adsorb dissociatively on Cu in the investigated temperature range according to Equation 8. Water dissociation was verified by H$_2$ TPD experiments over Cu/ZrO$_2$ with an onset temperature of 180 °C in our previous reports.[41,42] In addition, similar metallic Cu surface oxidation by H$_2$O during the water gas shift reaction over Cu-based catalysts has been proposed based on both kinetic experiments and DFT calculations.[43-45] Thus, the positive effect of H$_2$ is ascribed to the formation of empty sites required for dissociative glycerol adsorption. Further studies using *operando* XPS to determine the Auger parameter are considered helpful to verify the oxidation state of Cu.

$$Cu_{surf} + H_2O \rightleftharpoons Cu_{surf} - O_{ads} + H_2 \tag{8}$$

3.3 Effect of the reaction temperature

Temperature variation experiments over Cu/ZrO$_2$ were conducted to investigate the influence on glycerol conversion and product selectivities. These kinetic data were used to derive the apparent activation energies for the HDO and hydrogenolysis routes. As previously reported, metallic Cu is identified to be the active site for the consecutive dehydration-hydrogenation pathway.[32] In order to further verify this assumption, the reaction kinetics was additionally studied over pure metallic Cu obtained by the reduction of commercial CuO nanopowder and compared with the kinetics over Cu/ZrO$_2$.

3.3.1 Cu/ZrO$_2$ catalyst

The results of the temperature variation experiments using Cu/ZrO$_2$ are summarised in Table 1. Without catalyst, glycerol was not converted at 200 °C even after 20 h. An increase of the reaction temperature significantly increased glycerol conversion from 9.9% at 175 °C to 93.0% at 225 °C. Similar to the pressure variation experiments, the selectivity of the direct C-C bond hydrogenolysis of glycerol to ethylene glycol marginally increased from 4.5% to 7.2%. Consequently, the glycerol HDO pathway is favoured over the C-C hydrogenolysis at lower temperature. The selectivity to acetol gradually increased from 0.4% to 5.4% with increasing temperature, indicating that the consecutive hydrogenation to 1,2-PDO is limited at higher temperature. This incomplete hydrogenation of acetol to 1,2-PDO can be attributed to a lower H$_2$ partial pressure at higher reaction temperature at 40 bar total pressure. The selectivity to 1,2-PDO remained rather constant at around 95% up to 200 °C, and

a further temperature increase to 225 °C led to a slight decrease by 7%. This decrease is caused by the incomplete hydrogenation of acetol and by the increasing selectivity of ethylene glycol at 225 °C. The TOF for the HDO pathway increased from 2.5 to 21.5 h^{-1} with increasing temperature over Cu/ZrO$_2$. These values are larger compared with literature reports under similar reaction conditions in the aqueous phase, e.g., 2.1 h^{-1} for Cu/ZnO at 200 °C and 50 bar H$_2$ pressure[30], 2.6 h^{-1} for Cu/Al$_2$O$_3$ at 220 °C and 70 bar H$_2$ pressure[46], pointing to the relatively high activity of Cu/ZrO$_2$. Vasiliadou et al.[28] reported higher TOF values of 30 and 50 h^{-1} after 5 h using two types of Cu/SiO$_2$ in n-butanol, which can be ascribed to the employed harsher reaction conditions (240 °C and 80 bar H$_2$ pressure) and the possible solvent effect. The TOF values for 1,2-PDO formation over Cu powder are comparable with that over Cu/ZrO$_2$.

3.3.2 Comparison of Cu/ZrO$_2$ with metallic Cu powder

Corresponding to Cu/ZrO$_2$, the conversion of glycerol over metallic Cu powder (Table 1) was also significantly enhanced from 2.7% to 56.7% with increasing temperature. However, the selectivity to 1,2-PDO was much lower (56 to 63%), whereas the selectivity to ethylene glycol was much higher (30 to 42%). The detailed kinetic results at 225 °C using Cu/ZrO$_2$ and Cu powder are shown in Figures 5a and 5b, respectively. It has to be pointed out that this specific comparison was conducted using equal numbers of active sites. Since the specific Cu surface areas of Cu/ZrO$_2$ and metallic Cu powder determined by N$_2$O frontal chromatography measurements amount to 4.2 and 0.73 m^2 g^{-1} (ratio of 5.75), respectively, 0.4 g Cu/ZrO$_2$ and 2.3 g CuO were used for this study accordingly. For both catalysts the conversion of glycerol increased linearly with increasing reaction time, again pointing to zero-order kinetics for the overall glycerol consumption. More interestingly, the linear correlation in case of pure Cu powder further supports the dominant role of metallic Cu as the active site in the HDO of glycerol. Similar degrees of conversion of 93% (Cu/ZrO$_2$) and 95% (Cu powder) were achieved after 8 h, but the selectivity to 1,2-PDO and ethylene glycol showed a strong dependence on the catalyst. Using Cu/ZrO$_2$ resulted in approximately 90% selectivity to 1,2-PDO and 6% selectivity to ethylene glycol, whereas metallic Cu led to around 60% and 40% selectivity to 1,2-PDO and ethylene glycol, respectively. This observation indicates that the unsupported metallic Cu powder facilitates both HDO and the competing C-C bond hydrogenolysis, whereas Cu/ZrO$_2$ mainly favours the selective HDO to 1,2-PDO.

The shift from HDO to C-C hydrogenolysis may be due to the different sizes of the metallic Cu particles. The Cu particle size of Cu/ZrO_2 is 5 nm, whereas the particle size of the Cu powder was derived as 42 nm from the corresponding XRD pattern using the Scherrer equation.[32, 40] It is obvious that the HDO pathway is favoured over smaller Cu particles, whereas C-C bond hydrogenolysis is significantly enhanced over larger Cu particles. Glycerol HDO to 1,2-PDO requires the adsorption of one OH-group on the active site. This mode of adsorption is probably less sterically hindered than the coordinative adsorption of two carbon atoms, which is required to initiate C-C bond hydrogenolysis. Consequently, the higher HDO selectivity on smaller Cu particles is presumably attributed to the suppression of C-C hydrogenolysis due to sterical hindrance. A similar correlation between Cu particle size and 1,2-PDO selectivity was observed for Cu/ZnO catalysts.[47] With increasing Cu particle size from 26 to 33 nm the selectivity to 1,2-PDO was found to decrease from 78% to 28%. In another study using Cu/MgO catalysts, the selectivity to 1,2-PDO was also found to decrease by 5%, when the Cu particle size increased from 12 to 30 nm.[48]

Figure 6 shows the 1,2-PDO yields as a function of reaction time at three different temperatures using the same amount of Cu/ZrO_2 (a) and metallic Cu powder (b). Linear correlations between the yields of 1,2-PDO and reaction time are observed, suggesting a zero-order dependence for the HDO route with respect to glycerol concentration. The apparent activation energies E_{a1} for glycerol HDO over both catalysts were derived from the Arrhenius plots (Figure 7). The apparent activation energies of glycerol HDO over Cu/ZrO_2 and metallic Cu powder were found to be 106 and 105 kJ mol^{-1}, respectively. The rather similar activation energies further indicate that the sequential dehydration and hydrogenation (HDO) is catalysed by the same active site on both catalysts, which is identified as fully adsorbate-covered metallic Cu. In addition, the temperature dependence for C-C bond hydrogenolysis was analysed over both catalysts. The kinetic parameters for both catalysts and the two different reaction pathways are summarized in Table 2. Although the apparent activation energy of glycerol hydrogenolysis over metallic Cu powder (109 kJ mol^{-1}) is larger than that over Cu/ZrO_2 (97 kJ mol^{-1}), the selectivity to ethylene glycol is significantly higher for Cu powder. This is ascribed to the fact that the pre-exponential factor for metallic Cu powder is roughly two orders of magnitude larger, thus resulting in a higher rate constant.

4. Conclusions

The reaction kinetics of glycerol hydrodeoxygenation and the competing C-C hydrogenolysis was studied over a co-precipitated Cu/ZrO_2 catalyst under aqueous conditions. The kinetic experiments were performed by varying the reaction parameters such as temperature (175 – 225°C), H_2 partial pressure (25 – 35 bar) and initial glycerol concentration (2 – 8 wt%). Glycerol conversion was strongly influenced by temperature and H_2 pressure leading up to 93% conversion at 225 °C and 25 bar H_2 pressure. The selectivity to 1,2-PDO slightly decreased from 95% to 88% with increasing temperature and pressure, while the selectivity to ethylene glycol produced from the competing C-C bond hydrogenolysis increased from 4% to 7%.

These two parallel routes were considered for the kinetic study and a power-law model was applied. The apparent activation energy for the HDO pathway was determined to be 106 kJ mol^{-1} over Cu/ZrO_2. For unsupported pure metallic Cu as catalyst, the apparent activation energy was found to be 105 kJ mol^{-1} for the HDO route. The similar HDO activation energies over both catalysts indicate the dominant role of fully adsorbate-covered metallic Cu as the active site for the consecutive dehydration-hydrogenation of glycerol to 1,2-PDO. The hydrogenolysis of glycerol to ethylene glycol is found to be structure-sensitive, being favoured for larger Cu particles.

The overall glycerol consumption shows a zero-order dependence on the initial glycerol concentration and a nearly first-order dependence on H_2 concentration. Furthermore, the formation rate of 1,2-propanediol is also independent of the glycerol concentration. These results imply that the high selectivity to the HDO product 1,2-PDO is due to the high coverage of glycerol inhibiting product readsorption. The role of H_2 is assumed to be two-fold: it is required for fast hydrogenation of the formed intermediate acetol and to create empty sites for dissociative glycerol adsorption by removing adsorbed atomic oxygen originating from water dissociation.

References

[1]   Y. Nakagawa, X. Ning, Y. Amada, K. Tomishige, Appl. Catal. A: Gen. 433 (2012) 128-134. https://doi.org/10.1016/j.apcata.2012.05.009

[2]   D.T. Johnson, K.A. Taconi, Environ. Prog. 26 (2007) 338-348. https://doi.org/10.1002/ep.10225

[3]   Y. Nakagawa, K. Tomishige, Catal. Sci. Technol. 1 (2011) 179-190. https://doi.org/10.1039/C0CY00054J

[4]   A.M. Ruppert, J.D. Meeldijk, B.M.W. Kuipers, B.H. Erne, B.M. Weckhuysen, Chem. Eur. J. 14 (2018) 2016-2024. https://doi.org/10.1002/chem.200701757

[5]   W. Fang, S. Wang, A. Liebens, F. De Campo, H. Xu, W. Shen, M. Pera-Titus, J.-M. Clacens, Catal. Sci. Technol. 5 (2015) 3980–3990. https://doi.org/10.1039/C5CY00534E

[6]   J.-M. Clacens, Y. Pouilloux, J. Barrault, Appl. Catal. A: Gen. 227 (2002) 181-190. https://doi.org/10.1016/S0926-860X(01)00920-6

[7]   M. Trejda, K. Stawicka, M. Ziolek, Appl. Catal. B: Environ. 103 (2011) 404-412. https://doi.org/10.1016/j.apcatb.2011.02.003

[8]   W.D. Bossaert, D.E. De Vos, W.M. Van Rhijn, J. Bullen, P.J. Grobet, P.A. Jacobs, J. Catal. 182 (1999) 156-164. https://doi.org/10.1006/jcat.1998.2353

[9]   F. Cai, D. Pan, J.J. Ibrahim, J. Zhang, G. Xiao, Appl. Catal. A: Gen. 564 (2018) 172-182. https://doi.org/10.1016/j.apcata.2018.07.029

[10]   E.S. Vasiliadou, A.A. Lemonidou, WIREs Energy Environ. 4 (2015) 486-520. https://doi.org/10.1002/wene.159

[11]   Y. Wang, J. Zhou, X. Guo, RSC Adv. 5 (2015) 74611-74628. https://doi.org/10.1039/C5RA11957J

[12]   A. Corma, G.W. Huber, L. Sauvanauda, P.O'Connor, J. Catal., 257 (2008) 163-171. https://doi.org/10.1016/j.jcat.2008.04.016

[13]   E. Tsukuda, S. Sato, R. Takahashi, T. Sodesawa, Catal. Comm. 8 (2007) 1349-1353. https://doi.org/10.1016/j.catcom.2006.12.006

[14]   N.P. Rajan, G. Srinivasa Rao, V. Pavankumar, K.V.R. Chary, Catal. Sci. Technol. 4 (2014) 81-92. https://doi.org/10.1039/C3CY00430A

[15]   Y. Shinmi, S. Koso, T. Kubota, Y. Nakagawa, K. Tomishige, Appl. Catal. B: Environ. 94 (2010) 318-326. https://doi.org/10.1016/j.apcatb.2009.11.021

[16]   M. Checa, F. Auneau, J. Hidalgo-Carrillo, A. Marinas, J.M. Marinas, C. Pinel, F.J. Urbano, Catal. Today 196 (2012) 91-100. https://doi.org/10.1016/j.cattod.2012.02.036

[17]   E.S. Vasiliadou, A.A. Lemonidou, Org. Process Res. Dev. 15 (2011) 925-931. https://doi.org/10.1021/op2000173

[18]   D. Sun, Y. Yamada, S. Sato, W. Ueda, Appl. Catal. B: Environ. 193 (2016) 75-92. https://doi.org/10.1016/j.apcatb.2016.04.013

[19]   W. Yu, J. Xu, H. Ma, C. Chen, J. Zhao, H. Miao, Q. Song, Catal. Comm. 11 (2010) 493-497. https://doi.org/10.1016/j.catcom.2009.12.009

[20]   X. Guo, Y. Li, R. Shi, Q Liu, E. Zhan, W. Shen, Appl. Catal. A: Gen. 371 (2009) 108-113. https://doi.org/10.1016/j.apcata.2009.09.037

[21]   I. Gandarias, P.L. Arias, J. Requies, M.B. Güemez, J.L.G. Fierro, Appl. Catal. B: Environ. 97 (2010) 248-256. https://doi.org/10.1016/j.apcatb.2010.04.008

[22]   M. Balaraju, V. Rekha, P.S. Sai Prasad, B.L.A. Prabhavathi Devi, N. Lingaiah, Appl. Catal. A: Gen. 354 (2009) 82-87. https://doi.org/10.1016/j.apcata.2008.11.010

[23]   F. Cai, W. Zhu, G. Xiao, Catal. Sci. Technol. 6 (2016) 4889–4900. https://doi.org/10.1039/C6CY00085A

[24]   M. Balaraju, V. Rekha, P.S. Sai Prasad, R.B.N. Prasad, N. Lingaiah, Catal. Lett. 126 (2008) 119–124. https://doi.org/10.1007/s10562-008-9590-6

[25]   D. Durán-Martín, M. Ojeda, M. López Granados, J.L.G. Fierro, R. Mariscal, Catal. Today 210 (2013) 98-105. https://doi.org/10.1016/j.cattod.2012.11.013

[26]   Z. Xiao, J. Xiu, X. Wang, B. Zhang, C.T. Williams, D. Su, C. Liang, Catal. Sci. Technol. 3 (2013) 1108–1115. https://doi.org/10.1039/C2CY20788E

[27]   R.V. Sharma, P. Kumar, A.K. Dalai, Appl. Catal. A: Gen. 477 (2014) 147-156. https://doi.org/10.1016/j.apcata.2014.03.007

[28]   E.S. Vasiliadou, T.M. Eggenhuisen, P. Munnik, P.E. de Jongh, K.P. de Jong, A.A. Lemonidou, Appl. Catal. B: Environ. 145 (2014) 108-119. https://doi.org/10.1016/j.apcatb.2012.12.044

[29]   E.S. Vasiliadou, A.A. Lemonidou, Chem. Eng. J. 231 (2013) 103-112. https://doi.org/10.1016/j.cej.2013.06.096

[30]   A. Bienholz, F. Schwab, P. Claus, Green Chem. 12 (2010) 290-295. https://doi.org/10.1039/B914523K

[31]   C. Wang, H. Jiang, C. Chen, R. Chen, W. Xing, Chem. Eng. J., 264 (2015) 344-350. https://doi.org/10.1016/j.cej.2014.11.113

[32]   T. Gabrysch, B. Peng, S. Bunea, G. Dyker, M. Muhler, ChemCatChem 10 (2018) 1344-1350. https://doi.org/10.1002/cctc.201701748

[33]   O.Hinrichsen, T. Genger, M. Muhler, Chem. Eng. Technol. 23 (2000) 956–959. https://doi.org/10.1002/1521-4125(200011)23:11<956::AID-CEAT956>3.0.CO;2-L

[34]   Y. Amada, Y. Shinmi, S. Koso, T. Kubota, Y. Nakagawa, K. Tomishige, Appl. Catal. B: Environ. 105 (2011) 117-127. https://doi.org/10.1016/j.apcatb.2011.04.001

[35]   D.G. Lahr, B.H. Shanks, Ind. Eng. Chem. Res. 42 (2003) 5467–5472. https://doi.org/10.1021/ie030468l

[36]   X. Jin, B. Subramaniam, R.V. Chaudhari, P.S. Thapa, AIChE J. 62 (2016) 1162-1173. https://doi.org/10.1002/aic.15114

[37]   N.N. Pandhare, S.M. Pudi, S. Mondal, K. Pareta, M. Kumar, P. Biswas, Ind. Eng. Chem. Res. 57 (2018) 101-110. https://doi.org/10.1021/acs.iecr.7b03684

[38]   H.A. Pray, C.E. Schweickert, B.H. Minnich, Ind. Eng. Chem. 44 (1952) 1146-1151.
        https://doi.org/10.1021/ie50509a058

[39]   E.E. Gonzo, M. Boudart, J. Catal. 52 (1978) 462–471. https://doi.org/10.1016/0021-
        9517(78)90352-4

[40]   S. S. Toor, L. Rosendahl, A. Rudolf, Energy 36 (2011) 2328-2342.
        https://10.1016/j.energy.2011.03.013

[41]   J. Schittkowski, K. Tölle, S. Anke, S. Stürmer, M. Muhler, J. Catal. 352 (2017) 120-129.
        https://doi.org/10.1016/j.jcat.2017.05.009

[42]   J. Schittkowski, D. Buesen, K. Tölle, M. Muhler, Catal. Lett. 146 (2016) 1011-1017.
        https://doi.org/10.1007/s10562-016-1712-y

[43]   N.A. Koryabkina, A.A. Phatak, W.F. Ruettinger, R.J. Farrauto, F.H. Ribeiro, J. Catal. 217 (2003)
        233–239. https://doi.org/10.1016/S0021-9517(03)00050-2

[44]   C.-S. Chen, T.-W. Lai, C.-C. Chen, J. Catal. 273 (2010) 18-28.
        https://doi.org/10.1016/j.jcat.2010.04.019

[45]   C.-H. Lin, C.-L. Chen, J.-H. Wang, J. Phys. Chem. C. 115 (2011) 18582-18588.
        https://doi.org/10.1021/jp2034467

[46]   R.B. Mane, A.M. Hengne, A.A. Ghalwadkar, S. Vijayanand, P.H.Mohite, H.S.Potdar, C.V. Rode,
        Catal. Lett. 135 (2010) 141-147. https://doi.org/10.1007/s10562-010-0276-5

[47]   S. Wang, H. Liu, Catal. Lett. 117 (2007) 62-67. https://doi.org/10.1007/s10562-007-9106-9

[48]   M. Balaraju, K. Jagadeeswaraiah, P.S. Sai Prasad, N. Lingaiah, Catal. Sci. Technol. 2 (2012)
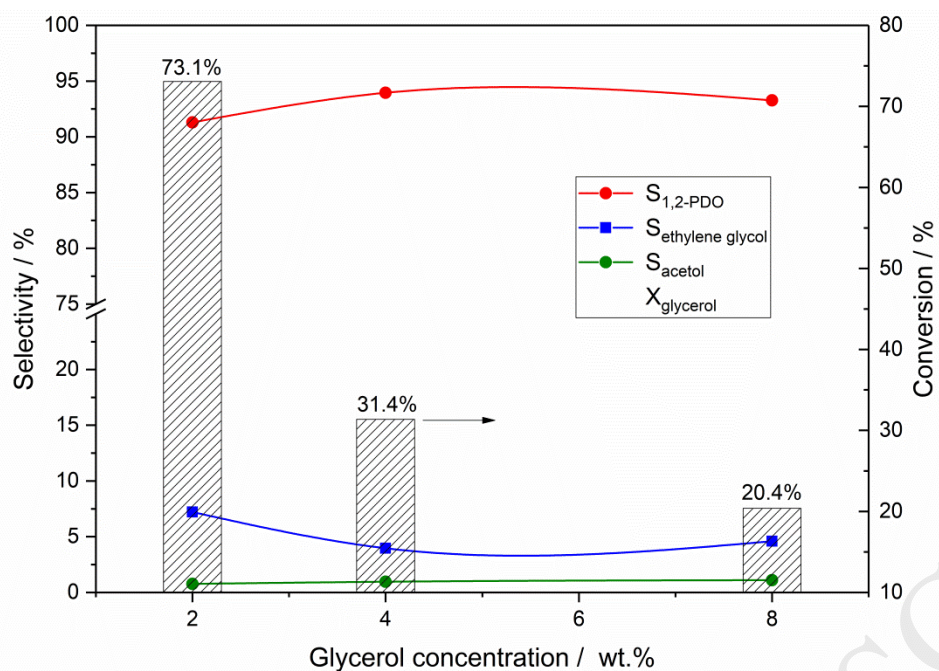   1967-1976. https://doi.org/10.1039/C2CY20059G

Figure 1. Effect of initial glycerol concentration on the degree of conversion after 8 h reaction time and liquid product selectivities. Reaction conditions: 20 mL of 2-8 wt% aqueous glycerol solution, 400 mg of 18 wt% CuO/ZrO_2 (pre-reduced), 200 °C, 25 bar H_2 pressure, 750 rpm stirring speed.
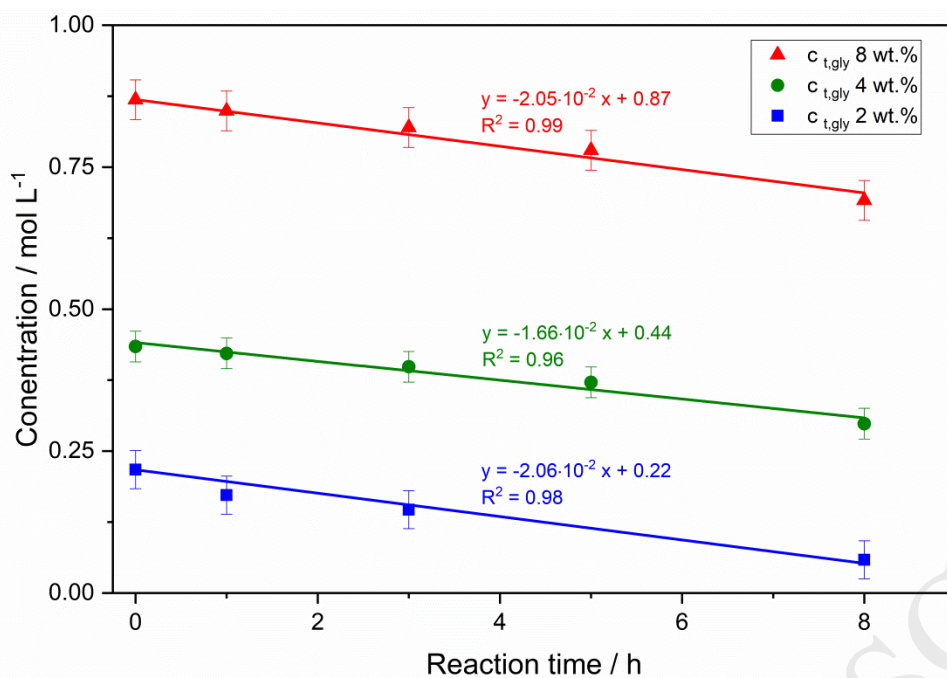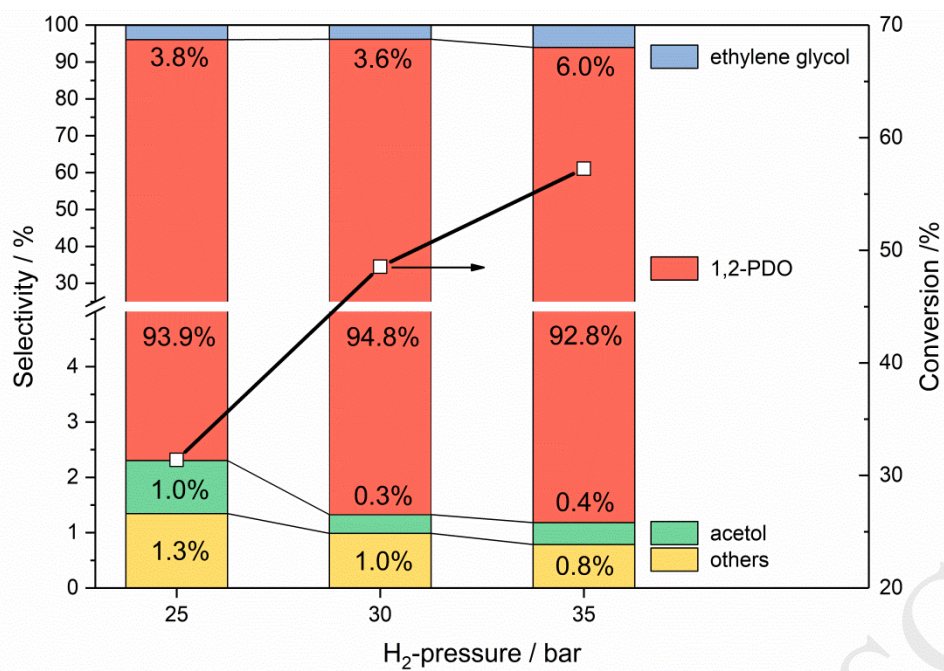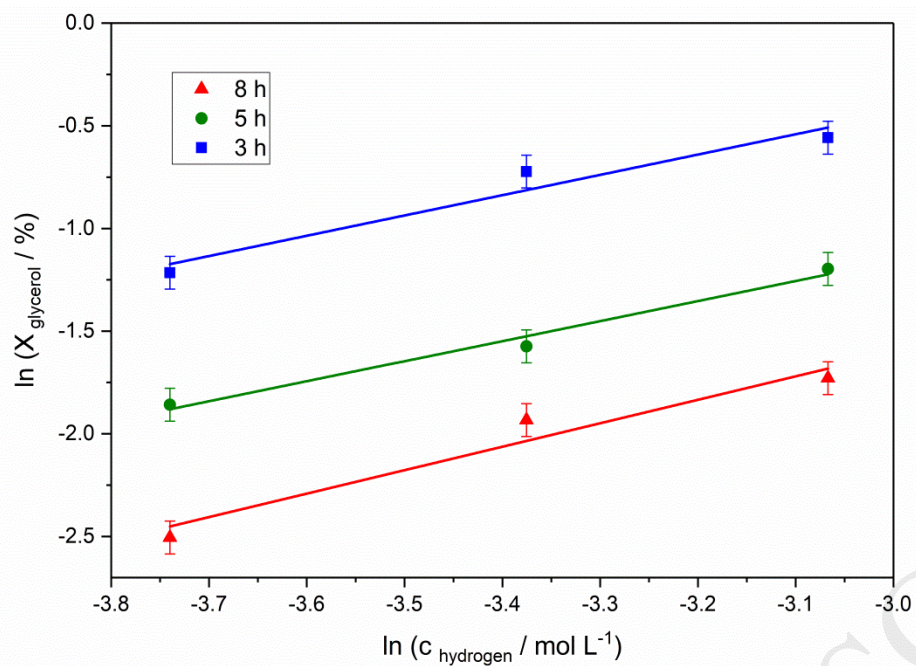
Figure 2. Glycerol concentration as a function of reaction time with varying initial glycerol concentrations (2-8 wt%). Reaction conditions: 20 mL of 2-8 wt% aqueous glycerol solution, 400 mg of 18 wt% CuO/ZrO_2 (pre-reduced), 25 bar H_2 pressure, 200 °C, 750 rpm stirring speed.

Figure 3. Effect of H$_2$ pressure on glycerol conversion and liquid product selectivities. Reaction conditions: 20 mL of 4 wt% aqueous glycerol solution, 400 mg of 18 wt% CuO/ZrO$_2$ (pre-reduced), 200 °C, 750 rpm stirring speed and 8 h.
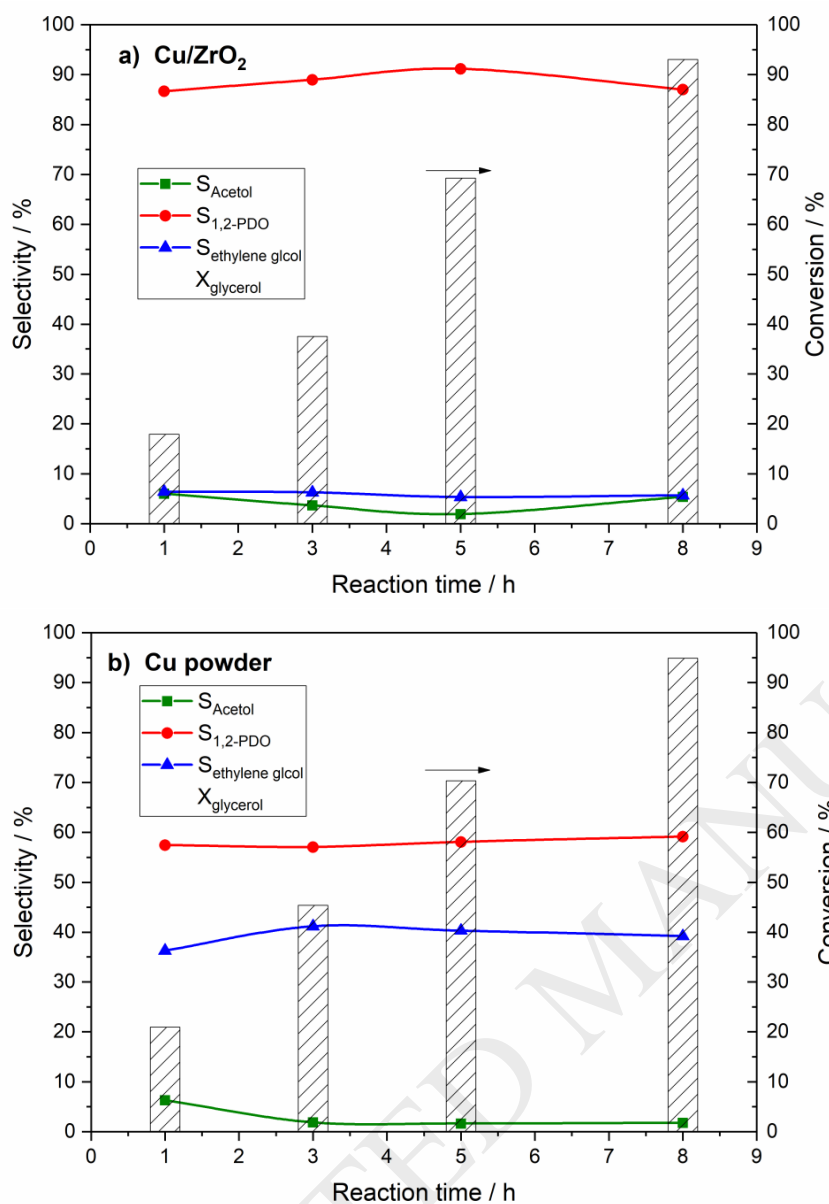
Figure 4. Log-log plot of glycerol conversion with hydrogen concentration in the aqueous phase at varying H_2 pressure (25 to 35 bar); liquid samples were taken after 3, 5, and 8 h reaction time. Reaction conditions: 20 mL of 4 wt% aqueous glycerol solution, 400 mg of 18 wt% CuO/ZrO_2 (pre-reduced), 200 °C and 750 rpm stirring speed.

Figure 5. Glycerol conversion and liquid product selectivities as a function of time over a) 18 wt% CuO/ZrO$_2$ (pre-reduced) and b) metallic Cu powder. Reaction conditions: 20 mL of 4 wt% aqueous glycerol solution, 400 mg of 18 wt% CuO/ZrO$_2$ and 2.3 g of CuO (both reduced prior to reaction), 225 °C, 750 rpm stirring speed and 8 h.
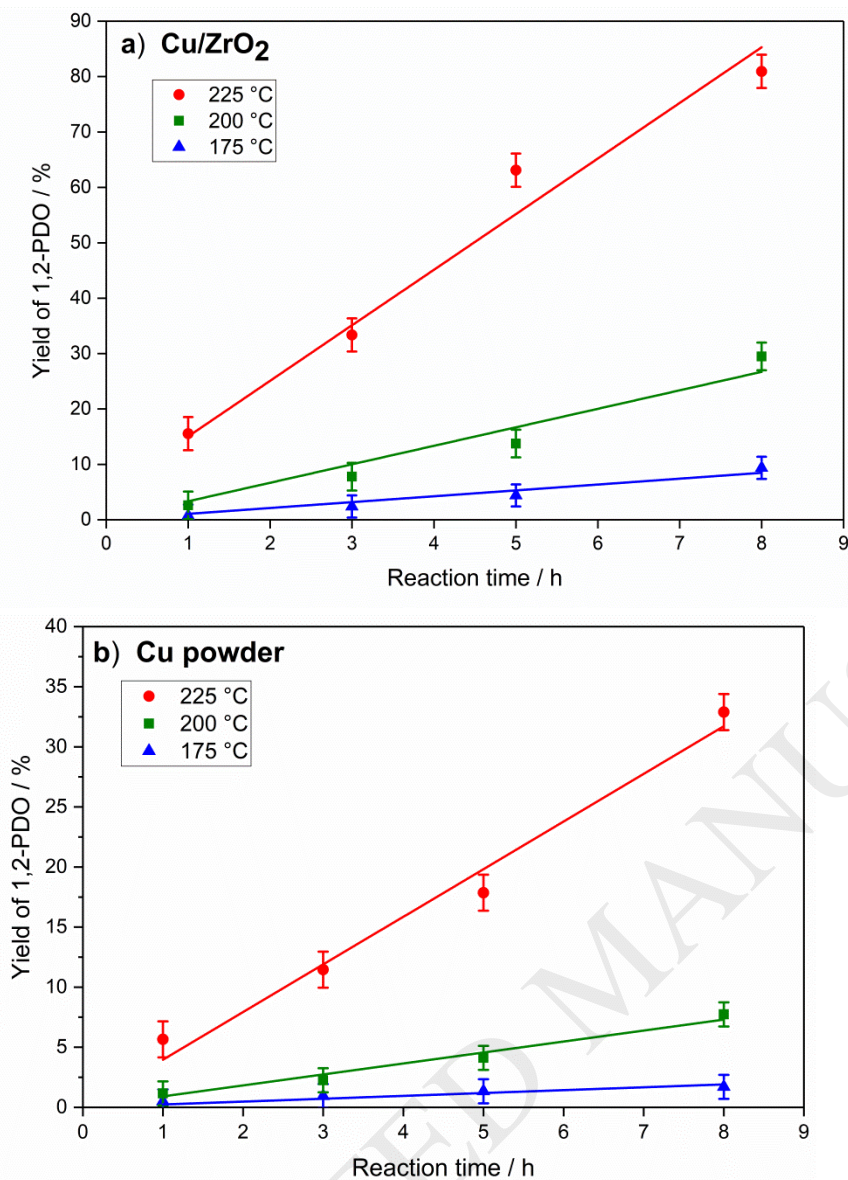
Figure 6. Plots of the 1,2-PDO yield against reaction time for varying reaction temperatures over a) 18 wt% CuO/ZrO$_2$ and b) metallic Cu powder. Reaction conditions: 20 mL of 4 wt% aqueous glycerol solution, 400 mg of unreduced precursor (reduced prior to the reaction), 25 bar H$_2$ pressure and 750 rpm stirring speed.
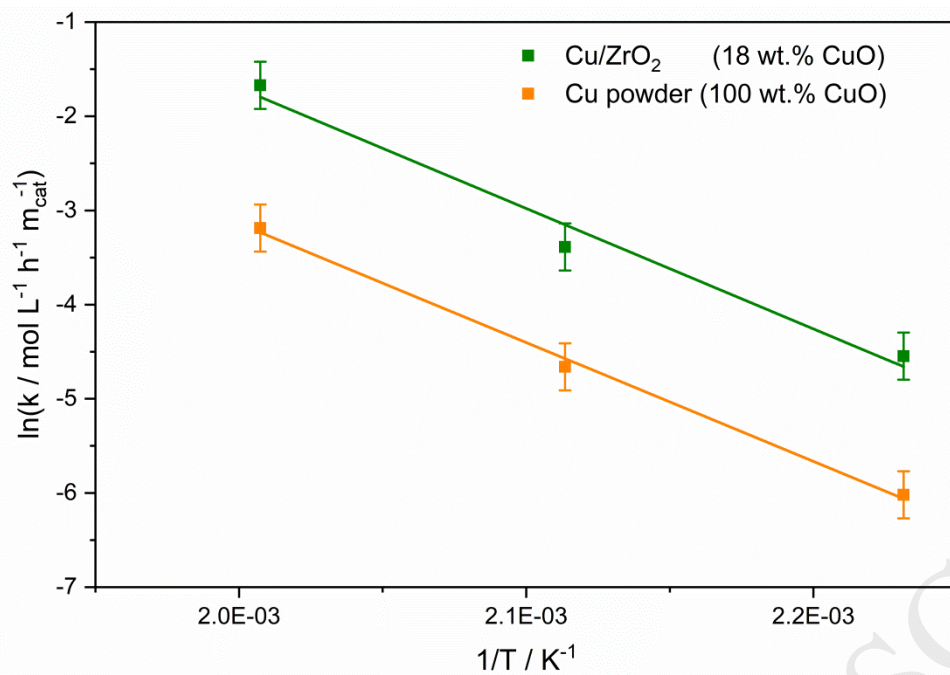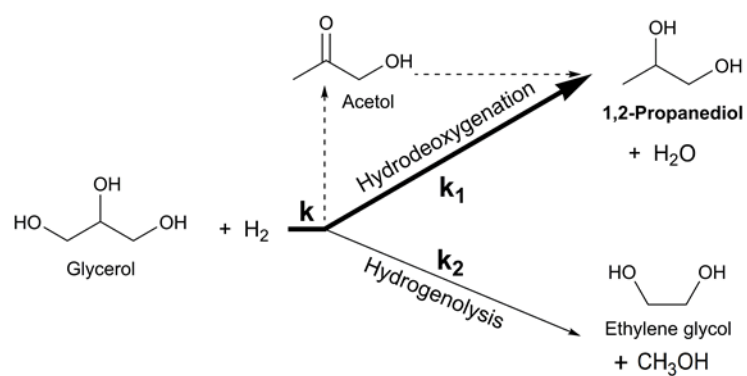
Figure 7. Arrhenius plots for the selective HDO of glycerol to 1,2-PDO over Cu/ZrO$_2$ (green line) and metallic Cu powder (orange line). Reaction conditions: 20 mL of 4 wt% aqueous glycerol solution, 400 mg of unreduced precursor (reduced prior to the reaction), 25 bar H$_2$ pressure and 750 rpm stirring speed.

Scheme 1: Simplified reaction pathways of hydrodeoxygenation and hydrogenolysis of glycerol over Cu-based catalysts.

Table 1: Effect of reaction temperature on glycerol conversion, TOF for HDO and liquid product selectivities after 8 h over Cu/ZrO$_2$ and metallic Cu powder. Reaction conditions: 20 mL of 4 wt% aqueous glycerol solution, 400 mg of unreduced catalyst (reduced prior to the reaction), 40 bar total pressure, 750 rpm stirring speed.

| T / °C | Cu/ZrO$_2$ | | | | | | Cu powder | | | |
| | Conv. / % | TOF* / h^{-1} | Selectivity / % | | | Conv. / % | TOF* / h^{-1} | Selectivity / % | | |
			Acetol	1,2-PDO	Ethylene glycol			Acetol	1,2-PDO	Ethylene glycol
175	9.9	2.5	0.4	94.2	4.5	2.7	2.5	1.4	63.0	30.6
200	31.4	7.8	1.0	93.9	4.0	12.2	10.1	1.0	56.6	41.6
225	93.0	21.5	5.4	87.0	7.2	56.7	41.7	2.3	56.0	29.9

* The TOF for the HDO pathway was calculated after 8 h based on the molar amount of exposed metallic copper atoms

Table 2: Derived kinetic parameters for glycerol HDO and hydrogenolysis over Cu/ZrO_2 and metallic Cu powder.

Catalyst	Hydrodeoxygenation		Hydrogenolysis	
	A_1	E_{a1} / kJ mol^{-1}	A_2	E_{a2} / kJ mol^{-1}
Cu/ZrO_2	2.3×10^{10}	106 ± 2.1	9.1×10^7	97 ± 2.9
Cu	4.0×10^9	105 ± 2.1	6.3×10^9	109 ± 2.2