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8, 4891Promoting effect of solvent on Cu/CoO catalyst
for selective glycerol oxidation under alkaline
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Cu/CoO catalysts were employed for the selective oxidation of glycerol in the aqueous phase under basic conditions. The effect of the solvent on the catalytic performance was investigated and the impact on the catalyst was thoroughly elucidated. Detailed characterization of the catalysts by HR-TEM, XRD, and XPS analysis before and after the reaction revealed that the addition of co-solvents (ethanol, *n*-propanol, or *tert*-butanol) drastically altered the catalyst properties. In particular, the amount of the catalytically active CoO(OH) phase generated during the reaction depends on the co-solvent used. Generally, the co-solvent has a beneficial effect on the catalytic activity and improves the glycerol conversion by a factor of up to 1.8, which could be linearly correlated to the $E_T(30)$ solvent polarity.

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Introduction

The inevitable depletion of fossil fuels and other environmental concerns have boosted the search for alternative sustainable processes to generate fuels and chemical feedstocks from biomass. Biodiesel, as a renewable resource derived from biomass, emerged over the last few decades as a replacement for fossil fuels. Biodiesel is produced by the transesterification of fats and oils, where glycerol is concomitantly formed as a side-product with high amounts (10 wt%) of biodiesel.¹ Consequently, the increased biodiesel production resulted in the well-known glycerol glut, drastically dropping the market prices for glycerol.^{2,3} Hence, a demand arose to convert glycerol into value-added derivatives in order to make the biodiesel production more economically feasible.

Besides the various valorization routes (hydrogenolysis, dehydration, polymerization, esterification, *etc.*),^{1,4–7} the selective oxidation of glycerol plays a crucial role in the scientific field and has been thoroughly investigated.^{8–10} Even non-conventional photocatalytic pathways have been studied to find an efficient and sustainable way to valorize glycerol.^{11–18} Recently, we demonstrated that plasmonic photocatalysis, utilizing noble metals as light absorbers and active centers, is a promising alternative to thermocatalytic glycerol oxidation.^{19,20}

To date, mainly noble metal catalysts have been investigated for the selective oxidation of glycerol in the aqueous phase^{1,9,10} and only a few reports were published focusing on cost-efficient transition metal-based catalysts.^{21–27} McMorn *et al.* showed that transition metal-containing silicalite and aluminophosphate catalysts are capable of glycerol oxidation in the presence of H₂O₂ with high selectivities for formic acid and mono-formate-esters.²¹ More recently, Jin *et al.* reported that Co catalysts supported on Mg–Al hydrotalcite structures show high glycerol oxidation conversion with remarkable selectivities to tartronic acid.²⁶ Davis and co-workers showed that non-precious metal atoms (M = Fe, Cu, Cr, Co, Ni) dispersed on a nitrogen-containing carbon matrix catalyzed the oxidation of benzyl alcohol and 5-hydroxymethylfurfural.²⁸ However, they also investigated the oxidation of other alcohols over these catalysts and observed that the catalytic performance for glycerol oxidation was poor, emphasizing the fact that finding active non-noble metal catalysts for glycerol oxidation is a challenging task.

We previously reported metallic Cu nanoparticles supported on ordered mesoporous CoO as active catalysts for glycerol oxidation with decent selectivities for glyceric, glycolic, and formic acid.²⁹ Intrigued by these results, the study was extended to CuCo-based materials prepared by a facile co-precipitation method where the catalysts were further investigated in more detail.³⁰ Several post-treatments were applied to CuCo-based catalysts, resulting in different crystalline phases, which were investigated for selective glycerol oxidation.

Investigations on the solvent effect for heterogeneous, noble and non-noble metal catalysts are only scarcely

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† Electronic supplementary information (ESI) available: Tabulated selectivities, fitted XPS spectra, XRD patterns of reference materials, conversions and selectivities of recycling experiments. See DOI: 10.1039/c8cy01284a



available.^{31,32} A few studies have been reported where the role of the solvent was investigated for polyol oxidation over noble metal catalysts. D'Agostino *et al.* showed that for 1,3-propanediol oxidation over Au/TiO₂, both adsorption and reactant diffusivity have to be considered when selecting the solvent composition.³¹ Furthermore, in a study on the catalytic oxidation of 1,4-butanediol over Au/TiO₂ catalyst, it was reported that adsorption of the reactant and the solvent are crucial for improving the catalytic performance.³² Moreover, Dumeignil and co-workers investigated the impact of crude glycerol for the selective oxidation over Pt/Al₂O₃ catalyst.³³ One conclusion of their studies was that adding methanol as co-solvent into the reaction medium promoted the catalytic performance. In stark contrast, by using Au/Al₂O₃ and Ag/Al₂O₃ catalysts, they could show that methanol as the co-solvent had a detrimental effect on the activity.³⁴ Lately, we also investigated the effect of co-solvents on the catalytic activity of Cu/Al₂O₃-based catalysts towards the selective oxidation of glycerol and could demonstrate a good correlation between the solvent polarity and the catalytic activity.³⁵ To learn more about the effect of the presence of a co-solvent on the catalytic activity of Cu-based catalysts, we have studied the solvent-effect on a different Cu-based catalyst, namely Cu/CoO, and the results are reported herein.

The exploration of the role of different solvents can shed light on the reaction mechanism and determine the influence that the solvent can have. Furthermore, crude glycerol contains impurities like methanol or ethanol. The development of catalysts that are resistant to these or other solvents is an important step for valorizing glycerol by heterogeneous catalysts without purification pre-treatments. Hence, the examination of the solvent effect for non-noble metal catalysts cannot be neglected if these catalysts shall be regarded as promising materials for glycerol oxidation.

From an industrial point of view, it is most interesting to investigate the effect of methanol and ethanol on the catalytic performance of glycerol oxidation catalysts, since these alcohols are used for the transesterification process to yield biodiesel.^{36,37} On the other hand, from the academic perspective, the use of a homologous series of alcohols, deduced from methanol (such as ethanol and *n*-propanol) and mono-functional alcohols with different structures (like *tert*-butanol), can give further insight into the reaction mechanism and the enhancing or impeding effects of the solvent. Hence, these solvents were selected in order to investigate the solvent effect for glycerol oxidation over CuCo-based catalysts.

Herein, we investigate the solvent effect on glycerol oxidation in the aqueous phase over Cu/CoO catalysts. The detailed characterization of the materials before and after glycerol oxidation experiments shed light on the role of the solvent in the catalytic performance. Moreover, the solvent effect on the change of crystal phase and surface species of the catalysts, the Cu leaching, and the catalytic activity of leached Cu species was investigated.

Experimental section

Catalyst preparation

Co(NO₃)₂·6H₂O (>98%, Sigma-Aldrich), Cu(NO₃)₂·3H₂O (99–104%, Sigma-Aldrich), NaOH (pellets, VWR Chemicals), H₂O₂ (35 wt%, J. T. Baker) were used without further purification.

The detailed preparation of Cu/CoO catalysts was described previously.³⁰ An aqueous NaOH solution (3.2 M, 20.8 mL) was prepared in a 250 mL beaker and heated up to 50 °C under stirring. Co(NO₃)₂·6H₂O (1.21 g) and Cu(NO₃)₂·3H₂O (0.502 g) were dissolved in DI water (10.4 mL) and added dropwise into the NaOH solution and stirred for 20 min. Afterwards, H₂O₂ (35 wt%; 29.7 mL) was added dropwise into the solution within 20 min. The solution was further stirred for 20 min at 50 °C. Then, the precipitated black powder was filtered and washed with DI water (500 mL). The material was dried for 24 h at 110 °C and further calcined at 350 °C for 2 h with a heat ramp of 5 °C min⁻¹. Finally, the calcined powder was treated with an ethanol reduction procedure developed in our group.^{29,38,39} High-temperature ethanol decomposition (similar to steam reforming process) results in H₂ over copper-cobalt oxide and reduces the material selectively to Cu/CoO in the process of producing metallic CuCo. The sample was placed in a tube oven and calcined at 270 °C for 4 h with a heating ramp of 5 °C min⁻¹. N₂ was used as the carrier gas with a gas stream of 100 mL min⁻¹. Prior to reaching the sample in the oven, the gas stream was bubbled through a round bottom flask (500 mL) containing 250 mL of pure ethanol.

Catalyst characterization

Transmission electron microscopy (TEM) studies were performed on a Hitachi H-7100 with 100 kV acceleration voltage. High-resolution TEM analysis was performed on an HF-2000 field emission electron microscope with an acceleration voltage of 200 kV. Analysis of the reaction solution for the determination of the Cu content was performed by "Mikroanalytisches Laboratorium Kolbe" in Mülheim an der Ruhr, Germany. The X-ray powder patterns for qualitative phase analysis for glycerol oxidation experiments were collected on a Stoe STADI P transmission diffractometer using Mo radiation (0.7093 Å). The instrument was equipped with a primary Ge (111) monochromator (MoKα₁) and a position sensitive Mythen1K detector. Data were collected in the range between 5 and 50° 2θ with a step width of 0.015° 2θ. Measuring times per step were varied between 20 and 60 s. For each sample, 8 scans were collected and summed after data collection. For the measurements, the samples were filled into glass capillaries (Ø = 0.3 mm). The measured patterns were evaluated qualitatively by comparison with entries from the ICDD PDF-2 powder pattern database and by comparison with simulated data (crystal structure data were taken from the ICSD database). XPS measurements were performed with a Kratos HSi spectrometer with a hemispherical analyzer. The monochromated Al K_α X-ray source (*E* = 1486.6 eV) was operated at 15 kV and 15 mA. For the narrow scans, analyzer pass



energy of 40 eV was applied. The hybrid mode was used as the lens mode. The base pressure during the experiment in the analysis chamber was 4×10^{-7} Pa. To account for charging effects, all spectra were referred to C1s at 284.5 eV.

Catalytic glycerol oxidation

Glycerol oxidation experiments were performed as follows. Stainless steel autoclaves (ca. 36 mL total volume) with Teflon inlets were loaded with the catalyst (15 mg), the reaction solution (0.05 M aqueous glycerol solution (DI water), 4:1 mol mol⁻¹ = NaOH:glycerol, 15 mL) and a stirring bar. The sealed autoclaves were purged with pure O₂ at 10 bar three times before they were pressurized at 10 bar, unless otherwise indicated. The autoclaves were positioned in preheated heating mantles at 90 °C and the stirring speed was adjusted to 750 rpm unless otherwise indicated. The reaction was performed for 1 h and subsequently, cooled to 0 °C in an ice bath and depressurized. The reaction solution was centrifuged (9000 rpm, 15 min) to separate the catalyst from the solution. Blank glycerol oxidation experiments without catalyst, but otherwise identical reaction conditions, showed no conversion. The catalysts were recovered by hot filtration for the recycling experiments. For the investigation of the solvent effect, different amounts of co-solvents (methanol, ethanol, *n*-propanol, *tert*-butanol) were mixed with the aqueous glycerol solution, thereby maintaining the total reaction volume of 15 mL. Product analysis in the liquid phase was performed *via* HPLC (Shimadzu) with a 300 × 6.5 mm Metacarb 67H with guard cartridge. Aqueous 0.1% trifluoroacetic acid solution was used as the eluent with a flow rate of 0.8 mL min⁻¹ at 323 K. Each sample (10 µL) was injected and peaks were detected with a refractive index detector. Products were identified by comparison with reference samples.

Results and discussion

CuCo-based materials were modified by different post-treatments and used for glycerol oxidation in the aqueous phase; we provided a detailed characterization and relevant reaction mechanism in our previous report.³⁰ Herein, we selected the most active catalyst, Cu/CoO with a Co/Cu atomic ratio of 2, prepared *via* a facile co-precipitation method and a thermal post-treatment, to explore the effect of the co-solvent for the glycerol oxidation reaction. As shown in Fig. 1, the catalyst consisted of metallic Cu nanoparticles in close contact with CoO and small amounts of an unknown phase, which might be a composite based on copper and cobalt. N₂ physisorption analysis revealed a BET surface area of 65 m² g⁻¹.

In order to investigate the role of the solvent in the catalytic performance of Cu/CoO for glycerol oxidation, different solvents with diverse solvent/water ratios were used to dilute glycerol. The homologous series from methanol to *n*-propanol and additionally *tert*-butanol were investigated with Cu/CoO as the solid catalyst. As presented in Fig. 2a), catalytic reactions with 50 vol% solvent content for ethanol,

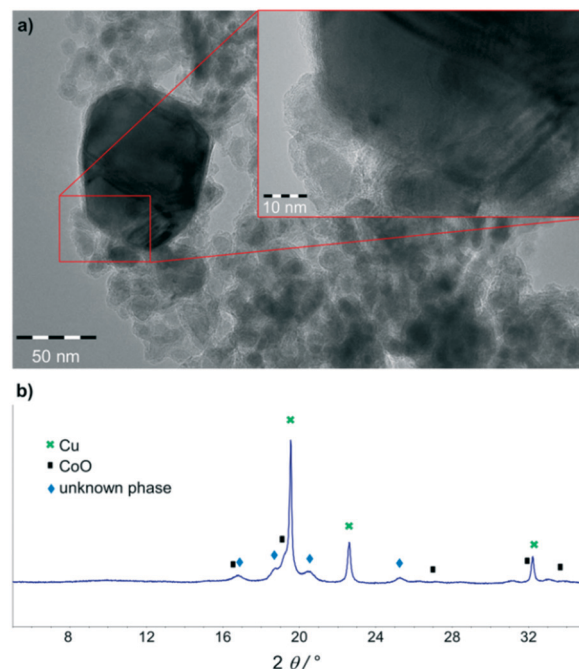


Fig. 1 a) HR-TEM micrographs and b) XRD diffractogram (MoKα₁ radiation) of the Cu/CoO catalyst with a Co/Cu ratio of two.

n-propanol, and *tert*-butanol over Cu/CoO showed remarkable increases in glycerol conversion compared to the reaction performed in water. The conversion continuously increased with higher solvent content. At 50 vol% solvent content, *n*-propanol and ethanol exhibited the highest conversion. In stark contrast, methanol as the co-solvent had a detrimental impact on the catalytic performance even at low concentrations. It has been reported that by using AuPd/TiO₂ as the catalyst, glycerol can be oxidized preferentially in comparison to 1,3-propanediol or *n*-propanol.⁴⁰ Several reasons were suggested for this behavior based on the promoting effect of the secondary hydroxyl group present in glycerol. The vicinal diols could improve the formation of a complex with the catalyst surface or simply weaken the C–H bond due to an improved electron withdrawal effect of the secondary OH-group. This is in line with our observation that mono-functional alcohols were not oxidized and only glycerol was converted (Fig. 2b).

Skrzynska *et al.* used Pt/Al₂O₃ as the catalyst and observed a beneficial effect on glycerol conversion by adding methanol to the aqueous solution, which is in contradiction to our results.³³ They concluded that a higher O₂ solubility was achieved by adding methanol, which increased the conversion. This beneficial effect of higher O₂ solubility was also generally attributed to other solvents like ethanol, *n*-propanol and *tert*-butanol.^{41,42} On the other hand, the same group reported elsewhere that the addition of methanol as co-solvent resulted in decreased conversions for Au/Al₂O₃ and Ag/Al₂O₃ catalysts.³⁴ However, we can exclude the explanation based on the improved O₂ solubility caused by methanol addition due to this being the reason for the increased



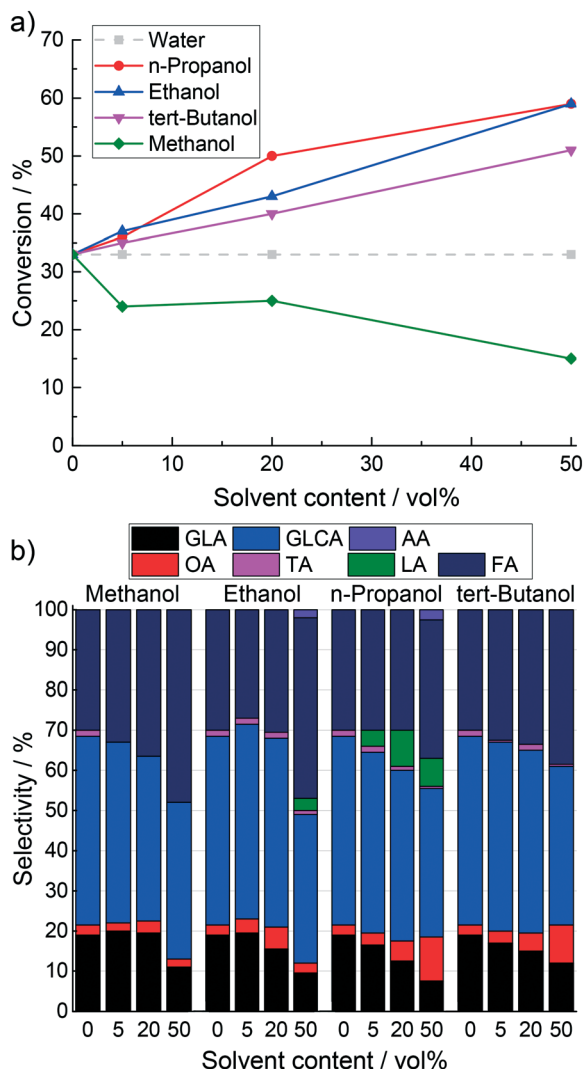


Fig. 2 a) Glycerol conversions and b) selectivities for glycerol oxidation experiments over Cu/CoO catalysts with a Co/Cu ratio of 2. GLA: glyceric acid; GLCA: glycolic acid; AA: acetic acid; OA: oxalic acid; TA: tartaric acid; LA: lactic acid; FA: formic acid. The indicated solvent content is related to the added amount of the specified alcohol in the aqueous phase. Reaction conditions: 1 g L⁻¹ catalyst, 15 mL of 0.05 M aqueous glycerol solution, 4 : 1 NaOH to glycerol ratio, 90 °C, 10 bar pure O₂, 1 h reaction time, 750 rpm stirring speed.

conversions. We performed glycerol oxidation experiments over Cu/CoO with different O₂ pressures up to 20 bar and could not observe any change in activity or selectivity above 10 bar.³⁰ A linear relationship between the applied pressure in the gas phase and the dissolved O₂ in solution is assumed to be plausible, according to the literature;^{43,44} thus, we could show that a higher O₂ solubility could not be the origin of the increased conversions. The solvent polarity or the change in the nature of the catalyst during the reaction could play some role for the higher conversion, which is discussed later.

The selectivities for the different reactions are illustrated in Fig. 2b) (see Table S1, ESI[†] for listed values). Note that additional reactions with the different solvent mixtures were performed without glycerol in order to determine the selectiv-

ities for glycerol oxidation without falsified values by oxidized solvent products. No significant amounts of typical glycerol oxidation or solvent oxidation products were detected. Hence, all selectivities determined for reactions with solvent mixtures originated from the oxidation of glycerol and not from the solvent. It is remarkable that the Cu/CoO catalyst is not capable of oxidizing any solvent even at high concentrations, emphasizing the fact that CuCo-based catalysts preferentially oxidized glycerol.

Generally, a decrease in the glyceric acid and glycolic acid selectivity was observed with higher solvent content, while selectivities toward oxalic acid and formic acid increased. This indicates that glyceric and glycolic acids were further oxidized to oxalic and formic acid. In the case of methanol and ethanol as co-solvents, the oxalic acid selectivity decreased at 50 vol% solvent content, whereas the selectivity toward formic acid increased more steeply compared to the reactions conducted with *n*-propanol and *tert*-butanol. This means that the further oxidation of oxalic acid to formic acid was more favored with methanol and ethanol as co-solvents. The changes in the selectivities with increased conversions are in good accordance with a consecutive reaction pathway for glycerol oxidation.³⁰ Glyceric and glycolic acid were formed as primary products. The formation of C₂ products (glycolic acid) concomitantly led to C₁ products, *i.e.*, formic acid and CO₂; carbon mass balances were well above 95% so we can exclude large amounts of CO₂ formation.

The trend and role of co-solvent are in good agreement with our previous study on the Cu/Al₂O₃ catalyst where the enhanced activity was attributed to the varied solvent polarity upon the addition of a co-solvent. The same behaviour was also found for the reaction performed over the Cu/CoO catalyst reported in this study. Fig. 3 shows a plot of the glycerol

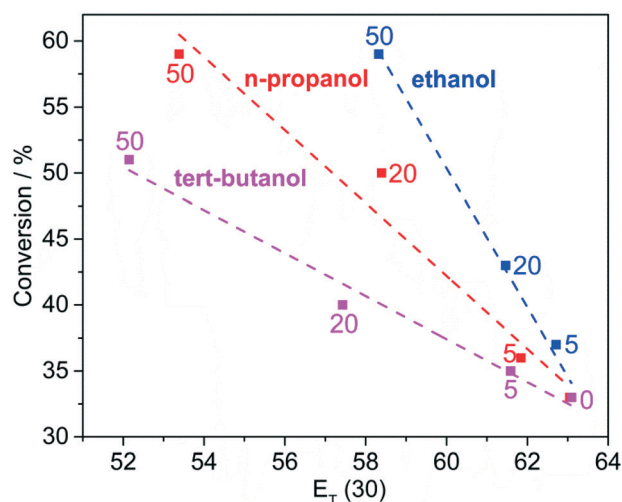


Fig. 3 Glycerol conversion in water/co-solvent mixtures with different vol% of the co-solvent (indicated as numbers next to data point) as a function of the solvatochromic parameter $E_T(30)$ together with the linear regression lines. Reaction conditions: 1 g L⁻¹ catalyst, 15 mL of 0.05 M aqueous glycerol solution, 4 : 1 NaOH to glycerol ratio, 90 °C, 10 bar pure O₂, 1 h reaction time, 750 rpm stirring speed.



conversion against the $E_T(30)$ solvent polarity, in which the glycerol conversion in the individual co-solvent/water mixtures with different ratios showed good linear correlations with the solvent polarity. The decreased solvent polarity can result in a lower degree of solvation of the polar reactant glycerol, which facilitates the interaction between glycerol and the catalyst surface. It should be kept in mind that if the solvent polarity was the only factor that impacts the catalytic activity, similar conversions at similar solvent polarities would be expected for all solvents. However, in the case of methanol, a lower conversion was observed. Thus, the solvents were expected to have an additional effect, which will be evaluated in detail in the following section.

CuCo-based catalysts undergo drastic changes in crystal phases during glycerol oxidation reactions, which are beneficial for the catalytic activity. In particular, we could determine that CoO(OH) in contact with Cu species are the active phases for glycerol oxidation.³⁰ Cu/CoO is not stable under oxidative and alkaline reaction conditions and it is transformed to its oxide and oxyhydroxide counterparts. Accordingly, it was investigated herein whether the reaction medium had an effect on the formation of different crystal phases and if this could be the reason for the higher conversion and for the diminished conversion in the presence of methanol. As shown in Fig. 4, the fresh Cu/CoO catalyst consists of metallic Cu, and CoO and small amounts of an unknown phase. Generally, after 1 h reaction time in various solvent mixtures, CoO(OH) and CuO were formed, whereas the amount of metallic Cu diminished. Additionally, small amounts of Co_3O_4 and/or $\text{Cu}_x\text{Co}_y\text{O}_4$ spinel were formed. It should be kept in mind that due to the very similar lattice parameters, it is not possible to distinguish between the Co_3O_4 and $\text{Cu}_x\text{Co}_y\text{O}_4$ spinel phases solely by XRD analysis.^{29,30} It is evident that the various crystal phases were formed to different extents depending on the nature of the solvent. Moreover,

the XRD analysis revealed that the extent of diminished metallic Cu also varied depending on the solvent. Pure water as the reaction solvent retained the highest amount of metallic Cu in the sample, while XRD patterns for reactions performed in methanol or *tert*-butanol as co-solvent showed no reflections for metallic Cu, whereas the patterns for ethanol and *n*-propanol still had small reflections.

Remarkably, in 50 vol% methanol as the reaction solvent, Cu/CoO catalysts exhibited intense reflections of Co_3O_4 and/or $\text{Cu}_x\text{Co}_y\text{O}_4$ spinel but no reflections of the catalytically active CoO(OH) phase, as evidenced by the missing reflection at 22.5° . As mentioned before, the CoO(OH) phase is important to obtain an active catalyst for glycerol oxidation. Indeed, by employing solely the spinel phase of $\text{Cu}_x\text{Co}_y\text{O}_4$ (obtained by only using the calcined sample; see Experimental section) for glycerol oxidation in water under the same conditions as depicted in Fig. 2, only 5% conversion was obtained. This is in line with the poor catalytic activity observed for the catalyst suspended in methanol as co-solvent (Fig. 2a). Consequently, the lower conversion in the presence of methanol can be explained by the suppression of the formation of the active CoO(OH) phase.

Materials suspended in 50 vol% *n*-propanol and *tert*-butanol showed a noticeably higher CoO(OH) content after 1 h reaction time compared to the catalyst suspended in water. This might be an indication of the improved catalytic performance in these co-solvents. On the other hand, in the case of 50 vol% ethanol as co-solvent, the XRD pattern was comparable to the pattern obtained after 1 h reaction in water, except for the stronger diminished reflections for metallic Cu. Thus, the solvent polarity and the influence of the co-solvent on the formation of the catalytically active phases both play important roles in the Cu/Co system. Fresh catalysts and catalysts used for glycerol oxidation experiments in water, 50 vol% methanol/water, 50 vol% ethanol/water, and 50 vol% *n*-propanol/water mixtures were further analyzed by XPS (Fig. 5) in order to examine any changes in the catalyst surface induced by the solvent. A detailed deconvolution of the XPS signals in order to quantify the amount of each surface species can lead to ambiguous results due to the overlap of the signals from different species present in the catalyst. Hence, no quantification of the various species was performed in this study.

The Co 2p spectra are depicted in Fig. 5a). The co-existence of $\text{Co}_3\text{O}_4/\text{Cu}_x\text{Co}_y\text{O}_4$ and CoO(OH) (as determined by XRD analysis) and, with this, the overlap of Co^{2+} and Co^{3+} species in the photoelectron spectra complicate the accurate and reliable fitting of the spectra. For the identification of Co oxidation states, not the main Co 2p photopeaks but the satellite peaks are essential. Despite the fact that the samples experienced different solvent environments, the spectra obtained for all four samples after the reaction were nearly identical. On the other hand, distinct differences were observed for the fresh catalyst. The surface of the fresh catalyst consisted of Co^{2+} in the form of CoO, as determined by XRD analysis (Fig. 4). This became clear by comparing the profiles

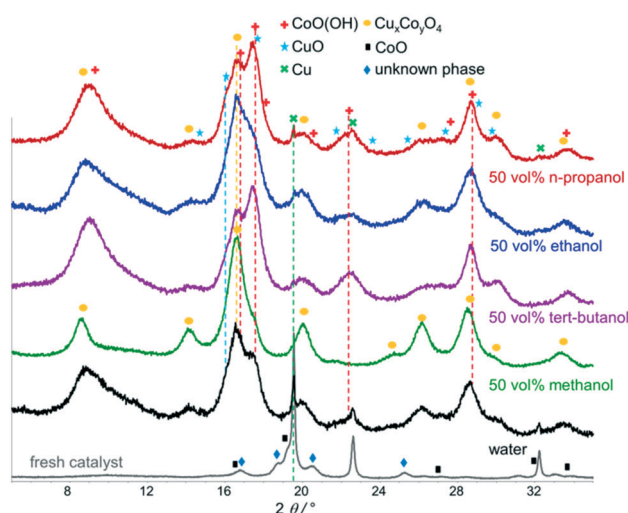


Fig. 4 XRD diffractograms ($\text{MoK}\alpha_1$ radiation) for freshly prepared Cu/CoO and after glycerol oxidation experiments in pure water and in different solvent mixtures. For reaction conditions see the caption of Fig. 2.



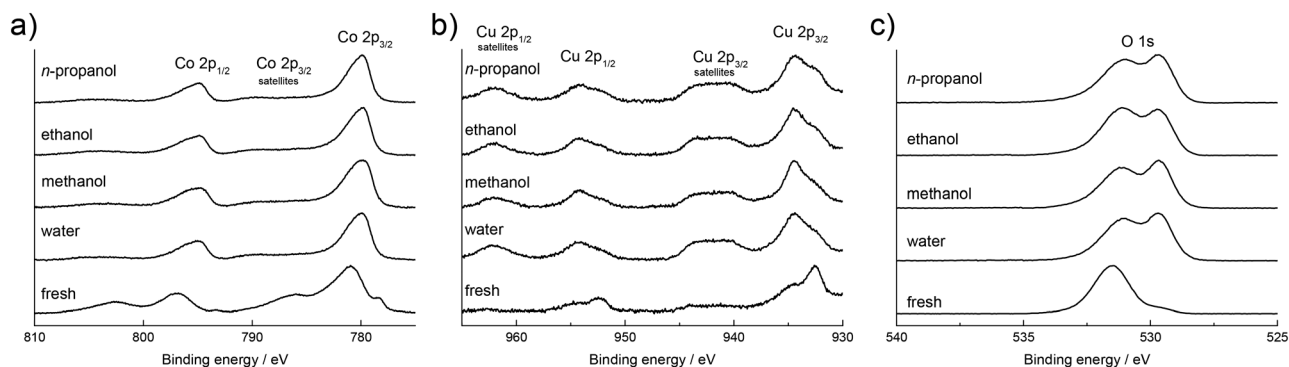


Fig. 5 XPS spectra of Cu/CoO catalysts (Co (a), Cu (b) and O (c)) before (fresh) and after glycerol oxidation experiments in water, 50 vol% methanol/water, 50 vol% ethanol/water and 50 vol% *n*-propanol/water mixtures.

with the Co(OH)_2 reference material where Co^{2+} is present (ESI† Fig. S1) and with the XPS spectra for CoO reported by Biesinger *et al.*⁴⁵ Furthermore, the peak at 778.4 eV reveals that Co was present in small amounts on the surface most probably in the form of metallic Co, which could not be observed in the XRD pattern. Apparently, metallic Co was formed in small crystallites that were below the detection limit of the XRD analysis. In the case of the spent catalysts, it was concluded by comparing the XPS spectra with results reported in the literature^{45–47} and with reference materials that the surfaces consisted of a mixture of Co^{2+} and Co^{3+} species as expected for Co_3O_4 . Due to the similar Co 2p spectra of Co_3O_4 and $\text{Cu}_x\text{Co}_y\text{O}_4$, it is not possible to distinguish the phases by XPS analysis.^{48,49} The presence of CoO and Co(OH)_2 in the spent catalysts can be excluded due to the shape of the $\text{Co}^{3+}/\text{Co}^{2+}$ shake-up satellites between 785 and 790 eV (reference XPS spectra of neat Co_3O_4 , CoO(OH) , and Co(OH)_2 are presented in the ESI† Fig. S1). Indeed, the oxidizing conditions during the reaction make it unlikely that CoO and Co(OH)_2 could persist on the surface. This was also confirmed by the XRD results, which also do not show any reflections of these phases (reference patterns of samples consisting of neat Co(OH)_2 , CoO(OH) , and Co_3O_4 crystalline phases are presented in the ESI† Fig. S2). It is important to emphasize that the XRD results for the spent catalysts show a higher CoO(OH) content for samples used in *n*-propanol than for the samples used in ethanol mixtures. XPS analysis confirmed that the surface composition of the catalyst changes slightly after catalytic reactions. The reaction in water resulted in a cobalt to copper atomic ratio of 2.1, while this ratio increased for water–alcohol mixtures, which indicates that surface copper was leached out significantly in the presence of alcohol as co-solvent.

The comparison of the Cu 2p XPS spectra showed no significant changes in the Cu $2p_{3/2}$, $2p_{1/2}$, and satellite signals collected for catalysts used in water and in the solvent mixtures (Fig. 5b). By comparison with the XPS spectra of Cu/Cu₂O, CuO, and Cu(OH)_2 and fitted Cu $2p_{3/2}$ signals reported by Biesinger *et al.*,⁵⁰ it can be concluded that the surface of the spent catalysts consisted of a mixture of Cu^{2+} incorporated in CuO and in Cu(OH)_2 . The $2p_{3/2}$ binding energies for

both species are very close to each other but the shapes of the satellites are significantly different. Beside Cu^{2+} , Cu^0 or Cu^+ were also present as the shoulders of the main Cu $2p_{3/2}$ peak at around 932.4 eV. Cu^0 and Cu^+ can only be distinguished unambiguously by their Auger peaks but the Auger peak overlaps with the signal coming from Cu^{2+} . This makes the assignment difficult. The fresh catalyst contained higher amounts of Cu^0/Cu^+ on the surface, which is consistent with the XRD pattern where metallic Cu was detected. For the fresh catalyst, the surface also contained CuO or Cu(OH)_2 as revealed by the weak satellite peaks.

The O 1s spectra do not show distinct differences between the spent catalysts (Fig. 5c). The profiles show a superposition of the O 1s signals for Co_3O_4 , CoO(OH) , CuO, Cu(OH)_2 , and Cu_2O . Thus, an accurate assignment of the signals to each species is difficult. The shape of the O 1s peak at 529.7 eV resembles the profile reported by Yang *et al.* for CoO(OH) ⁴⁷ and is in good agreement with the assigned species derived from the Cu 2p and Co 2p spectra. A comparison with the O 1s values reported by Biesinger *et al.*^{45,50} and the reference spectra presented in the ESI† (Fig. S1), showed that the peak at 531.1 eV can be assigned to the O 1s signal of Cu(OH)_2 and/or CuO. It has to be emphasized that the O 1s profile for pure Co_3O_4 (ESI† Fig. S1) looks significantly different from the O 1s profiles presented in Fig. 5c). Hence, this is clear evidence that CoO(OH) and Cu(OH)_2 species had to also be present on the catalyst surface. The fresh catalyst contained Co(OH)_2 and/or Cu(OH)_2 species on the surface, which was deduced by comparing the XPS spectrum with the reference spectra (ESI†) and with the profiles reported in the literature.^{45,47} The amount of CoO was expected to be quite low according to the spectrum. It should be emphasized that the Co 2p and Cu 2p spectra do not exclude the presence of Co(OH)_2 and Cu(OH)_2 on the surface. A further impact of the co-solvent lies in the dissolved ions during the catalytic reaction. Cu ions tend to leach out from solid CuCo-based catalysts to a certain extent during glycerol oxidation experiments, whereas no Co species can be found in the reaction solution.³⁰ The dissolved ions might contribute to the catalytic activity resulting in a cocktail-type system of catalysts – a phenomenon reported in the literature.⁵¹ Furthermore, the



Table 1 Leached Cu amounts in ppm during glycerol oxidation (1 h reaction time) over Cu/CoO catalysts in pure water or solvent mixtures (50% water/50% solvent). Reaction conditions: 1 g L⁻¹ catalyst, 15 mL of 0.05 M aqueous glycerol solution, 4:1 NaOH to glycerol, 90 °C, 10 bar pure O₂, 1 h reaction time, 750 rpm stirring speed

Solvent	Cu concentration/ppm
Water	33
Methanol	72
Ethanol	63
<i>n</i> -Propanol	48
<i>tert</i> -Butanol	95

capability of homogeneous Cu complexes in the presence of oxidants to oxidize glycerol was reported as well.⁵² Hence, it is of interest to elucidate whether the different solvent mixtures have an influence on the Cu ion dissolution and their catalytic activity. After the separation of the solid catalyst, the reaction solution was further analyzed for dissolved Cu species. As listed in Table 1, reactions performed in water for 1 h showed a Cu concentration of 33 ppm, whereas reactions performed in 50 vol% alcohol/water mixtures showed a significantly increased Cu concentration of up to 95 ppm. Experiments under the same reaction conditions were performed with dissolved Cu(NO₃)₂ to investigate the contribution of the homogeneous Cu species (Table 2).

An influence of the counter ion NO₃⁻ was excluded since the reactions conducted with CuSO₄ showed the same catalytic performances. As seen in Table 2, the reactions conducted in water showed a glycerol conversion of 26%. Please note that a Cu concentration of 50 ppm was used for these experiments, which was higher than the determined concentration of dissolved Cu in pure water for the heterogeneously catalyzed reactions (Table 1). Furthermore, it is important to mention, that the Cu concentrations presented in Table 1 are the values after 1 h of reaction. Consequently, since Cu is expected to leach out during the course of the reaction, the mean concentration of dissolved Cu species is expected to be much lower. The catalytic results shown in Table 2 reveal that the solvent indeed had an effect on the catalytic activity of the dissolved Cu ions. The use of methanol as co-solvent resulted in a total loss in activity with no glycerol conversion. This supports the conclusions obtained by XRD analysis. Apparently, the methanol not only alters the bulk phase of the catalyst into the undesired Co₃O₄/Cu_xCo_yO₄

crystal phase but also hinders the dissolved Cu species to contribute to the reaction process. It has been shown that using methanol as solvent (compared to dimethyl sulfoxide, tetrahydrofuran, and acetonitrile) resulted in a drastic drop in activity for the oxidative cleavage reactions of secondary alcohols to acids over homogeneous Cu catalysts.⁵³ This is in line with our observations for glycerol oxidation over Cu(NO₃)₂ catalysts.

The homogeneously catalyzed reaction with the co-solvent *tert*-butanol showed the same glycerol conversion as obtained in pure water (Table 2) when the same amount of Cu(NO₃)₂ was used. However, the fact that more Cu ions were leached from the solid catalyst for the reaction performed in *tert*-butanol (Table 1) implies that the homogeneously catalyzed reaction had a higher contribution to the glycerol conversion, compared to the reaction performed in water. On the other hand, the reaction performed with *n*-propanol exhibited a glycerol conversion of only 15% (Table 2), which is far below the conversion obtained over the solid Cu/CoO catalyst (Fig. 1a). Also, in the case of pure water as the solvent, the glycerol conversion obtained with Cu(NO₃)₂ did not reach the value obtained with Cu/CoO. Hence, a solvent effect that only affects the dissolved Cu species can be excluded.

In addition, by assuming the sole interaction of the solvent with the dissolved Cu species, the reactions performed with *tert*-butanol should show higher glycerol conversions compared to the reactions performed with *n*-propanol, which was not observed. We showed in our previous study, by investigating the recyclability of the materials and by filtration tests, that the solid catalyst is crucial for the catalytic performance, despite the detected leached Cu species.³⁰ Also, we conducted recycling experiments (ESI,† Fig. S3) and it is clearly shown that for reactions conducted in pure water and 50 vol% ethanol/water mixtures, no decrease in glycerol conversion occurred for the first recycling run, which was performed in water. This implies that the solid catalyst plays a dominant role in the reaction, although a cocktail type of catalyst seems to be present for this system. Hence, it is reasonable to assume that the interaction of the solvent with the solid catalyst plays an important role. Apparently, the opposing and in some cases synergistic effects of the solvents on the solid catalyst and on the leached Cu species resulted in the observed catalytic performances presented in Fig. 1.

Table 2 Conversions and selectivities for glycerol oxidation over dissolved Cu(NO₃)₂ ions (50 ppm) in pure water or solvent mixtures (50% water/50% solvent). Reaction conditions: 15 mL of 0.05 M aqueous glycerol solution, 4:1 NaOH to glycerol, 90 °C, 10 bar pure O₂, 1 h reaction time, 750 rpm stirring speed

Solvent	Conversion/%	Selectivity/%						Carbon mass balance/%
		Glyceric acid	Oxalic acid	Glycolic acid	Tartronic acid	Formic acid	Lactic acid	
Water	26	27.5	2	53	2	15.5	0	99
Methanol	0	—	—	—	—	—	—	100
Ethanol	51	13.5	5	34	4	40	3.5	95
<i>n</i> -Propanol	15	25	5	42	3.5	18.5	6	98
<i>tert</i> -Butanol	24	50	0	46	4	0	0	87



In conclusion, the role of leached Cu species in the reaction medium cannot be neglected for the explanation of the increased activity of the solid catalysts for glycerol oxidation depending on the solvent. For instance, a 50 vol% ethanol/water reaction mixture not only results in higher amounts of leached Cu species in the reaction solution but also, most probably, in the improved catalytic performance of the dissolved Cu species by the solvent. However, the effect of the reaction medium on the crystal phase changes of the solid materials also plays an important role. The interplay of all these influences introduced herein results in the improved catalytic performance of the materials.

Conclusions

We have shown that it is possible to improve the catalytic performance of Cu/CoO catalysts by changing the reaction environment. Different monofunctional alcohols (methanol, ethanol, *n*-propanol, and *tert*-butanol) in various solvent/water ratios were used to evaluate the improvement in the glycerol oxidation reaction. Generally, the catalytic activity relates linearly to the solvent polarity for the individual co-solvents. In contrast, the presence of methanol resulted in a diminished catalytic activity. These contradicting behaviors can be explained by the formation of catalytically active CuO(OH), which forms in the presence of ethanol, *n*-propanol, and *tert*-butanol, but not in the presence of methanol and by the disabled catalytic activity of the dissolved Cu species in methanol containing solvents. The results presented herein give valuable insights into the effect of co-solvents on the crystal structure of Cu/Co-based catalysts and its activity towards the selective oxidation of glycerol, which can be employed to improve the cost-efficiency of transition metal-based catalysts by alteration of the solvent.

Conflicts of interest

There are no conflicts to declare.

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References

- G. Dodekatos, S. Schünemann and H. Tüysüz, *ACS Catal.*, 2018, **8**, 6301–6333.
- D. T. Johnson and K. A. Taconi, *Environ. Prog.*, 2007, **26**, 338–348.
- R. Ciriminna, C. Della Pina, M. Rossi and M. Pagliaro, *Eur. J. Lipid Sci. Technol.*, 2014, **116**, 1432–1439.
- C. H. Zhou, J. N. Beltramini, Y. X. Fan and G. Q. Lu, *Chem. Soc. Rev.*, 2008, **37**, 527–549.
- F. Jerome, Y. Pouilloux and J. Barrault, *ChemSusChem*, 2008, **1**, 586–613.
- D. M. Alonso, S. G. Wettstein and J. A. Dumesic, *Chem. Soc. Rev.*, 2012, **41**, 8075–8098.
- M. Besson, P. Gallezot and C. Pinel, *Chem. Rev.*, 2014, **114**, 1827–1870.
- B. Katryniok, H. Kimura, E. Skrzynska, J. S. Girardon, P. Fongarland, M. Capron, R. Ducoulombier, N. Mimura, S. Paul and F. Dumeignil, *Green Chem.*, 2011, **13**, 1960–1979.
- S. E. Davis, M. S. Ide and R. J. Davis, *Green Chem.*, 2013, **15**, 17–45.
- A. Villa, N. Dimitratos, C. E. Chan-Thaw, C. Hammond, L. Prati and G. J. Hutchings, *Acc. Chem. Res.*, 2015, **48**, 1403–1412.
- V. Augugliaro, H. A. H. El Nazer, V. Loddo, A. Mele, G. Palmisano, L. Palmisano and S. Yurdakal, *Catal. Today*, 2010, **151**, 21–28.
- V. Augugliaro, M. Bellardita, V. Loddo, G. Palmisano, L. Palmisano and S. Yurdakal, *J. Photochem. Photobiol. C*, 2012, **13**, 224–245.
- C. Minero, A. Bedini and V. Maurino, *Appl. Catal., B*, 2012, **128**, 135–143.
- A. Molinari, A. Maldotti, A. Bratovcic and G. Magnacca, *Catal. Today*, 2013, **206**, 46–52.
- Y. Zhang, N. Zhang, Z. R. Tang and Y. J. Xu, *Chem. Sci.*, 2013, **4**, 1820–1824.
- N. A. Hermes, A. Corsetti and M. A. Lansarin, *Chem. Lett.*, 2014, **43**, 143–145.
- T. Jedsukontorn, V. Meeyoo, N. Saito and M. Hunsom, *Chem. Eng. J.*, 2015, **281**, 252–264.
- B. Zhou, J. Song, H. Zhou, L. Wu, T. Wu, Z. Liu and B. Han, *RSC Adv.*, 2015, **5**, 36347–36352.
- S. Schünemann, G. Dodekatos and H. Tüysüz, *Chem. Mater.*, 2015, **27**, 7743–7750.
- G. Dodekatos and H. Tüysüz, *Catal. Sci. Technol.*, 2016, **6**, 7307–7315.
- P. McMorn, G. Roberts and G. J. Hutchings, *Catal. Lett.*, 1999, **63**, 193–197.
- C. H. Zhou, J. N. Beltramini, C. X. Lin, Z. P. Xu, G. Q. Lu and A. Tanksale, *Catal. Sci. Technol.*, 2011, **1**, 111–122.
- G. Wu, X. Wang, Y. Huang, X. Liu, F. Zhang, K. Ding and X. Yang, *J. Mol. Catal. A: Chem.*, 2013, **379**, 185–191.
- G. M. Lari, C. Mondelli and J. Pérez-Ramírez, *ACS Catal.*, 2015, **5**, 1453–1461.
- C. Crotti and E. Farnetti, *J. Mol. Catal. A: Chem.*, 2015, **396**, 353–359.
- X. Jin, M. Zhao, C. Zeng, W. J. Yan, Z. W. Song, P. S. Thapa, B. Subramaniam and R. V. Chaudhari, *ACS Catal.*, 2016, **6**, 4576–4583.
- X. L. Wang, G. D. Wu, X. F. Liu, C. F. Zhang and Q. B. Lin, *Catal. Lett.*, 2016, **146**, 620–628.
- J. H. Xie, K. H. Yin, A. Serov, K. Artyushkova, H. N. Pham, X. H. Sang, R. R. Unocic, P. Atanassov, A. K. Datye and R. J. Davis, *ChemSusChem*, 2017, **10**, 359–362.



- 29 X. Deng, G. Dodekatos, K. Pupovac, C. Weidenthaler, W. N. Schmidt, F. Schüth and H. Tüysüz, *ChemCatChem*, 2015, 7, 3832–3837.
- 30 G. Dodekatos and H. Tüysüz, *ChemCatChem*, 2017, 9, 610–619.
- 31 C. D'Agostino, T. Kotionova, J. Mitchell, P. J. Miedziak, D. W. Knight, S. H. Taylor, G. J. Hutchings, L. F. Gladden and M. D. Mantle, *Chem. – Eur. J.*, 2013, 19, 11725–11732.
- 32 C. D'Agostino, M. R. Feavioir, G. L. Brett, J. Mitchell, A. P. E. York, G. J. Hutchings, M. D. Mantle and L. F. Gladden, *Catal. Sci. Technol.*, 2016, 6, 7896–7901.
- 33 E. Skrzynska, A. Wondolowska-Grabowska, M. Capron and F. Dumeignil, *Appl. Catal., A*, 2014, 482, 245–257.
- 34 E. Skrzynska, S. Zaid, J.-S. Girardon, M. Capron and F. Dumeignil, *Appl. Catal., A*, 2015, 499, 89–100.
- 35 S. Schünemann, F. Schüth and H. Tüysüz, *Catal. Sci. Technol.*, 2017, 7, 5614–5624.
- 36 H. Fukuda, A. Kondo and H. Noda, *J. Biosci. Bioeng.*, 2001, 92, 405–416.
- 37 J. M. Encinar, J. F. González, J. J. Rodríguez and A. Tejedor, *Energy Fuels*, 2002, 16, 443–450.
- 38 H. Tüysüz, Y. Liu, C. Weidenthaler and F. Schüth, *J. Am. Chem. Soc.*, 2008, 130, 14108–14110.
- 39 H. Tüysüz, C. Weidenthaler and F. Schüth, *Chem. – Eur. J.*, 2012, 18, 5080–5086.
- 40 N. Dimitratos, J. A. Lopez-Sanchez, S. Meenakshisundaram, J. M. Anthonykutti, G. Brett, A. F. Carley, S. H. Taylor, D. W. Knight and G. J. Hutchings, *Green Chem.*, 2009, 11, 1209–1216.
- 41 J. Tokunaga, *J. Chem. Eng. Data*, 1975, 20, 41–46.
- 42 R. W. Cargill, *J. Chem. Soc., Faraday Trans. 1*, 1976, 72, 2296–2300.
- 43 M. Geng and Z. Duan, *Geochim. Cosmochim. Acta*, 2010, 74, 5631–5640.
- 44 D. Tromans, *Hydrometallurgy*, 1998, 48, 327–342.
- 45 M. C. Biesinger, B. P. Payne, A. P. Grosvenor, L. W. M. Lau, A. R. Gerson and R. S. Smart, *Appl. Surf. Sci.*, 2011, 257, 2717–2730.
- 46 N. S. McIntyre and M. G. Cook, *Anal. Chem.*, 1975, 47, 2208–2213.
- 47 J. Yang, H. Liu, W. N. Martens and R. L. Frost, *J. Phys. Chem. C*, 2010, 114, 111–119.
- 48 M. De Koninck, S. C. Poirier and B. Marsan, *J. Electrochem. Soc.*, 2006, 153, A2103–A2110.
- 49 A. La Rosa-Toro, R. Berenguer, C. Quijada, F. Montilla, E. Morallón and J. L. Vázquez, *J. Phys. Chem. B*, 2006, 110, 24021–24029.
- 50 M. C. Biesinger, L. W. M. Lau, A. R. Gerson and R. S. C. Smart, *Appl. Surf. Sci.*, 2010, 257, 887–898.
- 51 V. P. Ananikov and I. P. Beletskaya, *Organometallics*, 2012, 31, 1595–1604.
- 52 M. V. Kirillova, A. M. Kirillov, D. Mandelli, W. A. Carvalho, A. J. L. Pombeiro and G. B. Shul'pin, *J. Catal.*, 2010, 272, 9–17.
- 53 M. Wang, J. Lu, L. Li, H. Li, H. Liu and F. Wang, *J. Catal.*, 2017, 348, 160–167.

