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Catalytic hydrothermal transformations of polyols to organic acids and hydrogen in aqueous alkaline media

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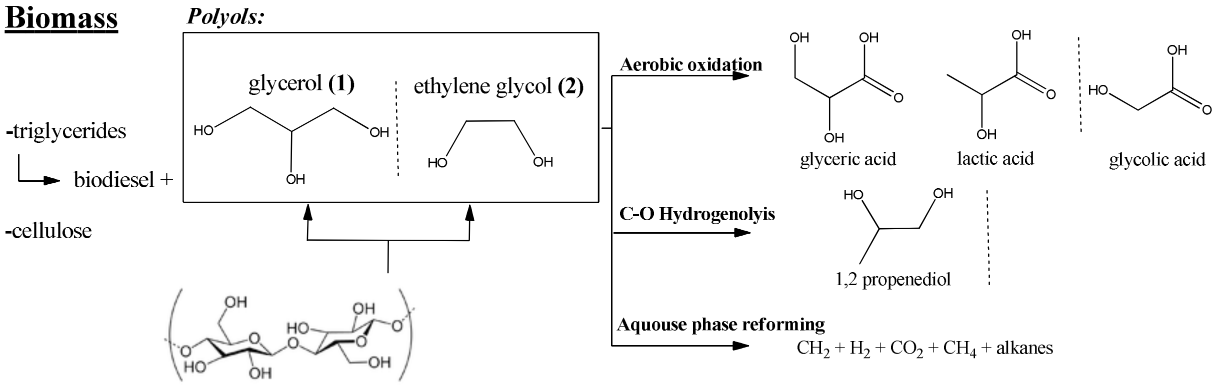
In this paper we show that carbon nanofiber supported copper and nickel nanoparticles can selectively transform ethylene glycol and glycerol into value added oxygenates (organic acids) under anaerobic aqueous conditions. During aqueous phase oxidation Cu based catalysts showed a nearly quantitative yield (96% selectivity at 82% conversion) of glycolic acid from ethylene glycol. The reaction was carried out under alkaline conditions at relatively mild temperatures (150-180 ºC) and produced H_2 as co-product. The high selectivity towards glycolic acid was independent of the temperature. For glycerol oxidation a high selectivity (67% at full conversion) towards lactic acid was observed using Cu with competitive formation of glyceric acid, 1,2-propanediol tartronic acid and formation of H_2 as co-product. The activity of Ni was comparable to that of Cu but it was less selective for the formation of desired oxygenates, glycolic acid (31%) and lactic acid (24%), due to the formation of formic acid.

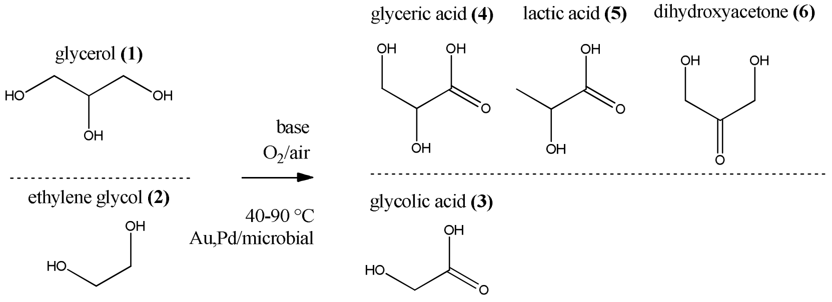
Introduction

Plant derived biomass can serve as a primary source for the synthesis of renewable chemicals and fuels. Cellulose is of special interest in this regard as it is one of the major components in biomass and does not compete directly with food production. It has been shown that cellulose can be directly converted into smaller polyols like glycerol **(1)** and ethylene glycol **(2)** [1-3] which can serve as renewable building blocks for the fine-chemical industry. In addition glycerol is widely available as a by-product from biodiesel production (see scheme 1). Known strategies for the valorisation of these polyols are outlined in scheme 1 and include oxidation, hydrogenolysis of a C-O bond [4, 5] and aqueous phase reforming [6].



Scheme 1: Roadmap summarizing different strategies for the valorization of glycerol and ethylene glycol obtained from cellulose or biodiesel production via aqueous phase processes; (an)aerobic oxidation, hydrogenolysis and aqueous phase reforming.

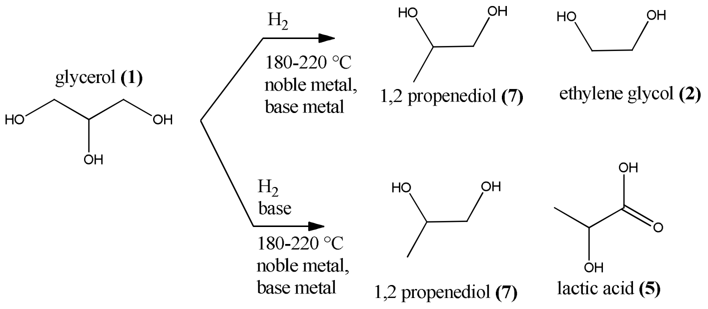
The aerobic oxidation (scheme 2) of small polyols can be accomplished via chemical and biochemical routes. For instance, glycolic acid (2-hydroxyethanoic acid) **(3)** can be produced by aerobic fermentation of ethylene glycol with high selectivity [7, 8]. Value added glycerol derivatives like glyceric acid (2,3-dihydroxypropanoic acid) **(4)** [9] and lactic acid **(5)** [10, 11] can be produced via a variety of microbial processes [12]. These chemicals are valuable products for the pharmaceutical, cosmetic and polymer industry [13].



Scheme 2. Possible products obtained by the catalytic transformation of glycerol and ethylene glycol via chemical or biochemical aerobic oxidation.

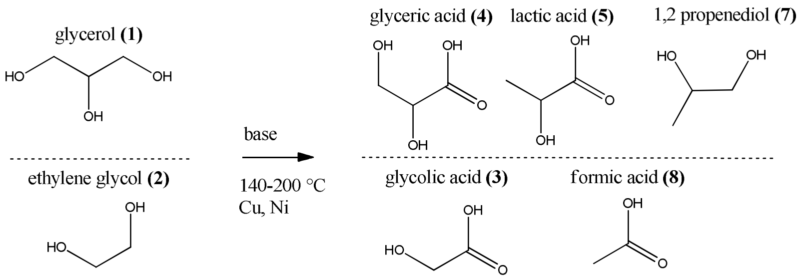
Since these biochemical processes suffer from low space-time-yields alternative chemical processes using heterogeneous catalysts have also been explored. The liquid phase catalytic oxidation of glycerol with heterogeneous Au and Pd catalysts yields dihydroxy acetone **(6)** plus a variety of organic acids, most notably glyceric acid **(4)** [14, 15]. High yields (85%) of lactic acid **(5)** have also been reported with an Au-Pt/TiO_2 catalyst [16].

A chemical route is also known for the selective production of glycolic acid **(3)** by catalytic oxidation of ethylene glycol using Cu [17] or precious metal (Au Pd, and Au–Pd bimetallic) catalysts [18] and with Au and Pd supported on carbon [13, 19]. These processes are conducted at low temperatures (40-90 ºC) using molecular oxygen and typically require alkaline conditions to in order to achieve appreciable activity.



Scheme 3. Possible products obtained via the hydrogenolysis of glycerol.

Next to oxidation the hydrogenolysis of polyols is another route for the production of value added chemicals (scheme 3). This process requires the addition of hydrogen at high pressures (20-50 bar) at 180-220 °C. For instance the production of 1,2-propanediol **(7)** from glycerol has been investigated extensively with noble and base metal catalyst [3, 4, 20-24]. However d'Hondt et al. were, to the best or our knowledge, the first to report that hydrogenolysis also proceeds without external H_2 addition in inert atmosphere. In that case aqueous phase reforming [6] of a part of the glycerol feed to H_2 and CO_2 yields the required hydrogen in-situ [25], which has since then been corroborated by others [26-28]. Glycerol hydrogenolyis has been studied under acidic [29] and alkaline [21] conditions and, besides the type of catalysts, also pH and gas phase composition were shown to affect selectivity [30, 31]. Higher 1,2-propanediol **(7)** and ethylene glycol selectivities were obtained under hydrogen atmosphere while more gaseous hydrocarbons were formed under inert atmosphere. Interestingly also lactic acid **(5)** was observed as a by-product in the hydrogenolysis of glycerol without external hydrogen addition [26]. Several studies showed that the presence of base significantly enhanced the reaction rate but shifted the selectivity from 1,2-propanediol **(7)** to lactic acid **(5)** as major product, both with a hydrogen atmosphere [21] or under inert atmosphere (i.e. no external hydrogen addition) [31, 32].



Scheme 4. Possible products obtained via hydrothermal anaerobic oxidation of glycerol and ethylene glycol.

The synthesis of lactic acid without external oxygen or hydrogen using metal catalysts is an interesting alternative to the aerobic chemical routes and to the biochemical route for application where enantio pure lactic acid **(5)** is not required, e.g. when lactic acid is converted further into propionic acid or acrylic acid. In most cases noble metals (Pt and Ru [21] or Ir and Rh [30, 31] were investigated. Obviously the use of non-noble metal catalyst would be advantageous. Recently Roy et al. [33] showed that copper catalysts are active and selective for the production of lactic acid **(5)** from glycerol in alkaline aqueous solutions and reported high selectivities at relatively low temperatures (200-240 ºC). Unfortunately only bulk copper catalysts were stable and supported Cu/SiO_2 and CuO/Al_2O_3 deactivated due to support degradation in the alkaline reaction medium.

In this paper we investigate both ethylene glycol and glycerol transformations (scheme 4) using copper and nickel nanoparticles supported on carbon nanofibers (CNF) as catalysts. The main advantage of the CNF support is its inertness under the basic conditions applied [34-36]. We show for the first time that ethylene glycol can be nearly quantitatively converted to glycolic acid **(3)** in alkaline aqueous solutions under anaerobic conditions at temperature between 150-180 °C over Cu while over Ni also formic acid **(8)** was observed as product. Pathways for the conversion of ethylene glycol and glycerol over Ni and Cu catalysts will be discussed.

Experimental procedures

Catalyst preparation

Carbon nanofibers were prepared by via a procedure explained elsewhere [35, 37]. The catalysts were prepared by incipient wetness impregnation of surface oxidized carbon nanofibers (CNF) with aqueous solutions of $Ni(NO_3).6H_2O$ (Acros 99%) or $Cu(NO_3).3H_2O$ (Acros 99.5%) to obtain metal loadings of 10 wt%. The impregnated samples were dried at 120 °C for 16 hours in static air. The dried samples were then reduced in a 150 ml/min flow of 30% v/v H_2/N_2 at 300 °C during 2 hours. Part of the reduced sample (Cu/CNF, Ni/CNF) was removed from the reactor in a glove box under nitrogen atmosphere and stored before further use. Prior to characterization part of the sample was slowly passivated by diffusion of air into the reactor through a 26 cm long tube with a 3 mm inner diameter (Cu/CNFp, Ni/CNFp). Part of the passivated sample was then calcined in static air at 250 °C for 2 hours to obtain the CuO/CNF and NiO/CNF catalyst.

Catalyst characterization

X-ray powder diffraction (XRD) was carried out using a Bruker-AXS D2 Phaser powder X-ray diffractometer with Co Kα radiation (λ = 1.79026 Å), between 2theta 20 – 80°. The experimental data was fitted with a pseudo-Voight function using a linear combination of the support (CNF) and metal contributions and a correction for instrumental broadening. Crystallite sizes were estimated from the Scherrer equation using a shape factor of 0.89.

Hydrogen chemisorption was performed on a Micromeretics ASAP 2020C instrument. The catalysts were reduced in H_2 (60 ml/min) at 300 °C for 2 h after which the system was outgassed (<1 Pa) at that temperature for 2 h. Subsequently the system was cooled to 150 °C and outgassed for another 0.5 h before the measurement was started. The monolayer H_2 uptake was found by extrapolating the linear part of the isotherm (150-600 mbar) to zero pressure. The monolayer uptake was calculated assuming a stoichiometry Ni:H of 1.

Transmission Electron Microscopy (TEM) analysis was carried out on an FEI Technai20F operated at 200 KeV. The samples were ground to a fine powder in a mortar and a small amount of powder was supported onto a thin carbon film on a copper grid.

Catalyst testing

Catalytic performance was evaluated using 10 ml batch autoclave reactors. The reactors were loaded in glove box with reduced catalyst (10-100 mg), base additive (0-0.65 M KOH) and substrate (0.1-10 wt%), typically a KOH/substrate molar ratio of 2 and a total liquid volume of 5 ml was used. The reactors were placed in a preheated oil bath and the reaction mixture was stirred using a magnetic spinner (1000 rpm). The reaction was continued at the desired temperature (150-180 ºC) for 0.5-15 h after which the reactors were quenched and depressurized. The reaction mixture was diluted 10x with water and adjusted to pH 2-3 by addition of diluted H_2SO_4.

The composition of the liquid phase was analysed by HPLC using a refractive index detector and an Animex Column (0.55 ml/min of 0.005 M H_2SO_4 at 60 °C and 35 bar). The substrate conversion ($X_{substrate}$) was calculated as moles of substrate reacted / moles of substrate fed x 100%. The product yields ($Y_{product}$) were calculated on a carbon basis as moles of carbon in the formed product / n times the moles of substrate fed to the reaction x100%, with n=2 for ethylene glycol and n=3 for glycerol. The selectivity ($S_{product}$) was calculated as $S_{product}= Y_{product}/ X_{substrate}$ x100%.

The gas phase composition was investigated by preforming the reaction in an Autoclave Engineers 100 ml batch EZE seal batch reactor. The reactor vessel was filled with 0.5 g catalyst (Ni/CNF or Cu/CNF) and 50 ml 1 wt% aqueous solution of ethylene glycol or glycerol. The reactor was pressurized to 5 bars with N_2 and heated (10 °C/min) to 150 °C and the reaction was continued for 4 hours before cooling down to room temperature. An increase in pressure was observed. To analyze the gas phase the reactor was depressurized via a back pressure regulator (BPR) and the gas composition was measured using an online GC (dual channel Intersience CompactGC with Poraplot Q and Molsieve 5A columns, equipped with TCD detectors using He and N_2 as carrier gas).

Turn-over-frequencies (TOFs) were calculated based on the moles of glycerol converted per hour and normalized by the number of metal surface sites of the fresh catalyst as measured by H_2 chemisorption (Ni) or calculated based on the average crystallites size observed from XRD (Cu).

Results and discussion

Effect of base promoters

The effect of the concentration and nature of the base on the conversion of ethylene glycol and on the product formation was investigated first. Table 1 shows the conversion of ethylene glycol and the corresponding product yields after 2 hours. Without base addition (entries 1-2), at neutral pH, almost no ethylene glycol was converted (<1%) over the Ni/CNF or Cu/CNF catalyst. We also performed blank experiments with base but without metal catalyst (entry 3-4). At a KOH: ethylene glycol ratio of 2 no activity was observed (conversion <1%). This is not surprising since the non-catalytic hydrothermal process (i.e without metal catalyst) is known to occur only at significantly higher temperatures (e.g 300 ºC) [16, 38, 39]. The CNF support did show some activity (conversion 5%) but no products were detected in significant quantity. Therefore we concluded that the observed conversion is due to the formation of undetectable condensation products or the result of adsorption of reactant on the support.

For the pre-reduced Cu/CNF catalyst different base to ethylene glycol ratios were explored (table 1, entry 5-8). The activity increased with increasing base concentration up to a ratio of 2 mole KOH per mole ethylene glycol. The maximum achievable conversion under the applied conditions was 20%. Glycolic acid and trace amounts of glycolaldehyde (2-hydroxyacetaldehyde) and oxalic acid (ethanedioic acid) were the only products observed. The type of base (KOH, NaOH or $Ca(OH)_2$ also affected the activity (table 1, entry 7, 9-10). We found that KOH was comparable to NaOH and superior to $Ca(OH)_2$. This is in agreement with effectiveness of base additives in the non-catalytic high temperature hydrothermal process [38] and probably mainly the result of the difference in pH as a result of the solubility of the base.

With Ni/CNF, at a KOH: ethylene glycol ratio of 2, a high conversion (49%) was realized in 2 hours and besides glycolic acid also formic acid was observed (entry 11). These results clearly show that the formation of glycolic acid from ethylene glycol requires both the metal catalyst and the base at this temperature. Therefore all further experiments were performed at a KOH: substrate ratio of 2.

Table 1. Effect of the substrate base ratio on the product yield and conversion of ethylene glycol.

Entry	Catalyst	Base	Base /EG (mol/ mol)	Conversion (%)	GOA yield (%C)
1	Cu/CNF	None	0	<1	<1
2	Ni/CNF	None	0	2	<1
3	None	KOH	2	<1	<1
4	CNF	KOH	2	5	<1

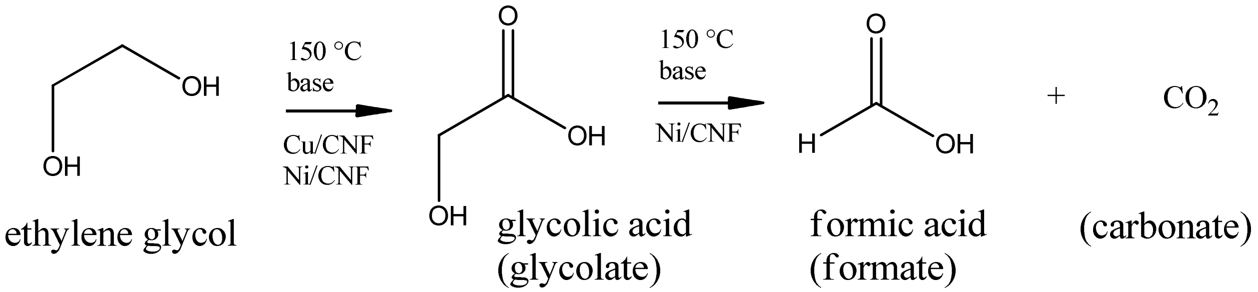
5	Cu/CNF	KOH	1.1	14	12
6	Cu/CNF	KOH	1.5	18	17
7	Cu/CNF	KOH	2	20	20
8	Cu/CNF	KOH	3	16	14
9	Cu/CNF	NaOH	2	17	16
10	Cu/CNF	$Ca(OH)_2$	2	8	7
11	Ni/CNF	KOH	2	49	29

Reaction conditions: 1 wt% EG, 150 ºC, 100 mg pre-reduced catalyst (Cu/CNF or Ni/CNF), reaction time 2 hours;

EG = ethylene glycol, GOA = glycolic acid.

Reaction profiles: Ni versus Cu

The activity of pre-reduced Ni/CNF and Cu/CNF was studied over time in order to gain insight into the evolution of the reaction products (figures 1 and 2). Figure 1 shows the conversion of ethylene glycol and product yield between 1 and 15 hours over (a) Ni/CNF and (b) Cu/CNF. For Ni/CNF we observed the formation of glycolic acid (as glycolate) and formic acid (as formate). Glycolic acid is the major product and reached an optimum yield of 37% after 4 hours and then decreased again to a final yield of 31% after 15 hours. Glycolic acid is apparently prone to secondary reactions. The decrease in glycolic acid yield between 4 and 16 hours was accompanied by an increase in formic acid yield. The formic acid yield continued to increase over the whole course of the reaction and a yield of 24% was reached after 15 hours. This suggests that glycolic acid is the intermediate product and degrades to formic acid (scheme 5). With Cu/CNF (figure 1b) glycolic acid was also formed but, unlike with Ni/CNF, did not react further to formic acid and glycolic acid was quantitatively obtained (scheme 5).



Scheme 5: Product formation in the anaerobic oxidation of ethylene glycol with Cu/CNF and Ni/CNF catalysts in aqueous alkaline media.

The product selectivities and carbon balances after 15 hour using the Cu and Ni catalyst and ethylene glycol and glycerol as feedstock are reported in table 2. With ethylene glycol as reactant and Cu/CNF as catalyst the selectivity towards glycolic acid was 98% while with Ni/CNF the selectivity was only 31%. In addition the carbon balance of the liquid phase shows a significant carbon deficit with the Ni/CNF catalyst. This might be explained by the formation of CO_2 which is captured by the base as will be discussed below. Table 2 also list the initial activity expressed as turn-over-frequency (TOF) at 20% conversion. These rates are normalized by the number of surface Ni and Cu atoms (288 µmol/g and 58 µmol/g respectively) estimated from H_2-chemisorption (Ni) and the XRD (Cu). The TOFs were comparable for the Ni and Cu catalyst, 11 and 14 h^{-1} respectively.

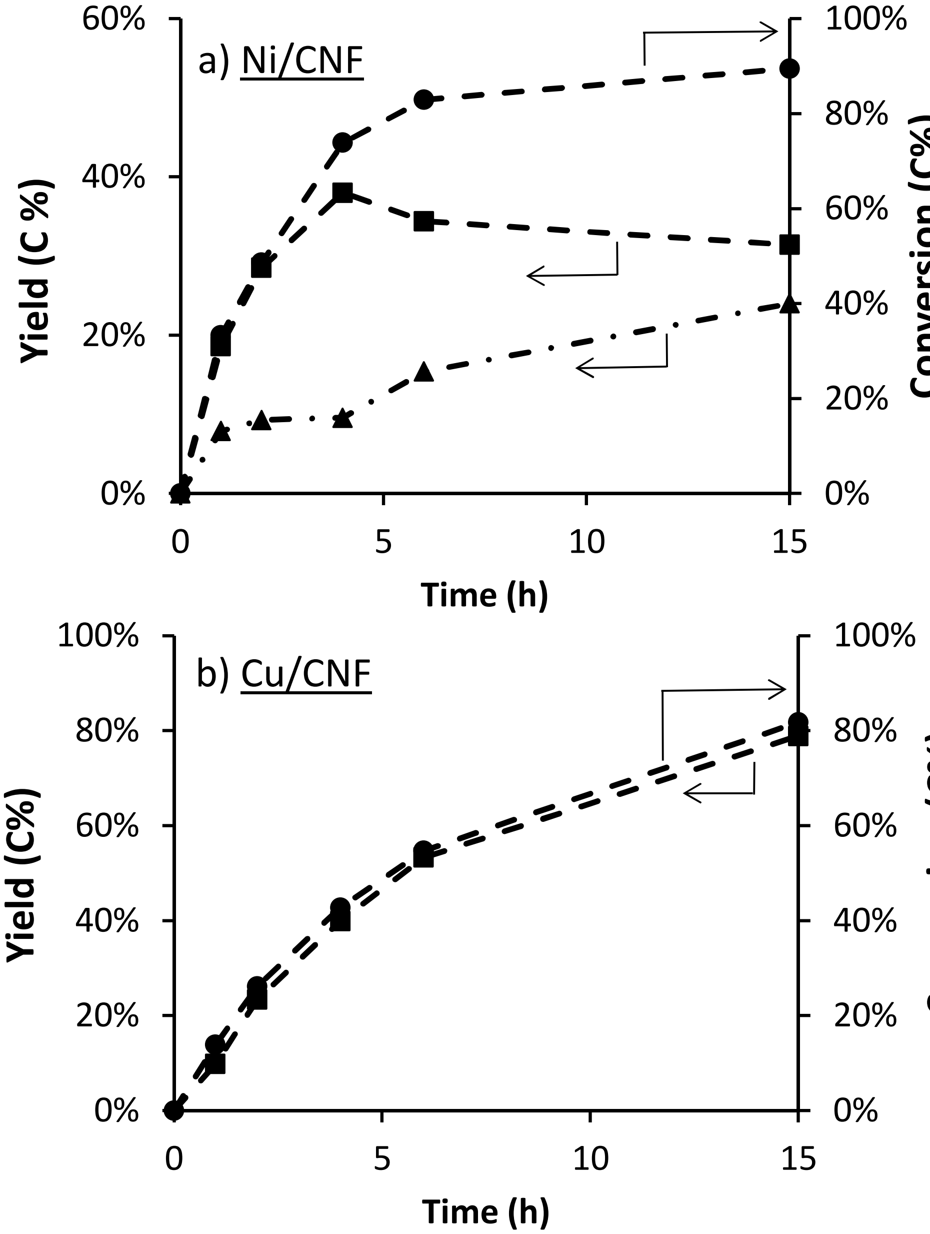
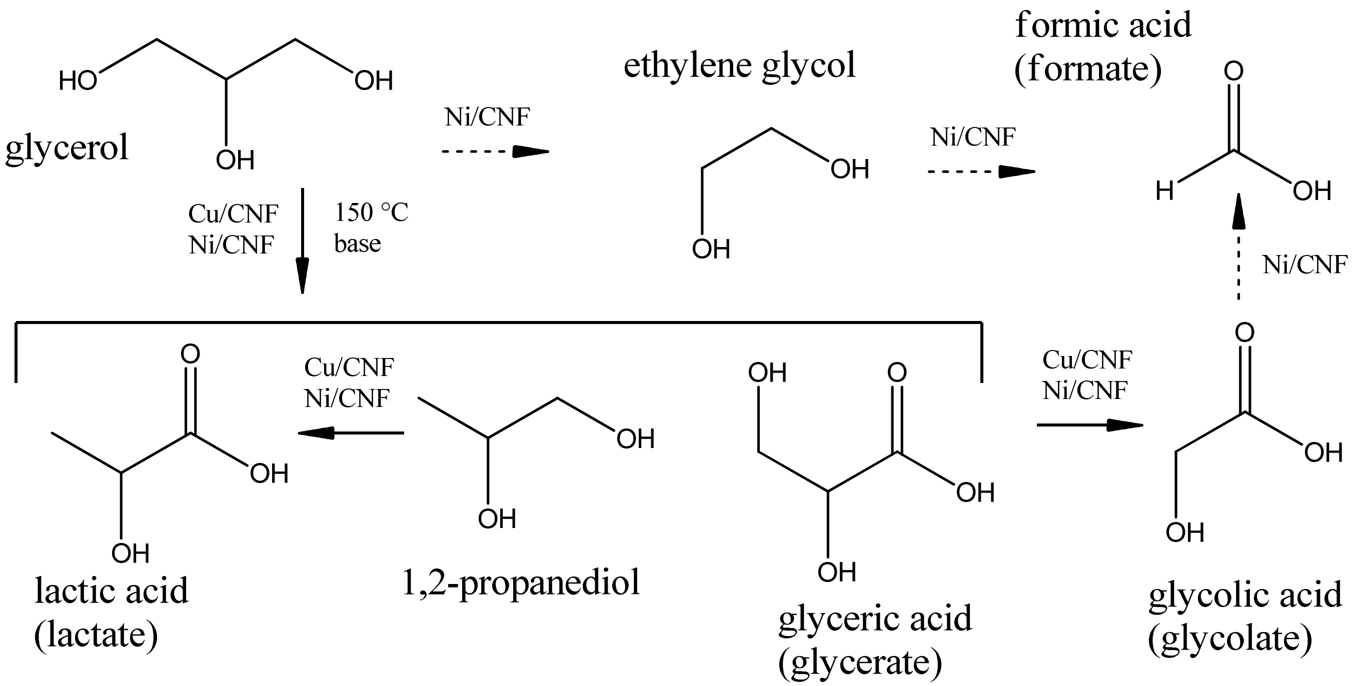


Figure 1. Conversion profiles of (●) ethylene glycol and (carbon based) product yields of (■) glycolic acid and (▲) formic acid. Reaction conditions: KOH:EG=2, 1 wt% EG in water, 150 °C, 100 mg catalyst.

Figure 2 shows the conversion profiles of glycerol and product yields between 1 and 15 hours over Ni/CNF (a) and Cu/CNF (b). With Ni/CNF complete conversion of glycerol was obtained after 2 hours and the product spectrum is dominated by the C_3 products lactic acid (as lactate) and 1,2PDO and glyceric acid (as glycerate). Also significant quantities of C_2 (glycolic acid and ethylene glycol) and C_1 (formic acid) products were formed. This shows that C-C cleavage is an important pathway over the nickel catalyst. With the exception of glyceric acid these products have been reported previously in the transformation of glycerol to lactic acid using Rh/C [30, 31], Ir/C [31, 32], Pt and Ru on carbon [21] and Cu catalysts [33]. Lactic acid and 1,2PDO yields increased to 19% for both products in the first 2 hours. At this point almost complete conversion of glycerol was realized, however the lactic acid yield increased further to 24% after 15 hours whereas the 1,2PDO yield decreased to 9% during this period. The yields of ethylene glycol and glyceric acid also decreased after full glycerol conversion was realized while formic acid and glycolic acid yields increased continuously over the whole course of the reaction.

With Cu/CNF complete glycerol conversion was achieved within 6 hours (figure 2b). The major products formed were lactic acid and glyceric acid and also significant amounts of 1,2PDO and glycolic acid were formed. Also here the formation of lactic acid increased even after complete glycerol conversion was realized and a final yield of 52% was obtained. Glyceric acid and 1,2PDO yield decreased after glycerol was fully converted.



Scheme 6: Product formation in the anaerobic oxidation of glycerol with Cu/CNF and Ni/CNF catalysts in aqueous alkaline media.

When the product distributions over Cu and Ni are compared (scheme 6) it appears that 1,2PDO can react to lactic acid and glyceric acid can degrade to form glycolic acid over both catalysts. Formation of additional C-C cleavage products, formic acid and ethylene glycol, occurs only with the Ni catalyst. Ethylene glycol might be formed directly from glycerol and formic acid could be formed from ethylene glycol via glycolic acid. The selectivity after 15 hours toward desirable lactic acid and glyceric acid was thus also higher with the Cu catalyst than with the Ni catalyst, 52% versus 24% (table 2). Again the carbon balance was closed for the Cu catalyst (99%) while a significant carbon deficit was observed with Ni (carbon balance 59%), likely due to formation of CO_2 and subsequent capture of CO_2 by KOH as (bi)carbonate.

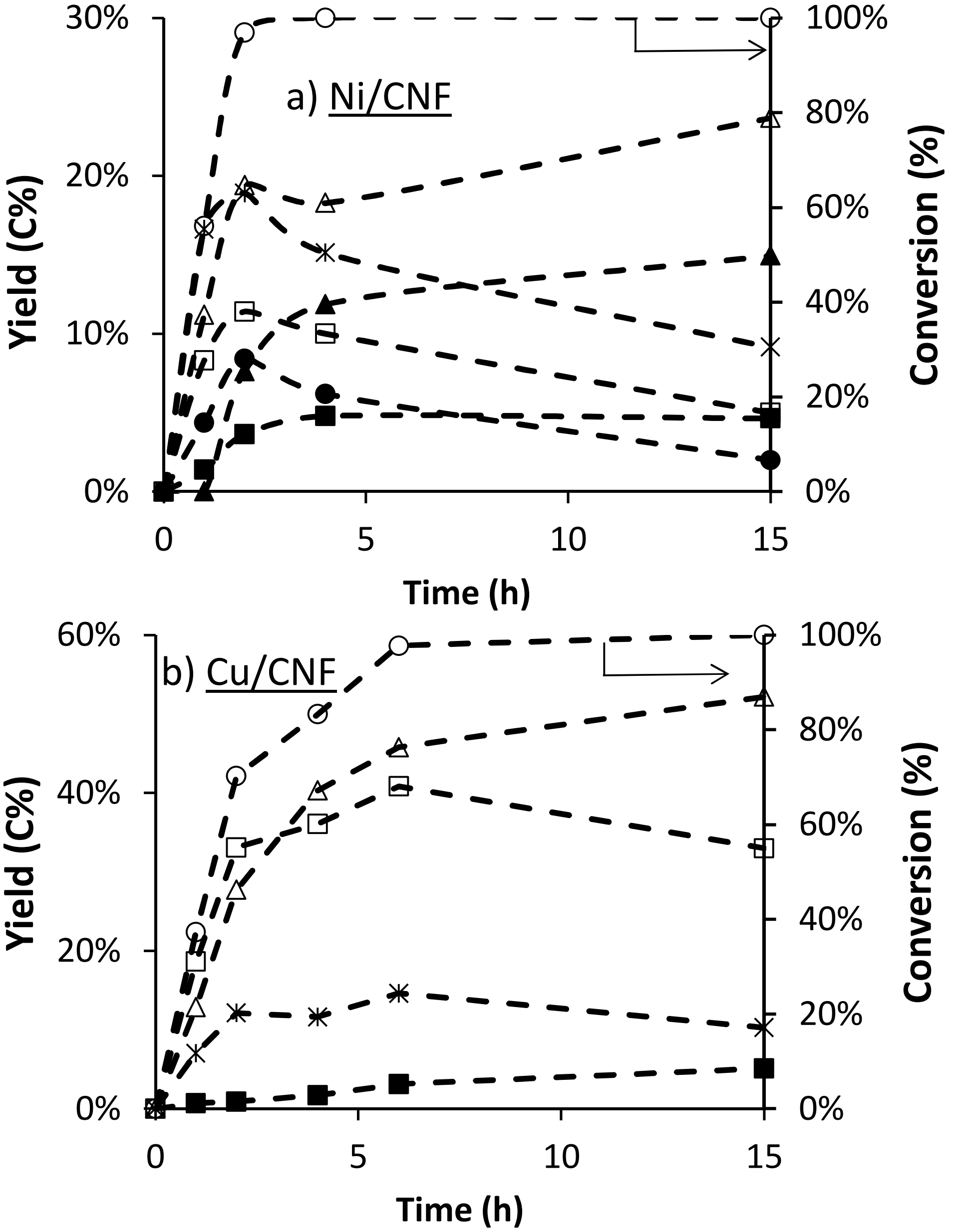


Figure 2. Conversion profiles of glycerol (○) and product yields (carbon based) of (Δ) lactic acid, (▲) formic acid, (*) 1,2-propanediol, (□) glyceric acid (•) ethylene glycol, and (■) glycolic acid. a) Ni/CNF and b) Cu/CNF. Conditions: KOH: glycerol=2, 1-15 hours, 1 wt% glycerol, 150 °C, 100 mg catalyst.

Table 2. Product selectivities in the processing of ethylene glycol and glycerol over Ni/CNF and Cu/CNF catalysts

#	Reactant	Catalyst	X	TOF[1] (h^{-1})	Product selectivity (%)						C$_{bal}$ (%)[2]
			(%)		GOA	FA	LA	GEA	1,2PDO	EG	(%)
1	EG	Ni/CNF	89	11	31	27	0	0	0	0	65
2	EG	Cu/CNF	82	14	96	0	0	0	0	0	98
3	GLY	Ni/CNF	100	n.a	5	15	24	5	9	2	59
4	GLY	Cu/CNF	100	30	5	0	52	33	10	0	99

[1] Activity expressed as turn-over-frequency (TOF) at ±20% conversion. [2] Percentage of carbon accounted for in the liquid phase after 15 hours reaction. Reaction conditions: 150 °C, 1 wt % solutions, 15 hours, 100 mg catalyst. EG = ethylene glycol, GLY = glycerol, GOA= glycolic acid, FA = formic acid, LA = lactic acid, GEA = glyceric acid, EG = ethylene glycol. N.a = not available.

Hydrogen formation

Organic acids are the main products from both glycerol and ethylene glycol under the prevailing conditions. Apparently the oxidation of these polyols proceeds in the absence of molecular oxygen and should thus be accompanied by hydrogen production. Overall the reaction can be written as (1) for the formation of glycolic acid from ethylene glycol and (2) for the formation of lactic acid from glycerol. We also observed the formation of 1,2PDO from glycerol which is accompanied by consumption of hydrogen (3).

$C_2H_6O_2$ (ethylene glycol) + $H_2O \rightarrow C_2H_4O_3$ (glycolic acid) + $2H_2$ (1)

$C_3H_8O_3$ (glycerol) $\rightarrow C_3H_6O_3$ (lactic acid) + H_2 (2)

$C_3H_8O_3$ (glycerol) + $H_2 \rightarrow C_3H_8O_2$ (12PDO) + H_2O (3)

During aqueous phase hydrogenolysis of glycerol without external H_2 in alkaline conditions Roy et al. [33] detected small amounts of hydrocarbons and CO_2 but did not report the production of H_2. Auneau et al. [31] on the other hand reported the formation of H_2 during glycerol hydrogenolysis both in inert and hydrogen containing atmosphere. Since we also observed a pressure increase in the reactor during the experiments the composition of the gas phase was investigated for the reactions of ethylene glycol and glycerol with both Cu and Ni catalyst. H_2 was the only gas formed in significant amounts. Figure 3 shows the H_2 selectivity expressed as mole of H_2 produced per mole of converted substrate. For the copper catalyst the observed production of 1.9 mole of H_2 per mole of ethylene glycol is in good agreement with the stoichiometry of the formation of glycolic acid from ethylene glycol (reaction 1). For the reactions with glycerol lower H_2 selectivities were obtained as compared to starting with ethylene glycol. This is because the formation of lactic acid only yields one mole of H_2 and also the production of 1,2PDO from glycerol consumes 1 mole of H_2 per mole converted glycerol. With the nickel catalyst the H_2 selectivity was always higher. This is in agreement with the observation that significant amounts of formic acid are formed which results in additional production of H_2.

Since only H_2 was detected in the gas phase the observed carbon deficiency with the Ni/CNF catalyst cannot be attributed to the formation of hydrocarbons. It is therefore most likely that with the Ni catalyst also partial reforming to H_2 and CO_2 occurs, possibly via decaboxylation or decabonylation of the acid or aldehyde intermediates [40]. The formed CO_2 is not observed in the gas phase under alkaline conditions due to the formation of carbonates [41].

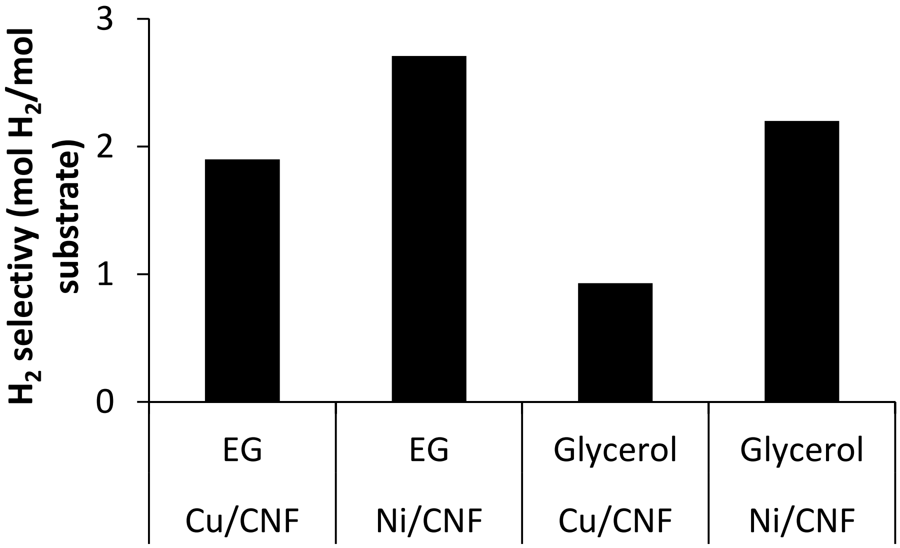


Figure 3. Hydrogen selectivity expressed as mole H_2 per mole converted substrate for ethylene glycol and glycerol using Cu/CNF and Ni/CNF catalysts at 150 °C. Reaction conditions: 150 °C, 1 wt % solutions, 4 hours, KOH: substrate ratio 2.

Effect of temperature and concentration

The influence of temperature on the activity and selectivity was investigated for Cu/CNF, the most selective catalyst towards the desired oxygenated products (i.e. glycolic acid and lactic acid). Table 3 summarizes the activity and product distribution as function of temperature. It was already shown in figure 1 that at 150 ºC ethylene glycol was converted selectively to glycolic acid at a rate of 14 h^{-1} (table 2, entry 2). By increasing the temperature to 180 ºC (table 3, entry 1) the TOF increased to 39 h^{-1} while still maintaining high selectivity (97%). Thus the temperature increased the activity while maintaining the high selectivity.

The effect of the reaction temperature on the reactivity of glycerol in the range 150-180 ºC is also shown in table 3 (entries 2-4). The glycerol TOF increased from 33 h^{-1} at 150 °C to 124 h^{-1} at 180 °C. With Cu/CNF complete conversion was obtained at 160 ºC after 4 hours. From 150-180 ºC the lactic acid selectivity increased steadily from 42% to 64% while the selectivity to glyceric acid and 1,2PDO decreased. The increase in lactic acid selectivity can be partially attributed to the higher conversions at higher temperature and the conversion of 1,2PDO to lactic acid (figure 1). Since at higher temperature the increase in selectivity towards lactic acid is larger than the corresponding decrease in 1,2PDO selectivity it must be concluded that lactic acid formation is also favoured over the formation glyceric acid. In addition above 150 °C the formation of tartronic acid (2-hydroxypropanedioic acid), becomes significant. This also contributes to the decrease in glyceric acid selectivity.

Table 3. Influence of temperature on the glycerol conversion and product selectivities over Cu/CNF.

Entry	Reactant	T (°C)	X (%)	TOF[1] (h^{-1})	Selectivity (%)				
					LA	GEA	12PDO	TA	GOA
1	EG	180	76	39	0	0	0	0	97
2	GLY	150	68	33	42	39	16	2	1
3	GLY	160	100	50	51	24	9	11	5
4	GLY	180	100	124	64	7	2	14	13

[1] Surface normalized reaction rates expressed as turn-over-frequency (TOF) at ±20% conversion. Reaction condition: 1 wt % solutions, 100 mg Cu/CNF, 4 hours, 120-180 °C. LA = lactic acid, GEA = glyceric acid, 12PDO = 1,2-propanediol, TA = tartronic acid and GOA = glycolic acid.

Since the use of dilute (1 wt%) feed solution is not economical (e.g. glycerol from trans-etherification typically contains only 20 wt% water) we also investigated the use of higher feedstock concentrations. The effect of the initial glycol concentration on the reaction rate and lactic acid yield is shown in table 4. When the glycerol concentration was increased from 5 to 10 wt% (entry 1-2) the glycerol TOF at 20% conversion almost doubled from 106 to 203 h^{-1}. The use of even higher glycerol concentrations would also require higher base concentrations and therefore risk severe corrosion of the reactor. We note that such limitation can easily be overcome for an industrial process in which the pH can be controlled for instance by operating in semi-batch mode. The use of more concentrated glycerol solutions did not affect the lactic acid yield which was ~50%. By increasing the reaction temperature to 180 °C almost full conversions was achieved after 4 hours with a lactic acid selectivity of 67%. Thus by increasing the glycerol concentration and temperature lactic acid could be produced at high selectivity and with high reaction rate (765 h^{-1}). We note that these reaction rates are comparable to highly active noble metals, e.g 600 h^{-1} for Au-Pd bimetallic catalyst [18], during aerobic oxidation reaction at 60 °C. Further enhancement of these rates is expected at higher concentrations and temperatures because, unlike the aerobic oxidation, the reaction is not limited by oxygen diffusion.

Table 4. Effect of initial glycerol concentration on conversion and lactic acid selectivity with Cu/CNF.

Entry	Time (h)	$C_{i,GLY}$ (wt%)	T (°C)	X_{GLY}(%)	TOF[1] (h^{-1})	S_{LA} (%C)
1	2	5	150	22	106	49
2	2	10	150	21	203	50
3	4	10	180	100	765	67

[1]Surface normalized reaction rates expressed as turn-over-frequency (TOF) at ±20% conversion. Reaction conditions: 150-180 ºC, 2 hours, 50 mg Cu/CNF. X_{GLY} = Glycerol conversion. S_{LA} = selectivity toward lactic acid.

Reaction thermodynamics

To further illustrate the benefit of the oxidation of polyols in water we calculated the Gibbs free energy and enthalpy for the transformations of ethylene glycol and glycerol. The most important reaction products detected in this study were glycolic acid from ethylene glycol and lactic acid from glycerol. Table 5 lists the standard Gibbs free energy ($\Delta_r G^o$) and enthalpy ($\Delta_r H^o$) of these reactions for a neutral reaction media (rxn 1 and 5) and for the reaction including the neutralization in alkaline media (rnx 2 and 6). The aerobic oxidation reactions (with molecular oxygen) are given as a reference (rxn 3 and 7). The aerobic oxidation of both ethylene glycol [18] and glycerol [14] also requires the addition of base and thus forms the corresponding carboxylic salts and are therefore more accurately written as reactions 4 and 8.

Table 5. Standard reaction Gibbs free energies and enthalpies of reaction for transformations of ethylene glycol and glycerol.

Rxn No.	Reaction	$\Delta_r G^o$ (kJ/mol substrate)	$\Delta_r H^o$ (kJ/mol substrate)
	Ethylene glycol to glycolic acid:		
1[a]	$C_2H_6O_2(l) + H_2O(l) = C_2H_4O_3(l) + 2H_2(g)$	8	101
2[a]	$C_2H_6O_2(l) + KOH(ia) = KC_2H_3O_3(a) + 2H_2(g)$	-63	68
3[b]	$C_2H_6O_2(l) + O_2(g) = C_2H_4O_3(a) + H_2O(l)$	-410	-466
4[b]	$C_2H_6O_2(l) + O_2(g) + KOH(ia) = K(C_2H_3O_3)(a) + 2H_2O(l)$	-498	-520
	Glycerol to lactic acid:		
5[a]	$C_3H_8O_3(l) = C_3H_6O_3(a) + H_2(g)$	-89	-4
6[a]	$C_3H_8O_3(l) + KOH(ia) = KC_3H_5O_3(a) + H_2(g) + H_2O(l)$	-155	-27
7[b]	$2C_3H_8O_3(l) + O_2(g) = 2C_3H_6O_3(a) + 2H_2O(l)$	-301	-294
8[b]	$2C_3H_8O_3(l) + O_2(g) + 2KOH(ia) = 2KC_3H_5O_3(a) + 4H_2O(l)$	-360	-338

Calculated using HSC Chemistry for Windows [42]. Reaction temperature: ([a]) 160 º C and ([b]) 60 ºC. Aggregation states (a) aqueous (ia) aqueous dissociated, (l) liquid, (g) gaseous.

The Gibbs free energies are lower for the reaction of both substrates if KOH addition (i.e neutralization) is taken into account. The Gibbs free energy for the formation of glycolic acid from ethylene glycol (160 ºC) has a small positive value (8 kJ/mol) and thus the equilibrium lies on the side of ethylene glycol and the reaction does not proceed (with any significant conversion). This explains our experimental finding that without the addition of base the reaction does not proceed (table 1). From glycerol the formation of lactic acid is favourable even without KOH addition (-89 kJ/mol). Experimentally however no glycerol conversion was observed over Ni or Cu without KOH (table 1). The transformation of glycerol is thus kinetically limited over Ni and Cu catalysts in the absence of the base as co-catalyst. The same is true for the aerobic oxidation reactions (rxn 4 and 8) which have very negative Gibbs free energies values and are thus very favourable. The role of the base in lowering the activation energy for these reactions has been discussed in literature [14]. When we compare the enthalpy ($\Delta_r H^o$) of these reactions we see that the aerobic oxidation reactions are also very exothermic (large negative $\Delta_r H^o$ value). This implies that such a process requires a large cooling duty and, because of the low reaction temperature used to prevent over oxidation (e.g. 60 ºC), thus produces substantial amounts of low temperature waste heat. The anaerobic process uses water as the oxidant and does not require molecular oxygen. As a consequence the heat produced in the reaction of glycerol to lactic acid is significantly lower (-27 kJ/mol versus -338 kJ/mol for the aerobic reaction). In case of the aerobic glycolic acid production from ethylene glycol the reaction becomes endothermic by 68 kJ/mol (versus -520 kJ/mol for the aerobic reaction). In fact the difference in reaction enthalpy between the aerobic and the hydrothermal process equals the heat of combustion of H_2. Since both process require stoichiometric amounts of base the anaerobic hydrothermal process can be viewed as advantageous compared to the aerobic process because, instead of low temperature heat (which cannot be used economically), this process produces hydrogen as a valuable co-product. For the production of glycolic acid from ethylene glycol part of the hydrogen can be combusted in order to drive the reaction while the remainder can be used elsewhere in a bio-refinery system.

Effect of metal oxidation state

Copper was previously reported to be active both as metallic (Cu^0) and metal oxide (Cu_2(I)O and Cu(II)O) catalyst for glycerol transformation to lactic acid [33]. The effect of the oxidation state of our Cu catalyst was investigated by comparing the activity of the catalyst in a reduced, passivated and oxidized state. XRD was used to confirm the presence of the metallic (Cu^0) and Cu(II)O crystalline phases. When a reduced catalyst was exposed to air at room temperature, formation of a CuO phase was observed in addition to the metallic Cu phase (Cu/CNFp). When this catalyst was calcined in static air at 250 °C the metallic phase disappeared completely and CuO was the only phase observed (CuO/CNF). The highest conversion at 150 °C was observed for the reduced catalyst both with Ni/CNF (97%) and with Cu/CNF (83%). The passivated Ni catalyst (Ni/CNFp) was slightly less active (90% conversion) than the reduced catalyst, whereas the activity of the passivated Cu catalyst (Cu/CNFp) was significantly lower (29% conversion). The CuO and the NiO catalysts were almost inactive. A possible explanation for the lower activity of the passivated catalysts is that the CuO layer of the passivated metal catalyst first needs to be reduced in-situ by the substrate subsequently yielding the active metal catalyst. It is expected that the in-situ reduction of CuO/CNF and NiO/CNF is more difficult which explains that these catalyst were inactive. We therefore conclude that the metallic Cu is most likely the active phase. The activity of the aforementioned Cu(II)O catalyst might be due to the higher temperature (200-240 ºC) compared to this study (150 ºC).

Table 6: Effect of metal oxidation state on catalytic activity.

	Catalyst					
	Ni/CNF	Ni/CNFp	NiO/CNF	Cu/CNF	Cu/CNFp	CuO/CNF
X_{GLY} (%)	97	90	0	68	29	6

Reaction conditions: 4 hours, 150°C, 1 wt% glycerol solution and KOH:glycerol ratio 2.

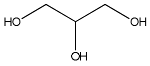
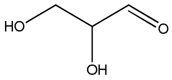
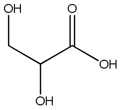
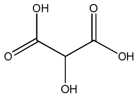
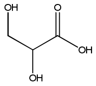
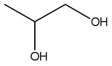
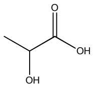
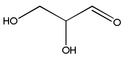
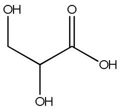
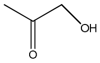
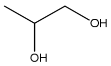
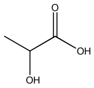
Intermediate and stability study

In order to gain more insight into the possible reaction route in the conversion of glycerol and to attempt to differentiate between reactions taking place on the catalyst surface and in the solution we investigated the reactivity of the observed products (lactic acid, 1,2PDO and glyceric acid) and possible intermediates; glyceraldehyde (2,3-dihydroxypropanal) and acetol (1-hydroxyacetone) at low concentrations (1 g/L). Glycolaldehyde was observed in some experiments but only in trace amounts. Acetol was not observed but both glyceraldehyde and acetol have been proposed as intermediate in the transformation of glycol to lactic acid [21, 39]. We investigated the reactivity of the possible intermediates and reaction products in aqueous solutions, in alkaline aqueous solutions and in alkaline aqueous solution in the presence of Cu/CNF. The results are summarized in table 7. Only glyceraldehyde was converted under solely hydrothermal conditions (i.e without metal catalyst and base) or with only the base. For all other intermediates activity was only observed in the presence of both the base and the Cu catalysts. Under solely hydrothermal conditions the observed products for glyceraldehyde were lactic acid (89%) and 1,2PDO (11%) however only 40% of the carbon could be accounted for probably due to condensation/polymerization reactions (entry 1), indeed the formation of solids was observed for these reactions. With the addition of base (KOH) and without metal catalyst only lactic acid formation was observed from glyceraldehyde but again most of the starting carbon could not be accounted for (entry 2) and again solid formation was observed. The fact the no 1,2PDO was formed with base only suggests that the formation of lactic acid is enhanced much more significantly by the presence of base then the formation of 1,2PDO.

Next we discuss the stability of the substrates when tested with both the copper and the base catalyst (entry 3-7). Under these conditions glycerol was one of the products obtained from glyceraldehyde (entry 4). This shows that the glycerol dehydrogenation is reversible. However, next to glycerol, mostly oxidation products, glyceric acid, glycolic acid and tartronic acid were observed. This implies that also H_2 must be formed which is then likely the source of the hydrogen required to hydrogenate the glyceraldehyde to glycerol. It also shows that the metal catalyst is essential to catalyse the formation of glyceric acid. Starting with glyceric acid as substrate tartronic and glycolic acid were formed, indicating that the formation of glyceric acid from glyceraldehyde is not reversible since no lactic acid and 1,2PDO were observed. This shows that formation of glycolic acid might occur through C-C cleavage of glyceric acid, although it cannot be excluded that additionally it forms directly from glyceraldehyde.

The reactivity of acetol was investigated since it is the product that would be formed if glycol undergoes a base catalysed dehydration reaction. Both 1,2PDO and lactic acid were formed. Thus both acetol and glyceraldehyde are possible intermediate in the formation of lactic acid and 1,2PDO from glycerol. Finally, the reaction with 1,2PDO as substrate (entry 6) showed that it was partially converted to lactic acid whereas the lactic acid (entry 7) was found to be stable product under reaction conditions. This is in agreement with previous reports [31] and it can be concluded that the formation of lactic acid from glyceraldehyde is irreversible.

Table 7. Reactivity of intermediates and products over a Cu/CNF catalyst under alkaline hydrothermal reaction conditions.

Entry		Product distribution (%)							C_{bal}[1]
	Reactant	GLY	GLYAL	GEA	TA	GOA	12PDO	LA	
									(%)
1[a]	GLYAL	0	0	0	0	0	11	89	40
2[b]		0	0	0	0	0	0	100	24
3[c]		17	0	63	4	6	1	9	85
4[c]	GEA 	0	0	50	34	16	0	0	94
5[c]	Acetol 	0	0	0	0	0	5	95	94
6[c]	12PDO 	0	0	0	0	0	40	60	98
7[c]	LA 	0	0	0	0	0	0	100	95

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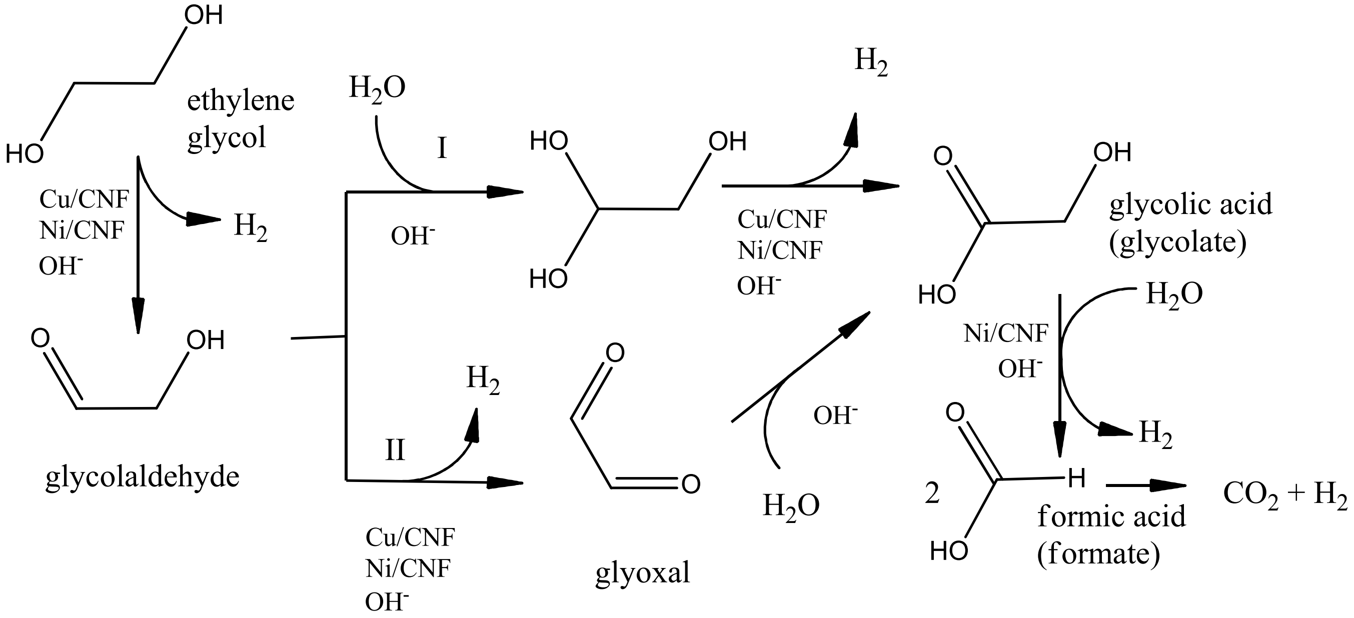
[1] Percentage of carbon accounted for in the liquid phase after 15 hours reaction. Reactions with 1 g/L of substrate at 150 ºC for 4 hours in; [a] water [b] aqueous solution of KOH (KOH:substrate ratio 2) [c] with 50 mg Cu/CNF and KOH: substrate ratio 2. GLYAL = glyceraldehyde, GLY = glycerol, GEA = glyceric acid, TA = tartronic acid, GOA = glycolic acid, 12PDO = 1,2-propanediol and LA = lactic acid.

Reaction route

Based on the experimental results and literature a reaction route is proposed for the formation of glycolic acid from ethylene glycol (scheme 7) and for the reactions of glycerol (scheme 8). From ethylene glycol we found that glycolic acid was formed exclusively with Cu and both glycolic acid and formic acid were formed using Ni. Based on the identification of trace amount of glycolaldehyde in some of the reaction mixtures and the formation of H_2 gas it is reasonable to assume that the formation of glycolic acid proceeds via the dehydrogenation of ethylene glycol to glycolaldehyde [33], catalysed by both Ni and Cu. In a previous study we also observed the formation of glycolaldehyde as a by-product in the aqueous phase reforming of ethylene glycol [35]. The fact that the dehydrogenation only occurs in alkaline media can be explained based on the work of Davis et al. [14] on the oxidative dehydrogenation of ethanol. These authors show that O-H bond activation for ethanol in aqueous media over Pt/C catalysts is unlikely but the dissociative adsorption is facilitated in the presence of surface hydroxides. The resulting alkoxide intermediate can also be formed by deprotonation of ethylene glycol in strong alkaline solution (the pKa of ethylene glycol is ~14). Subsequent activation of the C-H of the alkoxide intermediate then yields the glycolaldehyde. The activation barrier for this step is also lowered due to the presents of adsorbed OH groups [14]. The formation of glycolic acid might proceed via a base catalysed Cannizzaro reaction of the glyceraldehyde by disproportionation of two aldehydes form an alcohol and an acid. However the base alone cannot catalyse this reaction and it is therefore more likely that the reaction takes place on the metal surface where oxygen insertion could occur via addition of hydroxide to the aldehyde, after which a hydrogen abstraction will yield the acid [14]. Since aldehydes are partially hydrated to geminal diols in aqueous solution it was suggested that the reaction proceeds through a diol intermediate (scheme 7 route I) [43, 44]. Another explanation is that the reaction proceeds via the metal catalysed dehydrogenation of glyceraldehyde to glyoxal (ethanedial) which is then followed by a rapid and irreversible internal disproportionation [19] (scheme 7 route II). The difference between the oxidative dehydrogenation and the anaerobic hydrothermal process lies in the removal of the adsorbed hydrogen. During the aerobic oxidation of alcohols oxygen is not directly involved in the mechanism but is required to remove the hydrogen for the catalyst surface [44]. The adsorbed hydrogen atoms are removed from the surface by reaction with dissociatively adsorbed oxygen and close the catalytic cycle by regenerating surface-bound hydroxide ions [14, 18]. It has been established that in the absence of molecular oxygen no reaction occurs at reaction temperatures typical for catalytic oxidation of alcohols (60-90 °C). We show that at higher temperatures it becomes possible to remove the adsorbed hydrogen atoms from the metal as molecular hydrogen.

The difference between the Cu and Ni catalyst is the additional formation of formic acid with the latter which was shown to proceed via glycolic acid. Because Ni is effective for C-C cleavage (opposed to Cu) the formation of formic acid might proceed via as oxalic acid (as oxalate, not shown) [45, 46] which was detected in trace amounts. Decomposition of formic acid then yields CO_2 (as (bi)carbonate) and H_2 [47].



Scheme 7. Proposed reaction route for the formation of glycolic acid from ethylene glycol. For clarity products are shown as free acids.

Scheme 8 shows the proposed mechanism starting from glycerol based on that of Davis et al [21] and adjusted to incorporate the products observed in this study. Glycolic acid was not reported in previous studies on the transformation of glycerol in alkaline media with external hydrogen addition [21, 30] or in inert atmosphere [30, 33] but was observed in this study with both Ni and Cu catalysts. The formation of glyceric acid from glycol can proceed via a mechanism equivalent to the formation of glycolic acid from ethylene glycol (scheme 7). Glycerol is first dehydrogenated to glyceraldehyde over the metal (both Ni and Cu) catalyst which reacts further to glyceric acid. Glyceric acid can follow the same route again with oxidation of the primary alcohol to obtain tartronic acid although higher temperatures were required for this reaction. The formation of glycolic acid was suggested to proceed through a retro-aldol reaction of the glyceraldehyde [21] since Cu is not effective for C-C bond cleavage. This will yield glycolaldehyde which can reacts to glycolic acid as shown in scheme 7. Our experiments confirm that glycolic acid is one of the products when starting from glyceraldehyde but it is also formed from glyceric acid and only in the presence of the Cu catalyst. Since glyceric acid can react to form glyceraldehyde and this reaction is irreversible, it appears that glycolic acid formation actually proceeds via glyceric acid.

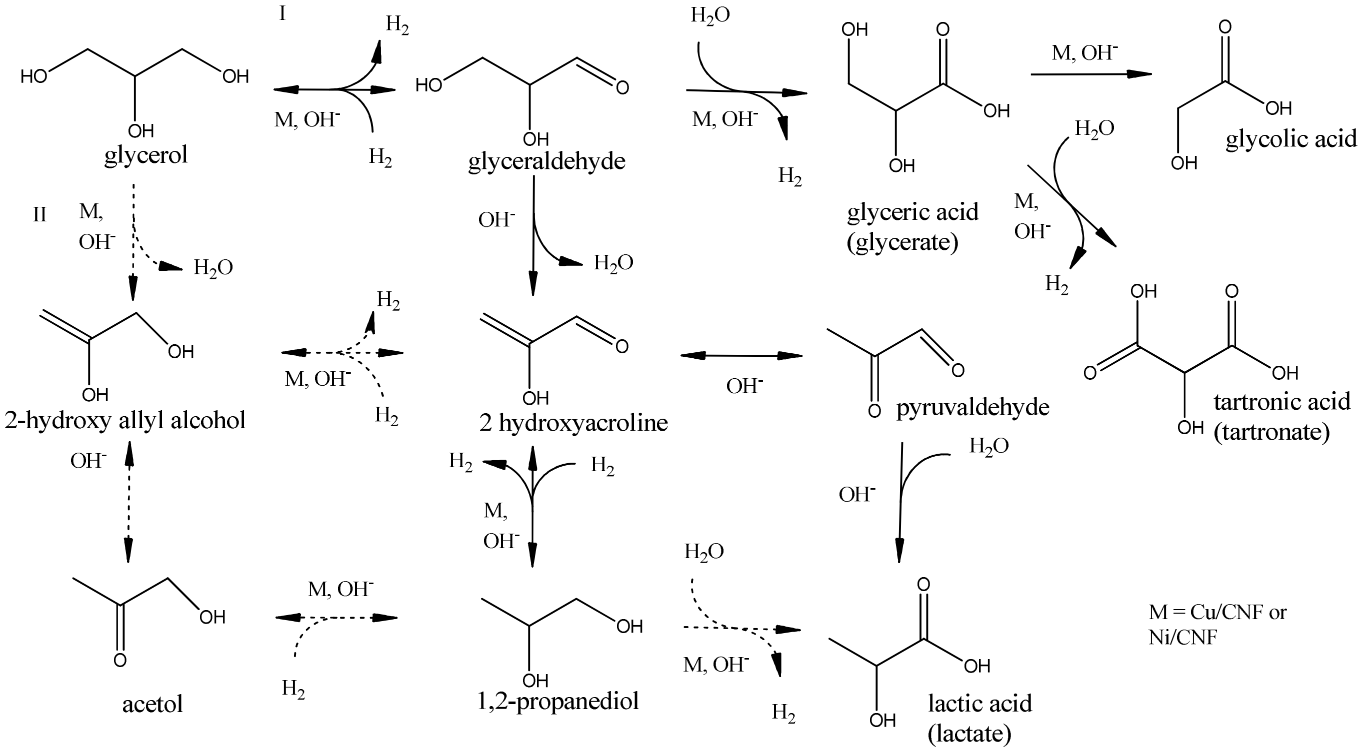
The reaction path for hydrogenolysis of a C-O bond in glycerol to form 1,2PDO has also been discussed in literature. Montassier proposed a mechanism for the hydrogenolysis of polyols with Cu catalysts. They found that metallic copper is responsible for the (de)hydrogenation and copper surface hydroxyl groups are responsible for dehydroxylation via dehydration follow by hydrogenation [23]. Whether this reaction proceeds first via a dehydration (scheme 7, route I) or a dehydrogenation (scheme 7, route II) has also been investigated. As noted by Davis et al. the dehydration of glycerol is unlikely in dilute aqueous glycerol solutions due to the unfavourable equilibrium [21]. Anneau et al. showed that the reaction rate for glycerol hydrogenolyis in alkaline media was actually increased when the gas phase is switched from hydrogen to inert, which point towards a dehydrogenation as the first step. They evaluated reaction mechanisms over Ir and Rh catalyst by calculation of the energy of the intermediates and the transition states using DFT. They concluded that the dehydrogenation pathway is kinetically favoured and the formation of glyceraldehyde intermediate was favoured over dihydroxyacetone [30, 31] although the role of the base was not taken into account. The formation of glyceraldehyde as the first step is also in agreement with our results since it is also required to explain the formation of glyceric acid. In order to form 1,2PDO a competing reaction occurs where instead of glyceric acid formation the aldehyde intermediate can then undergo a base catalysed dehydration reaction to form pyruvaldehyde (2-oxopropanal), which is in equilibrium with the enol, 2 hydroxyacroline via keto-enol tautomerization. Hydrogenation of these intermediates then gives 1,2PDO. For this reaction the metal catalyst is required which explains why 1,2PDO was not formed from glyceraldehyde with only the base.

Route I can also explain the formation of lactic acid which, starting from glyceraldehyde can be formed without metal catalyst. The isomerization of glyceraldehyde to lactic acid may occurs through dehydration of the glyceraldehyde with subsequent disproportionation via intermolecular Cannizario rearrangement of pyruvaldehyde [30, 31], also referred to as benzilic rearrangement [33]. This step is the equivalent of the formation of glycolic acid from glyoxal in the mechanism for ethylene glycol (scheme 7). The base catalysed elimination of water from glyceraldehyde is expected to be easier than the direct dehydration of glycerol because of the more acidic α-hydrogens of glyceraldehyde [48]. However when this reaction was performed with only the base it also leads to the formation of solid by-products, which is not the case in the presence of the metal catalyst. The metal catalyst thus also facilitates the formation of lactic acid, possibly by providing a different dehydration pathway.

Base on isotope studies Zhang et al. [39] came to the opposite conclusion and suggest that lactic acid formation proceeds via dehydration as the first step (scheme 2, route II). The dehydration of glycerol will yield acetol (in equilibrium with 2-hydroxy allyl alcohol via keto-enol tautomerization) which was never observed in this study. However their study was performed without metal catalyst in basic solutions at much higher temperatures (300 °C). Because glycerol dehydration is endothermic it is possible that at higher temperature dehydration becomes the dominant pathway.

The difference between the Cu and Ni catalyst is the formation of additional C-C cleavage products with Ni; ethylene glycol and formic acid (not shown in scheme 8). Ethylene glycol can be formed by direct hydrogenolysis of glycerol [21, 22] with Ni/CNF and can subsequently react to formic acid as shown in scheme 7. However more research is required to identify the additional pathway availably over the Ni/CNF catalyst in more detail.

In conclusion we propose that the formation of glycolic and glyceric acid from polyols proceeds via a mechanism similar to the oxidative dehydrogenation but hydrogen is desorbed from the surface as molecular hydrogen. The mechanism for C-O scission leading to 1,2PDO and lactic acid is under debate but the metal catalyst is required for both the dehydration and hydro-dehydrogenantion steps, suggesting that the mechanism takes place entirely on the metal surface although the assistance of base is required.



Scheme 8: Proposed reaction routes for glycerol. For clarity products are shown as free acids. M denotes the metal catalyst.

Catalyst stability

Since Cu is the most promising catalyst for the selective production of glycolic acid from ethylene glycol and lactic acid from glycerol we focussed our stability studies on the Cu/CNF catalyst. The catalyst was characterized with Transmission Electon Microscopy (TEM) as shown in figure 4. For both the fresh and the spent catalyst Cu particles with sizes of 10-100 nm were observed evenly distributed over the CNF support. The Cu particles appeared to be somewhat larger for the spent catalyst which was also apparent from XRD.

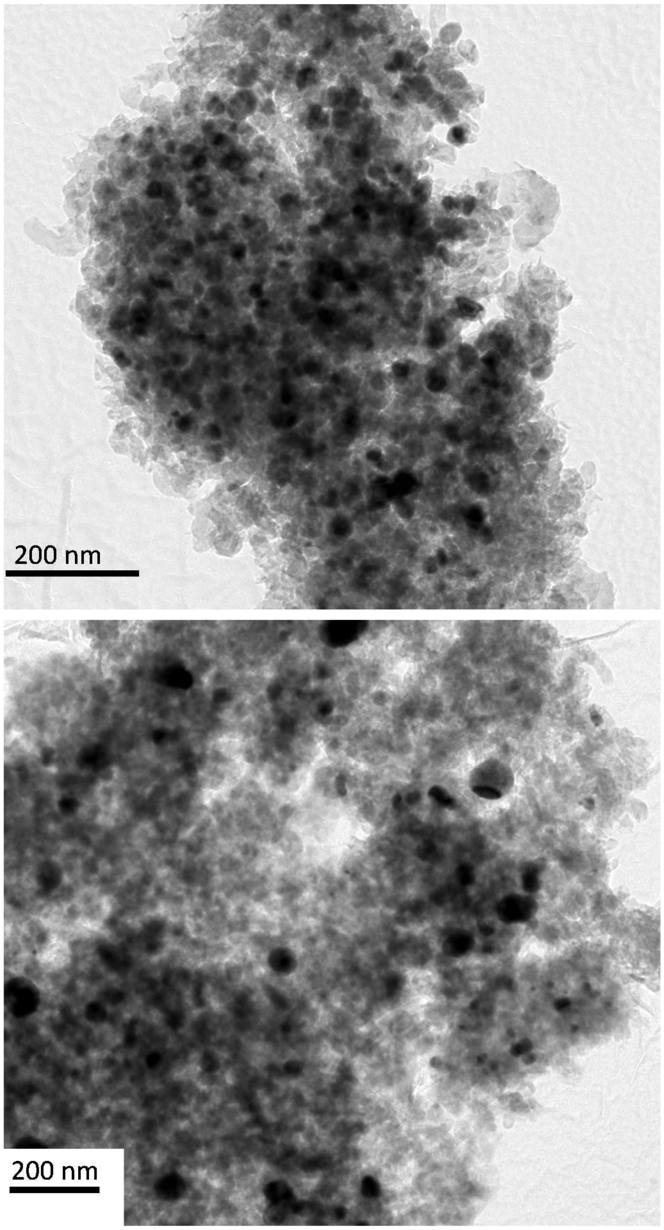


Figure 4. TEM micrographs of passivated Cu/CNF catalysts; fresh catalyst (top) and spent catalyst after 15 hours reaction (bottom).

Figure 5 shows the XRD diffractograms of the fresh catalysts and of the spent catalyst after 15 hours reaction. We observed mainly diffraction lines at 51° and 59° 2θ attributed to the metallic Cu phase. In addition broad contributions due to CuO at 41° and 45° 2θ were present. This is likely the result of the passivation treatment before the measurement and indicates a layer of CuO exist on the metallic nano-particles. However we cannot exclude that a fraction of the smallest particles is completely oxidized by the passivation treatment. By applying the Scherrer equation an average value of ~30 nm was obtained for the metal crystallites of the fresh catalyst. An increase to 44 nm was found was found after 15 hours reaction. The loss of dispersion was also evident from the decrease in catalytic activity when the catalyst was reused. A decrease in conversion was observed from 40% to 13% after using the catalyst in four consecutive runs (see table 8).

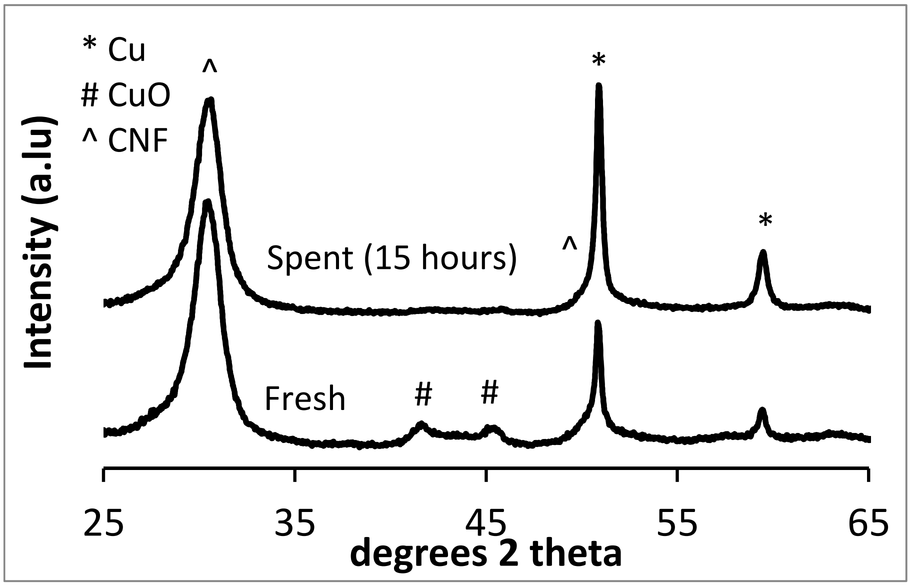


Figure 5. XRD diffractograms of the fresh catalysts and of the spent catalyst after 15 hours reaction.

Table 8. Recycle experiment for Cu/CNF.

Run#	Conversion (%)
1	40±2
2	27±2
3	15±1
4	13±1

Reaction conditions: T=150 °C, 1 wt% glycerol solution, run time 4 hours.

Conclusion

Anaerobic oxidation of polyols into mainly glycolic acid and lactic acid proceeds with high selectivity in alkaline aqueous media at low temperatures, 150-180 ºC, using CNF supported Ni and Cu catalyst. The combination of both supported metal catalyst and homogeneous base is essential. From ethylene glycol we can produce glycolic acid with near 100% selectivity at high conversion levels (82 %) with Cu supported on CNF. Compared to the aerobic process for the production of glycolic acid (oxygen atmosphere, 60 °C) the use of anaerobic conditions at somewhat higher temperatures has the benefit of producing hydrogen as valuable co-product, however stoichiometric amounts of base are required in both processes. Starting from glycerol mainly lactic acid is formed with glyceric acid and 1,2-propanediol as by-products. Higher temperatures and longer reaction times favour the production of lactic acid for which a maximum selectivity 67% was be obtained at full glycerol conversion using Cu/CNF. With the Ni/CNF catalyst C-C cleavage products, formic acid and ethylene glycol, were also formed resulting in high hydrogen selectivity but lower selectivity to valuable glycolic and lactic acid.

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† Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/

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