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Insights into the reaction pathways of glycerol hydrogenolysis over Cu–Cr catalysts

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ABSTRACT

In order to well understand reaction pathways of glycerol hydrogenolysis over Cu–Cr catalysts, hydrogenolysis of glycerol was investigated as a function of the molar ratios of Cu to Cr, reaction time, reaction temperature, hydrogen pressure, and glycerol concentration. The intermediates in glycerol hydrogenolysis were identified under Ar atmosphere or relatively mild condition. Hydrogenolysis of propanediols was also investigated for understanding the formation of propanols as by-products. The structure of Cu–Cr catalysts, prepared by an epoxide-assisted route, was determined by X-ray diffraction and scanning transmission electron microscopy. The high conversion of 85.9% and high selectivity toward 1,2-propylene glycol of 98.5% was achieved over the CuCr(4) catalyst in the hydrogenolysis of glycerol. As expected, extending reaction time, or elevating temperature and hydrogen pressure favored the conversion of glycerol. Interestingly, the conversion of glycerol and the selectivity to 1,2-propanediol increased with increasing the glycerol concentration at the same ratio of catalyst to glycerol. It was found that the hydrogenolysis of glycerol not only involved glycerol directly dehydrated and hydrogenated to 1,2-propanediol (DH route), but also involved glycerol dehydrogenation to glyceraldehyde, which was subsequently dehydrated and hydrogenated to 1,2-propanediol (DDH route), while 1,2-propanediol was further converted to propanol through H^+ transfer from alcohol compounds.

1. Introduction

Glycerol is the major byproduct of vegetable oil transesterification and accounts for 10 wt.% of the biodiesel product [1]. Therefore, the utilization of glycerol to produce high value-added chemicals may partially compensate for the production costs of biodiesel. The global projection in glycerol production estimated by Procter & Gamble in 2010 show that the markets are reacting strongly to the increased availability of this feedstock [2]. The resulting sharp decrease of glycerol prices from increasing production of biodiesel is expected to elevate glycerol as a major platform chemical. Indeed, glycerol has been recently identified by the US DOE as an important building block for future biorefineries [3,4]. Recently, there has been growing interest regarding catalytic glycerol conversion. The hydrogenolysis of glycerol would be one attractive pathway for the production of renewable high value-added chemicals.

In previous studies, copper chromite catalysts have also been reported to have a superior performance in glycerol hydrogenolysis [5–9]. This is due to their poor activity for C—C bond cleavage and high efficiency for C=O bond hydrogenation and dehydrogenation. For the first time, Suppes et al. [5] reported that copper chromite catalyzes glycerol hydrogenolysis with good conversion (54.8%) and propanediol selectivity (85.0%) under relatively mild reaction conditions (i.e. 200 °C, 1.4 MPa). Liang and co-workers showed that Cu–Cr catalysts prepared by sol–gel route and carbon templating method resulted in different performance [6–8]. More recently, the high glycerol conversion (80.3%) and selectivity to 1,2-propanediol (83.9%) obtained by using Cr promoted Cu catalysts was reported by Yi et al. [9], while the kinetic mechanism, as a point of debate for a long time, was not discussed in these reports. There are two mechanisms that have been proposed for glycerol hydrogenolysis to 1,2-propylene glycol in the literature. The most commonly proposed involves a dehydration–hydrogenation (DH) mechanism [10–19], although a dehydrogenation–dehydration–hydrogenation (DDH) mechanism has some support [20,21]. Clearly, these two routes require different catalytic functions, and a systematic study of the activity and selectivity of this reaction over Cu–Cr catalysts is required. Obviously, besides the catalyst structure, the pH of solution has a significant influence on the hydrogenolysis mechanism of glycerol as well [22]. Under alkaline conditions, 1,2-propanediol is formed via glyceraldehyde, through an initial dehydrogenation followed by water elimination and finally two reduction steps [23]. While under

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acidic conditions, 1,2-propanediol is formed by direct dehydration and subsequent hydrogenation [24].

Herein, in order to systematic understand the catalytic performance of the Cu–Cr catalysts, the hydrogenolysis of glycerol was investigated as a function of the molar ratios of Cu to Cr, reaction time, reaction temperature, hydrogen pressure, and glycerol concentration. For further exploring the reaction pathways of glycerol hydrogenolysis and determine the intermediates, the hydrogenolysis of glycerol was performed under Ar atmosphere or relatively mild condition. The formation of by-products (propanols) was also investigated by employing propanediols as reaction substrates. It was found that hydrogenolysis of glycerol not only involved glycerol directly dehydrated and hydrogenated to 1,2-propanediol, but also involved glycerol dehydrogenation to glyceraldehyde, which was subsequently dehydrated and hydrogenated to 1,2-propanediol, while 1,2-propanediol was further converted to propanol through H^+ transfer reaction.

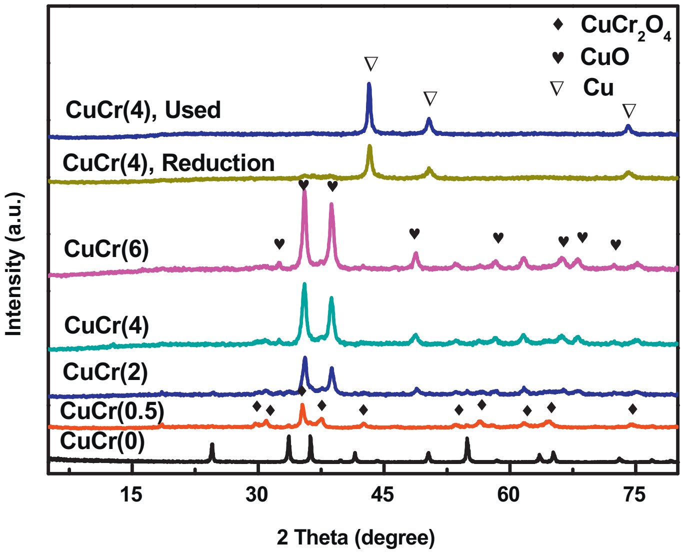


Fig. 1. XRD patterns of the CuCr(*X*) catalysts with various Cu/Cr molar ratios.

2. Experimental

2.1. Catalyst preparation

The Cu–Cr catalysts were synthesized by sol–gel route [7,8]. In a typical synthesis, 2.9 g $Cu(NO_3)_2\cdot 3H_2O$ and 9.8 g of $Cr(NO_3)_3\cdot 9H_2O$ at a desired molar ratio (Cu/Cr = 0.5) were dissolved in 47 mL of ethanol at 60 °C to give a clear dark blue solution. After adding 18 mL of 1,2-propylene oxide to the solution, a dark green transparent gel formed within a few minutes. The obtained wet gel was aged under air atmosphere and subsequently dried at 75 °C for 15 h, and the resulting xerogel was calcinated at 500 °C for 120 min. The as-prepared oxides were reduced by 10% H_2 in Ar at 300 °C for 2 h in a fluidized bed reactor to obtain the final Cu–Cr catalysts. The prepared catalysts were designated as CuCr(*X*), where *X* denotes as the molar ratio of copper to chromium.

2.2. Catalyst characterization

X-ray diffraction (XRD) patterns of the samples were measured in a D/MAX-2400 diffractometer with a Cu Kα monochromatized radiation source (λ = 1.5418 Å), operated at 40 kV and 100 mA.

Composition analysis was performed in the scanning transmission electron microscopy (STEM) mode in combination with energy dispersive X-ray spectroscopy using an analyzer system (EDAX) in the same microscope. High-resolution TEM (HRTEM) and energy dispersive X-ray spectroscopy (EDX) were performed by using a Philips CM200 FEG transmission electron microscope operated at 200 kV.

2.3. Catalytic reaction

Glycerol catalytic conversion was performed in a 100 mL stainless steel autoclave with mechanical stirrer and an electric temperature controller, operated under H_2 pressure of 4.1 MPa at 210 °C for 600 min. About 60 mL aqueous solution of 60 wt.% glycerol and 5 wt.% (based on glycerol) of the catalysts was charged into the autoclave. The reactor was sealed and pressurized to the required hydrogen pressure, and then heated to the desired temperature. After the reaction, the autoclave was cooled to ambient temperature, then brought to atmospheric pressure and opened to allow the reaction mass to be discharged and centrifuged for removing the catalyst. The products were analyzed with a Bruker 450-GC gas chromatograph equipped with a flame ionization detector. ChemStation software was used to collect and analyze the data. A FFAP GC column (30 m × 0.32 mm × 0.5 μm) was used for separation. The analysis was carried out using n-butanol as the internal standard. The conversion of the glycerol was calculated as follows:

$$\text{Conversion}\,(\%) = \frac{\text{sum of moles of all products}}{\text{sum of moles of reactant}} \times 100$$

The selectivity to each product was defined based on carbon as follows:

$$\text{Selectivity}\,(\%) = \frac{\text{moles of carbon in specific product}}{\text{moles of carbon in all products}} \times 100$$

3. Results and discussion

3.1. Characterization of Cu–Cr catalysts

The crystalline structures of the CuCr(*X*) catalysts were investigated by XRD measurements. Fig. 1 shows XRD patterns of calcined CuCr(*X*) catalysts with various molar ratios. The CuCr(0) catalyst showed a single phase of Cr_2O_3. As the copper ratio was increased, the characteristic peaks corresponding to Cr_2O_3 phase decreased and new characteristic peaks of the copper chromite ($CuCr_2O_4$) spinel phase appeared at ca. 18.6°, 29.6°, 31.1°, 37.7°, 42.3°, 61.4° and 64.8° for the CuCr(0.5) catalyst, corresponding to the (1 1 1), (2 2 0), (0 2 2), (1 1 3), (4 0 0), (4 4 0) and (4 0 4) planes, respectively [25]. This indicates that the formation of the $CuCr_2O_4$ spinel phase is energetically favorable in mixtures of Cu and Cr. Further increases in the copper ratio resulted in a decrease in the $CuCr_2O_4$-related coupled with the appearance of the CuO phase. On the basis of these observations, it is apparent that the phase composition is significantly affected by increasing Cu/Cr molar ratios. Apart from the CuCr(0), the higher the loading of copper was, the sharper the diffraction peaks were, indicating a greater degree of crystallinity and crystallite growth.

Typically, TEM, HRTEM, STEM, elemental maps, and EDX analysis were used to determine the catalyst structural properties, e.g. the CuCr(4) sample was shown in Figs. 2 and 3. The HRTEM image in Fig. 2c revealed that the $CuCr_2O_4$ and CuO phases were formed, which was coincide with XRD result. Meanwhile the structure of CuO supported $CuCr_2O_4$ was observed. The *d*-spacing of 0.476, 0.256 and 0.301 nm for $CuCr_2O_4$ corresponding to the (1 0 1), (2 1 1) and (2 0 0) planes, and lattice spacing of *d* = 0.251 nm was identified as CuO $(1\,1\,\bar{1})$. EDX, STEM and elemental maps results indicated that the dispersion of Cu and Cr species was homogeneous. It was

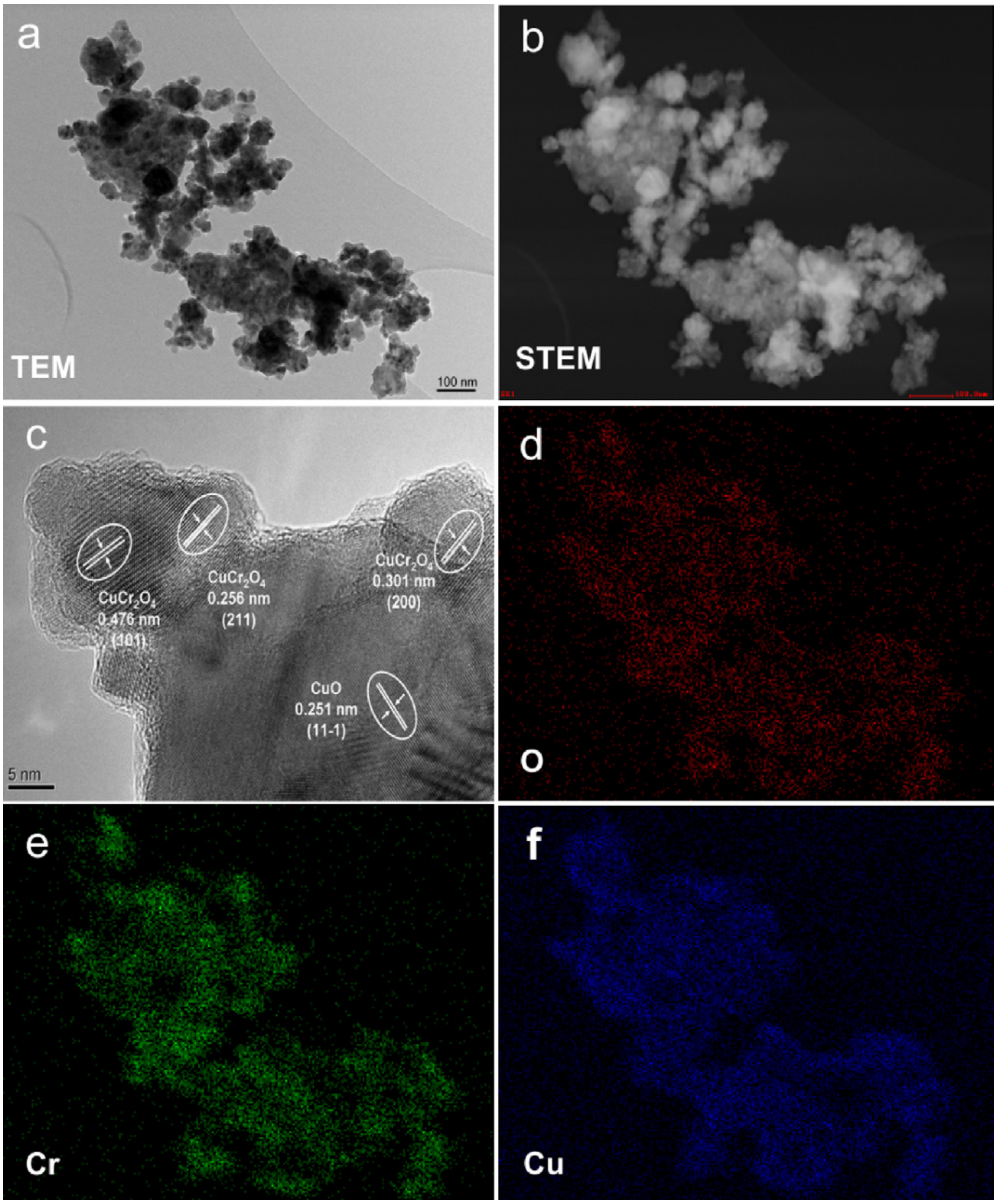


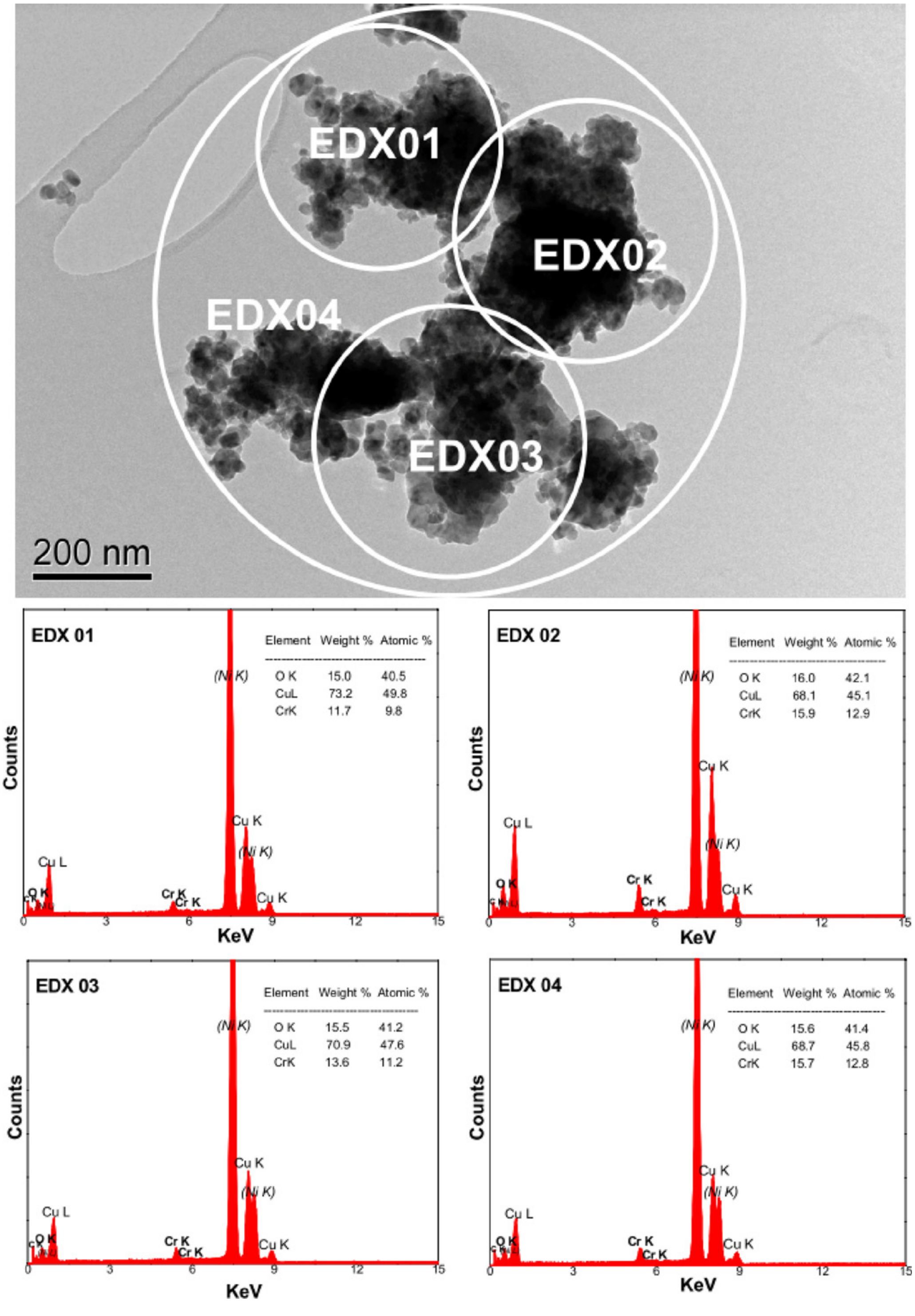
Fig. 2. TEM (a), STEM (b), HRTEM (c) and elemental maps (d–f) analysis of the CuCr(4) catalyst.

noteworthy, however, that content ratio (Cu/Cr) of about 3.6 in the EDX results was lower than the theoretical value of 4, which likely resulted from experimental errors, or the special structure of $CuCr_2O_4$/CuO led to the increased of surface chromium.

3.2. *Hydrogenolysis of glycerol over Cu–Cr catalysts*

Given those interesting structural changes, glycerol hydrogenolysis over these CuCr(*X*) catalysts were investigated as shown in Fig. 4. Not surprisingly, there was no activity for glycerol hydrogenolysis over CuCr(0) catalyst. However, as loading of copper increased, there was a uniform increase in the glycerol conversion from 32% over CuCr(0.5) catalyst to 49% over CuCr(4) catalyst. The similar tendency for 1,2-propanediol (1,2-PD) selectivity was observed, it successive increased from 55% to 68%. Glycerol can also be dehydrated into acetol, and then hydrogenated to propylene glycol over copper metal catalysts [6,26,27]. Thus, we believe that the increase of glycerol conversion is likely due to the increase of active copper in the catalyst. Further increasing the Cu/Cr ratio to 6 resulted in no obvious difference in glycerol conversion and selectivity, which may be a result of increase in particle size (the same as XRD results), even though the increase of active copper.

From that on, the CuCr(4) catalyst gave the maximum activity with the best selectivity of 1,2-PD. Thus, the CuCr(4) catalyst was further explored to determine the influence of reaction parameters on glycerol hydrogenolysis. Fig. 5a shows the results of glycerol hydrogenolysis with increasing reaction time. About 44% of conversion and 82% selectivity toward 1,2-PD were achieved within 3 h. As expected, the glycerol conversion increased with increasing the reaction time, reaching a value of about 56% in 17 h. At the same time, the selectivity to 1,2-PD and acetol decreased with time. While the selectivity to the byproduct 1-propanol (1-PO) increased with time, due to the gradual formation from 1,2-PD, which would be discussed in the following. There was no obvious change observed for 2-propanol (2-PO) selectivity.



EDX 01

Element	Weight %	Atomic %
O K	15.0	40.5
CuL	73.2	49.8
CrK	11.7	9.8

EDX 02

Element	Weight %	Atomic %
O K	16.0	42.1
CuL	68.1	45.1
CrK	15.9	12.9

EDX 03

Element	Weight %	Atomic %
O K	15.5	41.2
CuL	70.9	47.6
CrK	13.6	11.2

EDX 04

Element	Weight %	Atomic %
O K	15.6	41.4
CuL	68.7	45.8
CrK	15.7	12.8

Fig. 3. EDX analysis of the CuCr(4) catalyst.

The effect of reaction temperature on hydrogenolysis of glycerol was also investigated, and the results are presented in Fig. 5b. Glycerol conversion greatly improved from 9% to 64% in the range of 180–230 °C, while the selectivity to 1,2-PD decreased from 94% to 45%. As an intermediate in the first dehydration step, the selectivity of acetol increased with temperature since the formation of acetol is thermodynamically favorable, while the acetol hydrogenation is limited by thermodynamic equilibrium [28]. Due to the enhancement of dehydration at elevating temperature, the combined selectivity to 1-PO and 2-PO was increased, e.g. from 7% to 54%. These results are probably due to hydrogenation of acetol being favored at low reaction temperature and high hydrogen partial pressure from the viewpoint of chemical equilibrium [28], while the dehydration of glycerol favors high temperatures [17,28].

As shown in Fig. 5c, reaction pressure had a significant positive effect on glycerol conversion and a negative effect on 1,2-PD selectivity. As the pressure increased from 2 to 5 MPa, glycerol conversion increased from 32% to 58%, and subsequent 1,2-PD selectivity decreased from 84% to 44%. In contrast, the combined selectivity to 1-PO and 2-PO increased with pressure. This further

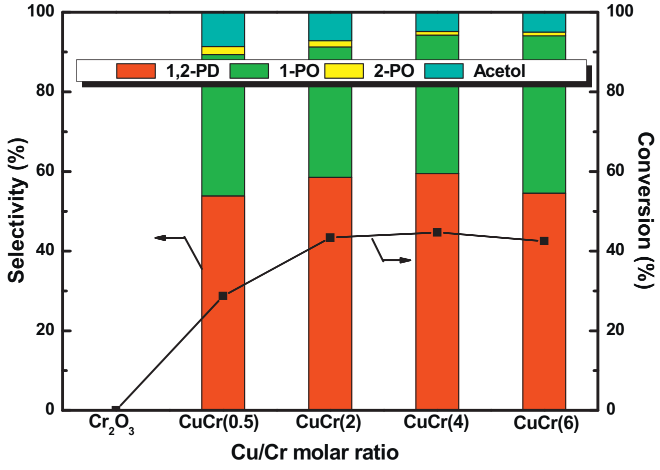


Fig. 4. Effect of molar ratios on hydrogenolysis of glycerol over the CuCr(*X*) catalyst (reference conditions: 60 mL 60 wt.% aqueous glycerol solution, 5 wt.% catalyst (based on glycerol), 210 °C, 4.1 MPa H_2, 10 h, 150 r/min).

suggested that more byproducts were formed at higher pressure. Vannice has also proposed that active hydrogen species on metal sites increase with increasing hydrogen pressure [29], with a resultant increase in the rate of acetol hydrogenation. This is the reason of a decrease in the acetol selectivity with increasing pressure.

The effect of glycerol concentration on the performance of glycerol hydrogenolysis was examined as shown in Fig. 5d. It was previously reported that the conversion of glycerol decreased with increasing glycerol concentration [5]. In contrast, increasing the glycerol concentration from 20% to 100% led to an increase in conversion from 32% to 92%. The reason is that, in the previous report, the amount of catalysts was not changed regardless of glycerol concentration, while the ratio of both was identical in our studies. The similar results had been reported by Zhou et al. [30], in which the glycerol concentration had a positive effect on conversion, when the substrates with identical molar ratio Ag to glycerol were injected. As a solvent, water has a diluting effect, which is detrimental to the conversion of glycerol. Considering that water is a byproduct of the glycerol hydrogenolysis, vast amounts of water in solution can impede the equilibrium in the forward direction. Interestingly, the selectivity to 1,2-PD exhibited the same tendency as the conversion of glycerol, increasing from 10% to 85%. While about 7% of others were detected for solvent-free glycerol hydrogenolysis, which were not identified due to polymerization [5]. According to previous report [31], glycerol had a higher affinity for adsorption sites than 1,2-PD. The catalysts had sufficient reaction sites for glycerol and 1,2-PD conversion at low glycerol concentration. As the concentration increased, the reaction sites for 1,2-PD converting to 1-PO were occupied by glycerol, resulting in the increased of 1,2-PD selectivity.

3.3. *Reaction pathways of the glycerol hydrogenolysis*

In the previous reports, several mechanisms have been suggested for glycerol hydrogenolysis. Since acetol can be hydrogenated to 1,2-PD over metal catalysts, it is regarded as a key intermediate for 1,2-PD. The formation of acetol generally involves

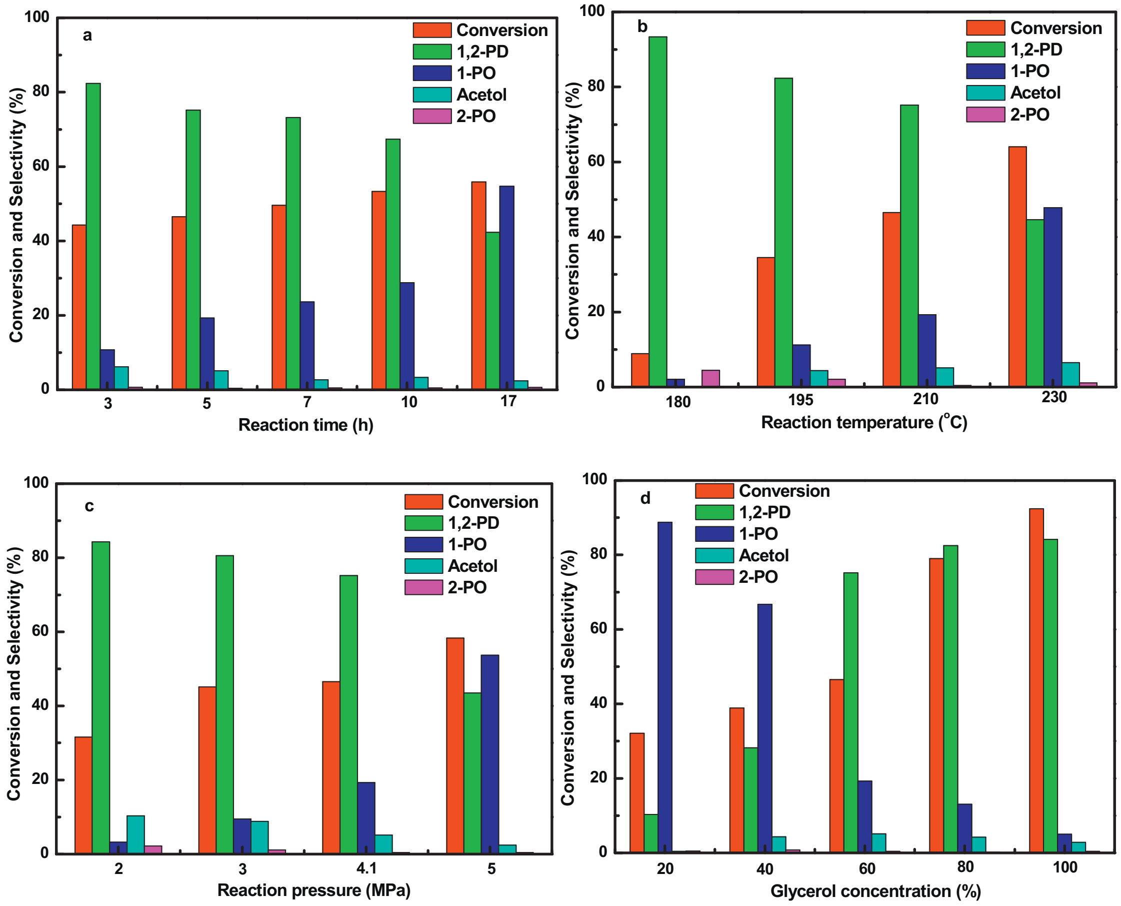


Fig. 5. Effect of reaction time (a), temperatures (b), hydrogen pressure (c), and glycerol concentration (d) on hydrogenolysis of glycerol over the CuCr(4) catalyst (reference conditions: 60 mL 60 wt.% aqueous glycerol solution, 5 wt.% catalyst (based on glycerol), 210 °C, 4.1 MPa H_2, 5 h, 150 r/min).

Table 1
Hydrogenolysis of 1,2-PD and 1,3-PD over the CuCr(0.5) and CuCr(4) catalysts.

Reactant	Catalysts	Selectivity (%)			Conversion (%)
		1-PO	Acetol	2-PO	
1,2-PD[a]	CuCr(0.5)	89.0	6.5	4.5	0.3
1,3-PD[a]	CuCr(0.5)	99.5	–	0.5	10.5
1,2-PD[a]	CuCr(4)	80.5	6.0	13.5	0.3
1,3-PD[a]	CuCr(4)	99.9	–	0.1	50.7
1,2-PD + ethylene glycol[b]	CuCr(4)	94.6	3.3	2.1	34.5
1,2-PD + n-butanol[b]	CuCr(4)	91.3	6.3	2.4	5.1
1,2-PD + cyclohexane[b]	CuCr(4)	95.1	4.4	0.5	0.5

[a] Reaction conditions: 60 mL 60 wt.% aqueous reactant solution, 5 wt.% catalyst, 4.1 MPa H_2, 210 °C, 5 h, 150 r/min.

[b] Reaction conditions: 60 mL 60 wt.% aqueous reactant solution (40 wt.% of 1,2-PD), 5 wt.% catalyst, 4.1 MPa H_2, 210 °C, 5 h, 150 r/min.

two routes. One is direct dehydration of glycerol [10–13,32–35]. In the other route, glycerol dehydrogenates to glyceraldehyde followed by dehydration and subsequent hydrogenation into acetol [20,36,37]. Therefore, it is very significant to determine the formation route of acetol for understanding the mechanism of glycerol hydrogenolysis. On the basis of the current understanding mechanism, the glycerol hydrogenolysis product 1,2-PD was also detected on CuCr(4) catalyst under Ar (other conditions are the same), e.g. about 67% selectivity to 1,2-PD and 15% selectivity to acetol at 9% conversion of glycerol, indicating that acetol may be formed not solely from the direct dehydration of glycerol. H_2 is required for acetol to be hydrogenated to propylene glycol under Ar, which should be derived from glycerol through its dehydrogenation on the metallic Cu surfaces. However, no dehydrogenated intermediate (e.g. glyceraldehyde) was detected, which was likely due to its known high reactivity and instability relative to acetol and propanediol under the given conditions [36]. To verify the mechanism, the solvent-free glycerol hydrogenolysis was also performed under mild conditions (2 MPa, 130 °C), interestingly, a small amount of glyceraldehyde was detected.

Tomishige et al. proposed that 1-PO and 2-PO originated from 1,3-PD over Ru/C with an ion-exchange resin catalysts [13,38]. However, 1-PO and 2-PO were observed over Pt/ASA catalysts via dehydration of 1,2-PD and subsequent hydrogenation [39]. In agreement with the previous results, 1-PO and 2-PO were also detected in this study. Therefore, we attempted to elucidate the pathways of glycerol converted to 1-PO and 2-PO over Cu–Cr catalysts. The performance of CuCr(0.5) and CuCr(4) catalysts for 1,2-PD and 1,3-PD catalytic conversion has been investigated as shown in Table 1. Surprisingly, 1,2-PD conversion was much lower under the given conditions, irrespective of the employed catalysts. However, there was no obvious changed of glycerol conversion after 3 h, the selectivity of 1,2-PD decreased with increasing reaction time as shown in Fig. 5a, while the selectivity of 1-PO increased. As known, the selectivity is proportional to the concentration at identical conversion, namely the corresponding concentration exhibited the same variation trend as well. Thus, it was reasonable that 1,2-PD could convert to 1-PO. This is contrary with the results in Table 1. It was likely that the conversion of 1,2-PD promoted by presenting some molecules. In the case of 1,3-PD as reactant, the CuCr(4) catalyst gave much superior 1,3-PD conversion compared with the CuCr(0.5). Nevertheless, most of 1,3-PD had converted to 1-PO and a trace amount of 2-PO was detected, reflecting that 2-PO may be originated from 1,2-PD. Based on these results, the formation of 1-PO is likely favored from the conversion of 1,3-PD and/or 1,2-PD, while the formation of 2-PO is favored from the conversion of 1,2-PD.

For a detailed view of the origin of 1-PO, a shortened reaction time and less forcing reaction conditions are required for detecting the intermediates. Therefore, glycerol hydrogenolysis was investigated under hydrogen pressure of 3 MPa and 190 °C as shown in Fig. 6. Unexpectedly, apart from the final products, no intermediates were observed, such as 3-hydroxypropanal, acrolein and allyl alcohol (intermediates in producing 1,3-PD), which were detected in the literature [40]. In addition, a more mild condition (3 MPa and 160 °C) was also employed for glycerol hydrogenolysis, and again there were no intermediates. Therefore, this strongly supports that the origin of 1-PO is via dehydration of 1,2-PD and subsequent hydrogenation, rather than from conversion of 1,3-PD.

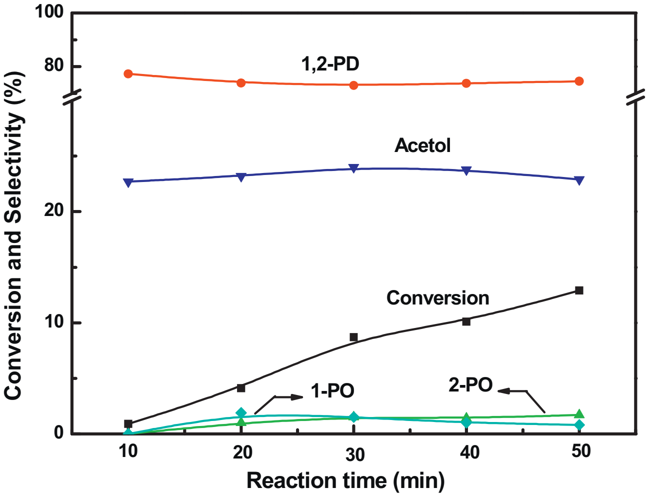
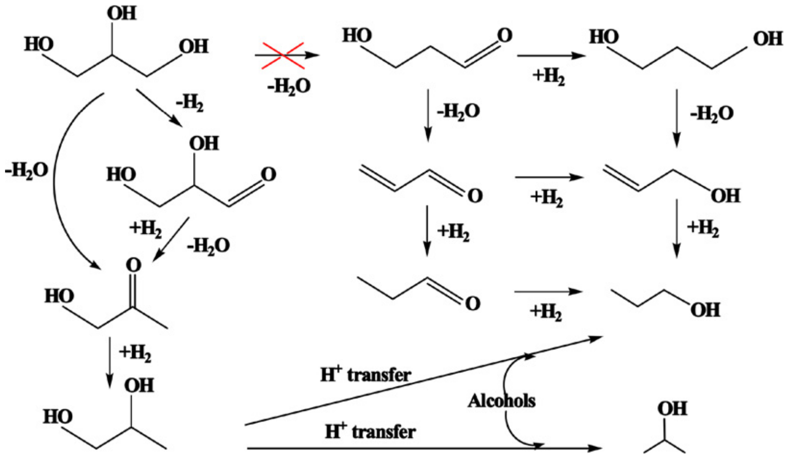


Fig. 6. Glycerol hydrogenolysis over the CuCr(4) catalyst (60 mL 60 wt.% aqueous glycerol solution, 5 wt.% catalyst (based on glycerol), 190 °C, 3 MPa H_2, 150 r/min).

A promotion mechanism was proposed by Schüth et al. [41], where allyl alcohol could be obtained from acrolein through a hydrogen transfer reaction with an alcohol as a hydrogen donor. Whether the similar mechanism presents in the conversion of 1,2-PD, which needs to be further investigated. Thus, we had conducted the conversion of 1,2-PD over CuCr(4) catalyst under the existence of other compounds (ethylene glycol, n-butanol and cyclohexane) as shown in Table 1. Surprisingly, 1,2-PD conversion was greatly improved upon injection of ethylene glycol with ca. 35% of 1,2-PD conversion, whereas it increased only to 5% after adding n-butanol. However, a promotion had been observed. Besides, 1,2-PD conversion was not obvious changed as injecting cyclohexane. These results indicated that 1,2-PD was further converted to propanols through H^+ transfer of an alcohol as reported in the literature [42], in which 2-propanol could function as a hydrogen donor molecule in the transfer hydrogenation process to selectively convert glycerol into 1,2-propanediol under N_2 pressure. On the basis of the above discussion, we propose that glycerol hydrogenolysis to 1,2-PD proceeds as shown in Scheme 1 by its dehydrogenation to glyceraldehyde, and the subsequently dehydration and hydrogenation to acetol, or direct dehydration and hydrogenation to acetol, which is then hydrogenated to 1,2-PD, while 1,2-PD was further converted to propanols through H^+ transfer of an alcohol.

3.4. Effect of mass transfer on the hydrogenolysis of glycerol

It easy to find the above results were not showed superiority comparing to previous study [9]. The difference is likely due to mass transfer limitations in liquid-phase catalytic hydrogenations. Therefore, a thorough study should be made of the influence of mass transfer on the catalyst performance. The influence of the stirring rate on glycerol hydrogenolysis is presented in Table 2. At stirring rate of below 300 rpm, the glycerol conversion significantly increased with increasing the stirring rate, and subsequently increased gradually with the stirring rate increase up to 900 rpm.



Scheme 1. Reaction pathways of glycerol hydrogenolysis over the Cu–Cr catalysts.

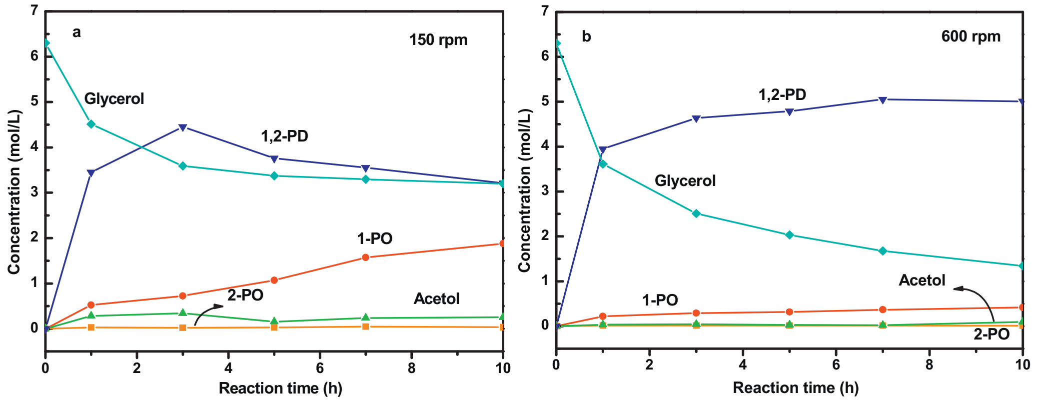


Fig. 7. Effect of stirring rate on hydrogenolysis of glycerol over the CuCr(4) catalyst (reference conditions: 60 mL 60 wt.% aqueous glycerol solution, 5 wt.% catalyst (based on glycerol), 210 °C, 4.1 MPa H_2).

This effect may be due to the diffusion retardation of the reaction, namely that the mass transfer resistances of hydrogen at the gas/liquid interface and of glycerol at the liquid/solid interface was minimized [43]. Significantly, however, the selectivity to 1,2-PD increased monotonically from 60% to 98%. These observations can be explained by the effect of mass transfer of the organic reactants on the reaction rates [44]. Whereas the hydrogen concentration on the catalyst surface is in equilibrium with the bulk concentration at high conversion. The influence of gas–liquid mass transfer can be neglected. Under low stirring rate, insufficiently fast diffusion of glycerol to the catalyst surface from the bulk and of the desorbed 1,2-PD to the bulk leads to lower $C_{\text{glyerol}}/C_{\text{1,2-PD}}$ in the liquid–solid diffusion layer compared to the kinetic regime and, thus, to a lower catalyst surface coverage with glycerol and higher with 1,2-PD. Therefore, in this case of mass transfer limitations, the over hydrogenation of 1,2-PD to 1-PO will be occurred. Otherwise, the mass transfer limitation is eliminated, leads to the increased of 1,2-PD selectivity. The curve of concentration as a function of reaction time at different stirring rate was shown as in Fig. 7, which suggested that higher stirring rate gave superior hydrogenation rate.

Table 2
Effect of the stirring rate on catalytic performance for glycerol hydrogenolysis.[a]

Stirring rates (rpm)	Selectivity (%)				Conversion (%)
	1,2-PD	1-PO	Acetol	2-PO	
150	59.7	34.9	4.7	0.7	49.2
300	84.6	12.7	2.5	0.2	73.4
600	90.6	7.5	1.7	0.2	78.7
900	98.5	1.1	0.4	0	85.9

[a] Reaction conditions: 60 mL 60 wt.% aqueous glycerol solution, 5 wt.% CuCr(4) catalyst (based on glycerol), 4.1 MPa H_2, 210 °C, 10 h.

Catalyst recycle use is important for liquid-phase reactions in batch reactor. Therefore, the recycling experiments of the CuCr(4) catalyst were conducted under the optimal conditions (4.1 MPa H_2, 210 °C, 900 rpm, 10 h). After three recycling, the glycerol conversion was slightly decreased from 85.9% to 81.1%, while the selectivity of 1,2-PD maintained at about 98%. This result indicated that the Cu–Cr catalyst had good stability, which was also proved by the XRD results as shown in Fig. 1. After reaction, there was no obvious change in XRD pattern compared to the reduced catalyst, apart from an increase in the intension of diffraction peaks, indicating that the particle size of Cu–Cr catalyst increased after reaction.

4. Conclusions

The copper species are mainly responsible for the glycerol conversion, which is confirmed by the results of glycerol hydrogenolysis over Cu–Cr catalysts with various Cu/Cr molar ratios. The CuCr(4) catalyst exhibits the best activity due to an increased number of active sites. The glycerol conversion is increased monotonically with increasing the reaction temperature and hydrogen pressure. An antiparallel correlation is also observed for the selectivity toward 1,2-PD. These results indicate that the dehydration or formation of acetol favors high temperatures, while hydrogenation of acetol favors low reaction temperature and high hydrogen partial pressure. The same tendency is shown for glycerol conversion and 1,2-PD selectivity under different glycerol concentration, which is due to the reaction equilibrium and competition adsorption. In addition, the hydrogenolysis mechanism apparently involves glycerol dehydrogenation to glyceraldehyde, which is subsequently dehydrated and hydrogenated to 1,2-PD (DDH route), or glycerol is directly dehydrated to acetol and hydrogenated to 1,2-PD (DH route). The 1,2-PD can then be further dehydrated and hydrogenated to 1-PO and 2-PO, which is promoted by presenting alcohols through H^+ transfer of hydroxyl.

Acknowledgements

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