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Article (Dedicated to Professor Yi Chen on the occasion of his 80th birthday)

Efficient catalytic hydrogenolysis of glycerol using formic acid as hydrogen source

Jing Yuan, Shushuang Li, Lei Yu, Yongmei Liu, Yong Cao *

Department of Chemistry, Shanghai Key Laboratory of Molecular Catalysis and Innovative Materials, Fudan University, Shanghai 200433, China

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ABSTRACT

We describe a sustainable, cost-effective, and highly efficient H₂-free protocol for catalytic hydrogenolysis of glycerol to 1,2-propanediol (1,2-PDO) using formic acid (FA) as the H₂ source. The process is catalyzed by an earth-abundant and robust Cu-based metal oxide catalyst, in which the high performance of the Cu catalyst for the in situ generation of H₂ gas in the system by highly selective decomposition of FA in an aqueous medium is essential. The activity test results showed that a synergy effect of well-dispersed Cu and amphoteric ZrO₂ is essential for FA decomposition as well as for glycerol conversion to 1,2-PDO. The Cu content of the Cu/ZrO₂ catalyst prepared by the oxalate gel method has a significant role in the FA-mediated glycerol conversion to 1,2-PDO, and a Cu content of 20 wt% on ZrO₂ was identified as the optimum Cu content. Moreover, the creation and maintenance of high component dispersion is essential for high glycerol hydrogenolysis activity of the Cu/ZrO₂ system. Because selective hydrogenolysis with minimum use of external fossil-fuel H₂ is a critical issue in the realization of biorefinery concepts, the procedure described here is expected to be of broad applicability in biomass use.

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1. Introduction

Diminishing petroleum reserves and growing concerns about global climate change necessitate the development of fuel and chemical production pathways based on renewable resources such as biomass materials [1,2]. In this respect, glycerol, obtained as a high-volume by-product in the biodiesel process, has emerged as a promising abundant feedstock for the renewable chemicals industry [3–5]. Among various transformations already reported for glycerol, hydrogenolysis to propanediols (PDOs) is of particular interest because of the large numbers of applications of 1,2- and 1,3-PDO (Scheme 1). 1,2-PDO is a major commodity chemical that is currently obtained through the selective hydrolysis of propylene oxide [6–8]. 1,3-PDO has traditionally been considered a specialty

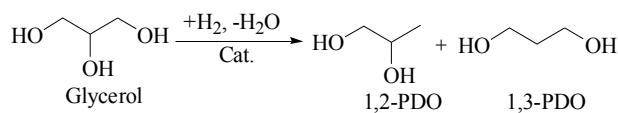
chemical [9,10]; however, it is fast emerging as a significant building block for the manufacture of polyesters such as poly(trimethylene terephthalate). Glycerol hydrogenolysis has mainly been performed using molecular hydrogen (H₂) [4,11–14]. However, high H₂ pressures are generally required to reach acceptable conversion and selectivity. As well as this practical inconvenience, the use of H₂ has some other important drawbacks. First, most of the currently available H₂ gas is still produced from fossil fuels, which makes the process dependent on fossil carbon. In addition, it ignites easily and has high diffusivity, and therefore presents considerable hazards when working at high pressures.

One interesting alternative that could minimize external fossil-fuel H₂ consumption is the use of formic acid (FA), one of the major products formed during biomass processing, as the

* Corresponding author. Tel: +86-21-55665287; Fax: +86-21-65643774; E-mail: yongcao@fudan.edu.cn

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Scheme 1. Reaction for conversion of glycerol to PDOs.

H₂ source. FA has recently attracted considerable interest in the area of green and sustainable chemistry because of its potential as a H₂ carrier and as a means of using CO₂ [3,15]. FA is liquid at room temperature, so it has the added technical advantage that its use as a replacement for H₂ would not be limited by storage and delivery problems [15,16]. Compared with the impressive progress being made in glycerol hydrogenolysis with H₂, very few reports dealing with the direct hydrogenolysis of glycerol using FA as a H₂ source are available. In related previous studies, bimetallic Ni-Cu supported on Al₂O₃ was used as an efficient catalyst for direct hydrogenolysis of glycerol with FA [17]. However, this catalyst has a low inherent efficiency, and the system requires the use of a heavily loaded catalyst and prolonged reaction times at high temperatures (up to 24 h at 220 °C) to improve the hydrogenolysis kinetics. From both practical and economic points of view, a more efficient catalytic transformation that can be carried out at lower reaction temperatures using stoichiometric amounts of FA and glycerol is preferable.

As part of our ongoing interest in the development of new catalytic methods that enable controlled and selective transformations of highly functionalized bio-derived feedstocks, we recently discovered an efficient heterogeneous catalytic system for the direct conversion of bio-derived aqueous levulinic acid/FA streams to γ -valerolactone, catalyzed by ZrO₂-supported high-dispersed Au nanoparticles (NPs), in which high performance of the supported Au NPs for in situ generation of H₂ gas via selective FA decomposition under mild conditions is essential [18]. This Au/ZrO₂-FA protocol is also a suitable method for selective hydrogenolysis of glycerol to 1,2-PDO in high yields. However, the high cost and limited availability of Au have necessitated the development of earth-abundant base-metal alternatives for these applications. Simple Cu-based catalysts are promising candidates because they have high activities toward FA decomposition in the vapor phase [19–22]. Moreover, it is also well established that Cu catalysts are very selective for catalytic hydrogenolysis of glycerol under a H₂ atmosphere [23,24]. In this paper, we report that a simple Cu–Zr nanocomposite featuring high component dispersion can be used as an efficient catalyst in the selective conversion of glycerol to 1,2-PDO using bio-derived FA as a convenient H₂ source.

2. Experimental

2.1. Catalyst preparation

The catalysts were prepared using the conditions and methods listed in Table 1.

2.1.1. Oxalate gel (OG) coprecipitation (CP) method [25].

Briefly, an alcoholic solution of 20% excess oxalic acid was

injected rapidly into an alcoholic solution of zirconium (cerium) nitrate (0.1 mol/L) containing the desired amount of copper (iron, cobalt, nickel) nitrate at room temperature under vigorous stirring. After stirring for 2 h, the resultant gel-like precipitates were separated by filtration, followed by air drying at 110 °C overnight. The as-obtained materials were then calcined in a muffle oven at 500 °C for 4 h.

2.1.2. Na₂CO₃ CP method

Typically, a mixed aqueous solution of copper nitrate and zinc nitrate (each 0.1 mol/L) and a solution of Na₂CO₃ (0.1 mol/L) were added slowly and simultaneously to 150 mL of deionized water at 80 °C under vigorous stirring. The pH was kept constant at 6.5–7.0. After stirring for 4 h, the precipitates were separated by filtration, followed by drying at 110 °C overnight. The as-obtained material was then calcined in a muffle oven at 500 °C for 4 h.

2.1.3. Incipient wetness impregnation (Imp) method

In a typical procedure, a certain amount of ZrO₂ support or SiO₂ support was soaked in an aqueous solution of copper nitrate of appropriate concentration. The mixture was stirred for 4 h at room temperature and then stirred at 85 °C until the mixture was dry. The samples were dried in an oven at 110 °C overnight.

2.1.4. Urea deposition-precipitation (urea DP) method

Typically, a mixed aqueous solution of copper nitrate (0.1 mol/L) and urea (10 mol/L), and ZrO₂ (or P25) were added to 200 mL of deionized water at 90 °C under vigorous stirring for 4 h. The solids were separated by filtration, followed by drying in an oven at 110 °C overnight. The as-obtained materials were

Table 1
FA conversions and CO contents for different catalysts.

Catalyst	Preparation method	FA conversion ^a (%)	CO concentration ^b (ppm)
Cu/ZnO-Al ₂ O ₃ ^c	Na ₂ CO ₃ CP	7	5
30%Cu/ZnO-Al ₂ O ₃	Na ₂ CO ₃ CP	9	11
30%Cu/ZnO	Na ₂ CO ₃ CP	15	47
30%Fe/ZrO ₂	OG CP	1	45
30%Co/ZrO ₂	OG CP	1	57
30%Ni/ZrO ₂	OG CP	2	55
30%Cu/SiO ₂	Imp	1	50
30%Cu/CeO ₂	OG CP	20	32
30%Cu/TiO ₂	Urea DP	5	30
30%Cu/ZrO ₂	Urea DP	10	40
30%Cu/ZrO ₂	Imp	1	52
30%Cu/ZrO ₂	OG CP	50	12

Reaction conditions: FA 18 mmol, H₂O 40 mL, $n_{FA}/n_{metal} = 24$, 160 °C, 5 h.

^aAnalyzed by a HPLC (HP 1100, Agilent, USA) equipped with a refractive index detector (RID) and a Platisil ODS C18 column.

^bMeasured by using a GC analysis system equipped with a methanizer and a flame ionization detector (detection limit ~1.0 ppmv).

^cSupplied by Research Institute of Nanjing Chemical Industrial Group.

then calcined at 500 °C for 4 h.

Prior to reaction, all samples were prereduced with 5% H₂/Ar at 300 °C for 2 h.

2.2. Characterization

X-ray diffraction (XRD) analysis of the catalysts was carried out on a Bruker D8 Advance (Germany) X-ray diffractometer using Ni-filtered Cu K α radiation, with a scanning angle (2θ) of 20–80°, a scanning speed of 2°/min, and a voltage and current of 40 kV and 20 mA, respectively. Hydrogen temperature-programmed reduction (H₂-TPR) experiments were carried out using a laboratory-made apparatus, as described elsewhere [26]. The specific surface areas of the prepared catalysts were determined by adsorption-desorption of N₂ at –196 °C using a Micromeritics TriStar 3000 system. Sample degassing was carried out at 300 °C for 4 h prior to acquiring the adsorption isotherm. X-ray photoelectron spectroscopy (XPS) analysis was performed with a Perkin Elmer PHI 5000C system equipped with a hemispherical electron energy analyzer using Mg K α ($h\nu = 1253.6$ eV) radiation operated at 15 kV and 20 mA. The energy scale was internally calibrated by setting the C 1s peak at 284.6 eV.

The specific surface area of metallic Cu was measured based on the adsorption and decomposition of N₂O on the surface of metallic Cu as follows: 2Cu(s) + N₂O → N₂ + Cu₂O(s). The pulse titration technique was employed. Pure N₂ was used as the carrier gas, and a thermal conductivity detector (TCD) was used to detect the amount of N₂O consumed [25,27]. The specific area of metallic Cu was calculated from the total N₂O consumption, with 1.46×10^{19} Cu atoms per m². The Cu dispersion was calculated based on the specific surface. The solution after reaction was analyzed by inductively coupled plasma atomic emission spectroscopy (ICP-AES) using a Thermo Electron IRIS Intrepid II XSP spectrometer.

2.3. Decomposition of FA and hydrogenolysis of glycerol

For decomposition of FA, a mixture of FA (18 mmol), water (40 mL), and the prereduced supported metal catalyst (metal 4.2 mol%) was charged into a 50 mL Hastelloy C high-pressure Parr reactor and stirred at a rate of 800 r/min. The mixture of the substrate and the catalyst was heated to 160 °C for less than 15 min. After the given reaction time, the concentration of residual FA was analyzed using a high-performance liquid chromatography (HPLC; HP 1100, Agilent, USA) system consisting of a Platisil ODS C18 column and a refractive index detector. H₂SO₄ (0.5 mmol/L) was used as the mobile phase at a flow rate of 1 mL/min. The temperatures of the column and the detector were both 40 °C. The gaseous products were analyzed using a GC equipped with a TDX-01 column and a TCD. The carrier gas was He. A standard gas sample consisting of 33.3% H₂, 33.3% CO, and 33.3% CO₂ was used to calibrate the GC. The composition of gaseous products was determined based on the standard gas. Very low CO concentrations can be reliably measured using a GC analysis system equipped with a methanizer and a flame ionization detector (FID, detection limit

~1.0 ppmv).

For hydrogenolysis of glycerol, a mixture of glycerol (5 mmol), FA (a certain amount, according to the experimental requirements), the prereduced supported metal catalyst (metal 10 mol%), 2-methoxyethyl ether (2.5 mmol, internal standard), and water (10 mL) was charged into a 25 mL Hastelloy C high-pressure Parr reactor and stirred at a rate of 800 r/min under a 0.5 MPa N₂ atmosphere for a given reaction time. The mixture of substrate and catalyst was heated to the desired temperature in less than 15 min. The liquid products were analyzed using a Shimadzu GC-17A gas chromatograph equipped with a capillary column HP-FFAP (30 m × 0.25 mm) and an FID. The identification of the products was performed using GC-mass spectrometry.

3. Results and discussion

We commenced our study by investigating the selective decomposition of FA in an aqueous medium over various Cu-based solid catalysts. As early as the 1960s, the decomposition of FA was widely investigated as a probe reaction for characterizing the surface properties of metals and metal oxides. Among these reports, two different pathways, namely dehydrogenation (HCOOH → H₂ + CO₂, $\Delta G = -48.4$ kJ/mol) and dehydration (HCOOH → H₂O + CO, $\Delta G = -28.5$ kJ/mol), were identified [16]. From the stand point of catalysis, what is of particular interest is that the selectivities for the two possible pathways can be controlled by the choice of catalyst. In the specific use of FA as a H₂ source for chemical synthesis, the key point is selective decomposition of liquid-phase FA to H₂ and CO₂, while avoiding undesirable formation of CO. In general, studies of heterogeneous FA decomposition have mostly concentrated on gas-phase catalysis. For the liquid-phase decomposition of FA by heterogeneous catalysts, a number of supported as well as unsupported noble metals, including Pd, Pt, Au, and their corresponding bimetallic alloys such as Pd–Au, have been reported to be effective [28–30]. The development of new non-noble catalytic systems that give fast, selective decomposition of FA under mild aqueous conditions is therefore still of great interest.

In a first set of experiments, the decomposition of a diluted aqueous solution of FA (0.43 mol/L) for 5 h at 160 °C was studied in a batch autoclave reactor. The results in terms of the direct production of H₂ and CO₂ over various Cu-based catalysts are compiled in Table 1. The H₂/CO₂ molar ratios (n) obtained from most catalysts under these conditions were around 1:1, with very low CO contents, indicating that the selective decomposition of FA can take place under these reaction conditions. However, most catalysts were not very active in the direct dehydrogenation of FA (conversion level < 30%) under our experimental conditions. Conventional 30%Cu/ZnO, 30%Cu/ZnO–Al₂O₃, and industrial Cu/ZnO–Al₂O₃ methanol synthesis catalysts gave either low activities or high CO contents. It is interesting to note that the Cu/ZrO₂-based catalyst prepared using the OG CP method gave good FA conversion, with a consistently low CO content (< 20 ppm); this is of particular interest for the direct use of FA as a convenient source of

H₂. Moreover, a clear advantage of the 30%Cu/ZrO₂-OG catalyst over other first-row Group VIII metals (base metals) with the same metal loading was also observed when aqueous FA was subjected to decomposition using identical OG-derived Fe/ZrO₂, Ni/ZrO₂, or Co/ZrO₂ under otherwise identical conditions.

To further improve the FA conversion while minimizing undesirable CO formation, Cu/ZrO₂ catalysts with different Cu loadings were prepared, and their performance in FA decomposition was measured. As indicated in Fig. 1, the catalytic performance was strongly dependent on the Cu contents. Among the catalysts examined at this stage of the study, the Cu/ZrO₂-OG catalyst containing 20 wt% Cu exhibited by far the best catalytic performance, and it was found that 100% FA conversion was achieved within 3 h at 180 °C. This result is significant, especially as, similar to all these experiments, only a very low level of CO (< 20 ppm) was detected in the gas-phase products. The reaction parameters were further optimized for FA decomposition by varying the feed concentration, which is very important for the product distribution in the glycerol hydrogenolysis reaction; this will be discussed further. It was found that even more efficient FA decomposition was achieved by using a FA solution of higher concentration.

To clarify the origin of their high FA decomposition activities, the (10–50 wt%)Cu/ZrO₂-OG catalysts were characterized in detail. Typical data such as BET specific surface areas and Cu metal surface areas (determined from chemical N₂O titration) are summarized in Table 2. It can be seen that there is only a weak relationship between the specific surface area and the performance of the Cu/ZrO₂-OG samples, indicating that the external texture is not the key factor governing the catalytic performance of the samples prepared using the OG CP method. However, there is a strong positive correlation between Cu dispersion and FA decomposition activity (not shown). The fact that a specific composition of 20%Cu/ZrO₂-OG can maximize exposure of the fraction of catalytically active species at the catalyst surface is crucial for achieving high activity in FA decomposition, in line with the many literature reports docu-

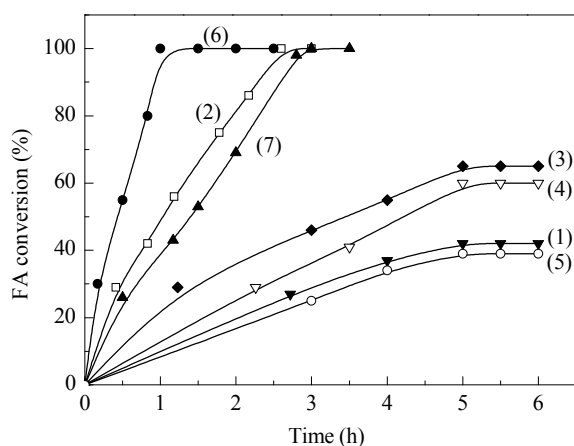


Fig. 1. Time profiles of FA decomposition over Cu/ZrO₂ catalysts with different Cu loadings. (1) 10%Cu/ZrO₂; (2) 20%Cu/ZrO₂; (3) 30%Cu/ZrO₂; (4) 40%Cu/ZrO₂; (5) 50%Cu/ZrO₂; (6) 20%Cu/ZrO₂ (FA 18 mmol, H₂O 20 mL); (7) 20%Cu/ZrO₂ (FA 9 mmol, H₂O 40 mL). Reaction conditions: FA 18 mmol, H₂O 40 mL, $n_{FA}/n_{metal} = 24$, 180 °C.

Table 2
Physiochemical properties of various Cu/ZrO₂ catalysts.

Catalyst	S_{BET} (m ² /g)	S_{Cu}^a (m ² /g _{Cu})	D_{Cu} (%)	d_{Cu}^b (nm)
10%Cu/ZrO ₂ -OG	28	28.0	4.3	11.2
20%Cu/ZrO ₂ -OG	40	47.5	7.4	12.3
30%Cu/ZrO ₂ -OG	37	41.7	6.5	14.6
40%Cu/ZrO ₂ -OG	63	36.7	5.7	20.8
50%Cu/ZrO ₂ -OG	36	33.8	5.2	21.6
30%Cu/ZrO ₂ -DP	31	4.0	0.6	25.3
30%Cu/ZrO ₂ -Imp	20	3.3	0.5	79.0

^a Determined by N₂O titration.

^b Estimated from XRD data using the Scherrer equation.

menting the structure-activity relationships of supported Cu catalysts [25,27,31,32].

The XRD patterns of the calcined forms of the as-synthesized catalysts showed only tetragonal ZrO₂ and CuO crystallites (not shown). After prereduction under a 5% H₂/Ar atmosphere at 300 °C for 2 h, a strong peak at 43.3°, ascribed to the Cu (111) lattice plane of metallic Cu, appeared. This, together with the fact that no diffraction features of CuO could be identified in the reduced form of the catalyst (Fig. 2), indicates that CuO was completely reduced to metallic Cu in the working sample. H₂-TPR (Fig. 3) showed that 20%Cu/ZrO₂ can be completely reduced at a lower temperature (200 °C), which indicates stronger Cu-Zr interactions; this was considered to be the most important reason for FA decomposition over Cu/ZrO₂ catalysts without leaching of Cu.

Based on the above results, we next focused on the direct use of FA as the sole H₂ source to facilitate the hydrogenolysis of glycerol in an aqueous medium. Figure 4 shows plots of glycerol conversion versus temperature in the presence of 20%Cu/ZrO₂-OG for 5 h. With increasing temperature, the reaction rate increased, but the selectivity for 1,2-PDO decreased significantly as a result of formation of appreciable amounts of *n*-propanol as a by-product. As a result, 200 °C was found to be the optimum temperature for targeted 1,2-PDO formation. The molar ratio of FA to glycerol, which might be very important for the product distribution, was also investigated to maximize the 1,2-PDO yield. As shown in Fig. 5, the conversion of glycerol

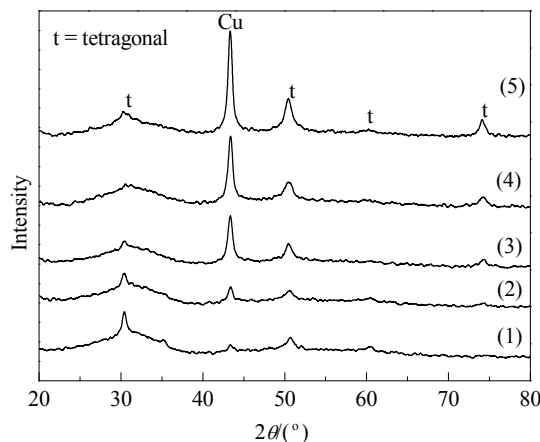


Fig. 2. XRD patterns of reduced Cu/ZrO₂ catalysts with different Cu loadings prepared by the OG CP method. (1) 10%Cu/ZrO₂; (2) 20%Cu/ZrO₂; (3) 30%Cu/ZrO₂; (4) 40%Cu/ZrO₂; (5) 50%Cu/ZrO₂.

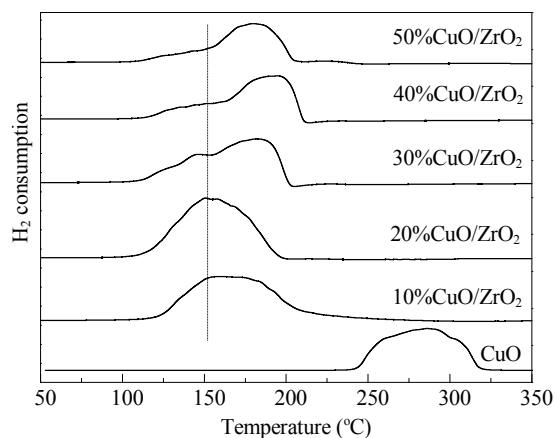


Fig. 3. TPR profiles of CuO/ZrO₂ catalysts with different Cu loadings prepared by the OG CP method.

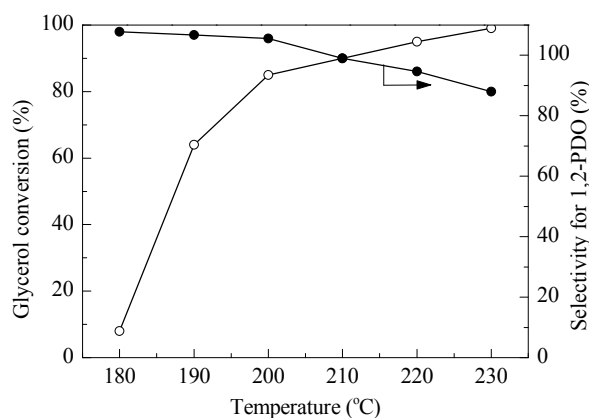


Fig. 4. Glycerol conversions and 1,2-PDO selectivities at different temperatures. Reaction conditions: glycerol 5 mmol, H₂O 10 mL, FA 5 mmol, 0.5 MPa N₂, $n_{\text{glycerol}}/n_{\text{metal}} = 10$, 5 h.

increased from 69% to 89% when the molar ratio of FA to glycerol changed from 1:2 to 3:1; this is consistent with the results in Fig. 1, which shows that FA decomposition is more favored at high FA concentrations. The selectivity for 1,2-PDO was quite low when $n_{\text{FA}}/n_{\text{glycerol}} = 1:2$ because the lack of H₂ could favor the undesirable degradation of glycerol to other products. However, more 1,2-PDO was converted to *n*-propanol by excess H₂ ($n_{\text{FA}}/n_{\text{glycerol}} > 1$). The highest selectivity (96%) for 1,2-PDO was obtained with $n_{\text{FA}}/n_{\text{glycerol}} = 1$. Given the fact that the yield of the target product can be up to 94%, it appeared that complete use of FA was achieved in this particular case.

To explore the reaction performed with 20%Cu/ZrO₂-OG in detail, the product evolution for the direct hydrogenolysis of glycerol with FA at 200 °C was followed by continuous sampling using GC. As shown in Fig. 6, the conversion of glycerol reached 85% within 5 h. The reaction rate then leveled off and an extended time of 18 h was required to attain a conversion of 97%. Throughout the process, the 1,2-PDO selectivity remained above 95%, and an approximately 94% yield of 1,2-PDO was achieved after reaction for 18 h at 200 °C using FA. It is important to emphasize that this value was much better than that reported by Gandarias et al. [17] (conversion of 90% and 1,2-PDO selectivity of 82% after operating for 24 h at 220 °C by

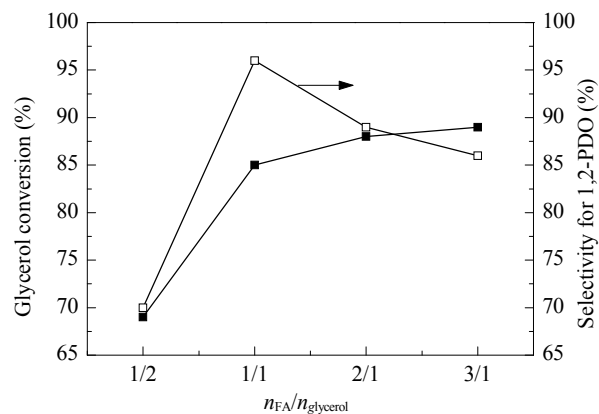


Fig. 5. Glycerol conversions and 1,2-PDO selectivities with different molar ratios of FA and glycerol. Reaction conditions: glycerol 5 mmol, H₂O 10 mL, 0.5 MPa N₂, $n_{\text{glycerol}}/n_{\text{metal}} = 10$, 200 °C, 5 h.

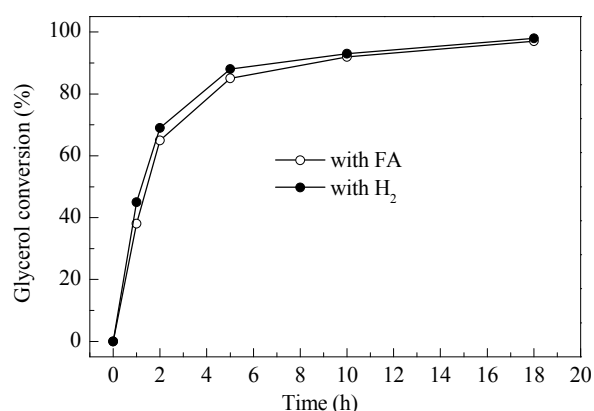


Fig. 6. Profiles of glycerol hydrogenolysis over time using FA and H₂ as sources. Reaction conditions: glycerol 5 mmol, H₂O 10 mL, FA 5 mmol (or 0.8 MPa H₂; $n_{\text{H}_2} = n_{\text{FA}}$), $n_{\text{glycerol}}/n_{\text{metal}} = 10$, 200 °C.

continuously introducing FA). As stability is critical for the efficient use of any catalyst, possible metal leaching during the reaction was studied. As can be seen from Fig. 7, the conversion of glycerol and selectivity for 1,2-PDO remained essentially the same after five cycles. Catalyst leaching was not observed by ICP-AES analysis. This finding demonstrates the high stability of the 20%Cu/ZrO₂-OG catalyst and rules out the possibility of catalyst deactivation during the reaction.

To further understand the reaction pathways involved in the FA-mediated reduction, we investigated a separate hydrogenolysis of an aqueous solution of glycerol (0.5 mol/L) at 200 °C under a H₂ atmosphere (0.8 MPa). As shown in Fig. 6, the hydrogenolysis performance of Cu/ZrO₂ using H₂ closely resembled that observed with FA as the reductant. It is important to note that the pressure inside the autoclave reactor increased rapidly from 0.5 MPa to a maximum value of ca. 4 MPa in the first hour of reaction during the hydrogenolysis of glycerol over 20%Cu/ZrO₂, an indication that significant FA decomposition, leading to H₂/CO₂ formation, occurred in the initial stage of the reaction. A set of control experiments indicated that the FA concentration was constant at 200 °C in the absence of catalysts. Taken together, these results demonstrated that the hydrogenolysis of glycerol with FA did not proceed through

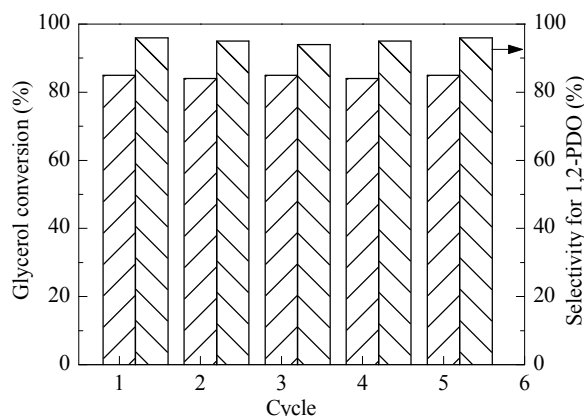


Fig. 7. Recycling study of glycerol hydrogenolysis. Reaction conditions: glycerol 5 mmol, water 10 mL, FA 5 mmol, $n_{\text{glycerol}}/n_{\text{metal}} = 10$, 200 °C, 5 h.

Cu-catalyzed transfer hydrogenolysis, as emphasized by Gandarias et al. [17], but rather through indirect hydrogenolysis of glycerol with H_2 generated in situ by FA decomposition. More specifically, the fact that the Cu/ZrO₂ catalyst can substantially facilitate the crucial FA dehydrogenation appeared to be the key factor for achieving high activity in glycerol hydrogenolysis.

4. Conclusions

We have demonstrated that a highly active, robust, non-noble, Cu/ZrO₂-based catalyst can be used to convert glycerol to 1,2-propanediol (1,2-PDO) in excellent yields using bio-derived formic acid (FA) as a convenient H_2 source. It was observed that there is an optimum FA/glycerol molar ratio (1:1) and an optimum temperature that maximize the yield of 1,2-PDO (94% yield after 18 h at 200 °C). This catalyst can be reused at least five times. The similar performance of the Cu/ZrO₂ catalysts in glycerol hydrogenolysis to 1,2-PDO under a H_2 atmosphere and using FA confirms that the present glycerol reaction with FA proceeds through a straightforward hydrogenolysis of glycerol by H_2 generated in situ by FA decomposition. The present findings form the basis for cost-competitive production of 1,2-PDO from glycerol and the development of new sustainable,

affordable processes for the targeted conversion of bio-derived feedstock, with minimum use of external fossil-fuel-based H_2 sources.

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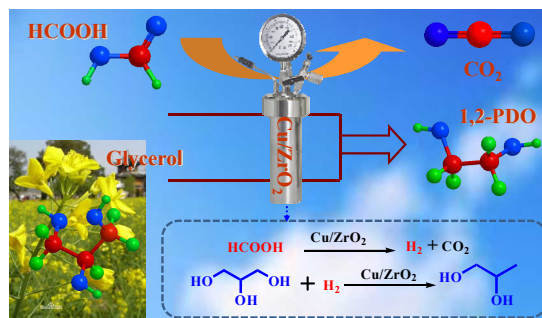
Graphical Abstract

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Efficient catalytic hydrogenolysis of glycerol using formic acid as hydrogen source

Jing Yuan, Shushuang Li, Lei Yu, Yongmei Liu, Yong Cao*
Fudan University

Biorenewable formic acid as a convenient H_2 source and cheap and earth-abundant Cu-based catalysts can be used for the facile conversion of glycerol to 1,2-propanediol (PDO). The present findings form the basis of cost-competitive production of 1,2-PDO from glycerol and the development of new sustainable, affordable processes for the targeted conversion of bio-derived feedstock, with minimum use of external fossil-fuel-based H_2 sources.



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