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Hydrogenolysis of glycerol to propanediols over supported Ag–Cu catalysts

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Abstract Hydrogenolysis of glycerol to 1,2-propanediol and 1,3-propanediol has significant scientific importance and commercial interest due to the huge surplus of glycerol and the various application of propanediols. A series of supported Ag-Cu catalysts synthesized by impregnation method were studied for hydrogenolysis of glycerol to propanediols. The catalysts were characterized by H₂-TPR, NH₃-TPD, XRD, BET, N₂O chemisorption, TG, ICP and SEM. It was observed that the loading of 5% Ag-Cu-based catalysts facilitated the reduction, surface acidity and dispersion of the Cu particles, which improved the conversion of glycerol and promoted the generation of propanediols. It was also found that when loading Ag and Cu simultaneously on Al₂O₃, the catalyst had a better performance for the reaction because of the higher acidity, dispersion and surface area of the Cu species on the catalyst surface. In addition, effects of metal concentrations, metal impregnation sequence, reaction temperature, reaction pressure, reaction time, solvent and pH value of the solution on glycerol hydrogenolysis together with the recyclability of catalyst were investigated in detail. The optimal 5Ag-15Cu/Al₂O₃ achieved 66.4% glycerol conversion with 68.2% 1,2-propanediol and 3.1% 1,3-propanediol selectivity at 200 °C under 3.5 MPa in ethanol for 8 h.

Keywords Glycerol \cdot Hydrogenolysis \cdot PDO \cdot Ag–Cu \cdot Al₂O₃ \cdot Catalyst

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Introduction

With the rapid development of modern society, one of the main problems the whole world facing now is the energy crisis. As a result, renewable biomass materials are receiving more and more attention. Glycerol, which is a major by-product of biodiesel production, has been identified as a promising alternative to petroleum and natural gas for the production of commodity chemicals (Marinoiu et al. 2013).

Hydrogenolysis of glycerol to 1,2-propanediol (1,2-PDO) and 1,3-propanediol (1,3-PDO) is a potential route being studied by many scientists. Propanediol is a valuable product used in many fields, such as polymers, cosmetics, resins and antifreeze (Sharma et al. 2014). The main side products of the reaction are methanol, ethanol, ethylene glycol (EG) and hydroxyacetone (HA). There are a large number of reports on hydrogenolysis of glycerol to propanediols using supported metal catalysts like Cu, Co, Zn and Ni. Cu-based catalyst shows a high conversion and selectivity to propanediols because of its lower activity for C–C bond cleavage (Rekha et al. 2015; Yuan et al. 2010; Montassier et al. 1995; Monstassier et al. 1991). Zhu et al. (2013a, b) found that boron oxide-loaded Cu/SiO₂ catalyst can get 98% selectivity to 1,2-PDO with a complete conversion at 200 °C at H₂ pressure of 5.0 MPa. Considering the good performance and cheap price of Cu catalysts, modification of Cu-based catalysts by a promoter to enhance the catalytic activity for glycerol hydrogenolysis is of great interest. And according to previous studies, noble metals like Pt, Pd and Au are highly selective for glycerol conversion toward propanediols. Ag is an important metal used in many fields, but there are not enough studies on hydrogenolysis of glycerol over Ag catalysts (Yadav et al. 2012). Zhou et al. (2012) reported that about 46%

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conversion and 96% 1,2-PDO selectivity were achieved at 220 °C over Ag/Al_2O_3 . Although Ag catalysts have a good performance for glycerol conversion, the high price of Ag metal limits their application. It is interesting to investigate if the introduce of Ag into Cu catalysts could improve the performance of Cu catalysts.

In addition, Sun et al. (2014) found that Ag loading on commercial Cu/Al₂O₃ catalyst had a good performance in a fixed bed reactor. But as the Ag-Cu/Al₂O₃ consists of two active components, impregnation sequence may have a great influence on the chemical and physical properties of the catalyst. It is desired to know the electronic interaction between the two metals and their activity in a batch reactor. Zhou et al. (2010) tested Ag–Cu catalysts without reduce or pretreatment and they took deionized water as solvent. The main problem of Zhou's study is that the conversion of glycerol was only 27% and no 1,3-PDO was detected. To achieve a higher conversion, generate 1,3-PDO and improve the yield of propanediols, in this work, the prepared Ag–Cu catalysts were first reduced in H₂ atmosphere at 350 °C for 2 h and alcohols were used as solvents. With respect to the hydrogenolysis of glycerol to 1,2 and 1,3propanediol, current studies mainly focus on the preparation methods, types of metal, conditions optimization etc., but give little attention to the effects of solvent on the reaction (Bienholz et al. 2010). This paper studied factors like support, solvent and solution pH together with the recyclability of the Ag-Cu/Al₂O₃ catalyst for the first time.

Experimental

Catalyst preparation

The Ag–Cu catalysts were prepared by an incipient wetness impregnation method with aqueous solutions of Cu(NO₃)₂·3H₂O, AgNO₃ and the supports. The supports include γ -Al₂O₃, MnO₂, SiO₂ and TiO₂. After impregnation, the catalysts were dried at 120 °C for 8 h and calcined at 400 °C in air for 4 h. The percentage of Ag and Cu was calculated based on the weight of Ag and Cu compared to the supports. The prepared catalysts were denoted as *x*Ag– *y*Cu/Al₂O₃, in which *x* and *y* represent the percentage of Ag and Cu loaded on Al₂O₃.

Catalytic activity test

Prior to the reaction, catalysts were pretreated in H_2 flow at 350 °C for 2 h. The catalytic reaction of glycerol was carried out in a stainless-steel autoclave (200 mL) equipped with mechanical stirring, pressure indicator, speed controller and temperature controller. In a typical run, a solution of 30 g glycerol and 70 g ethanol along with 1 g

catalyst were loaded into the reactor. Nitrogen was purged into the reactor three times to remove air before the reaction, and then the reactor was pressurized with hydrogen and heated to the desired temperature. The products were analyzed by a gas chromatograph GC-6890 with a flame ionization detector (FID). A GC column of SE-30 was used with a known amount of 1,4-butanediol as internal standard (Niu et al. 2013). The conversion and selectivity were calculated as follows:

Conversion of glycerol (%)

$$=\frac{\text{Moles of glycerol converted}}{\text{Initial moles of glycerol}} \times 100$$
(1)

Selectivity (%)

$$= \frac{\text{Moles of glycerol converted to product}}{\text{Total moles of glycerol converted}} \times 100 \quad (2)$$

Catalyst characterization

Powder X-ray diffraction (XRD) patterns of the catalysts were recorded on a Rigaku D/max-A instrument with Cu Ka radiation operated at 50 kV and 30 mA. The scanning range was from 10° to 70° .

 H_2 temperature-programmed reduction (H_2 -TPR) studies were carried out in TP-5076 instrument. For each run, 0.05 g catalyst was pretreated in a flow of He (30 mL/min) at 400 °C for 1 h to remove undesired physisorbed species, and after being cooling to 50 °C, the TPR profiles of catalysts were measured from 50 to 500 °C under a flow of 10% H_2/N_2 with a ramping rate of 10 °C/min.

Temperature-programmed desorption of NH₃ (NH₃-TPD) was conducted by TP-5076 apparatus. About 0.05 g sample was loaded and pretreated under a flow rate of He at 400 °C for 1 h. After being cooled to 100 °C, the tube was saturated with pure NH₃ for 1 h at 50 °C and then purged with He to eliminate physisorbed species. Finally, the sample was heated from 100 to 600 °C under He flow with a heating rate of 10 °C/min.

The BET surface area (S_{BET}) and pore volume (V_{p}) were measured by N₂ adsorption at -196 °C with a micromeritics apparatus. Before the measurement, the samples were treated at 200 °C under vacuum for 12 h to eliminate the adsorbed species.

The surface area of copper (S_{Cu}/g_{cat}) and Cu dispersion were determined by dissociative N₂O chemisorption (Liu et al. 2016; Zhu et al. 2013a, b; Wang and Liu 2014; Xia et al. 2013). Before measurement, 0.05 g sample was reduced by flowing H₂ at 250 °C for 2 h, followed by purging with He for 1 h. After cooling at room temperature, the sample was exposed to N₂O flow for 0.5 h. Subsequently, the reactor was flushed with flowing He for 0.5 h to remove the oxidant. Subsequently, H₂-TPR was performed to reduce Cu_2O to Cu by increasing the temperature to 400 °C with a 5% H_2/N_2 flow.

The X-ray photoelectron spectroscope (XPS) measurements were performed on an Escalab 250Xi equipped with AI K α anode. The non-monochromatized AI K α X-ray source (h ν = 1486.6 eV) was operated at 12.5 kV. The spectra were recorded with a passing energy of 110 eV and an X-ray spot size of 500 µm.

Scanning electron microscopy (SEM) was performed on Hitachi S-4800 with an acceleration voltage of 15 kV.

Thermogravimetric (TG) curve was measured by SDT-Q600 instrument. A small quantity of sample was heated to 600 $^{\circ}$ C at a rate of 10 $^{\circ}$ C/min in air.

ICP optical emission spetroscopy (optimal 2100DV, PerkinEler) were performed to measure the chemical compositions of calcined samples.

Results and discussion

Study of catalyst preparation

Effect of Ag/Cu mass ratios

XRD patterns of calcined Ag-Cu/Al₂O₃ catalysts with various Ag to Cu mass ratios are showed in Fig. 1a. The 20Cu/Al₂O₃ catalyst presented the typical diffraction peaks of CuO at $2\theta = 35.5$ and 38.7° (PDF No. 44-0706) and the 20Ag/Al₂O₃ catalyst showed a weak signal of Ag₂O $(2\theta = 32.8^\circ)$ (PDF No. 43-0997) and strong signals of Ag $(2\theta = 38.2 \text{ and } 44.3^{\circ})$ (PDF No. 04-0783). While there were no peaks related to Ag or Ag₂O being detected in 5Ag-15Cu/Al₂O₃ catalyst, which is in accordance with Sun et al.'s report (2014). It seems that Ag was highly dispersed on 5Ag-15Cu/Al₂O₃. And with 5% Ag loading, CuO diffraction peaks became weaker, indicating the better dispersion of Cu particles. When the Ag loading was more than 5%, peaks related to Ag or Ag₂O were detected. XPS in Fig. 2 was used to identify surface chemical state of Ag and Cu of the calcined Ag-Cu/Al2O3 catalysts. According to Fig. 2a, the Cu2p binding values at 953.8 and 933.5 eV ascribed to Cu²⁺ were found for both 20Cu/Al₂O₃ and 5Ag-15Cu/Al₂O₃ (Zhu et al. 2013a, b; Liu et al. 2016). It displayed that valence state of surface Cu particles did not change with 5% Ag loading. Curve-fitting procedure was adopted to distinguish chemical states of Ag. As shown in Fig. 2b, the binding energy at 374 and 368 eV indicated the existence of Ag(0). And the spin-orbit split peaks at 373.7 and 367.7 eV were assigned to Ag(1+) (Zhou et al. 2010). In addition, the amount of Ag(0) is almost as much as Ag(1+). It can be concluded that the surface Cu species are in the state of Cu(2+) and surface Ag species are Ag(0)



Fig. 1 XRD patterns of calcined (a) and reduced (b) Ag–Cu/Al $_2O_3$ catalysts

and Ag(1 +), which is in accordance with XRD tests of calcined Ag-Cu/Al₂O₃ catalysts.

XRD patterns of reduced Ag-Cu/Al₂O₃ catalysts are shown in Fig. 1b. The reduced 20Cu/Al₂O₃ and 5Ag-15Cu/Al₂O₃ presented peaks of Cu at $2\theta = 43.4$ and 50.5° (PDF No. 04-0836), while no diffraction related to CuO was found, which proved that CuO particles were reduced completely. It was obvious that the Cu diffraction became weaker while Ag diffraction became stronger with the increase of Ag addition. In addition, no diffraction peaks of Ag were detected for 5Ag-15Cu/Al₂O₃, which indicated that Ag particles were still highly dispersed in the catalyst after reduction. The Cu dispersion, specific surface area and particle size were listed in Table 1. The BET test showed that 5Ag-15Cu/Al₂O₃ has the largest surface area and pore volume. It can be observed that all the Ag promoted catalysts had higher dispersion than 20Cu/Al₂O₃. It may be concluded that Ag addition promoted the Cu dispersion. And the Cu surface area declined when Cu content



Fig. 2 a Cu2p XPS spectra of calcined $20Cu/Al_2O_3$ and $5Ag-15Cu/Al_2O_3$, b Ag3d XPS spectra of calcined $5Ag-15Cu/Al_2O_3$

decreased, except for $5Ag-15Cu/Al_2O_3$. It is interesting to note that $5Ag-15Cu/Al_2O_3$ had the highest Cu surface area and Cu dispersion among tested catalysts, which might be because that 5% Ag adding promoted the dispersion of Cu particles greatly.

Figure 3 showed the TPR profiles of Ag–Cu/Al₂O₃ catalysts with different Ag–Cu mass ratios. The reduction peak of 20Cu/Al₂O₃ catalyst was observed at about 292 °C, which was ascribed to the reduction of CuO to Cu. The reduction peak shifted from higher temperature to lower temperature with 5% Ag loading. The 5Ag–15Cu/Al₂O₃ displayed a peak centered at about 250 °C, which started from about 200 °C and ended at about 300 °C. The shift of the reduction temperature could be due to the electronic interaction between Ag and Cu, which was in accordance with the results of XRD and N₂O chemisorption tests (Liu et al. 2016; Zhu et al. 2013a, b; Fernández et al. 2015). The 10Ag–10Cu/Al₂O₃ and 15Ag–5Cu/Al₂O₃ catalysts showed

two peaks related to the reduction of Ag_2O and CuO, respectively. While $20Ag/Al_2O_3$ just showed a peak corresponding to the reduction of Ag_2O . It is believed that small amount of Ag loading not only eases the reduction of the catalyst, but also increases the dispersion and surface area of Cu species, which improves the performance of the Cu-based catalysts (Zhou et al. 2010). And according to former researches, surface acidity, Cu dispersion and Cu surface area are the key for the good performance of Cu-based catalysts (Vasiliadou and Eggenhuisen 2014; Liu et al. 2016; Zhu et al. 2013a, b; Wang et al. 2015; Yuan et al. 2010).

The catalytic performances of Ag–Cu/Al₂O₃ catalysts with different Ag/Cu mass ratios were displayed in Table 2. It can be observed that the optimal $5Ag-15Cu/Al_2O_3$ achieved 66.4% glycerol conversion with 68.2%1,2-propanediol and 3.1% 1,3-propanediol selectivity, which is superior to the monometallic catalysts (i.e., $20Ag/Al_2O_3$ and $20Cu/Al_2O_3$). The reason could be that 5% Ag addition benefited Cu reduction, surface acidity, Cu dispersion and Cu surface area. When the Ag addition continued rising, the selectivity of EG, HA and 1-propanol increased while PDOs selectivity decreased. Therefore, $5Ag-15Cu/Al_2O_3$ catalyst was selected for further studies.

Effect of catalyst support

The Ag–Cu bimetal catalysts with various supports (Al₂O₃, SiO₂, MnO₂ and TiO₂) were prepared for glycerol hydrogenolysis. It can be observed from Table 2 that 5Ag-15Cu/Al₂O₃ catalyst showed the highest yield of PDO. The NH₃-TPD profiles of the catalysts are displayed in Fig. 4. Desorption peaks from 150 to 450 °C were presented on 5Ag-15Cu/Al₂O₃ catalyst, which were ascribed to the adsorption of NH₃ on weak acid sites (50-250 °C) and medium strength acid sites (250-450 °C) on the surface of catalyst (Feng et al. 2013; Zhu et al. 2013a, b; Oliveira et al. 2011). However, in the case of MnO_2 and TiO_2 as support, the amounts of total acidity decreased significantly. The 5Ag-15Cu/SiO₂ catalyst only showed a weak desorption peak at about 170 °C, which was attributed to the presence of weak acid sites on the catalyst surface. The presence of acidic sites is necessary for the dehydration of glycerol to acetol, which subsequently is hydrogenated to 1,2-propanediol (Delgado et al. 2013). Physicochemical properties of the catalysts with different supports in Table 1 showed that 5Ag-15Cu/Al₂O₃ had the highest surface area, Cu surface area and Cu dispersion among 5Ag-15Cu catalysts. The BET results showed that the surface area of the supports were in the order of Al₂- $O_3 > SiO_{2>} MnO_2 > TiO_2$. However, the surface acidity of the supports did not present a huge variation.

Catalysts	$S_{\rm BET} ({\rm m^2/g})^{\rm a}$	$V_{\rm p} ({\rm cm}^3/{\rm g})^{\rm a}$	Cu dispersion (%) ^b	$S_{\rm Cu}/g_{\rm cat} \ ({\rm m}^2/{\rm g})^{\rm b}$	$d_{\mathrm{Cu}} (\mathrm{nm})^{\mathrm{c}}$	$d_{\rm Ag} ({\rm nm})^{\rm c}$	Total acidity (µmol/g _{cat}) ^d
20Cu/Al ₂ O ₃	154.8	0.73	7.3	7.9	14.6	_	11.7
5Ag-15Cu/Al ₂ O ₃	167.5	0.82	10.3	8.4	11.8	-	12.5
10Ag-10Cu/Al ₂ O ₃	153.3	0.79	7.9	4.3	13.7	12.4	9.1
15Ag-5Cu/Al ₂ O ₃	138.4	0.63	8.5	2.3	12.9	13.9	7.8
20Ag/Al ₂ O ₃	151.2	0.57	-	_	-	15.8	4.4
5Ag-15Cu/SiO ₂	140.8	0.71	9.2	7.6	12.1	-	3.7
5Ag-15Cu/TiO ₂	123.7	0.65	7.8	6.4	13.5	-	1.9
5Ag-15Cu/MnO ₂	91.1	0.41	6.6	5.4	15.6	-	1.5
Al_2O_3	174.2	0.98	-	_	-	-	1.1
SiO ₂	154.5	0.89	-	_	-	-	0.9
TiO ₂	143.5	0.78	-	_	-	-	0.7
MnO ₂	132.7	0.69	-	-	-	-	0.6

Table 1 Physicochemical properties of different supported Ag-Cu catalysts

^a Measured from BET method

^b Measured from N₂O chemisorption

^c Measured from XRD

^d Measured from NH₃-TPD



Fig. 3 TPR profiles of Ag–Cu/Al₂O₃ catalysts with different Ag–Cu mass ratios: a 0.20, b 5.15, c 10.10, d 15.5, e 20.0

It can be concluded that $5Ag-15Cu/Al_2O_3$ catalyst showed the best activity for the reaction, because the strongest acidity, largest surface area and smallest Cu particles are presented on $5Ag-15Cu/Al_2O_3$ catalyst.

Effect of metal impregnation sequence

It is proposed that the loading of Ag in Cu/Al₂O₃ alter the chemical and physical properties of the surface (Sun et al. 2014). Since the Ag-Cu/Al₂O₃ consists of two active components, their impregnation sequence may have effect on the performance of the catalyst. According to Table 3, the catalyst prepared by simultaneously impregnation showed a higher activity than loading Ag and Cu separately, no matter which one was the first. Figure 5 was XRD patterns of calcined 5Ag-15Cu/Al₂O₃ with different impregnation sequences. It was clear that when loading Cu first the catalyst showed diffraction peaks of Ag and CuO. While other two catalysts just presented the diffraction peaks of CuO, proving the good dispersion of Ag species on the surface of the catalysts. TPR profiles in Fig. 6 showed that the catalyst in which Cu was impregnated first showed two peaks at about 180 and 300 °C related to the reduction of Ag₂O to Ag and CuO to Cu, respectively. While the other two catalysts just showed one wide peak in Fig. 6 related to the reduction of CuO to Cu. And when loading Ag first, the reduction peak of the catalyst was wider and its CuO diffraction in Fig. 5 was stronger, indicting the worse dispersion of Cu particles.

Study of reaction conditions

Through studies above, 5Ag–15Cu/Al₂O₃ prepared by simultaneously impregnation method showed a better performance for the hydrogenolysis of glycerol to PDO. It not

 Table 2
 Catalytic performance
 of different supported Ag-Cu catalysts

Catalysts	Conv. (%)	Selectivity (%)						
		1,2-PDO	1,3-PDO	EG	HA	1-propanol	Others	
20Cu/Al ₂ O ₃	63.1	60.1	1.5	10.3	12.5	4.4	11.2	
5Ag-15Cu/Al ₂ O ₃	66.4	68.2	3.1	6.9	12.3	3.8	5.7	
10Ag-10Cu/Al ₂ O ₃	52.5	57.5	3.2	8.5	17.7	5.8	7.3	
15Ag-5Cu/Al ₂ O ₃	50.1	59.2	2.5	9.7	18.2	5.7	4.7	
20Ag/Al ₂ O ₃	41.3	58.1	3.5	11.2	19.6	7.1	0.5	
5Ag-15Cu/SiO ₂	32.3	68.7	2.3	6.6	5.6	6.4	10.4	
5Ag-15Cu/TiO ₂	28.3	70.1	2.1	5.7	6.5	3.1	12.5	
5Ag-15Cu/MnO ₂	19.6	69.8	9.2	11.3	5.7	2.7	2.2	

Reaction conditions: temperature, 200 °C; initial H₂ pressure, 3.5 MPa; stirring speed 600 rpm; reaction time, 8 h; glycerol ethanol solution of 30 wt %; others include methanol, ethanol, 2-propanol, etc



Fig. 4 NH₃-TPD profiles of 5Ag-15Cu catalysts on different supports: a Al₂O₃, b MnO₂, c SiO₂, d TiO₂

only had a good dispersion of Ag-Cu and a lower reduction temperature, but also had the strongest acidity. And in the following experiments, optimal reaction conditions to promote its conversion and selectivity were systematically studied.

Effect of reaction temperature

Table 3 Effect of metal

The influence of reaction temperature on hydrogenolysis of glycerol to PDO was investigated in the range of



Fig. 5 XRD patterns of calcined 5Ag-15Cu/Al₂O₃ with different impregnation sequences: a simultaneously, b Ag first, c Cu first

180-240 °C at 3.5 MPa for 8 h (Fig. 7). The glycerol conversion rate improved obviously from 20.7 to 85.5% with the increase in reaction temperatures, which demonstrated that the relatively high temperature is conducive to the conversion of glycerol. While the selectivity to PDO was found to decrease significantly from 83.1 to 52.2% as the temperature rose. This could be explained by the exothermicity of the reaction and the intensification of its decomposition reaction by C-C bond cleavage to the formation of byproducts during higher temperatures (Hnat

Table 3 Effect of metal impregnation sequence on the	Sequence	Conv. (%)	Selectivity (%)						
catalytic performance of 5Ag- 15Cu/AlaOa			1,2-PDO	1,3-PDO	EG	HA	1-Propanol	Others	
13Cu/Al ₂ O ₃	Simultaneous	66.4	68.2	3.1	6.9	12.3	3.8	5.7	
	Cu first	41.2	78.2	10.5	4.4	2.5	3.6	0.8	
	Ag first	50.8	53.8	3.4	21.3	15.1	5.6	0.8	

Reaction conditions: temperature 200 °C; initial H₂ pressure 3.5 MPa; stirring speed 600 rpm; reaction time 8 h; glycerol ethanol solution of 30 wt %; others include methanol, ethanol, 2-propanol, etc



Fig. 6 TPR profiles of $5Ag-15Cu/Al_2O_3$ with different impregnation sequences: **a** simultaneously, **b** Ag first, **c** Cu first

et al. 2013). When the temperature was 200 °C, the yield of propanediols was the highest. Therefore, 200 °C was chosen as the optimal reaction temperature.

Effect of reaction pressure

The effect of hydrogen pressure on hydrogenolysis of glycerol was studied from 2.5 to 4.5 MPa at 200 °C for 8 h (Fig. 7). It can be observed that the conversion of glycerol increased from 55.1 to 66.1% as the hydrogen pressure increased from 2.5 to 3.5 MPa, then it increased slowly. It also can be observed that the selectivity of PDO increased from 46.3 to 76.8% as the hydrogen pressure increased from 2.5 to 3 MPa. But it decreased when the hydrogen pressure continued to increase. The reason could be that with the increase of the hydrogen pressure, hydrogen solubility in the ethanol increases and more hydrogen is available to be adsorbed in catalyst surfaces, which leads to the increase of the selectivity to 1,2-PDO and 1,3-PDO. However, relatively higher pressure could also promote the hydrogenation of unsaturated intermediates as well as the further degradation of glycols (Chen et al. 2013). Therefore, 3.5 MPa is the optimal hydrogen pressure for this reaction system.

Effect of reaction time

The reaction time is one of the most important factors affecting the hydrogenolysis of glycerol. Hydrogenolysis of glycerol was carried out at 3.5 MPa and 200 °C with different reaction hours. It is clear from Fig. 7 that with the extension of reaction time, the conversion of glycerol increased gradually. When the hydrogenolysis reaction was carried out for 8 h, the reaction gave 66.4% glycerol



Fig. 7 Effect of reaction temperature, pressure and time on 5Ag– 15Cu/Al₂O₃ catalyst

conversion with 71.3% PDO selectivity. When further prolonging the reaction time to 10 h, the conversion increased, however, the selectivity to PDO decreased due to the happening of side reactions. It is suggested that too much contact time tends to decrease the selectivity of PDO and increase the selectivity of undesired products, such as methanol, ethanol, propanols and acetone, which might be caused by the enhancement of further hydrogenolysis (Priya et al. 2015). Therefore, 8 h was chosen as the optimal reaction time.

Solvent	Conv. (%)	1,2-PDO selectivity (%)	1,3-PDO selectivity (%)	Catalyst acidity $(\mu mol/g_{cat})^a$
Methanol	43.4	45.4	2.1	6.9
Ethanol	66.4	68.2	3.1	9.1
EG	42.3	31.4	4.1	5.3
1-Propanol	50.7	40.6	2.1	7.3

Table 4 Effect of solvent on the catalytic performance of 5Ag-15Cu/Al₂O₃ catalyst

Reaction conditions: temperature 200 °C; initial H_2 pressure 3.5 MPa; stirring speed 600 rpm; reaction time 8 h; glycerol solution of 30 wt %; others include methanol, ethanol, 2-propanol, etc

^a Measured from NH₃-TPD

Effect of solvent

Solvent can play an important role in determining the catalytic performance for many reactions. According to former study, glycerol conversion and selectivity to PDO varied with different solvents (Wang et al. 2015). Methanol, ethanol, EG and 1-propanol were used as solvents for the reaction. All these solvents have good dissolving ability with both glycerol and PDO. And they are also the side products of the reaction, so it is desirable to understand which of them could affect the side reactions most and improve the selectivity to PDO. Table 4 shows the performance of the catalyst in different solvents. It indicates that using ethanol as solvent could hamper the happening of side reactions most, as it has the highest selectivity. It is also clear that reaction in ethanol achieved highest conversion, which may be due to its best solubility for hydrogen.

To find the properties of the $5Ag-15Cu/Al_2O_3$ catalyst in different solvents, the same amount of catalyst were put into these four solvents for 8 h without reaction and retrieve them by filtration followed by drying in N₂ atmosphere at 80 °C for 30 min. Then the acidities of the catalysts were detected via NH₃-TPD. According to NH₃-TPD patterns in Fig. 8, catalyst dipped in ethanol had the strongest weak and medium acid sites, which may be another reason why it had the best activity (Table. 4).

Effect of solution pH

Acid–base property of the reaction system is another important variable that affects the reaction (Maris and Davis 2007). A small amount of acid (CH₃COOH), ethanol and base (Na₂CO₃) were added into the reaction system separately. The pH values of these systems were 4, 7 and 10. The reaction results are shown in Table 5. It can be seen that the maximum glycerol conversion and selectivity were acquired in a neutral solvent. To observe the microscopic morphology of Ag–Cu/Al₂O₃ catalyst under different solution acid–base properties, 5Ag–15Cu/Al₂O₃ catalysts were immersed in glycerol/ethanol solution of different pH values for 8 h without reaction. After filtering



Fig. 8 NH₃-TPD patterns of $5Ag-15Cu/Al_2O_3$ catalysts after immersed in different solvents: **a** methanol, **b** ethanol, **c** EG, **d** 1-propanol

and drying in N₂ atmosphere at 80 °C for 30 min, physicochemical properties of the catalysts were tested (Table 6). Compared to neutral condition, catalyst in acidic solution had larger surface area and smaller particle size, while the one under basic condition had smaller surface and larger particle size. It is believed that surface area, pore volume and particle size have a significant correlation with activity of catalysts, which caused that catalyst under basic condition did not have a good glycerol conversion and selectivity to PDO. The reason why the catalyst in acidic system with larger surface area and smaller Cu particle size did not have a better performance was the formation of ester, which was detected by the gas chromatograph.

Study of catalyst recyclability

According to the literature, copper catalysts in glycerol hydrogenolysis reaction suffer from serious deactivation problems (Vasiliadou and Eggenhuisen 2014). To study the recyclability of the catalysts, 5Ag–15Cu/Al₂O₃ catalyst was separated from the reaction system by centrifugation after reaction. Subsequently, it was washed by ethanol for

Table 5Effect of solution pHon glycerol hydrogenolysis over5Ag-15Cu/Al2O3 catalyst

Table 6 Physicochemical properties of 5Ag–15Cu/Al₂O₃ catalyst after immersed in solutions of different pH

Solution pH	Conv. (%)	Selectivity (%)							
		1,2-PDO	1,3-PDO	EG	HA	1-Propanol	Others		
4	46.7	36.2	2.7	10.5	19.2	6	25.4		
7	66.4	68.2	3.1	6.9	12.3	3.8	5.7		
10	57.2	54.3	2.2	9.4	15.7	5	13.4		

Reaction conditions: temperature 200 °C; initial H_2 pressure 3.5 MPa; stirring speed 600 rpm; reaction time 8 h; glycerol solution of 30 wt %; others include methanol, ethanol, 2-propanol, etc

Solution pH	$S_{\rm BET} ({\rm m}^2/{\rm g})^{\rm a}$	$V_{\rm p} ({\rm cm}^3/{\rm g})^{\rm a}$	$S_{\rm Cu/Cat} ({\rm m}^2/{\rm g})^{\rm b}$	$d_{\rm Cu} (\rm nm)^b$
4	164.8	0.80	50.9	12.1
7	157.9	0.76	50.3	12.7
10	138.4	0.69	47.6	12.9

^a Measured from BET method

^b Measured from N₂O chemisorption

Table 7 Study of the recyclability of 5Ag-15Cu/Al₂O₃ catalyst

Reused times	Ag loading	Cu loading $(mg_{Cu}/g_{cat})^a$	Total acidity $(\mu mol/g_{cat})^{b}$	Conv. (%)	Selectivity (%)				
	$(mg_{Ag}/g_{cat})^{a}$				1,2-PDO	1,3-PDO	EG	HA	1-Propanol
Fresh	36	119	12.5	66.4	68.2	3.1	6.9	12.3	3.8
1	27	96	10.1	36.7	42.8	1.4	7.3	1.3	4.1
2	18	78	7.2	32.1	30.5	1.2	9.7	2.5	7.1
3	12	64	6.7	27.1	18.1	4.1	17.2	1.6	11.2

Reaction conditions: temperature 200 °C; initial H₂ pressure 3.5 MPa; stirring speed 600 rpm; reaction time 8 h; glycerol solution of 30 wt %

^a Measured from ICP method

^b Measured from NH₃-TPD

three times, dried at 80 °C and reduced at 350 °C for 2 h. Then the regenerated catalyst was used for the hydrogenolysis of glycerol again at the same conditions. According to Table 7, the conversion of glycerol and PDO selectivity had a sharp decrease while the selectivity of byproducts like EG and 1-propanol increased after three cycles of reusing, which might be caused by the handling losses of the catalyst as well as active metal aggregation during the reaction (Dam et al. 2013). SEM characterization of fresh and spent samples (Fig. 9) showed that the particles became much larger after reaction, which indicated that accumulation of species did happen. And the XRD characterization (Fig. 10) also showed that the Cu diffraction became stronger and Ag signals appeared after reusing, proving the existence of the accumulation of Ag and Cu particles during the reaction, which may also explain the deactivation of the catalyst.

The thermogravimetric analysis of catalysts after reaction is shown in Fig. 11. The weight loss from room temperature to $150 \,^{\circ}$ C is ascribed to the loss of ethanol absorbed on catalyst surface. The weight decrease from 150 to 300 °C is associated with the presence of strong absorbed glycerol and PDOs. Finally, about 6% weight change happened at more than 300 °C was assigned to the coke formed during the reaction (Vasiliadou and Eggenhuisen 2014). The happening of coke formation also contributed to the deactivation of the catalyst. In addition, Table 7 showed that surface acidity of the catalysts decreased a lot after three cycles of regeneration. It also indicated the content of both Ag and Cu declined after reaction, proving the existence of metal leaching during the reaction.

Conclusions

Supported Ag–Cu catalysts over different supports were prepared by impregnation method and evaluated for the glycerol hydrogenolysis into 1,2-PDO and 1,3-PDO. The addition of 5% Ag to Cu-based catalysts promoted the dispersion and surface area of the Cu species, facilitated



Fig. 9 SEM images of 5Ag-15Cu/Al₂O₃: a before reaction, b after reaction



Fig. 10 XRD patterns of $5 Ag {-} 15 Cu / Al_2 O_3$ catalyst before and after reaction

the reduction of the Cu species and improved the surface acidity of the catalyst. When 5% Ag and 15% Cu were loaded simultaneously on the Al₂O₃, the catalyst had a stronger surface acidity and better species dispersion. Studies on reaction parameters disclosed that reaction temperature, pressure, time and solvent had significant effect on glycerol hydrogenolysis. It was found that higher reaction temperature, pressure and time was conducive to glycerol conversion, but tended to decrease the selectivity of PDO. And the optimal 5Ag–15Cu/Al₂O₃ achieved a 73.1% selectivity to propanediols with a 66.4% glycerol conversion under the optimal reaction conditions of 3.5 MPa initial hydrogen pressure at 200 °C in ethanol for 8 h.



Fig. 11 Thermogravimetric analysis of supported $5\mathrm{Ag15Cu/Al_2O_3}$ catalysts after reaction

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