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Article

Hydrogenolysis of glycerol to propanediols over Cu-MgO/USY catalyst

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ABSTRACT

A series of acid-base bifunctional catalysts composed of USY with different Cu and MgO loadings were prepared, characterized, and tested for the hydrogenolysis of glycerol. The USY support retained the Y zeolite structure, and the introduction of MgO enhanced the dispersion of Cu in the support. At 200 °C, 3.5 MPa H₂, 10 h and with a 6% 0.2Cu-MgO/USY catalyst, 83.6% conversion of glycerol with 40% selectivity to 1,2-propanediol (1,2-PDO) and 19.4% selectivity to 1,3-propanediol (1,3-PDO) was achieved.

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1. Introduction

The increasing depletion of fossil resources and the environmental pollution caused by their combustion have detrimental consequences on environmental protection and social development. Therefore, the development of a substitute energy source such as biodiesel has attracted much attention [1,2]. Owing to the large surplus of glycerol as a byproduct in the production of biodiesel, in recent years, more attention has been focused on new application of glycerol. Propanediols, epichlorohydrin, carboxylic acid esters of glycerol, pyruvate, and other important chemical intermediates can be synthesized from glycerol [3–6]. Among these, propanediols derived from glycerol is a sustainable process with potential application.

The hydrogenolysis of glycerol to 1,2-PDO and 1,3-PDO has good potential and development prospects due to its environment-friendly and low cost of production. Compared with 1,2-PDO, 1,3-PDO is more valuable as it can be used in the pro-

duction of polyester fibers and other important chemicals. There are two existing chemical synthesis routes for 1,3-PDO based on fossil fuels: the Degussa-DuPont process via the hydration of acrolein and the Shell process via the hydroformylation of ethylene oxide, which are in industrial production [7,8]. Less attention has been paid to the fermentation processes to produce 1,2-PDO and 1,3-PDO with its low reaction rate and product concentration [9].

On the basis of previous research [4,10,11], 1,2-PDO is the main product in the hydrogenolysis of glycerol. Wang and Liu [12] reported the hydrogenolysis of glycerol with a Cu-ZnO catalyst prepared by the coprecipitation method in a glycerol water solution. At a reaction condition of 200 °C, 4.2 MPa H₂, and 20 wt% glycerol concentration, 22.5% conversion of glycerol and 83.6% selectivity to 1,2-PDO was achieved. They also used NaOH and H₂SO₄ to alter the pH of the solution and obtained a series of reaction results, which indicated that the conversion of the glycerol and the selectivity to 1,2-PDO increased as the pH of the glycerol solution increased. Yuan et al.

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[13] reported 72.0% conversion of glycerol and 97.6% selectivity to 1,2-PDO over a Cu/MgO catalyst at 3 MPa H₂ initial pressure. Zhou et al. [14] found that a Al₂O₃ supported Ag catalyst exhibited a markedly high activity, giving 46 mol% glycerol conversion with a very high selectivity to 1,2-PDO that reached 96 mol%. Xia et al. [15] reported a solid base supported Rh and Cu catalyst with high conversions of glycerol and selectivity to 1,2-PDO that reached 91.0% and 98.7%, respectively, at 2.0 MPa H₂ and 180 °C, and this catalyst was stable in five consecutive hydrogenolysis tests in ethanol. Xia et al. [16] reported that the hydrogenolysis of glycerol to 1,2-PDO on a Pd_xCu_{0.4}/Mg_{5.6-x}Al₂O_{8.6-x} catalyst achieved 99.6% selectivity to 1,2-PDO and 88.0% conversion of glycerol at 180 °C and 2 MPa H₂ pressure. Generally, 1,2-PDO was the main product without any 1,3-PDO in most of the reports on the one step glycerol hydrogenolysis.

However, there were also some research, which showed that 1,3-PDO was the main product. Nakagawa et al. [17] reported the rhenium oxide-modified iridium nanoparticles supported on silica catalyzed the direct hydrogenolysis of glycerol to 1,3-PDO in an aqueous media. The selectivity to 1,3-PDO at the initial stage reached (67±3)%. The yield of 1,3-PDO reached 38% at 81% conversion of glycerol after 36 h. Kurosaka et al. [18] produced a Pt/WO₃/ZrO₂ catalyst to catalyze the hydrogenolysis of glycerol to 1,3-PDO with a yield of 24% at 170 °C and 8 MPa H₂. Zhu et al. [19] reported the hydrogenolysis of glycerol to 1,3-PDO on a Pt-H₄SiW₁₂O₄₀/SiO₂ catalyst and achieved 31.4% yield of 1,3-PDO with glycerol conversion of 81.2% at 200 °C and 6 MPa H₂.

These works [11,20–22] showed that glycerol is transformed into 1,2-PDO in basic solution or when catalyzed by a catalyst with an alkaline support while it is more likely to be transformed into 1,3-PDO with the presence of a solid acid and noble metals. Furthermore, most of the previous efforts to produce 1,3-PDO have been performed in a high boiling point solvent, which increased the separation difficulty and cost of production. Based on that an alkaline or acid support can be used to get 1,2-PDO or 1,3-PDO selectively, we designed a new kind of acid-base bifunctional catalyst loaded with a non-noble metal, which is both inexpensive and novel to increase the conversion of glycerol and the selectivity to propanediols, especially 1,3-PDO under mild conditions.

In this work, we carried out a detail study of the hydrogenolysis of glycerol to propanediols over a Cu-MgO/USY acid-base bifunctional catalyst in an autoclave. The effects of MgO content and Cu loadings on the catalytic performance were examined.

2. Experimental

2.1. Catalyst preparation

Ultrastable Y type zeolite (USY), SiO₂, and MCM-41 (purchased from Nankai Catalyst Factory) were used as supports. The Cu-MgO/USY catalyst was synthesized by the coprecipitation method with Cu(NO₃)₂·3H₂O (AR, Sinopharm), Mg(NO₃)₂·6H₂O (AR, Sinopharm), and USY as raw materials. An aqueous solution of mixed Cu(NO₃)₂·3H₂O, Mg(NO₃)₂·6H₂O, and USY

power was simultaneously added into a glass reactor. An aqueous solution of Na₂CO₃ was dropped into the reactor with vigorous stirring at 65 °C until a pH value of 9. The slurry was aged for 24 h and dried at 110 °C for 12 h and then calcined at 550 °C in air for 3 h. The catalyst was designed as (X)Cu-(Z)MgO/USY, in which X and Z represented the mass amount (g) of Cu and MgO, respectively, per gram USY used. The catalysts Cu/USY, Cu/MgO, Cu/SiO₂, Cu/MCM-41, and Cu-MgO/SiO₂ prepared with the same method were used as contrast catalysts.

2.2. Catalyst characterization

Fourier transform infrared (FT-IR) spectra of various catalysts were recorded with a Nicolet 5700 spectrophotometer in the transmission mode using a KBr wafer. The spectra were obtained in the wavenumber range from 4000 to 400 cm⁻¹ at a resolution of 2 cm⁻¹. Powder X-ray diffraction (XRD) patterns of the catalysts were collected on a D8 Discover X-ray diffractometer using Cu K_α radiation at 40 kV and 30 mA with λ of 0.15406 nm. The scanning range was 5° to 90° with a scan rate of 2°/min. Temperature-programmed desorption of ammonia (NH₃-TPD) was carried out using a Micromeritics Autochem II 2920 instrument. In a typical experiment, about 0.025 g sample was placed in the tube and pretreated under a flow rate of helium at 500 °C for 2 h. After the system was cooled to 120 °C, the tube was saturated with pure NH₃ for 1 h at 120 °C and then purged with He to eliminate physisorbed species. Subsequently, the sample was heated from 120 to 850 °C at a heating rate of 10 °C/min. Transmission electron microscopy (TEM) was carried out on a JEOL JEM-2011 electron microscope operated at an acceleration voltage of 120 kV. A small amount of samples were prepared by ultrasonically suspending the powder in ethanol, and drops of the suspension were deposited on a copper grid dried at room temperature before analysis.

2.3. Catalytic test

The activity of the catalysts was tested by the hydrogenolysis of glycerol in a 100 ml autoclave with mechanical stirring. Ultrahigh purity hydrogen and nitrogen gases were used in this test. The catalysts were pretreated in H₂ flow at 350 °C for 2 h. In a typical operation, an amount of glycerol solution with absolute ethyl alcohol as solvent and pretreated catalyst were added into the autoclave. Nitrogen was purged into the reactor three times to remove air, and then the reactor was pressurized with hydrogen to 3.5 MPa at room temperature. Then the autoclave was heated to 200 °C and maintained at this temperature for 10 h under continuous stirring at 300 r/min. After the reaction, the products were cooled to room temperature and separated from catalyst by filtration. The products were analyzed by a gas chromatograph GC-6890 (Teng Hai, Shandong, China) with a flame ionization detector (FID). A GC column of SE-54 was used with a known amount of 1,4-butanediol as internal standard. 1,2-PDO and 1,3-PDO were the main products with some other byproducts such as water, glycol, and isopropanol.

3. Results and discussion

3.1. Results of characterization

The XRD patterns of USY, Cu/MgO, and 0.2Cu-(Z)MgO/USY catalysts with different mass ratios of MgO to USY are shown in Fig. 1. All the 0.2Cu-(Z)MgO/USY catalysts had the characteristic peaks of zeolite Y, which showed that the framework structure of the support was kept. The characteristic peaks of zeolite Y from 5° to 33° were weakened as the MgO content increased, which indicated an interaction of the alkaline active component and the acid sites of USY. Meanwhile, the diffraction peaks of MgO and CuO changed with the decrease of MgO content. It can be seen in Fig. 1 that the characteristic peaks of CuO at 36° and 38.3° were enhanced while the MgO peaks at 42.8°, 62.2°, and 78.6° were weakened. The characteristic peaks at 42.8°, 62.2°, and 78.6° became very weak when the mass ratio of MgO to USY was decreased to 0.4 (0.2Cu-0.4MgO/USY). Comparing with the results of the hydrogenolysis of glycerol with 0.2Cu-(Z)MgO/USY in Fig. 7, it can be seen that the conversion of glycerol decreased as the characteristic peaks weakened, from which it can be deduced that Cu-MgO is the active site of the catalyst.

The XRD patterns of the (X)Cu-MgO/USY catalysts with different Cu loadings are shown in Fig. 2. From Fig. 2, we can see that all the catalysts showed the obvious characteristic peaks of zeolite Y, which indicated that the structure of the USY was kept. The characteristic peaks of Cu-MgO appeared at 35°–80° after loading with Cu and MgO. The intensity of the characteristic peaks of CuO at 36° and 38.3° increased as the Cu loadings increased. However, the 10Cu-100MgO/USY catalyst had very weak peaks at these two angles, and it showed poor activity in the hydrogenolysis of glycerol. Therefore, Cu plays an important role in the hydrogenolysis of glycerol [23].

The FT-IR spectra of 0.2Cu-(Z)MgO/USY with different mass

Fig. 1. XRD patterns of USY, 0.2Cu/MgO, and 0.2Cu-(Z)MgO/USY catalyst. (1) 0.2Cu/MgO; (2) 0.2Cu-0.4MgO/USY; (3) 0.2Cu-0.6MgO/USY; (4) 0.2Cu-0.8MgO/USY; (5) 0.2Cu-MgO/USY; (6) 0.2Cu-1.2MgO/USY; (7) USY.

Fig. 2. XRD patterns of (X)Cu-MgO/USY with different Cu loadings. (1) 0.1Cu-MgO/USY; (2) 0.15Cu-MgO/USY; (3) 0.2Cu-MgO/USY; (4) 0.25Cu-MgO/USY; (5) 0.3Cu-MgO/USY; (6) USY.

ratios of MgO to USY and (X)Cu-MgO/USY with different Cu loadings are shown in Fig. 3 and Fig. 4, respectively. The typical peak at 3400 cm^{-1} can be assigned to the OH of USY. The three obvious peaks at 450, 810, and 1100 cm^{-1} were assigned to Si-O. The intensity of these Si-O vibrations weakened as the MgO contents and Cu loadings increased. However, the wavenumber of the Si-Mg peak increased and the intensity was enhanced for the vibration at 1400 cm^{-1} , which indicated interaction between MgO and Cu with the USY.

The NH_3 -TPD results of the 0.2Cu-(Z)MgO/USY, 0.2Cu/MgO, and USY samples are shown in Fig. 5. There was no desorption peak of NH_3 in the 0.2Cu/MgO, which indicated that there were no acid sites on this catalyst. Two desorption peaks of NH_3 appeared at 150–200 °C and 275–325 °C, which were attributed to the adsorption of NH_3 on weak acid sites and medium strength acid sites on the USY surface, with the obvious result

Fig. 3. FT-IR spectra of 0.2Cu-(Z)MgO/USY with different mass ratios of MgO to USY. (1) USY; (2) 0.2Cu-0.4MgO/USY; (3) 0.2Cu-0.6MgO/USY; (4) 0.2Cu-0.8MgO/USY; (5) 0.2Cu-MgO/USY.

Fig. 4. FT-IR spectra of (X)Cu-MgO/USY with different Cu loadings. (1) USY; (2) 0.1Cu-MgO/USY; (3) 0.2Cu-MgO/USY; (4) 0.25Cu-MgO/USY; (5) 0.3Cu-MgO/USY.

Fig. 5. NH₃-TPD profiles of 0.2Cu-(Z)MgO/USY, 0.2Cu/MgO, and USY. (1) 0.2Cu-MgO; (2) 0.2Cu-1.2MgO/USY; (3) 0.2Cu-MgO/USY; (4) 0.2Cu-0.8MgO/USY; (5) 0.2Cu-0.6MgO/USY; (6) 0.2Cu-0.4MgO/USY; (7) USY.

that the amount of weak acid sites was much more than that of the medium strength acid sites. After loading with MgO, the amount of both acid sites decreased although the weak acid sites decreased much more obviously with the medium

Table 1

Hydrogenolysis of glycerol over the catalysts.

Catalyst	Conversion of glycerol (%)	Selectivity (%)	
		1,2-PDO	1,3-PDO
0.2Cu/MgO	57.0	29.1	—
0.2Cu/SiO ₂	34.2	19.4	—
0.2Cu/USY	39.3	51.4	4.5
0.2Cu/MCM-41	46.5	20.8	—
0.2Cu-MgO/SiO ₂	44.1	25.0	—
0.2Cu-MgO/USY	83.7	40.0	19.4

Reaction conditions: 40 wt% ethanol solution of glycerol 100 g, 2.4 g catalyst, 3.5 MPa H₂, 200 °C, 10 h.

strength acid sites, which shifted to a low temperature. When the mass ratio of MgO to USY was increased to 1:1, the medium strength acid became dominant in the catalyst, and the conversion of glycerol and selectivity to 1,3-PDO reached their maxima, which can be seen from the hydrogenolysis results of 0.2Cu-MgO/USY in Fig. 7. Therefore, the improved selectivity to 1,3-PDO was caused by the interaction between the acidic USY and alkaline MgO, which were well matched when the mass ratio of these was 1:1, and the appropriate amount and strength of the acid sites promoted the generation of 1,3-PDO.

Figure 6 shows the TEM images of 0.2Cu/USY, 0.2Cu/MgO, and 0.2Cu-MgO/USY. From the images of Fig. 6(a) and (b), we can see good dispersion of Cu with uniform particle size on the USY or MgO supports. After loaded with Cu and MgO, a fairly obvious interaction between USY and MgO appeared in image of Fig. 6(c), which altered the surface appearance of the catalyst and led to a better dispersion and more capacity of Cu. Because the 0.2Cu-MgO/USY catalyst showed the highest conversion of glycerol and selectivity to 1,3-PDO, which can be seen in Table 1. We deduced that the good dispersion of Cu [24] and new surface morphology caused by the interaction between MgO and USY led to the high activity of the catalyst.

3.2. Catalytic activity of the catalysts

The mechanism of the hydrogenolysis of glycerol [25] indicated that 1,2-PDO is the main product in an alkaline catalytic system although both 1,2-PDO and 1,3-PDO were generated in an acid catalytic system, which was shown by our reaction results (Table 1). No 1,3-PDO was generated when a neutral or alkaline material was used as support, which can be seen from the results of 0.2Cu/MCM-41, 0.2Cu/SiO₂, and 0.2Cu/MgO.

Fig. 6. TEM images of different catalysts. (a) 0.2Cu/USY; (b) 0.2Cu/MgO; (c) 0.2Cu-MgO/USY.

Fig. 7. Effect of mass ratio of USY and MgO on the hydrogenolysis of glycerol over the 0.2Cu-(Z)MgO/USY. Reaction conditions: 40 wt% ethanol solution of glycerol 100 g, 2.4 g catalyst, 3.5 MPa H₂, 200 °C, 10 h.

However, a small amount of 1,3-PDO was generated after an acidic material USY was used as support, indicated by the hydrogenolysis result of catalysis over 0.2Cu/USY. In order to obtain an appropriate acidity and improve the selectivity to propandieols of glycerol, MgO was used to improve the performance of the 0.2Cu/USY catalyst as it showed fairly high activity in the hydrogenolysis of glycerol with a conversion of 39.3% and selectivity to 1,2-PDO of 51.4%, 1,3-PDO of 4.5%, respectively.

Figure 7 exhibits the influence of the mass ratio of MgO to USY with the Cu loading fixed at 20 wt%. It has been suggested that an appropriate acidity, especially the amount of medium strong acid sites [19], is essential for the selective hydrogenolysis of glycerol to 1,3-PDO due to the bifunctional process [26–28]. Meanwhile, an appropriate basicity can increase the conversion of glycerol and selectivity to 1,2-PDO [15] in the hydrogenolysis of glycerol. Therefore, both 1,2-PDO and 1,3-PDO were generated from the hydrogenolysis of glycerol as a result of the synergy between acid and base. From Fig. 7, the conversion of glycerol increased as the mass ratio of MgO to USY increased and reached a maximum when the mass ratio was 1:1. The selectivity to 1,2-PDO decreased at first and then increased, which was opposite to that of 1,3-PDO. This can be explained by that the synergy between acid and base reached an optimum when the mass ratio of MgO to USY was 1:1.

The effect of Cu loading on glycerol hydrogenolysis was investigated. The results are shown in Fig. 8. The mass ratio of MgO and USY in the catalyst was fixed at 1:1. With the increase of Cu loading, the conversion of glycerol increased at first and then decreased. The maximum value (83.7%) was obtained when the Cu loading was 20%. This can be explained by that the introduction of Cu provided extra active sites and accelerated the reaction process. However, the conversion of glycerol decreased as the Cu loading exceeded 20%. This may be caused by that excess Cu generated agglomerates, which blocked the acid sites and reduced the dispersion of Cu. However, the selec-

Fig. 8. Effect of different Cu contents on the hydrogenolysis of glycerol over (X)Cu-MgO/USY. Reaction conditions: 40 wt% ethanol solution of glycerol 100 g, 2.4 g catalyst, 3.5 MPa H₂, 200 °C, 10 h.

tivity to 1,2-PDO rose at first and then decreased when the Cu loading exceeded 15%. The selectivity to 1,3-PDO showed the same variation as the conversion of glycerol and was maximum at 19.4% at 20% Cu loading.

4. Conclusions

Cu-MgO/USY gave better activity and selectivity than other non-noble catalysts. The catalyst with 0.2 g Cu and 1.0 g MgO per gram USY calcined at 550 °C (denoted as 0.2Cu-MgO/USY) gave the highest activity and selectivity. Under the reaction condition of 200 °C, 3.5 MPa initial H₂ pressure, and 10 h, 83.7% conversion of glycerol with 40% selectivity to 1,2-PDO and 19.4% selectivity to 1,3-PDO was achieved. This was attributed to the appropriate acidity and alkalinity of the catalyst and good dispersion of Cu. Although 1,2-PDO was the main product of the hydrogenolysis of glycerol in a neutral or alkaline catalytic medium, the good dispersion of Cu and appropriate interaction between the acidic USY and alkaline MgO promoted the generation of 1,3-PDO over our catalyst.

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Graphical Abstract

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Hydrogenolysis of glycerol to propanediols over Cu-MgO/USY catalyst

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Well dispersed Cu-MgO/USY catalysts have been prepared by the coprecipitation method and used in the hydrogenolysis of glycerol, which showed a relatively high activity and selectivity to propanediols.

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Cu-MgO/USY催化甘油氢解制丙二醇

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摘要: 以USY为载体制备了一系列不同Cu和MgO负载量的酸碱双功能催化剂Cu-MgO/USY用于甘油氢解制丙二醇反应, 并采用X射线粉末衍射、透射电镜、傅里叶红外光谱、NH₃程序升温脱附等手段对该催化剂进行了表征。结果表明, 负载后的USY载体其Y沸石特征峰保持完整, 且MgO的加入提高了Cu在载体表面的分散度。在200 °C, 3.5 MPa H₂下反应10 h以及6% 催化剂0.2Cu-MgO/USY (0.2 g Cu与1.0 g MgO负载于1.0 g USY上面)用量的条件下, 甘油转化率达到83.6%, 1,2-丙二醇及1,3-丙二醇的选择性分别为40%和19.4%。

关键词: 甘油氢解; 甘油; 1,2-丙二醇; 1,3-丙二醇

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