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Hydrogenolysis of Glycerol to Propylene Glycol on Nanosized Cu–Zn–Al Catalysts Prepared Using Microwave Process

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Cu–Zn–Al catalysts were prepared using microwave-assisted process and co-precipitation methods. The prepared catalysts were characterized by XRD, BET, XPS and TPD of ammonia and their catalytic activity for the hydrogenolysis of glycerol to propylene glycol was also examined. The XRD patterns of Cu/Zn/Al mixed catalysts show CuO and ZnO crystalline phase regardless of preparation method. The highest glycerol hydrogenolysis conversion is obtained with the catalyst having a Cu/Zn/Al ratio of 2:2:1. Hydrogen pre-reduction of catalysts significantly enhanced both glycerol conversions and selectivity to propylene glycol. The glycerol conversion increased with an increase of reaction temperature. However, the selectivity to propylene glycol increased with an increase of temperature, and then declined to 30.5% at 523 K.

Keywords: Hydrogenolysis, Propylene Glycol, Glycerol, Cu–Zn–Al Catalyst, Microwave Process.

1. INTRODUCTION

Biodiesel fuel has attracted considerable attention as a renewable and environmentally friendly source of energy. However, a large amount of glycerol will be produced from the biodiesel industry as byproduct in next decades. About 10% of crude glycerol will be formed during the synthesis of biodiesel from triglycerides.[1–6] In the near future, a huge amount of crude glycerol is expected to be produced as a byproduct from biodiesel industries and may be of little value. The utilization of crude glycerol may partially compensate for the production costs of biodiesel, making it economically feasible as well as overcoming the disposal problem of the surplus crude glycerol from biodiesel industries.[7] Among the plentiful chemicals derived from glycerol, propylene glycol has attracted much attention from researchers because of its wide applications in pharmaceuticals, anti-freezers, foods, agricultural etc.[8–10] Selective hydrogenolysis of glycerol to propylene glycol requires cleavage of C—O bonds by hydrogen without attacking C—C bonds in the glycerol molecule. For this purpose, a number of solid catalysts have been explored. For example, CuO/ZnO,[11] Raney Ni,[12] sulfide Ru,[13] Ru/C,[14] and copper chromite[15] catalysts have been tested. Among these catalysts, CuO-containing mixed oxides exhibit the higher activity compared to other catalysts.

Microwave heating has lately popular in the crystallization of materials such as zeolites and other inorganic materials,[16] due to its higher yields, cleaner synthetic method and shorter crystallization time compared with the conventional method. In addition, the synthesis of metal oxides with microwave heating has many advantages such as fast crystallization, increased phase purity and selectivity, narrow size distribution and facile morphology control.

In this study, Cu–Zn–Al catalysts were prepared using microwave-assisted process and we have synthesized them

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using co-precipitation methods for comparing the effect of preparation method. The synthesized metal oxides were characterized and their catalytic activity on the hydrogenolysis of glycerol to propylene glycol in the presence of hydrogen was also examined along with the effect of reaction conditions.

2. EXPERIMENTAL DETAILS

$Cu(NO_3)_2 \cdot 2.5H_2O$, $Zn(NO_3)_2 \cdot 6H_2O$ and $Al(NO_3)_3 \cdot 9H_2O$ ($>98\%$, Sigma-Aldrich) were dissolved 50 ml of distilled water and then, 2.0~6.0 M of malic acid was added to the solution. The solution was irradiated by microwave during 15 min with stirring. Microwave synthesis was performed using 600 W, 2.45 GHz home-made microwave digestion system (LG Electronic Co.). After irradiation, the samples were calcined in an atmosphere of air at 450 °C for 6 h. The hydrotalcite type catalysts were prepared by typical co-precipitation method at constant pH as a reference catalysts.

The metal composition of the catalysts was determined by X-ray Fluorescence Spectrometer (XRF). The crystal structures of the prepared mixed oxides were examined by powder X-ray diffraction (XRD) with Cu-Kα radiation (Rigaku Co. Model DMax). The BET surface area of the prepared catalysts was determined by nitrogen physisorption data at 77 K using a NOVA 1000 e (Quantachrome Co., USA). Temperature-programmed desorption (TPD) of ammonia experiments were carried out using 100 mg catalysts under a gas flow (100 ml/min) of NH_3 (2000 ppm) diluted with helium. Mass spectrometer (HPR 20) was used to monitor the ammonia desorption amount.

The hydrogenolysis of glycerol to propylene glycol was carried out in a home-made glass-lined stainless steel autoclave reactor (Hanwoul Co., Korea). Each reactor with a capacity 150 mL is equipped a stirrer, a heater and a temperature controller. The reactor were flushed several times with nitrogen followed by hydrogen. Then the reactor was heated to the desired reaction temperature and pressurized with hydrogen to the necessary pressure. The speed of the stirrer was set constant 700 rpm throughout the reaction. Unless specially mentioned, all catalysts without pretreatment by hydrogen stream were used in this work.

Reactants and products were analyzed by VARIAN 3800 Gas Chromatography (U.S.A) equipped with a flame ionization detector (FID). The separation of reactant and products were performed on an Agilent HP-FFAP capillary column (25 m × 0.32 mm × 0.5 um) with the oven isothermal at 180 °C. Detected liquid products mainly include propylene glycol, ethylene glycol, and trace of amounts of 1,3-propanediol, 1-propanol, 2-propanol, methanol and ethanol. Conversion of glycerol is defined as the ratio of the number of moles of glycerol consumed in the reaction to the total moles of glycerol initially present. Selectivity is defined as the ratio of the number of moles of the product formation to that of the glycerol consumed in the reaction. Selectivity to propylene glycol, acetol and ethylene glycol were discussed in this study by considering both the amounts detected and commercial importance.

3. RESULTS AND DISCUSSION

Figure 1 shows the XRD patterns of Cu/Zn/Al (2/2/1) catalysts prepared by different method. The XRD patterns shows CuO and ZnO crystalline phase regardless of preparation method. CuO crystalline phase was observed at $2\theta = 35.5°$ and $38.5°$ corresponding to the most intense reflection of tenorite CuO.[17] When the catalyst is prepared by microwave process, a mixed oxide phase is detected at $2\theta = 11.2$ and $24.2°$. Corresponding to JCPDS data, it is identified to have a crystalline phase of $Cu_{0.4}Al_{0.7}Zn_{1.85}O_5$.

As shown in Figure 2, the catalysts reduced by hydrogen shows Cu crystallite diffraction peak at 43.1 and 50.1° instead of CuO peaks. This result indicates the active Cu metallic species can be obtained from the hydrogen reduction at 300 °C for 3 h.

The BET surface areas of Cu/Zn/Al catalysts are measured and are shown in Table I. The surface areas of catalysts increase with an increase of the amount of aluminum oxide regardless of the preparation method. In addition, the catalysts prepared by co-prepitation method have higher surface area than those prepared by microwave process.

Table I shows glycerol hydrogenolysis conversion and selectivities to acetol, propylene glycol and ethylene glycol at 473 K on various catalysts used in this study.

Bulk CuO and ZnO show very poor activity for glycerol hydrogenolysis. It is well known that the conversion of glycerol via a dehydration reaction to acetol (hydroxylacetone) followed by a hydrogenation reaction to selectively produce propylene glycol.[11] The catalyst for the dehydration of alcohol should have either strong Lewis or Bronsted acid sites. ZnO shows an activity solely for glycerol dehydration without forming any hydrogenolysis

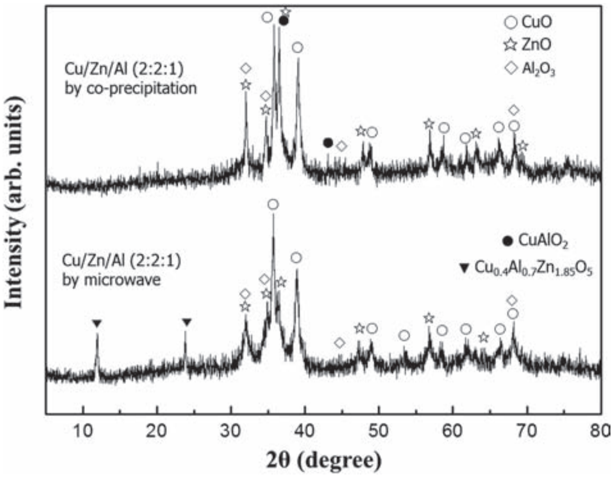

Figure 1. X-ray diffraction patterns of Cu/Zn/Al (2/2/1) catalysts prepared different method.

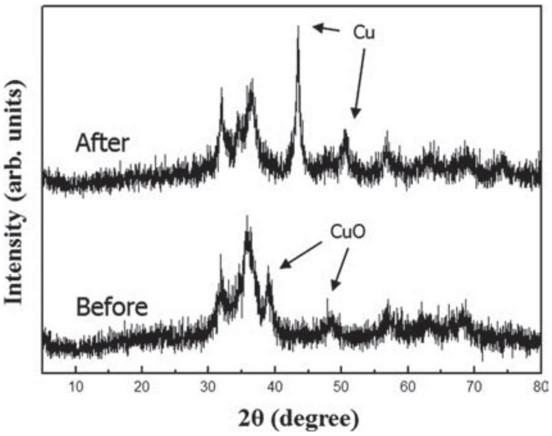

Figure 2. X-ray diffraction patterns of Cu/Zn/Al(2/2/1) catalysts with and without hydrogen pre-reduction.

product, indicating that ZnO only plays a role on dehydration of glycerol. However, CuO shows the formation of propylene glycol, indicating that it has the catalytic ability of the hydrogenation reaction.

The glycerol hydrogenolysis conversion and selectivity to propylene glycol is increased on the Cu/Zn mixed oxide. This result shows the synergy effect of CuO and ZnO mixed oxides. In addition, the addition of aluminum oxide into Cu/Zn mixed oxide significantly enhanced both the conversion of glycerol and the selectivity to propylene glycol. It is thought that Cu/Zn mixed oxides were well incorporated into aluminum oxide in order to achieve bifunctional nature of the catalyst with dehydration and hydro-genolysis properties. In addition, the increase in the Cu/Zn composition of the catalyst also enhances the glycerol hydrogenolysis conversion and selectivity to propylene glycol. Dalai et al. reported that the variation in the Cu/Zn composition of Cu/Zn/Al mixed oxides might have an effect on the hydrogenolysis of glycerol by modifing the acidic and hydrogenation properties. As shown in Table II, the highest glycerol hydrogenolysis conversion is obtained with the catalyst having a Cu/Zn/Al ratio of 2:2:1.

Table I. Physical properties and catalytic activity of catalysts used in this study.

Preparation method	Cu/Zn/Al catalyst (molar ratio)	Surface area (m^2/g)	Malic acid (M)	Conversion (%)	Selectivity (%)		
					Acetol	PG	EG
Precipitation	Cu/Zn (1/1)			13.2	4.9	28.6	2.6
	CuO			6.5	–	5.6	–
	ZnO			1.4	–	–	–
Co-precipitation	Cu/Zn/Al (1/1/4)	131	–	37.5	2.2	66.2	1.7
	Cu/Zn/Al (1/1/1)	62	–	51.2	0.8	50.3	2.0
	Cu/Zn/Al (2/2/1)	79	–	64.4	4.7	51.0	2.4
Microwave process	Cu/Zn/Al (1/1/4)	89	6	28.3	1.7	39.2	1.9
	Cu/Zn/Al (1/1/1)	41	6	41.7	1.5	40.5	1.4
	Cu/Zn/Al (2/2/1)	–	3	31.5	–	23.3	–
	Cu/Zn/Al (2/2/1)	43	6	43.4	2.9	66.4	3.5

Notes: Reaction conditions: 5 wt% catalysts, 20 wt% glycerol aqueous solution, 250 psig H_2, reaction time 20 h, reaction temperature 473 K.

Table II. Catalytic activities of Cu/Zn/Al catalysts prepared by microwave process for hydrogenolysis of glycerol to propylene glycol with and without hydrogen pre-reduction.

	Cu/Zn/Al catalyst (molar ratio)	Conversion (%)	Selectivity (%)		
			Acetol	PG	EG
Non pre-reduction	Cu/Zn/Al (1/1/1)	41.7	1.5	40.5	1.4
	Cu/Zn/Al (2/2/1)	43.4	2.9	66.4	3.5
Pre-reduction	Cu/Zn/Al (1/1/1)	54.9	1.2	51.3	2.2
	Cu/Zn/Al (2/2/1)	72.6	0.5	76.4	7.6

Notes: Reaction conditions: 5 wt% catalysts, 20 wt% glycerol aqueous solution, 250 psig H_2, reaction time 20 h, reaction temperature 473 K.

The microwave-assisted process in the preparation of metal oxides had some advantages compared to the conventional method. In this study, we have prepared the Cu/Zn/Al catalysts using microwave process and the catalytic activity is shown in Table I. The catalysts prepared using microwave process show lower glycerol hydrogenolysis conversion than those prepared using co-precipitation method. This result can be explained in Figure 3. The conversion of glycerol hydrogenolysis is dependent on the acidic property of the catalyst. As shown in Figure 3, the ammonia TPD peak of the catalyst prepared using co-precipitation method is larger than that prepared using microwave process. The Cu/Zn/Al catalyst prepared by co-precipitation method has large amount of acid sites and then shows higher conversion.

Table II shows the glycerol conversions and selectivities at 473 K on Cu/Zn/Al catalysts with and without hydrogen pre-reduction before it was loaded to the reactor. Hydrogen pre-reduction of catalysts significantly enhances both glycerol conversions and selectivity to propylene glycol. As shown in Figure 2, Cu metallic species are obtained instead of CuO particles, indicating that metallic Cu is much more active than the copper oxides on the hydrogenolysis of glycerol.

Figure 4 shows the effect of reaction temperature on glycerol conversion and selectivities to products on Cu/Zn/Al (2/2/1) catalyst prepared using microwave process. The glycerol conversion increased with an increase of

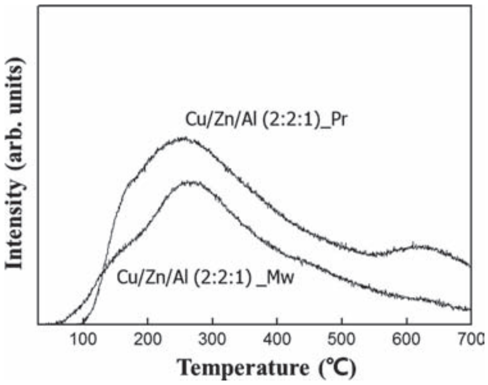

Figure 3. Ammonia TPD patterns of Cu/Zn/Al (2/2/1) catalysts prepared by different method.

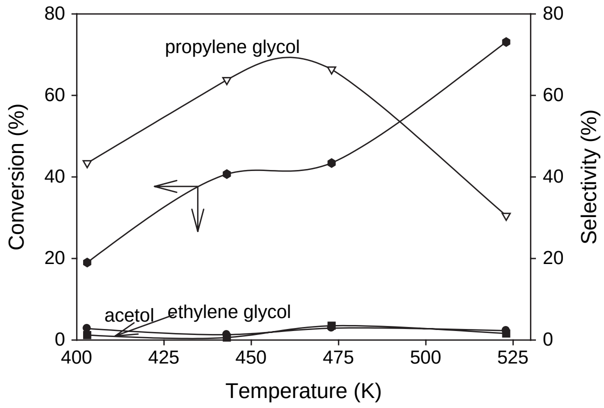

Figure 4. Effect of reaction temperature on glycerol conversion and selectivities to products on Cu/Zn/Al (2/2/1) catalyst prepared using microwave process.

reaction temperature. However, the selectivity to propylene glycol increased with an increase of temperature, and then declined to 30.5% at 523 K. This result indicates that high propylene glycol selectivity requires optimal reaction temperature. It is thought that the dehydrated glycerol intermediates were decomposed to over-hydrogenolyzed products by breaking their C—C and C—O bonds at higher reaction temperature.

4. CONCLUSIONS

We have prepared Cu–Zn–Al catalysts by microwave-asisited process and co-precipitation methods. The prepared catalysts were characterized and their catalytic activity for the hydrogenolysis of glycerol to propylene glycol was also examined. The XRD patterns of Cu/Zn/Al mixed catalysts show CuO and ZnO crystalline phase regardless of preparation method. The highest glycerol hydrogenolysis conversion is obtained with the catalyst having a Cu/Zn/Al ratio of 2:2:1. Hydrogen prereduction of catalysts significantly enhanced both glycerol conversions and selectivity to propylene glycol. The glycerol conversion increased with an increase of reaction temperature. However, the selectivity to propylene glycol increased with an increase of temperature, and then declined to 30.5% at 523 K.

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