

Effect of preparation method on structure and catalytic activity of Cr-promoted Cu catalyst in glycerol hydrogenolysis

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Abstract—Relationships between surface structure and catalytic properties were investigated for a series of copper chromium catalysts. The catalysts were prepared using methods involving impregnation and precipitation, and their catalytic activities were evaluated for the hydrogenolysis of glycerol. Catalyst (10I and 50I) prepared by the impregnation method contained a mixed phase of both individual copper and chromium oxide structures, while the catalyst (50P) prepared by precipitation showed a single phase, with a copper chromite spinel structure (CuCr_2O_4). XPS data indicated that, after the reduction step, the copper species in the impregnated catalyst was reduced to Cu^0 , but the catalyst prepared by the precipitation method retained a spinel structure evidenced by the large amount of Cu^{2+} species. In hydrogenolysis reactions, the precipitated catalyst showed a higher catalytic activity than the impregnated catalyst. Thus, the reduced copper chromite spinel structure, which constitutes a single phase, appears to be responsible for the high catalytic activity in the hydrogenolysis of glycerol to propylene glycol.

Key words: Copper Catalyst, Chromium, Hydrogenolysis, Glycerol, Propylene Glycol

INTRODUCTION

Biodiesel fuel has attracted considerable attention as a renewable and environmentally friendly source of energy [1-4]. Such materials can serve as an alternative energy source for fossil diesel and as a fuel additive in preparation for future tightened environmental legislation [5]. However, one of the major problems in biodiesel production is that a byproduct is 10% glycerol. The rapidly increased production of biodiesel has led to a drastic surplus of glycerol in the chemical markets. For this reason, numerous studies have been reported, in attempts to develop the processes for the value-added chemical production of useful chemicals from glycerol [6-8].

A variety of valuable chemicals can be produced from glycerol [5,9]. One of these, propylene glycol, is a major commodity widely used in the production of unsaturated polyester resins, functional fluids (antifreeze, de-icing, and heat transfer), pharmaceuticals, foods, cosmetics, liquid detergents, tobacco humectants, flavors and fragrances, personal care, paints and animal feed [10,11]. The majority of propylene glycol is currently produced via the hydration of propylene oxide derived from propylene by either the chlorohydrin or hydroperoxide process [12]. Because of the cost of these processes, the hydrogenolysis of the biodiesel by-product, glycerol, has great potential for the cost-effective production of propylene glycol.

Several groups have reported on the production of propylene glycol from glycerol via hydrogenolysis. Dasari et al. [10] examined a series of commercially available catalysts and reported that copper chromite catalysts showed a high catalytic activity. Although they

reported high catalytic activities, our overall knowledge of the relationship between catalytic properties and performance remains limited. The physical and chemical states of both copper and chromium species can be altered, based on the preparation method used. Examples of this include the copper species deposited on a chromium support or the case of a copper-chromium solid solution of each oxide species. Chromium, which plays a role as support material, can confer a geometric promotion effect providing structural stability and has an effect on metal-support interactions. On the other hand, when copper and chromium form a solid solution, the resulting structure is a copper chromite spinel structure. The catalytic activity of such a structure would be expected to be different from that of a catalyst composed of a mixture of elemental copper and chromium. In addition, the copper chromite spinel structure was previously reported to catalyze other reactions such as hydrogenation/dehydrogenation [13,14].

In this study, copper catalysts promoted by chromium were prepared by different synthesis methods. The structures and compositions of each catalyst were found to be changed, based on the different synthesis methods employed. The objective of this work was to investigate the relationships between surface structure properties and the catalytic activities of the prepared catalysts in the hydrogenolysis of glycerol to propylene glycol.

EXPERIMENTAL

1. Catalysts Preparation

Two types of catalysts were prepared using different synthesis methods: impregnation and precipitation. An impregnated catalyst was prepared by the incipient wetness impregnation of aqueous copper nitrate ($\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$, Riedel-de Haën) solutions onto a

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chromium(III) oxide support (Cr_2O_3 , Samchun chemical). After impregnation, the samples were dried overnight and then calcined in an atmosphere of air at 550°C for 6 h. To control the amount of copper on the catalyst surface, the amount of copper used was adjusted to a 1 : 10 and 1 : 2 in molar ratio with the chromium species of the support. The 10% copper impregnated catalyst (Cu : Cr=1 : 10 molar ratio) and 50% copper impregnated catalyst (Cu : Cr=1 : 2 molar ratio) are denoted as 10I and 50I, respectively. For the preparation of precipitated catalysts, a known amount of copper nitrate was dissolved in distilled water. A calculated amount (Cu : Cr=1 : 2 molar ratio) of chromium nitrate ($\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, Sigma-Aldrich) was added to copper metal salt solution under vigorous stirring. A sodium hydroxide solution was then added to the metal salt solution. The precipitates were filtered, washed and dried overnight. The dried solid materials were powdered and calcined to yield the catalysts. The prepared catalysts are designated as 50P. Prior to the reactions, all the catalysts used in this study were reduced at 320°C for 2 h with mixed gas (10% H_2 in N_2) in a flow reactor. After the reduction, all catalysts were passivated with the N_2 flow with very small amount of O_2 (<1% O_2 in N_2) for 1 h. Reduced and passivated catalysts were used for the reaction test.

2. Characterization

The X-ray diffraction (XRD) patterns of the powder catalysts were recorded using a D-MAX2500-PC, Rigaku Corporation instrument equipped with Cu $K\alpha$ radiation ($\lambda=1.5405 \text{ \AA}$). To examine the reducibility of the synthesized catalysts, temperature-programmed reduction (TPR) measurements were performed in a conventional flow system with a moisture trap connected to a thermal conductivity detector (TCD). The flow rate of the mixed gas (10% H_2 in N_2) was fixed at 20 ml/min and the heating rate was $5^\circ\text{C}/\text{min}$. X-ray photoelectron spectroscopy (XPS) spectra were recorded on a KRATOS AXIS electron spectrometer equipped with Mg $K\alpha$ radiation for exciting photoelectrons. All binding energies (BE's) are referred to the adventitious C 1s line at 284.6 eV.

3. Hydrogenolysis of Glycerol

The conversion of glycerol to propylene glycol by hydrogenolysis was carried out in a Hastelloy-C autoclave with a magnetic stirrer and heater. The autoclave was filled with glycerol (50 g, SIGMA-Aldrich, Tech., 90%) and catalyst (1 g, 2 wt%); the system was then purged with hydrogen gas for 30 min. The reactor pressure increased with hydrogen to the set point pressure (80 bar) and the suspension heated to the desired reaction temperature (220°C).

The reaction products were removed from the autoclave and centrifuged (HA-500, Hanil Science Industrial) to remove the catalyst. These samples were then analyzed by gas chromatography (DS 6200, DONAM INSTRUMENT INC.) and the products detected using a flame ionization detector (FID). SGE BP20 (WAX) GC Capillary Columns ($25 \text{ m} \times 0.53 \text{ mm} \times 1 \mu\text{m}$) were used for the separations.

RESULTS AND DISCUSSION

The crystal structures of the calcined catalysts were confirmed by XRD analysis and representative XRD patterns are shown in Fig. 1. In the case of the impregnated catalysts (10I and 50I), copper and chromium were present in separate form in the oxide states. The peak intensity of the copper oxide phase was proportional to the copper content in the catalyst. Catalyst 50I showed a much higher

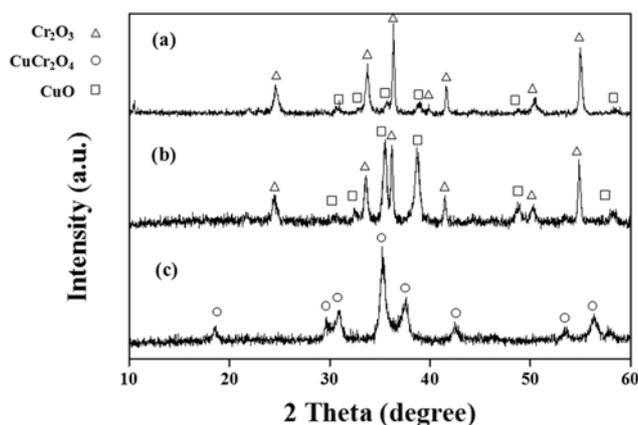


Fig. 1. XRD patterns of synthesized catalysts prepared by different methods. (a) 10I (Cu : Cr=1 : 10), (b) 50I (Cu : Cr=1 : 2) and (c) 50P (Cu : Cr=1 : 2).

CuO diffraction peak intensity than that of 10I. In the case of 50P, which was prepared by the precipitation method, strong characteristic peaks assigned to a copper chromite spinel phase were observed at 18.6° , 29.6° , 31.1° and 37.7° which corresponds to (111), (220), (022) and (113) planes, respectively. These results indicate that the copper species in the impregnated catalysts on the catalyst surface are independent of the chromium species, while elemental copper in the precipitated catalyst formed a solid solution with chromium.

The reducibility of the synthesized catalysts was examined by conducting H_2 -TPR, as shown in Fig. 2. In the case of catalyst 10I, a small amount of surface copper species underwent reduction at temperatures below 200°C , while the TPR profile of catalyst 50I indicated the contribution of more than one reduction characteristic. This suggests that a variety of copper species are present in the catalyst, including bulk state copper and copper species that interacted with the chromium support. Compared to the impregnated catalyst, 50P showed a single peak which began to be reduced at a higher temperature region than the impregnated catalysts. In addition, the reduction of 50P occurred in a narrow temperature range, indicating that the copper and chromium species in the precipitated

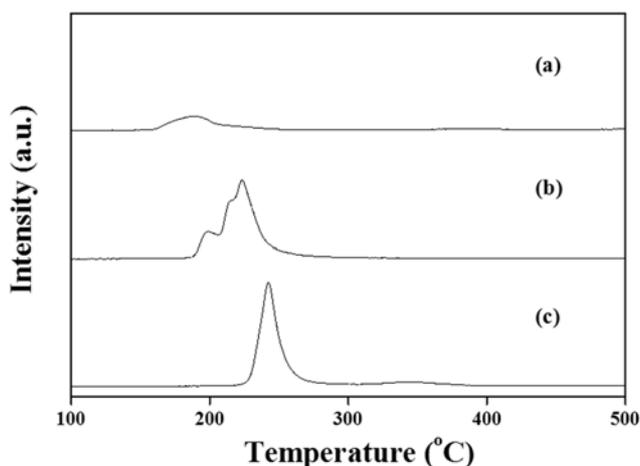


Fig. 2. H_2 -TPR profiles of synthesized catalysts. (a) 10I (Cu : Cr=1 : 10), (b) 50I (Cu : Cr=1 : 2) and (c) 50P (Cu : Cr=1 : 2).

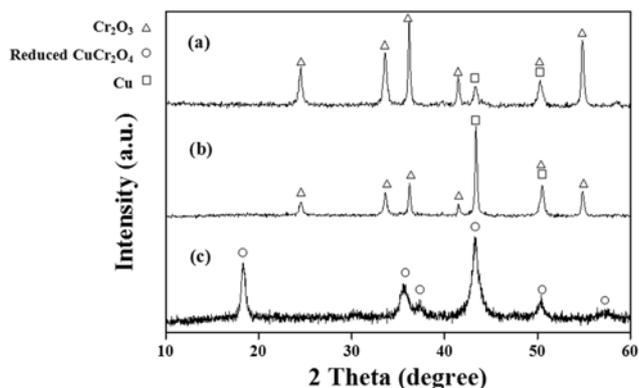


Fig. 3. XRD patterns of synthesized catalysts after reduction. (a) 10I (Cu : Cr=1 : 10), (b) 50I (Cu : Cr=1 : 2) and (c) 50P (Cu : Cr=1 : 2).

catalyst formed a single phase structure, a finding that is consistent with the XRD results. Differences in the reducibility of the catalysts can be attributed to differences in surface composition, which can affect catalytic performance.

All of the prepared catalysts were reduced before conducting the test reactions, and the crystal structures of the reduced catalysts were confirmed by XRD analysis, as shown in Fig. 3. In the case of catalysts 10I and 50I, all of the CuO species supported on the chromium oxide support were reduced to Cu⁰ after the reduction at 320 °C. In the case of catalyst 50P, changes in the diffraction pattern were observed, as a result of the transformation from a tetragonal spinel phase to a cubic spinel phase [14]. This indicates that copper species in a spinel structure are not easily reduced to Cu⁰ with its solid solution structure being maintained. The low reducibility of 50P is consistent with the TPR results, which began to be reduced at a higher temperature than that for the impregnation catalysts. Such different reduction behavior also indicates the existence of different copper species in each catalyst.

Physical properties of prepared catalysts are summarized in Table 1. BET surface areas of all catalysts are found to be small less than 20 m²/g. However, catalyst 50P showed relatively higher surface area than 10I and 50I by ca. 4 m²/g. Crystalline sizes of prepared catalysts before and after reduction process were calculated by Scherrer equation, which were also listed in Table 1.

The chemical states of the surface copper species after reduction were investigated by XPS analysis (Fig. 4). The characteristic profile of the Cu 2p region and satellite peaks by the shaken up effect can be found in this result [15]. As shown in the deconvolution profiles, Cu 2p spectra consist of two peaks with BE's of 932.4 and 934.0 eV, which correspond to Cu⁰ and Cu²⁺, respectively [16]. In the

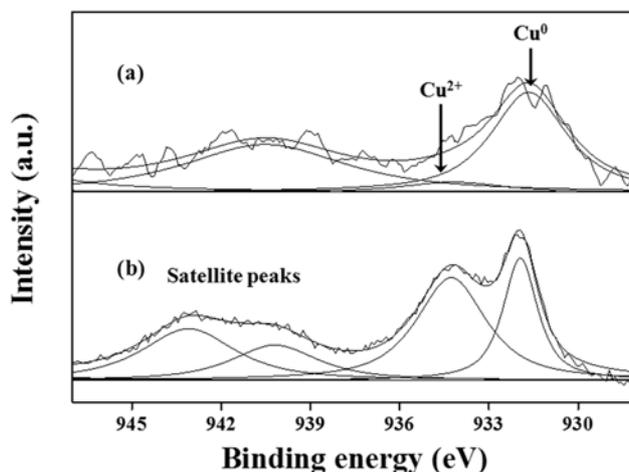


Fig. 4. X-ray photoelectron spectra (Cu 2p region) of synthesized catalysts after reduction process. (a) 50I (Cu : Cr=1 : 2) and (b) 50P (Cu : Cr=1 : 2).

case of catalyst 50I, most of the surface copper species are present as Cu⁰, due to the complete reduction of surface CuO. On the other hand, although Cu⁰ species are also present in 50P, a large amount of Cu²⁺ species remain, even after the reduction. The reduction properties of copper chromite spinel structure have been reported elsewhere [14,17]. During the partial reduction process, hydrogen atoms are incorporated into the crystalline structure and copper species are partially reduced and change their position in the spinel structure. Consequently, the main spinel structures are transformed to a cubic spinel phase without the loss of oxygen species [17]. As a result, a large amount of Cu²⁺ state species were detected after the completion of the reduction. Such reduction process of copper chromite spinel structure is known as a reversible process. It is believed that this reduction characteristic has a positive effect on the catalytic reaction involving hydrogen [14].

The hydrogenolysis of glycerol to propylene glycol was used in this study, to evaluate catalytic activity. Among the impregnated catalysts, the catalytic activity of 50I was higher than that for 10I in terms of conversion, selectivity and yield. Since elemental copper showed catalytic activity to some extent in our preliminary test of this reaction, it is likely that the large amount of copper species in 50I is mainly responsible for its higher catalytic activity. However, the catalytic activity of 50P was found to be considerably higher than that of 50I, even though both catalysts contain the same amounts of copper. Such a difference in catalytic activity can be attributed to the state of the copper species in the catalyst. As evidenced by the XRD, TPR and XPS data, copper oxide and chromium oxide are present as separate oxides species in the impregnated catalysts, and chromium oxide is thought to play the role of a support material. A support material can enhance catalytic activity since it can confer both geological and electronic promotion effects in the system. However, no significant promotion effect of chromium oxide was found for the impregnated catalyst. It is likely that the enhancement in catalytic activity between 10I and 50I is largely due to the amount of active copper species present. A relatively large fraction of side-products were produced in the reaction results of 10I and 50I, mainly composed of ethanol, 1-propanol, ethylene glycol, and some poly-

Table 1. Physical properties of prepared catalysts

Catalyst	BET surface area (m ² /g)	Crystalline size (nm) ^a	
		Before reduction	After reduction
10I	15.4	14	23.8
50I	15.1	19.5	45.7
50P	19.3	14.5	13.4

^aCalculated from the XRD results by Scherrer equation

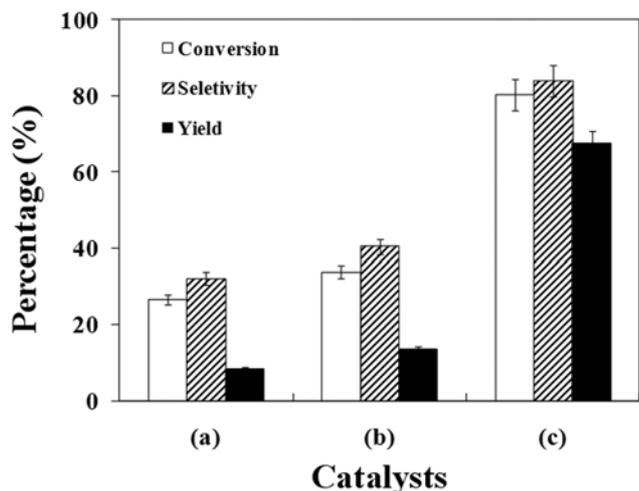


Fig. 5. Catalytic performance of synthesized catalysts in the hydrogenolysis of glycerol to propylene glycol. (a) 10I (Cu : Cr=1 : 10), (b) 50I (Cu : Cr=1 : 2) and (c) 50P (Cu : Cr=1 : 2).

merized compound. When only copper catalyst was used in the reaction, no polymerized product was found. Therefore, productions of cracked and polymerized side-products are thought to be the effect of Cr_2O_3 support. In the case of the precipitated catalyst, copper is mixed with chromium to form a spinel structure. Even after the reduction process, the spinel structure of copper and chromium is maintained and the overall promotion effect is greatly improved in 50P, which shows a much higher catalytic activity than 50I. Catalyst 50P showed high selectivity to propylene glycol, and a very small fraction of side-products were observed such as ethylene glycol and 1-propanol. As a result, it appears that the spinel structure of 50P is a major factor in the increased activity for the hydrogenolysis of glycerol to propylene glycol among the catalysts studied here.

CONCLUSION

To investigate the relationships between surface structure properties and catalytic activities in the conversion of glycerol to propylene glycol by hydrogenolysis, copper catalysts promoted by chromium were prepared using different synthesis methods, namely, impregnation (10I and 50I) and precipitation (50P). Based on the characterization results, the surface properties of the synthesized catalysts change, depending on the method used to prepare them. In the impregnated catalysts, the copper species is supported on a chromium oxide support, in the form of two separate oxide phases, while copper and chromium species form a single spinel phase in the precipitated catalyst. After the reduction process, CuO on the impregnated catalyst was completely reduced to Cu^0 , while the copper species in the precipitated catalyst was partially reduced and the spinel phase was maintained. In hydrogenolysis reaction tests,

the precipitated catalyst shows a much higher catalytic activity than impregnated catalysts. Differences in surface structure affected the catalytic activities in hydrogenolysis, and it can be concluded that a single phase of a reduced copper chromite spinel structure is mainly responsible for the increase in catalytic activity.

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