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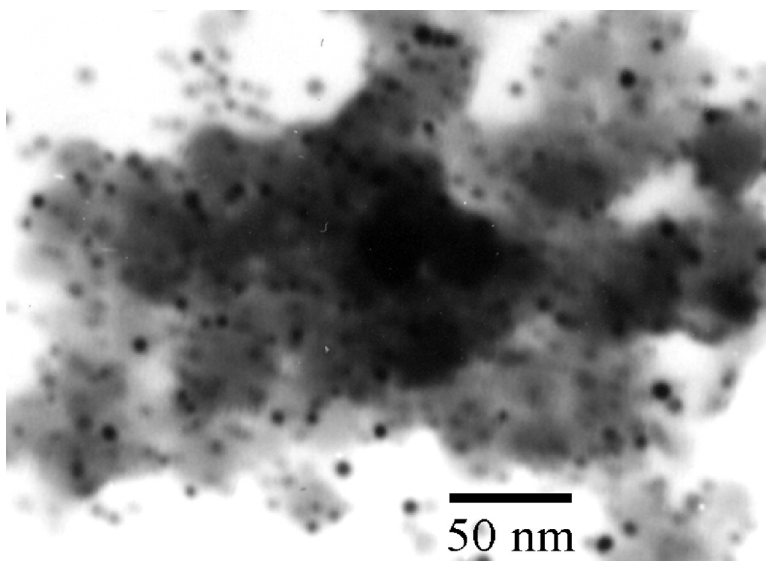
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Highly Dispersed Silica-Supported Copper Nanoparticles Prepared by Precipitation–Gel Method: A Simple but Efficient and Stable Catalyst for Glycerol Hydrogenolysis

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Highly dispersed copper nanoparticles supported on silica were successfully prepared by a simple and convenient precipitation–gel technique, and their physicochemical properties and activity were compared to those of a catalyst prepared by the conventional impregnation method. As a consequence of the preparation method, the texture (BET), dispersion (dissociative N₂O adsorption), morphology (TEM), reduction behavior (TPR, XRD), state of copper species (XPS), and catalytic performance (glycerol hydrogenolysis) differ between samples. Both samples showed high selectivity (>98%) toward 1,2-propanediol in glycerol reaction. Because of a much smaller particle size, a higher dispersion of copper species with a strong metal–support interaction, and more resistance to sintering, the CuO/SiO₂ catalyst prepared by precipitation–gel method presented a much higher activity and remarkably better long-term stability in glycerol reaction than did the catalyst prepared by impregnation method. The catalytic behavior of calcined and reduced samples and the structure changes of these samples after reaction allow the understanding of the stability toward sintering as well as the possible mechanism of the reaction.

1. Introduction

Metal nanoparticles are attractive catalysts because of the large surface area of the particles. Nanocatalysis (in which nanoparticles are used to catalyze reactions) is considered to be a bridge between homogeneous and heterogeneous catalysis, and the field of nanocatalysis has been very active lately.^{1–3} Dispersed copper catalysts have been of great interest due to their good activities and selectivities in a wide range of reactions such as steam reforming,^{4–6} dehydrogenation of alcohols,^{7–9} methanol synthesis,^{10,11} ester hydrogenolysis,^{12,13} reduction of NO_x,^{14–16} oxidation of CO and hydrocarbons,^{17,18} and so forth. A wide variety of methods are used to prepare dispersed copper catalysts, the most

common of which are impregnation, adsorption, ion-exchange, sol–gel, and (co)precipitation. By conventional methods for catalyst preparation such as impregnation, however, inhomogeneous agglomeration of active species at grain boundary of support occurs especially at higher content, resulting in large-sized particles.¹⁹ With the ion-exchange method, copper species can be stabilized by the silica support and lead to a better dispersion of copper on the silica support than does the wet impregnation method,²⁰ nevertheless, wide use of this method is restricted because of the low loading due to the limited terminal –OH groups on the surface of silica. Although the sol–gel technique offers some advantages in stabilizing the active phase in supported copper catalyst,¹⁵ lower activities were usually observed due to encapsulation of active phase in some sol–gel catalysts.²¹

Herein, we report a simple and convenient method using a precipitation–gel (PG) technique for the preparation of

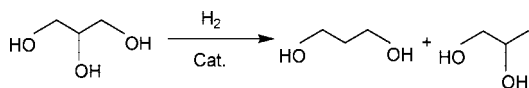
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Scheme 1. Selective Hydrogenolysis of Glycerol to Propanediols

silica-supported copper catalyst with highly dispersed nanoparticles. This method involves the addition of an aqueous NaOH solution to the solution of $\text{Cu}(\text{NO}_3)_2$ to form a precipitate, and the addition of colloidal silica to the solution of the precipitate to stabilize the microparticles of the precipitate and simultaneously form a gel. So this method is different from the previous deposition–precipitation method, which involves the suspension of a support material in the solution of a metal salt and the precipitation of the metal ions onto the support.^{22,23} The stability of the active phase in supported catalysts not only depends on the support, the preparation method, but also depends on the thermal treatment such as calcination, reduction. Accordingly, this work was undertaken with the aim of exploring the capability of the PG method for the preparation of CuO/SiO_2 catalyst and to see whether such a method can yield copper species dispersed and stabilized by the carrier.

Glycerol is a main byproduct in the biodiesel production by transesterification of vegetable oils and animal fats, and large quantities of glycerol become available due to the rapid development of biodiesel process. Until now, a great deal of effort has been put toward the utilization of glycerol.^{24–26} One of the attractive outlets of glycerol is to produce glycols, especially propanediols, by an alternative route involving selective hydrogenolysis of glycerol (Scheme 1). This process provides a clean and economically competitive route for the production of these commercial chemicals from renewable glycerol instead of from nonrenewable petroleum.^{27–29} Supported noble metals such as Ru, Rh, Pt, and their bimetals are well-known as active catalysts in the hydrogenolysis of glycerol,^{27,29–33} so these catalysts are extensively investigated. Unfortunately, these catalysts often promote excessive C–C cleavage, resulting in a low selectivity to propanediols. As a less expensive alternative, copper-based catalysts have been reported to have a superior performance in this reaction

due to their poor activity for C–C bond cleavage and high efficiency for C–O bond hydro-dehydrogenation.^{34,35} Recently, Suppes and co-workers effectively converted glycerol to 1,2-propanediol (1,2-PDO) with a copper–chromite catalyst.²⁸ Nowadays, however, chromium-containing catalysts are called into question because of environmental reasons. More recently, Wang et al.³⁶ reported that Cu/ZnO catalysts prepared by coprecipitation are active in this reaction; nonetheless, the catalytic activity and selectivity are unsatisfactory, and, moreover, these catalysts are not so stable as the active species are easy to sinter during the reaction. Despite much research on copper-based catalysts, up to now, few reports were seen on using environmentally friendly CuO/SiO_2 catalyst for glycerol hydrogenolysis. In the present work, selective hydrogenolysis of glycerol, as a model reaction, has been carried out over the highly dispersed CuO/SiO_2 nanoparticles prepared by PG method to study their catalytic properties, and their activity, selectivity, and long-term stability were compared to those of a catalyst prepared by the conventional impregnation (IM) method. Characterization of the catalyst structures by a variety of chemical and physical techniques, including N_2 adsorption, N_2O chemisorption, infrared spectroscopy, X-ray powder diffraction, X-ray photoelectron spectroscopy, temperature-programmed reduction, and transmission electron microscopy, has been used to correlate the microstructure of the solids with their catalytic performance in the hydrogenolysis of glycerol.

2. Experimental Section

Catalyst Preparation. The PG catalyst was prepared as follows. First, an aqueous solution of NaOH (4 mol/L) was dropped in a solution of $\text{Cu}(\text{NO}_3)_2$ (0.5 mol/L) at a constant rate under vigorous stirring to form a precipitate. Next, a calculated amount of colloidal aqueous silica solution (SiO_2 , 40.0 wt %, Guangzhou Renmin Chemical Plant, China) was added to the solution of the precipitate to form a gel, and then the gel was allowed to age at 363–373 K for 4 h. Finally, the slurry of the gel was filtered, thoroughly washed with hot distilled water, dried at 393 K overnight, and calcined at 723 K under air for 3 h. A reference catalyst IM was prepared by impregnating dry silica gel (Qingdao Haiyang Chemical Co., China, 442 m^2/g) with an aqueous solution of $\text{Cu}(\text{NO}_3)_2$ to obtain the required final copper oxide loading. The sample was dried and calcined under the same conditions as the catalyst prepared by PG method. The metal loadings in terms of metal oxide determined by X-ray fluorescence spectroscopy (XRF, PANalytical Magix PW 2403) were 30.0 and 31.4 wt % for IM and PG catalyst, respectively.

Catalyst Characterization. Fourier transform infrared (FTIR) spectra were recorded at room temperature on powdered samples using the KBr wafer technique in a Nicolet Nexus 870 FTIR spectrometer. Spectra were recorded in the 4000–400 cm^{-1} range working with a resolution of 4 cm^{-1} . The X-ray powder diffraction (XRD) of the samples was carried out on a PANalytical X'pert Pro diffractometer using nickel filtered $\text{Cu K}\alpha$ radiation with a scanning angle (2θ) of 15–80° (for dried samples from 10–80°),

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a scanning speed of 2°/min, and a voltage and current of 40 kV and 30 mA. The particle sizes of CuO and Cu were calculated by using the Scherrer equation. X-ray photoelectron spectra were obtained using a VG ESCALAB 210 spectrometer equipped with a Mg K α X-ray radiation source ($h\nu = 1253.6$ eV) and a hemispherical electron analyzer. The spectra were recorded in the constant pass energy mode with a value of 20 eV, and all binding energies were calibrated using the Si2p peak at 103.4 eV as the reference. The BET surface area measurements were performed on a Micromeritics ASAP 2010 instrument at liquid nitrogen temperature. Temperature-programmed reduction (TPR) experiments were conducted on an Altamira AMI-100 catalyst characterization instrument. A sample of 100 mg of catalyst precursor was pretreated in a He flow of 50 mL/min at 523 K for 1 h and then cooled to room temperature. After that, a reducing gas composed of 20% H₂/Ar was employed at a flow rate of 50 mL/min, with a heating rate of 10 K/min from ambient to 673 K. The hydrogen consumption was continuously monitored by quadrupole mass spectrometers (Ametek Instruments, Dycor system 1000). For comparison, CuO powder (obtained by calcining of Cu(NO₃)₂·3H₂O at 723 K for 3 h) as a reference compound was also performed for TPR measurement. The number of surface metallic copper sites was determined by dissociative N₂O adsorption at 363 K using the procedure described by Van Der Grift et al.³⁷ The catalysts were first reduced at 673 K for 1 h. Afterward, they were flushed with He and the temperature was decreased to 363 K. Next, 5 vol % N₂O (99.995% purity) in N₂ (99.999% purity) was admitted to the reactor at this temperature and allowed to flow (50 cm³/min) for 30 min. Finally, the samples were again flushed with He and cooled to room temperature to start a TPR run. Transmission electron microscopic (TEM) investigations were carried out using a Hitachi H-600 electron microscope. The powder of copper catalysts was suspended in alcohol with an ultrasonic dispersion for 30 min, and then the resulted solution was dropped on a carbon film of copper grid.

Catalytic Activity Testing. The discontinuous glycerol reaction was carried out in a 200 mL stainless steel autoclave at a stirring speed of 400 rpm. Unless specifically stated, CuO/SiO₂ samples with prereduction by H₂ stream at 553 K for 3 h were used as the catalysts in this work. The standard reaction was carried out under the following reaction conditions: 453 K, 6.4 MPa of initial H₂ pressure, 80 g of 80 wt % glycerol aqueous solution, 4 g of reduced catalyst, 12 h. After being purged, the reactor was heated to the reaction temperature, and the H₂ pressure was increased to about 9.0 MPa and maintained during the reaction. The liquid-phase products were analyzed by using a gas chromatograph with a SE-54 capillary column (50 m \times 0.32 mm) and a flame ionization detector. The gas products were analyzed by using a gas chromatograph (Porapak Q column (4 m \times 3 mm)) equipped with a thermal conductivity detector. Products were also identified on a HP 6890/5793 GC-MS with a DB-5MS column. The detected liquid products mainly included 1,2-propanediol, ethylene glycol, and small amounts of acetol, 1,3-propanediol, 1-propanol, 2-propanol, ethanol, and methanol, while gas products only consisted of small amounts of CO₂ and CH₄. Conversions and selectivities were calculated on the basis of a carbon described by Miyazawa et al.²⁹ The continuous glycerol reaction was preformed in a fixed-bed reactor at 6.0 MPa total pressure, employing 3–4 g of catalyst (20–40 mesh). The reactor tube was 36 cm long and 1.2 cm in inner diameter. The reactor was packed with the catalyst between two plugs of glass wool. Before the reaction, the catalysts were

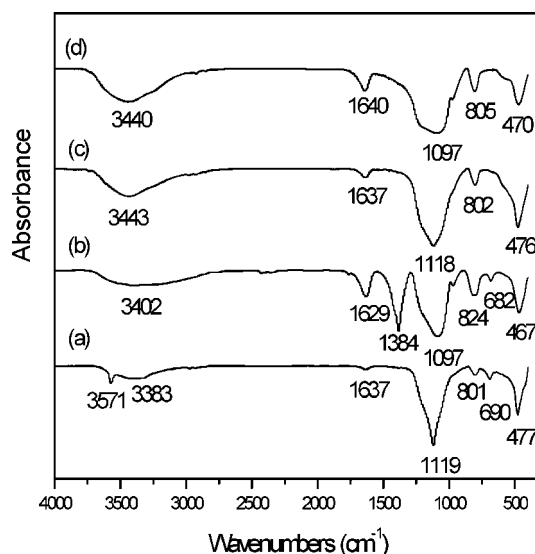


Figure 1. FTIR spectra of (a) dried PG sample, (b) dried IM sample, (c) calcined PG sample, and (d) calcined IM sample.

reduced with a hydrogen flow under atmospheric pressure at 553 K for 3 h. To increase the fluidity of the reaction media, 40 wt % glycerol in 10 wt % water and 50 wt % methanol were used. Standard reaction conditions were: WHSV of 0.25 h⁻¹, glycerol to hydrogen ratio 1:22, 453 K. The reaction products were analyzed as indicated above, ignoring the small amount of methanol generated during the reaction.

3. Results and Discussion

3.1. FTIR. The IR spectra of dried and calcined samples of PG and IM catalysts are given in Figure 1. The absorption bands at approximately 1100, 800, and 470 cm⁻¹ are assigned to the different vibration modes of the Si–O bonds in the amorphous SiO₂.^{15,21} The broad absorption band in the range 3600–3200 cm⁻¹ is due to the overlapping of the OH stretching vibration of adsorbed water and silanols.²¹ The wideness of the band is related to the degree of hydrogen bonding with neighboring OH groups. The dried PG sample showed a complex band in this region, with a fine and intense peak at 3571 cm⁻¹, corresponding to a nearly single hydroxyl, while other wider bands centered at 3383 cm⁻¹ indicate hydrogen-bonded OH groups.³⁸ Similarly, the band near 1640 cm⁻¹ corresponds to the bending mode of OH groups of adsorbed water.³⁹ Because of their structural OH groups, IR spectroscopy is well-adapted to discriminate between copper hydroxide, copper nitrate hydroxide, and copper hydrosilicate (chrysocolla).⁴⁰ Therefore, for silica-supported copper materials, the discrimination between copper hydroxide and copper hydrosilicate can be made from the frequencies of the δ_{OH} bands (for copper hydroxide at around 938 and 694 cm⁻¹, for copper hydrosilicate at near 670 cm⁻¹), while the presence of copper nitrate hydroxide can be distinguished by its strong and sharp NO₃ bands.⁴⁰

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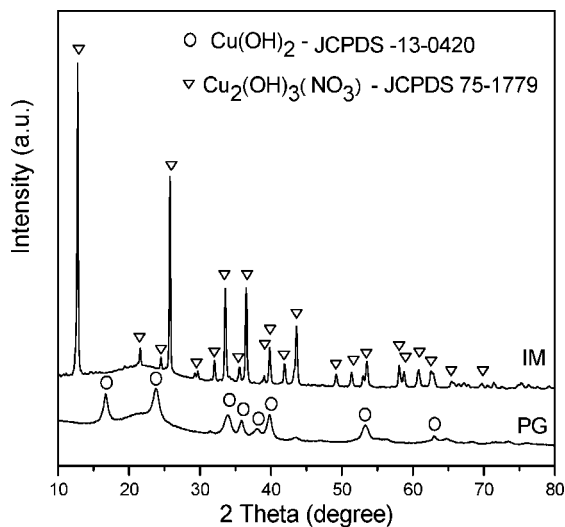


Figure 2. XRD profiles of the dried precursors of PG and IM catalysts. As can be seen from Figure 1, the bending absorption of Cu—O—H bond of the dried PG sample appears at 690 cm^{-1} , suggesting the presence of $\text{Cu}(\text{OH})_2$. In the case of the dried IM sample, both bending absorption of Cu—O—H bond at 682 cm^{-1} and a sharp absorption at 1384 cm^{-1} related to NO_3 groups are characteristic of the presence of $\text{Cu}_2(\text{OH})_3\text{NO}_3$. Thus, the spectra shown in Figure 1 and discussed later clearly show that the copper species in the dried precursors of PG and IM are mainly present in the form of $\text{Cu}(\text{OH})_2$ and $\text{Cu}_2(\text{OH})_3\text{NO}_3$, respectively, but not copper hydrosilicate, which is known to form in the CuO/SiO_2 catalysts prepared by ion-exchange⁴¹ and precipitation-deposition²² methods.

The absorption bands associated with bending absorptions of Cu—O—H bonds for both dried precursors and the band related to NO_3 groups for the dried IM sample disappeared after calcination at 723 K. Because of the presence of a broadband at 470 cm^{-1} from the support, the vibration of CuO bonds that appear at 575, 500, and 460 cm^{-1} cannot be observed.¹⁵ In both spectra of the calcined samples, a shoulder around 600 cm^{-1} is observed, and this could be an indication of $\text{Cu}(\text{II})\text{—O}$ species.³⁹

3.2. XRD. Because of a different preparation procedure, the copper species in the dried precursors of PG and IM catalysts are different from each other, and the XRD patterns of them are shown in Figure 2. The dried PG sample exhibits a bright-blue color. The diffraction pattern of this sample reveals the formation of a highly dispersed copper hydroxide $\text{Cu}(\text{OH})_2$ phase. Differently, the precursor of IM sample is green-blue, indicating the formation of copper hydroxynitrate $\text{Cu}_2(\text{OH})_3(\text{NO}_3)$ upon drying at 393 K.⁴¹ This sample seems to be composed of one single phase of $\text{Cu}_2(\text{OH})_3\text{NO}_3$ as evidenced by a strong 001 reflection at $2\theta = 12.9^\circ$. Other reflections that correspond to the $\text{Cu}_2(\text{OH})_3\text{NO}_3$ phase are at $2\theta = 25.8, 33.6, 36.5$, and 43.6° . The results are in line with the observations made by FTIR.

The XRD patterns of the calcined and reduced PG and IM catalysts are shown in Figure 3. After calcination at 723 K, copper species in both dried precursors were converted

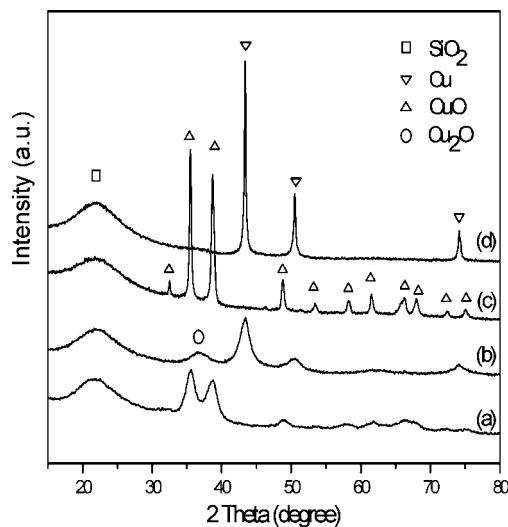


Figure 3. XRD patterns of calcined and reduced PG and IM catalysts: (a) calcined PG sample; (b) calcined PG sample reduced at 553 K for 3 h; (c) calcined IM sample; and (d) calcined IM sample reduced at 553 K for 3 h.

to CuO (Figure 3a,c). The diffraction peaks of CuO for PG catalyst are much broader and less intense than those of the IM catalyst, suggesting that CuO/SiO_2 prepared by the PG method shows much smaller crystalline size (5.7 vs 20.7 nm) and higher metal dispersion than those of the sample prepared by impregnation. Diffraction pattern of SiO_2 is only seen at around $2\theta = 21.7^\circ$ with a broad and diffuse diffraction peak, which is attributed to amorphous silica for both catalysts. After reduction, the peaks of copper oxides for both calcined samples disappeared and the peaks of metallic copper appeared (Figure 3b,d); in addition, a diffraction peak at $2\theta = 36.8^\circ$ attributed to Cu_2O is also observed in the reduced PG catalyst. These findings infer the complete and inadequate reduction of Cu^{2+} species in the calcined IM and PG catalysts upon H_2 -reduction at 553 K, respectively. Because of a low interaction between the Cu^0 crystallites and the silica support and the mobility of metallic copper during the reduction process,⁷ copper species in IM catalyst aggregated to larger particles (27.0 nm). In contrast, Cu^0 in PG catalyst decreased to smaller particles (about 4.2 nm) upon reduction, and the reason for the decrease has been reported elsewhere.⁴² The sintering of copper for IM catalyst during the reduction process contrasts with the good stability of Cu particles for PG catalyst.

3.3. XPS. The XP spectra of calcined and H_2 -reduced PG and IM samples as well as the Auger spectra of the reduced samples are reported in Figure 4. The intense and broad photoelectron peak at somewhat above 933.4 eV ($\text{Cu}2\text{p}_{3/2}$) along with the presence of the characteristic shakeup satellite peaks suggests that the copper oxidation state is +2 in both calcined samples.¹⁴ However, the shapes of the XP spectra of the two samples are different from each other. Considering the asymmetry of the $\text{Cu}2\text{p}_{3/2}$ envelope, the peak of the calcined PG sample can be deconvoluted into two contributions centered around 936.0 and 934.1 eV , indicating the existence of two Cu^{2+} species with different valence states.

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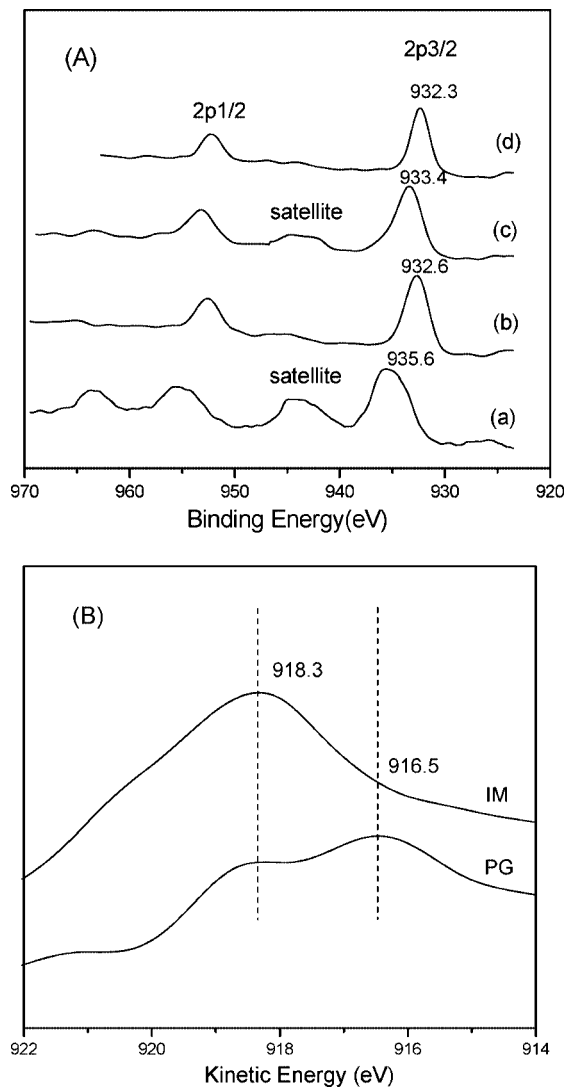


Figure 4. XPS spectra of calcined and reduced PG and IM catalysts: (A) Cu2p spectra of (a) calcined PG sample, (b) calcined PG sample reduced at 553 K for 3 h, (c) calcined IM sample, and (d) calcined IM sample reduced at 553 K for 3 h; (B) Auger kinetic energy of calcined PG and IM samples reduced at 553 K for 3 h.

CuO species was determined at BE = 934.1 eV; thus the relatively large positive BE shift of the Cu2p core level for the calcined PG catalyst is indicative of a charge transfer from the metal ions toward the support matrix, that is, a strong interaction between the metal ions and the matrix.⁴³ Therefore, the XPS result inferred the presence of well-dispersed Cu²⁺ ions interacting with the silica support (936.0 eV) in the calcined PG sample, besides CuO species.⁴⁴ Judging from the Cu2p core level and the shape and area of the Cu2p satellites, some X-ray and ion bombardment-induced reduction of CuO phase may occur during the analysis of the outgassed samples and more specifically for the sample of the calcined IM catalyst in which the BE of Cu2p was lower than that of CuO species and the intensity of the satellites was rather weak.^{14,15}

In the case of the reduced samples, the BE of Cu2p_{3/2} core levels reduced to 932.3–932.6 eV and the satellite lines disappeared, indicating that copper became reduced (Cu⁺ or Cu⁰). Because the BE values of Cu⁺ and Cu⁰ are almost identical, the distinction between these two species present on the catalyst surface is feasible only through examination of the Auger spectra.^{15,45} Two overlapping Cu LMM Auger kinetic energy peaks centered at about 918.6 and 916.5 eV are observed in the reduced PG catalyst, whereas only one peak at 918.3 eV is observed in the reduced IM catalyst (Figure 4B). These results indicate that both Cu⁰ and Cu⁺ coexist on the surface of the reduced PG catalyst, while Cu⁰ is mainly present on the surface of the reduced IM catalyst.^{18,45,46} It is difficult to draw firm conclusions based on this observation, as surface oxidation of the catalyst cannot be excluded, although the reduced catalysts were kept in nitrogen atmosphere during the transfer to XPS instrument. Nevertheless, we believe that inadequately reduced Cu²⁺ species exist on the surface of the reduced PG catalyst, because dispersed Cu²⁺ ions with strong metal–support interaction in the calcined PG catalyst are more difficult to reduce than is bulk CuO, as will be illustrated later.

XPS intensity ratios of the metal cations in the supported metal oxide to those in the oxide support can provide important information regarding the dispersion and crystallite size of supported particles.⁴⁷ The Cu/Si ratio on the calcined PG sample obtained by XPS analysis is 0.425, which is 6.2 times that of the calcined IM sample (0.069) with essentially the same composition, suggesting that the PG method can greatly improve the dispersion of Cu²⁺ species on SiO₂ and thus generate more active sites on the support surface. After reduction, only an appreciable decrease of Cu/Si ratio (0.425 vs 0.413) on the reduced PG catalyst was seen, supporting the observation made by XRD that the PG catalyst showed good resistance to sintering. In contrast, further sintering of copper species seems to occur in the reduced IM sample, as the Cu/Si ratio (0.056) decreased by 19% upon reduction, thus indicating low-level stability of copper in IM catalyst.

3.4. H₂-TPR. The H₂-TPR profiles of both calcined samples are illustrated in Figure 5. As can be seen, each sample exhibits two hydrogen consumption peaks, and the shapes of the peaks differ between samples. These findings indicate that at least two different Cu species are present in each sample. Because the XRD results have already shown the presence of large crystalline sized CuO in the calcined IM sample, for this sample the peaks centered at 518 and 549 K can be attributed to the reduction of highly dispersed CuO with small size and the reduction of bulk CuO with large size, respectively.^{7,14} The calcined PG catalyst showed a broader hydrogen consumption region than that of the calcined IM catalyst, and its reduction began at a lower temperature, whereas it ended in a higher temperature. The minor shoulder peak at 569 K, which is higher than that

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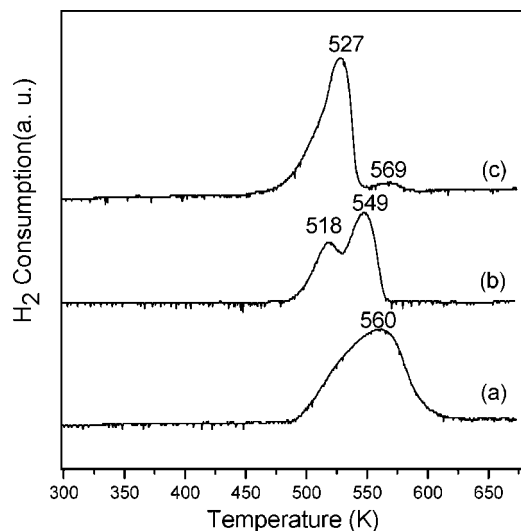


Figure 5. H₂-TPR profiles of (a) CuO, (b) calcined IM catalyst, and (c) calcined PG catalyst.

associated with the reduction of unsupported bulk CuO, seems to indicate some copper species other than CuO. Bond et al.⁴⁸ and Chang et al.⁴⁹ demonstrated that Cu²⁺ ions with strong metal–support interaction were more difficult to reduce than bulk CuO. Because the XPS results mentioned above have revealed the presence of well-dispersed Cu²⁺ ions on the calcined PG catalyst, the reasonable explanation for the high temperature reduction peak is the reduction of the supported Cu⁺ (arising from partial reduction of Cu²⁺ ions chemically interacting with the support surface) to Cu⁰.^{15,49,50} So the main peak at 527 K most probably contributed to the one-step reduction of low interacted copper oxide (CuO → Cu⁰) and the partial reduction of highly dispersed and surface interacted copper species (Cu²⁺ → Cu⁺). From the intensities of the peaks, it can be seen that besides a small amount of hard-reducible copper species, probably a form of copper silicate, the main copper species present in the calcined PG catalyst is highly dispersed CuO, whereas that in the calcined IM catalyst is largely bulk CuO.

The formation of large CuO crystallite with weak or no metal–support interaction in the calcined catalyst IM as illustrated above is most probably due to a poor interaction between the precipitated species copper hydroxynitrate and the surface of the silica support.⁵¹ Because under high temperature (363–373 K), high pH conditions (>7) during the preparation procedure (aging) both the silica surface and microparticles of the copper oxide precursor (Cu(OH)₂) are of high reactivity,²² they may further react to form a small amount of hard-reducible copper silicate. Additionally, copper silicate can also be formed during the calcination procedure. It should be noted that there is no detection of the copper silicate phase in the spectrum of XRD; it may be amorphous or very small.

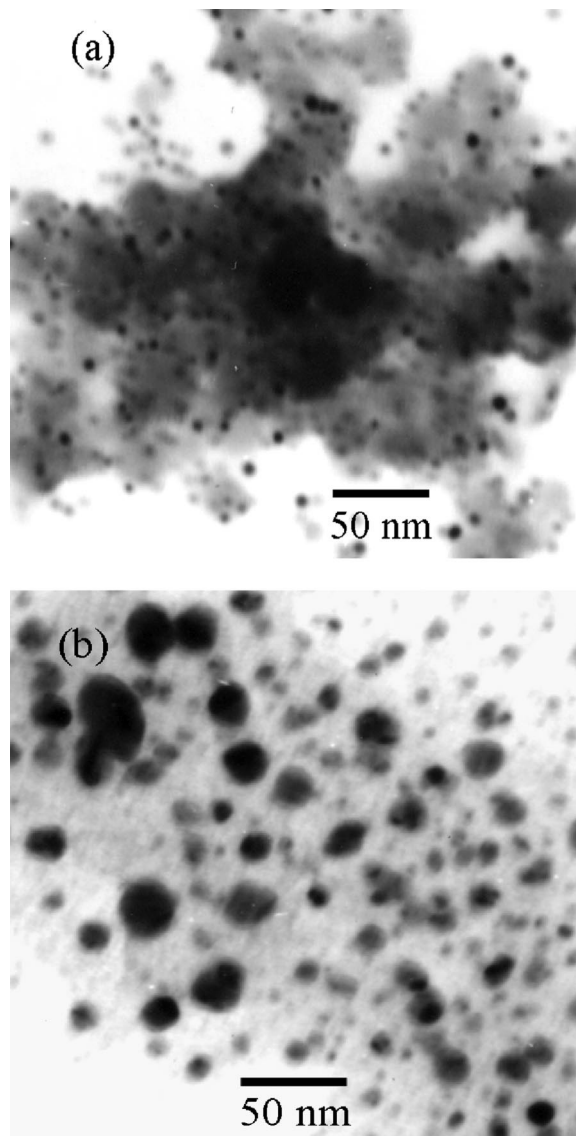


Figure 6. TEM images of (a) calcined PG catalyst and (b) calcined IM catalyst.

3.5. TEM. The morphologies of the calcined PG and IM samples are shown in Figure 6. The copper species in the calcined PG catalyst display spherical shapes and are distributed uniformly over the SiO₂ support. The copper particles exhibit a narrow size distribution of 3–8 nm with an average diameter of 6 nm. In the case of the calcined IM catalyst, aggregation of a few isolated CuO crystallites was observed due to sintering. The CuO particles show a wide size distribution of 3–40 nm with an average diameter of about 20 nm. The differences in morphologies of the catalysts can be attributed to the different preparation methods. To prepare the IM catalyst, a Cu(NO₃)₂ solution in the 2–3 pH range was used, which is below the zero charge point of silica (pH 3).⁵² In this pH range, copper is found primarily as CuOH⁺ and Cu²⁺, and the silica surface is positively charged. After thermal treatment (calcination), a single deposition phenomenon then could lead to a wider copper oxide particle size distribution, resulting in a lower copper metal dispersion. In the case of the PG catalyst preparation,

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Table 1. Textural Properties, Turnover Frequencies, and Apparent Activation Energies of PG and IM Catalysts

catalyst	BET surface area ^a (m ² /g)	dispersion ^b (%)	copper surface area ^b (m ² /g Cu)	copper particle size ^b (nm)	TOF ^c (h ⁻¹)	E _a ^d (kJ/mol)
IM	275	5.7	38.6	17.5	0.34	94
PG	181	29.4	198.9	3.5	1.49	48

^a BET method. ^b Calculated from dissociative N₂O adsorption. ^c TOF (mol of 1,2-PDO produced per mol of copper per hour) for glycerol reaction at 453 K. ^d Determined in the 433–493 K range.

microparticles (diameter <10 nm) of the copper oxide precursor (Cu(OH)₂) with uniform size distribution were formed during the first precipitation procedure. In the second dispersing and stabilizing step, colloidal silica of high pH (ammonium stabilized type, pH 9–9.5) was used, well above the zero charge point; thus the silica surface is negatively charged, favoring the adsorption of copper cations. After the slurry of the gel was well mixed, highly dispersed catalyst precursor was formed. Thus, by using this method a catalyst precursor with small particle size and high dispersion can be easily obtained. The TEM results support the observations made by XRD, XPS, and TPR.

3.6. BET and N₂O Adsorption. The textural properties of both calcined catalysts including the specific surface area, metal dispersion, metal surface area, and particle size of copper are summarized in Table 1. Although the BET surface area of PG catalyst is lower than that of IM catalyst, it is still as high as 181 m²/g. The high surface area of the IM catalyst should be attributed to the high surface area of the support itself. Chemisorption of N₂O indicates that the CuO/SiO₂ prepared by PG method showed much higher dispersion and as result higher copper surface area; both values are approximately 5 times that of the catalyst prepared by IM method. Thus, the present results are in well agreement with the dispersion determined by XPS method. The average copper particle size obtained from chemisorption is considerably small for PG catalyst, which is 3.5 nm, while large particle is shown for IM catalyst. These values for both samples are smaller, but generally in agreement with the results obtained from XRD and TEM.

3.7. Catalytic Activity. Glycerol hydrogenolysis reaction was carried out to study the catalytic properties of both PG and IM catalysts, and their activity and selectivity as a function of temperature were shown in Figure 7. Because of a much higher dispersion of copper species with significantly small particle size mentioned above, PG catalyst presented a much higher activity in glycerol reaction at each given temperature than did the IM catalyst. Even at 433 K, which is significantly lower than those reported in the literatures^{25,28} (usually temperatures higher than 473 K are needed to achieve high activity), PG catalyst showed a high activity (19% conversion) for glycerol hydrogenolysis with 98% of 1,2-PDO selectivity. Nevertheless, only 2% of glycerol conversion with a slightly higher selectivity (99%) toward 1,2-PDO was obtained over IM catalyst at this temperature. The TOF calculated at 453 K for PG catalyst is 1.49 h⁻¹, which is approximately 4.4 and 372 times higher than that of the IM catalyst prepared and the CuO/ZnO catalyst reported earlier,²⁷ respectively. These results clearly show the high efficiency of the PG catalyst in glycerol hydrogenolysis. The apparent activation energy for IM catalyst is 94 kJ/mol in the range 433–493 K, whereas it is

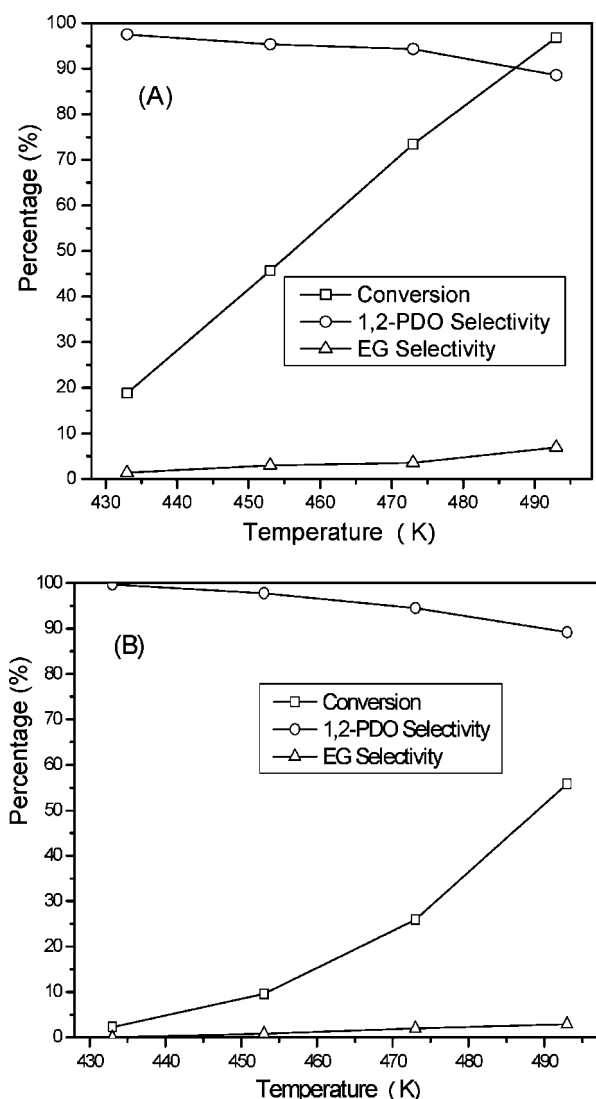


Figure 7. The activity and selectivity of glycerol reaction as a function of temperature carried out in an autoclave for (A) PG catalyst and (B) IM catalyst. Reaction conditions: 80% aqueous solution of glycerol 80 g, total pressure 9.0 MPa, reduced catalyst 4 g, 12 h.

nearly one-half that for PG catalyst, which is 48 kJ/mol. Note the activation energy for Rh/C was calculated to be 98 kJ/mol in the range 453–513 K.²⁷ The reason for the significant decrease of activation energy for PG catalyst as compared to IM catalyst most probably originates from the dramatic decrease of the particle size for PG catalyst. Because the active sites with higher activity require lower activation energy, the number of active sites with higher activity such as the corners of crystallites increases as the particle size decreases,⁵³ thus giving a good explanation for the large decrease of activation energy for PG catalyst. Park et al.⁵⁴

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Table 2. Glycerol Reaction over Calcined and Reduced PG and IM Catalysts, Copper Powder, and Silica Support, and Their Characterizations after Reaction^a

catalyst	conversion (%)	selectivity (%)			phases ^b	crystallite size ^c (nm)
		1,2-PDO	EG	acetol		
calcined PG	52.7	93.1	5.2	trace	Cu ⁰	19.6
reduced PG	73.4	94.3	3.6	trace	Cu ⁰ /Cu ₂ O	9.0 (0.380)
calcined IM	22.9	94.5	2.0	0.3	Cu ⁰	35.2
reduced IM	25.6	95.2	2.0	0.3	Cu ⁰	31.1 (0.043)
Cu ^d	1.6	78.6	2.6	3.6	Cu ⁰	58.2
SiO ₂	—	—	—	—	ND	ND

^a Reaction conditions: 80 wt % aqueous solution of reactant 80 g, 4 g of reduced catalyst, total pressure 9.0 MPa, 473 K, 12 h (ND = not determined.) ^b Determined by XRD. ^c Determined by X-ray diffraction method using the Scherrer equation. The data given in the parentheses are the Cu/Si ratio obtained from XPS analysis. ^d Purchased from market and prereduced in H₂ steam at 553 K for 1 h before being used in the reaction.

also observed that the activation energy of aluminum nanoparticles oxidation reaction decreased as the aluminum particle size decreased. It should be noted that both catalysts showed high selectivity (>89%) toward 1,2-PDO even at high temperature (493 K), thus suggesting the high selectivity of CuO/SiO₂ catalysts in glycerol reaction. The increase of the selectivity of ethylene glycol (EG, the main byproduct) at the cost of 1,2-PDO selectivity with increasing temperature indicates that at high temperature the degradation of glycerol and excessive hydrogenolysis of the products are also high.²⁸ Ni⁵⁵ and Co⁵⁶ were reported to be active in glycerol hydrogenolysis. Silica-supported Ni and Co catalysts were prepared by PG method with essentially the same metal oxide content as that of CuO/SiO₂, and the reaction was carried out at 453 K under H₂ pressure. Although these catalysts also showed high dispersion and small particle size (estimated by XRD to be <4 and 8.6 nm for Ni and Co catalysts, respectively), the activities in terms of conversion on these catalysts were low, only 4% and 5% for Ni and Co catalyst, respectively. The selectivities to 1,2-PDO over these catalysts were also very low with only 54% for Ni catalyst and 78% for Co.

Activation treatment has a significant effect on the structure as well as the activity of CuO/SiO₂ catalysts prepared by both PG and IM methods. To study the phase change and the stability of the active phase during the reaction, both calcined and reduced CuO/SiO₂ catalysts prepared by different methods after reaction were measured by XRD and XPS (for prereduced samples only). The structure data of the used catalysts along with the catalytic results of the catalysts pretreated under different conditions are compiled in Table 2. Interestingly, both copper catalysts without prereduction also showed good activity and high selectivity in glycerol hydrogenolysis at 473 K under H₂ pressure. Wang et al.³⁶ reported that prereduction of Cu/ZnO catalyst before glycerol reaction can greatly increase the selectivity to 1,2-PDO as compared to the nonprereduced one, while the conversion of glycerol seems not to be affected much by the prereduction treatment. Inversely, in our condition, prereduction of the CuO/SiO₂ catalysts could increase the activity of the catalysts, more pronounced for

PG catalyst (increased about 20% after reduction), while the selectivity toward 1,2-PDO for both catalysts seems not to be affected much by the prereduction treatment (Table 2). The crystallite sizes of the catalysts after reaction listed in Table 2 show that more serious sintering of copper species was seen for the calcined samples as compared to their prereduced ones. Thus, we can see that prereduction of the CuO/SiO₂ catalysts in H₂ before hydrogenolysis reaction helps to retard the sintering of copper particles during reaction. As the copper particle sizes of the used IM catalyst with and without prereduction were not affected much (31.1 vs 35.2 nm), so were their activities for glycerol reaction. It seems that the reactive surface that is generated in situ during the reaction in the calcined sample is not very different from that generated in a prereduced sample. The difference in activities for the calcined and reduced samples is most probably due to the different extent of sintering. Therefore, as compared to the PG catalyst prereduced at 553 K, it is clear that the much lower activity of the calcined PG catalyst was caused mainly by the quick aggregation of the Cu particles in a reaction stream with high reducibility. Although after reaction some extent of sintering was observed in both prereduced samples, the PG catalyst presented a much better resistance to sintering during the aqueous reaction as the mean crystallite size had not grown up to more than 10 nm. XPS examination of the reduced PG catalyst after use showed, as the Cu/Si ratio given in Table 2, a smaller extent of sintering as compared to that seen in the used IM catalyst, which agrees with the XRD results.

It should be remarked here that acetol with high selectivity (3.6%) was observed over copper powder (metallic copper)-catalyzed glycerol reaction, thus indicating that Cu⁰ can catalyze the dehydration of glycerol to acetol, a reaction intermediate, which is subsequently hydrogenated to 1,2-PDO. Dasari et al.²⁸ validated acetol as the intermediate in converting glycerol to 1,2-PDO over copper–chromite catalyst. Miyazawa et al.²⁹ and Wang et al.³⁶ reported that the formation of 1,2-PDO proceeded via an acid-catalyzed dehydration of glycerol to form the reaction intermediate of acetol. To study the effect of the silica support in glycerol hydrogenolysis, the silica support was solely used as a catalyst to carry out the reaction. It was found that almost no reaction took place over the silica support (Table 2), thus indicating that copper promotes the dehydration of glycerol. From the present results, however, the acid sites for the dehydration of glycerol that are generated in situ from H₂ in PG and IM catalysts cannot be excluded. Fukuoka et al.⁵⁷

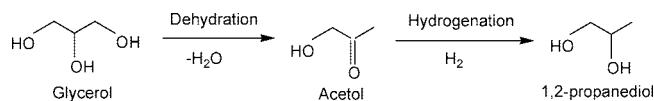
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Scheme 2. Proposed Reaction Mechanism for Conversion of Glycerol to 1,2-Propanediol



reported that besides the acidic surface sites intrinsic in the support, the acid sites for the hydrolysis of cellulose also can be generated in situ from H_2 . Because the $C=O$ group in acetol is readily reduced by Cu with H_2 giving an almost stoichiometric amount of 1,2-PDO, it is reasonable to propose that the surface Cu^0 species combined with the acidic sites generated in situ from H_2 catalyze the dehydration of glycerol to acetol, which is a rate-determining step (Scheme 2). Moreover, from the above results, we can see that highly dispersed surface metal sites are prerequisite for a high glycerol reaction activity, while the acidic surface sites intrinsic in the support for dehydration are dispensable. A surface consisting of only Cu^0 for the prereduced IM catalyst displayed high activity in glycerol reaction, while copper powder also showed mild activity in this reaction (Table 2), thus suggesting that Cu^0 is the active site for glycerol hydrogenolysis. Taking the high activity of the calcined samples into consideration, the only Cu^0 phase determined in these samples after reaction also supports the idea that Cu^0 species are the active phase in the hydrogenolysis of glycerol. The much higher copper surface area of PG catalyst listed in Table 1 explains its excellent activity as compared to that of IM catalyst.

Montassier et al.⁵⁸ reported that the formation of Cu_2O during glycerol reaction is one of the reasons for the deactivation of Cu/C catalyst. In our cases, Cu_2O species was only found in the used PG catalyst that was prereduced in H_2 at 553 K (Figure 8). Because there was no detection of Cu_2O in the reduced IM catalyst after reaction as well as both calcined catalysts after reaction, the Cu_2O species detected in the reduced PG catalyst after use is not likely formed during the reaction but rather formed during the prereduction treatment. In fact, Cu_2O species was detected in the reduced PG catalyst by both XRD and XPS (Figures 3 and 4). Fridman et al.⁸ reported that monovalent copper species presents an activity in the cyclohexanol dehydrogenation reaction significantly higher than that of metallic copper. Cunningham et al.⁴⁶ observed that Cu^+ has a synergistic effect with Cu^0 during isopropanol dehydrogenation reaction. As demonstrated above, the superior activities for the reduced samples are mainly due to a lower extent of sintering as compared to their corresponding calcined samples. The relationship between crystallite size and glycerol reaction activity listed in Table 2 suggests that the Cu^+ formed during the reduction treatment, which may be catalytically inactive in glycerol reaction, helps to inhibit the sintering of copper particles during the reaction rather than exhibit an activity superior to that of Cu^0 or has a synergistic effect with Cu^0 during reaction. Kohler et al.⁴² also suggested that the low deactivation rate for Cu/SiO₂ prepared by ion-exchange is related to a strong interaction between small

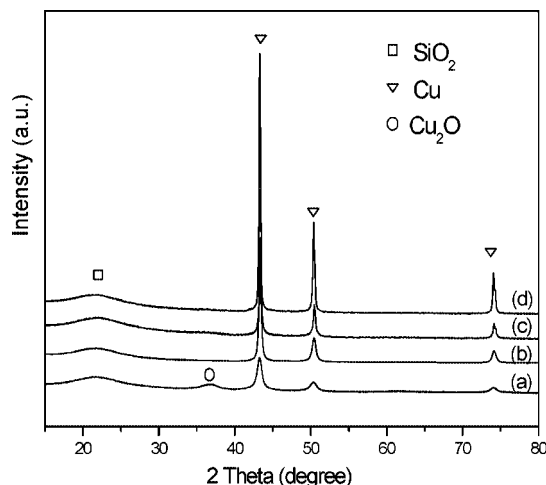


Figure 8. XRD profiles of calcined and reduced PG and IM catalysts after glycerol reaction: (a) reduced PG catalyst after reaction; (b) calcined PG catalyst after reaction; (c) reduced IM catalyst after reaction; and (d) calcined IM catalyst after reaction.

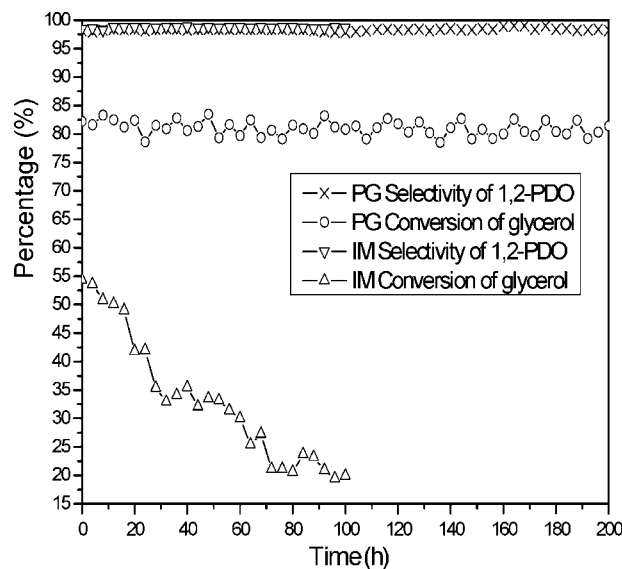


Figure 9. Time on-stream behavior of PG and IM catalysts. Reaction conditions: WHSV of 0.25 h⁻¹, glycerol to hydrogen mol ratio 1:22, total pressure 6.0 MPa, 453 K.

copper particles and the ion-exchanged Cu(I) present on the silica surface. Therefore, the above results indicate that stabilization of active species through the support due to the preparation method and to the activation treatments has important implications on the activity of the catalyst and the resistance of the active phase toward sintering.⁴¹ In addition, the selectivity to 1,2-PDO seems to be independent of the particle size of the supported copper catalysts as shown by the results listed in Table 2. The activity in terms of conversion, however, is size-dependent, with smaller copper domains leading to higher activities. The same effect of particle sizes in the glycerol reaction was seen on Cu/ZnO catalysts.³⁶

To study the long-time stability of both catalysts, the reaction was carried out by using a fixed-bed flow reactor. As shown in Figure 9, the catalyst prepared by the PG method showed much higher activity and remarkable stability in time on-stream when compared to the catalyst prepared

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by impregnation. No appreciable decrease in the activity was observed over PG catalyst even after 200 h of time on-stream; in contrast, a severe loss of activity (more than one-half of the initial activity) was seen over IM catalyst after only 100 h of time on-stream, thus indicating that the active phase in the catalyst prepared by PG method is much more stable than that in the catalyst prepared by IM method. Because in a continuous system degradation of the reactants and further reaction of the 1,2-PDO products could be limited due to a lower contact time, thus a higher selectivity of 1,2-PDO (>98%) was obtained on both CuO/SiO₂ catalysts as compared to the results obtained from a discontinuous (autoclave) reactor. In catalyst prepared by IM method, a serious loss of metal surface area and consequently a decrease in the number of active sites due to significant sintering could easily explain its behavior. Because the PG method can provide a catalyst precursor with much smaller particle size and high dispersion, this method offers the possibility of stabilizing active phases by the support. Therefore, we can speculate that highly dispersed copper species stabilized by the support, as a consequence of the preparation method, are responsible for the stable catalytic behavior of the sample when compared to the catalyst prepared by IM method. Moreover, the formation of a hard-reducible silicate compound from reaction of the precursor of CuO with the support during the heat treatment in the PG catalyst as determined in the XPS and TPR characterization techniques also can contribute to the high stability of PG catalyst.⁴¹ Therefore, both the highly dispersed CuO particles and the small amount of Cu²⁺ ions with strong metal–support interaction are supposed to be needed to achieve optimum performance (good activity and long time stability) in glycerol hydrogenolysis.

4. Conclusion

In summary, we have demonstrated a simple and convenient method using a precipitation–gel technique for the preparation of highly dispersed silica-supported copper nanoparticles. This method can be widely used to prepare

highly dispersed transition metal nanoparticles even at high loadings. FTIR and XRD spectra illustrate that Cu(OH)₂ and Cu₂(OH)₃NO₃ are mainly present in the dried precursors of the catalyst prepared by PG and IM methods, respectively. After being calcined at 723 K, two types of copper species, highly dispersed CuO and Cu²⁺ ions with strong metal–support interaction, were present in the catalyst prepared by PG method, while dispersed and bulk CuO were present in the catalyst prepared by IM method. After being prereduced in H₂ at 553 K, both reduced Cu⁰ and inadequately reduced Cu⁺ coexisted on the surface of the PG catalyst, whereas only Cu⁰ was present on the IM catalyst. CuO/SiO₂ catalysts prepared by both PG and IM methods showed high selectivity (>98%) toward 1,2-propanediol in glycerol hydrogenolysis, while the catalyst prepared by PG method presented a much higher activity and remarkably better long-term stability than those of the catalyst prepared by IM method. The good performance of the PG catalyst can be ascribed to a much small particle size, high dispersion of copper species with strong metal–support interaction, and high resistance to sintering. The Cu⁰ formed during the prereduction treatment and/or generated in situ during the reaction is believed to be the active site for glycerol reaction; and high copper surface area leads to high reactivity. The Cu⁺ species formed during the prereduction treatment that may be catalytically inactive in glycerol reaction is suggested to help to inhibit the sintering of active phases during the reaction. The reaction is likely to proceed via a metallic copper, and the in situ generated acidic sites catalyzed dehydration of glycerol to form an intermediate of acetol, which subsequently hydrogenated to 1,2-propanediol over copper surface. Efficient and stable CuO/SiO₂ prepared by the precipitation–gel technique is an attractive potential catalyst for this reaction.

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