

Research Article

Effect of Copper Nanoparticles Dispersion on Catalytic Performance of Cu/SiO₂ Catalyst for Hydrogenation of Dimethyl Oxalate to Ethylene Glycol

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Cu/SiO₂ catalysts, for the synthesis of ethylene glycol (EG) from hydrogenation of dimethyl oxalate (DMO), were prepared by ammonia-evaporation and sol-gel methods, respectively. The structure, size of copper nanoparticles, copper dispersion, and the surface chemical states were investigated by X-ray diffraction (XRD), transmission electron microscopy (TEM), temperature-programmed reduction (TPR), and X-ray photoelectron spectroscopy (XPS) and N₂ adsorption. It is found the structures and catalytic performances of the catalysts were highly affected by the preparation method. The catalyst prepared by sol-gel method had smaller average size of copper nanoparticles (about 3–4 nm), better copper dispersion, higher Cu⁺/C⁰ ratio and larger BET surface area, and higher DMO conversion and EG selectivity under the optimized reaction conditions.

1. Introduction

Ethylene glycol (EG) is widely used as solvent, antifreezer, polyester fibers, and precursors in lubricant and polyester manufacture [1]. At present, a universal industrial approach to EG is the direct hydrate from ethylene oxide obtained by oxidation of ethylene with air or oxygen, while the ethylene comes from the petroleum cracking process. However, as petroleum resources shrink and the demand for EG constantly increases, the synthesis of EG from syngas attracts considerable attention because it provided an alternative non-petroleum route to produce EG [2]. Two steps are included in this route: first, the coupling of CO with methanol to oxalates; second, hydrogenation of oxalates to EG [3, 4]. Considerable efforts have been focused on the second step. The hydrogenation process can be completed by both homogeneous and heterogeneous catalysis reactions. Compared with homogeneous hydrogenation, heterogeneous process has advantages of easy to separate product and low cost. Therefore, much attention has been focused investigation on the heterogeneous catalysts [5–7]. It is known that hydrogenolysis of monoalkyl ester to alcohol has been in

successful industrial operation and the copper-based catalysts are suitable for the process [8]. However, compared with hydrogenolysis of monoalkyl ester to alcohol, hydrogenolysis of dialkyl ester is more difficult considering that this selective hydrogenation has to be sufficient to reduce the dialkyl ester and avoid overhydrogenolysis of glycol to ethanol and other by-products [9, 10].

Previous studies have shown that the copper loading, Ni species doping, preparation temperature, and support acidity have an influence on texture, structure, and catalytic performance of the catalyst [11, 12]. To achieve high catalytic activity, it is important to disperse fine metal particles on the surface of a support even at higher metal loading [13]. Although various preparation methods have been reported, including sol-gel, ammonia-evaporation, deposition-precipitation, impregnation, and coprecipitation [14–16], few reports focus on the influence of the copper nanoparticles dispersion on the Cu/SiO₂ catalysts for hydrogenation of DMO to EG.

In the present study, for comparison purpose, we adopted the sol-gel and ammonia-evaporation methods to prepare Cu/SiO₂ catalysts with same Cu loadings and evaluate their catalytic properties for the hydrogenolysis of DMO to EG,

respectively. In an attempt to understand the effect of Cu nanoparticles dispersion and preparation methods on the catalyst structure and catalytic performance, we characterized these catalysts by means of the techniques such as nitrogen physisorption, X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), temperature-programmed reduction (TPR), and transmission electron microscopy (TEM). This work not only can provide a research foundation for the development of industrial catalysts for the synthesis of EG via a nonpetroleum route but also can provide some deep insight for the design of high active copper-based catalysts for other reactions.

2. Experimental Section

2.1. Catalyst Preparation. All the reagents used are analytically pure. Cu/SiO₂ catalysts were prepared by ammonia-evaporation and sol-gel methods, with the same nominal copper loading of 30 wt% (CuO/(CuO + SiO₂)), respectively. The ammonia-evaporation method was carried out as follows. At room temperature, 13.6 g Cu(NO₃)₂·3H₂O (Sinopharm Chemical Reagent Ltd.) was dissolved in 150 mL of deionized water. 42 mL of 28% ammonia aqueous solution (Sinopharm Chemical Reagent Ltd.) was added and stirred for 30 min. Then 42.0 g of silica sol (JA-25, Qingdao Haiyang Chemical Ltd.) was added to the copper ammonia complex solution and the initial pH of the suspension was 11–12. The suspension was stirred for another 3 h. Then the suspension was heated to 363 K and kept at this temperature for the evaporation of ammonia. The evaporation process was not terminated until the pH decreased gradually to 6–7. Then the product was filtered, washed by deionized water for several times, and dried at 393 K for 12 h. Then the product was calcined in a muffle oven at 723 K for 4 h. After calcination, the catalyst was pelletized, crushed, and sieved to 20–40 mesh. The catalyst was referred to as Cu/SiO₂-AE.

The sol-gel method was carried out as follows. Tetraethoxysilane (TEOS, Sinopharm Chemical Reagent Ltd., China) and copper nitrate trihydrate were used as the silica and copper sources, respectively. The mixture of ethanol (C₂H₅OH) and water (H₂O) was used as solvent, the mass ratio of TEOS/C₂H₅OH/H₂O was 1/1/1. The mixture was stirred homogeneously and kept at room temperature for 20 h for gelation. Then the product was filtered, washed by deionized water for several times and dried at 393 K for 12 h. Then the product was calcined in a muffle oven at 723 K for 4 h. After calcination, the catalyst was pelletized, crushed, sieved to 20–40 mesh. The catalyst is referred to as Cu/SiO₂-SG.

2.2. Catalyst Characterization. XRD measurements were performed on a Bruker D8 X-ray diffractometer with Cu-K α radiation ($\lambda = 1.54156 \text{ \AA}$) at a scan rate of 4° min^{-1} at 45 kV and 40 mA.

BET surface areas were measured by N₂ adsorption at 77 K using a Micromeritics SSA-4000 instrument. Before measurements, samples were degassed under vacuum at 298 K for 3 h.

The XPS measurements were performed on a Perkin-Elmer PHI 5000 ESCA photoelectron spectrometer using an Al K α ($h\nu = 1,486.6 \text{ eV}$) source. The binding energies of the elements on the surfaces of the catalysts were corrected by using the carbon C1s value, 285 eV, as an internal standard.

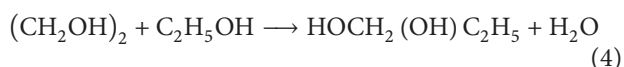
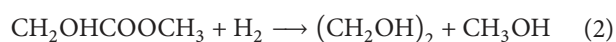
TEM images were obtained on a JEOL JEM 2010 transmission electron microscope with accelerating voltage of 200 kV.

H₂-TPR was also conducted to examine the catalyst reducibility. 50 mg of the catalyst was heated in He at 673 K for 60 min, followed by cooling to room temperature. The temperature was then raised in 50 mL/min of 10% H₂/Ar using a ramp rate of 10 K/min to 823 K. H₂ consumption was detected using TCD.

2.3. Catalyst Testing. Activity and selectivity measurements for DMO hydrogenation to EG were carried out in a continuous-flow fixed-bed reactor made of stainless steel (i.d. = 7 mm). 1.2 g catalyst was placed into the reactor. The reaction pressure was 2.0 MPa, and the reaction temperature is 453 K. Prior to the catalytic measurements, the catalyst was reduced in a stream of 10% H₂/N₂ at 553 K for 4 h under atmospheric pressure. After cooling to the reaction temperature, the catalyst bed was fed with 10% DMO in methanol and H₂, and H₂/DMO is 80 (mol/mol). The DMO in methanol was supplied by a syringe pump (SSI), vaporized, and mixed with the H₂ feed in an electrical heated stainless steel preheater at 443 K. The hydrogen feed was controlled by the mass flow controllers. The exit gases were cooled down to room temperature in a water-cooled condenser. The liquid product was collected and analyzed by gas chromatograph (Beijing Benfenruili Ltd., 3420) equipped with an FID detector.

3. Results and Discussion

3.1. Performance of Different Cu/SiO₂ Catalysts. The catalytic properties for DMO hydrogenation to EG over the Cu/SiO₂-AE and Cu/SiO₂-SG catalysts were tested. For the synthesis process of EG from hydrogenation of DMO, it can be expressed by the following reactions [17]:



During reaction process, first methyl glycolate (MG) is produced by hydrogenation of DMO, then further hydrogenation of MG to EG, while EG can dehydrate to ethanol (ET). At certain conditions, EG and ET can dehydrate to 1,2-butanol (BDO). MG is known as a partial hydrogenation product, while ET and BDO are called the excess hydrogenation products. The EG is a major product, and the other products are side products in our experiments. The conversion of DMO, the selectivity of EG and the yield of EG on Cu/SiO₂ are shown in Table 1. Compared with

TABLE 1: The catalytic activities of the Cu/SiO₂ catalysts prepared by different methods.

Catalyst	X _{DMO} /%	S _{EG} /%	Y _{EG} /%
Cu/SiO ₂ -AE	98	96	94.1
Cu/SiO ₂ -SG	96	93	89.3

Reaction conditions: $T = 353$ K, $P = 2.0$ MPa, $H_2/DMO = 80$ (mol/mol), $LHSV = 0.6$ h⁻¹.

Cu/SiO₂-AE catalyst, the Cu/SiO₂-SG catalyst exhibits higher activity. Conversion of DMO and selectivity of 98% and 96% are obtained on Cu/SiO₂-SG catalyst at optimal reaction conditions. It is well known that the catalytic performance of the Cu/SiO₂ catalysts is highly dependent on structure, size, and dispersion of copper species and surface chemical states of the catalysts. The different catalytic performance of the two Cu/SiO₂ catalysts could be resulted from their different structures. And further discussion will be carried out in the following parts. In addition, compared with other copper-based catalysts prepared various methods, the Cu/SiO₂-SG catalyst here also exhibits equal or higher activity [2, 10, 11].

Under the reaction temperature of 453 K, reaction pressure of 2, and Mpa and H₂/DMO molar ratio of 80, the effect of different liquid hourly space velocity (LHSV) on the performance of the Cu/SiO₂ catalysts is investigated and the results are shown in Figure 1. It can be clearly seen that conversion of DMO decreases gradually while the selectivity of EG first increases and then decreases with increasing LHSV over both Cu/SiO₂ catalysts. The EG selectivity of each catalyst reaches the maximum when the LHSV is 0.6 h⁻¹. This changing trend of the selectivity can be understood from the point of view of residence time. When the LHSV is lower, a longer residence time for reactants is obtained, resulting in overhydrogenation of EG and the production of ET and BDO, and the EG selectivity is consequently lower; While under higher LHSV, the residence time is shorter, leading to partial hydrogenation of DMO and the production of MG but not EG, and therefore the selectivity is also lower. By comparison it is found that both of the conversion of DMO and the selectivity for EG over the Cu/SiO₂-SG catalyst are greater than those of the Cu/SiO₂-AE catalysts.

3.2. The Characterization of the Cu/SiO₂ Catalysts

3.2.1. Textural Properties and Morphology. Figure 2 shows the XRD patterns of the reduced Cu/SiO₂ catalysts prepared with different methods. The strong and sharp peaks observed (see Figure 2) confirm that the catalysts are all well crystallized. For Cu/SiO₂-AE, the diffraction peaks appearing at 43.3°, 50.4°, and 74.1° can be indexed to Cu phase (JCPDS 85-1326), and the broad and diffuse diffraction peak at around 21.7° can be attributed to amorphous silica phase (JCPDS 88-1535), as shown in Figure 2. It is also found the diffraction peaks intensities of the Cu/SiO₂-SG catalyst are much weaker than those of Cu/SiO₂-AE, which implies the copper dispersion of the Cu/SiO₂-SG catalyst is higher than that of Cu/SiO₂-AE.

The physicochemical properties of the calcined catalysts are summarized in Table 2. It is clearly shown in Table 2 that

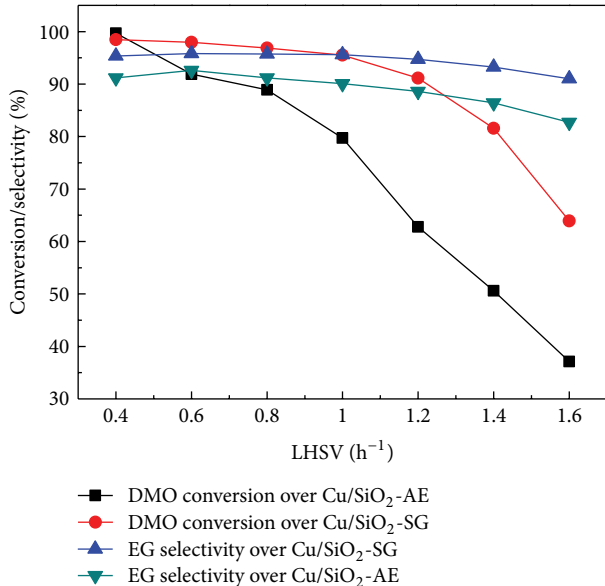


FIGURE 1: Effects of DMO LHSV on catalytic performances of Cu/SiO₂ catalysts. Reaction conditions: $P = 2.0$ MPa, $T = 453$ K, $H_2/DMO = 80$ (mol/mol).

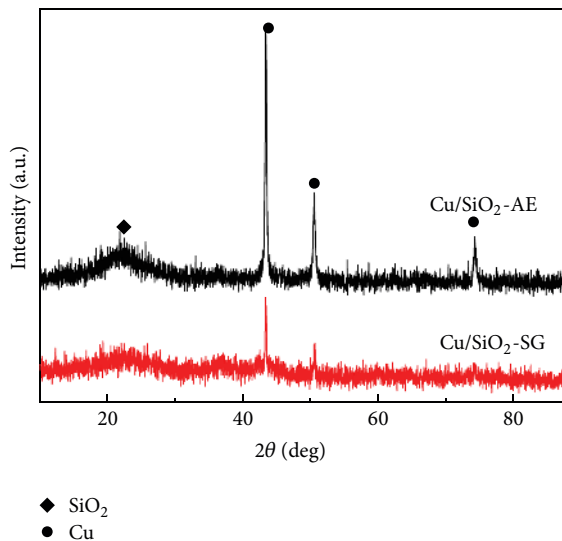


FIGURE 2: XRD patterns of the reduced Cu/SiO₂ catalysts prepared with different methods.

TABLE 2: The physicochemical properties of the Cu/SiO₂ catalysts prepared by different methods.

Catalyst	BET surface area (m ² /g)	Pore volume (cm ³ /g)	Average pore size (nm)
Cu/SiO ₂ -AE	144.0	0.51	14
Cu/SiO ₂ -SG	216.8	0.31	5.6

the BET surface area of the Cu/SiO₂-SG catalyst is much larger than that of Cu/SiO₂-AE catalyst. However, the average diameter of Cu/SiO₂-SG catalyst is much smaller than that of

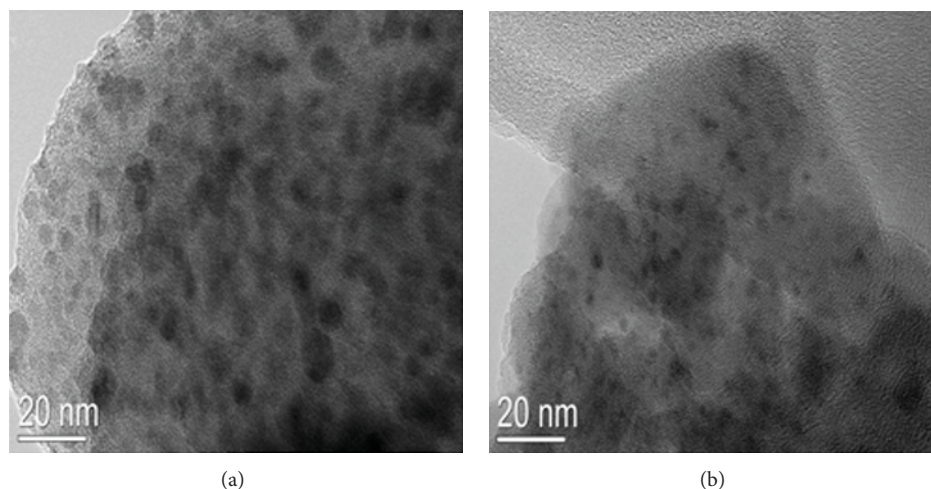


FIGURE 3: TEM images of reduced Cu/SiO₂ catalysts: (a) Cu/SiO₂-AE and (b) Cu/SiO₂-SG.

Cu/SiO₂-AE catalyst, and the average pore diameters are 14 and 5.6 nm, indicating that the two catalysts have mesoporous structures.

The copper dispersion can also be observed from the TEM images. Figure 3 shows the images of the reduced Cu/SiO₂ catalysts prepared by ammonia-evaporation method (Figure 3(a)) and sol-gel method (Figure 3(b)), respectively. It is observed that the copper species are distributed uniformly over the Cu/SiO₂-SG catalyst; the average particle size is about 3-4 nm. On the contrary, the average Cu particle size in the Cu/SiO₂-AE catalyst is about 10 nm; in addition, some Cu particles obviously aggregate together, implying poor Cu dispersion of the catalyst. The copper particles are highly distributed on the surrounding silica supports, which might increase the interaction between the copper species and the support and consequently improve the activity of the catalyst [18].

3.2.2. The Reducibility. TPR measurements were carried out to investigate the reducibility of the copper species in the Cu/SiO₂ catalysts prepared by different methods. Figure 4 presents the reduction profiles of the catalysts. As shown in Figure 4, there are two reduction peaks in the TPR profiles of the catalysts: one occurs in the range of 495–515 K and the other occurs in the range of 530–540 K, which are denoted as α peak (the low-temperature reduction peak) and β peak (the high-temperature reduction peak), respectively, implying the presence of different CuO species with slight differences in ease of reducibility. The α peak can be assigned to the reduction of well-dispersed CuO species and β peaks can be attributed to the reduction of bulk CuO. The similar assignments have also been reported for other copper based catalysts [19]. For Cu/SiO₂-AE catalyst, the area of α peak is much smaller than that of β peak, demonstrating that the quantity of larger CuO particles is much more than the smaller ones. In contrast, for Cu/SiO₂-SG catalyst, the trend changes conversely, suggesting the fractions of highly dispersed CuO species is much higher than those of bulk

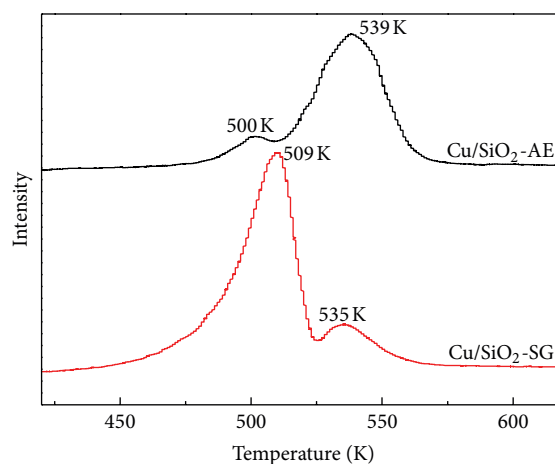


FIGURE 4: TPR profiles of different Cu/SiO₂ catalysts.

ones. The observed shift in reduction temperature may be ascribed to the different copper particle sizes, different interactions between copper oxide and silica, and different copper oxide dispersions. The TPR results further elucidate that the Cu/SiO₂ catalyst prepared by the sol-gel method can result in a better-dispersion of copper species on the SiO₂ support. In addition, the TPR results are consistent with TEM results.

3.2.3. The Surface Chemical States of the Catalysts. The XPS spectra as well as X-ray-induced Auger spectra (XAES) of the reduced catalysts are illustrated in Figures 5 and 6, respectively. As it can be seen from Figure 5, the binding energy values of Cu2p_{3/2} core levels are 932.4 and 932.7 eV of Cu/SiO₂-AE and Cu/SiO₂-SG, implying that copper has been reduced to Cu⁺ and/or Cu⁰ [20, 21]. Because the binding energy values of Cu⁺ and Cu⁰ are almost identical, the distinction between these two species present on the catalyst surface is impossible on the basis of the Cu2p level. In

TABLE 3: Surface Cu component of the reduced catalysts based on Cu LMM deconvolution.

Catalysts	KE (eV) ^a		α' (eV) ^b		Cu 2p _{3/2} BE (eV)	XCu ⁺ /Cu ^{0c} (mol/mol)
	Cu ⁺	Cu ⁰	Cu ⁺	Cu ⁰		
Cu/SiO ₂ -AE	916.3	918.3	1848.7	1850.7	932.4	1.79
Cu/SiO ₂ -SG	916.5	919.1	1849.2	1851.8	932.7	1.96

^aKinetic energy. ^bModified Auger parameter. ^cCu⁺/(Cu⁰) * 100%.

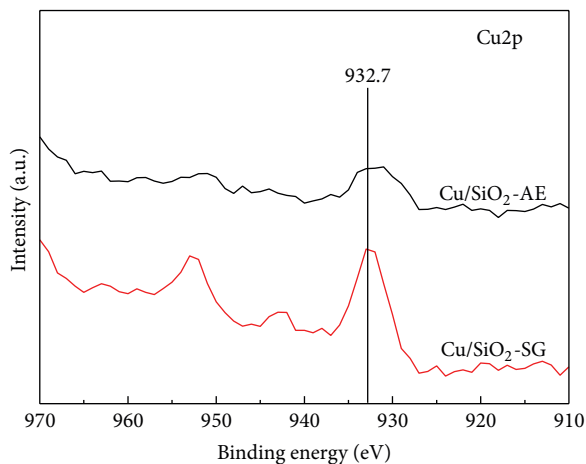


FIGURE 5: Cu2p photoelectron spectra of the reduced Cu/SiO₂ catalysts.

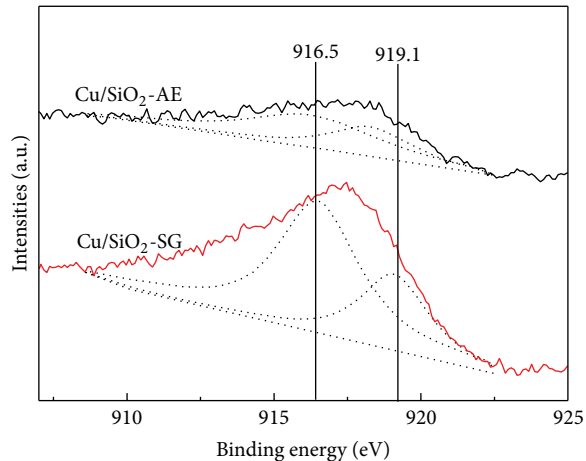


FIGURE 6: Cu LMM XAES spectra of the reduced Cu/SiO₂ catalysts.

general, Cu⁺ and Cu⁰ species can be distinguished through their kinetic energies in the XAES Cu LMM line position or the modified Auger parameters (α') [22]. It is reported that α' is ca. 1851.0 eV for Cu⁰ and 1849.0 eV for Cu⁺ [23]. As it can be seen from Figure 6, the Cu LMM spectra of catalysts show a broad and asymmetrical peak, implying the coexistence of Cu⁺ and Cu⁰ in the surface of the catalyst. Two symmetrical peaks centered at near 916 and 919 eV can be obtained by deconvolution of the original Cu LMM peaks, which are corresponding to Cu⁺ and Cu⁰ species [24]. The

deconvolution results are summarized in Table 3. As shown in Table 3, the α' value at ca. 1849 eV is ascribed to Cu⁺ and 1851 eV to Cu⁰. Compared with bulk Cu⁺, the α' values of Cu⁺ in the catalysts are 2-3 eV lower, indicating strong interaction between Cu⁺ and silica supports [25]. The Cu⁺/Cu⁰ area ratios derived from fitting the Cu LMM peaks are listed in Table 3. It is noted that the Cu⁺/Cu⁰ area ratio on the surface of reduced Cu/SiO₂-SG is 9.4% more than that of reduced Cu/SiO₂-AE, which might be one reason for the enhancement in catalytic activity for the catalyst. It is reported that higher activity can be obtained on the Cu/SiO₂ catalyst with proper ratio of Cu⁺/Cu⁰ due to their synergetic effect. The XPS and XAES results are in good agreements with TPR results. It can be concluded that the surface chemical states of the catalysts are highly affected by the preparation methods.

4. Conclusions

In summary, the Cu/SiO₂ catalysts for the synthesis of EG from hydrogenation of DMO were prepared by two methods: one was prepared by ammonia method and the other was prepared by sol-gel method. It is found that the structure, the reducibility of CuO, the particle size of Cu, and the surface chemical state are highly affected by the preparation method. By comparison, the catalyst prepared by sol-gel method exhibited higher activity and EG selectivity, and 98% DMO conversion and 96% EG selectivity can be obtained under the optimized hydrogenation conditions, due to its smaller Cu particles size, larger BET surface area, and higher dispersion in silica.

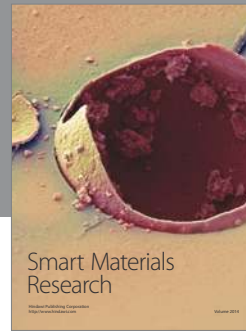
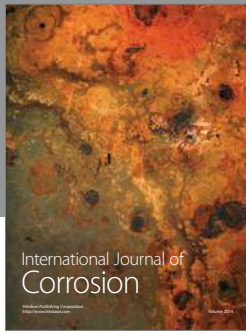
Acknowledgments

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