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Article

Highly active Cu/SiO₂ catalysts for hydrogenation of diethyl malonate to 1,3-propanediol

Tongmei Ding, Hengshui Tian*, Jichang Liu, Wenbin Wu, Jintao Yu

School of Chemical Engineering, East China University of Science and Technology, Shanghai 200237, China

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ABSTRACT

Cu/SiO₂ catalysts prepared by the ammonia evaporation method were applied to hydrogenation of diethyl malonate to 1,3-propanediol. The calcination temperature played an important role in the structural evolution and catalytic performance of the Cu/SiO₂ catalysts, which were systematically characterized by N₂ adsorption-desorption, inductively coupled plasma-atomic emission spectroscopy, N₂O chemisorption, X-ray diffraction, Fourier transform infrared spectroscopy, H₂ temperature-programmed reduction, transmission electron microscopy, and X-ray photoelectron spectroscopy. When the Cu/SiO₂ catalyst was calcined at 723 K, 90.7% conversion of diethyl malonate and 32.3% selectivity of 1,3-propanediol were achieved. Compared with Cu/SiO₂ catalysts calcined at other temperatures, the enhanced catalytic performance of the Cu/SiO₂ catalyst calcined at 723 K can be attributed to better dispersion of copper species, larger cupreous surface area and greater amount of copper phyllosilicate, which results in a higher ratio of Cu⁺/Cu⁰. The synergetic effect of Cu⁰ and Cu⁺ is suggested to be responsible for the optimum activity.

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1. Introduction

1,3-Propanediol (1,3-PDO), which has transformed from a traditional specialty chemical to a commodity chemical [1], is widely used in polyester fibers, resins, cosmetics, lubricants and engine coolants [2–5]. Oleochemical synthesis processes of 1,3-PDO use ethylene oxide [6,7] or acrolein as feedstocks [8,9]. The main problem lies in residual carbonyls to the extent of a few thousand parts per million, which is extremely troublesome in the production of polytrimethylene terephthalate (PTT). A synthesis process involving hydrogenation of diethyl malonate (DEM) to 1,3-PDO has been discussed in detail and could prevent this problem. Wang et al. [10] reported that DEM conversion could reach 55.9% at 6.7 MPa over CuZn_{0.4}Al_{0.6}O_x catalysts. However, the relationships between the catalyst structure and performance, and the catalyst life and its deactivation have not been investigated.

Copper sites account for selective hydrogenation of C–O bonds and are inactive for hydrogenolysis of C–C bonds, so Cu-based catalysts have been recently investigated for vapor-phase hydrogenation reactions [11]. The typical application of Cu-based catalyst is hydrogenation of dimethyl oxalate (DMO) to ethylene glycol [12–16]. Among the various reported catalysts, silica-supported Cu catalysts have widespread applications in this area because of the moderate interaction between copper and the silica support, which has relatively weak acidity and is favorable for constructing catalytic active sites [17–19]. In addition, mesoporous materials such as MCM-41 [20,21], hexagonal mesoporous silica [22], and SBA-15 [23] have been used as supports. However, the preparation process of these mesoporous supports is complicated and time-consuming. Cu/SiO₂ has been intensively investigated and attracted considerable attention owing to its excellent selectivity, green benefits and low cost. Various preparation techniques

* Corresponding author. Tel: +86-21-64252198; E-mail: hstian@ecust.edu.cn

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have been used to fabricate Cu/SiO₂ catalyst, such as ammonia evaporation, ion exchange, sol-gel processes, deposition precipitation, and impregnation [24]. Notably, the ammonia evaporation method can effectively disperse copper and provide high copper loading on the support.

Copper species undergo complicated changes during the ammonia evaporation process. The preparation conditions, such as the initial precipitation temperature [25], Cu loading [26], ammonia evaporation temperature [27], and amount of ammonia [28] have a profound effect on Cu dispersion, the Cu⁰/Cu⁺ ratio, and the interaction between copper and silica. The effect of the calcination temperature on DMO hydrogenation has been discussed by Zhu et al. [29]. They suggested that large stable Cu particles formed and the number of Cu sites decreased under high calcination temperature. The effect of the calcination temperature on other reaction systems has also been investigated. Yuan et al. [30] reported that the calcination temperature significantly influenced the properties and performance of the catalyst, and higher calcination temperature caused agglomeration of CuO species in dimethyl adipate hydrogenation to 1,6-hexanediol. The catalytic activity of toluene combustion on Cu–Mn/MCM-41 is significantly affected by the calcination temperature [31]. Choi et al. [32] reported the effect of calcination temperature on catalyst performance, and better catalytic stability was closely related to formation of nickel hydrosilicate. Kaneko et al. [33] suggested that catalysts calcined at moderate temperature gave the highest Pt dispersion, further enhancing the activity.

In this paper, Cu/SiO₂ catalysts were prepared by the ammonia evaporation method. Few studies have been published regarding the structure–performance correlation of Cu/SiO₂ catalysts under different calcination temperatures in the hydrogenation of DEM to 1,3-PDO. To elucidate the effect, systematic investigations of the structure behavior and catalytic performance were performed.

2. Experimental

2.1. Catalyst preparation

Cu/SiO₂ catalysts were prepared by the ammonia evaporation method. In brief, 24.16 g of Cu(NO₃)₂·3H₂O (Shanghai Lingfeng Chemical Reagent Co. Ltd., Shanghai, China) was dissolved in 200 mL of deionized water at 313 K with vigorous stirring. Ammonia solution (25 wt% Shanghai Lingfeng Chemical Reagent Co. Ltd.) was then added dropwise. Subsequently, 64 g of silica sol (JN-30, Qingdao Ocean Chemical Co. Ltd., Qingdao, China) was added to the cuprammonia solution and the solution was stirred for 4 h. The suspension was then heated in a water bath preheated to 363 K to allow evaporation of ammonia and consequent deposition of copper species on silica. The evaporation process was terminated when the pH value of the suspension decreased to 7. The precipitates obtained were filtered and washed five times with deionized water one time with ethanol. Prior to calcination in air for 4 h, the obtained powder was dried at 393 K for 12 h. The obtained samples were pressed, crushed, and sieved through 40–60

meshes. The catalysts are denoted as Cu/SiO₂-*T*, where *T* is the calcination temperature (K).

2.2. Catalyst characterization

Copper loading of all catalysts was determined by the inductively coupled plasma–atomic emission spectroscopy (ICP–AES) method (Agilent 725ES, USA). Samples were dissolved in HF, and then diluted with water.

Nitrogen adsorption–desorption isotherms at 77 K were measured with a Micromeritics ASAP 2020 instrument after degassing at 423 K for 1 h in vacuum to remove physically adsorbed impurities. The specific surface area was calculated by the Brunauer–Emmett–Teller (BET) method. The Barrett–Joyner–Halenda (BJH) method was used to calculate the pore size distributions according to the desorption branches of the isotherms.

Wide-angle X-ray diffraction (XRD) scanning was performed on a German Bruker D8 FOCUS X-ray diffractometer operating with Cu K_α radiation at 40 kV and 100 mA. The angle ranged from 10° to 80° with a continuous scanning speed of 0.02°/min. The mean crystallite sizes of CuO and Cu were calculated with the Scherrer equation.

Fourier transform infrared (FT–IR) spectroscopy was performed on Nicolet 5700 spectrometer (USA) with a KBr beam splitter. The spectral resolution was 2 cm^{–1} and 32 scans were recorded for each spectrum.

The reducibility of the calcined samples was determined by H₂ temperature-programmed reduction (TPR) on a Micromeritics Autochem II ASAP 2090 instrument. Calcined Cu/SiO₂ catalyst (50 mg) was outgassed at 473 K under Ar for 1 h. After the catalyst was cooled to room temperature under argon, 10% H₂/Ar was introduced at a flow rate of 50 mL/min and then the temperature was linearly increased from ambient temperature to 723 K at a rate of 10 K/min.

N₂O chemisorption was carried out in Autochem II 2920 apparatus (Micromeritics, USA). Briefly, the catalyst sample was reduced in 5% H₂/Ar at 723 K with a heating rate of 2 K/min. After cooling to 323 K under Ar, 10% N₂O/He was introduced at a rate of 50 mL/min for 40 min, ensuring that surface Cu atoms were completely oxidized according to the reaction $2\text{Cu}_{(\text{s})} + \text{N}_2\text{O} \rightarrow \text{Cu}_2\text{O}_{(\text{s})} + \text{N}_2$. Hydrogen pulse reduction of surface Cu₂O to metallic Cu was performed at 723 K under 10% H₂/Ar to ensure that chemisorbed oxygen on the surface immediately reacted with hydrogen. Hydrogen pulse dosing was repeated until the pulse area did not change. The consumed amount of hydrogen was the value obtained by subtracting the small area of the first few pulses from the area of the other pulses. The specific surface area of Cu was estimated from the total amount of N₂O consumption with 1.46×10^{19} copper atoms per square meter.

Transmission electron microscopy (TEM) was performed on a JEM-2100 transmission electron microscope (JEOL, Japan) with an operating voltage of 200 kV. The samples were ultrasonically dispersed in ethanol at room temperature for 15 min and deposited on copper grids coated with amorphous carbon films.

Table 1Physicochemical properties of the calcined Cu/SiO₂ catalysts.

Sample	Cu loading ^a (wt%)	<i>A</i> _{BET} (m ² /g)	<i>V</i> _p (cm ³ /g)	<i>d</i> _p (nm)	<i>I</i> ₆₇₀ / <i>I</i> ₈₀₀ ^b	<i>d</i> _{Cu} ^c (nm)	<i>d</i> _{Cu} ^d (nm)	Cu dispersion ^e (%)	<i>S</i> _{CuO} ^e (m ² /g)
Cu/SiO ₂ -623	21.9	273.4	0.62	7.8	0.171	17.1	15.0	14.9	21.2
Cu/SiO ₂ -723	21.8	360.6	1.14	10.4	0.258	13.8	9.5	24.5	34.7
Cu/SiO ₂ -823	20.1	223.2	0.52	6.8	0.079	16.4	13.9	13.2	18.6
Cu/SiO ₂ -923	22.2	309.7	0.76	8.3	0	17.7	14.0	12.6	17.8
Cu/SiO ₂ -1023	23.0	260.1	0.66	9.0	0	36.6	32.1	6.2	8.8

^a Determined by ICP-AES.^b By integration of the fitted peaks at 670 and 800 cm⁻¹ in the FT-IR spectrum.^c Cu crystallite size calculated by the Scherrer formula after reduction.^d Cu particle size after reduction measured by TEM.^e Determined by N₂O chemisorption.

X-ray photoelectron spectroscopy (XPS) and X-ray Auger electron spectroscopy (XAES) were performed on a ESCALAB 250Xi system (Thermo Fisher, USA) operated at a pass energy of 100 eV and equipped with an Al *K*_α X-ray source radiation source (*E* = 1486.6 eV). The carbonaceous C 1s line (284.8 eV) was used as the reference to calibrate the binding energies (BEs). The catalysts were heated to 573 K in pure hydrogen at 100 mL/min and reduced at this temperature for 4 h. After reduction, the catalysts were kept under nitrogen and transferred into the XPS sample holder using a sealed bottle.

2.3. Activity tests

DEM hydrogenation was performed in a continuous flow unit equipped with a stainless-steel fixed-bed tubular reactor (inner diameter 10 mm, length 700 mm). Typically, 2.5 g of catalyst (40–60 meshes) was loaded into the tubular reactor with a thermocouple inserted into the catalyst bed for better control of the actual pretreatment and reaction temperatures. Catalyst activation was performed at 573 K for 4 h in flowing H₂ (100 mL/min). The temperature was then decreased to the reaction temperature of 473 K, and 10 wt% DEM (purity > 99%) in ethanol was pumped into the reactor by an advection pump along with H₂ at a H₂/DEM molar ratio of 440 and a system pressure of 2.0 MPa. The liquid hourly space velocity (LHSV) of DEM was set to 1.80 h⁻¹. The products were con-

densed and analyzed by a gas chromatograph (GC9800, Kechuang Chromatogram Instruments Co. Ltd., Shanghai, China) fitted with an HT-5 capillary column (30 m × 0.32 mm) and a flame ionization detector.

3. Results and discussion

3.1. Textural properties of the catalysts

The copper contents in the Cu/SiO₂ catalysts were determined by ICP-AES (Table 1). The bulk weight loadings of copper on the support were slightly lower than the nominal value (25 wt%). During the washing procedure, the filtrate was dark blue during the first two washings, indicating partial loss of copper species.

The textural properties, including the pore volume, pore diameter, and BET surface area, have a profound influence on the catalytic behavior of catalysts. Figure 1 shows typical N₂ adsorption-desorption isotherms and the corresponding pore size distributions of the calcined Cu/SiO₂ catalysts. As shown in Fig. 1(a), all of the catalysts show a type IV Langmuir adsorption isotherm with an H3-type loop, corresponding to a typical large-pore mesoporous material [34]. Capillary condensation of nitrogen occurred inside the mesopores, suggesting a typical mesoporous structure with uniform pore diameters [35]. The Cu/SiO₂-723 catalyst showed the most uniform pore size dis-

Fig. 1. (a) N₂ adsorption-desorption isotherms and (b) BJH pore size distributions of the calcined catalysts: (1) Cu/SiO₂-623; (2) Cu/SiO₂-723; (3) Cu/SiO₂-823; (4) Cu/SiO₂-923; (5) Cu/SiO₂-1023.

tribution for the relative long saturated adsorption platform. As shown in Fig. 1(b), pores with diameters of ~ 3.3 and ~ 17 nm are the main contributors to the total pore volume of the Cu/SiO₂-723 catalyst. The size of the larger pores (i.e., those ~ 17 nm in size for Cu/SiO₂-723) decreased to 7.2 nm for a calcination temperature of 823 K, indicating aggregation of copper species. The smaller pore size in Cu/SiO₂-623 than Cu/SiO₂-723 indicates that low calcination temperature is detrimental for the formation of large-volume pores.

The BET surface areas, pore volumes, and average pore diameters of samples are summarized in Table 1. The BET surface area increased from 273.4 to 360.6 m²/g and the pore volume increased from 0.62 to 1.14 cm³/g when the calcination temperature was increased from 623 to 723 K, and then decreased with further increase of the calcination temperature. However, there was a nonmonotonic change when the calcination temperature increased from 823 to 1023 K. Hence, we deduced that the structure and species of the catalysts markedly changed with calcination temperature.

Metallic copper dispersion and the cupreous surface areas of the Cu/SiO₂ catalysts were determined by N₂O chemisorptions (Table 1). Copper dispersion and the cupreous surface area increased with increasing calcination temperature from 623 to 723 K, and then decreased with increasing calcination temperature from 823 to 1023 K. Cu/SiO₂-723 showed the highest dispersion (24.5 %) and largest Cu⁰ surface area (34.7 m²/g). Cu/SiO₂-1023 showed significantly lower copper dispersion and cupreous surface area than the other catalysts, which is most probably because of copper particle aggregation at high calcination temperature.

3.2. Wide-angle XRD

XRD patterns of Cu/SiO₂ catalysts calcined at different temperatures are shown in Fig. 2(a). For catalysts calcined from 723 to 923 K, no obvious diffraction peaks are observed except for a broad diffraction peak at 22° from amorphous silica, indicating homogeneous dispersion of copper species on the support. At a calcination temperature of 1023 K, diffraction peaks at 35.3° and 38.7° assigned to CuO (JCPDS 05-0661) are ob-

served [36], indicating aggregation of Cu nanoparticles. The CuO crystallite size based on the Scherrer equation is about 12.7 nm. Additionally, extremely weak and broad diffraction peaks at 31°, 34.8°, 57.2°, and 63.3° are assigned to the copper phyllosilicate (Cu₂Si₂O₅(OH)₂) phase over the Cu/SiO₂-623 catalyst [28]. The results show that high calcination temperature facilitates formation of CuO while copper phyllosilicate forms at low calcination temperature.

XRD patterns of the reduced Cu/SiO₂ samples are shown in Fig. 2(b). The diffraction peaks of copper oxide and copper phyllosilicate observed in the calcined samples disappeared. Diffraction peaks at 43.2° and 50.3° ascribed to the Cu phase and a diffraction peak at 36.5° attributed to the Cu₂O phase are observed [11], indicating that Cu²⁺ species are reduced to Cu⁰ and Cu⁺ in the reduced catalysts. The intensities of the Cu diffraction peaks are the highest at a calcination temperature of 923 K and the intensity of the Cu⁺ diffraction peak is the highest for Cu/SiO₂-723. The calcination temperature affects the ratio of Cu⁰/Cu⁺, which directly affects the catalytic activity. As shown in Table 1, the Cu particle size calculated by the Scherrer equation decreases from 17.1 to 13.8 nm when increasing the calcination temperature from 623 to 723 K, and then increases with further increasing calcination temperature, indicating that the Cu particle size is the smallest in the Cu/SiO₂-723 catalyst after reduction.

3.3. FT-IR spectroscopy

Interestingly, the color of the calcined catalysts changed from blue to dark blue with increasing calcination temperature, indicating the appearance of at least two copper species. For Cu/SiO₂-1023, the sample was nearly black, which is attributed to the presence of CuO. To gain further insight into the structure, FT-IR spectra of the calcined samples were recorded, as shown in Fig. 3. The band at 1637 cm⁻¹ corresponds to the bending mode of OH groups of absorbed water [27,37] and the absorption bands at approximately 1119, 800, and 472 cm⁻¹ are assigned to different vibration modes of Si–O bonds of amorphous silica [38]. For the Cu/SiO₂-623, Cu/SiO₂-723, and Cu/SiO₂-823 catalysts, the single δ_{OH} band at 672 cm⁻¹ and ν_{SiO}

Fig. 2. XRD patterns of catalysts after (a) calcination and (b) reduction: (1) Cu/SiO₂-623; (2) Cu/SiO₂-723; (3) Cu/SiO₂-823; (4) Cu/SiO₂-923; (5) Cu/SiO₂-1023.

Fig. 3. FT-IR spectra of the different catalysts: (1) Cu/SiO₂-623; (2) Cu/SiO₂-723; (3) Cu/SiO₂-823; (4) Cu/SiO₂-923; (5) Cu/SiO₂-1023.

shoulder peak at 1038 cm⁻¹ indicate the presence of copper phyllosilicate. Formation of copper phyllosilicate indicates that copper could insert into the framework of the silica support and link with the support by chemical bonds, so a metal-support interaction exists between copper and the support. According to the XRD and N₂O analyses, we deduced that copper dispersion and the active sites could be changed by setting the calcination temperature in a different range.

The relative amount of copper phyllosilicate was calculated by considering the integrated intensity of the δ_{OH} band at 670 cm⁻¹ normalized to the integrated intensity of the symmetric ν_{SiO} band of amorphous silica at 800 cm⁻¹, which is referred to I_{670}/I_{800} [39]. From integration fitting Table 1, the relative amount of copper phyllosilicate increased when the calcination temperature was increased from 623 to 723 K, decreased when

the calcination temperature was increased from 723 to 823 K, and was zero for calcination temperatures ≥ 923 K.

3.4. TEM results

Figure 4 shows TEM images of the support, calcined catalysts, and reduced catalysts. Figure 4(a) shows the orderly morphology of the support. Copper species appear as spherical particles over the other samples (Fig. 4(b)–(e)). Copper species in the Cu/SiO₂-623 and Cu/SiO₂-723 catalysts are uniformly dispersed over the support and the particle sizes are in the range 2–6 nm. For the Cu/SiO₂-823 and Cu/SiO₂-923 catalysts, aggregation of a few copper species is observed. For the Cu/SiO₂-1023 catalyst, copper species form bulk crystals, indicating that large copper particles (> 300 nm) form at high calcination temperature. The results are in agreement with the N₂O chemisorption and XRD analyses. For the Cu/SiO₂-623 catalyst, the typical filandrous morphology of copper phyllosilicate [27] is observed, which is more apparent in the Cu/SiO₂-723 sample. It is not present in Cu/SiO₂-1023 and Cu/SiO₂-923. For the reduced catalysts (Fig. 4(g)–(i)), copper particles aggregate, except for Cu/SiO₂-723. The Cu particle sizes measured by TEM are shown in Table 1. The copper particles are the smallest in Cu/SiO₂-723, which possesses the highest thermal stability. The results were in good agreement with the XRD analysis.

3.5. Redox properties of the catalysts

H₂-TPR is a very useful technique to investigate the redox properties of catalysts. Figure 5 shows TPR profiles of the calcined Cu/SiO₂ catalysts. For the catalyst calcined at 623 K, the spectra exhibits a narrow and nearly symmetrical reduction

Fig. 4. TEM images of the support, and calcined and reduced Cu/SiO₂ catalysts: (a) support; (b) Cu/SiO₂-623; (c) Cu/SiO₂-723; (d) Cu/SiO₂-823; (e) Cu/SiO₂-923; (f) Cu/SiO₂-1023; (g) Cu/SiO₂-623 after reduction; (h) Cu/SiO₂-723 after reduction; (i) Cu/SiO₂-1023 after reduction.

Fig. 5. TPR profiles of the Cu/SiO₂ catalysts: (1) Cu/SiO₂-623; (2) Cu/SiO₂-723; (3) Cu/SiO₂-823; (4) Cu/SiO₂-923; (5) Cu/SiO₂-1023.

peak at ca. 464 K, indicating good dispersion of copper species with small particle sizes. For the Cu/SiO₂-823 catalyst, the main reduction peak shifts to lower temperature and there is a shoulder peak at ca. 478 K, indicating that at least two different Cu species are present. The reduction peak shifted to high temperature at a calcination temperature of 923 K and it is symmetrical, which can be ascribed to well-dispersed CuO. For Cu/SiO₂-1023, the main reduction peak is at ca. 488 K and there is a shoulder peak at 503 K. There is an additional reduction peak at ca. 549 K for Cu/SiO₂-723 and Cu/SiO₂-823. This peak can be attributed to the reduction of bulk CuO [40]. The low reduction temperature strongly suggests that the ammonia evaporation method can be used to finely disperse cupreous on silica for Cu/SiO₂ catalysts, which can be easily reduced to provide more active sites.

It has been reported that the Cu/SiO₂ catalyst shows a reduction peak at 463 K [41]. Zhang et al. [26] reported that the reduction of Cu/SiO₂ catalyst samples from 482 to 512 K consisted of reduction of copper phyllosilicate to Cu⁺ and well-dispersed CuO directly to Cu⁰. Ma et al. [20] reported that only one strong reduction peak at ca. 480 K can be attributed to reduction of Cu–O–Si overlapped with the reduction peak of well-

dispersed copper oxide. Combining with the FT-IR and TEM analyses, the strong and symmetrical reduction peaks for Cu/SiO₂-623 and Cu/SiO₂-723 can be attributed to the reduction of copper phyllosilicate to Cu⁺ overlapped with reduction of well-dispersed CuO to Cu⁰. The reduction peak of well-dispersed CuO is present in the spectrum of Cu/SiO₂-923 and the reduction peak of poorly dispersed CuO exists in the spectrum of Cu/SiO₂-1023. However, the shoulder peak in the TPR profile of Cu/SiO₂-823 may indicate the presence of poorly dispersed copper phyllosilicate.

3.6. Surface chemical states

The surface composition and oxidation states of the catalysts were investigated by XPS. XPS and XAES spectra of the reduced Cu/SiO₂ catalysts are shown in Fig. 6. In Fig. 6(a), the two intensive photoelectron peaks located at 932.8 and 952.6 eV are ascribed to the Cu 2p_{2/3} and Cu 2p_{1/2} binding energies of Cu⁺ or Cu⁰ species. For all of the catalysts, there are no satellite peaks at 944–945 eV [42] related to Cu²⁺, suggesting that Cu²⁺ species were reduced to a lower valence state of +1 or 0. The amounts of Cu⁰ and Cu⁺ species can be determined from the XAES spectra. As shown in Fig. 6(b), asymmetric and broad peaks are observed and can be deconvoluted into two symmetrical peaks centered at around 914 and 916 eV, corresponding to Cu⁺ and Cu⁰ species. These results indicate that both Cu⁺ and Cu⁰ coexist on the surface silica, which is in agreement with the XRD and TPR analyses.

The modified Auger parameter α' , which represents the sum of the kinetic energy of the Cu LMM Auger electron and the binding energy of the Cu 2p_{2/3} photoelectron, was used to distinguish Cu⁺ and Cu⁰ species. Generally, $\alpha' = \sim 1851.0$ eV for Cu⁰ and $\alpha' = \sim 1849.0$ eV for Cu⁺. It has been reported that when copper (+2, +1, and 0 valence states) is in a highly dispersed state and in intimate contact with a support, α' can be 2–3 eV lower than the bulk value [43]. As listed in Table 2, copper species with $\alpha' = \sim 1849$ eV are ascribed to Cu⁰ and those with $\alpha' = \sim 1847$ eV are ascribed to Cu⁺. The lower values for Cu⁺ and Cu⁰ than the bulk values are attributed to the strong interaction between copper species and the support. The Cu⁺/(Cu⁺ + Cu⁰)

Fig. 6. (a) Cu 2p XPS and (b) Cu LMM auger spectra of the reduced Cu/SiO₂ catalysts: (1) Cu/SiO₂-623; (2) Cu/SiO₂-723; (3) Cu/SiO₂-823; (4) Cu/SiO₂-923; (5) Cu/SiO₂-1023.

Table 2

Surface Cu components of the reduced Cu/SiO₂ catalysts based on Cu LMM deconvolution.

Catalyst	KE ^a (eV)		AP ^b (eV)		BE of Cu 2p _{3/2} ^c (eV)	X _{Cu⁺} ^d (%)
	Cu ⁺	Cu ⁰	Cu ⁺	Cu ⁰		
Cu/SiO ₂ -623	913.6	916.4	1846.3	1849.1	932.7	41.3
Cu/SiO ₂ -723	914.2	916.3	1847.1	1849.2	932.9	45.5
Cu/SiO ₂ -823	914.1	916.2	1846.9	1849.0	932.8	36.9
Cu/SiO ₂ -923	914.1	916.4	1846.9	1849.2	932.8	35.1
Cu/SiO ₂ -1023	914.0	916.4	1846.8	1849.2	932.8	47.6

^a Kinetic energy.

^b Auger parameter.

^c Binding energy of Cu.

^d Peak area ratio, X_{Cu⁺} = Cu⁺/(Cu⁰ + Cu⁺).

intensity ratio obtained by fitting the Cu LMM peaks increases when increasing the calcination temperature from 623 to 723 K. Combining with the FT-IR analysis, there were more copper phyllosilicate in Cu/SiO₂-723, so more Cu⁺ can be obtained. Although no copper phyllosilicate is present in Cu/SiO₂-1023, highest amount of Cu⁺ can be ascribed to the reduction difficulty of aggregated CuO.

3.7. Catalyst evaluation

Vapor-phase DEM hydrogenation to 1,3-PDO involves several cascade reactions, including hydrogenation of DEM to 3-hydroxyethyl propionate (3-HPE) as an intermediate, hydrogenation of 3-HPE to 1,3-PDO, and deep hydrogenation of 1,3-PDO to *n*-propanol (NPA) (Scheme 1). The ethyl propionate (EP) byproduct is synthesized by further hydrogenation of 3-HPE.

DEM conversion and 1,3-PDO selectivity over the Cu/SiO₂ catalysts are summarized in Table 3. All of the catalysts show high conversion (> 90%) of DEM, indicating the high activity of Cu/SiO₂ catalysts prepared by the ammonia evaporation method. DEM conversion increases with increasing amount of Cu⁰ and is the highest for the Cu/SiO₂-923 catalyst. The selectivity of 1,3-PDO increases when increasing the calcination temperature from 623 to 723 K, and then decreases when the calcination temperature is further increased to 1023 K. Among the catalysts used, Cu/SiO₂-723 shows the best performance with 1,3-PDO selectivity of 32.3%. The selectivity of 3-HPE is the highest for Cu/SiO₂-923. The selectivity of 1,3-PDO decreases with increasing selectivity of NPA and EP, indicating that inhibition of over hydrogenation is the key factor for catalyst modification.

Because stability is critical for practical application of catalysts for DEM hydrogenation, the long-term performance of the optimal catalyst Cu/SiO₂-723 was investigated. As shown in Fig. 7, the Cu/SiO₂-723 catalyst remained stable for about 99 h under the optimum reaction conditions. When the reaction time increased to 104 h, DEM conversion decreased to 74.1% and the 1,3-PDO yield decreased to 26.7%.

Scheme 1. Hydrogenation of DEM to 3-HPE, 1,3-PDO, and *n*-propanol.

Table 3

Catalytic performance of the Cu/SiO₂ catalysts.

Catalyst	DEM conversion (%)	Selectivity (%)			
		1,3-PDO	3-HPE	NPA	EP
Cu/SiO ₂ -623	91.9	29.3	10.6	31.6	22.4
Cu/SiO ₂ -723	90.7	32.3	38.9	8.9	13.9
Cu/SiO ₂ -823	95.2	27.3	35.6	18.7	18.2
Cu/SiO ₂ -923	96.5	18.0	41.6	14.6	19.2
Cu/SiO ₂ -1023	90.3	8.0	19.0	34.9	31.4

Reaction conditions: *p*(H₂) = 2.0 MPa, *T* = 473 K, H₂/DEM = 440 (mol/mol), LHSV = 1.8 h⁻¹.

From XRD measurements (Fig. 8), the Cu particle size increases from 13.8 nm after reduction to 36.1 nm after DEM hydrogenation (deactivation) owing to aggregation of copper species. TEM images of reduced and deactivated catalysts are shown in Fig. 9. Copper particles are uniformly dispersed on the Cu/SiO₂-723 catalyst after reduction and they agglomerate after deactivation. Large copper particles with an average diameter up to 90 nm are present over the used Cu/SiO₂-723 catalyst. We conclude that aggregation of copper particles is the main factor for catalyst deactivation [44,45]. However, copper phyllosilicate can enhance dispersion of copper species and interaction between copper and the support [42], leading to the relatively long-term catalytic stability of 99 h for the Cu/SiO₂-723 catalyst.

Fig. 7. Catalytic performance of the Cu/SiO₂-723 catalyst as a function of reaction time. Reaction conditions: *p*(H₂) = 2.0 MPa, *T* = 473 K, H₂/DEM = 330 (mol/mol), LHSV = 1.8 h⁻¹.

Fig. 8. XRD patterns of the Cu/SiO₂-723 catalyst (1) after reduction and (2) after deactivation.

Fig. 9. TEM images of the Cu/SiO₂-723 catalyst (a) after reduction and (b) after deactivation.

3.8. Discussion

3.8.1. Formation of copper phyllosilicate on calcined Cu/SiO₂ catalysts

Toupance et al. [46] showed that two types of supported Cu²⁺ species formed in calcined samples: grafted Cu²⁺ ions and copper phyllosilicate. Both Cu²⁺ species lead to small metal particles after reduction. Grafted Cu²⁺ arises from electrostatic interaction between [Cu(NH₃)₂]²⁺ and two SiO⁻ groups, while copper phyllosilicate is synthesized by the heterocondensation reaction of Si(OH)₄ with the Cu(OH₂)(H₂O)₄ complex. Trouillet et al. [47] reported that Cu^{II} complexes exist as [Cu(NH₃)₄(H₂O)₂]²⁺ and have electrostatic interactions with the silica support in solution, which can be transformed to (≡SiO)₂Cu^{II}(H₂O)₄ after calcination in air. Copper phyllosilicate can also form during the ammonia evaporation method [27].

In the present work, the silica surface and microcrystallites of the copper oxide precursor reacted to form difficult-to-reduce copper phyllosilicate, which was characterized by FT-IR and TEM. The filandrous structure characteristic of copper phyllosilicate became predominant on samples prepared at low calcination temperature. The relative amount of copper phyllosilicate showed a volcano-type trend with increasing calcination temperature and was maximum in the Cu/SiO₂-723 catalyst. It was not present when the calcination temperature was higher than 923 K. When the catalyst was calcined at 1023 K, formation of large CuO particles can be attributed to aggregation of loosely bound well-dispersed CuO. Formation of copper phyllosilicate indicates the strong interaction between copper and the support, and the good dispersion of copper species, resulting in the Cu/SiO₂-723 catalyst showing the highest catalytic performance.

3.8.2. Copper species after reduction

Chen et al. [27] found that well-dispersed CuO can be reduced to Cu⁰, and copper phyllosilicate can be reduced to Cu⁺. Van der Grift et al. [48] suggested that copper phyllosilicate and well-dispersed CuO can be reduced to Cu⁺ and Cu⁰, respectively. Toupance et al. [46] suggested that grafted Cu²⁺ ions and copper phyllosilicate transformed to Cu⁰ and Cu⁺, respectively, after reduction. Initially, [Cu(NH₃)₂]²⁺ adsorbs on the pore surface of SiO₂ by strong electrostatic adsorption. After calcination, grafted Cu²⁺ transforms to CuO, and copper phyllosilicate strongly adsorbs on the silica surface by formation of Cu–O–Si bonds. From XPS and XRD analyses, under a hydrogen atmosphere, CuO and copper phyllosilicate can be reduced to Cu⁰ and

Cu⁺, respectively.

The amount of copper phyllosilicate increases when the calcination temperature is increased from 623 to 723 K, resulting in a strong interaction between copper and silica. The specific surface area and ratio of Cu⁺/Cu⁰ are the highest for the Cu/SiO₂-723 catalyst. Compared with the Cu/SiO₂-723 catalyst, the amount of copper phyllosilicate and Cu dispersion decrease for the Cu/SiO₂-823 catalyst, leading to a smaller specific surface area and an asymmetrical reduction peak in the TPR profile. Copper phyllosilicate is not present and CuO is well dispersed on the surface of the Cu/SiO₂-923 catalyst, resulting in a large specific surface area and a symmetrical reduction peak. Aggregation of CuO is severe in the Cu/SiO₂-1023 catalyst and blocks the pore channels of silica, so reduction of CuO is not efficient.

3.8.3. Active sites for DEM hydrogenation

The optimal catalytic activity involves the cooperative effect of Cu⁰ and Cu⁺ to dissociate hydrogen and activate DMO [27]. It has been suggested that a suitable ratio of Cu⁰/Cu⁺ can greatly improve the catalytic performance [14,20]. The catalytic stability is greatly enhanced by boric acid with an optimal Cu/B atomic ratio, because of formation and preservation of appropriate distributions of Cu⁺ and Cu⁰ species on the catalyst surface [24]. Yin et al. [39,40,49] showed that metallic Cu and Cu⁺ are responsible for the high catalytic efficiency. Cu⁺ may play an important role in the DMO hydrogenation reaction. Moreover, Cu⁺ may act as electrophilic or Lewis acid sites to polarize the C=O bond via the lone pair on the oxygen atom, thereby improving the reactivity of the ester group in DMO [50]. In methyl acetate hydrogenation, Poels et al. [51] reported that while H₂ dissociatively adsorbed to Cu⁰, Cu⁺ stabilized methoxy and acyl species, which are important intermediates in DMO hydrogenation. XRD and XPS characterizations showed that Cu²⁺ could be completely absent after reduction and abroad and asymmetric peak in the Cu LMM auger spectra indicated that Cu⁰ and Cu⁺ coexist in the reduced catalysts. By deconvolution of the Cu LMM auger spectra, the Cu/SiO₂-723 catalyst showed the optimum Cu⁺/(Cu⁰+Cu⁺) ratio because of the highest amount of copper phyllosilicate in the calcined sample, while there was more Cu⁰ in Cu/SiO₂-923 than in the other catalysts. Activity results showed that a catalyst with a relatively large ratio of Cu⁺/(Cu⁰+Cu⁺) could increase the selectivity of 1,3-PDO and more Cu⁰ could increase DEM conversion. Therefore, we tentatively propose that the optimal catalytic activity over the Cu/SiO₂-723 catalyst is because of the synergetic effect between Cu⁰ and Cu⁺, and more Cu⁺ could enhance the reactivity of the ester group in DEM. From TPR, the lower reduction temperature of Cu/SiO₂-723 catalyst indicated that it contained more active sites, leading to the highest catalytic performance.

Ammonia evaporation is an effective way to prepare the Cu/SiO₂-723 catalyst with high Cu loading, good dispersion of copper species, and large copper surface area, which may be important for the catalytic performance. The particles of Cu/SiO₂ catalysts calcined at temperatures higher than 823 K could aggregate, leading to an increase of the particle size and decrease of the copper surface area and copper dispersion.

4. Conclusions

The calcination temperature has a profound effect on the texture, composition, and structure of Cu/SiO₂ catalysts prepared by the ammonia evaporation method. Copper species can react with silicic acid to form copper phyllosilicate, which is instrumental in promoting dispersion of copper species and obtaining more Cu⁺ after reduction. Among the catalysts prepared under different calcination temperature, the Cu/SiO₂-723 catalyst showed the highest catalytic performance for DEM conversion of 90.7% and the highest 1,3-PDO selectivity of 32.3%. The trend of the catalytic activity with the ratio of Cu⁺/(Cu⁰+Cu⁺) suggests a synergetic effect between Cu⁰ and Cu⁺. Moreover, other factors could not be ruled out, such as the larger specific surface area, better dispersion of copper species, larger cupreous surface area, and greater number of active sites in the Cu/SiO₂-723 catalyst. The catalytic performance of the Cu/SiO₂-723 catalyst in gas hydrogenation remained stable for about 99 h.

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Graphical Abstract

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Highly active Cu/SiO₂ catalysts for hydrogenation of diethyl malonate to 1,3-propanediol

Tongmei Ding, Hengshui Tian*, Jichang Liu, Wenbin Wu, Jintao Yu
East China University of Science and Technology

Cu/SiO₂ catalysts prepared via the ammonia evaporation method were applied in diethyl malonate hydrogenation. The optimum catalytic performance could be obtained over Cu/SiO₂ calcined at 723 K, acquiring better copper species dispersion, larger cupreous surface area and larger ratio of Cu⁺/Cu⁰.

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高活性 Cu/SiO₂ 催化剂应用于丙二酸二乙酯加氢制 1,3-丙二醇

丁同梅, 田恒水*, 刘纪昌, 吴文滨, 余锦涛

华东理工大学化工学院, 上海 200237

摘要: 作为聚对苯二甲酸丙二醇酯 (PTT) 的不可替代原料, 1,3-丙二醇 (1,3-PDO) 广泛应用于聚酯、树脂、化妆品、润滑剂和制冷剂等领域。采用丙二酸二乙酯 (DEM) 一步加氢合成 1,3-PDO 可避免传统化学工艺中醛类副产物的生成和生物法中产品纯度不高的问题, 进而满足下游 PTT 的品质要求。Cu/SiO₂ 催化剂因铜与载体间的强相互作用以及硅胶的弱酸性有利于催化活性中心的建立而被广泛应用于气相加氢反应, 可以选择性地活化 C–O 键而不活化 C–C 键。因此, 本文将 Cu/SiO₂ 催化剂应用于 DEM 加氢反应, 重点考察了焙烧温度对催化剂结构与性能影响的本质原因。

采用蒸氨法制备 Cu/SiO₂ 催化剂, 将一定量氨水滴加到硝酸铜水溶液中形成铜氨溶液后滴加 JN-30 硅溶胶, 经老化、过滤、洗涤、烘干、焙烧、压片成型后得到 40–60 目的催化剂。将不同温度 (623–1023 K) 焙烧的 Cu/SiO₂ 催化剂装填入自制连续高压固定床反应器中进行 DEM 加氢反应, 并采用 N₂ 物理吸附脱附、电感耦合等离子体发射光谱、N₂O 化学吸附、X 射线衍射、傅里叶红外光谱、H₂ 程序升温还原 (TPR)、透射电镜及 X 射线光电子能谱等手段对不同温度焙烧催化剂进行表征。结果表明, 在 723 K 焙烧的催化剂具有最大的比表面积和最均一的孔径分布, 其铜组分分散均匀, 活性铜表面积最大, 焙烧后可以形成最多的页硅酸铜, 导致还原后 Cu⁺/Cu⁰ 比例较高。在该催化剂作用下, 于 473 K、2.0 MPa、氢酯摩尔比 330 和液体空速 1.8 h⁻¹ 条件下, DEM 转化率为 90.7%, 1,3-PDO 选择性为 32.3%。

焙烧温度对 Cu/SiO₂ 催化剂组成、织构、结构、形貌及还原后的价态有较大影响。在焙烧温度为 623–1023 K 时, 低温焙烧有利于生成页硅酸铜, 而高温焙烧则有利于形成 CuO。在焙烧温度升高的过程中, 铜组分形态会发生较大变化, 在 623–723 K 焙烧的催化剂中页硅酸铜含量不断增加; 继续升高温度至 823 K, 页硅酸铜含量减少, 但是分散变差, 导致铜的比表面积、孔体积和孔径最小; 进一步升高温度至 923 K, 页硅酸铜消失, CuO 分散均匀, H₂-TPR 的还原峰窄且对称; 当温度升高到 1023 K 时, 铜晶体迅速长大而较难被还原。

关键词: 铜; 硅胶; 丙二酸二乙酯; 加氢; 1,3-丙二醇; 焙烧温度

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*通讯联系人. 电话: (021)64252198. 电子信箱: hstian@ecust.edu.cn

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