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bition of copper phyllosilicate and better dispersion of copper species.

Short Communication

Effect of promoters on hydrogenation of diethyl malonate to 1,3-propanediol over nano copper-based catalysts

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ABSTRACT

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1. Introduction

1,3-propanediol(1,3-PDO) is described as an important chemical intermediate with potential uses in resins, cosmetics, foods, lubricants, medicines, engine coolants and so on [1–2]. Moreover, it is mostly applied in the synthesis of polytrimethylene terephthalate (PTT) [3–5]. Three major production pathways of 1,3-PDO consist of ethylene oxide hydroformylation, acrolein hydration and hydrogenation and glycerol or glucose fermentation [6–11]. High pressure, high temperature, expensive catalysts and unstable intermediates are the disadvantages in the former two petrochemical processes. We focused on 1,3-PDO synthesis from diethyl malonate (DEM) hydrogenation in a continuous fixed-bed reactor, which avoids the unstable intermediate formation and the byproduct (ethanol) could be recycled.

Cupreous active sites are considered to be active for the selective hydrogenation of carbon-oxygen bonds and relatively inactive for the hydrogenolysis of carbon-carbon bonds [12–14]. So copper-based catalysts have been intensively investigated and promoters are added to obtain the desired properties. Chromium is regularly applied as an additive in copper containing catalyst for fatty ester hydrogenolysis, but it is toxic and harmful for environmental protection. Therefore, research is focused on the development of chromium free catalysts with good activity and thermal stability. Addition of ZnO to Cu/SiO₂ catalysts resulted in increased activity and lower by-product formation in the hydrogenolysis of methyl acetate [15]. Nickel [16], boron [17], silver

[18], aluminum [19] could also promote the catalytic performance in the hydrogenation of dimethyloxalate. Moreover, addition of promoters enhanced the activity and selectivity in the hydrogenation of methyl 3-hydroxypropionate to 1,3-PDO for better dispersion and stability of the active sites in the catalysts [20].

Copper-based catalysts were prepared via ammonia evaporation co-precipitation method. Structure evolutions

of the catalysts were systematically characterized by XRD, FTIR, TG, SEM, N₂-physisorption, ICP-AES, N₂O chem-

isorption and XPS focusing on the influence of promoters on the catalytic behavior in the hydrogenation of

diethyl malonate to 1,3-propanediol. The results showed that diethyl malonate conversion and 1,3-propanediol

selectivity could reach 96.71% and 29.76% respectively at 473 K with 2.0 MPa and 1.8 h⁻¹ with boron as promoter. The improved catalytic performance of Cu-B/SiO₂ catalyst could be attributed to more Cu⁰ formed with the inhi-

In this paper, copper-based catalysts were prepared by ammonia evaporation co-precipitation method. The effects of promoters on the catalytic activity were systematically investigated with a series of physico-chemical characterizations. To the best of our knowledge, it is the first time to discuss the influence of promoters on DEM hydrogenation to 1,3-PDO.

2. Experimental

2.1. Catalyst preparation

The copper-based catalysts were prepared by ammonia evaporation co-precipitation (AECP) method with copper nitrate trihydrate and aluminum nitrate nonahydrate, zinc nitrate hexahydrate, nickel nitrate hexahydrate, silver nitrate, ammonium heptamolybdate or boric acid dissolving in deionized water. 25 wt.% ammonia solution was added dropwisely at 313 K. JN-30 colloidal silica was added with constant stirring for another 4 h. Then raise the temperature to 363 K to evaporate ammonia until pH value of the solution as 7–8. After cooling, the suspension was filtered and washed with water for five times and with ethanol once followed by drying at 393 K for 12 h. The catalyst precursors were calcined at 723 K for 4 h, pressed, crushed and sieved to 40–60 meshes. All the catalysts were prepared as described and denoted typically by adding different promoters.





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2.2. Catalyst characterization

The copper-based catalysts with different promoters were characterized by different techniques as follows. The wide-angle XRD were conducted on a Bruker D8 FOCUS X-ray diffractometer with Cu-K α radiation, operating at a voltage of 40 kV and a current of 100 mA. The angle ranged from 10 to 80° with a continuous scanning speed of 0.02°/min. TG analysis was measured on Simultaneous Q600 DSC-TGA equipment with air atmosphere at 10 K/min heating rate. Flourier transform infrared spectroscopy (FT-IR) was performed on Nicolet5700 spectrometer with KBr beam splitter. Scanning electron micrograph (SEM) was conducted on Nova Nano SEM 450 and the sample was gold-plated before measurement. The specific surface areas and pore size distributions were measured on a Micromeritics ASAP2020 instrument following the BET method and BJH method respectively. The real content of copper and boron was determined by inductively coupled plasma-atomic emission spectroscopy method (ICP-AES: Agilent 725ES). N₂O chemisorption was carried out in Autochem II 2920 apparatus. 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. X-ray photoelectron spectroscopy (XPS) was conducted on a ESCALAB 250Xi system (Thermo Fisher) operated at a pass energy of 100 eV with an Al K_{α} X-ray source radiation source.

2.3. Activity test

The catalytic activity test was conducted on a fixed-bed reactor. Before reaction, 5 mL 40–60 meshes copper-based catalysts with different promoters were loaded into a stainless steel tubular reactor, the void of which was filled with quartz sand. The reactor was heated with three stage heater in order to control the reaction temperature. And the catalyst was deoxidized with H₂ at 573 K for 4 h. Then dropping to the reaction temperature, DEM in ethanol was pumped by an advection pump to the reactor and combined with H₂ at a H₂/DEM molar ratio of 440. The system temperature was set at 473 K and the system pressure was 2.0 MPa. And the liquid hourly space velocity (LHSV) of DEM was set at 0.72 h⁻¹ and 1.80 h⁻¹. The products were condensed and analyzed on a gas chromatograph fitted with HT-5 capillary column (30 m \times 0.32 mm \times 0.5 µm) and a flame ionization detector.

3. Results and discussion

3.1. Catalytic activity

Vapor phase hydrogenation of DEM to 1,3-PDO comprises several cascade reactions as shown in Scheme 1, including DEM hydrogenation to 3-hydroxy ethyl propionate (3-HPE), 3-HPE hydrogenation to 1,3-PDO and deep hydrogenation of 1,3-PDO to n-propanol (NPA). Moreover, the other side product ethyl propionate (EP) could be produced as the hydrogenation of hydroxyl group in 3-HPE. So it is important to choose a proper promoter inhibiting the side reactions to increase the selectivity of 1,3-PDO.

The catalytic performance of different promoters on DEM hydrogenation to 1,3-PDO is shown in Table 1. At a low LHSV of 0.72 h^{-1} , different promoters exhibited high catalytic activities (>80%). Nickel and

Table 1

Activity of different promoters adding to copper-based catalyst.

Catalyst	IUSV(b-1)	Conversion (%)	Selectivity (%)			
Catalyst	LHSV (II)	CONVERSION (%)	1,3-PDO	3-HPE	NPA	EP
Cu-B/SiO ₂	0.72	97.22	19.48	15.26	18.86	5.12
	1.80	96.71	29.76	16.69	22.12	21.03
Cu-Ag/SiO ₂	0.72	96.03	12.83	8.75	32.13	6.30
	1.8	93.46	6.47	16.01	18.84	13.12
Cu-Zn/SiO ₂	0.72	80.37	6.88	13.54	10.25	6.92
	1.8	35.98	21.81	63.03	9.14	6.10
Cu-Al/SiO ₂	0.72	92.16	4.77	4.15	2.53	15.41
	1.80	74.29	14.49	19.66	2.17	12.67
Cu-Ni/SiO ₂	0.72	96.62	0.00	5.37	15.30	5.08
	1.8	93.29	0.00	10.50	18.10	14.52
Cu-Mo/SiO ₂	0.72	93.39	0.00	11.96	16.64	6.48
	1.8	85.72	14.43	34.51	9.62	6.56
Cu/SiO ₂	0.72	94.38	18.07	6.35	37.90	7.91
	1.8	92.17	28.96	21.43	20.01	14.44

Reaction conditions: $P(H_2) = 2.0$ MPa, T = 473 K, $H_2/DEM = 440$ (mol/mol).

molybdenum as prompters showed zero selectivity of 1,3-PDO and a certain selectivity for 3-HPE and side-products. During other four promoters, the selectivity of 1,3-PDO varied considerably in the following order: B > Ag > Zn > Al. At a high LHSV of 1.8 h^{-1} , most promoters showed high conversion (>74%) but a significantly decrease for zinc. The activity decline of Cu-Zn/SiO₂ catalyst indicated that it was easier to deactivate, ascribing to the activation, storage or spillover of hydrogen [13]. The selectivity of 1,3-PDO and 3-HPE could increase for most promoters at higher LHSV.

Compared with Cu/SiO_2 catalyst, the selectivity of 1,3-PDO increased from 28.96% to 29.76% and the selectivity of 3-HPE decreased from 21.43% to 16.69% under Cu-B/SiO₂, while other chosen promoters had an adverse effect on the selectivity of 1,3-PDO. It is obvious that boron showed the highest selectivity of 1,3-PDO in the chosen copper-based catalysts. In order to find out the related information, several characterization techniques have been carried out below.

3.2. XRD analysis

The XRD patterns of calcined catalysts with different promoters are shown in Fig. 1A. All catalysts show a broad and diffuse peak at 22° , dedicating that SiO₂ as the support is amorphous. No CuO diffraction peak is observed in Cu-B/SiO₂ and Cu/SiO₂ catalysts, indicating well dispersion of copper particles or very small particle size [21]. Two visible peaks at 35.5° and 38.7° belonging to CuO with the crystal planes of (111) and (200) are observed in Cu-Al/SiO₂ catalyst. Aluminum oxide could incorporate into the framework of SiO₂ to form tetrahedral coordination bonded Si atoms by oxygen bridges [22], so it might increase the steric hindrance of copper oxide particles precipitated on the surface of support. The characteristic peaks of copper oxide also appear in Cu-Zn/SiO₂ and Cu-Ni/SiO₂. So we conclude that the addition of aluminum, zinc and nickel played an adverse effect on copper dispersion in Cu/SiO₂ catalysts.

The XRD patterns of typical samples after reduction are presented in Fig. 1B. The reduced catalysts show diffraction peaks at 43.2° and 50.3° ascribed to Cu phase and a diffraction peak at 36.5° attributed to Cu₂O phase. The intensity of Cu peak is stronger and the intensity of Cu₂O



Scheme 1. Reaction scheme for the hydrogenation of DEM to 3-HPE, 1,3-PDO and n-propanol.





Fig. 1. XRD patterns of the calcined (A) and reduced catalysts (B) with different promoters.

peak becomes much weaker after boron being added in Cu/SiO₂ catalyst and both are weaker in Cu-Mo/SiO₂ catalyst, indicating that Cu⁰ played a significant effect in the hydrogenation of DEM. Toupance et al. [23] suggested that grafted Cu²⁺ ions and copper phyllosilicate were transformed to Cu⁰ and Cu⁺ respectively after reduction. And Li [24] considered that the conversion of esters was depended on Cu⁺ and the selectivity of alcohols was depended on Cu⁰. So we tentatively deduced that boron as promoters inhibited the formation of phyllosilicate to a certain extent and promoted more grafted Cu²⁺, which could be hydrogenated to Cu⁰ as the active sites.



Fig. 2. FTIR spectra of the calcined catalysts.

3.3. FTIR analysis

The species of the calcined catalyst can be verified by the FTIR spectra. The typical samples are shown in Fig. 2. The broad absorption band at 3448 cm⁻¹ and 1637 cm⁻¹ attributes to OH groups in absorbed water [25]. And the absorption bands at approximately 1119, 800 and 472 cm⁻¹ are assigned to different vibration modes of the Si-O bonds in amorphous silica [26]. Cu(OH)₂ exhibits two δ_{OH} bands characteristic of structural hydroxyl groups at 938 and 694 cm^{-1} whereas chrysocolla is characterized by a single δ_{OH} band at 670 cm^{-1} and the ν_{SiO} shoulder peak at 1027 cm⁻¹ on the low frequency side of the v_{SiO} asymmetric stretching band of silica [23]. From Fig. 2, Cu(OH)₂ was absent and copper phyllosilicate was manifested in Cu-B/SiO₂ and Cu/SiO₂ catalysts. The relative amount of copper phyllosilicate is calculated by the integrated intensity of the δ_{OH} band at 670 cm^{-1} normalized to the symmetric v_{SiO} band at 800 cm⁻¹, which is termed as I_{670}/I_{800} [27]. According to the integration fitting, I_{670}/I_{800} of Cu/SiO₂ and Cu-B/SiO₂ are 0.245 and 0.184 respectively, dedicating that boron could decrease the formation of copper phyllosilicate on the silica. These results were corresponding to XRD analysis.

3.4. TG analysis

TG is used to investigate the influence of hydroxyl group amounts on the catalytic hydrogenation performance over catalysts. Fig. 3 shows the TG profiles of Cu-B/SiO₂ and Cu/SiO₂ catalysts. Below 373 K, the weight loss about 4 wt% is related to the loss of physical adsorbed water in both catalysts. The weight loss of the chemical bonded water between 523 K and 873 K [28] is 2.95 wt% in Cu-B/SiO₂, which is lower than Cu/SiO₂ catalyst (3.73%). And higher than 873 K could be considered as the loss of different hydroxyl group [18]. It is obvious that the amount of the hydroxyl group in Cu-B/SiO₂ is less than Cu/SiO₂ catalyst. Copper phyllosilicate (Cu₂Si₂O₅(OH)₂) formed in solution through the reaction between silicic acid arising from silica dissolution and [Cu(OH)₂(H₂O)₄]⁰ complex, so there is more copper phyllosilicate formed in Cu/SiO₂ catalyst. This finding is well consistent with XRD and FTIR results discussed in the context.

3.5. SEM analysis

To visually investigate the morphology of the catalysts after calcination and reduction, SEM experiments were carried out. As seen from Fig. 4 A and C, all samples could maintain sphere-like shape of silica. And no copper species could be detected on the surface, indicating that copper species dispersed well after calcination. The results were in good agreement with XRD analysis. After reduction, the particles



Fig. 3. TG profiles of calcined Cu/SiO₂ and Cu-B/SiO₂ catalysts.



Fig. 4. SEM images for catalysts: (A) calcined Cu/SiO₂ catalyst, (B) reduced Cu/SiO₂ catalyst,

attributed to Cu species could be obviously observed on both catalysts. It is apparent over Cu/SiO₂ catalyst but not so distinct in Cu-B/SiO₂ catalyst (even under high expansion), which could be ascribed to improved dispersion after boron incorporating into the framework of copper species.

(C) calcined Cu-B/SiO₂ catalyst, (D) reduced Cu-B/SiO₂ catalyst.

3.6. Textual properties of the catalysts

As shown in Table 2, the actual Cu content determined by ICP-AES was slightly lower than the theoretical values because cupric ions weakly adsorbed on the silica were eluted during washing process. The nitrogen adsorption-desorption isotherms of the calcined Cu/SiO₂ and Cu-B/SiO₂ catalysts and the corresponding pore size distribution were illustrated in Fig. 5. Both samples exhibit Langmuir type IV isotherms with H3-type hysteresis loop [29] in Fig. 5A. The hysteresis loop of Cu-B/SiO₂ catalyst does not change a lot, which indicate that introduction of boron would not affect the pore shape of the support. The BET specific surface area, pore volume and pore diameter of the calcined catalysts are summarized in Table 2. Cu/SiO₂ catalyst was found to possess a

relatively high BET surface area and pore volume, which decreased to $334.3 \text{ m}^2 \text{ g}^{-1}$ and $0.64 \text{ cm}^3 \text{ g}^{-1}$ respectively after boron being added. Compared with Cu/SiO₂ catalyst, the average pore diameter of Cu-B/SiO₂ decreased from 9.55 nm to 6.42 nm. As shown in Fig. 5B, the main contributions of pores to the total pore volume pore size were at ~3.0 nm for both catalysts. And the amount of micropores between 10 and 20 nm in Cu/SiO₂ catalyst decreased to 7.0 nm in Cu-B/SiO₂ catalyst, which resulted in the decrease of pore diameter after boron adding. Thus boron could play an important role in promoting the dispersion of copper species, which is in accordance with the analysis of XRD and SEM. This result could also be confirmed by N₂O chemisorption. As shown in Table 2, the higher copper dispersion (27.9%) and Cu⁰ surface area (37.6 m² g) were obtained over Cu-B/SiO₂ catalyst, which afforded the higher 1,3-PDO yield than Cu/SiO₂ catalyst.

3.7. Chemical state of copper and reduction behavior

XPS analysis is carried out to elucidate the chemical states of the reduced catalyst. The XPS and XAES spectra of reduced Cu/SiO₂ and

Table 2

Physicochemical properties of Cu/SiO_2 and $Cu-B/SiO_2$.

Catalyst	Cu loading ^a (wt.%)	S_{BET} (m ² .g ⁻¹)	d _{pore} (nm)	V _{pore} (cm ³ .g ⁻¹)	Cu dispersion ^b (%)	$\frac{S_{Cu0}^{b}}{(m^2/g)}$	TOF ^c (s ⁻)
Cu/SiO ₂	21.8	378.8	9.55	1.14	24.5	34.7	0.76
Cu-B/SiO ₂	23.5	334.3	6.42	0.64	27.9	37.6	0.89

^a Determined by ICP-AES.

^b Determined by N₂O chemisorption.

^c TOF is moles of 1,3-PDO converted per mole of surface Cu sites and per hour. Reaction conditions: 453 K, 2.0 MPa, H₂/DEM = 440 (mol/mol), LHSV = 1.8 h⁻¹.



Fig. 5. $N_{\rm 2}$ sorption isotherms (A) and BJH pore size distribution (B) of the calcined catalysts.

Cu-B/SiO₂ catalysts are illustrated in Fig. 6. The two peaks centered at binding energy of ca.933 eV and 953 eV (Fig. 6A) strongly suggested that most Cu²⁺ species were reduced to Cu⁺ and Cu⁰ [30]. The amount of Cu⁺ and Cu⁰ can be determined via XAES spectra [31]. In the Cu LMM XAES spectra shown in Fig. 6B, two overlapping Cu LMM Auger Kinetic energy peaks centered at about 914 eV and 916 eV, corresponding to Cu⁺ and Cu⁰ species. From the deconvolution results in Table 3, the mole ratio of surface Cu⁰/(Cu⁰ + Cu⁺) increased dramatically when boron was added to Cu/SiO₂ catalyst, which is in accordance with XRD analysis. The auger parameter of copper species α value at ca.1849 eV was ascribed to Cu⁰ and ca.1847 eV to Cu⁺. The smaller value for Cu⁺ and Cu⁰ than the bulk value was attributed to the strong interaction between copper species and support.

Turnover frequency (TOF) is calculated to reflect the intrinsic activity. The results are listed in Table 2. Compared with Cu/SiO₂, TOF of Cu- B/SiO_2 increased from 0.76 h⁻¹ to 0.89 h⁻¹, which could confirm the promoting effect of boron. According to the pore size distribution, the larger pores (10-20 nm) in Cu/SiO₂ decreased to ~7 nm when boron was added. The decrease of average pore diameter in Cu-B/SiO₂ could be attributed to better dispersion of copper species by N₂O chemisorption characterization results. It is documented that the reduction of cupreous species with H_2 involved the processes as following: Cu^{2+} to Cu⁰, Cu²⁺ to Cu⁺ and Cu⁺ to Cu⁰ [32]. Combining with the analysis from FTIR and XRD, we deduced that the introduction of boron into the silica framework would increase the ratio of Cu⁰ to Cu⁺, which could be confirmed by XPS analysis. The better catalytic performance for Cu-B/SiO₂ compared to Cu/SiO₂ most probably originated from the higher dispersion of copper particles, which could provide more active sites for DEM and H₂ than Cu/SiO₂. And more Cu⁰ generating from the



Fig. 6. Cu2p XPS (A) and Cu LMM Auger spectra (B) of the reduced catalysts.

grafted Cu²⁺ after reduction could also enhance the selectivity of 1,3-PDO in Cu-B/SiO₂ catalyst.

4. Conclusions

Suitable promoter such as boron could improve the catalytic performance of Cu/SiO₂ in the hydrogenation of DEM to 1,3-PDO. The conversion of DEM, the selectivity of 1,3-PDO and the selectivity of 3-HPE could reach 96.71%, 29.76% and 16.69% respectively at 473 K with 2 MPa and 1.8 h⁻¹ liquid hourly space velocity over Cu-B/SiO₂ catalyst. As demonstrated by XRD, FTIR, TG and XPS measurement, boron as a promoter could increase the formation of Cu⁰ after reduction with the decrease of the amount of copper phyllosilicate, which played an important role in the selectivity improvement of 1,3-PDO. The pore structure could maintain well and the dispersion of copper could be improved after the addition of boron by the characterization of SEM, N₂ adsorption and N₂O chemisorption.

Table 3	
Surface Cu component of the reduced	catalysts based on XPS results.

Catalyst	K.E.(eV) ^a		A.P.(eV) ^b		Cu 2p _{2/3}	$X_{Cu}^{0}\left(\%\right)^{d}$	
	Cu ⁺	Cu ⁰	Cu ⁺	Cu ⁰	BE (eV) ^c		
Cu/SiO ₂ Cu-B/SiO ₂	914.0 913.7	916.0 916.0	1847.1 1846.6	1849.1 1848.9	933.1 932.9	51.9 67.5	

^a Kinetic energy.

^b Auger parameter.

^c Binding energy of Cu.

^d Peak area ratio: $X_{Cu}^0 = Cu^0/(Cu^0 + Cu^+)$.

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