



Short communication

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



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ABSTRACT

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 chemisorption 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 inhibition of copper phyllosilicate and better dispersion of copper species.

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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].

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. Fourier 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 × 0.32 mm × 0.5 μ m) 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	LHSV (h ⁻¹)	Conversion (%)	Selectivity (%)			
			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(H₂) = 2.0 MPa, T = 473 K, H₂/DEM = 440 (mol/mol).

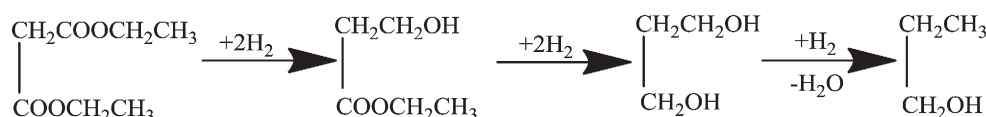
molybdenum as promoters showed zero selectivity of 1,3-PDO and a certain selectivity for 3-HPE and side-products. During other four promoters, the selectivity of 1,3-PDO varied considerably in the following order: B > Ag > Zn > Al. At a high LHSV of 1.8 h⁻¹, most promoters showed high conversion (>74%) 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/SiO₂ 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.

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