Chinese Journal of Catalysis 37 (2016) 484–493

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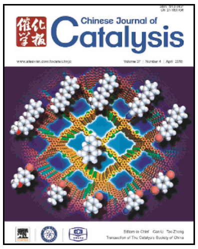

Article

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

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ARTICLE INFO

Article history:
Received 3 December 2015
Accepted 13 February 2016
Published 5 April 2016

Keywords:
Copper
Silica
Diethyl malonate
Hydrogenation
1,3-Propanediol
Calcination temperature

ABSTRACT

Cu/SiO_2 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/SiO_2 catalysts, which were systematically characterized by N_2 adsorption-desorption, inductively coupled plasma-atomic emission spectroscopy, N_2O chemisorption, X-ray diffraction, Fourier transform infrared spectroscopy, H_2 temperature-programmed reduction, transmission electron microscopy, and X-ray photoelectron spectroscopy. When the Cu/SiO_2 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/SiO_2 catalysts calcined at other temperatures, the enhanced catalytic performance of the Cu/SiO_2 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^+/Cu^0. The synergetic effect of Cu^0 and Cu^+ is suggested to be responsible for the optimum activity.

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 $CuZn_aAl_bO_c$ 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/SiO_2 has been intensively investigated and attracted considerable attention owing to its excellent selectivity, green benefits and low cost. Various preparation techniques

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DOI: 10.1016/S1872-2067(15)61053-1 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 37, No. 4, April 2016

have been used to fabricate Cu/SiO_2 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 Cu^0/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/SiO_2 catalysts were prepared by the ammonia evaporation method. Few studies have been published regarding the structure–performance correlation of Cu/SiO_2 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/SiO_2 catalysts were prepared by the ammonia evaporation method. In brief, 24.16 g of $Cu(NO_3)_2\cdot3H_2O$ (Shanghai Lingfeng Chemical Reagent Co. Ltd., Shanghai, China) was dissolved in 200 mL of deionized water at 313 K with vigorousstirring. 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/SiO_2-*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 H_2 temperature-programmed reduction (TPR) on a Micromeritics Autochem II ASAP 2090 instrument. Calcined Cu/SiO_2 catalyst (50 mg) was outgassed at 473 K under Ar for 1 h. After the catalyst was cooled to room temperature under argon, 10% H_2/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.

N_2O chemisorption was carried out in Autochem II 2920 apparatus (Micromeritics, USA). Briefly, the catalyst sample was reduced in 5% H_2/Ar at 723 K with a heating rate of 2 K/min. After cooling to 323 K under Ar, 10% N_2O/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 $2\ Cu_{(s)} + N_2O \rightarrow Cu_2O_{(s)} + N_2$. Hydrogen pulse reduction of surface Cu_2O to metallic Cu was performed at 723 K under 10% H_2/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 N_2O 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.