Applied Catalysis A, General 555 (2018) 161–170

Contents lists available at ScienceDirect

Applied Catalysis A, General

journal homepage: www.elsevier.com/locate/apcata

Enhancement of diethyl malonate hydrogenation to 1,3-propanediol using mesoporous Cu/SBA-15 as catalyst

Jintao Yu, Jingshun Cao, Lihui Du, Yongmei Wei, Tao Wang, Hengshui Tian*

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

ARTICLE INFO

Keywords:
Hydrogenation
SBA-15
1,3-Propanediol
Copper-based catalyst

ABSTRACT

SBA-15 is considered as an ideal support to ensure a copper-based catalyst with high activity and selectivity. In this work, the hydrogenation of diethyl malonate (DEM) to 1,3-propanediol (1,3-PDO) over Cu/SBA-15 catalysts was investigated. Compared to the conventional Cu/SiO_2 catalyst, the Cu/SBA-15 catalysts exhibited higher DEM conversions (up to 95%), better 1,3-PDO selectivities (up to 61%), and longer lifetime (over 180 h). These improvements were ascribed to the well-ordered tubular channel structure, better copper active-site dispersion, and appropriate Cu^+/Cu° ratio in the Cu/SBA-15, affording higher TOFs and copper species surface areas, which was confirmed by N_2-physisorption, X-ray diffraction, inductively coupled plasma-atomic emission spectroscopy, N_2O titration, transmission electron microscopy, H_2 temperature-programmed reduction, Fourier-transform infrared spectroscopy, and X-ray photoelectron spectroscopy analyses. The Cu/SBA-15 in this work advances the prospects of DEM hydrogenation as a promising method to produce 1,3-PDO on industrial scale.

1. Introduction

1,3-Propanediol (1,3-PDO) is a crucial industrial chemical that finds wide-ranging application in materials as varied as dry-set mortars, resins, water-based inks, and engine coolants [1]. Among these applications, the vast majority of 1,3-PDO is used to manufacture polytrimethylene terephthalate (PTT), a polyester which shows many excellent properties including superior stretchability, lower dyeing temperature, wider color range accommodation, and greater stain resistance [2,3]. To date, the main commercial processes for the production of 1,3-PDO include two chemical methods (Degussa and Shell processes) and a bio-fermentation method (DuPont) [4]. Both the Degussa and Shell processes [5–7] suffer from disadvantages such as high pressures (10 MPa), high costs, toxic cobalt-based catalysts, and serious environmental pollution. More importantly, a number of aldehyde side products are produced by these chemical methods, lowering the production quality below the desirable polymer- and fiber-grade levels (99.9 wt%) [1]. Bio-fermentation technology has also been developed to produce 1,3-PDO through glucose or glycerol conversion [8,9]. Although the bio-fermentation method can produce one-tenth of the aldehyde impurities (0.003 wt%) in the 1,3-PDO compared to the chemical methods, its low yield and complex separation steps remain serious drawbacks [1]. Therefore, the development of an alternative or novel approach to overcome the problems of the chemical and bio-fermentation methods remains necessary.

Currently, an alternative method involving the green hydrogenation of esters using a copper-based catalyst to produce 1,3-PDO has received considerable attention [10–12]. Specifically, this process involves the initial hydrogenation of diethyl malonate (DEM) to form ethyl 3-hydroxypropanoate (HPE), followed by the hydrogenation of HPE to generate 1,3-PDO. DEM is a green and safe chemical feedstock that has been synthetized from syngas or by biomass methods on commercial scale. Compared to the conventional processes, the DEM hydrogenation method usually proceeds under mild reaction conditions. In particular, no aldehydes are contained in the 1,3-PDO product. In addition, the low-cost, non-toxic, copper-based catalysts can selectively activate carbon-oxygen bonds, and thus, have been widely utilized in ester hydrogenation processes (such as dimethyl oxalate (DMO) and diethyl oxalate (DEO)) [13,14], which would make the DEM hydrogenation method a cost-competitive and environmentally friendly process for the production of 1,3-PDO. Nevertheless, the selectivity for 1,3-PDO and lifetime of the copper-based catalyst are still great challenges for DEM hydrogenation before large-scale use [12]. Concerning these problems, previous studies on Cu/SiO_2 catalysts suggested that the calcination temperature, metal loading, and promoter metal play important roles in the selectivity for 1,3-PDO and catalyst lifetime. For example, Ding et al. investigated the effect of the calcination temperature on the transformation of copper species in a DEM hydrogenation process, resulting in a DEM conversion of 90.7% and 1,3-PDO selectivity of 32.3% [10]. Zheng et al. studied metal loading in a dimethyl malonate (DMM)

---

* Corresponding author.
E-mail address: HengshuiTian@163.com (H. Tian).

https://doi.org/10.1016/j.apcata.2018.02.020
Received 18 October 2017; Received in revised form 7 February 2018; Accepted 19 February 2018

hydrogenation process, achieving a 1,3-PDO yield as high as 41.7% [12]. From these studies, the amorphous Cu/SiO_2 catalyst was found to show unsatisfactory selectivity for 1,3-PDO. Furthermore, the Cu/SiO_2 catalyst had a relatively low specific surface area (~350 m^2/g), and the low melting point of the copper metal could easily lead to sintering deactivation, thus reducing the catalyst lifetime. Therefore, it is still a challenge to develop or design copper-based catalysts with higher selectivity for 1,3-PDO and longer lifetimes for the ester hydrogenation process.

Generally, two major strategies can be employed to modify the copper-based catalyst. The first involves the promoter metal. For example, Cu-Cr, Cu-Ni, Cu-Ag, and Cu-Au bimetal catalysts using amorphous silicate as the support can form intermetallic or alloy phases with synergistic effects, which can be resistant to copper sintering and contribute to better catalytic performance in the ester hydrogenation process [15–18]. According to previous reports, the addition of a small amount of noble metal enabled full DMO conversion with over 95% ethylene glycol (EG) selectivity, and the modified catalyst remained active over 150 h [16,17]. Unfortunately, some bimetal-site catalysts exhibited better catalytic performance for ester hydrogenation only under lower liquid hourly space velocities (LHSV) (0.2 h^{-1}) and higher H_2/ester molar ratios (100 mol/mol). Furthermore, noble or toxic metals inevitably face higher cost, safety, and environmental challenges.

As another strategy, mesoporous silicate materials as supports have been considered to hold promise for enhancing the quality of copper-based catalysts. Specifically, the mesoporous silicate families, including HMS, M41S, and SBA-*n*, possess regular hexagonal mesostructures and huge specific surface areas (over 700 m^2/g), allowing their wide application as adsorbents [19,20], carrier materials [21], and catalysts [22–26]. Typically, when used as supports, these materials provide a means to eliminate internal diffusion and improve the metal dispersion in heterogeneous catalysis [27]. In the ester hydrogenation process, Cu/HMS, Cu/MCM-41, and Cu/SBA-15 catalysts have been found to exhibit better activities and more stable catalytic performance. For example, the HMS-support catalyst reported by Yin et al. achieved 100% ester conversion and 92% EG selectivity in the DMO hydrogenation process [28]. In Ma et al.'s study, the Cu/MCM-41 catalyst produced a 92% yield of EG with a lifetime of over 100 h even at an LHSV as high as 3.0 h^{-1} [29]. For the SBA-15-supported catalyst, in particular, it was found that even at a copper loading of 50 wt%, the copper particle size remained at 22 nm, while the copper species were simultaneously highly dispersed [30]. Besides, a 66.1% yield of 1,4-BDO was achieved using Cu/SBA-15 as catalyst in the dimethyl maleate hydrogenation process, which was much higher activity compared to the conventional catalysts [31]. Among the mesoporous silicates, SBA-15 is considered as a promising support; synthesized using a recyclable surfactant template, SBA-15 possesses a high surface area (700–1000 m^2/g), tunable channel size (3–30 nm), and unique framework with a well-defined pore arrangement [32]. In fact, when used as a support, SBA-15, exhibits higher thermal and hydrothermal stabilities, as well as better catalyst reusability [33,34]. Owing to these advantages over HMS and MCM-41, SBA-15 would be expected to enhance copper-based catalyst activity and selectivity, and prolong the lifetime of the catalyst in the DEM hydrogenation process. Furthermore, the SBA-15 support with its tunable tubular framework structure should be suitable for probing structure-activity relationships. However, to the best of our knowledge, very few studies have focused on copper-based catalysts using the mesoporous silicate SBA-15 support in the DEM hydrogenation process. Thus, there may be enormous potential in using SBA-15 as a support to overcome the unsatisfactory selectivity for 1,3-PDO and the poor stability of the Cu/SiO_2 catalyst in the DEM hydrogenation process.

Therefore, in the present work, Cu/SBA-15 catalysts with extremely large specific surface areas and well-dispersed active sites on the ordered silicate framework were synthesized by the ammonia evaporation method. Subsequently, the effects of the pressure, temperature, H_2/ester ratio, and LHSV on the DEM hydrogenation process over the Cu/SBA-15 catalysts were investigated. In particular, the lifetimes of the Cu/SBA-15 catalysts in the DEM hydrogenation were assessed. To fully characterize and understand the structure-activity performance of the Cu/SBA-15 catalysts, N_2-physisorption, X-ray diffraction (XRD), inductively coupled plasma-atomic emission spectroscopy (ICP-AES), N_2O titration, transmission electron microscopy (TEM), temperature-programmed reduction (H_2-TPR), Fourier-transform infrared spectroscopy (FT-IR), and X-ray photoelectron spectroscopy (XPS) analyses were performed.

2. Experimental

2.1. Catalyst preparation

SBA-15: Mesoporous SBA-15 with a tubular channel structure was synthesized according to Zhao et al. [32]. Tri-block polymer P123 (12.08 g, $EO_{20}PO_{70}EO_{20}$, $M_{av} = 5800$; Aldrich), deionized H_2O (311 mL), and HCl (60 mL, 36–38%, Adamas-Beta) were mixed in a flask for 4 h. Next, tetraethyl orthosilicate (25.6 g, TEOS, > 98%, Adamas-Beta) was added dropwise into the solution and aged for 24 h. Then, the mixture was transferred into a PTFE container and hydrothermally treated for 72 h. After filtration and washing with deionized water and ethanol, the obtained powder was heated at 823 K for 5 h.

Cu/SBA-15: An appropriate amount of $Cu(NO_3)_2{\cdot}3H_2O$ (> 99%; Sinopharm Chemical) was dissolved in deionized water (100 mL) to afford a copper loading of 10, 15, 20, or 25 wt% with respect to the SBA-15 powder. Aqueous ammonia (25 wt%) was added to adjust the pH to 11.0. Then, SBA-15 powder (6.4 g) was added into the solution and stirred for 4 h. Thereafter, the mixture was heated to 363 K to evaporate the ammonia until pH value was 7.5. After filtration and washing with deionized water and ethanol, the obtained solid was dried in an oven at 373 K for 12 h and calcined at 723 K for 4 h. The different copper-loaded samples were labelled as *x*Cu/SBA-15, where *x* represents the loading amount (wt%).

2.2. Catalyst characterization

Inductively coupled plasma-atomic emission spectroscopy (ICP-AES, Agilent 725ES) was used to analyze the actual copper contents. Before the analysis, samples were dissolved in HF, and then diluted with water.

FT-IR was conducted using a Nicolet 5700 instrument equipped with a KBr beam splitter at a resolution of 2 cm^{-1}. Each sample was mixed with KBr and pressed into a self-supported wafer, placed into a sample holder and scanned 32 times in the 400–4000 cm^{-1} range.

N_2O titration, in which surface copper atoms are oxidized through the reaction $2Cu_{(s)} + N_2O \rightarrow Cu_2O_{(s)} + N_2$, was conducted with a Micromeritics Autochem II 2920. The calcined catalysts were first reduced under a 10% H_2/Ar flow for 1.5 h at 573 K. After cooling to 323 K under Ar flow, a flow of 10% N_2O/He was introduced at a rate of 50 mL/min to oxidize the surface copper atoms to Cu_2O. The content of Cu_2O was then determined through a H_2 reduction process at 623 K under 10% H_2/Ar flow. The copper atom's surface area and dispersion of Cu were determined by H_2 consumption, and 1.46×10^{19} copper atoms per square meter were assumed [35].

N_2 adsorption-desorption isotherms of the calcined catalysts were obtained at 77 K using a Micromeritics ASAP2020 instrument. Vacuum degassing was first conducted at 423 K for 1 h. The specific surface area (A_{BET}) was calculated by the Brunauer-Emmett-Teller (BET) method. Pore volumes (V_P) were derived from the adsorbed N_2 volume at a relative pressure of 0.99. Pore volume distributions were calculated by the Barrett-Joyner-Halenda (BJH) method.

XRD profiles were obtained with a Bruker D8 FOCUS diffractometer equipped with Cu K_α radiation in a scanning angle range of 10–80° at a scan rate of 2°/min. The working voltage and current were 40 kV and 100 mA, respectively. The Cu crystallite size $d_{Cu}(nm)$ was calculated