



Original article

Low-temperature hydrogenation of maleic anhydride to succinic anhydride and γ -butyrolactone over *pseudo*-boehmite derived alumina supported metal (metal = Cu, Co and Ni) catalysts



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ARTICLE INFO

Article history:

Received 15 February 2016
 Received in revised form 8 March 2016
 Accepted 11 March 2016
 Available online 19 March 2016

Keywords:

Maleic anhydride
 Hydrogenation
 Succinic anhydride
 Nickel

ABSTRACT

The *pseudo*-boehmite derived alumina supported metal (Cu, Co and Ni) catalysts prepared by the impregnation method were investigated in hydrogenation of maleic anhydride (MA) to succinic anhydride (SA) and γ -butyrolactone. The catalysts were characterized by ICP-AES, N_2 adsorption-desorption, XRD, H_2 -TPR, CO-TPD, dissociative N_2O adsorption and TEM and the results showed that the alumina possessed mesoporous feature and the metal species were well dispersed on the support. Compared to Cu/Al_2O_3 and Co/Al_2O_3 , Ni/Al_2O_3 exhibited higher catalytic activity in the MA hydrogenation with 92% selectivity to SA and nearly 100% conversion of MA at 140 °C under 0.5 MPa of H_2 with a weighted hourly space velocity of $2\ h^{-1}$ (MA). The stability of Ni/Al_2O_3 catalyst was also investigated.

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1. Introduction

Developing highly active catalysts for hydrogenation of maleic anhydride (MA) under low temperature is significant for the production of important industrial chemicals [1–3]. The reaction products such as succinic anhydride (SA), γ -butyrolactone (GBL), tetrahydrofuran (THF), and 1,4-butanediol (BDO) are widely used as solvents or raw materials for polymer synthesis.

Noble metal-based catalysts, such as Ru/C [2], Pd/SiO_2 [4] and Pd/Al_2O_3 [5], have been reported as effective catalysts in hydrogenation of MA. The reaction is generally carried out at temperature of 100–240 °C and pressure of 0.2–5 MPa and the main products are SA and GBL. Although the noble metal catalysts exhibited good catalytic performance for the MA hydrogenation, high cost and limited resource of noble metal restrict their application. Recently, more attention has been drawn on developing non-noble metal catalysts, such as Cu/SiO_2 [6], Co/SiO_2 [7], $Ni/HY-Al_2O_3$ [8] and Ni/CeO_2 [9], generally operated at temperature of 190–210 °C and pressure of

0.1–5 MPa. Among these catalysts, Cu-, Co- and Ni-containing catalysts have shown remarkable catalytic activity.

It is well known that supports generally facilitate the catalysts with high dispersion and stability of the active species [10]. Much attention has been paid into the selection of suitable catalyst support for the MA hydrogenation. Various supports, such as CeO_2 [9], SBA-15 [11], hydroxylapatite [11], MCM-41 [11], TiO_2 [12] and Al_2O_3 [13] have been investigated for the MA hydrogenation to SA and GBL. Among these supports, alumina was widely used and showed good stability in the hydrogenation of MA [5,13–16]. *Pseudo*-boehmite is usually employed as the precursor to prepare different types of alumina supports [17].

In this work, we reported a novel and simple method to prepare *pseudo*-boehmite derived alumina supported Cu-, Co- and Ni-containing catalysts (Cu/Al_2O_3 , Co/Al_2O_3 and Ni/Al_2O_3) used for the hydrogenation of MA. We aimed to explore the effective catalyst for hydrogenation of MA under low temperature and pressure.

2. Experimental

2.1. Catalyst preparation

The Al_2O_3 support was obtained through the calcination of *pseudo*-boehmite (Shangdong City Star Petroleum Chemical Technology Co., Ltd.) precursor at 750 °C for 3 h as Al_2O_3 prepared

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at this temperature has high surface area and large pore volume along with high crystallinity (Fig. S1 and Table S1 in Supporting information). All the catalysts were prepared by the wet impregnation method. To prepare Ni/Al₂O₃, 5.6 mL of 0.32 mol L⁻¹ 1 aqueous solution of Ni(NO₃)₂·6H₂O was added into a suspension containing 2 g of Al₂O₃ and 32 mL of H₂O. The mixture was magnetically stirred for 12 h at room temperature. After evaporation of water at 70 °C, the sample was dried at 120 °C overnight and then calcined in air at 450 °C for 3 h. To prepare Cu/Al₂O₃ and Co/Al₂O₃, the same procedure of preparing Ni/Al₂O₃ was followed except using the equimolar of Cu(NO₃)₂·3H₂O and Co(NO₃)₂·6H₂O instead, respectively.

2.2. Catalyst characterization

Elemental analysis was performed on a Thermo Elemental IRIS Intrepid inductively coupled plasma atomic emission spectrometer (ICP-AES). N₂ adsorption–desorption isotherms were obtained at -196 °C using a Quantachrome Quadrasorb S1 apparatus. The pore volume was calculated from the amount of N₂ adsorbed at a relative pressure of 0.99. The pore size distribution was calculated with the Barrett–Joyner–Halenda (BJH) model from the desorption branch. The powder X-ray diffraction (XRD) patterns were recorded on a Bruker D8 Advance X-ray diffractometer using Cu-K α radiation with a voltage of 40 kV and a current of 40 mA. The transmission electron microscope (TEM) images of Cu/Al₂O₃ and Co/Al₂O₃ catalysts were obtained from a FEI Tecnai G2 F20 S-TWIN microscope, while those of Ni/Al₂O₃ catalyst were derived from a JEOL JEM2011 microscope. H₂ temperature programmed reduction (H₂-TPR) profiles of the calcined catalysts were recorded using a Micromeritics Chemisorb 2720 apparatus. 50 mg of sample was placed in a quartz reactor and heated at 10 °C min⁻¹ up to 200 °C under a He flow of 50 mL min⁻¹, and held at this temperature for 2 h. The reactor was then cooled down to 100 °C. H₂-TPR was performed using a 10% H₂/Ar mixture at a flow rate of 50 mL min⁻¹ while the temperature was linearly ramped from 100 °C to 950 °C at 3 °C min⁻¹. The dispersion of Ni/Al₂O₃ and Co/Al₂O₃ was analyzed by the temperature programmed desorption of carbon monoxide (CO-TPD) with the assumption of CO:Ni or CO:Co (surface) stoichiometry of 1:1. The dispersion of Cu/Al₂O₃ catalyst was determined by the dissociative N₂O adsorption method [18].

2.3. Catalytic reaction

Catalytic activity test was carried out in a fixed-bed reactor. In each run, 0.25 g of catalyst (60–80 mesh) was placed at the center of the reactor tube between two layers of silica sands. The reaction temperature was continuously monitored using a thermocouple touching the catalyst bed firmly. Prior to the reaction, the catalyst was pre-reduced under a flow of 5% H₂/Ar (50 mL min⁻¹) for 2 h at

450 °C for Cu/Al₂O₃ and Co/Al₂O₃ and 750 °C for Ni/Al₂O₃. After reduction, the catalyst was cooled down to a desired reaction temperature (120–200 °C) and a mixture consisting of MA and GBL with a weight ratio of 15:85 were fed continuously into the reactor with a H₂/MA molar ratio of 24. The products were collected at intervals of 1 h and analyzed by gas chromatography (GC) with a flame ionization detector and a HP-5 capillary column. Based on the GC results the conversion of MA and the selectivity to the product *i* were calculated according to

$$\text{Conversion (MA)} = (\text{MA}_{\text{in}} - \text{MA}_{\text{out}}) / \text{MA}_{\text{in}} \times 100\% \quad (1)$$

$$\text{Selectivity (i)} = \text{Product}_{i,\text{out}} / (\text{MA}_{\text{in}} - \text{MA}_{\text{out}}) \times 100\% \quad (2)$$

where, MA_{in}, MA_{out} and Product_{*i*,out} represent the molar concentration of inlet reactant, outlet reactant and outlet products, respectively.

3. Results and discussion

3.1. Characterization

The chemical compositions and textural properties of the Cu/Al₂O₃, Co/Al₂O₃ and Ni/Al₂O₃ catalysts before H₂ reduction and Al₂O₃ support are summarized in Table 1. As seen in Table 1, the surface area for the Al₂O₃ support is 214 m² g⁻¹ and pore volume is 1.14 cm³ g⁻¹. Three catalysts, Cu/Al₂O₃, Co/Al₂O₃ and Ni/Al₂O₃, show slightly smaller surface area and pore volume after the impregnation of metal species. The N₂ adsorption–desorption results for the support and catalysts are shown in Fig. 1. All isotherms are of type IV, which indicates that the samples maintain the mesoporous structure after metal impregnation and calcination treatment. Metal dispersion is also a crucial factor in determining catalytic performance [9,19]. Based on the TEM images of reduced Cu/Al₂O₃, Co/Al₂O₃ and Ni/Al₂O₃ catalysts (Fig. S3 in Supporting information), the nanoparticle size of Co species is much bigger than those for Cu and Ni species, suggesting the relatively poor Co dispersion. Moreover, the calculated dispersion degree of Cu, Co and Ni species after H₂ reduction is 24.8%, 8.2% and 14.4%, respectively, which is consistent with the TEM results.

The XRD patterns for the support and catalysts before H₂ reduction are shown in Fig. 2A. For the Al₂O₃ support, the diffraction peaks at 2 θ of 37.4°, 39.7°, 45.8° and 67.3° may be assigned to (3 1 1), (2 2 2), (4 0 0) and (5 2 2) diffractions of γ -Al₂O₃ (PDF No. 04-0880), respectively [20–22]. In the case of the calcined Co/Al₂O₃, in addition to the diffractions of Al₂O₃ the peaks appeared at 2 θ of 31.3°, 36.8°, 44.8°, 59.4° and 65.2° are attributed to Co₃O₄ (PDF No. 43-1003) [23,24]. The nickel and copper oxide phases were not observed, indicating the metal species are highly dispersed on the support, which are in agreement with the Ni/Al₂O₃ and Cu/Al₂O₃ catalysts dispersion results.

Table 1

The physicochemical properties and catalytic performance of Cu/Al₂O₃, Co/Al₂O₃ and Ni/Al₂O₃ catalysts.

Samples	Metal loading ^a (wt%)	S _{BET} (m ² g ⁻¹)	V _{pore} (cm ³ g ⁻¹)	Dispersion (%)	MA Con (%)	TOF (h ⁻¹) ^b
Al ₂ O ₃	–	214	1.14	–	–	–
Cu/Al ₂ O ₃	4.9	185	0.88	24.8 ^c	25.8 ^d	28
Co/Al ₂ O ₃	4.8	186	0.84	8.2 ^e	38.7 ^d	120
Ni/Al ₂ O ₃	4.9	165	0.85	14.4 ^e	>99 ^d	171
					84.8 ^f	434

^a Calculated based on the ICP-AES results.

^b TOF = moles of MA converted in the 7th h per mole of Cu, Co and Ni calculated from their dispersion.

^c Determined by the dissociative N₂O adsorption.

^d Reaction conditions: temperature = 140 °C, H₂ pressure = 0.5 MPa, WHSV = 2 h⁻¹ (MA).

^e Determined by the CO-TPD method.

^f Reaction conditions: temperature = 140 °C, H₂ pressure = 0.5 MPa, WHSV = 6 h⁻¹ (MA).

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