

Gas phase hydrogenation of maleic anhydride to γ -butyrolactone by Cu–Zn–Ti catalysts

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Abstract

Cu–Zn–Ti catalysts were prepared by coprecipitation method. The calcined and reduced Cu–Zn–Ti catalysts were characterized by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), temperature-programmed reduction (TPR), and N₂ adsorption. The calcined Cu–Zn–Ti catalysts were composed of CuO, ZnO, and amorphous TiO₂. There were two kinds of CuO species present in the calcined Cu–Zn–Ti catalyst. At a lower copper content, CuO species interacted with ZnO and TiO₂; at a higher copper content, both the surface-anchored and bulk CuO species were present. After reduction, metallic copper (Cu⁰) appeared in all Cu–Zn–Ti catalysts. Cu⁰ produced by reduction of the surface-anchored CuO favored the deep hydrogenation of maleic anhydride. ZnO and TiO₂ had synergistic effect on the catalytic activity of Cu–Zn–Ti catalysts in hydrogenation of maleic anhydride.

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1. Introduction

Hydrogenation of maleic anhydride has attracted a great deal of attention recently, since the hydrogenation products, such as γ -butyrolactone, 1,4-butanediol, and tetrahydrofuran, are important intermediate chemicals and solvents in food, pharmaceuticals, and textile industries [1]. Among the hydrogenation products, γ -butyrolactone is widely used as a starting material for the production of *N*-methyl-2-pyrrolidone, 2-pyrrolidone, *N*-vinyl-2-pyrrolidone, polyvinylpyrrolidone, herbicides, and rubber additives.

γ -Butyrolactone is produced worldwide mostly in two processes. The first is the hydrogenation of diethyl or dimethyl maleate (Davy McKee process) and the second is the dehydrogenation of 1,4-butanediol [2,3]. The Davy McKee process includes two reactions, the esterification in

the presence of ion exchange resin and the hydrogenation in the presence of Cu–Cr catalyst. The majority of γ -butyrolactone is currently produced by the dehydrogenation of 1,4-butanediol which is produced by the classical Reppe process using explosive acetylene and possibly cancerogenic formaldehyde as feedstocks. These disadvantages of the already established processes led to intensive searches for alternative synthesis routes over last decades. The directly selective hydrogenation of maleic anhydride to γ -butyrolactone should be an eco-friendly and economical alternative to the already established processes because maleic anhydride is now produced by selective oxidation of *n*-butane or benzene in a large scale and at a low price.

Many researches aiming at the hydrogenation of maleic anhydride to γ -butyrolactone have been well carried out by using noble metals [2–8] and copper-based catalysts in gas phase [9–12], in liquid phase [3–5,7,8,13], and in supercritical CO₂ medium [6]. Noble metals catalysts, such as PdRe/C, Pd/C, and Ru/C, have been found more active than

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copper-based catalysts [4]. It is also reported that Pd–Sn/SiO₂ is active and selective in the hydrogenation of maleic anhydride to γ -butyrolactone [3,5]. But the cost of the noble metal catalysts is higher than that of the copper-based catalysts.

It is reported that Cu–Cr (copper chromite) and Cu–Mg₂SiO₄ catalysts favor the formation of succinic anhydride and γ -butyrolactone in hydrogenation of maleic anhydride [13] and that the presence of ZnO in Cu–Zn–Cr catalysts promotes the formation of γ -butyrolactone, accompanied with the formation of 1,4-butanediol, tetrahydrofuran, and *n*-butanol [4,9,13]. The activity of Cu–Zn–Cr catalysts for the hydrogenation of maleic anhydride is comparable with that of noble metal catalysts [4]. Unfortunately, Cr-containing catalysts are of environmental problems because of the toxic nature of the spent catalysts, related to the chromium content. Replacement of Cr-containing catalysts by eco-friendly ones has been paid a great effort recently. For example, Cu–Zn–Al catalyst exhibits better performance in conversion of maleic anhydride to γ -butyrolactone than Cu–Zn–Cr catalyst does [10]. But the γ -butyrolactone selectivity is not very high in heterogeneously catalytic hydrogenation of maleic anhydride due to the formation of many by-products, such as *n*-butanol, butyric acid, and tetrahydrofuran caused by the hydrogenolysis and the over-hydrogenation reactions [2,9–11,13].

It is well known that TiO₂ is a widely used material as a catalyst support or as a catalyst itself. Lu et al. [12] recently reported that TiO₂ modified γ -Al₂O₃-supported Cu catalyst showed higher selectivity for γ -butyrolactone in the gas phase hydrogenation of maleic anhydride. Therefore, it is reasonable to predict that TiO₂ as an alternative to Cr or Al present in copper-based catalyst should have a positive impact on the selective hydrogenation of maleic anhydride. In the present work, the investigation of maleic anhydride hydrogenation catalyzed by Cu–Zn–Ti catalysts was carried out. A major objective of this work was to gain an insight into the catalytic activity of Cu–Zn–Ti catalysts in the hydrogenation of maleic anhydride to γ -butyrolactone.

2. Experimental

2.1. Catalyst preparation

All Cu–Zn–Ti catalysts were prepared by a continuous coprecipitation method. A mixed solution of Cu(NO₃)₂·3H₂O, Zn(NO₃)₂·6H₂O, and TiCl₄ salts with a given atomic ratio was used as a precursor solution and a Na₂CO₃ solution (1 M) was added as a precipitating agent. Coprecipitation was performed at 75 °C and the flow rates of the two solutions were adjusted to give a constant pH of ca. 8.5. The resultant precipitates were washed with distilled water until the conductivity of the filtrate was less than 2 mS/m, dried at 120 °C for 12 h, and then calcined at 350 °C for 2 h. The calcined catalysts were pressed at 24.5 MPa to form pellets and crushed to form small-sized particles with particle sizes ranging from 0.4 to 0.8 mm for characterization by XRD,

Table 1

The compositions, specific surface areas, and average pore diameters of the calcined Cu–Zn–Ti catalysts

Samples	Atomic ratios			Specific surface areas m ² /g	Average pore diameters nm
	Cu	Zn	Ti		
C1	1	2	0.5	139.51	3.83
C2	1	2	1	172.87	3.83
C3	1	2	1.5	182.05	3.81
C4	1	2	2	210.6	3.83
C5	2	2	0.5	135.50	3.44
C6	2	2	1	148.86	3.40
C7	2	2	1.5	186.04	3.42
C8	2	2	2	186.32	3.41
C9	1	0	2	184.62	3.41

XPS, TPR, and catalytic test. For XRD and XPS characterization of the H₂-reduced Cu–Zn–Ti catalysts, the calcined Cu–Zn–Ti catalysts were reduced under the same reduction procedures as those described in the catalytic test. The reduced Cu–Zn–Ti catalysts were cooled to ambient temperature in a N₂ stream and sealed in plastic bags before XRD and XPS characterization. The compositions of the as prepared Cu–Zn–Ti catalysts according to those in their precursors are listed in Table 1.

2.2. Characterization

X-ray diffraction (XRD) was used to examine the bulk structures of the calcined and reduced catalysts. The XRD data were recorded by a Rigaku D/Max-III B diffractometer (Japan) with Ni filter and Cu K α radiation, scanning from 20° to 80°.

X-ray photoelectron spectroscopies (XPS) of the calcined and reduced catalysts were recorded on a PHI-5300 ESCA spectrometer (Perkin Elmer, USA) using Mg K α radiation (35.75 eV). The binding energies were calculated with respect to C 1s peak at 285 eV with a precision of ± 0.2 eV.

The reduction behaviors of the calcined catalysts were investigated by temperature programmed reduction (TPR) technique using a mixed H₂/N₂ flow (10:90 v/v) of 50 ml/min and 20 mg of the calcined catalyst at a temperature ramp of 10 °C/min from 25 to 400 °C. H₂ consumption was determined by analyzing the effluent gas with a thermal conductivity detector. The calcined samples were preheated in air at 400 °C before the TPR measurement in order to eliminate impurities and adsorbed water.

The specific surface areas and the average pore sizes of the calcined catalysts were measured on a NOVA 2000e physical adsorption apparatus by BET and BJH methods, respectively, and the results are listed in Table 1.

2.3. Catalytic test

The catalytic test was carried out in a stainless steel tubular fixed-bed reactor with diameter and length of 8 and 200 mm, respectively, packed with 5 ml of catalyst with par-

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