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Bimetallic Pt–Sn/γ-alumina catalyst for highly selective liquid phase hydrogenation of diethyl succinate to γ-butyrolactone

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Abstract

Platinum–tin bimetallic catalyst on γ-alumina support was prepared by impregnation method and was reduced by sodium borohydride at room temperature. XRD and XPS characterization revealed that platinum was reduced to Pt^0 while, tin was probably partially reduced to Sn^{2+} due to the low temperature reduction method and Sn^0 was completely absent, avoiding the formation of Pt–Sn alloy. Pt–Sn/γ-alumina (Pt 1%, Sn 9%) thus prepared was found to give almost complete selectivity to γ-butyrolactone in liquid phase hydrogenation of diethyl succinate. A plausible reaction pathway is proposed involving Pt–O–Sn state and high selectivity to GBL is due to the Lewis acidity of $Sn^{2+/4+}$.

Keywords: Bimetallic Pt–Sn catalyst; Liquid phase hydrogenation of diethyl maleate; γ-Butyrolactone selectivity; XPS of Pt–Sn; XRD of Pt–Sn

1. Introduction

The hydrogenation of esters of C_3–C_6 dicarboxylic acids is an industrially important route in the manufacture of fine and medium volume commodity chemicals [1–4]. The diols are formed as the major products along with other intermmediate products such as monohydroxy acids, lactones and cyclic ethers in the catalytic hydrogenation of dicarboxylic acids/esters. These hydrogenations are generally carried out at high temperature (>230 °C) and pressure (3–8 MPa) conditions and use of non-specific catalysts leads to excessive hydrogenation of ethers/diols giving undesired products such as alcohols and hydrocarbons [5,6]. Hydrogenation of diethyl succinate is one such example for the production of γ-butyrolactone, 1,4-butanediol and tetrahydrofuran as main products alongwith undesirable side products such as *n*-butanol, propanol and methane. Among these products, γ-butyrolactone (GBL) is in great demand (approx. 120,000 tons by 2005) due to its major use for the production of *N*-methylpyrrolidone. Both gas as well as liquid phase hydrogenation of maleic, succinic acids and their dialkyl esters have been reported in the literature mainly using copper based catalysts [7–10]. γ-Butyrolactone (GBL) is commercially produced via the dehydrogenation of 1,4-butanediol starting either from acetylene (Reppe process) or diethyl maleate. Selective hydrogenation of diethyl maleate would be the direct method for the production of GBL and also more environmentally safe as compared to the conventional Reppe process. It was shown that copper catalysts with zinc oxide promoter could enhance GBL selectivity in vapor phase hydrogenation of diethyl succinate[11]. Liquid phase hydrogenation of dialkyl maleate/succinate has also been investigated using noble metal catalysts such as Pd, Re or Ru with formation of a mixture of GBL, THF and BDO alongwith other side products [12,13]. In case of liquid phase hydrogenation, higher selectivities to GBL have been claimed by using various bimetallic catalysts such as Pd–Re, Ni–Co as well as Pt–Sn [14–16]. Generally, the reduction of metal precursors in Pt–Sn catalyst described in the literature is by hydrogen under high temperature which has usually led to Pt–Sn alloy formation [17–19]. In our work, among the various noble metals along with tin on

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various supports screened, Pt–Sn/Al_2O_3 (Pt 1%, Sn 9%) was found to be highly selective for the hydrogenation of diethyl succinate to GBL. We therefore undertook a detailed work on characterization of the Pt–Sn bimetallic system before and after use for identifying the various surface species and type of bimetallic state formed and their role for enhancing the selectivity to GBL. Based on these data, a plausible reaction pathway for the formation of GBL is also proposed in this paper.

2. Experimental

2.1. Catalyst preparation

The bimetallic Pt–Sn catalysts on different supports were prepared by wet impregnation method. 1% Pt–Sn (Pt:Sn, 1:10) on γ-alumina catalyst was prepared by stirring the aqueous solution of 0.1858 g of $PtCl_2$ with 10 g of activated alumina for 16 h at room temperature. Then the slurry was dried in a rotavap to get a solid impregnated with $PtCl_2$. Aqueous solution of 0.94 g of $SnCl_4 \cdot 2H_2O$ was contacted with platinum salt loaded alumina under stirring again for 16 h. During this impregnation procedure, pH of the slurry was maintained at nine using aqueous 2 N NaOH for fixing the metal chlorides. The reduction of platinum chloride was carried out using six times molar (Pt + Sn) excess of 10% aqueous sodium borohydride solution drop wise to the aqueous slurry of the impregnated support. The reduced catalyst was then filtered, washed several times with water followed by ethanol and finally dried in an oven at 413 K for 5 h. Following this procedure various catalysts were prepared using silica gel, Kieselguhr supports and Ru, Pt and Pd metals. In case of platinum on alumina catalyst, Pt:Sn ratio was varied from 1:5 to 1:20.

2.2. Activity testing

The various bimetallic catalysts prepared were tested for their activity and selectivity for the hydrogenation of diethyl succinate in a high pressure, high temperature 250 ml Parr autoclave, provided with automatic temperature control, safety rupture disc and liquid sampling facility. The progress of the reaction was monitored by measuring the drop in hydrogen pressure in the gas reservoir as a function of time and also by intermediate liquid sampling. The liquid samples were analysed by gas chromatography (HP 5840) using a 10% OV–17 on chromosorb SS column.

2.3. Catalyst characterization

The catalyst samples were characterized before and after the hydrogenation reaction. XRD patterns were recorded on Phillips (Model 1730) and Ni-filtered Cu Kα (0.1530 nm) radiation with proportional counter detector at a scan rate of 2°/min. The XPS analysis was carried out on a VG Microtech ESCA 3000 instrument using Mg Kα radiation (photoenergy 1253.6 eV) at a constant energy of 50 eV. The binding energy values were charge-corrected to the C_{1s} signal (284.9 eV). JEOL JSM 200 instrument was used for SEM analysis.

3. Results and discussion

Bimetallic catalysts with various noble metals (Ru, Pt and Pd) and tin supported on γ-alumina were evaluated for the hydrogenation of diethyl succinate and the results are shown in Table 1. The specific activity (expressed as moles of substrate converted per g of catalyst per h) for Ru was highest however, the selectivity to GBL was highest (98%) for the platinum–tin system. In case of Ru and Pd catalysts (Table 1), the other major product formed was 1,4-butanediol (BDO). For ruthenium containing bimetallic catalysts, highest activities have been reported and major products formed were 1,4-butanediol (BDO) and tetrahydrofuran (THF) indicating further hydrogenation of GBL takes place over Ru catalysts [16,20]. Over hydrogenation of GBL to BDO has also been reported for homogeneous ruthenium complex catalyzed hydrogenation of succinic anhydride that is attributed to the catalyst itself [21]. Since, Pt–Sn (1:10) on alumina was found to give highest (>98%) selectivity to GBL, its detailed characterization before and after use was carried out to further understand the influence of the structural properties of platinum–tin/alumina catalyst on its activity and selectivity pattern.

The low intensity XRD patterns of Pt–Sn catalyst before and after use shown in Fig. 1 indicate the very high dispersion of the metal particles in the prepared samples. The peaks at $2\theta = 39.3°$ and 45.5° in the fresh sample (Fig. 1A) correspond to Pt^0 (111 and 200 respectively) while there was no peak attributable to PtO_2 indicating the complete reduction of platinum precursor to Pt^0. Both the peaks at $2\theta = 39.3°$ and 45.5° (Fig. 1B) are retained in the catalyst sample after hydrogenation reaction which indicates the stability of Pt^0 state. The broadness of the Pt^0 peaks suggest very small size of Pt crystallites and that Pt component was well dispersed over the alumina support. The peak at 26.6° in the fresh sample (Fig. 1A) is attributed to SnO_2 which disappeared in the used catalyst sample (Fig. 1B) probably due to the reduction to SnO under

Table 1
Screening of alumina supported catalysts for DES hydrogenation

Catalyst	Specific activity, mol g^{-1} h^{-1}, $\times 10^3$	Conversion (DES) %	Selectivity %	
			GBL	Others[a]
Ru–Sn	13.3	17	40	59.2
Pt–Sn	2.8	17.4	98	2
Pd–Sn	3.0	23	5.5	93.5

Reaction conditions: temperature, 513 K; H_2 pressure, 13.78 MPa. Catalyst loading, 10% (w/w); DES concentration. 10% by mol; metal:Sn, 1:10.

[a] Side products include succinic acid, monoethyl succinate, γ-hydroxybutyraldehyde and were detected by GC/HPLC.