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Hydrogenation of methyl propionate over Ru–Pt/AlOOH catalyst: Effect of surface hydroxyl groups on support and solvent

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ABSTRACT

A ruthenium–platinum bimetallic catalyst supported on boehmite was prepared by co-impregnation and hydrothermal reduction and characterized by XRD, TEM and TG–DTG. Reduction time of the catalyst affected the conversion of γ-Al_2O_3 to boehmite and the specific surface area of the catalyst, and consequently influenced the catalytic performance of the catalyst. Under the same conditions, the Ru–Pt/AlOOH catalyst showed much higher activity and selectivity than the Ru–Pt/γ-Al_2O_3 in aqueous hydrogenation of methyl propionate. The selectivity to 1-propanol of 97.8% could be obtained at methyl propionate conversion of 89.1% over Ru–Pt/AlOOH at 453 K under 5 MPa of H_2 for 6 h. It is postulated that the high performance of this novel catalyst is related to the cooperation of the hydroxyl groups of support surface and water solvent.

1. Introduction

Hydrogenation of carboxylic acids or their esters to corresponding alcohols is an industrially important process [1]. Usually, heterogeneous hydrogenation of esters carried out over copper-containing, mixed-oxide catalysts under a high hydrogen pressure (20–30 MPa) and reaction temperature (473–573 K) [2,3]. Therefore, many attempts have been made to develop some highly efficient catalyst systems. Several homogenous catalytic systems have been used for ester hydrogenation, which allow more moderate reaction temperature and hydrogen pressure [4–6]. However, large amounts of additives, such as an organic base [4], inorganic acid [4], salt [5], and zinc [6] are needed in these systems to obtain high yield of alcohols. For example, the hydrogenation of methyl propionate to 1-propanol in a system of $Ru(acac)_3$ (acac = acetylacetonate) with $CH_3C(CH_2PPh_2)_3$ as a ligand could be carried out at 192 °C under hydrogen pressure of 1000 psig for 15 h [7]. Another possibility is the application of bimetallic catalysts. For example, Louessard et al. [8] firstly reported that Ru–Sn/SiO_2 was effective for the hydrogenation of ethyl acetate to ethanol. Later on, the hydrogenation of fatty esters to fatty alcohols catalyzed by Ru–Sn–B was investigated in detail [9,10]. Tahara et al. [1,11] also found that the Sn precursor can affect the hydrogenation of CHDC (1,4-cyclohexanedicarboxylic acid dimethyl ester) to CHDM (1,4-cyclohexanedimethanol). In recent years, Fraga et al. [12–14] have intensively studied the hydrogenation of dimethyl adipate and found that only the Ru–Sn catalysts exhibited appreciable selectivity towards diol. Fan et al. [15,16] also reported the promoting role of Sn to Ru catalyst for the hydrogenation of ethyl lactate to 1,2-propanediol.

In most of the previous studies, traditional carriers such as TiO_2, γ-Al_2O_3, SiO_2, ZrO_2, and active carbon were often used. In addition, all of the hydrogenation of esters was performed in organic solvents. In the present work, boehmite supported Ru–Pt catalyst Ru–Pt/AlOOH is firstly used for the ester hydrogenation. Especially, the reaction is carried out in water solvent to give a good conversion and selectivity for the hydrogenation of methyl propionate. It is found originally that the cooperation between the surface hydroxyl groups on boehmite and water solvent played an important role in the hydrogenation of methyl propionate. It improved not only the catalyst activity but also the selectivity to 1-propanol.

2. Experimental

2.1. Catalyst preparation

All of the chemicals (A.R.) were commercially obtained and were used as received. γ-Al_2O_3 was calcined at 500 °C for 4 h prior to use. The purity of hydrogen was 99.99%. The bimetallic catalyst Ru–Pt/AlOOH with a metal content of 6.3 wt.% was prepared by co-impregnation, hydrothermal reduction method. Typically, 1.0 g of γ-Al_2O_3 was dispersed in 30 ml alcohol solution containing $RuCl_3 \cdot x$-H_2O (51.8 mg of Ru) and $H_2PtCl_6 \cdot 6H_2O$ (11.2 mg of Pt) (Kunming

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Institute of Precious Metals, China). The mixture was stirred overnight at room temperature. Next, the solvent was slowly removed under vacuum. The resulted solid was dried overnight at 120 °C and calcined at 400 °C in air for 4 h. Thereafter, the calcined catalyst Ru–Pt/γ-Al_2O_3 was reduced in water with hydrogen of 3 MPa at 180 °C for 2 h, and then filtered and dried in vacuum for 10 h to give catalyst Ru–Pt/AlOOH.

2.2. Catalyst characterization

XRD studies were performed on a Rigaku D/max-rA instrument with a Cu Kα radiation (λ = 0.1542 nm) and in the scan range of 10–70°. The X-ray photoelectron spectra (XPS) were recorded with a Kratos XSAM800 spectrometer (Al Kα X-ray radiation (1215 eV), operating at 15 mA and 12 kV). All binding energy values were referenced to the C1s peak of contaminant carbon at 284.6 eV. Transmission electron microscopy (TEM) images and selected area electron diffraction (SAED) were obtained in JEM-1200EX at 100 kV. The TG and DTG curves were determined by using 10 mg of sample at a heating rate of 10 °C/min (SDT Q600) to elucidate the dehydration behavior of the catalyst. The characterization of the porous structure of supports was carried out on a Micromeritics ASAP 2010 apparatus and by physical adsorption of N_2 at −196 °C. Before the measurement, the samples were preheated at 150 °C for 2 h in vacuum. The specific surface area (S_{BET}) was calculated by BET method in the relative pressure (P/P_0) range from 0.05 to 0.3.

2.3. Catalytic test

Catalytic hydrogenation of methyl propionate was carried out in a 60 ml stainless autoclave equipped with a magnetic stirrer and an electric temperature controller. In a typical experiment, the catalyst (73 mg), methyl propionate (0.2 ml), and solvent (3 ml) were added to the autoclave. It was purged with H_2 for three times, pressurized with H_2 to the designed pressure, and then heated to the desired temperature. The stirring rate was set a constant of 1000 rpm. Methyl propionate conversion and product selectivity were determined by GC-6890 (Agilent) with FID detector and quartz capillary column (SE-30, 30 m × 0.25 mm). Reactants and products were identified by comparison with the standard samples and GC–MS.

3. Results and discussion

3.1. Catalyst characterization

The results of XPS are shown in Table 1. Both the fresh (reduced in water for 2 h) and used Ru–Pt/AlOOH catalysts exhibit the Ru $3d_{5/2}$ peak at 280.1 eV, which is assigned to Ru^0 [17]. The signal at 71.0 eV (Pt $4f_{7/2}$) in XPS spectra of Pt 4f is attributed to Pt^0, but it is only detected in the used catalyst. While the peak at 72.5 eV (Pt $4f_{7/2}$), which can be ascribed to an electron deficient Pt^{n+} ($0 < n < 2$) species [18], is observed in the fresh as well as the used catalyst. These results indicate that Pt is not completely reduced to zero valence in water with H_2 at 180 °C even after the hydrogenation.

Fig. 1a is the XRD pattern of Ru–Pt catalyst reduced in ethanol for 2 h. The peaks at 2θ = 19.6°, 37.6°, 45.8° and 66.8° can be attributed to γ-Al_2O_3 (γ-Al_2O_3, JCPDS Card No. 29-63). It indicates that γ-Al_2O_3 does not convert into AlOOH. Fig. 1b–f show XRD profiles of Ru–Pt catalysts reduced in water for different times and after hydrogenation. The peaks at 2θ = 14.4°, 28.1°, 38.3°, 48.9°, 54.9°, and 64.2° in these XRD patterns, which become sharper and stronger with the extension of reduction time, are assigned to boehmite (AlOOH, JCPDS Card No. 21-1307). Except a peak at 2θ = 44.0°, all the peaks appearing in the XRD pattern of the used catalyst (Fig. 1f) can be attributed to boehmite. These results indicate that γ-Al_2O_3 has transformed into AlOOH with a good crystallization state under the hydrothermal reduction conditions. With the extension of reduction time, a broad and diffuse peak at 2θ = 44.0°, which is assigned to Ru^0 (JCPDS Card No. 6-0663), starts to appear and its intension also increases. It suggests that Ru^0 species starts to be formed and its particles grow up with the extension of the reduction time, but the size of Ru crystallite is very small and Ru is well dispersed over the support. In any cases, no peaks corresponding to Pt^0 or Pt^{n+} species can be detected due to low Pt loading or high dispersion.

The TG and DTG curves of the Ru–Pt catalyst (reduced in water for 2 h) are shown in Fig. 2. The thermal analysis of the Ru–Pt catalyst shows three decomposition steps. The first step, with a mass loss of 2% at around 60 °C, is attributed to desorption of physically adsorbed water. The weak DTG step at about 330 °C is responsible for the decomposition of bayerite to η-Al_2O_3 [19,20], which suggests existence of a small amount of bayerite. The last step at about 490 °C, with a mass loss of 11.4% in DTG curve, is consistent with the theoretical value for conversion of AlOOH to Al_2O_3 [21,22] and corresponds the removal of hydroxyl bridges among layer structure of boehmite.

The TEM images of the Ru–Pt catalysts reduced in water for 2 h (a) and after hydrogenation (b) show the nanoflakes of boehmite with the width of tens of nanometers and a few nanofibers of γ-Al_2O_3 in Fig. 3, which is in accordance with the XRD pattern in Fig. 1. The SAED pattern in Fig. 3, exhibiting symmetrically scattered spots, shows the good crystallization of the boehmite [23]. In addition, metal particles around 2–3 nm are homogeneously dispersed on the surface of boehmite.

Table 1
XPS Analysis of the fresh and used Ru–Pt/AlOOH catalysts.

Catalyst	Ru $3d_{5/2}$	Pt $4f_{7/2}$	
	Ru^0 (%)	Pt^0 (%)	Pt^{n+} (%)[c]
A[a]	100	–	100
B[b]	100	45.4	54.6
BE (eV)	280.1	71.0	72.5

[a] Fresh catalyst (reduced in water for 2 h).
[b] Catalyst after hydrogenation in water for 6 h.
[c] $0 < n < 2$.

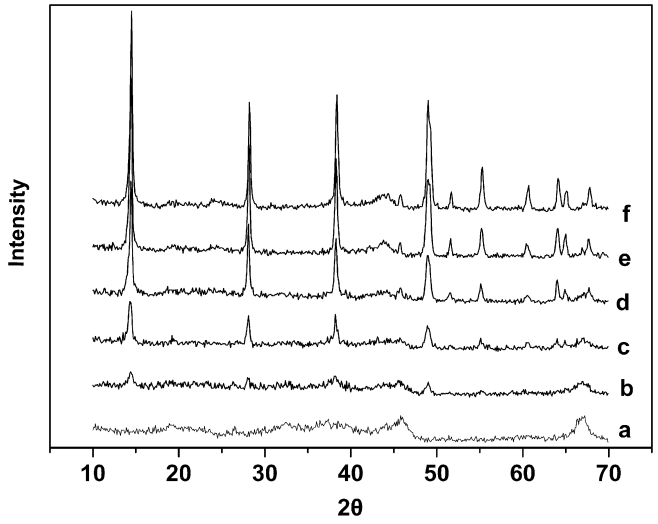

Fig. 1. XRD patterns of Ru–Pt catalyst reduced in ethanol for 2 h (a) and in water for: 1 h (b); 2 h (c); 3 h (d); 5 h (e) and (f) after hydrogenation in water for 6 h.