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A comparative study on Pt/CeO_2 and Pt/ZrO_2 catalysts for crotonaldehyde hydrogenation

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ABSTRACT

Vapor-phase hydrogenation of crotonaldehyde was carried out over Pt/CeO_2 and Pt/ZrO_2 catalysts. It was found that both catalysts suffered deactivation, with the conversion of crotonaldehyde decreasing from 31 to 6% over the Pt/CeO_2 catalyst and 20 to 7% over the Pt/ZrO_2 catalyst, which was due to the formation of organic compounds on the catalyst surface as revealed by temperature programmed oxidation technique on the spent catalysts, and the poisoning effect of CO chemisorptions on Pt atoms via decarbonylation reaction. For the Pt/ZrO_2 catalyst, selectivity to crotyl alcohol reached 48% and kept stable during the reaction, while for the Pt/CeO_2 catalyst, the selectivity to crotyl alcohol decreased dramatically from 51 to 33%. The decrease of selectivity for the Pt/CeO_2 catalyst was attributed to carbon deposit formed on the catalyst surface by the reaction between CO and reduced Ce^{3+} ion in CeO_2. However, for the Pt/ZrO_2, no carbon deposit was formed on the catalyst surface, which could account for the stable selectivity during the reaction process.

1. Introduction

Selective hydrogenation of α-, β-unsaturated aldehyde to α-, β-unsaturated alcohol is an important reaction in industrial production, because α-, β-unsaturated alcohols are vital intermediates in pharmaceutical, fragrance and fine chemicals [1–4]. As a typical type of α-, β-unsaturated aldehydes, crotonaldehyde ($CH_3{-}CH{=}CH{-}CHO$) is often used in model reaction of selective hydrogenation. Containing the conjugated C=O bond and C=C bond, the selective hydrogenation of crotonaldehyde usually produces three major products, namely, the partial hydrogenation as crotyl alcohol (C=O bond) and butanal (C=C bond), and the deep hydrogenation as butanol (C=C and C=O bond). Generally, hydrogenation of the C=C bond is much easier than that of the C=O bond in respect of thermodynamic and kinetic factors, so it is difficult for selective hydrogenation of the carbonyl bond while keeping the C=C double bond intact in the hydrogenation of crotonaldehyde.

Supported Pt [5–7] catalysts have been frequently used in the selective hydrogenation of crotonaldehyde to crotyl alcohol in recent years. The catalytic activity of Pt/SnO_2 catalyst deactivated quickly in the hydrogenation of crotonaldehyde, while an increasing selectivity to crotyl alcohol was observed due to the formation of PtSn alloys [8]. A Pt/ZnO catalyst also gave a rapid deactivation during the hydrogenation progress, but its selectivity to crotyl alcohol could reach a value as high as 75–80% because of the alloying and chlorine effect [9]. In our recent work, it was suggested that Lewis acidic sites generated by chlorine species may be the key factor to the high crotyl alcohol selectivity [10]. For the Pt/Cr/ZnO catalyst, a high crotyl alcohol selectivity of 80% could be obtained and maintained during the hydrogenation reaction, due to the change of electronic structure of the active Pt metal [11]. For $Pt/ZnCl_2/SiO_2$ catalyst, the selectivity to crotyl alcohol was above 68%, but the catalytic activity did not change significantly with the change of reduction temperature [12].

It can be summarized from the above findings that the catalytic behaviors of the Pt catalysts are quite different during the reaction. For example, some supported Pt catalysts can give steady activity and selectivity, while some catalysts suffer severe deactivation and loss of selectivity. To better understand the causes of catalyst deactivation and the factors governing the selectivity, we designed two supported Pt catalysts, Pt/CeO_2 and Pt/ZrO_2, and applied them to the gas phase selective hydrogenation of crotonaldehyde. The different catalytic behaviors of these two catalysts relating to the catalyst property were compared and discussed.

2. Experimental

2.1. Catalyst preparation

CeO_2 and ZrO_2 supports were obtained by thermal decomposition of $Ce(NO_3)_3{\cdot}6H_2O$ and $Zr(NO_3)_4{\cdot}5H_2O$ in air at 400 °C for 4 h, with a specific surface area of 66 m^2/g and 73 m^2/g,

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respectively. Both the Pt/CeO_2 and Pt/ZrO_2 catalysts were prepared by an impregnation method. The support was impregnated with H_2PtCl_6 aqueous solution with a nominal Pt content of 3 wt%. Excess water solution was removed by a mild evaporation. Finally, the resulting solid was dried overnight at 120 °C, and was denoted as Pt/CeO_2 and Pt/ZrO_2 catalysts.

2.2. Catalyst characterizations

The specific surface areas of catalysts were determined by nitrogen adsorption at −196 °C on a Quantachrome Autosorb-1 apparatus. X-ray diffraction (XRD) patterns were recorded using a PANalytic X'Pert PW3040 diffractiometer with Cu K_α radiation operating at 40 kV and 40 mA. The patterns were collected in a 2θ range from 20° to 110°, with a scanning step of $0.15^\circ\ s^{-1}$. Particle sizes of Pt in the Pt/CeO_2 and Pt/ZrO_2 catalysts were measured by CO chemisorption on a Chembet 3000 instrument. The sample was reduced in a H_2—N_2 mixture gas (5 vol% H_2, 30 ml/min) at 500 °C for 1 h and cooled down to 30 °C under pure He flow (30 ml/min), then pulse of CO was injected. Pt dispersion was evaluated from the consumption of CO, assuming that CO: Pt = 1. The Pt particle size was estimated using the cubic Pt particle model with the calculated Pt metal dispersion. The reduction properties of the samples were measured by hydrogen temperature-programmed reduction (H_2-TPR) experiments. The sample was placed in a quartz reactor, and then heated from room temperature to 550 °C at a rate of 10 °C/min in a H_2—N_2 gas (5 vol% H_2; 30 ml/min). The hydrogen consumption during the reduction was determined by a gas chromatograph with a thermal conductivity detector. Raman spectra were obtained on a Renishaw RM1000 confocal microscope with exciting wavelength of 514.5 nm and scanning range of 200–2000 cm^{-1} under an ambient condition. In order to study the carbon deposit, in situ Raman spectroscopy of CO adsorption was carried in a Renishaw RM1000 confocal microscope with an excitation wavelength of 514.5 nm and a scanning range of 200–2000 cm^{-1}. The sample was reduced in a H_2—N_2 mixture (5 vol% H_2, 30 ml/min) stream at 500 °C for 1 h and cooled down to 25 °C in a He flow (30 ml/min). Then the sample was exposed CO—N_2 (1 vol% CO) 30 min at 50 °C. For the temperature-programmed oxidation (TPO) study, 50 mg of the used catalyst was placed in the middle of a quartz microreactor with a inner diameter of 6 mm. The outlet was analyzed on-line by mass spectrometry (Qic-20 Benchtop, Hiden Analytical). Then the sample was subsequently flushed by O_2 (20 ml/min) from room temperature to 600 °C at a rate of 10 °C/min. The mass numbers of 44 and 18 were selected to monitor the desorption of CO_2 and H_2O fragments, respectively.

2.3. Catalytic test

The gas phase crotonaldehyde hydrogenation was performed in a fixed bed reaction system at atmospheric pressure, using a quartz tube (8 mm i.d.) reactor. 100 mg of catalyst was loaded in the reactor with a thermal couple placed in the middle of the catalyst bed to monitor the reaction temperature. Before running the catalytic test, the catalyst was reduced at 500 °C for 1 h in ultrapure H_2 (20 ml/min) and then it was cooled down to 50 °C. The crotonaldehyde was introduced in a trap set before the reactor tube and maintained at 0 °C to achieve a constant crotonaldehyde partial pressure (1.06 kPa), therefore, aldehyde at constant partial pressure was carried over the catalyst by hydrogen flow (26 ml/min). The gas line was kept at about 50 °C to avoid any condensation. The reaction products and reactant were analyzed on line using a gas chromatography (Shimazu GC-2014) equipped with a flame ionization detector (FID) and a DB-Wax capillary column (30 m × 0.25 mm × 0.25 μm).

Table 1
Physical properties of Pt/CeO_2 and Pt/ZrO_2 catalysts.

Catalyst[a]	Pt content (wt%)	Particle size (nm)[a]	Surface area (m^2/g)
Pt/CeO_2	2.90	4.4	58
Pt/ZrO_2	2.84	3.1	62

[a] Sample reduced at 500 °C.
[b]Determined by CO adsorption.

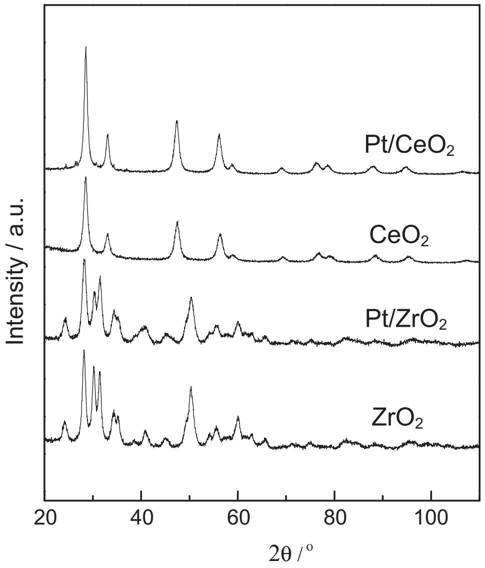

Fig. 1. XRD patterns of Pt/CeO_2 and Pt/ZrO_2 catalysts reduced at 500 °C.

3. Results and discussion

3.1. Physical properties of catalysts

Table 1 lists the physical properties of the Pt/CeO_2 and Pt/ZrO_2 catalysts reduced at 500 °C. The actual Pt contents in the Pt/CeO_2 and Pt/ZrO_2 catalysts are 2.90 and 2.84 wt%, respectively, which are close to the nominal values. By CO chemisorption measurement, the Pt particle sizes in the Pt/CeO_2 and Pt/ZrO_2 are 4.4 and 3.1 nm, respectively. The specific surface areas of the Pt/ZrO_2 and Pt/CeO_2 catalysts are 62 and 58 m^2/g, respectively. Fig. 1 shows the XRD patterns of Pt/CeO_2 and Pt/ZrO_2 catalysts reduced at 500 °C. For both catalysts, only diffraction peaks of the support (CeO_2 and ZrO_2) are observed. Diffraction peaks of PtO_2 or Pt are not detected, which indicates that the Pt species are highly dispersed on the catalyst surface.

Fig. 2 shows the H_2-TPR profiles of Pt/ZrO_2 and Pt/CeO_2 catalysts and their corresponding supports. The ZrO_2 support shows no reduction peak up to 550 °C [13], while the pure CeO_2 shows one reduction peak at around 470 °C, which can be assigned to the reduction of surface ceria [14]. As for the supported catalysts, a reduction peak at 200 °C is observed for the Pt/ZrO_2 catalyst, and two reduction peaks appear at 180 (α) and 410 °C (β) for the Pt/CeO_2 catalyst.

Assuming that the initial Pt oxidation state in the catalysts is Pt^{4+} (PtO_2), the nominal hydrogen consumptions of the Pt/ZrO_2 and Pt/CeO_2 catalysts are 291.2 and 297.3 $\mu mol_{H2}\ g_{cat}{}^{-1}$, respectively. According to the TPR profiles in Fig. 2, the actual hydrogenation consumptions (α peak) calibrated by the known amount of CuO powder for the Pt/ZrO_2 and Pt/CeO_2 catalysts are 288.8 and 608.0 $\mu mol_{H2}\ g_{cat}{}^{-1}$, respectively. For the Pt/ZrO_2 catalyst, it can be seen that the nominal hydrogen consumption is very close to the actual consumption, suggesting that the reduction peak at 200 °C