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Promoting effect of Ir on the catalytic property of Ru/ZnO catalysts for selective hydrogenation of crotonaldehyde

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ABSTRACT

A series of ZnO supported Ru–Ir bimetal catalysts were prepared and tested for vapor-phase selective hydrogenation of crotonaldehyde. The addition of Ir could effectively promote the catalytic performance, especially the catalyst stability. A Ru–0.5Ir/ZnO catalyst showed the highest activity (a conversion of 63.3%) and selectivity to crotyl alcohol (94.4%) after 30 h reaction. The enhanced stability was attributed to the modified electronic property of Ru by the formation of RuIr alloy as the X-ray photoelectron spectroscopy results showed charge transfer from Ru to Ir, as well as the weakened surface acidity in the Ru–Ir/ZnO catalyst as evidenced by NH_3 temperature-programmed desorption technique. Besides, the deactivation of the catalysts was due to the strong chemisorption of CO on the metal surface via decarbonylation reaction and deposition of organic compounds on the catalyst surface, which was characterized by CO poisoning experiment, CO temperature-programmed desorption and temperature-programmed oxidation methods.

1. Introduction

The preferred hydrogenation of C=O group in the presence of a C=C bond in α,β-unsaturated aldehydes is of special interest for the chemical industry because the partially hydrogenated products, are used for the production of fine chemicals, pharmaceuticals, and perfumes [1]. Nowadays, α,β-unsaturated alcohols are mostly produced through α,β-unsaturated aldehydes reduced by the $NaBH_4$ or $AlLiH_4$ in industry [2]. Although this method can get high yield of α,β-unsaturated alcohols, there are some serious drawbacks, namely, not only the reaction conditions are difficult to be controlled, but also a large amount of environment pollutants are generated [3].

The development of catalysts with high activity and high selectivity for these reactions is not only important from an industrial point of view, but also of fundamental scientific interest for catalysis because the thermodynamic and kinetic reasons favor the formation of the non-desired saturated aldehyde [4]. Intensive studies have been made to develop catalyst systems for selective hydrogenation of α,β-unsaturated aldehydes, in which noble metal catalysts are most commonly employed in this reaction. According to reports in the literature, Pt-based catalysts are used mostly for crotonaldehyde hydrogenation [5–7]. For example, 80% selectivity to crotyl alcohol could be obtained on a $Pt/ZnCl_2/SiO_2$ reduced at 400 °C [8]. Au catalysts supported on various oxides [9–12], as well as supported Ir [13–15] and Ru [16,17] catalysts are also applied for the selective hydrogenation of crotonaldehyde. Ramos-Fernández et al. [16] reported that gas phase hydrogenation of crotonaldehyde over a Ru/ZnO catalyst using $RuCl_3$ as the precursor resulted in a catalytic activity of 80 $\mu mol\, g_{Ru}^{-1}\, s^{-1}$ at the initial state and a selectivity to crotyl alcohol of 80%. The catalyst showed better catalytic performance compared to a Ru/ZnO catalyst using Cl-free Ru precursor ($Ru(acac)_3$) and the authors attributed the enhancement to a well controlled metal–support interaction. Also, bimetallic catalysts have been reported to improve the catalytic performance of the catalysts. Metals such as Fe [18], Sn [19–21], or Zn [22] were added to group VIII metal catalysts to inhibit the C=C hydrogenation. This has been explained on the basis of alloy formation, which results in the weakening of the adsorption through the olefinic bond, and the presence of acid Lewis centers (the more electropositive metal atoms on surface) interacting with the oxygen atom of the carbonyl bond and favoring its hydrogenation [23].

Although great efforts have been paid, the main problem of the current catalyst systems employed for selective hydrogenation of crotonaldehyde is rapid deactivation during the reaction. Usually the catalysts for selective hydrogenation of crotonaldehyde suffer severe deactivation. For example, Pt catalysts in the literature lost about 80% of initial activity in 5 h reaction [5,24–26]. Similar deactivation was also observed on Au [11,27] and Ir [13,14] systems. Generally, the catalyst deactivation is due to the strong

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adsorption of reactant/product molecules on the catalyst surface due to the interaction of the molecules with strong surface acid sites [28], and decarbonylation of crotonaldehyde to form CO molecules which could strongly chemisorb on the metal surface and poison the active sites [15].

As mentioned above, well designed catalysts with properly modified surface properties are required in order to improve the catalytic performance, especially the catalyst stability. In this study, a series of ZnO supported Ru–Ir bimetal catalysts were prepared and tested for selective hydrogenation of crotonaldehyde. It was found that the addition of Ir could effectively promote the activity and inhibit the catalyst deactivation to some extent. The promotion was discussed based on the interaction between Ru and Ir, which influences the electronic property and surface acidity of the catalyst. Besides, the deactivation was discussed based on the surface properties of the catalysts.

2. Experimental

2.1. Catalysts preparation

The ZnO support was prepared by a homogeneous precipitation method. In a typical procedure, a 0.2 M aqueous solution of Na_2CO_3 was drop-wise added into a 0.2 M aqueous solution of $Zn(NO_3)_2{\cdot}6H_2O$ at 60 °C in water bath until the precipitation was completed, then the precipitate was filtered and washed with plenty of deionized water, dried at 120 °C for 12 h and then calcined in air at 450 °C for 2 h. The final ZnO powder had a surface area of 11 $m^2\,g^{-1}$.

The Ru–*x*Ir/ZnO catalysts were prepared by impregnating the ZnO support with aqueous solution of $RuCl_3$ and H_2IrCl_6 for 12 h. The nominal content of Ru in the catalyst was 3 wt.%, and the value of *x* was the molar ratio of Ir/Ru (*x* = 0, 0.125, 0.5 and 1). Excess solvent was removed by mild evaporation, and then the samples were dried at 60 °C for 12 h and then calcined at 400 °C for 2 h in air. The obtained precursor solids were denoted as Ru–*x*Ir/ZnO(P). Before characterizations as well as prior to the reaction, the solids were reduced in ultra-pure H_2 (99.995%) at 200 °C for 1 h and the final catalysts were denoted as Ru–*x*Ir/ZnO. A reference Ir/ZnO catalyst with a nominal Ir content of 3 wt.% was synthesized in a similar manner.

2.2. Catalyst characterizations

Elemental compositions of the reduced catalysts were determined by X-ray fluorescence (XRF) analysis on an ARLADVANT'X Intelli Power 4200 scanning X-ray fluorescence spectrometer. The results were analyzed using UniQuant non-standard sample quantitative analysis software.

X-ray diffraction (XRD) patterns were recorded using a PANalytic X'Pert PW3040 diffractiometer with Cu Kα radiation operated at 40 kV and 40 mA. The patterns were collected in a 2θ range from 10° to 75° with a scanning step of 0.014°.

Transmission electron microscopy (TEM) analysis was performed on a JEM-2100F microscopy with a field emissive gun, operated at 200 kV and with a point resolution of 0.24 nm. The reduced samples were suspended in ethanol. The dispersion was then immersed for 10 min in an ultrasonic bath in order to disperse the powder particles. Finally, one drop was placed on a Formvar/carbon copper grid. Various regions of the grid were observed and the particle sizes were measured from the observation of 100 particles.

X-ray photoelectron spectra (XPS) were recorded using a VGESCALAB MK-2 spectrometer with Al Kα radiation (1486.6 eV). The voltage and the power for the measurements were 12.5 kV and 250 W, respectively. The obtained spectra were treated by removing the background and then fitted to Lorentzian and Gaussian lines to obtain the number of components, peak position, and their areas. The adventitious C 1s line at 285.0 eV was used as an internal standard.

The acidic properties of the catalysts were measured by ammonia temperature-programmed desorption (NH_3-TPD) on a home-made apparatus. 50 mg of catalyst was filled in a quartz tubular reactor (i.d. = 6 mm) prior to the measurement, and was in situ reduced in a H_2–Ar mixture (20 ml min^{-1}, 10 vol% H_2) at 200 °C for 1 h. Then it was cooled down to 50 °C. A flow of NH_3 (20 ml min^{-1}) was introduced for 30 min. The gaseous or physisorbed NH_3 was removed by purging Ar flow (30 ml min^{-1}) at 100 °C for 90 min. Then the sample was heated to 700 °C with a ramp of 10 °C min^{-1}. The desorbed NH_3 was monitored continuously via a TCD detector. The total amount of NH_3 desorbed was determined by reaction with an excess of dilute hydrochloric acid and back titration with sodium hydroxide solution. The sensitive indicator contains a mixture of 0.1% brom-cresol green ethanol solution and 0.2% methyl red ethanol solution with a volume ratio of 3:1.

The CO chemisorption properties of the catalysts were measured by CO temperature-programmed desorption (CO-TPD) on a home-made apparatus. 100 mg of catalyst was filled in a quartz tubular reactor (i.d. = 6 mm) prior to the measurement, and was in situ reduced in a H_2–Ar mixture (20 ml min^{-1}, 10 vol% H_2) at 200 °C for 1 h. Then it was cooled down to 30 °C. A flow of CO (30 ml min^{-1}) was introduced for 30 min. Then the sample was heated to 500 °C with a ramp of 10 °C min^{-1}. The desorbed CO was monitored continuously via a TCD detector.

Temperature-programmed oxidation (TPO) measurements were carried out in a quartz fixed-bed reactor with 6 mm inner diameter. 50 mg of the used catalyst was placed in the middle of the reactor, and O_2 gas with a flow rate of 20 ml min^{-1} was fed into the reactor at rising temperature from 30 to 500 °C at a rate of 10 °C min^{-1}. The gas at the outlet was analyzed on-line by mass spectrometry (Qic-20 Benchtop, Hiden Analytical). The mass numbers of 44 and 18 were selected to monitor the desorptions of CO_2 and H_2O, respectively.

Raman spectra were collected on a Renishaw RM1000 confocal microprobe under ambient conditions. The excitation wave length of laser was 514 nm. The power of each laser was kept at about 3 mW to prevent local heating effect and the resolution of the spectrometer was 1 cm^{-1} with the diameter of the analyzed spot being ca. 1 μm.

2.3. Catalytic test

Vapor-phase hydrogenation of crotonaldehyde was performed in a fixed bed quartz tube (8 mm i.d.) reactor at atmospheric pressure. 400 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 the catalytic performance test, the catalyst was reduced at 200 °C for 1 h in ultra-pure H_2 flow (99.999%, 20 ml min^{-1}) and then it was cooled down to 80 °C. Crotonaldehyde in a trap set maintained at 0 °C was introduced to the reactor by hydrogen flow (26 ml min^{-1}) with a constant crotonaldehyde partial pressure (1062 Pa). The reaction products and reactant were analyzed on line using a gas chromatography (Shimadzu GC-2014) equipped with a flame ionization detector (FID) and a DB-Wax column (30 m × 0.25 mm × 0.25 μm) capillary column.

3. Results and discussion

3.1. Composition and phase of Ru–xIr/ZnO catalysts

Table 1 lists surface areas and element contents in the catalysts. It can be seen that the surface areas of the catalysts are