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Study on the deactivation of supported amorphous Ni-B catalyst in hydrogenation

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Abstract

The MgO supported amorphous Ni-B catalyst was synthesized by a modified electroless plating method and its deactivation behavior in the hydrogenation of sulfolene and acetophenone (AP) was studied. The fresh and used catalysts were characterized by inductively coupled plasma atomic emission spectrometry (ICP-AES), X-ray powder diffraction (XRD), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), Fourier transform infrared spectra (FT-IR), and hydrogen chemisorption. Carbon disulfide was used to test the sulfur-poison-resistive property of the supported Ni-B/MgO catalyst. No significant sintering of the active component and crystallization of the amorphous structure was found in the hydrogenation. The deactivation of catalyst was ascribed to the sulfur-poisoning by SO_2 in the hydrogenation of sulfolene and the change of porous structure for Ni-B particles in the acetophenone hydrogenation.

Keywords: Amorphous alloy; Ni-B/MgO catalyst; Deactivation; Hydrogenation

1. Introduction

Amorphous alloy nanoparticles have received increasing attentions as a novel type of catalytic materials since 1980 [1–3]. Because of the unique isotropic structure and high concentration of coordinatively unsaturated sites, the amorphous alloy catalysts show superior catalytic properties to their crystalline counterparts [1–3]. Especially, the amorphous Ni-B alloy catalyst synthesized by chemical reduction method is superior to normal nickel-based catalysts, such as Raney Ni catalyst in activity, selectivity [4–6] and sulfur-poison-resistive properties [7,8]. Moreover, the thermal stability and cost of the amorphous Ni-B catalyst are improved by depositing Ni-B particles on supports with large surface area [1]. Therefore, various supported amorphous Ni-B catalysts have been prepared and investigated frequently.

Up to the present, the supported amorphous Ni-B catalysts have been mostly prepared by reducing the support impregnated with nickel ions with sodium or potassium borohydride solution. However, the surface of Ni-B particles synthesized by this method was usually covered with a layer of oxides [9–11], and it was adverse to the promotion of the catalytic properties of catalysts. Chen et al. modified such method by impregnating the mesoporous materials with potassium borohydride, followed by the reaction with nickel chloride solution [12,13]. The modification improved the catalytic properties of supported Ni-B catalysts in the hydrogenation of 2-ethylanthraquinone. In our previous work, we developed a method for synthesizing supported amorphous Ni-B catalysts by a modified silver-catalyzed electroless plating method [13,14]. The resulting catalyst showed superior hydrogenation activity to Raney Ni catalysts and the corresponding supported amorphous Ni-B/MgO catalyst synthesized by the chemical reduction method [13–16]. On the other hand, the practical application of a catalyst not only depended on its catalytic activity, but also on its stability. Therefore, the stability of the supported Ni-B/MgO catalyst in the catalytic reactions was focused in this paper.

For the amorphous Ni-B catalyst, besides the sintering and crystallization of active sites, its stability was also affected by the poison of hydrogenation reactants or products [7,17–19]. The present work emphasized on the investigation of the possible factors responsible for the deactivation of catalysts, such as the

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sintering, crystallization, sulfur-poisoning, and oxidation during the catalytic reactions. The results showed that the deactivation of Ni-B/MgO was mainly caused by the sulfur-poisoning and change of the porous structure for Ni-B particles.

2. Experimental

2.1. Catalyst preparation

The nickel(II) sulfate hexahydrate ($NiSO_4 \cdot 6H_2O$), potassium borohydride (KBH_4), ethylenediamine ($H_2NCH_2CH_2NH_2$), sodium hydroxide (NaOH), and silver nitrite ($AgNO_3$) were of reagent grade and used as received. The catalyst was prepared by the silver-catalyzed electroless plating method [13,14] as follows. The MgO support was pretreated by heating to 773 K for 4.0 h, and then Ag/MgO (0.2 Ag wt.%) was prepared according to reference [14]. For the preparation of supported amorphous Ni-B/MgO catalysts, the Ag/MgO was added into 200 mL plating solution with stirring at 323 K until no significant bubbles were observed. The resulting catalyst was washed thoroughly with distilled water until pH = 7, then washed with absolute alcohol to remove water and kept in absolute alcohol. The plating solution consisted of nickel(II) sulfate hexahydrate ($9\,g\,L^{-1}$), ethylenediamine ($12\,g\,L^{-1}$), and potassium borohydride ($3.75\,g\,L^{-1}$). The pH value of plating solution was adjusted to 13.5 by sodium hydroxide. The nickel loading was set at 12 wt.%.

2.2. Catalyst characterization

The chemical compositions of supported Ni-B catalysts were analyzed by inductively coupled plasma atomic emission spectrometry (ICP-AES) on an IRIS Intrepid spectrometer. The XRD patterns were recorded on a Rigaku D/max 2500 X-ray diffractometer (Cu Kα, $\lambda = 1.54178$ Å). Transmission electron microscopy (TEM) images of catalyst were acquired using a JEOL-2010 FEF high resolution transmission electron microscope equipped with an EDX system (EDAX) operating at 200 kV, with a point resolution of 0.23 nm. The selected area electron diffraction (SAED) pattern was taken at 80 kV with a beam size of ~40 nm to analyze the crystallinity. The FT-IR spectra were carried out on a NEXUS 870 spectrometer. X-ray photoelectron spectroscopy (XPS) was used to obtain detailed chemical analysis of surface electrical properties from charging studies. The XPS experiments were carried out with a Kratos Axis Ultra DLD spectrometer employing a monochromatic Al Kα X-ray source, hybrid (magnetic/electrostatic) optics and a multi-channel plate and delay line detector (DLD). To avoid the influence of the surface oxygen, argon etching for 10 min was performed to remove the surface passivation layer.

The active surface area (S_{Ni}) was determined by the hydrogen chemisorption, which was performed by using a dynamic pulse method [8,20–22]. The Ni-B/MgO catalyst was purged by a N_2 stream (purity of 99.999%) for 1.0 h at 473 K, which was far below its crystallization temperature. Then the sample was cooled to room temperature, and hydrogen pulses were injected at 303 K until the calculated areas of consecutive pulses became constant. According to the hydrogen chemisorption, S_{Ni} and the number of surface Ni atoms were calculated assuming H/Ni(s) = 1 and a surface area of $6.5 \times 10^{-20}\,m^2$ per Ni atom, based on an average of the areas for the (1 0 0), (1 1 0), and (1 1 1) planes [23].

2.3. Catalyst testing

The catalytic hydrogenation was carried out in a 100 mL stainless steel autoclave, equipped with a mass flow controller to record the hydrogen consumption rate during hydrogenations. The effect of stirring was preliminarily investigated. A stirring rate of 800 rpm was employed to eliminate the diffusion limitation. The hydrogen uptake rate, namely the hydrogen consumption per minute, was calculated according to the ideal gas equation.

In the hydrogenation of sulfolene, 1.0 g catalyst (dried at 353 K under 40 mL/min 99.9% N_2 flow) was transferred into the hydrogenation solution composed of 30.0 mL distilled water and 30.0 g sulfolene. After replacing the air with H_2 in the reactor, the reaction was performed with 2.0 MPa of hydrogen pressure at 328 K for 100 min.

For the acetophenone (AP) hydrogenation, 1.0 g dry catalyst (treated as above), 6.0 mL AP and 60.0 mL ethanol were mixed. Then the hydrogenation was carried out with 2.0 MPa H_2 pressure at 343 K for 4.0 h.

The hydrogenation product was filtered to remove the solid catalyst and analyzed by a gas chromatograph equipped with a flame ionization detector (FID).

3. Results and discussion

Fig. 1 shows the XRD patterns of the MgO support and supported Ni-B/MgO catalysts. In general, the present study indicates that the amorphous Ni–B alloy shows a broad peak

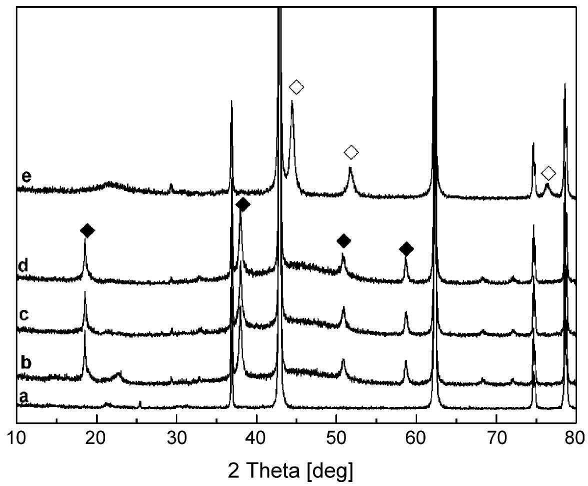

Fig. 1. XRD patterns of different samples: (a) MgO; (b) fresh Ni-B/MgO; (c) Ni-B/MgO used for sulfolene hydrogenation; (d) Ni-B/MgO used for hydrogenation of AP seven times; (e) Ni-B/MgO treated at 773 K under 40 mL/min N_2 flow for 2.0 h. The peaks of Ni are designated by ◇, and the peaks of $Mg(OH)_2$ are designated by ◆.