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Effect of TiO_2 Support on the Composition, Morphology and Catalytic Property of the NiB Amorphous Alloy Catalyst

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Abstract: Both the unsupported and supported NiB amorphous alloy catalysts (NiB and NiB/TiO_2) were prepared by the chemical reduction method. Their catalytic activities were tested by the hydrogenation of sulfolene. The interactions between the NiB alloy and TiO_2 were discussed for the first time by using XRD, ICP, SEM and TEM.

Keywords: NiB/TiO_2 amorphous catalyst, hydrogenation, sulfolene, interaction.

Amorphous alloy catalysts have attracted great attention in recent years because of their superior catalytic properties in hydrogenation [1-5]. Our previous studies revealed that the unsupported NiB alloys showed high activity during the hydrogenation of sulfolene to sulfolane[3]. However, their preparation conditions (at 268K, with N_2 protection) were very rigid, which limited their industrial application. In comparison with the unsupported NiB catalysts, supported NiB catalysts are promising in industrial applications because of their larger surface area, higher thermal stability, superior catalytic activities and lower cost. Furthermore, we had verified that the NiB/TiO_2 was an excellent catalyst in hydrogenation[4]. In the present work, we deposited the ultrafine NiB particles on TiO_2 by the impregnation-wetness-reduction method and chemical deposition method at 293K without N_2 protection. The unsupported NiB alloy was prepared by the chemical reduction method at the same condition. Their differences in the alloy composition, distribution, morphology and catalytic activity in the hydrogenation of sulfolene were identified and discussed.

Experimental

Catalyst Preparation

The NiB amorphous alloy catalyst was prepared by the chemical reduction method[3]. An aqueous solution of KBH_4 (2.0 mol/L) was added dropwise to the 0.1 mol/L $NiSO_4{\cdot}6H_2O$ aqueous solution. The molar ratio of B/Ni was 2:1 and the temperature was 293 K. NiB/TiO_2-1 was prepared by impregnation-wetness-reduction method[4]. NiB/TiO_2-2

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was prepared by the chemical deposition method. The mixture containing TiO_2 (5.0 g) and 0.1 mol/L $NiSO_4{\cdot}6H_2O$ solution was stirred vigorously for 4 h and then reduced by dropwise adding 2.0 mol/L KBH_4. All the preparation parameters including the molar ratio of B/Ni, temperature, adding rate, reaction time and the washing procedure were the same as the preparation of the NiB. The theoretical loading of Ni on TiO_2 was 10.0wt%.

Catalyst characterization

The XRD patterns were recorded on a D/MAX-2500 X-ray diffractometer with CuKα radiation. The nickel and boron contents were measured by ICP-AES (TJA ICP-9000 (N+M)). The surface morphology and the particle size were observed by both scanning electron microscopy (SEM Hitachi S-3500N) and transmission electron microscopy (TEM, Philips EM400ST).

Activity test

The hydrogenation of sulfolene was carried out in a stainless steel autoclave containing 60.0 mL distilled water, 30.0 g sulfolene and 1.0 g catalyst at 3.0 MPa of H_2 pressure and 328 K with vigorous stirring (600 rpm). The reaction lasted for 2.0 h. The products were analyzed by using a gas chromatograph equipped with FID, from which the yield of sulfolane was obtained.

Results and Discussion

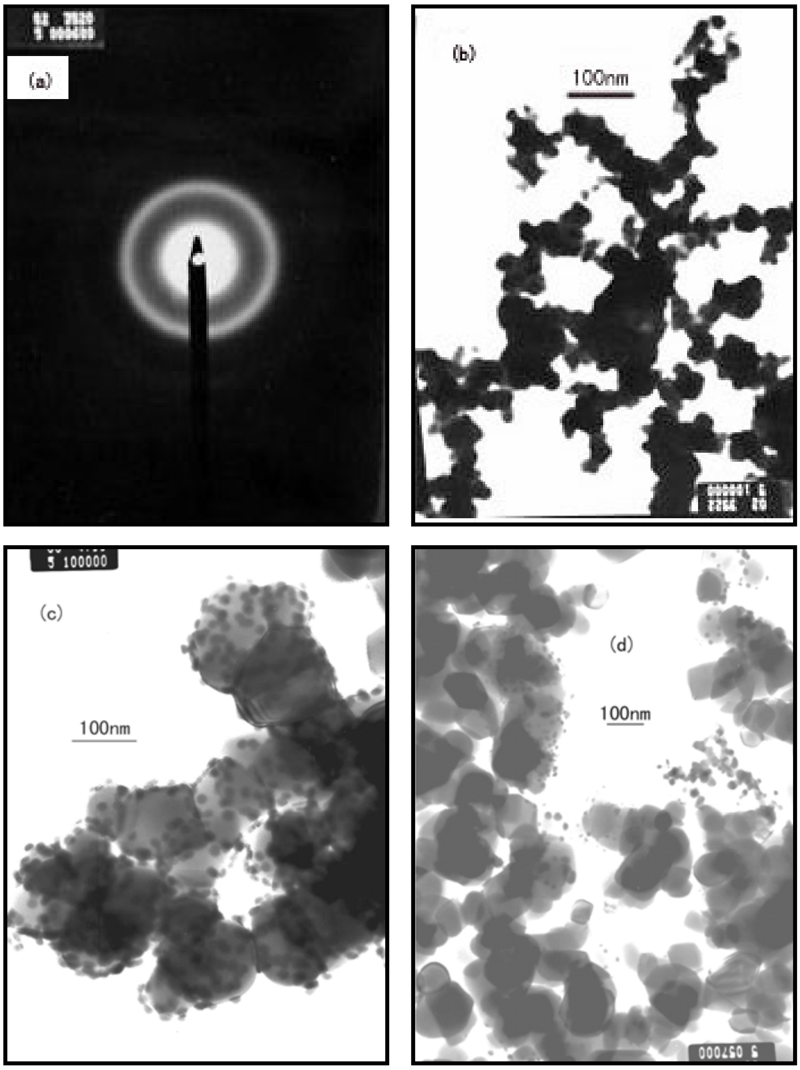
The XRD pattern of NiB alloy was typical of an amorphous substance with complete absence of any sharp crystalline peaks[2]. The broad peak around $2\theta=45°$in the pattern of NiB was due to the amorphous NiB alloy and the small profile around $2\theta=22°$was ascribed to the amorphous boron oxide, which was thought in the literature to be inevitably formed when the reduction was carried out in aqueous solution[5]. There was no significant difference between the XRD patterns of TiO_2 and that of NiB/TiO_2 because of the high dispersion of NiB on TiO_2 and the low loading of Ni, which was consistent with the results in the literature[4]. Selected area electronic diffraction (SAED) was also employed to verify the amorphous structure of NiB. There was a halo diffraction pattern rather than distinct dots in the SAED image of NiB (**Figure 1a**), in good agreement with the XRD result.

The bulk compositions of the catalysts were given in **Table 1**. Because both NiB and NiB/TiO_2-2 were prepared under the same conditions, their composition should be identical in theory. As shown in **Table 1**, no significant change in the composition of the NiB alloy was observed. It was also found that Ni loadings on NiB/TiO_2-1 and NiB/TiO_2-2 were different. The Ni loading on NiB/TiO_2-2 was identical with the theoretical value because there was no loss of the Ni during the preparation. But the Ni loading on NiB/TiO_2-1 was much lower than the theoretical value. The preparation procedures of NiB/TiO_2-1 were more complicated than that of NiB/TiO_2-2 and the loss of the nickel could not be avoided.

Table 1 The composition of NiB and NiB/ TiO_2 catalysts and their catalytic activities

Sample	Ni (wt.%)	Composition (wt.%)	Yield of sulfolane (%)
NiB	83.84	$Ni_{90.8}B_{9.2}$	70.3
NiB/TiO_2-1	6.10	$Ni_{86.4}B_{13.7}$	74.7
NiB/TiO_2-2	9.94	$Ni_{90.3}B_{9.7}$	65.9

Figure 1 SAED of (a) NiB and TEM of (b) NiB; (c) NiB/TiO_2-1; (d) NiB/TiO_2-2



TEM results showed that the unsupported NiB particles (**Figure 1b**) were spherical with the average particle size around 20 nm and appeared to be interconnected, which is the character of the nanoparticles. The NiB particles on NiB/TiO_2-1 (**Figure 1c**) were spherical with the average particle size about 10nm and the size distribution of them was very homogeneous. There were two kinds of NiB particles on NiB/TiO_2-2 (**Figure 1d**). Those particles in the free state were present in spherical shape with diameters ranging from 10 to 20 nm. Some NiB particles on NiB/TiO_2-2 were attached to the surface of the support and present in spherical shape with the average size around 10 nm. These two states of NiB particles on NiB/TiO_2-2 were ascribed to the preparation method of the chemical deposition, because not all the NiB particles prepared by the reduction of Ni^{2+} with KBH_4 would deposit on TiO_2. It was obvious that the gathering of the ultrafine NiB particles could be successfully inhibited owing to the introduction of the TiO_2 support. The differences in the morphology between the unsupported NiB and the supported NiB particles verified the promoting effect of the TiO_2 support on the dispersion of NiB alloy.

Both NiB and NiB/TiO_2 had very high hydrogenation activity under the reaction conditions used in the literature (Water/sulfolene = 10.0 mL/10.0 g) [3]. The yield of the sulfolane of each sample was over 99%. In order to distinguish their activities, the hydrogenation of sulfolene was performed at rigid condition (Water/sulfolene = 60.0 mL/30.0 g). The results (**Table 1**) showed that although the Ni loading on NiB/TiO_2-1 was much lower than that on NiB and NiB/TiO_2-2, the hydrogenation activity of NiB/TiO_2-1 was higher than NiB and NiB/TiO_2-2. The specific activities of Ni on both NiB/TiO_2-1 and NiB/TiO_2-2 were higher than the unsupported NiB. These results were ascribed to the dispersion and size of NiB particles on the support. As compared to that of NiB/TiO_2-1, the larger size and the lower dispersion of NiB particles on the NiB/TiO_2-2 would neutralize the increase of activity caused by the increase of the Ni loading. The above results showed that the activity of the supported NiB amorphous catalyst could be superior to the activity of the unsupported NiB amorphous catalyst under a low consumption of the nickel.

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