Preparation of Supported NiB Amorphous Alloy Catalysts by Powder Electroless Plating

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Amorphous alloys are potential heterogeneous catalysts in a variety of industrial processes [1-5]. Generally, amorphous alloys with a high surface area can be prepared by the chemical reduction method but the as-prepared alloys are costly and their thermal stability is poor [11]. In addition, aggregation of these ultrafine amorphous alloy particles is very serious [5], which greatly affects their catalytic activity. In order to overcome these drawbacks, we used two kinds of electroless plating baths to prepare two MgO-supported amorphous NiB alloy catalysts, NiB/MgO-1 and NiB/MgO-2, by the powder electroless plating method. For comparison, an unsupported NiB alloy was prepared by the traditional chemical reduction method. These catalysts were characterized by XRD, ICP and TEM. Their catalytic activity was measured using the liquid phase hydrogenation of sulfolene under moderate pressure.

The unsupported NiB amorphous alloy was prepared by using KBH₄ to reduce NiSO₄ in an aqueous solution at 293 K. For the preparation of NiB/MgO-1, precursor Ag₂O/MgO with a nominal loading of Ag on MgO of 2 000μg/g was made by impregnation and then was plated in a solution containing NiSO₄·6H₂O, KBH₄ and NH₄OH with stirring for 0.5 h. The resulting catalyst was washed thoroughly with distilled water and kept in absolute alcohol. NiB/MgO-2 was prepared by adding a measured amount of Ag₂O/MgO into a solution containing NiSO₄·6H₂O, KBH₄, NaOH and NH₂CH₂CH₂NH₂, stirring for 0.5 h and then washing with distilled water. The hydrogenation of sulfolene to sulfolane was carried out in a stainless steel autoclave containing 1.0 g catalyst, 30 g sulfolene and 60 ml distilled water at 3.0 MPa of H₂ pressure and 328 K with vigorous stirring. The reaction lasted 2.0 h. The products were analyzed using a gas chromatograph equipped with FID.

The XRD pattern of the NiB alloy is typical of an amorphous substance with the complete absence of any sharp crystalline peaks. The broad peak around θ = 45° is due to the amorphous NiB alloy [4,5]. In the cases of NiB/MgO-1 and NiB/MgO-2, no broad peak was found at θ = 45° because of the high dispersion of NiB on the support and the low Ni loading. However, a crystalline diffraction peak corresponding to metallic Ni appeared when NiB/MgO was treated at 773 K under Ar, indicating that Ni and B on the support existed in the amorphous state. These results are consistent with our previous studies [6].

The unsupported NiB particles (Fig 1(a)) are spherical with particle size of 10-60 nm and appear to be aggregated. The size of NiB particles on NiB/MgO-1 (Fig 1(b)) ranges from 30 to 90 nm, whereas those on NiB/MgO-2 (Fig 1(c)) are 20-50 nm. The size distribution of NiB nanoparticles on NiB/MgO-2 is more uniform than that on NiB/MgO-1. These are attributed to the different stability and plating speed of the two plating baths. The dispersion of NiB particles on MgO is better than that of unsupported NiB particles, which can be understood by considering the function of Ag. After adding Ag₂O/MgO to the plating bath, the Ag⁺ cation is first reduced rapidly by the BH₄⁻ anion to create crystalline nuclei of Ag, which catalyzes the reduction of Ni²⁺...
by BH₄. The process of electroless plating is a directional deposition⁷. Ag⁺ can anchor the initial NiB around it on the support. Thus, the powder electroless plating method of preparing supported NiB amorphous alloy catalysts can effectively inhibit the NiB particles from aggregation.

![TEM pictures of NiB, NiB/MgO-1, and NiB/MgO-2](image)

Fig 1 TEM pictures of NiB (a), NiB/MgO-1 (b) and NiB/MgO-2 (c)

The catalyst activity increases in the order NiB < NiB/MgO-1 < Raney Ni < NiB/MgO-2 (Table 1). The activity of the supported NiB amorphous alloy catalysts is higher than that of the unsupported NiB, which is attributed to the high dispersion of the supported amorphous alloy¹,²,⁴.

Table 1 Catalytic activity of samples for the hydrogenation of sulfonate to sulfonate

<table>
<thead>
<tr>
<th>Sample</th>
<th>Content (%)</th>
<th>Yield of sulfonate (%)</th>
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<tbody>
<tr>
<td>NiB</td>
<td>83.84</td>
<td>8.49</td>
</tr>
<tr>
<td>NiB/MgO-1</td>
<td>10.64</td>
<td>0.85</td>
</tr>
<tr>
<td>NiB/MgO-2</td>
<td>8.90</td>
<td>0.96</td>
</tr>
<tr>
<td>Raney Ni</td>
<td></td>
<td></td>
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In summary, the MgO-supported NiB amorphous alloy catalyst has a superior catalytic activity and a low consumption of Ni and it is a promising catalyst as a replacement for Raney Ni.

References