Preparation of amorphous Ni–Co–B alloys and the effect of cobalt on their hydrogenation activity

Zhong-Bin Yu, Ming-Hua Qiao, He-Xing Li, Jing-Fa Deng*

Department of Chemistry, Fudan University, Shanghai 200433, China

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Abstract

The bimetallic amorphous alloys Ni–Co–B were prepared by the chemical reduction of the solution containing both nickel and cobalt salts with aqueous potassium borohydride. Those samples were thoroughly characterized by ICP, BET, DSC, XRD, EXAFS, XPS, TEM and TPR. Superior to the rapid quenching techniques, the content of Co in Ni–Co–B alloys could be adjusted in a wide range by changing the initial concentration of cobalt salt in the solution. The catalytic activities of the as-prepared materials were measured through the hydrogenation of benzene under moderate pressure in liquid phase. By comparing with the activities of the corresponding pure Ni–B, Co–B and their mixture as well as the Ni–Co–B amorphous alloys with different contents of Co, both the inhibiting and promoting effects of Co on the hydrogenation activities in Ni–Co–B amorphous alloys have been observed and discussed according to the amount of the effective metal in the alloys and their structural characters, especially their surface properties. © 1997 Elsevier Science B.V.

Keywords: Ni–Co–B amorphous alloy; Cobalt; Hydrogenation of benzene; Catalytic activity

1. Introduction

Amorphous alloys represent a new class of materials with short-range ordering structure which may provide pathways to novel, more active and selective catalysts. In past few years, a lot of binary amorphous alloys with high hydrogenation activities have been obtained by rapid quenching techniques [1–4]. Although the modification of catalytic properties on the amorphous alloys by introducing an extra metal, which resulted in the ternary amorphous alloys, has been observed in many cases [5–7], the influencing mechanism of each metal in the ternary amorphous alloys was still not clear because those ternary amorphous alloys could be obtained only within a quite narrow composition range as limited by the compositions of the alloys at the eutectic point. Recently, a chemical reduction method by which transition metal ions are brought to the metallic state by reduction of KBH$_4$ in aqueous solution attracts keen interest because of its simple procedure and the particle size of the alloys obtained which is suitable for the catalysis [8]. Many amorphous alloys including both the binary and ternary systems, such as Ni–B, Ni–P, Co–P and Ni–W–P have been obtained by this way which exhibit high activity and selectivity...
during the hydrogenation of olefins [9–13]. The chemical reduction method also supplies a powerful way to investigate the effect of the metals existed in the ternary alloys because the composition of the amorphous alloys could be adjusted easily in a wide range. In the present paper, a series of Ni–Co–B amorphous alloys with different content of Co have been prepared by chemical reduction. The hydrogenation activities of those samples have been measured. Both the promoting and inhibiting effects of Co on the hydrogenation activity have been observed and discussed according to the relative content of metals in the alloys used as the catalysts and their structural characters.

2. Experimental

2.1. Catalyst preparation

The preparation method of Ni–Co–B was similar to that reported by Deng [11]. An aqueous solution of KBH$_4$ (2.0 M) was added dropwise into an aqueous solution containing both the nickel acetate and cobalt acetate. The initial molar ratio of KBH$_4$ to metallic salt was 5 : 2. The solution was kept in an ice water bath and stirred vigorously by a magnetic stirrer. The reaction was lasted for about 0.5 h until there was no gas released from the solution. The resulted black precipitate was washed several times with distilled water and subsequently with 99.9% ethanol (EtOH). The final product was kept in EtOH because it is easy to be oxidized and even pyrophoric in the air. The composition of the samples was adjusted by changing the initial ratio of Ni/Co in the solution. In the extreme, Ni–B and Co–B amorphous alloys were obtained when only nickel salt or cobalt salt was used in the solution, respectively.

2.2. Catalyst characterization

The as-prepared samples were characterized by the following methods:

1. X-ray diffraction (XRD) was executed on a Rigaku Dmax-rA powder diffractionmeter with Cu K$_\alpha$ radiation.
2. Differential scanning calorimetry (DSC) was conducted on a Perkin-Elmer Differential Scanning Calorimeter under N$_2$ atmosphere at the heating rate of 10°C/min.
3. Transmission electron micrograph (TEM) was performed on a Hitachi H 600 electron microscope.
4. EXAFS Spectra were measured on the BL-10B in the National Laboratory of High Energy Physics (KEK, Tsukuba, Japan) with the electron beam energy of 2.5 Gev and the stored current in the range of 360–260 mA. Monochrometer was a channel cut Si(3 1 1). Data were collected in the transmission mode using ion chambers of nitrogen (85%) and argon (15%) mixed gas at room temperature, then processed by using the EXAFS(II) program [14].
5. X-ray photoelectron spectroscopy (XPS) spectra were obtained with a Perkin-Elmer PH I 5000C ESCA system. All binding energy values were calibrated by using the value of contaminant carbon (C$_{1s}$=284.6 eV).
6. Temperature programmed reduction (TPR) was carried out in a flow of 3% H$_2$/Ar through a catalyst bed with the temperature ramp of 8 K/min. The hydrogen absorption during the reaction was recorded by a TCD. In those experiments, the catalysts were preoxidized at the temperature well below the crystallization point of the amorphous alloys in an oxygen flow.

2.3. Activity measurement

The catalytic activities of the amorphous alloys were evaluated through the hydrogenation of benzene which was performed in 40 ml 99.9% EtOH solution under an initial 1.0 MPa hydrogen at 373 K. In order to compare the hydrogenation activities for different catalysts, each reaction contained the same amount of catalyst (0.14 g) and the same concentration of benzene (2.24 mol/l). The hydrogenation was started by stirring the reaction mixture vigorously on a magnetic stirrer. The hydrogenation activity was observed by monitoring the change of the pressure inside the reaction tank versus the time, which was subsequently turned into the H$_2$ uptake rate by treating H$_2$ as the ideal gas. The reaction products in both liquid phase and gaseous phase were analyzed by a gas chromatographic method. Triple reproducing experiments show that the error in the test is within 2%.
Table 1
Composition and molar fraction of Ni–Co–B system and the solution

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Bulk comp.</th>
<th>(X^2_{\text{Co}}/(\text{Co}+\text{Ni}))</th>
<th>(X^2_{\text{Co}}/(\text{Co}+\text{Ni}))</th>
<th>Surf. area (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni–B</td>
<td>Ni₆₈.₄B₃₁.₆</td>
<td>0</td>
<td>0</td>
<td>12.0</td>
</tr>
<tr>
<td>Ni–Co–B–1</td>
<td>Ni₆₁.₆Co₅.₂B₳₃.₃</td>
<td>0.078</td>
<td>0.078</td>
<td>10.0</td>
</tr>
<tr>
<td>Ni–Co–B–4</td>
<td>Ni₄₉.₄Co₂₆.₃B₴₄.₆</td>
<td>0.40</td>
<td>0.37</td>
<td>8.0</td>
</tr>
<tr>
<td>Ni–Co–B–5</td>
<td>Ni₃₂.₂Co₀₈.₁B₳₳.₈</td>
<td>0.50</td>
<td>0.50</td>
<td>7.0</td>
</tr>
<tr>
<td>Ni–Co–B–6</td>
<td>Ni₃₆.₀Co₇₃.₈B₳₳.₇</td>
<td>0.60</td>
<td>0.60</td>
<td>6.₅</td>
</tr>
<tr>
<td>Ni–Co–B–8</td>
<td>Ni₄₀₌Co₄₁₆B₳₴₹.₀</td>
<td>0.₈₀</td>
<td>0.₈₀</td>
<td>₅.₀</td>
</tr>
<tr>
<td>Co–B</td>
<td>Co₇₅₃B₂₴₇</td>
<td>1.₀₀</td>
<td>1.₀₀</td>
<td>₄.₅</td>
</tr>
</tbody>
</table>

\(X^2_{\text{Co}}/(\text{Co}+\text{Ni})\) is the molar ratio of Co/(Co+Ni) in the alloy, \(X^2_{\text{Co}}/(\text{Co}+\text{Ni})\) is the molar ratio of Co/(Co+Ni) in the solution.

3. Results and discussion

The chemical compositions and surface areas of Ni–B, Co–B and Ni–Co–B systems were analyzed by induced coupled plasma (ICP) and BET method. Those results are summarized in Table 1. The compositions and cobalt molar fractions in Ni–Co–B samples changed with the initial concentration of cobalt salt in the solution which was subsequently reduced with KBH₄. The molar ratios of Co/(Co+Ni) in Ni–Co–B samples were almost the same as the corresponding molar ratios in the solution, indicating the complete reduction of metallic ions by KBH₄. Therefore the compositions of the Ni–Co–B alloys could be easily adjusted by changing the initial concentrations of the metallic salts in the solution. According to Table 1, the surface areas of the Ni–Co–B alloys decreased with Co content increasing.

The XRD patterns of Ni–B, Co–B and Ni–Co–B samples with various content of Co are illustrated in Fig. 1. The only one broad peak around 45° appeared in each pattern indicated the amorphous characters in all the as-prepared alloys. The amorphous structure of Ni–Co–B alloys was further confirmed by EXAFS, for it is powerful in investigating the fine structure of amorphous materials. Fig. 2 shows the radial distribution functions (RDF) of Ni–Co–B samples which were obtained from their \(\chi(k)k^3\) by the fast Fourier transformation. In each sample, only one broad peak with high FT amplitude for both Ni and Co in the first-neighbor (\(R=0.17–0.24\) nm) was observed, indicating that each sample has neither long-range order nor completely amorphous character. The materials obtained by chemical reduction are not the pure metals, but only the alloys with a rigid structure and short-range ordering confined in the first-neighbor atom layer [15].

Budurov reported that during the preparation of Ni–Co–P(B) alloys by rapid quenching techniques [7], the glass-forming occurred only in a quite narrow range of the compositions limited by the composition at the eutectic point. The highest content of Co in the amorphous alloys was about 8 at%, otherwise the crystallization occurred. The above results demonstrated that the chemical reduction supplied a new and powerful way to prepare bimetallic amorphous alloys in a wide range of the compositions. The content of Co in Ni–Co–B alloys obtained by chemical reduction could be changed from 0 to nearly 50 at% without changing their amorphous characters.

The morphologies of Ni–Co–B amorphous alloys were determined by TEM, as shown in Fig. 3. Each sample comprised of uniformly spherical particles with the average size of about 10 nm, indicating that the Ni–Co–B amorphous alloys existed as the nanometer particles, which was similar to those observed in Ni–B and Co–B amorphous alloys obtained by chemical reduction. No significant effect on the shape and particle size of Ni–Co–B alloys was observed with the increase of the Co content in the samples. The self-aggregation of some particles occurred in the samples due to the extremely high specific surface energy for the nanometer particles [16]. Some gel-like clusters were also observed in the samples. The amount of the clusters increased with increase in Co content in the samples. Those clusters were attributed to some hydroxides as they could be removed by dilute ammonia solution [4]. The gel-like clusters in the Ni–Co–B samples increased with increase in Co content because cobalt ion is easier to form hydroxides than nickel ion.
Fig. 1. XRD patterns of the samples: (a) Ni–B, (b) Ni–Co–B-1, (c) Ni-Co-B-5, (d) Ni-Co-B-8, (e) Co–B.

Those results caused the decrease of the surface areas of Ni–Co–B alloys with Co contain increasing, as shown in Table 1.

The crystallizing process of Ni–Co–B amorphous alloys was analyzed by DSC. As shown in Fig. 4, the DSC patterns changed significantly with the variation of $X_{\text{Co}}$, the molar ratio of Co/(Ni+Co). When $X_{\text{Co}}<10\%$, the DSC patterns of Ni–Co–B samples were quite similar to those of corresponding mixed Ni–B and CoB amorphous alloys, as shown in Fig. 4(a), (b) and (d), indicating that most of Ni and Co existed independently in Ni–Co–B amorphous alloys. When $X_{\text{Co}}>10\%$, the DSC patterns of Ni–Co–B amorphous alloys were different from either the pure Ni–B and Co–B or the mixture of Ni–B and Co–B amorphous alloys, indicating the interaction between Ni and Co in Ni–Co–B amorphous alloys.

The interaction of Ni and Co in Ni–Co–B amorphous alloys could be also analyzed by TPR. As shown in Fig. 5, when $X_{\text{Co}}<10\%$, three peaks on the TPR pattern of Ni–Co–B amorphous alloys were observed. The first peak at 585°C was attributed to Ni–B, while the other two peaks at 678°C and 780°C, respectively were corresponding to Co–B amorphous alloys. Thus the TPR curve of Ni–Co–B amorphous alloys was quite similar to those of mixed Ni–B and Co–B amorphous alloys, indicating the independent existence of Ni and Co in the Ni–Co–B samples. However, only one significant peak at about 650°C was observed for each Ni–Co–B sample when $X_{\text{Co}}>10\%$, indicating the interaction between Ni and Co in Ni–Co–B amorphous alloys.

Because hydrogenation occurred on the surface of the catalysts, the XPS was employed to investigate the surface states of Ni–Co–B amorphous alloys. The results were summarized in Fig. 6. In all the samples, two peaks appeared in Ni$_{2p^{3/2}}$, Co$_{2p^{3/2}}$ and B$_{1s}$ levels, indicating that nickel, cobalt and boron existed in both the elemental and oxidized states [15]. Those oxidized states do not disappear after Ar$^+$ sputtering, indicating...
that those oxidized states were not resulted from the oxidation on the surface but the oxidation occurred during the chemical reduction between metal salt and KBH4. No significant shift of binding energies in Co2p3/2 and B1s level was observed with XCo increasing. However, in Ni2p3/2 level, the shift of binding energies for elemental Ni to the lower value with XCo increasing (XCo>10%) was observed, as summarized in Table 2. When XCo<10%, the positive shift of the binding energy was also observed. The negative shift of binding energy for elemental Ni showed the existence of electronic effect caused by the introduction of Co, which resulted in the enrichment of electron on elemental Ni in the alloys. Besides the effect of Co on the valence state on the surface of Ni–Co–B, the effect on the surface compositions of Ni–Co–B amorphous
Fig. 3. TEM pictures of the samples: (a) Ni-Co-B-1, (b) Ni-Co-B-4.

Table 2

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Binding energy (eV)</th>
<th>Surf. comp.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni-B</td>
<td>852.0</td>
<td>Ni_{61.0}B_{39.0}</td>
</tr>
<tr>
<td>Ni-Co-B-1</td>
<td>852.4</td>
<td>Ni_{50.0}Co_{41.0}B_{45.9}</td>
</tr>
<tr>
<td>Ni-Co-B-4</td>
<td>852.1</td>
<td>Ni_{44.5}Co_{13.0}B_{42.5}</td>
</tr>
<tr>
<td>Ni-Co-B-5</td>
<td>851.9</td>
<td>Ni_{42.0}Co_{18.4}B_{39.6}</td>
</tr>
<tr>
<td>Ni-Co-B-8</td>
<td>851.7</td>
<td>Ni_{45.0}Co_{39.3}B_{44.8}</td>
</tr>
<tr>
<td>Co-B</td>
<td>—</td>
<td>Co_{53.6}B_{46.1}</td>
</tr>
</tbody>
</table>

alloys of Co content was also observed, as listed in Table 2. The molar ratio $(K_{Ni/Co})$ of $(Ni/Co)_{surf}/(Ni/Co)_{bulk}$ of Ni-Co-B amorphous alloys firstly increased and then decreased with $X_{Co}$ increasing, as shown in Fig. 7. As $K_{Ni/Co}$ is always more than 1.0, those results indicated that the introduction of Co to Ni-B alloy resulted in the enrichment of Ni on the surface of the as-prepared amorphous alloy.

The hydrogenation activities of Ni-B, Co-B, the mixed Ni-B and Co-B as well as Ni-Co-B amorphous alloys were investigated by measuring the hydrogen uptake rate during the hydrogenation of benzene. Because the cyclohexane is the only product during the hydrogenation determined in both the liquid and gaseous phase, it could be concluded that the selectivities of all those hydrogenation reactions were almost 100%. Therefore, the change of the pressure inside the reactor is mainly ascribed to the consumption of $H_2$ during the hydrogenation. In order to compare with each other, each reaction was performed under the same condition and with the same amount of amorphous alloy used as the catalyst. The effect of Co on the hydrogenation activities was observed by plotting the $H_2$ uptake rate versus $X_{Co}$ (Fig. 8(a) and compared with the hydrogen absorption rate when the mixture of Ni-B and Co-B amorphous alloys with the same content of Ni and Co as that in the corresponding Ni-Co-B were employed instead of Ni-Co-B as the catalyst in the hydrogenation (Fig. 8(b)). The hydrogenation activity of the mixed amorphous alloy catalysts decreased monologically with the increase of $X_{Co}$ in the mixture, quite similar to the average activity between Ni-B and Co-B amorphous alloys. According to Fig. 8, the following results could be obtained:

1. The hydrogenation activity of Ni-B amorphous alloy was much higher than the corresponding Co-B. In fact, no significant activity of Co-B amorphous alloy has been observed during the hydrogenation of benzene under the reaction conditions. The above results indicated that the hydrogenation activity of Ni-Co-B amorphous...
alloy was mainly dependent on Ni, especially the elemental Ni existed in the Ni–Co–B amorphous alloy, which has been reported to be the active site during the hydrogenation [16].

2. In general, the hydrogenation activities of the mixed Ni–B and Co–B amorphous alloys were less than that of the corresponding Ni–Co–B amorphous alloys used as the catalyst, showing the promoting effect of Co on the hydrogenation activity. In the mixed Ni–B and Co–B amorphous alloys, the hydrogenation activities decreased linearly with the increase of Co in the mixture.

3. When $X_{Co}<10\%$, the hydrogenation activities of Ni–Co–B amorphous alloys were less than the Ni–B amorphous alloys and even the corresponding mixture of Ni–B and Co–B amorphous alloys. The activities decreased rapidly with the increase of $X_{Co}$, indicating the inhibiting effect of small amount of Co on the hydrogenation activities of Ni–Co–B amorphous alloys.

4. When $50\%>X_{Co}>10\%$, the hydrogenation activities of Ni–Co–B amorphous alloys increased quickly with $X_{Co}$ increasing, indicating the promoting effect of Co on the hydrogenation activities. The maximum hydrogenation activity of Ni–Co–B amorphous alloys appeared at $X_{Co}\approx50\%$.

5. When $X_{Co}>50\%$, the hydrogenation activities of Ni–Co–B amorphous alloys decreased with the increase of $X_{Co}$, indicating the negative effect of excess Co on the hydrogenation activity. However, the hydrogenation activities of Ni–Co–B amorphous alloys with excess Co were still higher than those of the corresponding mixed Ni–B and Co–B amorphous alloys.
6. The specific hydrogenation activities of the as-prepared samples were calculated by dividing the H₂ uptaking rate by the corresponding surface area, as shown in Fig. 8(c). The change of the specific hydrogenation activity with $X_{Co}$ is similar to the change of hydrogenation activity, as shown in Fig. 8(a). However, it is found that the specific hydrogenation activity decreased slowly when $X_{Co} < 10\%$ or $X_{Co} > 50\%$ while increased quickly when $10\% < X_{Co} < 50\%$. Therefore, it could be concluded that although the introduction of Co to the Ni–B alloy had negative effect on the hydrogenation activities because of the decrease of the surface areas, it was not the most important factor because it did not change the shape of the curve, as shown in Fig. 8(a).

As mentioned above, the hydrogenation activity of Ni–Co–B amorphous alloys were mainly dependent
on the Ni, especially the elemental Ni in the alloys, therefore the effect of Co on the hydrogenation activity of Ni–Co–B amorphous alloys could be understood by considering the following factors:

1. As shown in Figs. 1–3, the introduction of Co into Ni–B amorphous alloys, which derived the bimetallic amorphous alloys, does not alter their amorphous structure and the particle size significantly. Thus, the effect of alternation of the amorphous characters and the particle size of the alloys on the hydrogenation activity caused by introducing various content of Co could be neglected.

2. Because the content of Ni in Ni–Co–B amorphous alloys decreased with $X_{\text{Co}}$ increasing, the real amount of Ni used in the hydrogenation was less than that of Ni–B amorphous alloys when the corresponding Ni–Co–B samples were used with the same amount (0.14 g) as that of Ni–B and it decreased with the increase of $X_{\text{Co}}$ in the alloys. As shown in Fig. 8(b), for the mixed Ni–B and Co–B amorphous alloys, the hydrogenation activities changed proportionally to the amount of Ni in the catalyst. Therefore, the hydrogenation activities of Ni–Co–B amorphous alloys would be less than the corresponding Ni–B amorphous alloys and decreased with the increase of Co in the alloys due to the decrease of Ni amount in the alloys used as the catalysts in the hydrogenation. On the other hand, the decrease of the hydrogenation activities of Ni–Co–B amorphous alloys also resulted from the decrease of the surface areas with Co content increasing, as shown in Table 1. This was confirmed by the specific activities of Ni–Co–B amor-

Fig. 6. XPS spectra of the samples: (a) Ni–Co–B-1, (b) Ni–Co–B-4, (c) Ni–Co–B-5, (d) Ni–Co–B-8, (e) Co–B.
phous catalysts, as shown in Fig. 8(c). Comparing with the corresponding hydrogenation activities, the hydrogenation activities per surface area decreased slowly and increased rapidly, indicating the negative effect of Co on the hydrogenation activities of Ni–Co–B amorphous alloys caused by the decrease of the surface areas.

3. As mentioned above, the introduction of Co to Ni–B amorphous alloys could change their structural properties in the following two ways:

1. The negative shift of binding energy of elemental Ni caused by introduction of Co in Ni–Co–B alloys referred to the relative rich in electron for elemental Ni on the surface of Ni–Co–B systems (Table 2). As reported in the study of hydrogenation activities of the Ni–B amorphous alloys, the electron donating effect to elemental Ni resulted in the increase of the hydrogenation activities of Ni–Co–B amorphous alloys [16].

2. The introduction of Co to Ni–B amorphous alloys resulted in the relative enrichment of Ni on the surface of Ni–Co–B amorphous alloys which subsequently resulted in the increase of their hydrogenation activities. This conclusion is strongly supported by comparing the relationship of $K_{Ni}X_{Co}$ and $R_{H2}X_{Co}$, as shown in Figs. 7 and 8.

In general consideration, the introduction of Co to Ni–B amorphous alloy exhibited both the negative and positive effects on the hydrogenation activities. The negative effect is resulted from the decrease of both the real amount of Ni and the surface areas. While, the positive effect is related the enrichment of Ni on the surface of the amorphous catalysts and the interaction
between Ni and Co in the Ni–Co–B amorphous alloys, which may alter the structural properties of the active sites. When $X_{Co}<10\%$, no significant effect on the structural property was observed by introducing Co to Ni–B amorphous alloys, which was confirmed by TPR and DSC as shown in Figs. 4 and 5. Ni and Co existed almost independently in Ni–Co–B amorphous alloys. Therefore the introduction of Co into Ni–B amorphous alloys was almost the same as the mixture of Ni–B and Co–B amorphous alloys. As the real amount of Ni in the amorphous alloys decreased and the surface areas decreased with $X_{Co}$ increasing, their hydrogenation activities also decreased. The hydrogenation activities of Ni–Co–B amorphous alloys were even less than those of the corresponding mixed Ni–B and Co–B amorphous alloys due to the relatively less amount of B in Ni–Co–B samples [16] and the positive shift of binding energy of elemental Ni, as
shown in Table 2. When 10%<X_{Co}<50%, the Ni and Co existed in an ensemble in Ni–Co–B amorphous alloys. The effect of Co on the structural property in the alloys became dominant. As mentioned above, the introduction of Co could modify the structure of the Ni–Co–B amorphous alloys which would improve their catalytic properties and result in the enrichment of Ni on the surface, therefore the hydrogenation activities of Ni–Co–B amorphous alloys were higher than the corresponding mixture of Ni–B and Co–B and even the pure Ni–B amorphous alloys and increased with the increase of X_{Co} in the Ni–Co–B samples, as exhibited in Fig. 8(a). When X_{Co}>50%, although there was still strong modification on the structure of Ni–Co–B amorphous alloys, the extremely decrease in the amount of Ni used in the hydrogenation caused by introduction of excess Co in Ni–Co–B amorphous alloys resulted in the decrease of hydrogenation activities. The hydrogenation activities of Ni–Co–B amorphous alloys were still higher than those of corresponding mixed Ni–B and Co–B amorphous alloys, indicating the existence of the effect of Co on the structural properties of Ni–Co–B amorphous alloys, as shown in Fig. 8(a).

Further study is underway in order to thoroughly understand the catalyzing mechanism of Ni–Co–B amorphous alloys.

4. Conclusions

A series of Ni–Co–B amorphous alloys have been prepared by chemical reduction. Their hydrogenation
activities have been measured and compared with the corresponding Ni–B and Co–B amorphous alloys. Experimental results indicated that the introduction of small amount of Co($X_{Co}$<10%) to Ni–B amorphous alloy would decrease the hydrogenation activity; while the introduction of moderate amount of Co(10%<$X_{Co}$<50%) to Ni–B amorphous alloy would increase the hydrogenation activity; however, the introduction of excess amount of Co($X_{Co}$>50%) would decrease the hydrogenation activity again. Both the positive and negative effects of Co on the hydrogenation activity of Ni–Co–B could be understood by considering the effects of Co introduction on the relative content of Ni which is the effective metal, the surface areas, the active site in Ni–Co–B amorphous alloys and their structural properties.

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References
