Evidence for the Antioxidation Effect of Boron on the Ultrafine Amorphous Ni–B Alloy Catalyst

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Introduction

Recently, amorphous metal alloys have gained much attention as promising novel catalytic materials. Their unique isotropic structure and high concentration of coordinatively unsaturated sites lead to superior catalytic activity and selectivity compared to their crystalline counterparts. Among them, ultrafine amorphous Ni–B catalysts have been most extensively studied on their activity and selectivity compared to their crystalline counterparts. In our previous papers,5,6 the amorphous alloy structure of the as-prepared Ni–B sample has been confirmed by various characterizations, such as X-ray diffraction (XRD), EXAFS, selective area electron diffraction (SAED), and differential scanning calorimetry (DSC). The transmission electron microscope (TEM) morphology demonstrated that the Ni–B alloy was present in the form of spherical particles with an average size of around 200 nm; i.e., the Ni–B alloy was present in the ultrafine powders (See Figure 1). Figure 2 shows the XPS spectra of B 1s under the exposing efficiency. After fixing it to the sample holder, the sample was transferred to the pretreatment chamber immediately. In the sample was degassed under 1 × 10−6 Torr for 4 h to remove the volatile contaminants. Then the sample was transferred without contacting the atmosphere into the analyzing chamber in which sample heating can be achieved by using an electric resistance heater through a tantalum slice equipped in the manipulator. A WR63WRt25 thermocouple was attached to the back of the sample for temperature measurement and control. After the sample was slightly sputtered to remove some involatile contaminants, exposure to O2 was performed while holding the sample at a certain temperature. XPS depth profiling was carried out by using an ion sputtering gun operated at 3.0 kV, 10 mA, and 5 × 10−5 Pa of Ar to give a nominal sputtering rate of 2 Å/min, as calibrated via a Ta2O5 standard. The surface composition was obtained by fitting the XPS spectra of the corresponding elements in the alloys by considering their sensitivity factors. In the fitting, a Gaussian–Lorentzian line shape is employed assuming a linear background.

Results and Discussion

In our previous papers,5,6 the amorphous alloy structure of the as-prepared Ni–B sample has been confirmed by various characterizations, such as X-ray diffraction (XRD), EXAFS, selective area electron diffraction (SAED), and differential scanning calorimetry (DSC). The transmission electron microscope (TEM) morphology demonstrated that the Ni–B alloy was present in the form of spherical particles with an average size of around 200 nm; i.e., the Ni–B alloy was present in the ultrafine powders (See Figure 1). Figure 2 shows the XPS spectra of B 1s under the exposing efficiency. After fixing it to the sample holder, the sample was transferred to the pretreatment chamber immediately. In the sample was degassed under 1 × 10−6 Torr for 4 h to remove the volatile contaminants. Then the sample was transferred without contacting the atmosphere into the analyzing chamber in which sample heating can be achieved by using an electric resistance heater through a tantalum slice equipped in the manipulator. A WR63WRt25 thermocouple was attached to the back of the sample for temperature measurement and control. After the sample was slightly sputtered to remove some involatile contaminants, exposure to O2 was performed while holding the sample at a certain temperature. XPS depth profiling was carried out by using an ion sputtering gun operated at 3.0 kV, 10 mA, and 5 × 10−5 Pa of Ar to give a nominal sputtering rate of 2 Å/min, as calibrated via a Ta2O5 standard. The surface composition was obtained by fitting the XPS spectra of the corresponding elements in the alloys by considering their sensitivity factors. In the fitting, a Gaussian–Lorentzian line shape is employed assuming a linear background.

Notes

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alloying form with metallic Ni ($B^0$) corresponding to
in Figure 2a, the boron species in the fresh Ni were present in both the oxidized form ($B_2O_3$) and the
As the $B_2O_3$ species could be observed even through the
binding energies (BE) of 192.5 and 188.2 eV, respectively.

Conclusions.4,6
nickel, which was in good agreement with the previous
XPS, indicating partial electron-transfer from boron to
positively by 1 eV as confirmed by the angle-dependent
value of elemental boron,8 the BE of alloying boron shifted
2b
increase in the treating temperature, as shown in Figure
ratio of $B^0/B_3$odynamically at 200 °C.9 As shown in
exposure (1.8 $10^5$ L, 1 L = $1 \times 10^{-6}$ Torr s). As shown in
Figure 2a, the boron species in the fresh Ni–B sample were present in both the oxidized form ($B_2O_3$) and the

Table 1. Surface Composition of Ni–B Amorphous Alloy
under Different Treating Conditions

<table>
<thead>
<tr>
<th>treating conditions</th>
<th>atomic ratio</th>
<th>atomic ratio</th>
<th>atomic ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>slightly Ar$^+$ sputtered</td>
<td>$B^0/Ni$</td>
<td>$B^0 + (B^3)^Ni$</td>
<td>$B^0/B^3$</td>
</tr>
<tr>
<td>100 °C/1.8 $10^5$ L</td>
<td>9.7/90.3</td>
<td>16.9/83.1</td>
<td>52.7/47.3</td>
</tr>
<tr>
<td>150 °C/1.8 $10^5$ L</td>
<td>8.6/91.4</td>
<td>22.6/77.4</td>
<td>32.2/67.8</td>
</tr>
<tr>
<td>200 °C/1.8 $10^5$ L</td>
<td>8.7/91.3</td>
<td>28.3/71.7</td>
<td>24.1/75.9</td>
</tr>
<tr>
<td>250 °C/1.8 $10^5$ L</td>
<td>10.7/89.3</td>
<td>33.2/66.8</td>
<td>24.7/75.8</td>
</tr>
</tbody>
</table>

Figure 2. B 1s spectra of amorphous Ni–B alloy under different treating conditions: (a) fresh sample after Ar$^+$ sputtering for 30 min; (b) 100 °C, O$_2$ 1.8 $10^5$ L; (c) 150 °C, O$_2$ 1.8 $10^5$ L; (d) 200 °C, O$_2$ 1.8 $10^5$ L; (e) 250 °C, O$_2$ 1.8 $10^5$ L; (f) 320 °C, O$_2$ 1.8 $10^5$ L.

different treating temperature but with the same O$_2$
exposure (1.8 $10^5$ L, 1 L = $1 \times 10^{-6}$ Torr s). As shown in
Figure 2a, the boron species in the fresh Ni–B sample were present in both the oxidized form ($B_2O_3$) and the

No distinctive influence on the shape of the B 1s
sputtering for 30 min; (b) 100 °C, O$_2$ 1.8 $10^5$ L; (c) 150 °C, O$_2$ 1.8 $10^5$ L; (d) 200 °C, O$_2$ 1.8 $10^5$ L; (e) 250 °C, O$_2$ 1.8 $10^5$ L; (f) 320 °C, O$_2$ 1.8 $10^5$ L.

Figure 3. Ni 2p spectra of amorphous Ni–B alloy under different treating conditions: (a) fresh sample after Ar$^+$ sputtering for 30 min; (b) 100 °C, O$_2$ 1.8 $10^5$ L; (c) 150 °C, O$_2$ 1.8 $10^5$ L; (d) 200 °C, O$_2$ 1.8 $10^5$ L; (e) 250 °C, O$_2$ 1.8 $10^5$ L; (f) 320 °C, O$_2$ 1.8 $10^5$ L.

ratio ($B^0 + B^3^+)/Ni$ kept on increasing (from 16.9/83.1 at
100 °C to 87.5/12.5 at 320 °C) with the treating temper-
aturature, showing the diffusion of the boron species from the
bulk to the surface during the treatment of the Ni–B
amorphous alloy in O$_2$ atmosphere.

Figure 3 presents the XPS spectra in Ni 2p3/2 level of the
Ni–B amorphous alloy treated under the same
conditions given in Figure 2. One can see that, unlike B
species, all the Ni species in the Ni–B alloy were present
in the metallic state, corresponding to a BE of 853.0 eV.6
When treated in the O$_2$ atmosphere, no oxidation of the
metallic Ni occurred until $B^0$ species were consumed
completely. In contrast, severe oxidation of metallic Ni
was observed when the pure Ni powders were treated
under the same conditions. These results clearly dem-
onstrated that the existence of alloying boron could delay
the oxidation of metallic Ni. Thus a longer lifetime for the
Ni–B amorphous alloy catalyst was expected as compared to
the pure Ni powder catalyst in an oxygen-containing
ambient.9 Furthermore, in contrast to the B 1s spectra,
the Ni 2p3/2 intensity decreased gradually with an

increase in treatment temperature in O₂ atmosphere, showing a decrease in the surface content of Ni species, which was mainly attributed to the diffusion of B species from the bulk to the surface, as mentioned above.

The XPS spectra demonstrated that, after thorough consumption of the bulk B⁰, the metallic Ni could be oxidized even when the sample was exposed in 1.8 × 10⁵ L O₂ atmosphere at the temperature as low as 150 °C. One can see from Figure 4 that the XPS peak corresponding to the metallic Ni disappeared, while a new broad peak indicative of the oxidized Ni (Ni³⁺) appeared at a BE of 855.6 eV. When the Ni–B sample was treated with Ar⁺ sputtering, the oxidized Ni disappeared and the metallic Ni appeared gradually with the increase of sputtering time, showing that the oxidation of the metallic Ni was started from the surface and gradually developed into the bulk. Such phenomena were also found in the Ni–P amorphous alloy.¹¹

The above experimental results demonstrated that, in the Ni–B amorphous alloy, the alloying B could effectively protect metallic Ni from oxidation, which could be understood by considering the following factors. On one hand, the alloying B was oxidized prior to the metallic Ni in the Ni–B sample. This may be partially ascribed to the electronic interaction between the alloying B and metallic Ni. As mentioned above, the XPS characterizations demonstrated that the alloying B donated partial electrons to metallic Ni. The DFT calculation by using the Ni₁₅B₁₅ cluster model further confirmed partial electron transfer from the 2s orbital of the B atom to 4s and/or 4p orbital of the Ni atom (the significant amount of B_{2}O₃ not considered in this model was due to its actual property in the alloy as discussed in the following).³ Thus, in the Ni–B amorphous alloy, the metallic Ni was electron-enriched,

while the alloying B was electron-deficient. Owing to the lone electron pair on the oxygen atom, the electron-enriched Ni would repel O₂, while the electron-deficient B would attract O₂ when the Ni–B sample contacted with O₂, making Ni free from oxidation. As we know, the affinity of boron for oxygen is larger than that of nickel (ΔH of B₂O₃ and NiO are −302.0 and −58.4 kcal/mol, respectively).¹² Moreover, the theoretical calculations using the DFT method also confirmed that oxygen atoms would preferentially react with boron in the Ni₅B₂ or Ni₁₅B₁₅ cluster, leading to the oxidation of boron to form B₂O₃. On the other hand, B⁰ may diffuse automatically from the bulk to the surface during the oxidation treatment to compensate for its oxidation on the surface. Such diffusion would continue until all the bulk B⁰ was consumed. From 100 to 150 °C, the B⁰/B³⁺ ratio decreased rapidly, since the oxidation of B⁰ was faster than its diffusion. From 150 to 250 °C, the B⁰/B³⁺ ratio remained unchanged, since the diffusion of B⁰ was equivalent to or slightly faster than its oxidation. Then the B⁰/B³⁺ ratio decreased again since most of the B⁰ in the bulk was consumed. Thus, the oxidation of metallic Ni occurred only after the bulk B⁰ was consumed completely.

The antioxidation property of the Ni–B amorphous alloy played a key role in keeping its activity during the hydrogenation reactions in the presence of trace O₂. This could be confirmed by comparing the catalytic performance of the Ni–B amorphous alloy with that of Raney Ni during liquid-phase selective hydrogenation of cyclopentadiene (CPD). As shown in Table 2, when the Ni–B sample was exposed to 6 × 10⁴ L of oxygen at 100 °C until all the B⁰ was oxidized, its specific activity (R_{H₂}⁻/S_{act}, the hydrogen consumption rate per second and per gram of Ni) decreased by about 50%. However, the Raney Ni catalyst lost its activity completely when it was treated under the same conditions. The disappearance of the activity of the Raney Ni catalyst could be understood by considering the complete oxidation of metallic Ni, since its active surface area (S_{act}) decreased to 0. However, the aforementioned XPS characterizations demonstrated that, owing to the presence of the alloying B, no significant oxidation of metallic Ni in the Ni–B amorphous alloy occurred under the present conditions. In addition, no significant change in S_{act} was observed, showing that the resulting B₂O₃ did not cover the Ni active sites but only served as the support of these Ni active sites. To exclude the effect of metal dispersion, the areal activity (R_{H₂}⁻/A, the hydrogen consumption rate per second and per meter square of active surface area) was also calculated. As shown in Table 2, the R_{H₂}⁻ decreased rapidly after the Ni–B sample was treated in O₂ atmosphere. Thus, the decrease in the specific
activity ($R_{O_{2}}^m$) of the Ni–B amorphous alloy during the oxidation treatment was mainly attributed to the change of the feature of the Ni active sites. As the alloying B would be oxidized in the presence of trace $O_2$, the Ni–B amorphous alloy would decompose into pure metallic Ni dispersed on $B_2O_3$ support. Our previous papers have proven that the Ni–B amorphous alloy exhibited higher activity than the pure metallic Ni powders, which was explained on the basis of both the electronic effect and the structural effect. The electronic effect referred to the electronic interaction between metallic Ni and alloying B, making Ni electron-enriched, which favored the adsorption of hydrogen and CPD molecules. The structural effect referred to, besides the unique amorphous structure of the Ni–B alloy, the structural modification of the alloying B on the Ni active sites, such as the highly unsaturated property and the strong synergistic effect between different Ni active sites. Thus, when the Ni–B amorphous alloy was treated under ambient $O_2$ atmosphere, the decrease in its activity during the CPD selective hydrogenation could be mainly attributed to the decomposition of the Ni–B amorphous alloy owing to the oxidation of the alloying B.

**Conclusion**

As a conclusion, our XPS results clearly demonstrated the strong antioxidation ability of the amorphous Ni–B alloy for the first time, in which the alloying B plays an essential role. Alloying B preferentially absorbed $O_2$ and those in the bulk would diffuse to the surface when the surface elemental boron was consumed, preventing nickel from oxidation. Such an attractive property of the amorphous Ni–B alloy originating from its special electronic structure makes it highly promising for practical catalytic processes.

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