Notes

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.[1] 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 special structural characteristics and surface properties. Based on modern techniques, such as extended X-ray absorption fine structure (EXAFS),[2] density function theory (DFT),[3] X-ray photoelectron spectroscopy (XPS),[4] etc., it is accepted that boron donates electrons to metallic nickel, and the presence of boron results in the short-range ordering and long-range disordering structure. In this paper, by means of XPS and using oxygen as the probing molecule, we unambiguously revealed that the alloying boron can readily prevent the oxidation of metallic nickel, which is a highly desirable property in practical catalytic processes.

Experimental Section

The Ni−B sample was prepared by a chemical reduction method. Details can be found elsewhere.[5] First, 1.0 mol dm^{-3} aqueous $Ni(CH_3COO)_2$ solution was added dropwise with 1.0 mol dm^{-3} aqueous KBH_4 in an ice−water bath under vigorous agitation. Then the mixture was heated to 90 °C and the black precipitate obtained was washed under open air with distilled water until pH = 7.0. The bulk atomic composition of the as-prepared sample was $Ni_{78}B_{22}$.

The XPS spectra were collected on an improved PHI 5000C ESCA system by using Al Kα radiation ($h\nu = 1486.6$ eV) with a base pressure of 1×10^{-9} Torr. Before the experiment, the Ni−B sample was pressed into a self-supported 1 × 10 mm disk and soaked in 99% ethanol to avoid the oxidation. The spectrometer was operated at 14 kV and 250 W with the pass energy of 46.95 eV. The spectrometer was calibrated with Cu 2p3/2 at a binding energy (BE) of 932.67 eV, Cu KLL at 567.96 eV, and Cu 3s at 75.13 eV. The analysis area was fixed at 4 × 10 mm. The accuracy of the BE values were within ±0.2 eV.

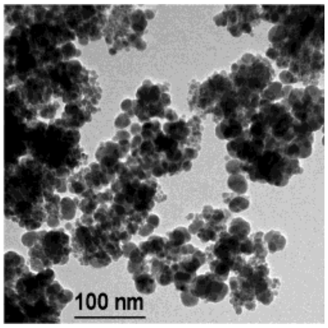

Figure 1. TEM photograph of the as-prepared amorphous Ni−B alloy.

The PHI 5000C ESCA system was modified for the XPS experiments. First, it was equipped with a pretreatment chamber for the sample degassing or prereaction, second, an Ar^+ sputtering gun was assembled for depth profiling, third, a high-temperature 5-dimensional specimen manipulator supplied a temperature on the sample of up to 800 K, and last, pure oxygen could be introduced to the sample surface through an O_2 doser which could be moved about 5 mm from the sample in order to increase the exposing efficiency. After fixing it to the sample holder, the sample was transferred to the pretreatment chamber immediately. In there 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 WRe3/WRe25 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 O_2 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 Ta_2O_5 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

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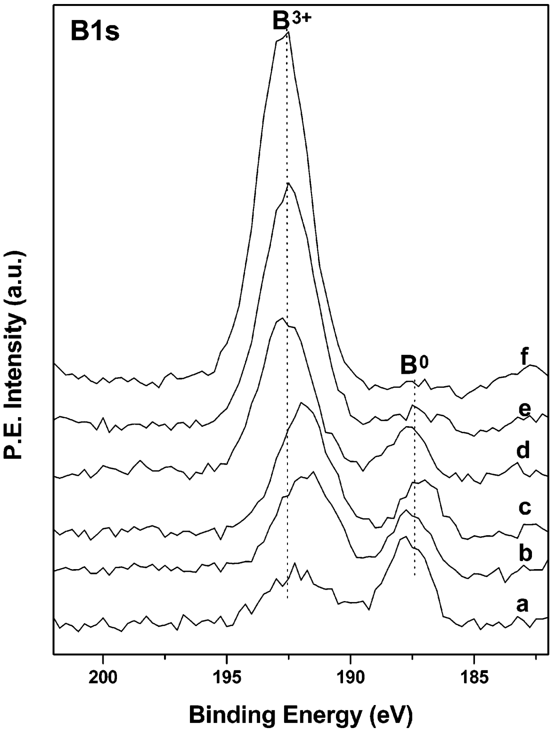

Figure 2. B 1s spectra of amorphous Ni−B alloy under different treating conditions: (a) fresh sample after Ar^+ sputtering for 30 min; (b) 100 °C, O_2 1.8×10^5 L; (c) 150 °C, O_2 1.8×10^5 L; (d) 200 °C, O_2 1.8×10^5 L; (e) 250 °C, O_2 1.8×10^5 L; (f) 320 °C, O_2 1.8×10^5 L.

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 alloying form with metallic Ni (B^0) corresponding to binding energies (BE) of 192.5 and 188.2 eV, respectively. As the B_2O_3 species could be observed even through the prolonged Ar^+ sputtering, one can conclude that the presence of such species was not due to the surface oxidation of the Ni−B amorphous alloy. Angle-dependent XPS results also supported this conclusion. Perhaps they resulted from the hydrolysis of borohydride, since the reduction of nickel ions by borohydride was performed in an aqueous solution.[7] Compared with the standard BE value of elemental boron,[8] the BE of alloying boron shifted positively by 1 eV as confirmed by the angle-dependent XPS, indicating partial electron-transfer from boron to nickel, which was in good agreement with the previous conclusions.[4,6]

No distinctive influence on the shape of the B 1s spectrum could be identified when the Ni−B sample was exposed to O_2 at room temperature. The relative atomic ratio of B^0/B^{3+} was determined as 52.7/47.3. With an increase in the treating temperature, as shown in Figure 2b−f and Table 1, the relative atomic ratio B^0/B^{3+} decreased abruptly until 24/76 at 150 °C. Then it remained unchanged up to 250 °C and, finally, decreased again until 0 when the temperature was further increased. However, unlike the change of the B^0/B^{3+} ratio, the relative atomic 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 temperature, 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.

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

	atomic ratio		
treating conditions	B^0/Ni	$(B^0 + B^{3+})/Ni$	B^0/B^{3+}
slightly Ar^+ sputtered	9.7/90.3	16.9/83.1	52.7/47.3
100 °C/1.8×10^5 L	8.6/91.4	22.6/77.4	32.2/67.8
150 °C/1.8×10^5 L	8.7/91.3	28.3/71.7	24.1/75.9
200 °C/1.8×10^5 L	10.7/89.3	33.2/66.8	24.2/75.8
250 °C/1.8×10^5 L	16.7/83.3	44.4/55.6	25.1/74.9
250 °C/3.6×10^5 L	14.8/85.2	48.4/51.6	18.5/81.5
300 °C/1.8×10^5 L	17.8/82.2	73.6/26.4	7.8/92.2
320 °C/1.8×10^5 L	0/100	87.5/12.5	0/100

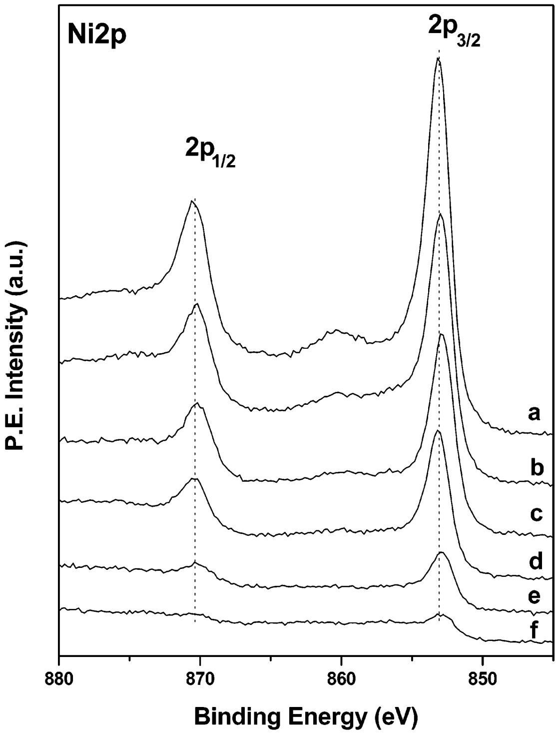

Figure 3. Ni 2p spectra of amorphous Ni−B alloy under different treating conditions: (a) fresh sample after Ar^+ sputtering for 30 min; (b) 100 °C, O_2 1.8×10^5 L; (c) 150 °C, O_2 1.8×10^5 L; (d) 200 °C, O_2 1.8×10^5 L; (e) 250 °C, O_2 1.8×10^5 L; (f) 320 °C, O_2 1.8×10^5 L.

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 demonstrated 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

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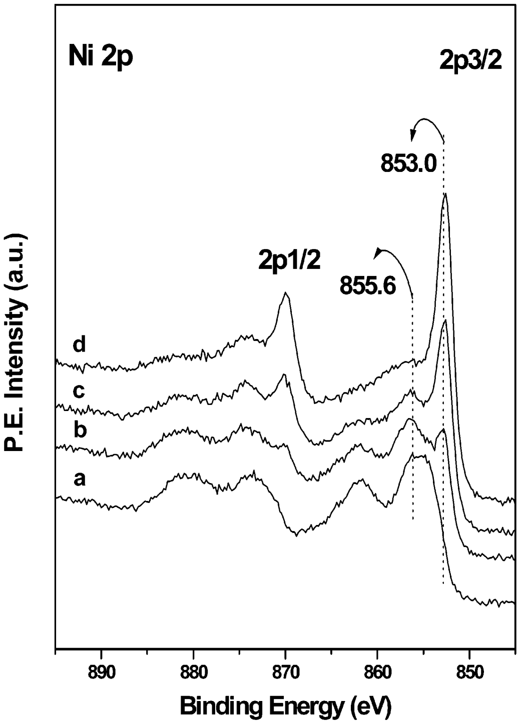

Figure 4. Ni 2p spectra of amorphous Ni−B alloy under different treating conditions after thorough consumption of the bulk B^0: (a) 1.8×10^5 L of O_2 at 150 °C; (b) sputtered for 5 min; (c) sputtered for 10 min; (d) sputtered for 15 min.

increase in treatment temperature in O_2 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 B^0, the metallic Ni could be oxidized even when the sample was exposed in 1.8×10^5 L O_2 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 (Ni^{3+}) appeared at a BE of 855.6 eV.[10] 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 Ni_mB_2 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_2O_3 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 O_2, while the electron-deficient B would attract O_2 when the Ni−B sample contacted with O_2, making Ni free from oxidation. As we know, the affinity of boron for oxygen is larger than that of nickel (ΔH_f of B_2O_3 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 Ni_4B_2 or Ni_8B_2 cluster, leading to the oxidation of boron to form B_2O_3. On the other hand, B^0 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 B^0 was consumed. From 100 to 150 °C, the B^0/B^{3+} ratio decreased rapidly, since the oxidation of B^0 was faster than its diffusion. From 150 to 250 °C, the B^0/B^{3+} ratio remained unchanged, since the diffusion of B^0 was equivalent to or slightly faster than its oxidation. Then the B^0/B^{3+} ratio decreased again since most of the B^0 in the bulk was consumed. Thus, the oxidation of metallic Ni occurred only after the bulk B^0 was consumed completely.

Table 2. Effects of Oxygen Treatment on the Catalytic Activity of Raney Ni and the Ni−B Amorphous Alloy[a]

catalysts	$R^m_{H_2}$,[c] mmol/s g of Ni	S_{act},[d] m²/g	$R^S_{H_2}$,[e] mmol/s m²
Raney Ni	0.350	21	0.017
Raney Ni[b]	∼0	0	∼0
Ni−B amorphous alloy	0.468	7.2	0.065
Ni−B amorphous alloy[b]	0.229	7.9	0.029

[a] Liquid phase selective hydrogenation of cyclopentadiene to cyclopentene. [b] After treatment with 6×10^4 L of O_2 at 100 °C. [c] The specific activity, the hydrogen consumption rate per second and per gram Ni. [d] The specific surface area, determined by the pulse hydrogen chemisorption method. [e] The areal activity, the hydrogen consumption rate per second and per meter square of active surface area.

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 O_2. 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 6×10^4 L of oxygen at 100 °C until all the B^0 was oxidized, its specific activity ($R^m_{H_2}$, 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 B_2O_3 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 ($R^S_{H_2}$, the hydrogen consumption rate per second and per meter square of active surface area) was also calculated. As shown in Table 2, the $R^S_{H_2}$ decreased rapidly after the Ni−B sample was treated in O_2 atmosphere. Thus, the decrease in the specific

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activity ($R^{m}_{H_2}$) 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.[5,6,8] 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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