Excellent Activity of Ultrafine Co-B Amorphous Alloy Catalyst in Glucose Hydrogenation

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The ultrafine Co-B amorphous alloy, doped or undoped with Mo or W, were prepared by chemical reduction with borohydride. Its catalytic performance in liquid phase hydrogenation of glucose to sorbitol has been investigated, which revealed (i)the higher activity than that of crystalline Co and the Ni-based catalysts, and (ii)the promoting effect of Mo and W dopants on the activity.

The hydrogenation of glucose to sorbitol is of great industrial importance because sorbitol is a valuable polyol used as additives in foods, drugs, and cosmetics or as a synthon for the preparation of vitamin C.[1] The most frequently used catalyst in the above hydrogenation is Raney Ni, but it is a fragile catalyst and a great number of attempts have been made to replace it by more resistant supported and unsupported catalysts.[2] Recently, the metal-metalloid amorphous alloy catalysts have been widely studied owing to their higher activity and better selectivity in various hydrotreating processes.[3-4] Most studies are focused on the Ni-based amorphous alloy catalysts, while the Co-based amorphous alloy catalysts cause much less attention.[5,6,7] The glucose hydrogenation over amorphous alloy catalysts has never been reported so far. In the present paper, we reported a novel ultrafine Co-B amorphous alloy prepared by chemical reduction. The as-prepared catalyst exhibited higher activity than not only the corresponding crystalline Co-B alloy but the Ni-based catalysts as well, such as Raney Ni and even the ultrafine Ni-B amorphous alloy catalysts, possibly owing to its higher affinity to oxygen. The promoting effect of Mo or W additive on the activity was also observed and investigated.

The Co-B amorphous alloy was prepared by adding dropwise 10 ml 1.0 M KBH_4 alkali solution to 10 ml 0.2 M $Co(Ac)_2$ solution at 273 K. The resulted black solid was then washed thoroughly with distilled water until pH = 7. Since the Co-B alloy is easy to be oxidized in air, it was kept in H_2O and used for characterization and activity test within 24 h. The ultrafine pure Co particles were prepared by the chemical reduction of $Co(Ac)_2$ by NH_2NH_2 alkaline solution at 363 K. The crystalline Co-B alloy was obtained by treating the fresh Co-B sample at 723 K in N_2 flow for 2.0 h. The promoted Co-B catalysts with Mo or W metal were prepared by using mixed Na_2WO_3 and $Co(Ac)_2$ or Na_2MoO_3 and $Co(Ac)_2$ in the solution before KBH_4 reduction. Raney Ni was available commercially from a sorbitol production factory in China. No further activation was attempted in the present work.

The TEM pictures revealed that the fresh Co-B sample was present in the spherical particles with the average diameter between 60 and 100 nm. Its amorphous structure was determined by XRD, as shown in Figure 1. Besides a small peak at 25° corresponding to the amorphous boron oxides, only one broad peak around $2\theta(\text{Cu K}\alpha) = 45°$ appeared, indicating a typical amorphous structure.[8] After being treated at high temperature, a lot of sharp diffractional peaks appeared, showing the occurrence of crystallization in which most of the Co-B alloy was decomposed into pure Co in well crystalline state and B in totally amorphous state. The amorphous structure was further confirmed by EXAFS, from which, the RDF curves could be obtained, as shown in Figure 2. Only one peak around R = 6.0 Åwas observed for the fresh Co-B sample, indicating it had no long-range but only short-range ordering structure. The shoulder peak was possibly attributed to the alloying B with Co metal. After being treated at high temperature, the intensity of the original peak greatly increased and a few of new peaks at longer range appeared, while the shoulder peak disappeared. Those results demonstrated that amorphous structure transferred to the highly ordering crystalline structure and the Co-B alloy decomposed at high

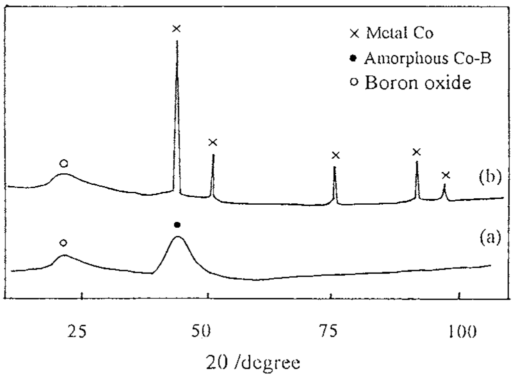

Figure 1. XRD patterns of Co-B samples (a) fresh (b) after being treated at 723 K in N_2 flow for 2.0 h.

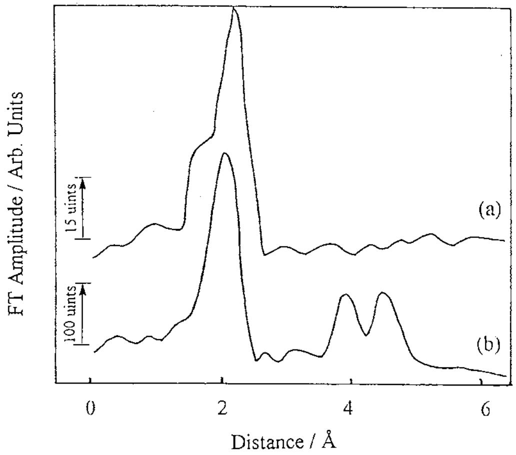

Figure 2. RDF curves of Co-B samples (a) fresh (b) after being treated at 723 K in N_2 flow for 2.0 h.

temperature. Similar results were also obtained for the doped Co-B samples, showing that effect of Mo or W additive on the amorphous structure could be neglected. However, the DSC analysis showed that the thermal stability of the Co-B amorphous alloy was greatly improved by those additives.

The XPS spectra revealed that both Co and B were present in two states. In B_{1S} level, it was found that besides small amount of boron oxide, most of B species were in elemental state corresponding to the binding energy(BE) of 188.2 eV. From $Co2P_{3/2}$ level, one can also see both the elemental Co at BE of 777.7 eV and the oxidized Co at BE of 780.9 eV. In comparison with the standard metal Co and amorphous boron powder, the BE of elemental B shifted positively about 1.0 eV while the BE of elemental Co shifted negatively about 0.5 eV. Therefor, it can be concluded that partial electron transferred from elemental B to metal Co in the Co-B amorphous alloy, making Co electron-rich. After being treated at high temperature, the XPS spectra of the crystallized Co-B sample were almost the same as those of pure Co and B. No significant electronic interaction between Co and B was observed, since most of the Co-B alloy has been decomposed, as confirmed by XRD in Figure 1.

The composition and the surface area of the as-prepared catalysts were determined by ICP analysis and BET method, respectively, as summarized in Table 1.

Liquid phase hydrogenation of glucose was performed at 393 K and 4.0 MPa in a stainless steel autoclave, which contained 1.0 g catalyst and 50 ml 50%(w/w) glucose aqueous solution. During the hydrogenation, the reaction mixture was stirred vigorously to eliminate the diffusion effects. Each reaction was lasted for 6.0 h. The initial hydrogenation activity was estimated by monitoring the drop of the pressure within the initial 1.0 h which was then turned to be the H_2 uptake rate(R_{H_2} = mmol/h·g) according to the ideal gas equation. The reaction products were analyzed by a gas chromatography equipped with a 25 m OV 101 capillary column and a FID, in which the oven temperature was programmed at a ramp of 4 K/min from 353 to 533 K. The sorbitol was the only product identified, showing that the selectivity is nearly 100%. The reaction was repeated for several times to evaluate the lifetime of the catalysts. The content of Co dissolved in the mixture after each cycle of reaction was also analyzed by ICP to determine the loss of active sites during the reaction. It was found that no significant decrease in activity of Co-B amorphous alloy catalyst was observed after reaction for 5 cycles and only less than 1.0 ppm Co was determined in the reaction mixture, showing the excellent durability of the Co-B amorphous alloy catalyst. By determining the remained glucose in the mixture after reaction for 6.0 h with Fehlings agent, the reaction conversion in each reaction was calculated and also listed in Table 1, which showed an excellent agreement with the H_2 uptake rate.

Table 1. Properties of the as-prepared samples

Catalyst	S_{BET} (m^2/g)	R_{H_2} (mmol/h·g)	Conv. (%)
$Co_{75.4}B_{24.6}$	26.2	26.8	89.0
$^aCo_{75.4}B_{24.6}$	19.5	7.8	23.5
$Co_{74.7}W_{1.2}B_{24.1}$	43.6	39.6	95.8
$Co_{74.8}Mo_{0.5}B_{24.7}$	35.0	31.0	90.8
Co	25.2	16.2	52.4
$Ni_{76.0}B_{24.0}$	32.0	9.0	27.0
Raney Ni	106.0	3.6	17.0

[a]After being treated at 723 K for 2.0 h in N_2 flow.

From Table 1, one can see that the fresh Co-B amorphous alloy exhibited higher activity in comparison with its corresponding crystalline form or pure Co catalyst and other Ni-based catalysts, such as Raney Ni and Ni-B amorphous alloy catalysts. According to the XRD patterns, as shown in Figure 1, after being crystallized at high temperature, the Co-B alloy was almost completely decomposed into crystalline metal Co and amorphous B. Therefore, the superior hydrogenation activity of amorphous Co-B alloy over its corresponding crystalline Co-B or the pure Co catalysts is mainly ascribed to its amorphous structure and its alloying B. On one hand, the high concentration of coordinately highly unsaturated sites and the strong metal-metal or metal-metalloid corporation in the amorphous structure promoted the hydrogenation activity.[4] On the other hand, the XPS spectra showed that the alloying B donated electron to metal Co, making Co electron-rich, which was favorable for the adsorption of the C=O double bond. The higher activity of Co-B amorphous alloy than that of Ni-B amorphous alloy and Raney Ni catalysts is possibly attributed to the larger affinity of Co to oxygen in C=O group than that of Ni as already reported in previous papers.[9,10] According to the XPS spectra, the Mo and W additives in the Co-B alloy were mainly present in their oxidized states. They have an influence on the enhancement of the specific surface area. Therefore, the promoting effects of those additives on the hydrogenation activity of Co-B amorphous alloy could be understood by considering the high distribution of Co active sites in those oxides. On the other hand, the metal dopant(Mo or W) at the state of a very divided oxide had a tendency to absorb the electron-rich oxygen in aldo group(C=O).[1,11] The hydrogen molecule would be dissociated on the Co surface and would migrate on the dopant oxide surface to the adsorbed aldo group where the reaction could take place. Further studies are being underway.

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References and Notes

1 P. Gallezot, P. J. Cerino, B. Blanc, G. Fleche, and P. Fuertes, *J. Catal.*, **146**, 93(1994).

2 J. Volf and J. Pasek, *Stud. Surf. Sci. Catal.*, **27**, 105(1986).

3 A. Molnar, G. V. Smith, and M. Bartok, *Adv. Catal.*, **36**, 329(1988).

4 J. F. Deng, H. X. Li, and W. J. Wang, *Catal. Today, in press.*

5 Y. Z. Chen and J. S. Wu, *J. Chin. I. Ch. E.*, **23**, 119(1992).

6 A. H. Uken and C. H. Bartholomew, *J. Catal.*, **65**, 402(1980).

7 J. F. Deng, J. Yang, S. Sheng, H. Chen, and G. Xiong, *J. Catal.*, **150**, 434(1994).

8 S. Yoshida, H. Yamashita, T. Funabiki, and T. Yonezawa, *J. Chem. Soc. Faraday Trans. 1*, **80**, 1435(1984).

9 M. Kajitani, N. Suzuki, T. Abe, Y. Kaneko, K. Kasuya, K. Takahashi, and A. Sugimori, *Bull. Chem. Soc. Jpn.*, **52**, 2343(1979).

10 Y. Nitta, T. Imanaka, and S. Teranishi, *Bull. Chem. Soc. Jpn.*, **53**, 3154(1980).

11 C. D. Bellefon and P. Fouilloux, *Catal. Rev.-Sci. Eng.*, **36**, 459(1994).