Structural Modification towards Metastable States and Catalytic Activity of an Amorphous Ni–B Alloy

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An amorphous Ni–B alloy pretreated thermally between 350 and 410 °C exhibits an unusual change in catalytic activity which is related to the presence of metastable structures between amorphous and crystalline states.

In a previous study on catalysis by amorphous alloys, we observed that the crystallization of amorphous Ni–P and Ni–B alloys resulted in a significant decrease in catalytic activity for the hydrogenation of alkenes.[1,2] A similar effect on crystallization was observed in the hydrogenations of carbon monoxide over iron or nickel based amorphous alloys,[3,4] and of *cis*-cyclododecene and (+)-apopinene over Pd–Si glasses.[5,6] In these studies the catalytic activity over amorphous alloys was compared with those of the fully crystallized alloys prepared by heating the amorphous alloys at very high temperatures, but the structural change from amorphous to fully crystallized states may occur stepwise *via* metastable states. We report here the preparation and catalytic activity of a Ni–B alloy in a metastable state and the importance of the structural modification of the amorphous alloy to the pre-crystallization state for generation of the maximum activity.

The hydrogenolyses of ethane and cyclopropane (structure sensitive reactions)[7] and the hydrogenations of ethene and isoprene (structure insensitive reactions) were carried out over a Ni_{62}–B_{38} amorphous alloy[1,2] to examine the structural changes of surface active sites caused by the thermal treatment of the alloy at different temperatures. The amorphous alloy was pretreated in the following order: (1) with 1.5 mol dm^{-3} HNO_3, (2) with heat at a temperature in the range 300—510 °C under hydrogen (100 Torr) for 2 h, (3) with heat under oxygen (50 Torr) at 200 °C for 1 h, and (4) with heat under

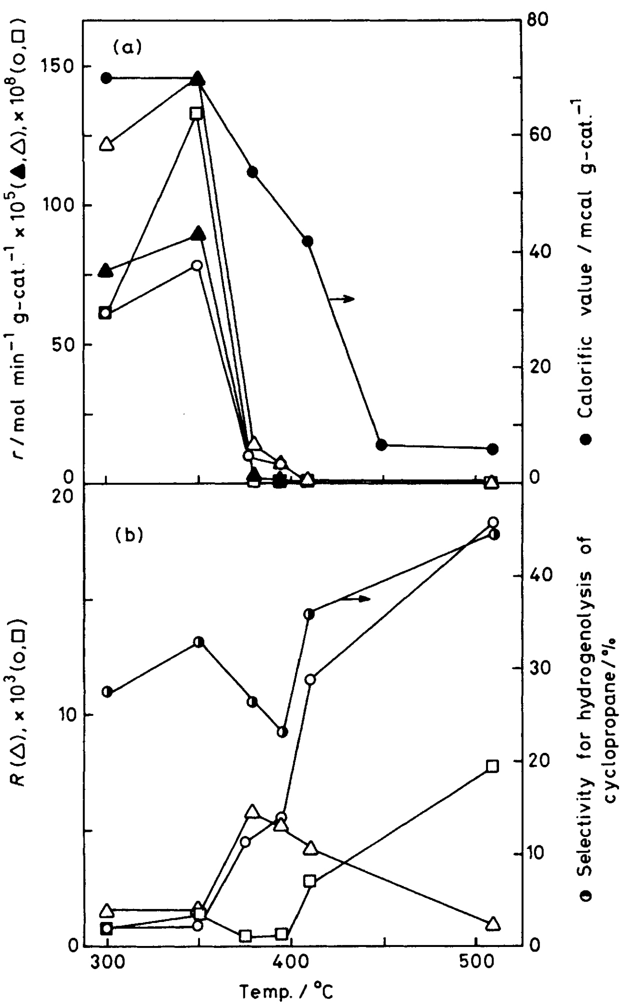

Figure 1. Effect of thermal treatment of an amorphous Ni–B alloy on the catalytic activity. (a) r = Initial rate; ▲ hydrogenation of ethene (P_{H_2} 145, $P_{C_2H_4}$ 55 Torr, at 100 °C), △ hydrogenation of isoprene (P_{H_2} 145, $P_{C_5H_8}$ 55 Torr, at 150 °C), □ hydrogenolysis of ethane (P_{H_2} 80, $P_{C_2H_6}$ 40 Torr, at 330 °C), ○ hydrogenolysis, accompanied with hydrogenation, of cyclopropane (P_{H_2} 80, $P_{C_3H_6}$ 40 Torr, at 300 °C); ● Calorific value (1 cal = 4.18 J). (b) R = Relative initial rate against the initial rate of hydrogenation of ethene; △ isoprene, □ ethane, ○ cyclopropane; ◑ Selectivity for hydrogenolysis in the reaction of cyclopropane.

hydrogen (100 Torr) at 300 °C for 2 h. The reactions were carried out in a conventional closed circulation system and the products were analysed by g.l.c. Initial rates of hydrogenolysis and hydrogenation were estimated from changes in the initial pressure and conversion, respectively. Differential thermal analyses (D.T.A.s) and X-ray diffraction (X.R.D.) studies were carried out to examine the amorphous and crystalline states of the pretreated alloys.

Figure 1(a) shows the effect of the thermal pretreatment temperature on the catalytic activity and on the calorific values estimated from D.T.A. The calorific values, which correspond to the heats evolved in the change from amorphous or metastable states to the fully crystallized state, began to decrease with the alloy pretreated at >350 °C. The catalytic activities increased with the treatment temperature up to 350 °C and decreased abruptly on treatment at the higher temperature. In the X.R.D. pattern, the alloy pretreated at 350 °C exhibited no peaks attributable to crystalline compounds, but those pretreated at 380 and 410 °C did. Intense peaks were observed in the latter case, along with the broad halo due to the presence of the amorphous alloy. Figure 1(b) shows the effect of the pretreatment temperature on the relative catalytic activities of the hydrogenolysis of ethane, hydrogenolysis of cyclopropane accompanied with hydrogenation, and hydrogenation of isoprene to that of the hydrogenation of ethene. The effect on the selectivity for hydrogenolysis in the reaction of cyclopropane is also shown. These values also exhibited great changes in trend between 350 and 410 °C.

The amorphous Ni–B alloy which exhibits the maximum activity does not involve crystalline compounds, but it is suggested that some rearrangement of the amorphous structure towards crystallization starts at <350 °C and the structure in the precrystallization state is the most favourable for catalytic activity. The catalytic activity of the amorphous alloy decreases greatly between 350 and 410 °C although the X.R.D. and D.T.A. data indicate that the alloy consists of not only the crystalline compounds but also the amorphous alloy. This suggests that local rearrangement of the surface structure takes place prior to full crystallization of the bulk alloy, reducing the number of the surface active sites. Since the structure sensitive reaction involves multiple adsorption,[7] the increase in the relative activity of hydrogenolysis to hydrogenation at >350 °C in Figure 1(b) indicates that the change of the surface structure involving the aggregation of nickel atoms is promoted by the treatment at the higher temperature. The aggregation of nickel atoms and the increase in the surface content of boron oxides, which was observed in the e.s.c.a. spectra,[8] reduce the number of active sites, and the aggregation eventually brings about the crystallization of the bulk alloy, leading to the low catalytic activity.

The change in activity of the hydrogenation of isoprene relative to that of ethane, exhibiting a maximum value at 380 °C, is unexpected because both reactions are structure insensitive. The selectivity for the hydrogenolysis of cyclopropane to ethane and methane exhibits a characteristic minimum value at 395 °C. These results observed with alloys pretreated between 350 and 410 °C seem to reflect delicate structural changes between amorphous and crystalline alloys, but further information about the structure of the metastable states is necessary for the explanation of the results above.

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References

1 S. Yoshida, H. Yamashita, T. Funabiki, and T. Yonezawa, *J. Chem. Soc., Chem. Commun.*, 1982, 964.
2 S. Yoshida, H. Yamashita, T. Funabiki, and T. Yonezawa, *J. Chem. Soc., Faraday Trans. 1*, 1984, 1435.
3 A. Yokoyama, H. Komiyama, H. Inoue, T. Masumoto, and H. M. Kimura, *J. Catal.*, 1981, **68**, 355.
4 A. Yokoyama, H. Komiyama, H. Inoue, T. Masumoto, and H. M. Kimura, *J. Chem. Soc. Jpn.*, 1982, **2**, 199.
5 G. V. Smith, W. E. Brower, M. S. Matyjaszczyk, and T. L. Pettit, in 'Proceedings of the 7th International Congress on Catalysis,' eds. T. Seiyama and K. Tanabe, Elsevier, Amsterdam, 1981, Part 1, p. 335.
6 G. V. Smith, O. Zahraa, A. Molnar, M. M. Khan, B. Rihter, and W. E. Brower, *J. Catal.*, 1983, **83**, 238.
7 V. Ponec and W. M. H. Sachtler, in 'Proceedings of the 5th International Congress on Catalysis,' ed. J. W. Hightower, North-Holland Publishing Company, Amsterdam, 1973, vol. 1, p. 645; J. H. Sinfelt, J. L. Carter, and D. J. C. Yates, *J. Catal.*, 1972, **24**, 283; J. M. Beelen, V. Ponec, and W. M. H. Sachtler, *ibid.*, 1973, **28**, 376; J. A. Dalmon and D. A. Marin, *ibid.*, 1980, **66**, 214.
8 H. Yamashita, T. Funabiki, and S. Yoshida, unpublished result.