

Hydrogenation of Olefins over Amorphous Ni-P and Ni-B Alloys Prepared by the Rapid Quenching Method

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Amorphous Ni-P and Ni-B alloys pretreated successively with dilute nitric acid, oxygen, and hydrogen are highly active for the hydrogenation of olefins; mono-olefins are more readily hydrogenated than diolefins, but the former are not hydrogenated in the presence of the latter, reflecting the stronger adsorption of the latter.

Ni-P and Ni-B alloys, known as useful hydrogenation catalysts, are usually prepared by chemical reduction of the metal salts, and it has been reported that the catalysts are formed in an amorphous state when the reductions are performed under mild conditions.^{1,2} However, the homogeneity of the state and its role in catalysis are uncertain. Recently, the rapid quenching method has been developed to prepare highly homogeneous amorphous metal alloys,³ but the catalytic properties of the alloys have been little studied.^{4,5} We report that amorphous Ni-P and Ni-B alloys are highly active for the hydrogenation of olefins, compared with the crystalline Ni-P and Ni-B compounds.

Amorphous Ni-P(Ni₈₁P₁₉) and Ni-B(Ni₆₂B₃₈) were prepared by the rapid quenching method as ca. 5 mm wide and 10–20 μm thick ribbons. The Ni-P and Ni-B alloys start to crystallize at 647 K and 783 K, respectively (differential thermal analysis), but both hold the amorphous state even after treatment with hydrogen at 573 K for 10 h. The Brunauer–Emmett–Teller (BET) surfaces of these alloys were 0.12 m² g⁻¹ for Ni-P and 0.094 m² g⁻¹ for Ni-B (measured by krypton physisorption at 77 K). Hydrogenation of olefins was carried out in a conventional closed circulation system at 20 kPa. Initial rates were estimated from the initial pressure change and products were analysed by g.l.c.

The virgin alloys showed no activity for the hydrogenation of olefins even after the hydrogen reduction of the alloys at 573 K for 6 h, but successive treatments of the alloys with dilute HNO₃, oxygen at 373–523 K, and hydrogen at 570 K brought about high catalytic activity. As shown in Table 1, the initial rate of hydrogenation over Ni-P decreased with increasing number of methyl substituents and diolefins were more difficult to hydrogenate than mono-olefins. The differ-

ences in the initial rates for the hydrogenation of olefins over Ni-B were not significant. Isomerization of the butenes was observed during the hydrogenation. Activities of crystallized Ni-P and Ni-B were studied for comparison. The former was less active than the amorphous Ni-P and the latter exhibited very little activity under the conditions employed. The decrease in activity probably results from a change in the surface electronic state or chemical composition of the surface, because the BET surface areas of the crystallized catalysts (0.12 m² g⁻¹ for Ni-P and 0.11 m² g⁻¹ for Ni-B) were essentially the same as those of the amorphous catalysts.

In the hydrogenation of buta-1,3-diene, but-1-ene was the main product (Table 2). The crystallization of alloys did not affect the selectivity. The product composition is similar to that over nickel phosphate on alumina reduced by hydrogen at 673 K, but different from that over the phosphate reduced at 923 K² and that over Raney Ni.⁶ The selectivity was constant until the conversion level of buta-1,3-diene had reached 95%, showing that no competitive hydrogenation and isomerization of butenes proceeded in the presence of buta-1,3-diene. This suggested stronger adsorption of buta-1,3-diene than of butenes, supported by the first and zeroth order dependences of the rate on hydrogen and buta-1,3-diene, respectively.

The effects of the pretreatments on the amorphous alloys were studied by observing ESCA spectra, which revealed that (i), treatment with dilute nitric acid was effective to remove the stable surface oxide layer, (ii), treatment with oxygen resulted in the partial oxidation of Ni, P, and B, and (iii), treatment with hydrogen reduced Ni ions to a metal state but did not reduce the oxidised P and B. The electron density of Ni atoms after the above treatments was suggested to be

Table 1. Initial rates in the hydrogenation of olefins over Ni-P and Ni-B.

Catalyst	Initial rate ^a /kPa min ⁻¹				
	ethene	propene	<i>cis</i> -but-2-ene	buta-1,3-diene	isoprene
Ni-P, amor. ^b	13.89	3.62	0.37	0.23	0.05
Ni-P, crys. ^c	8.79	2.47	0.30	0.08	0.01
Ni-B, amor. ^d	0.75	0.57	0.12	0.58	0.31
Ni-B, crys. ^e	<0.01	—	—	<0.01	—

^a Initial pressure: $p(\text{H}_2) = 19.3$ kPa, $p(\text{olefin}) = 7.3$ kPa. Reaction temperature: 373 K for Ni-P, 423 K for Ni-B. ^b Amorphous Ni-P (0.404 g), pretreated with 6M HNO₃ (aq), 6.7 kPa O₂ at 523 K for 2 h and 13.3 kPa H₂ at 573 K for 2 h, successively. ^c The above catalyst was crystallized by heat treatment at 723 K for 30 min under vacuum. ^d Amorphous Ni-B (0.322 g), pretreated with 1.5M HNO₃ (aq), 6.7 kPa O₂ at 423 K for 1 h, and 13.3 kPa H₂ at 573 K for 3 h, successively. ^e The above catalyst was crystallized by heat treatment at 793 K for 2 h under vacuum.

Table 2. Product distribution in the hydrogenation of buta-1,3-diene over Ni-P and Ni-B.^a

Catalyst	Conversion ^a (%)	Products (mol %)			
		butane	but-1-ene	<i>trans</i> -but-2-ene	<i>cis</i> -but-2-ene
Ni-P, amor. ^b	73	1.5	57.7	25.9	14.9
Ni-P, crys. ^c	77	1.4	59.9	26.0	12.7
Ni-B, amor. ^d	73	4.1	52.8	29.9	13.2

^a, ^b, ^c, ^d; see footnotes to Table 1. ^e Based on buta-1,3-diene introduced to the reactor.

lower than that of the pure Ni metal. These results indicate that the electron transfer from the electron rich Ni atom to the more electronegative P or B atom by alloying may be important to enhance the catalytic activity of the Ni atoms, which may be promoted by partial oxidation of B or P atoms. The high activity of the amorphous alloys may be ascribed to the specific formation of partially oxidised P or B atoms on the catalyst surface.

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