Skeletal Ni-P Amorphous Alloy(R-Ni-P) as a Hydrogenation Catalyst

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Ni-P amorphous alloy with skeletal structure like Raney nickel was prepared by alkali leaching of a Ni-Al-P amorphous alloy obtained by the rapid quenching method, which exhibits high selectivity and activity for the hydrogenation of the organic compounds with various unsaturated functional groups.

Raney nickel have been widely used in industrial process as a hydrotreating catalysts.[1] Recently, the Ni-based amorphous alloys, such as Ni-P, Ni-B etc., have caused much attention due to their superior hydrogenation activity and selectivity as well as the corrosion resistance.[2] However, their application in industry instead of Raney Ni is still quite limited due to the extremely low surface area(usually about 1.0 m^2/g) and poor thermal stability of the amorphous alloys obtained by rapid quenching techniques.[3] In the present paper, we report a novel Ni-P amorphous catalyst(R-Ni-P) by alkali leaching of an amorphous Ni-P-Al alloy obtained by the rapid quenching method. In comparison with all those Ni-P amorphous catalysts reported so far, the new catalyst exhibits great improvement on the hydrogenation activity and thermal stability due to the skeletal structure. Comparing with Raney Ni, its catalytic activity usually increases by 2-3 times. Excellent selectivity of R-Ni-P is also observed in the hydrogenation of hexanedinitrile to 1,6-hexanediamine.

The amorphous R-Ni-P sample was prepared by the procedure described as follows: The Ni-Al-P amorphous alloy containing 48.2%wt Ni, 48.7%wt Al and 3.1%wt P, in the form of ribbons ca. 5 mm wide and 10-20 μm thick, was prepared from a melting Ni-Al-P mixture at 1600~1700 K by the rapid quenching method at a cooling speed of 10^6 K/s using a single steel roll(2000~3000 rpm). The sample was ground to 200 meshes and dissolved in 6.0 M NaOH at 273 K very slowly. Then the reaction mixture was continued to stir at 343 K for 6.0 h in N_2 atmosphere for alkali leaching. The obtained amorphous R-Ni-P catalyst was washed free from alkali and aluminate with distilled water until pH = 7. It was further washed with ethanol(EtOH) to remove water, and finally, kept in EtOH for characterization and activity test. For comparison, Raney Ni catalyst was also prepared in the same way by alkali leaching of a commercial Ni-Al alloy(Ni/Al 50/50 w/w), and a regular Ni-P amorphous alloy was obtained by the rapid quench method as described elsewhere.[3]

The composition of the as-prepared catalysts was determined by inductively coupled plasma(ICP) analysis. The total surface area and the pore volume of the catalysts were determined by BET method. The active surface areas were measured by H_2 chemisorption. These results were summarized in Table 1. Both residual Al and P was observed in the as-prepared R-Ni-P catalyst. In comparison with the Ni-P amorphous alloy, the surface area of R-Ni-P increased by nearly two orders of magnitude due to its skeletal structure like Raney Ni catalyst. In comparison with Raney Ni, the slight decrease in the surface area and pore volume may be ascribed to the presence of residual P in the R-Ni-P catalyst.

Table 1. Some characters of the R-Ni-P and Raney Ni catalysts

Catalyst	Comp.	$S_T(m^2/g)$	V_{pore} (mL/g)	$S_{act}(m^2/g\ Ni)$
R-Ni-P	$Ni_{68}Al_{25}P_7$	87	0.050	38
Ni-P	$Ni_{88}P_{12}$	1.2	/	0.8
Raney- Ni	$Ni_{68}Al_{32}$	106	0.070	43

The amorphous character of R-Ni-P sample was determined by XRD. Only one broad peak around 2θ(Cu Kα) = 45° was observed in the XRD pattern, indicating a typical amorphous character.[2] The amorphous character was further confirmed by the EXAFS spectra at Ni K-edge. The radial distribution functions(RDF) of the samples were obtained from the $\chi(k)k^3$ by the fast Fourier transformation, as shown in Figure 1. Unlike Raney Ni catalyst in Figure 1c, only one broad peak with high FT amplitude in the first-near-neighbor(R = 0.15-0.25 nm) was observed in Figure 1a, indicating that the R-Ni-P sample has no long-range but only the short-range ordering structure confined within the first-near-neighbor atom layer.[4] Similar RDF curves of R-Ni-P and Ni-P samples in Figure 1a and b indicated the almost same structures between those two alloys. According to the DSC curves of R-Ni-P and Ni-P samples, the exothermic peaks show that both R-Ni-P and Ni-P amorphous alloys crystallized at high temperature due to their metastable structures. However, the crystallization temperature of R-Ni-P amorphous alloy is almost 80 K higher than the corresponding Ni-P amorphous alloy, showing the stabilizing effect of the skeletal structure on the Ni-P amorphous properties.

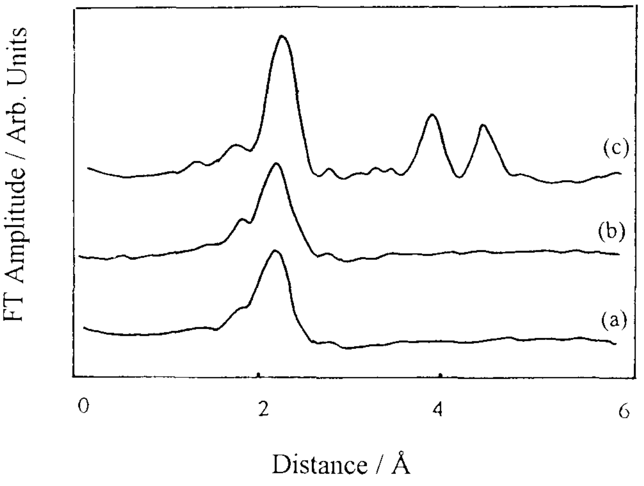

Figure 1. RDF curves of (a) R-Ni-P and (b) Raney Ni.

Liquid phase hydrogenation of organic compounds with various unsaturated functional groups, such as benzene, benzaldehyde, nitrobenzene, benzonitrile, was employed to evaluate the catalytic activity of R-Ni-P amorphous catalyst. The hydrogenation reaction was carried out at 373 K and 1.0 MPa of H_2 with 0.30 g catalyst mixed with 40 ml EtOH and 10 ml one of the organic compounds mentioned above. The hydrogenation was started by stirring the reaction mixture vigorously with a magnetic stirrer to eliminate the diffusion effects. Each reaction lasted for 4.0 h. The initial hydrogenation activity was determined by monitoring the change of the pressure with reaction time which was then turned to be the H_2 uptake rate(R_{H_2} = mmol /h·g of Ni).[5] The reaction products were analyzed by a gas chromatography, by which the conversion and selectivity were calculated. Reproducibility of the hydrogenation activity was better than 5%. The results were summarized in Table 2. Except for those products listed in Table 2, no by-products were detected. Since the selectivity in all those hydrogenation reactions was nearly 100%, the selective hydrogenation of hexanedinitrile to 1,6-hexanediamine at 353 K, used in nylon-6,6 manufacture, was employed to compare the selectivities of R-Ni-P, Ni-P and Raney Ni catalysts. The hydrogenation of hexanedinitrile in liquid phase is pretty complex. Besides the main product of 1,6-hexanediamine, various by-products, including 6-aminohexanenitrile and azacyloheptane etc., were observed. The results were listed in Table 3. According to Table 2 and 3, the hydrogenation activity of R-Ni-P is usually 60-80 times higher than that of Ni-P amorphous alloy, and 2-3 times higher than Raney Ni catalyst. The selectivity of R-Ni-P to 1,6-hexanediamine is similar to that of Ni-P, but about 30% higher than Raney Ni in the liquid phase hexanedinitrile hydrogenation.

Table 2. Catalytic activity of Ni-P(I), R-Ni-P(II) and Raney Ni(III) catalysts[a]

Organic Compound	Product	R_{H_2}(mmol/h·g Ni)[b]			TOF(S^{-1} × 10^{-3})[c]		
		I	II	III	I	II	III
Benzene	cyclohexane	~0[d]	48.0	17.2	/	2.5	0.70
Benzaldehyde	toulene	24.8	1186.0	378.5	77.2	78.0	28.2
Nitrobenzene	aniline	32.0	1560.3	688.2	95.4	96.0	29.0
Benzonitrile	benzylamine	11.2	568.7	146.8	24.0	25.0	6.3

[a]Reaction conditions: T = 373 K, PH_2 = 1.0 MPa, selectivity ≅ 100%. [b]Initial rate determined in the first one hour period. [c]The number of product molecules produced per second on each of surface Ni atoms. [d]The value is too small to be detected.

Table 3. Selective hydrogenation of hexanedinitrile to 1,6-hexanediamine[a]

Catalyst	H_2 Uptake (mmol/h·g Ni)	Spec. Activity (mmol/h·m^2 Ni)	Selectivity (%)	TOF (S^{-1})
R-Ni-P	1611.2	42.6	70	0.10
Ni-P	29.2	36.4	75	0.090
Raney Ni	720.0	24.1	40	0.033

[a]Reaction conditions: T = 353 K, P_{H_2} = 4.0 MPa, other conditions are given in Table 2.

Since the specific activities per active surface area and the TOF values of R-Ni-P are almost the same as those of Ni-P catalyst, the higher hydrogenation activities of R-Ni-P amorphous catalyst per gram Ni than those of the Ni-P catalyst could be understood in terms of the increase in the total surface area(BET) and the active surface area due to the skeletal structure and large pore volume existed in R-Ni-P catalyst. The similar selectivity of R-Ni-P to Ni-P is mainly ascribed to the same structures of those two catalysts, as shown in Figure 1. The residual Al, which was usually considered as both chemical and structural promoter in Raney Ni,[1] had very little or no effect on the specific activity and selectivity of R-Ni-P catalyst in comparison with the regular Ni-P catalyst without Al. However, the high dispersion of the Ni-P alloy powders and the presence of residual Al in R-Ni-P significantly improved the thermal stability of the Ni-P amorphous structure in which the crystallization temperature increased about 80 K, as determined by DSC curves. Since the similar surface areas of the R-Ni-P and Raney Ni catalysts, as shown in Table 1, the higher activity of R-Ni-P suggested a promoting effect of amorphous structure on the catalytic activity, which resulted in the higher activity per Ni atom, i.e., TOF value. According to the XPS spectra and the RDF curves from the EXAFS spectra, the electron-deficiency of Ni atoms caused by the electron transfer from Ni to P, the homogeneous distribution of active sites, and the highly coordinately unsaturated active centers in R-Ni-P, in comparison with Raney Ni catalyst, are main causes corresponding to the higher hydrogenation activity and TOF value as well as the selectivity of the as-prepared R-Ni-P amorphous catalyst than Raney Ni catalyst. Detailed results will be reported in the following papers.

More powerful Ni-based Raney type amorphous catalysts could be obtained by changing the leaching conditions and adding structural and/or chemical promoters in the present catalyst, such as Co, Cr and B etc. Those works are being underway.

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References and Notes

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