Journal of Catalysis **191,** 257–260 (2000)
doi:10.1006/jcat.1999.2792, available online at http://www.idealibrary.com on IDEAL®

RESEARCH NOTE

Glucose Hydrogenation to Sorbitol over a Skeletal Ni-P Amorphous Alloy Catalyst (Raney Ni-P)

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Received July 20, 1999; revised October 1, 1999; accepted October 6, 1999

A skeletal Ni-P amorphous alloy catalyst (Raney Ni-P) was prepared by alkali leaching of a Ni-Al-P amorphous precursor obtained by the rapid quenching technique of a melting solution containing Ni, Al, and P. This catalyst showed higher turnover rates (per surface Ni atom) than Raney Ni for the hydrogenation of glucose to sorbitol, apparently as a result of promotion of Ni-active sites by phosphorus. The Raney Ni-P catalysts gave turnover rates similar to those measured on Ni-P amorphous alloys without Al, but they had a significantly higher density of Ni surface atoms. As a result, Raney Ni-P catalysts showed superior specific hydrogenation rates (per gram catalyst) than either Raney Ni or Ni-P amorphous alloys.

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 (2). Up to now, many attempts have been made to improve its catalytic activity, including the employment of various dopants and preparation methods (3). Since the 1980s, the metal-metalloid amorphous alloy catalysts have been widely studied owing to their higher activity and better selectivity in various hydrogenation processes (4–10). However, those amorphous catalysts still cannot match Raney Ni in industrial application due to their extremely low surface area (ca. 1.0 m^2/g). Another important factor limiting their industrial application is the poor thermal stability of the amorphous alloys. In the present paper, we report a novel skeletal Ni-P amorphous alloy catalyst (denoted as Raney Ni-P) prepared by alkali leaching a Ni-P-Al amorphous alloy obtained by the rapid quenching technique. Its amorphous structure was confirmed by XRD, EXAFS, and DSC. Its activity was measured during the liquid-phase hydrogenation of glucose to sorbitol. The promoting effect of the skeletal structure on the hydrogenation activity of Raney Ni-P was determined by comparing its activity with that of the regular Ni-P, a pure Ni-P amorphous alloy prepared by the rapid quenching technique; while the promoting effects of the alloying P and the amorphous structure were determined by comparing its activity with that of the Raney Ni catalyst obtained by alkali leaching a crystalline Ni-Al alloy.

The Raney Ni-P sample was prepared by the procedure described as follows. A mixture containing 48.2 wt% Ni metal, 48.7 wt% Al metal, and 3.1 wt% red P was melted at 1673 K in an argon atmosphere. The melting solution was then cooled rapidly at the rate of 10^6 K/s by the rapid quenching technique (11) using a single steel roll at a very high stirring rate (2500 rpm), resulting in the Ni-Al-P amorphous alloy in the form of ribbons ca. 5 mm wide and 10–20 μm thick. Then, 6.0 g of the as-prepared Ni-Al-P sample was ground to 200-mesh powder and added very slowly over a 1.5-h period into 60 ml 6.0 M NaOH solution at 273 K. The alkali leaching process was carried out at 343 K in N_2 atmosphere with vigorous stirring for 6.0 h. No significant P species were determined in the leaching solution, showing that the loss of P during the leaching process could be neglected. The resulting Raney Ni-P was then washed free from alkali and aluminates with H_2O (until pH 7 was obtained). It was further washed with ethanol (EtOH) to remove water and finally kept in EtOH until time of use. Similar to the Ni-Al-P amorphous alloy preparation, the regular Ni-P amorphous alloy was also prepared by the rapid quenching technique from the melting solution containing only Ni metal and red P. The resulting Ni-P amorphous alloy was ground to 200-mesh powder and used for characterization and activity tests directly. The differences between the Raney Ni-P and the regular Ni-P catalysts could be described as follows. (i) Only the rapid quenching technique was employed in the regular Ni-P preparation, while both the rapid quenching technique and the alkali

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0021-9517/00 $35.00

leaching were employed in the Raney Ni-P preparation. (ii) The regular Ni-P was a pure Ni-P amorphous alloy, while Al additives were present in the Raney Ni-P sample even after alkali leaching for 6.0 h. The Raney Ni catalyst was prepared by alkali leaching a commercially available crystalline Ni-Al alloy (Ni/Al, 50/50, w/w) in the similar way to that used in the Raney Ni-P preparation.

The amorphous character of the Raney Ni-P sample was determined by X-ray powder diffraction (XRD, Rigaku Dmax-3C with Cu $K\alpha$ radiation). As shown in Fig. la, only one broad peak around $2\theta = 45^\circ$ was observed in the XRD pattern of the fresh Raney Ni-P, similar to that found in the regular Ni-P amorphous alloy (9), indicating a typical amorphous character. After being treated at 673 K for 2 h in N_2 flow, various sharp peaks corresponding to metal Ni, crystalline NiAl alloy, and NiP alloy were observed, as shown in Fig. 1b, indicating the occurrence of the crystallization of the Ni-P amorphous alloy at high temperatures. The amorphous structure of the Raney Ni-P was further confirmed by the extended X-ray absorption fine structure (EXAFS, BL-10B). Figure 2a shows the radial distribution functions (RDF) of the fresh Raney Ni-P obtained from the $\chi(k)k^3$ Ni edge by the fast Fourier transformation. Only one broad peak around $R = 2.1$ Å was observed, indicating that the sample has no long-range but only the short-range ordering structure confined within the first-near-neighbor atom layer (13). After being treated at 673 K, the strength of the original peak around $R = 2.1$ Å increased abruptly and two additional small peaks appeared at longer distances (ca. 3.7–4.6 Å), as shown in Fig. 2b, also indicating the occurrence of the crystallization. The differential scanning calorimetry (DSC, Perkin-Elmer), as shown in Fig. 3, also revealed that both the Raney Ni-P and the regular Ni-P samples were thermodynamically metastable since the crystallization corresponding to the exothermic peaks could be observed at high temperatures. However, the crystallization

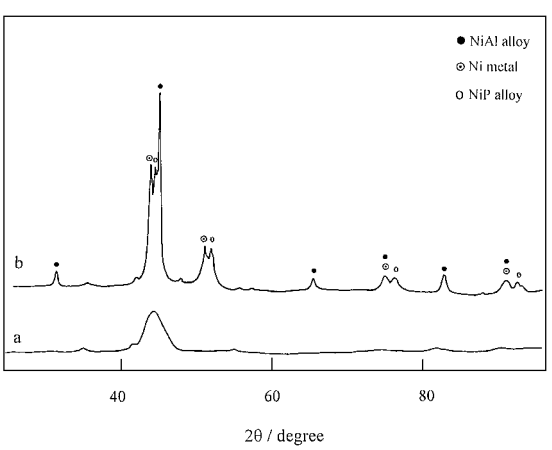

FIG. 1. XRD patterns of the Raney Ni-P samples: (a) fresh and (b) after being treated at 673 K for 2.0 h.

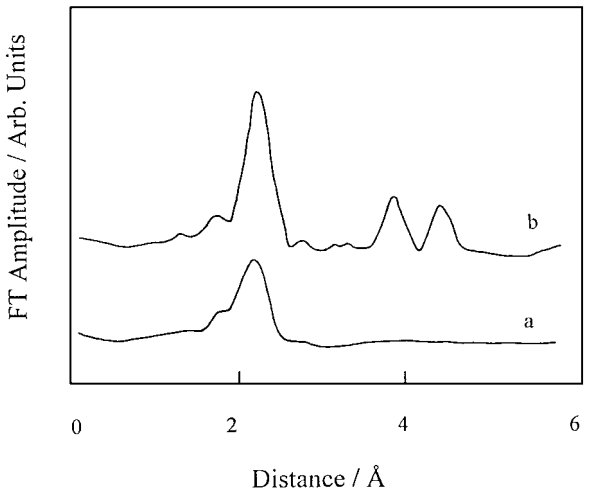

FIG. 2. RDF curves of the Raney Ni-P samples: (a) fresh and (b) after being treated at 673 K for 2.0 h.

temperature of the Raney Ni-P was nearly 70 K higher than that of the regular Ni-P, showing a better thermal stability of the Raney Ni-P amorphous alloy catalyst. This was possibly due to the presence of the skeletal structure and the residual Al species in the Raney Ni-P sample which could effectively inhibit the gathering of the small alloy particles and the migration of the alloy components. As reported previously (14), they were essential for the crystallization process of the Ni-P amorphous alloy.

The bulk composition of the as-prepared catalysts was determined by inductively coupled plasma (ICP) analysis. The BET surface area and the pore volume of the catalysts were determined by N_2 adsorption at 77 K using

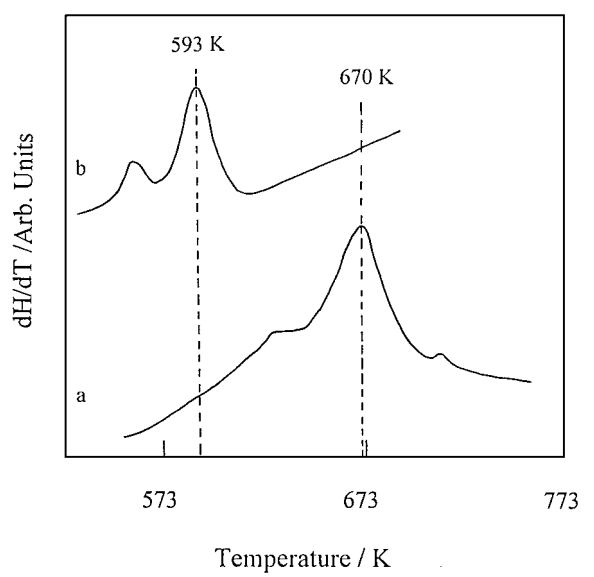

FIG. 3. DSC curves of (a) the Raney Ni-P and (b) the regular Ni-P samples.

TABLE 1

Structural Properties of the Different Catalysts

Sample	Composition	S_{BET} (m^2/g)	V_{pore} (ml/g)	S_{active} (m^2/g Ni)	Surface Ni atoms per gram Ni
Raney Ni-P	$Ni_{68}Al_{25}P_7$	87	0.050	38	5.58×10^{20}
Regular Ni-P	$Ni_{88}P_{12}$	1.2	$\sim 0^a$	0.8	1.20×10^{19}
Raney Ni	$Ni_{68}Al_{32}$	106	0.070	43	6.62×10^{20}

[a] Too small to be detected.

ASAP 2010 (Micro-meritics). The active surface area was measured by H_2 chemisorption, from which the number of surface active Ni atoms was also calculated assuming H/Ni(s) = 1 and a surface area of 6.5×10^{-20} m^2 per Ni atom, based on an average of the areas for the (100), (110), and (111) planes (12). These results are summarized in Table 1. One can see that a considerable amount of Al was still present in the Raney Ni-P catalyst after leaching for 6 h, showing that the alkali leaching for Al is not complete under the present condition. Similar to that of the Raney Ni, pronounced pore volume was also determined in Raney Ni-P, which accounted for its higher surface area (nearly 70 times) than that of regular Ni-P in which the pore volume was too small to be detected. In comparison with the Raney Ni obtained at the same alkali leaching conditions, the slightly lower BET surface area of the Raney Ni-P was possibly due to the presence of the extra P species which blocked some micropores in the catalyst. As can be seen from Table 1, the pore volume of Raney Ni-P is also slightly lower than that of Raney Ni catalyst.

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. The stirring effect was carefully investigated and a stirring rate of 1200 rpm was employed, which was found to be sufficient to stir the reaction system so that the higher stirring rate did not increase the reaction rate. The initial hydrogenation activity was estimated by monitoring the decrease of the pressure within the first 1.0-h period which was then turned to be the H_2 uptake rate per gram Ni($R^m_{H_2}$) or per meter square of the active surface area ($R^s_{H_2}$). 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 catalyst was found to be highly selective in the hydrogenation of glucose with almost the exclusive formation of sorbitol. The sorbitol was formed with selectivity up to 99.5%. The reaction conversion was obtained by determining the remaining glucose in the mixture after reaction for 6.0 h with Fehlings agent. In order to exclude the effect of metal dispersion, the turnover frequency (TOF) was also calculated according to the yield of sorbitol and the number of the surface-active Ni atoms. After reaction, the content of Ni dissolved in the mixture was analyzed by ICP. Only less than 1.0 ppm Ni was determined in the reaction solution, indicating that the leaching of the Ni-active sites during the glucose hydrogenation could be neglected. The catalyst was used repetitively until an abrupt decrease in the activity was observed. The number of repeat times (N) could reflect the lifetime of the catalyst. No significant decrease in activity was observed in the first 5 cycles of the hydrogenation, showing its excellent durability in the present reaction. It was also found that the deactivated catalyst could be easily regenerated by treating it again in 6.0 M NaOH solution.

The catalytic behaviors of the as-prepared three Ni-based catalysts are summarized in Table 2, from which the following orders in the hydrogenation activities could be obtained. (i) Hydrogen uptake rate per gram Ni($R^m_{H_2}$): Raney Ni-P > Raney Ni $\gg$ regular Ni-P. (ii) Hydrogen uptake rate per meter square of active surface area ($R^s_{H_2}$): Raney Ni-P $\cong$ regular Ni-P > Raney Ni. (iii) TOF value: Raney Ni-P $\cong$ regular Ni-P > Raney Ni.

According to our experimental results, the metallic Ni species were proved to be the active sites for the glucose hydrogenation since no significant activity was observed when the catalyst was preoxidized in O_2 flow and the high activity could be recovered after it was reduced in H_2 flow. Therefore, the hydrogenation activity of the as-prepared catalysts was mainly dependent on the the nature and the surface dispersion of these Ni-active sites. Thus, the higher hydrogenation rate per gram of Ni($R^m_{H_2}$) of Raney Ni-P than of the regular Ni-P catalyst was mainly attributed to the higher surface dispersion of Ni-active sites (i.e., the higher active surface area or the larger number of the surface-active Ni atoms). From Tables 1 and 2, one can see that the ratio of surface Ni atoms per gram of Ni in the Raney Ni-P and the regular Ni-P is 46.5, which is almost the same as the ratio of their ($R^m_{H_2}$) (47.7). However, since the active surface area of Raney Ni-P is even lower than that of Raney Ni catalyst, the different nature of Ni-active sites in the Raney Ni-P from that in Raney Ni catalyst should be considered in explaining the higher ($R^m_{H_2}$) of that of Raney Ni-P than that of Raney Ni. Since no significant electronic interaction between metallic Ni and P in Ni-P amorphous

TABLE 2

Hydrogenation Activities of Different Catalysts

Sample	$R^m_{H_2}$ per weight (mmol/h · g Ni)	$R^s_{H_2}$ per surface area (mmol/h · m^2 Ni)	Conv. (%)	TOF (s^{-1})
Raney Ni-P	10.5	0.28	55.8	0.40
Regular Ni-P	0.22	0.27	1.1	0.38
Raney Ni	3.6	0.084	17.2	0.11

Note. Reaction conditions: 1.0 g catalyst, 50 ml 50% (w/w) glucose aqueous solution, $T = 393$ K, $P_{H_2} = 4.0$ MPa, stirring rate = 1200 rpm, reaction time = 6.0 h.

alloy was observed (15, 16), the structural modification of the Ni-active sites in Raney Ni-P owing to the formation of the Ni-P amorphous alloy is possibly a key factor responsible for its higher activity. Detailed studies on the structural characteristics and the absorbing properties of Raney Ni-P as well as the reaction mechanism of glucose hydrogenation should be performed to elucidate the promoting effect of amorphous structure and the alloying P on the activity of Raney Ni-P catalysts. Those works are underway.

ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China and SINOPEC. We are also grateful to Prof. E. Z. Min and Dr. B. N. Zong in Research Institute of Petroleum Processing of China for help in preparing the regular Ni-P amorphous alloy and the Ni-Al-P amorphous alloy as the precursor of the present skeletal Ni-P catalyst.

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