Modification on Ni-P Amorphous Catalyst with SiO_2 and Pd

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Ni-P amorphous alloy is prepared by chemical reduction with hypophosphite and modified by introducing trace Pd to the alloy and depositing it on SiO_2, which results in the great improvement on both the thermal stability and hydrogenation activity. The stabilizing effect of SiO_2 and activating effect of Pd have been observed and discussed.

In many industrial processes, such as hydrotreating and hydrogenation, Ni-based catalysts are used extensively. In recent years, a number of papers have been published on amorphous Ni-based catalysts.[1-3] Although those catalysts exhibit high hydrogenation activity for various olefins,[4] however, the modification seems to be essential to improve the thermal stability and catalytic activity of the amorphous catalysts so that they are able to mach with the commercial catalysts such as Raney Ni and Pd/C etc. In the present work, we reported such a modification on Ni-P amorphous catalyst with trace Pd and SiO_2 support to form Ni-Pd-P/SiO_2 amorphous catalyst, which exibits great improvement on both the thermal stability and catalytic activity of Ni-P amorphous catalyst. It seems promising to be used instead of expensive Pd/C catalyst in the industrial refinement of TA.

Ni-P amorphous alloy in ultrafine particles is prepared by adding NaH_2PO_2 to $NiCl_2$ solution dropwise as reported elsewhere.[5] Its modified form, Ni-Pd-P/SiO_2 amorphous catalyst is obtained in the following procedures: SiO_2(40-60 mesh, 100 m^2/g) is impregnated with $NiCl_2$ solution containing trace $PdCl_2$(60 ppm) overnight, which was then dried at 623 K for 2.0 h and reduced with NaH_2PO_2 at 363 K. The Ni-Pd-P/SiO_2 is obtained by the electroless plating the treated SiO_2 in the solution containing 10.0 g/L $NiCl_2 \cdot 6H_2O$, 10.0 g/L $NaH_2PO_2 \cdot H_2O$, 10.0 g/L NaOAc and 10.0 g/L sodium citrate at 363 K. After plating for 2.0 h , the solid is filtrated and washed thoroughly with H_2O and EtOH subsequently. The final product is kept in EtOH for characterization and hydrogenation activity evaluation. Ni-P/SiO_2 amorphous catalyst is prepared in the similar way used in preparation of Ni-Pd-P/SiO_2 without $PdCl_2$ in the impregnating solution.

The XRD patterns of as-prepared samples are shown in Figure 1. By subtracting the broad peak from the amorphous SiO_2 support, only one broad peak around $2\theta=45°$ is observed for each of the samples, indicating the amorphous character of all the as-prepared samples. After heating the samples at high temperature for 2.0 h in the N_2 flow, a lot of sharp peaks corresponding to various crystalline forms(including Ni and Ni_3P etc.) appear on the XRD patterns indicating the occurrence of the crystallization process. It is noticed that the number and the strength of the sharp peaks increase with the heating temperature increasing. Therefore, the thermal stability of the amorphous catalysts can be evaluated by comparing Tc, the temperature at which significant sharp peaks are observed on the XRD patterns. The Tc values for the as-prepared samples are listed in Table 1.

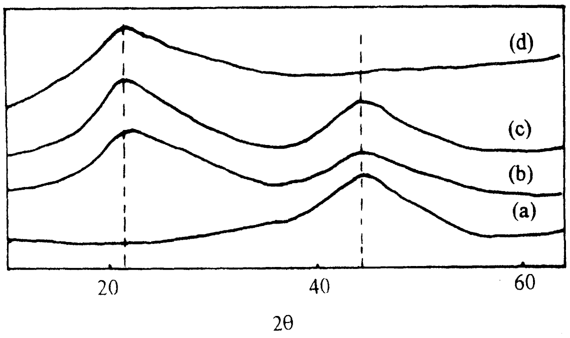

Figure 1. XRD patterns of as-prepared samples.
(a) Ni-P, (b) Ni-P/SiO_2, (c) Ni-Pd-P/SiO_2, (d) SiO_2.

The compositions of the amorphous alloy and their contents on SiO_2 are analyzed by ICP. The surface areas of the as-prepared samples are determined by BET. Those results are also summarized in Table 1.

Table 1. Some characters of the as-prepared samples

Sample	Composition	C(wt%Ni)	S(m^2/g)	Tc(K)
Ni-P	$Ni_{86}P_{14}$	/	21	550
Ni-P/SiO_2	$Ni_{85}P_{15}/SiO_2$	3.00	87	675
Ni-Pd-P/SiO_2	$Ni_{80}P_{20}/SiO_2$[a]	3.45	83	680

[a]Pd is not appeared in the composition because of its extremely low content(40 ppm).

The catalytic activity is measured through the hydrogenation of benzaldehyde(BA) in the following steps: 10 mL BA and 40 mL EtOH are mixed with certain amount of one of the Ni-based catalyst containing 0.050 g of Ni in a high pressure stainless steel reactor. The reactor is filled with H_2 up to 1.00 MPa and then heated slowly(80 K/h) in an oil bath until 393 K. The pressure inside increases with the temperature increasing. When it reaches a steady state again, the hydrogenation is started immediately by stirring the reaction mixture vigorously with the magnetic stirrer. The hydrogenation activity is measured by either monitoring the change of the pressure in the reactor with the time which is then turned to be the H_2 uptaking rate(r_{H_2}, mmol/hr·g of Ni) or determining the reaction conversion after 4.0 h. Those results are summarized in Table 2.

The hydrogenation activity of the as-prepared samples is also evaluated and compared with commercial Pd/C(0.5%) catalyst through the hydrogenation of 4CBA performed at the conditions used for the industrial refinement of TA (P_0 = 6.8 MPa, T=551 K, the reaction mixture is comprised of 1200 ml aqueous solution containing 400 g 4-carboxyl benzoic acid (TA) including 2000 ppm 4-carboxyl benzaldehyde (4CBA) and one of certain amount of the as prepared catalysts containing 0.020 g Ni or 0.020 Pd if Pd/C is used as the catalyst. The conversions of the 4CBA with different catalysts are listed in Table 3.

Table 2. Hydrogenation activity of the as-prepared samples

Sample	r_{H_2}(mmol/h.g)	Conv.(%)
Ni-P	81	4.6
Ni-P/SiO_2	76	4.4
Ni-Pd-P/SiO_2	137	7.8

Table 3. The conversion of 4CBA with different catalysts

Catalyst	Ni-P	Ni-P/SiO_2	Ni-Pd-P/SiO_2	Pd/C(0.5%)
Conv.(%)	61.0	57.0	82.5	86.5

According to above experimental results, the following conclusions could be obtained:

1. The modification on Ni-P catalyst with either trace Pd or silica support does not change its amorphous characters.
2. The thermal stability of Ni-P amorphous catalyst is greatly improved by depositing it on SiO_2. However, no significant promoting effect from SiO_2 on the hydrogenation activity has been observed.
3. The hydrogenation activity of Ni-P amorphous catalyst could be improved by introducing trace Pd to the Ni-P alloy while its thermal stability does not change.
4. The modified Ni-P amorphous catalyst supplies a new catalyst to be used instead of expensive Pd/C in the refinement of TA, because its catalytic activity is almost the same as Pd/C in the hydrogenation of 4CBA, as shown in Table 3.

The stabilizing effect from SiO_2 on the Ni-P amorphous catalysts could be understood by considering the interaction between the amorphous Ni-P alloy and SiO_2 support. On the other hand, it is partially ascribed to the high dispersion of the amorphous alloy on the support.

As various crystallites, such as Ni and Ni_3P etc., are formed simultaneously during the crystallization, the diffusion of the component elements in amorphous alloy is essential. Therefore, the thermal stability of supported Ni-P amorphous catalyst is much higher than that of the corresponding unsupported one because the diffusion is much more difficult due to the high dispersion of the amorphous alloy on the support.

The activating effect from trace Pd in Ni-Pd-P amorphous catalyst is not very clear so far. The hydrogenation activity resulted from Pd itself could be neglected because of its extremely low content in the alloy, which is confirmed by the experimental results with Pd/SiO_2 catalyst in which the content of Pd on SiO_2 is about 40 ppm obtained by the method mentioned above. Therefore, the change of the surface properties of the modified catalyst caused by trace Pd should be considered to explain the increase of the catalytic activity. The XPS spectra of Ni-P/SiO_2 and NiPd-P/SiO_2 are shown in Figure 2.

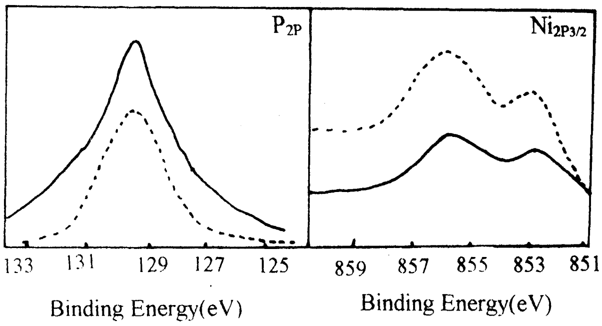

Figure 2. XPS spectra of the as-prepared samples.
(……)=Ni-P/SiO_2 , (——)=Ni-Pd-P/SiO_2.

No significant change in the biding energies for both Ni and P has been observed, indicating that the introduction of trace Pd to Ni-P amorphous alloy does not change its electronic structure on the surface. However, the significant change in the composition of the amorphous Ni-P alloy after modification with trace Pd has been observed, in which the molar ratio of P in the alloy increases a lot. It was also found that the active surface area of Ni-Pd-P/SiO_2 is 36 m^2/g, which is almost as twice as that of Ni-P/SiO_2 (20 m^2/g)determined by the hydrogen-oxygen titration. According to the reaction conversion in the same period(4.0 h), the turnover frequency(TOF) of both catalysts were almost the same. Therefore, we conclude that the improvement on the hydrogenation activity from the trace Pd is possibly attributed to the structural modification, such as the increase of the active surface area, the increase of P content in the alloy and so on. Further studies are being considered to explain the promoting effect from Pd by examining the surface properties with modern detecting techniques including EXAFS, STM, TPR, XPS, etc.

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References and Notes

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