Gas-Phase Adiponitrile Hydrogenation over Modified Ni–P/SiO_2 Amorphous Catalysts

Hexing Li,* Minghui Wang, and Yeping Xu
Department of Chemistry, Shanghai Normal University, Shanghai 200234, P. R. China

(Received May 29, 2000; CL-000517)

Gas-phase hydrogenation of adiponitrile was carried out in a fixed-bed reactor at 1 atm pressure, and in the absence of ammonia. In comparison with other Ni-based catalysts, the Ni–P/SiO_2 amorphous catalyst exhibited higher activity and/or better selectivity to 1,6-hexanediamine, which could be further improved by W or MgO-additives.

1,6-Hexanediamine (HMA) is the most important intermediate in the manufacturing of Nylon-6,6.[1] Large scale HMA is usually produced via adiponitrile (ADN) liquid phase hydrogenation and Raney Ni and Raney Co are probably the most frequently used catalysts.[2,3] Because these kinds of catalysts are subject to severe leaching by the aqueous reaction medium, substantial nickel losses and product cleanup are inevitable. The development of a fixed-bed catalyst system for ADN hydrogenation with a supported metal catalyst that was resistant for such leaching was believed to be feasible. However, the selectivity to HMA was very low (< 40%), where the catalyst was proved to be the key.[4–6] Recently, the amorphous alloy catalysts have caused much attention for their higher activity, better selectivity, and stronger sulfur resistance in hydrogenation reactions.[7–9] In this paper, we report a Ni–P/SiO_2 amorphous catalyst which seems more powerful in the gas-phase ADN hydrogenation to HMA due to its excellent activity and selectivity at 1 atm pressure and even in the absence of ammonia. Promoting effects of W- and MgO-additives were also observed.

The Ni–P/SiO_2 amorphous catalyst was prepared by the electroless plating described as follows: 1.0 g SiO_2 (40–60 meshes, 182 m^2/g) was impregnated with small amount of $NiCl_2$ solution overnight and dried at 423 K. After being calcined at 623 K for 2.0 h, the precursor was reduced by NaH_2PO_2 in alkaline solution to create crystalline nuclei. Then, the sample was transferred into 250 mL solution containing 40 g/L of $Na_3C_6H_5O_7 \cdot 2H_2O$ (sodium citrate), CH_3COONa, $NiCl_2 \cdot 6H_2O$, $NaH_2PO_2 \cdot H_2O$ (pH 4–5) with vigorous stirring for electroless plating at 363 K until the evolution of a gas had ceased, usually within 2 h. The resulting black solid was washed thoroughly with distilled H_2O until free from Cl^- ions, then washed with absolute alcohol (EtOH), and finally, dried at 363 K in the N_2 atmosphere. The Ni–P/SiO_2–MgO amorphous catalyst was obtained by using SiO_2–MgO (Si/Mg molar ratio = 7) instead of SiO_2, which was prepared by impregnating the SiO_2 support with desired amount of $Mg(NO_3)_2$ solution followed by a calcination at 773 K for 6 h. The W-doped Ni–P/SiO_2 amorphous catalyst (Ni–W–P/SiO_2) was prepared in the same procedure by adding desired amount of Na_2WO_4 into the plating solution.

For comparison, the crystallized Ni–P/SiO_2 catalyst was also prepared by treating the fresh Ni–P/SiO_2 sample at 873 K in N_2 flow for 2 h. The Ni/SiO_2 catalyst was prepared by H_2 reduction at 773 K for 2 h of the precursor obtained by a regular impregnation, where $Ni(NO_3)_2$ was used instead of $NiCl_2$ to avoid the poisoning effect from Cl^- ions.

The XRD patterns[9] revealed that the as-prepared Ni–P/SiO_2, Ni–W–P/SiO_2, and Ni–P/SiO_2–MgO samples were present in the typical amorphous structure as found in the Ni–P amorphous alloy obtained by the rapid quenching technique.[10] When these samples were treated at 873 K in N_2 flow, the crystallization occurred gradually since the amorphous structure is metastable thermodynamically. The radial distribution function (RDF) curves, obtained by the fast Fourier transformation based on the $\chi(k)k^3$ Ni edge EXAFS data, further confirmed the amorphous structure of the as-prepared Ni–P based samples since only one weak FT peak around R = 2.1 Å was observed for the fresh samples while very strong FT peak around R = 2.1 Å and two additional small peaks at longer distance (ca. 3.7–4.6 Å) were observed after being treated at 873 K,[9] showing that the fresh samples had no long-range but only short-range ordering structure, which may transfer to the well-ordered crystalline structure at high temperature.

The XPS spectra of the Ni–P/SiO_2, Ni–W–P/SiO_2 and Ni–P/SiO_2–MgO amorphous catalysts revealed that the nickel in all the as-prepared catalysts was mainly present in the metallic state with the binding energy (BE) of 853.1 eV ($Ni_{2P3/2}$ level) and the phosphorus was in the alloying state with Ni corresponding to 130.0 eV (P_{2P} level). Most of the W species was present in the W^{4+} state with BE of 32.8 eV in W_{4f} level. In comparison with the BE values of pure metallic Ni and red P,[11] no significant BE shift of both the metallic Ni and the alloying P was observed, indicating that electronic interaction between Ni and P in the Ni–P alloy was not significant.

Table 1. Structural characters of the as-prepared catalysts

No.	Sample	Composition /atom%	Ni loading /wt%	S_{act} /$m^2 \cdot g^{-1}$
A	Ni-P/SiO_2	$Ni_{86.0}P_{14.0}$	12.2	7.5
B	Ni-W-P/SiO_2[a]	$Ni_{81.6}P_{18.4}$	12.0	6.4
C	Ni-P/SiO_2-MgO[b]	$Ni_{86.0}P_{14.0}$	12.0	5.9
D	Cryst. Ni-P/SiO_2[c]	$Ni_{86.0}P_{14.0}$	12.2	4.8
E	Ni/SiO_2	Ni	12.2	5.2

[a] W/Ni molar ratio = 0.019. [b] Si/Mg molar ratio = 7. [c] Obtained by treating the Ni-P/SiO_2 sample at 873 K in N_2 flow for 2 h.

The Ni loading and the composition of the as-prepared catalysts were analyzed by ICP. The surface active area (S_{act}) was determined by hydrogen chemisorption assuming H/Ni(s) = 1. As shown in Table 1, the presence of W-dopant caused an increase in P content in the Ni–P alloy composition. The S_{act} of Ni–W–P/SiO_2 slightly decreased since partial surface Ni atoms were covered by W oxides. The lower S_{act} of Ni–P/SiO_2–MgO sample could be attributed to the decrease in the surface area of the support, leading to the decrease in the dispersion degree of the Ni active sites. The crystallization of the Ni–P/SiO_2 amorphous catalyst caused a considerable decrease in S_{act} owing to the gathering of Ni–P alloy particles at high temperature. Similar to the crystallized Ni–P/SiO_2, the Ni/SiO_2 catalyst also had low S_{act}

since the catalyst was prepared by H_2 reduction at high temperature (773 K).

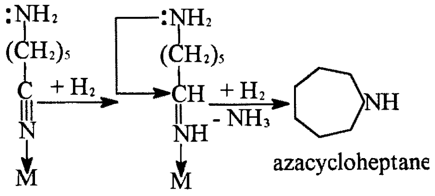
The ADN hydrogenation was carried out in a tubular glass fixed-bed reactor (0.8 cm i.d.) in a continuous process. Our preliminary study revealed that the catalyst did not show diffusion restrictions under present conditions. The ADN dissolved in EtOH was vaporized in a bubbling-type evaporator at 523 K, and then fed into the reactor with hydrogen mixture as a carrier gas (75 mL/min). The effluents were analyzed by means of an on-line gas chromatograph (GC 1102) with a flame ionization detector equipped with a 25 m OV 101 capillary column, and a 353–533 K oven temperature programmed at a ramp of 4 K/min. The reaction conditions and the experimental results are summarized in Table 2.

Table 2. Catalytic Behaviors of the as-prepared catalysts[a]

Catalyst	Conv. /%	Selectivity /%		
		HMA	6-aminohexanenitrile	azacycloheptane
A	69	65	19	16
B	83	68	10	22
C	70	78	18	4
D	34	45	40	15
E	22	34	50	16

[a] Reaction conditions: catalyst amount = 1.0 g, space velocity = 1700 h^{-1}, H_2/ADN = 37 (molar ratio), P = 1 atm, T = 473 K.

As shown in Table 2, besides the main product (HMA), two additional products, 6-aminohexanenitrile, and azacycloheptane were identified over each catalyst. The 6-aminohexanenitrile is an intermediate resulted from the half-hydrogenation of ADN in which only one cyano group ($C\equiv N$) was hydrogenated, while the azacycloheptane is a real side-product (a secondary amine), whose formation could be illustrated in the following scheme.[2]



Obviously, the high activity of the catalyst favors the further hydrogenation of 6-aminohexanenitrile to produce HMA. The polarization of the cyano group adsorbed on the catalyst seems to be favorable for the nucleophilic attack on the carbon atom by nitrogen atom in the NH_2 group on the other side of the ADN molecule and thus for the formation of the azacycloheptane.[12] Based on above assumption, the results in Table 2 could be explained as follows.

1. The Ni–P/SiO_2 amorphous catalyst exhibited higher activity than either the crystallized Ni–P/SiO_2 catalyst or the Ni/SiO_2 catalyst. As no significant electronic interaction between Ni and P in the Ni–P amorphous alloy was determined by XPS, the structural modification by the alloying P was considered as a main promoting factor. Such a structural modification resulted in (1) the higher dispersion degree (S_{act}), as shown in Table 1. However, this could not explain the higher TOF value of the Ni–P/SiO_2 amorphous catalyst (0.012 s^{-1}) than that of the Ni/SiO_2 catalyst (0.0029 s^{-1}); (2) the relatively weaker Ni–H bonging, as determined by TPD (the lower H_2 desorption peak on the Ni–P/SiO_2 amorphous catalyst in comparison with that on the Ni/SiO_2 catalyst), which facilitated the surface addition of dissociated H to $C\equiv N$ group; (3) the stronger interaction between Ni and Ni atoms owing to the shorter Ni–Ni bonding length in the Ni–P amorphous alloy than that in the pure Ni catalyst[6] and the more highly unsaturated Ni active sites, which were proved to be favorable for the hydrogenation.[7] Since no significant change in the azacycloheptane yield was observed, the better selectivity to HMA over the Ni–P/SiO_2 amorphous catalyst was mainly attributed to its higher activity which promoted the further hydrogenation of 6-aminohexanenitrile to HMA, as shown in Table 2. 2. Sueiras et al. reported that the higher acidity of the support favored the formation of azacycloheptane.[4,5] This may successfully account for the promoting effect of the MgO additive (an alkaline oxide) on the selectivity to HMA, since the formation of the azacycloheptane was effectively inhibited. 3. The role of the W-dopant in the Ni–W–P/SiO_2 amorphous catalyst is relatively complex. The XPS characterization revealed that most of the W modifiers were present in the form of the low-valent state (W^{4+}). On one hand, these electropositive W^{4+} species could strongly adsorb the cyano group, leaving more Ni active sites for adsorbing hydrogen. Our kinetic studies revealed that the ADN hydrogenation was first order with respect to hydrogen and zero order to ADN. Therefore, the activity was enhanced by W-dopant since more hydrogen molecules could be adsorbed and dissociated on the Ni active sites. The higher activity of the Ni–W–P/SiO_2 amorphous catalyst could also account for the lower yield of 6-aminohexanenitrile since it favored the further hydrogenation of 6-aminohexanenitrile to HMA, as discussed above. However, the W^{4+} species could act as Lewis adsorption sites.[12] the ADN molecule being adsorbed via the donation of a lone electron pair from the nitrogen of cyano group. This bonding polarized the $C\equiv N$ bond which was favorable for a nucleophilic attack on the carbon atom by the nitrogen atom with a lone electron pair in NH_2 group on the other side of the ADN molecule to form azacycloheptane. Therefore, no much improvement on the selectivity to HMA was observed due to the presence of larger amount of azacycloheptane, although the 6-aminohexanenitrile formation was effectively inhibited.

This work was supported by the National Natural Science Foundation of China (29973025), the Committee of Shanghai Education (98SG44), and the Natural Science Foundation of Shanghai, China (98QMA11402).

References

1 A. Baiker, J. De Pietro, M. Maciejewski, and B. Walz, *Stud. Surf. Sci. Catal.,* **67,** 169 (1991).
2 C. De Bellefon and P. Fouilloux, *Catal. Rev.—Sci. Eng.,* **36,** 459 (1994).
3 D. Gavroy, C. Joly-Vuillemin, G. Cordier, P. Fouilloux, and H. Delmas, *Catal. Today,* **24,** 103 (1995).
4 F. Medina, P. Salagre, and J. E. Sueiras, *J. Mol. Catal.,* **81,** 363 (1993).
5 F. Medina, P. Salagre, and J. E. Sueiras, *J. Chem. Soc. Faraday Trans.,* **90,** 1455 (1994).
6 H. X. Li, Y. P. Xu, and J. F. Deng, *New J. Chem.,* **23,** 1059 (1999).
7 A. Baiker, *Faraday Discuss. Chem. Soc.,* **87,** 239 (1989).
8 A. Molnar, G. V. Smith, and M. Bartok, *Adv. Catal.,* **36,** 329 (1989).
9 J. F. Deng, H. X. Li, and W. J. Wang, *Catal. Today,* **51,** 113 (1999).
10 S. Yoshida, H. Yamashita, T. Funabiki, and T. Yonezawa, *J. Chem. Soc., Chem. Commun.,* **1982**, 964.
11 H. Li, H. X. Li, W. L. Dai, W. J. Wang, Z. Fang, and J. F. Deng, *Appl. Surf. Sci.,* **152,** 25 (1999).
12 P. Gallezot, P. J. Cerino, B. Blanc, G. Fleche, and P. Fuertes, *J. Catal.,* **146,** 93 (1994).