

Pd-coated Ni nanoparticles by the polyol method: an efficient hydrogenation catalyst

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Pd-coated Ni nanoparticles of 50 ± 15 nm size are prepared by the polyol method and characterized by X-ray diffraction, transmission electron microscopy, X-ray photoelectron spectroscopy and thermogravimetry analysis. Surface coverage of Pd on Ni particles is less than a monolayer for 0.5 and 1 at% Pd-coated Ni. Quantitative conversion of nitrobenzene to aniline is observed over these Pd-coated Ni particles at 27 °C under one atmospheric pressure of hydrogen. 0.5 and 1 at% Pd-coated Ni exhibits 10 times greater activity than that of typical colloidal palladium and platinum catalysts and 2.5 times higher activity than commercial 5 wt% Pd/C.

Introduction

Palladium metal is a well-known hydrogenation catalyst.^{1,2} 5 to 10 wt% Pd/C or Pt/C are routinely employed as commercial hydrogenation catalysts in many hydrogenation reactions.^{3,4} Here palladium and platinum are present as finely dispersed metal particles on carbon. Even though Pd metal nanoparticles can be employed as catalyst, it is difficult to handle the nano materials and also to recover such nanoparticles from the reaction medium. There are several recent studies on bimetallic clusters of noble and light transition metals such as Pd/Ni, Pd/Cu which showed high hydrogenation activity. Miegge *et al.*⁵ and Michel *et al.*⁶ have shown the reactivity of Pd/Ni nanoparticles in the hydrogenation of buta-1,3-diene to butene and found that the reactivity of the alloy is greater than that of the pure metals. Toshima *et al.* reported the synthesis and catalytic activity of Pd/Ni and Pd/Cu for different hydrogenation reactions.^{7–10} In these bimetallic clusters, Pd content varies from 40 to 90 mol%. It has been shown that metal catalysis can be affected by adding a second metal, the additive component improves the activity, selectivity and stability of the metal catalyst.

Among the various chemical methods, which have been developed for the preparation of metal particles, the polyol process is a promising method with which to prepare mono dispersed metal particles.^{11,12} In this process, a metal precursor is heated in a high boiling alcohol. Mono dispersed Ni of 120 nm mean size can be prepared by the polyol method employing poly(*N*-vinyl-2-pyrrolidone) as a separating agent. However, by heterogeneous nucleation with Pd and Pt nuclei, using the same polyol process, Ni particles of 20–30 nm can be achieved.¹³ In this process, Ni nanoparticles are shown to be protected from oxidation by ethylene glycol.

Instead of making Ni-Pd bimetallic alloy clusters, coating Pd on Ni nanoparticles could improve the stability of the Ni particles in addition to Pd on Ni acting as a hydrogenation catalyst. With Pd being a noble metal, oxidation of Ni can be prevented, thus increasing the shelf-life of Ni nanoparticles. It may be possible to drastically reduce the amount of Pd by coating 0.5 to 1 monolayer of Pd on Ni nanoparticles. Since Ni (Raney Ni) itself is a hydrogenation catalyst, enhanced hydrogenation activity can be achieved due to the Pd–Ni interaction. Therefore we considered it worthwhile to investigate whether Pd can be coated over Ni nanoparticles by the polyol method. Herein we report the preparation of Pd-coated

Ni metal nanoparticles by the polyol method and show that 0.5 to 1 at% Pd-coated Ni is a highly efficient catalyst for the hydrogenation of nitrobenzene compared to the commercial 5 wt% Pd/C.

Experimental

Preparation of Pd-nucleated Ni and Pd-coated Ni metal particles

Pd-coated Ni nanoparticles were prepared by the polyol reduction method. Nickel(II) hydroxide (Aldrich) was used as the starting material. In a 500 mL three-necked flask, 10 g of poly(*N*-vinyl-2-pyrrolidone) (PVP) (Aldrich) and 2 g of Ni(OH)₂ were dissolved in 150 mL of ethylene glycol (EG). 1 mL of 2.5 M H₂SO₄ was added to increase the solubility of Ni(OH)₂. The solution was stirred and refluxed at 196 °C for 10 min. When the reaction mixture reached 190 °C, low boiling liquids and water impurities were distilled. This is an important step in the reduction of Ni(OH)₂ to Ni by EG. The reaction mixture was stirred at 300 rpm by a mechanical stirrer. The Pd(II) acetate (E. Merck India Ltd. 99.9%) was dissolved in EG. This solution was injected into the reaction mixture at 196 °C to the extent of 1 at% Pd with respect to Ni to achieve heterogeneous nucleation. The color of the reaction mixture instantly changed from green to black. Continuous refluxing for 30 min at 196 °C gave Ni particles by the reduction of Ni(OH)₂. After complete reduction of Ni(OH)₂, 0.5 and 1 at% Pd(II) acetate (relative to Ni) in EG was injected into the reaction mixture at 196 °C to coat Ni. The reaction was continued for 5 min. The mixture was cooled, the particles were centrifuged and washed with ethanol and acetone. A quantitative amount of Ni was obtained by this method. Similarly, Pd-nucleated Ni coated with 1 at% Pd was prepared. Pd and Pt nanoparticles were also prepared by this method.

Characterization of the Pd-coated Ni nanoparticles

X-Ray diffraction (XRD) of the catalysts was carried out with a Siemens D5005 diffractometer with Cu-K_α radiation ($\lambda = 1.5418 \text{ \AA}$) at a scan rate of 2° min^{-1} . A JEOL JEM-200CX operated at 200 kV was used to carry out TEM studies. X-Ray photoelectron spectra (XPS) of these materials were recorded on an ESCA-3 Mark II spectrometer (VG Scientific Ltd. England) using Al-K_α radiation (1486.6 eV). The oxidation

behaviour of the as prepared sample was examined by thermogravimetry analysis (TGA).

Hydrogenation of nitrobenzene

The hydrogenation of nitrobenzene (SD Fine Chemicals Ltd. India) was carried out in methanol at room temperature (27 °C) under one atmospheric pressure of hydrogen. In a typical experiment, ≈ 50 mg of Pd-coated Ni particles were dispersed in 5 mL of solvent. The contents were purged with H_2 . 2 mL of nitrobenzene was then added. The hydrogenation product was filtered to separate the solid catalyst and analyzed by a gas chromatograph [Mayura Analytical, Bangalore, India.] equipped with a flame ionization detector. A 30 m long, 0.53 mm diameter fused silica capillary column (DB[®] 624) was used. The injector and detector temperatures were 200 and 250 °C respectively. The oven temperature was maintained at 180 °C. The carrier gas used was ultra pure nitrogen at a flow rate of $10 \text{ cm}^3 \text{ min}^{-1}$. The retention time for nitrobenzene was 4 min and for aniline was 2.95 min under these operating conditions. Mixtures of known molar ratios of pure nitrobenzene and aniline were run in the GC. From the plot of molar ratio Vs area under the peak ratio, % conversion of nitrobenzene to aniline, was obtained.

The experiments were also performed with activated as well as as-received 5 wt% Pd/C (Lancaster), Pd and Pt particles prepared by the polyol method, uncoated Ni and Raney Ni for comparison. 5 wt% Pd/C was activated by hydrogen at 200 °C.

Results and discussion

XRD patterns of Pd nucleated Ni were recorded in the 2θ range from 5 to 100° . Diffraction lines due to only the Ni metal were observed and no lines due to unreacted $Ni(OH)_2$, Pd metal, oxides of either Pd or Ni were seen even on expanding the 2θ region where lines due to these impurities would be expected. Similarly, the XRD of Pd-coated Ni was also examined before and after the hydrogenation reaction. Here also no impurity peaks were seen. In Fig. 1 we show the XRD patterns of Pd-nucleated Ni (hereafterwards called uncoated Ni) before and after the hydrogenation reaction. 0.5 and 1 at% Pd-coated Ni are also shown. The pattern can be indexed as face centered cubic (FCC) Ni. The lattice parameter of Ni in all the cases is $3.520 \pm 0.002 \text{ \AA}$. There is no significant difference in the lattice parameters observed compared with those of pure Ni. A comparison of the Ni(111) and (200) diffraction lines of uncoated Ni before and after the hydrogenation reaction showed broadening of the peaks after the reaction indicating a decrease in particle size. Full width half maxima (FWHM) are indicated in the figure. Similarly, the FWHM of Ni coated with Pd increases after the reaction.

Transmission electron micrographs of the uncoated and 0.5 at% Pd-coated Ni before and after the hydrogenation reactions are shown in Fig. 2(a–c). The particles are homogeneous in size with a mean size of $50 \pm 15 \text{ nm}$. Faceted surfaces of Ni are clearly visible in the image. Pd metal particles over Ni are not seen. Further, there is no appreciable change in the morphology/size of Ni after the reaction [Fig. 2(c)]. The TEM studies confirm that the Pd is distributed on an atomic scale over the Ni surface. Careful examination of the electron diffraction pattern of 0.5 at% Pd-coated Ni in Fig. 2(d) shows that it can be indexed to FCC Ni. Even though Pd metal is present, no spots or even diffraction rings due to Pd were found in the electron diffraction pattern.

The Ni(2p) core level spectra of uncoated, 0.5 at% Pd-coated Ni before and after the hydrogenation reaction are given in Fig. 3. The binding energies of $Ni(2p_{3/2, 1/2})$ observed were 852.8 eV and 870.4 eV indicating Ni is in the metallic state. Generally Ni is oxidized on its surface and a small increase in the intensity of the $Ni^{2+}(2p_{3/2})$ peak at 855.0 eV due to NiO is

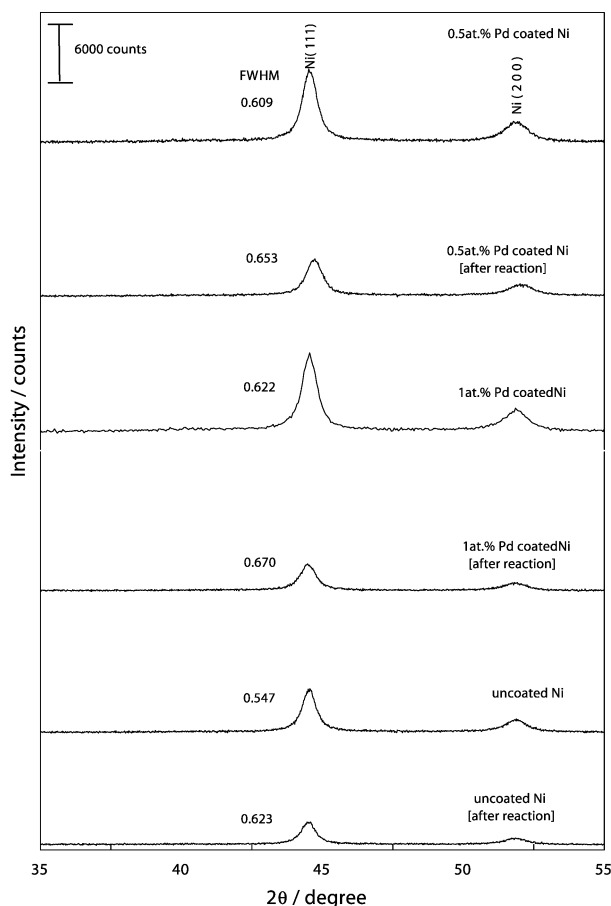


Fig. 1 X-Ray diffraction patterns of uncoated Ni, 0.5 at% Pd-coated Ni and 1 at% Pd-coated Ni before and after the hydrogenation reaction.

barely visible as indicated in the figure. In an earlier experiment on the surface oxidation of Ni metal foil, we had shown that even if two monolayers of NiO are formed on the Ni surface, the intensity of the $Ni^{2+}(2p)$ peak at 855.0 eV is greater than the $Ni^0(2p)$ peak at 852.8 eV.¹⁴ Therefore the extent of oxidation of Ni is much less than a monolayer. Even this amount of Ni oxidation may be due to oxygen associated with EG adsorbed on the Ni particles. Pd-coated Ni also showed a similar trend, showing Ni is in the metallic state. The Pd(3d) region of uncoated Ni, Pd-coated Ni before and after the hydrogenation reaction are presented in Fig. 4. The $Pd(3d_{3/2, 5/2})$ peak seen in the uncoated Ni is due to the Pd nuclei in the Ni nanoparticles. The $Pd(3d_{3/2, 5/2})$ peaks at 335.4 eV and 340.3 eV shows that Pd is in the metallic state. Pd(3d) peaks in the 0.5 at% Pd-coated Ni are of higher intensity compared to uncoated Ni. The intensity ratios of $Pd(3d_{3/2}) : Ni(2p_{3/2})$ peaks in the 0.5 at% Pd-coated Ni is about 3 times more with Pd-coated Ni compared to uncoated Ni which demonstrates that Pd is indeed present on the surface of Ni in the coated sample. The surface concentration of Pd from the integrated intensities of Pd(3d) and Ni(2p) is about 7% for 0.5 at% Pd-coated Ni.¹⁵ Thus the XPS study shows that Ni is in the metallic state and that for Pd-coated Ni, Pd is in the metallic state on the surface of Ni.

The stability of uncoated, 0.5 and 1 at% Pd-coated Ni particles was studied by thermogravimetry. Fig. 5 shows TGA curves of the above samples heated up to 500 °C at a rate of 5° min^{-1} in air. Uncoated Ni gained 11% weight after a 3% weight loss. The 3% weight loss is attributed to the desorption of adsorbed EG. A sharp weight gain occurred at 300 °C, approaching constant weight above 470 °C. The TGA curves for 0.5 and 1 at% Pd-coated Ni shows about 1.5% weight loss and 16% weight gain. The weight loss below 200 °C was less with Pd-coated Ni. This may be because of less desorption of

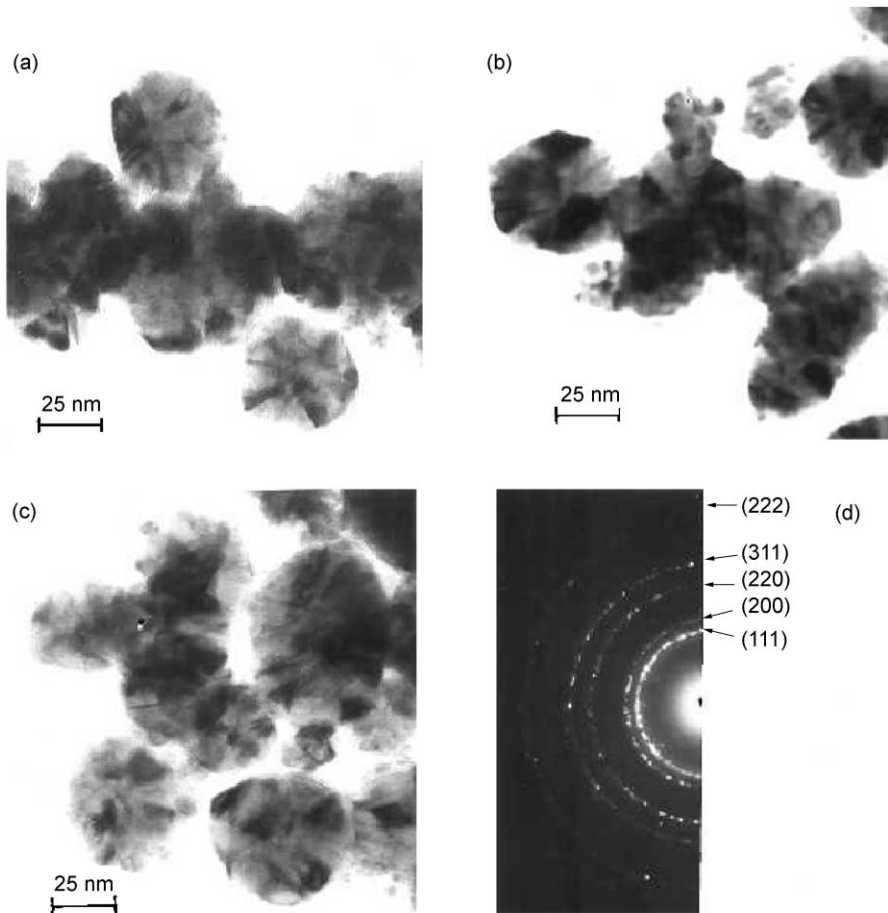


Fig. 2 Transmission electron micrographs of (a) uncoated Ni, (b) 0.5 at% Pd-coated Ni before the hydrogenation reaction (c) 0.5 at% Pd-coated Ni after the reaction and (d) electron diffraction of 0.5 at% Pd-coated Ni.

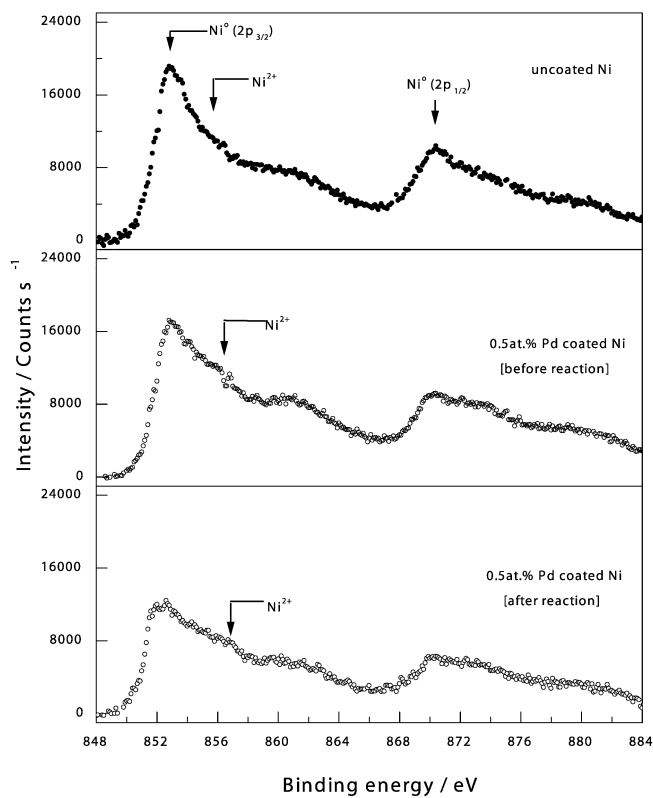


Fig. 3 Ni(2p) core level spectra of uncoated, and 0.5 at% Pd-coated Ni before and after the hydrogenation reaction.

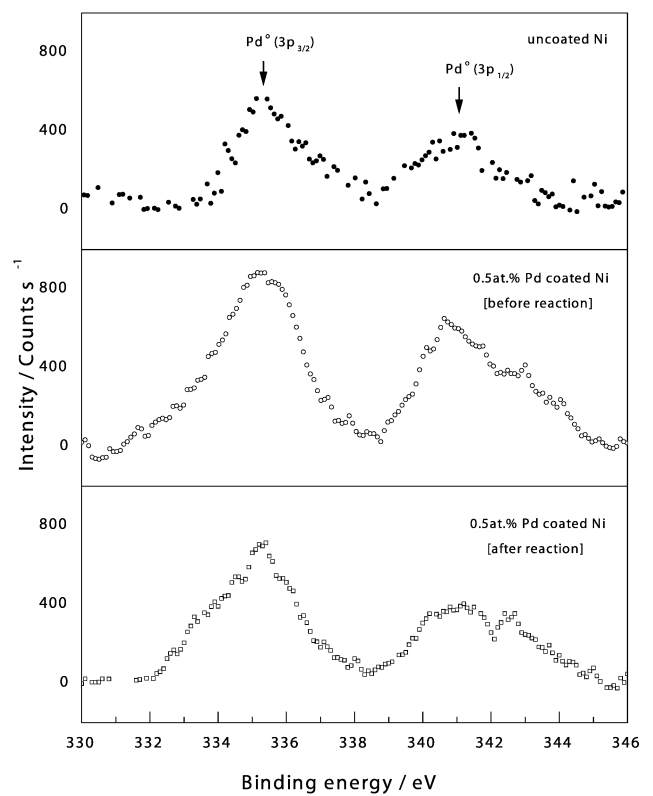


Fig. 4 Pd(3d) region of uncoated Ni, and 0.5 at% Pd-coated Ni before and after the hydrogenation reaction.

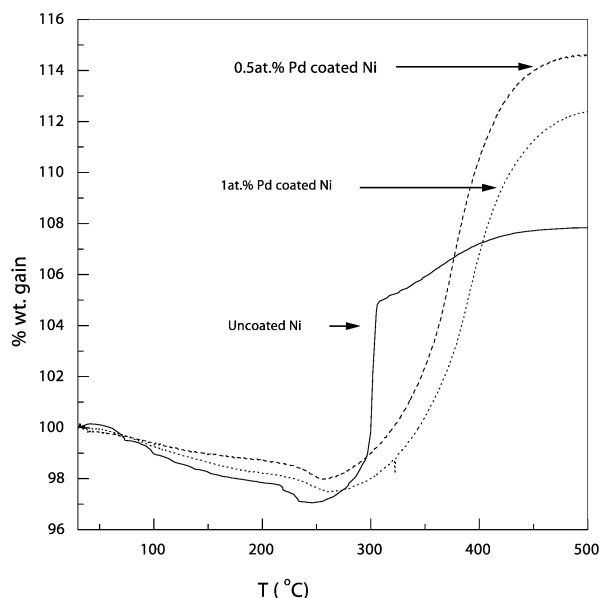


Fig. 5 TGA curves of uncoated, 0.5 and 1 at% Pd-coated Ni particles.

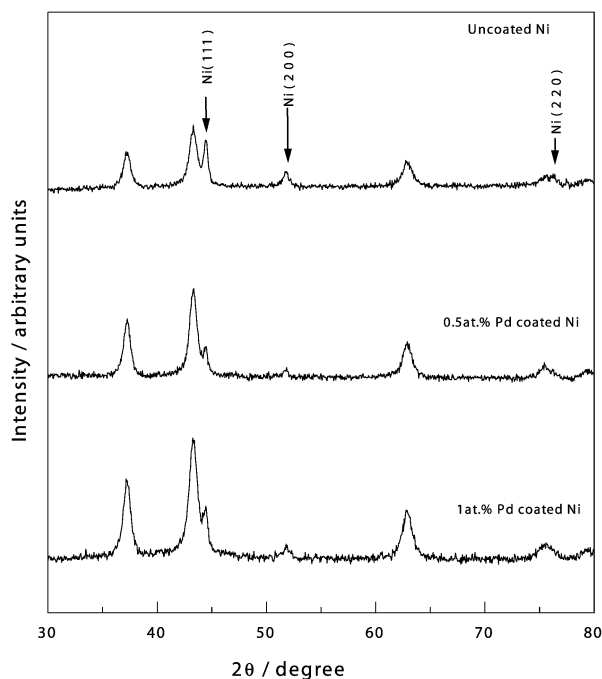


Fig. 6 XRD patterns of the oxidized samples in the TGA experiments.

EG on Pd-coated Ni. Oxidation of Pd-coated Ni occurs at a higher temperature than uncoated Ni. If Ni was completely oxidized to NiO, 28% weight gain should have been observed. A lower weight gain in all the three cases suggests that part of Ni is not oxidized due to a Ni/Pd alloying effect. XRD patterns of the oxidized samples from the TGA experiments are shown in Fig. 6. We can see diffraction lines due to NiO and the unoxidized Ni. No Pd metal lines are seen. Lines due to PdO are also not seen even after expanding the 2θ region where lines due to PdO would be expected. The TGA study thus shows that Pd-coated Ni is stable in air up to 300 °C.

Hydrogenation of nitrobenzene

Two forms of Ni, Pd/C catalysts, uncoated Ni and 0.5 and 1 at% Pd-coated Ni metal particles were employed the hydrogenation of nitrobenzene. Product analysis by gas

Table 1 Percentage conversion from nitrobenzene to aniline under 1.0 atm. H₂ (g) at room temperature in methanol solution after 6 hours reaction time

Catalyst	Amount/mg	% Conversion	TOF/s ¹
Bulk Ni (Fluka)	50	2.5	
Raney Ni	55	8.9	
Uncoated Ni	50	9.32	
Pd	4.2	55	0.013
Pt	5.9	45	0.014
5 wt% Pd/C as obtained	23	49	0.032
5 wt% Pd/C activated	25	100	0.076
0.5 at% Pd-coated Ni	50	90	0.172
1 at% Pd-coated Ni	50	100	0.102

chromatography has proved that nitrobenzene has been stoichiometrically converted to aniline, without any by-product. The results are given in Table 1. The reactions were carried out at 27 °C in each case. Ni metal powder of Fluka showed lowest conversion of 2.5%. Raney Ni and uncoated Ni made in this work gave ~9% conversions. 100% conversion of nitrobenzene to aniline was observed with 1 at% Pd-coated Ni. Therefore, Pd nuclei on which the Ni particle is grown has little influence on the hydrogenation reaction. The coating of Pd on Ni indeed enhances the activity. In order to compare the catalytic activity of Pd-coated Ni with pure Pd, Pt and Pd/C catalysts, the turnover frequencies [TOF = number of moles of products per second/number of moles of Pd] were calculated taking into account only the Pd in the coating of the nickel samples. TOF values for 0.5 and 1 at% Pd-coated Ni are almost 10 times that of pure Pd and Pt particles. Conversion with activated (hydrogen treated at 200 °C) 5 wt% Pd/C is twice that of unactivated (as received) Pd/C catalyst. The TOF of 0.5 at% Pd-coated Ni is 2.5 times higher than that of the activated Pd/C catalyst. Even the 1 at% Pd-coated Ni has a much higher TOF compared to the activated Pd/C. Therefore, the Pd-coated Ni is more efficient than Pd/C.

The average size of a Ni nanoparticle is 50 nm. Assuming that Pd is dispersed atomically on the surface of the Ni nanoparticles, surface coverage of Pd is calculated as follows. Assuming the Ni particles are spherical, and the surface consists of Ni (111), the number of Ni atoms on the surface of each Ni particle is 1.46×10^5 . Distributing the Pd equally over all the Ni particles in the 0.5 at% Pd-coated Ni, the number of Pd atoms per Ni particle is 3.26×10^4 . Thus the surface coverage of Pd over Ni is only about 0.22 for 0.5 at% Pd-coated Ni. Even 1 at% Pd-coated Ni, the surface coverage of Pd is 0.45. Thus, less than monolayer coverage of Pd over Ni nanoparticles shows high hydrogenation activity.

Ni nanoparticles prepared by the polyol method gave ~9% nitrobenzene conversion to aniline and with less than monolayer Pd coverage reactivity is enhanced to the extent of 100% conversion for the same reaction time. This is certainly due to the Pd–Ni interaction on the surface of the particle but the exact nature of the interaction is not clear to us. One possibility is that atomically dispersed Pd on the Ni surface is highly active.

0.5 and 1 at% Pd-coated Ni nanoparticles were stored in air. The % conversion of nitrobenzene to aniline using these stored samples in the catalytic reactions was the same as that of freshly prepared samples even after a year. Thus, surface of the catalyst is protected against oxidation. The shelf-life of the catalyst is high.

Conclusions

We have prepared Pd-coated Ni metal nanoparticles by the polyol method. These particles were employed to catalyze the hydrogenation of nitrobenzene. 0.5 to 1 at% Pd-coated Ni were found to be more active than commercial Pd/C for the

hydrogenation reaction. From the TOF values, we have shown that 2–3 times less Pd is sufficient to convert the same amount of nitrobenzene to aniline compared to the Pd/C catalyst.

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