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# Dispersing palladium nanoparticles using a water-in-oil microemulsion—homogenization of heterogeneous catalysis

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**Palladium nanoparticles dispersed by a water-in-oil microemulsion are very effective catalysts for hydrogenation of olefins in an organic solvent.**

Catalytic hydrogenation using metallic palladium particles is an important process in organic synthesis. Commercially available palladium catalyst is stabilized in activated carbon (Pd/C) that is traditionally used for heterogeneous catalysis including hydrogenation of olefins.[1] A recent report shows that palladium nanoparticles can be stabilized and dispersed in a water-in-$CO_2$ microemulsion for catalytic hydrogenation of olefins and nitro compounds with very fast reaction rates.[2] Efficient hydrogenation of olefins is most likely due to the fact that palladium nanoparticles in the microemulsion are uniformly dispersed and mixed with reactants resembling a homogeneous catalytic system. This concept of homogenization of heterogeneous catalysis utilizing microemulsion as a medium for dispersing metal catalysts should have important applications in conventional heterogeneous catalysis carried out in organic solvents. Sato et al. recently prepared ultrafine Pd particles in reverse micells using $KBH_4$ as a reducing agent and observed their catalytic activity for hydrogenation of allyl alchohol and styrene in isooctane.[3] The authors noted that the hydrogenation activity was inhibited by the AOT, bis(2-ethylhexyl) sulfosuccinate, surfactant. In another paper, de Jesus and Spiro showed the oxidation of TMPPD (*N*,*N*,*N′*,*N′*-tetramethyl-*p*-phenylenediamine) by $Co(NH_3)_5Cl^{2+}$ catalyzed by Pd nanoparticles in an aqueous/AOT/n-heptane microemulsion.[4] In this paper, we report the dispersion of palladium nanoparticles in a water/AOT/n-hexane microemulsion by hydrogen gas reduction of $PdCl_4^{2-}$ and its efficiency for hydrogenation of olefins in organic solvents.

Sodium tetrachloropalladate ($Na_2PdCl_4$) was purchased from Alfa. AOT was obtained from Aldrich and used as received. A Pd/C catalyst containing 10% Pd by weight was obtained from Aldrich. An Ocean Optics (OOI CHEM2000) UV-Vis spectrometer and a 300 MHz NMR (Bruker AMX300) were used for spectroscopic measurements. Transmission electron microscope (TEM) pictures were obtained using a Jeol (JEM-1200EXΠ) instrument. The procedure of preparation of the microemulsion is described as follows. Ten mL of hexane was first placed in a 25 mL round bottomed flask with a magnetic stirrer. After that, 40.5 μL of a 0.04 M aqueous $Na_2PdCl_4$ solution and 66.7 mg (0.15 mmol) of AOT were added to the flask that gave a *W* value ($[H_2O]$/[surfactant]) of 15. The system was stirred for 1 hour and the solution was optically transparent with a light yellowish color. To make Pd nanoparticles, the system was flushed with nitrogen gas under stirring followed by passing hydrogen gas (1 atm) through the system. Hydrogen gas is capable of reducing $Pd^{2+}$ to metallic Pd according to a previous study.[2] The UV/Vis spectra of the solution before and after addition of hydrogen gas are given in Figure 1(a). Palladium nanoparticles are known to absorb in the UV region with virtually no structure.[2,5] About 1 mL of the hexane solution after hydrogen reduction was taken for TEM study. The solution was shaken with a methanol–chloroform(1 : 1) mixture and samples were taken from the methanol phase and placed on copper grids. After evaporation to dryness, the copper grid samples were examined by TEM. Figure 1(b) shows the presence of spherical palladium metallic particles with diameters in the range 4–10 nm.

Three olefins (1-phenyl-1-cyclohexene, methyl *trans*-cinnamate, and *trans*-stilbene) were selected for this investigation and their structures are given in Table 1. A selected olefin (e.g. 1-phenyl-1-cyclohexene 23.7 mg or 0.15 mmol) was added to the hexane solution containing the microemulsion with

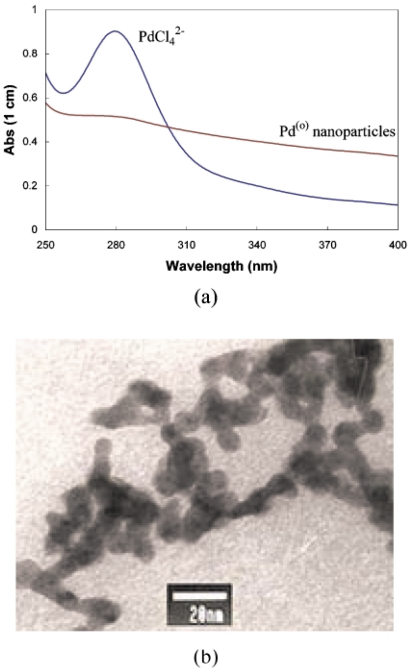
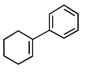
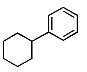
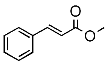
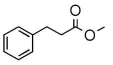
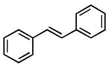
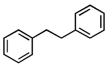


**Fig. 1** (a) UV-Vis spectra of $[PdCl_4]^{2-}$ and Pd nanoparticls in a water-in-oil microemulsion (0.04 M aq. $Na_2PdCl_4$, [AOT] = 0.15 mmol in 10 mL of n-hexane, *W* = 15) (b) TEM micrograph of Pd nanoparticles collected from the water-in-oil microemulsion system. (scale = 20 nm)

**Table 1** Catalytic hydrogenation of olefins with Pd nanoparticles in a water-in-hexane microemulsion

| Olefin | Catalyst | Reaction time | Conversion % | Product |
|---|---|---|---|---|
|  | Pd/ME[a] | 5 min | > 97 |  |
| | Pd/C[b] | 20 min | 50 | |
| | Pd/C[b] | 40 min | > 97 | |
|  | Pd/ME[a] | 6 min | > 97 |  |
| | Pd/C[b] | 25 min | 60 | |
| | Pd/C[b] | 45 min | > 97 | |
|  | Pd/ME[a] | 7 min | > 97 |  |
| | Pd/C[b] | 40 min | 68 | |
| | Pd/C[b] | 60 min | > 97 | |

[a] Molar ratio of olefin/AOT/$Na_2PdCl_4$ = 1/1/0.01 and 10 mL of n-hexane used as solvent (W = 15) at 30 °C. [b] 1.7 mg of Pd/C (0.17 mg or 1.6 μmol of Pd) in 10 ml of n-hexane.

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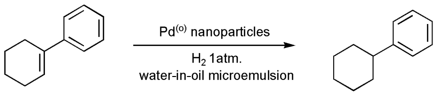
$Na_2PdCl_4$ in the water core. This is followed by bubbling hydrogen through the system. The system was stirred at 30 °C and samples were taken every minute to monitor the amounts of the reactant and the product using TLC and NMR spectroscopy. The amount of the olefin added to the solution was about two orders of magnitude greater than that of the total palladium present in the system. The hydrogen gas serves a dual purpose of reducing Pd ions as well as the starting material for the hydrogenation process as shown in Scheme 1.

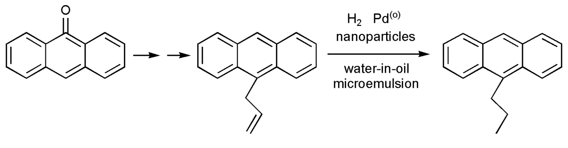
The results of hydrogenation of the three olefins catalyzed by the Pd nanoparticles dispersed in the hexane solution by the microemulsion are summarized in Table 1. In the case of 1-phenyl-1-cyclohexene, the reactant was not detectable by NMR after 5 minutes of reaction. Only the product 1-phenyl-1-cyclohexane shown in Scheme 1 was detected. From the detection limit of the NMR peak of the reactant, we estimated the conversion yield to be $>97\%$. A control experiment was also done without $Na_2PdCl_4$ in the water core of the microemulsion. In this case, only the reactant 1-phenyl-1-cyclohexene was detected under the specified experimental conditions indicating Pd nanoparticles were responsible for the catalytic hydrogenation. The hydrogenation reaction was also carried out using commercial Pd/C catalyst under the same conditions except in the absence of the microemulsion. About 1.7 mg of the Pd/C (0.17 mg, 1.6 μmol of Pd) was used in this experiment. The total amount of Pd in this case was the same equivalent for the microemulsion experiment. The system was stirred and samples were taken at different times and analyzed by the procedure described above. The conversion was about 50% after 20 minutes of reaction, After 40 minutes of reaction, the conversion was more than 97%. The palladium nanoparticles dispersed by the microemulsion in the organic solvent is obviously more efficient than the conventional Pd/C catalyst.



**Scheme 1** Hydrogenation of 1-phenyl-1-cyclohexene

The results of hydrogenation of the other two olefins, methyl *trans*-cinnamate and *trans*-stilbene, catalyzed by microemulsion dispersed palladium nanoparticles (Table 1) are similar to that of 1-phenyl-1-cyclohexene described above. Virtually all of the starting olefins were converted to the saturated hydrocarbons in 6–7 minutes. Using the conventional Pd/C catalyst, the conversion was 60% after 20 min for methyl *trans*-cinnamate and 68% after 40 min for *trans*-stilbene. Quantitative comparison of hydrogenation activity of the Pd nanoparticles in microemulsion versus conventional Pd/C catalysts requires detail knowledge about mass transport processes from the bulk solvent to the particle surface and the effective surface area that is not available at the present time. Research along this direction is currently in progress.

Another challenging test was the catalytic hydrogenation of monoalkylated anthracene, 10-(3-propenyl)anthracene as shown in Scheme 2. This molecule was synthesized from a monoalkylated anthrone derivative.[6] The monoalkylated anthracene derivative, 10-(3-propenyl)anthracene,[7] showed relatively poor hydrogenation in Pd/C catalyst. The conversion was less than 45% after 1 hour of reaction under the same reaction condition. In the case of the palladium nanoparticles dispersed by the water-in-oil microemulsion, however, the product, 10-propylanthracene,[8] was detected with more than 50% by NMR after 9 minutes of reaction.



**Scheme 2** Hydrogenation of 10-(3-propenyl)anthracene

The formation of palladium nanoparticles in the AOT microemulsion was also studied using different solvents including ethyl acetate, dimethyl formamide, toluene, chloroform and dichloromethane. Chloroform and dichloromethane are not able to form a stable water-in-oil microemulsion with AOT and a $Na_2PdCl_4$ solution. Ethyl acetate, dimethyl formamide and toluene are able to form water-in-oil microemulsion with AOT and a solution of $Na_2PdCl_4$. Other factors such as the $W$ value,[9] temperature,[10] amount and nature of surfactant[11] can also affect the stability of the microemulsion and consequently the catalytic efficiency of the metal nanoparticles. Extensive studies of these parameters are currently in progress.

The Pd nanoparticles formed in the water/AOT/n-hexane microemulsion at $W = 15$ was stable for about 15–20 minutes. After that aggregation of nanoparticles would occur and black Pd particles became visible in the solution. The Pd particles could be separated from the hexane solution by filtration. We could also recover AOT by adding an acid solution (e.g. 6 M HCl) to hexane and AOT would partition favorably in the acid solution.[12]

In conclusion, we have demonstrated that palladium nanoparticles dispersed by a water-in-oil microemulsion are very efficient catalysts for hydrogenation of olefins in an organic solvent. This approach can be applied to other metal catalyst systems including platinum, rhodium, nickel, etc. The concept of homogenation of heterogeneous catalysis by dispersing nanoparticles in solutions described in this paper may have a wide range of applications in organic synthesis and in industrial manufacturing processes.

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