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Swelled plastics in supercritical CO_2 as media for stabilization of metal nanoparticles and for catalytic hydrogenation

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Received (in Corvallis, OR, USA) 19th September 2003, Accepted 27th February 2004
First published as an Advance Article on the web 16th March 2004

Swelled plastics in supercritical carbon dioxide provide unique environments for stabilizing palladium and rhodium nanoparticles and for catalytic hydrogenation. Complete hydrogenation of benzene to cyclohexane can be achieved in 10 minutes using the plastic stabilized Rh nanoparticles at 50 °C in supercritical CO_2. High efficiency, reusability, and rapid separation of products are some advantages of the plastic stabilized metal nanoparticles for catalytic hydrogenation in supercritical CO_2.

There has been much interest recently in synthesizing nanometer-sized metal particles because of their potential applications as new catalysts for organic reactions.[1–3] The effect of size of metal nanoparticles on catalytic activities is one of the interesting aspects of the current research in this area.[4] However, nanometer-sized metal particles are unstable and tend to agglomerate without a suitable support. Different stabilizing approaches for nanoparticles have been reported in the literature including the use of chemical stabilizers,[3] dendrimers,[2] polymers[5] and microemulsions.[6]

In this communication, we report a novel approach of catalytic hydrogenation in supercritical CO_2 using palladium and rhodium nanoparticles stabilized in plastics. Since plastics swell in supercritical CO_2,[7,8] metal precursors dissolved in the fluid phase can penetrate into plastic structures. After hydrogen reduction of the metal precursors, the resulting metals are trapped as nanometer-sized particles and stabilized in the plastic structures. During catalytic hydrogenation, starting materials dissolved in CO_2 can penetrate into the swelled plastic structures and diffuse into the interior of the plastic containing metal nanoparticles for catalytic hydrogenation to take place effectively. Because the hydrodynamic diameters of metal nanaoparticles trapped in the plastic are much larger than that of starting materials (such as benzene and phenol), the plastic structures allow the reactants to diffuse into the interior but forbid metal nanoparticles to diffuse and to agglomerate. Therefore, not only do the metal nanoparticles exist on the surface of the plastic but they are also present in the interior of the plastic and are available for catalysis in supercritical CO_2. Consequently, the amount of metal nanoparticles per volume of the supporting plastic material can be extremely high compared with those of conventional active carbon and alumina supported metal catalysts. Thus, the plastic stabilized Pd and Rh nanoparticles can be used repeatedly without losing their catalytic capabilities. After reaction, the products of the catalytic hydrogenation diffuse away from the plastic structure. Finally the products can be easily separated from the plastic catalysts by rapid expansion of CO_2.

The plastic supported palladium and rhodium nanoparticles were prepared by hydrogen reduction of Pd(II) hexafluoroacetylacetonate [Pd(hfa)$_2$] and Rh(III) acetylacetonate [Rh(acac)$_3$] in supercritical CO_2. Watkins and McCarthy previously reported that nanometer-sized platinum particles could be uniformly deposited into poly(4-methyl-1-pentene) and poly(tetrafluoroethylene) in supercritical CO_2 by hydrogen reduction of a platinum precursor.[9] In our experiments, a 50 mL high-pressure stainless flat-bottom cell was used for the synthesis of the metal nanoparticles. High density polyethylene (HDPE) granules (3 mm diameter) and fluoropolymer (PFA) tube (6 mm diameter) obtained from Aldrich were used as supporting plastics. The PFA tubing was sliced into rings with a 1 mm width. The plastic materials were placed in a 50 mL high-pressure cell together with 250 mg of the metal precursor [Pd(hfa)$_2$ or Rh(acac)$_3$]. The 50 mL cell was then pressurized by 100 atm CO_2 to dissolve the Pd or Rh precursor in supercritical CO_2. Hydrogen gas (10 atm) was introduced into a separate injection vessel (10 mL volume) followed by pressurizing the injection vessel with 200 atm CO_2. By opening an interconnecting valve between the 50 mL high-pressure cell and the 10 mL injection vessel, hydrogen was injected into the 50 mL high pressure cell with the aid of the pressure difference between the two cells. The hydrogen reduction of Pd(hfa)$_2$ was performed at 200 atm and 50 ± 5 °C. After about 2 hours, Pd was successfully deposited into HDPE granules or PFA rings. The yellowish color caused by Pd(hfa)$_2$ became dark gray due to Pd metal particle formation as seen in Fig. 1a. A piece of the PFA with Pd nanoparticles was cut in half for observation. The whole cross section (width 1 mm) was also dark gray in color indicating that the Pd precursor penetrated deep into the whole PFA ring in supercritical CO_2 and deposited uniformly in the plastic as metal nanoparticles. Fig. 1b shows a TEM micrograph of the Pd nanoparticles deposited in HDPE. The method for TEM sample preparation was identical to that reported in the literature.[9] From the TEM micrograph, the size distribution of the metal nanoparticles was estimated to vary from 2 to 10 nm with the largest fraction in the range of 4–5 nm diameter.

In the synthesis of Rh nanoparticles, 3.5 mL chloroform was added to enhance the solubility of Rh(acac)$_3$ in supercritical CO_2. In addition, 10 mg of Pd(hfa)$_2$ was also added as a catalyst for hydrogen reduction of Rh(acac)$_3$. The Rh nanoparticle depositions in HDPE granule and PFA ring were performed at 110 and 150 °C, respectively. The plastic supported metal nanoparticles are very stable in air. No obvious agglomeration of the metal nanoparticles in the plastic materials was observed even after 3 months of storage in our laboratory based on TEM micrographs.

It should be noted that newly prepared plastic stabilized Pd and Rh catalysts must be washed thoroughly in supercritical CO_2 to remove possible byproducts produced from the reduction process. We recommend washing of the plastic catalysts with neat supercritical CO_2 at 100 atm and 50 °C repeatedly until the byproducts [hexafluoroacetylacetone from Pd(hfa)$_2$ and acetylacetone from Rh(acac)$_3$] are no longer detectable from the trapped solution. Hydrogenations of olefins, arenes and nitro compounds were studied using the plastic supported Pd or Rh nanoparticles prepared by the procedure given above. The plastic catalyst (4.5 g PFA or 3.0 g HDPE) and a starting material (the amounts are shown in Table 1) were placed in a 10 mL high-

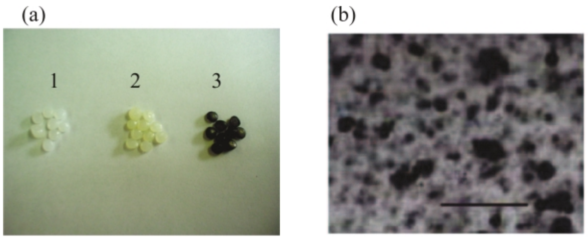


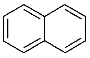
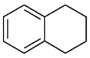
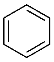
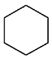
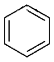
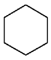
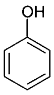
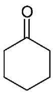
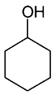
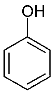
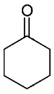
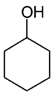
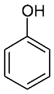
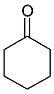
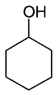
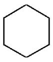
Fig. 1 (a) Optical image of HDPE, (1) original, (2) with Pd(hfa)$_2$, (3) with Pd nanoparticles. (b) TEM micrograph of Pd nanoparticles deposited in HDPE; scale = 50 nm.

DOI: 10.1039/b311522d

pressure stainless cell. The amounts of Pd and Rh in the PFA or HDPE were estimated to be 0.015–0.022 mmol based on the weight difference before and after deposition of the metal precursors in the plastic. The stainless cell was heated to a desired reaction temperature (*e.g.* 50 °C) in an oven. Hydrogen gas was flowed through the whole system to purge air and then was pressurized to 10 atm. Finally the reactor was pressurized by 100 atm of CO_2 to allow the starting material to dissolve in the CO_2 phase and for the hydrogenation reaction to occur. After a reaction time of 10–60 minutes, the reaction products were collected in a $CDCl_3$ solution by the RESS technique for NMR measurements using a 300 MHz NMR spectrometer (BRUKER AMX 300). The results of hydrogenation of arenes using the plastic supported Pd or Rh nanoparticles as catalysts are summarized in Table 1.

Using the plastic stabilized Pd nanoparticles as catalysts (in HDPE granule or in PFA ring), the hydrogenations of arenes proceed rapidly even at 50 °C. Hydrogenation of naphthalene to form tetralin was completed within 15 minutes under our experimental conditions. In order to examine the recyclability of the plastic supported metal nanoparticles, the hydrogenation of naphthalene using the HDPE supported Pd nanoparticle catalyst was repeated 10 times under the same experimental conditions. The conversion of naphthalene to tetralin was always >99 % and did not show an obvious decrease in hydrogenation efficiency. The fine structures of the plastic are effective for preventing diffusion and agglomeration of the nanoparticles in the plastic structures. On the other hand, the arenes can diffuse smoothly in the swelled plastic structures and can contact with nanoparticles, because of the extremely small hydrodynamic diameter compared with that of nanoparticles. The plastic stabilized Rh nanoparticles are more effective than the Pd nanoparticles for catalytic hydrogenation of arenes. The hydrogenation of benzene to cyclohexane using the PFA stabilized Rh nanoparticles was almost completed (99%) within 10 minutes at 50 °C with 10 atm H_2 and 100 atm CO_2. Using PFA stabilized Pd nanoparticles under the same reaction conditions, conversion of benzene to cyclohexane was 86% after 60 min. Fig. 2 shows a typical NMR spectrum of the reaction products found in the trap solution after hydrogenation of benzene using the Rh catalyst in supercritical CO_2. The only major peaks found in the NMR spectrum are cyclohexane (1.4 ppm) and chloroform from $CDCl_3$ (7.2 ppm). Two very small peaks at 1.5 ppm and 7.3 ppm are due to H_2O and the starting material benzene ($<$ 1%), respectively. This result clearly shows that the separation of the product from the plastic catalyst can be achieved by rapid expansion of CO_2. Despite repeated use of the same Rh catalyst throughout this series of experiments for hydrogenation of benzene (to determine the hydrogenation speed and to check the reproducibility), the PFA supported Rh nanoparticles did not show any observable changes in the catalytic activity. The Rh nanoparticles are also more effective than Pd for hydrogenation of phenol to cyclohexanone (major) and cyclohexanol (minor).

Table 1 Hydrogenation of arenes using the plastic supported metal nanoparticles

Metal	Plastic	Starting material	*T*/°C	*t*/min	Product (Conversion)
Pd	HDPE	 20 mg (0.15 mmol)	50	15	 (~100%)
Rh	PFA	 15 μL (0.17 mmol)	50	10	 (>99%)
Pd	PFA	 15 μL (0.17 mmol)	50	60	 (86%)
Pd	HDPE	 15 mg (0.16 mmol)	50	60	  (78%) (6%)
Pd	PFA	 15 mg (0.16 mmol)	50	50	  (62%) (38%)
Rh	PFA	 15 mg (0.16 mmol)	50	20	   (60%) (33%) (3%)

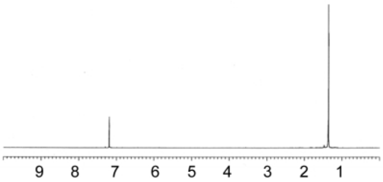


Fig. 2 NMR spectrum of hydrogenation of benzene using the Rh nanoparticles.

The hydrogenation of olefin and nitro compounds were also tested using PFA supported Pd nanoprticles. 4-methoxy cinnamic acid (15 mg) was converted to 4-methoxy hydrocinnamic acid ($>98\%$) in 5 minutes at 50 °C with 10 atm of H_2 and 100 atm of CO_2. Nitrobenzene (15 μL) was converted to aniline ($>98\%$) with minor products ($<2\%$) cyclohexyl amine and cyclohexane in 5 minutes under the same conditions in supercritical CO_2.

Although there are many kinds of nanoparticle catalysts with high catalytic activity as well as this research,[10,11] the plastic supported Pd and Rh nanoparticles may have great advantages over other nanoparticle catalysts in chemical synthesis and manufacturing processes, because of their stability, recyclability, easy handling and separation of products. The technique can be applied to other catalytic metals and different plastics. Since various forms of high temperature plastics such as polyimide, polytetrafluoroethylene and polybenzimidazole are commercially available, the plastic supported metal nanoparticles may be used for high temperature catalytic reactions.

This work was supported by Idaho NSF-EPSCoR and ARO-DEPSCoR programs.

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