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Hydrogenation of Olefins in Supercritical CO_2 Catalyzed by Palladium Nanoparticles in a Water-in-CO_2 Microemulsion

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Utilizing water-in-CO_2 microemulsions as templates for synthesizing metallic silver and copper nanoparticles in supercritical fluid CO_2 has been demonstrated recently.[1,2] The metal nanoparticles synthesized in the CO_2 microemulsions are uniformly dispersed in the supercritical fluid phase and are stable over an extended period of time.[1,2] One potential application of these metallic nanoparticles is for catalysis in supercritical CO_2, but no experimental evidence has been reported so far regarding this possibility. In our previous studies, the metal nanoparticles were synthesized by chemical reduction of appropriate metal ions dissolved in the water core of the microemulsion with an organic reducing agent such as sodium triacetoxyborohydride, sodium cyanoborohydride, or *N*,*N*,*N′*,*N′*-tetramethyl-*p*-phenylenediamine. These organic reagents are not ideal reducing agents for metal reduction in supercritical CO_2 because they generally have limited solubilities in supercritical CO_2 and may form byproducts that could complicate further utilization of the nanoparticles for chemical or materials applications. Recently, the reduction of $PdCl_4^{2-}$ by hydrogen gas followed by the formation of the Pd nanoparticles in aqueous solutions was reported.[3] We found that adding hydrogen gas to supercritical CO_2 can also cause reduction of a number of metal ions including Pd^{2+} dissolved in the water core of the microemulsion. Hydrogen gas is a very desirable reducing agent in comparison with the organic reagents used previously for metal reduction in supercritical CO_2 due to its miscibility with CO_2 and its chemical simplicity. After reduction, the hydrogen gas can also serve as a starting material for in situ hydrogenation in supercritical CO_2. The advantages of using supercritical CO_2 as a reaction medium for catalysis are described in a number of recent publications.[4,5] Catalytic hydrogenation in supercritical CO_2 using CO_2-soluble organorhodium and organoruthenium complexes is known in the literature.[6] In this communication, we report for the first time the preparation of nanometer-sized metallic palladium particles in a water-in-CO_2 microemulsion by hydrogen reduction of Pd^{2+} and the subsequent in situ hydrogenation of olefins (water-soluble or CO_2-soluble) catalyzed by the Pd nanoparticles in supercritical CO_2. This method of formation and dispersion of nanoparticles in supercritical CO_2 is simple and requires no organic synthesis and preparation of catalysts. The method is not limited to palladium; other metal nanoparticles can also be synthesized and dispersed in supercritical CO_2 using a similar approach for various catalyses.

The water-in-CO_2 microemulsion was prepared by mixing a certain amount of an aqueous Pd^{2+} solution (0.04 M) and a mixture of surfactants containing sodium bis(2-ethylhexyl)sulfosuccinate [AOT] (15 mM) and a cosurfactant perfluoropolyether phosphate [PFPE-PO_4] (30 mM) following the procedures described in the literature.[1,2] Two homemade high-pressure vessels were used for the synthesis of Pd(0) nanoparticles and the subsequent hydrogenation reactions. One vessel (9.5 mL volume) was equipped with a fiber-optic system (3 mm path length) connected to a CCD array UV−vis spectrometer (Spectral Instruments Inc., model SI-440, Tucson, AZ) for in situ spectroscopic measurements.[7] The other vessel with a volume of 50 mL was used to store hydrogen gas and the selected olefin. The surfactants and an aqueous $PdCl_2$ solution (total amount 2.2×10^{-3} mmol in the system for all experiments) were placed in the 9.5-mL fiber-optic cell. The solution was stirred for 1 h in CO_2 at 80 atm to ensure the formation of an optically transparent microemulsion. The 50-mL high-pressure vessel containing 4-methoxycinnamic acid (30 mg or 4.2 mmol near the saturation amount in liquid CO_2) and 10 atm hydrogen gas was pressurized to 200 atm by CO_2. The starting materials were forced into the fiber-optic cell by opening an interconnecting valve, and the pressure was kept constant at 200 atm by the ISCO pump. Immediately after completion of the injection (about 5 s), the fiber-optic cell was isolated by closing the interconnecting valve. In this process, about 10% of the starting materials in the 50-mL high-pressure vessel were injected into the fiber-optic cell.

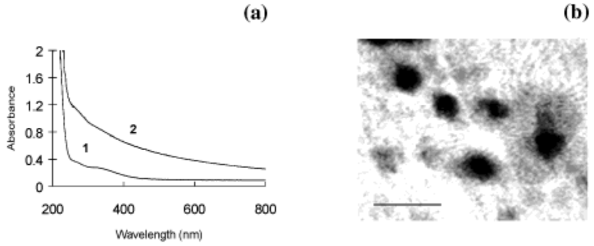

Figure 1. (a) UV−vis spectra of palladium (0.04 M Pd^{2+}) in the water-in-CO_2 microemulsion (with a water-to-surfactant ratio $W = 20$) before (spectrum 1) and after (spectrum 2) the injection of hydrogen in supercritical CO_2 at 50 °C and 200 atm. (b) TEM micrograph of the Pd nanoparticles collected in hexane using the RESS method (scale = 20 nm).

The formation of Pd(0) nanoparticles was confirmed by injecting only hydrogen gas into the fiber-optic cell containing the microemulsion with $PdCl_2$ in the water core. The surfactants absorb in the UV region as shown in Figure 1a. Palladium nanoparticles are known to absorb in the UV−vis region with hardly any structure. The broad absorption band in the visible region after injection of hydrogen was consistent with the reported spectra of Pd nanoparticles stabilized by a water-soluble stabilizer[3] in aqueous solution and a polymer[8] in a water/alcohol mixture solvent. The absorption band of Pd nanoparticles in the microemulsion system decreased gradually with time but lasted long enough (>1 h) for testing the catalytic capability of the nanoparticles in supercritical CO_2. The Pd nanoparticles were also collected in a hexane solution using the RESS (rapid expansion of supercritical solution) method[9] and studied by TEM. The TEM micrograph showed spherical Pd particles with a size range of about 5−10 nm (Figure 1b).

Hydrogenation of 4-methoxycinnamic acid to 4-methoxyhydrocinnamic acid catalyzed by Pd nanoparticles was performed first in liquid CO_2 at room temperature (20 °C). Spectra shown in Figure

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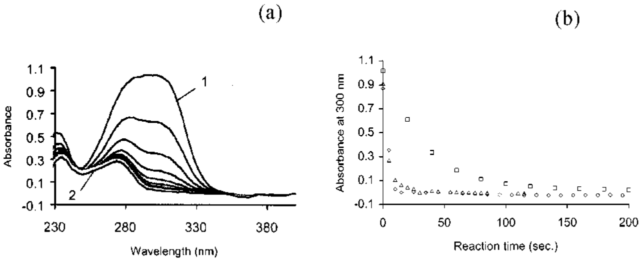
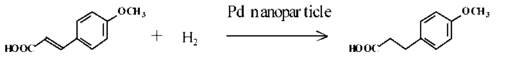


Figure 2. (a) Variation of UV−vis spectra of 4-methoxycinnamic acid with time during the hydrogenation process in CO_2 at 20 °C and 200 atm. Each spectrum was taken at 20-s intervals starting from zero time, spectrum 1. (b) Variation of the 4-methoxycinnamic acid absorption with time at 300 nm and 200 atm at (□) 20, (△) 35, and (◇) 50 °C.

2a were taken at 20-second intervals after the injection of hydrogen and 4-methoxycinnamic acid into the water-in-CO_2 microemulsion with $PdCl_2$ in the water core ($W = 20$). The first spectrum obtained immediately after the injection (spectrum 1) was identical to that of 4-methoxycinnamic acid dissolved in CO_2. The broad absorption peak centered around 300 nm decreased gradually and a new absorption peak centered around 270 nm appeared. After about 2 min, the absorbance at 300 nm dropped to the baseline level. The absorption peak (270 nm) in spectrum 2 (Figure 2a) was consistent with that of 4-methoxyhydrocinnamic acid. In the absence of $PdCl_2$ in the microemulsion, the absorption peak of 4-methoxycinnamic acid did not show a measurable decrease after the injection of the olefin and hydrogen into the fiber-optic reactor. The results indicate that the Pd nanoparticles formed in the water core of the CO_2 microemulsion are capable of catalyzing hydrogenation of 4-methoxycinnamic acid to 4-methoxyhydrocinnamic acid as shown in eq 1.



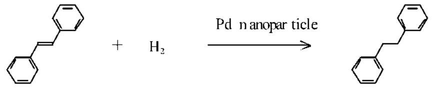
(1)

Figure 2b shows the decrease in the absorbance at 300 nm with time for the hydrogenation of 4-methoxycinnamic acid in liquid CO_2 at 20 °C and in supercritical CO_2 at 35 and 50 °C. The speed of the hydrogenation process is much faster in the supercritical CO_2 phase (35 and 50 °C) compared with that in the liquid CO_2 phase (20 °C). The hydrogenation process at 50 °C under the specific conditions was virtually completed in 20 s. The absorbance in logarithmic scale for both the liquid and supercritical CO_2 experiments decreases linearly with time, suggesting the hydrogenation process follows first-order kinetics. The apparent rate constants obtained from the slopes are about 1.1×10^{-2}, 6.9×10^{-2}, and 9.4×10^{-2} sec^{-1} at 20, 35, and 50 °C, respectively. The difference in the reaction rate between 20 and 35 °C was much larger than that between 35 and 50 °C. The hydrogenation reaction probably is controlled by the diffusion of the reactant from bulk CO_2 to the palladium nanoparticle surface. The diffusion coefficient of CO_2 dramatically changes at the critical point (31 °C).

Immediately after completion of the UV−vis spectrum change (after 20 s at 50 °C), the product was collected in acetone-d_6 via the RESS method for ^1H NMR spectroscopy (BRUKER, AMX 300).

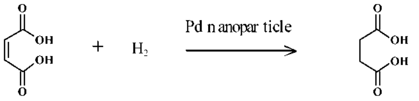
The NMR results are consistent with UV−vis spectra shown in Figure 2, indicating that hydrogenation of 4-methoxycinnamic acid to 4-methoxyhydrocinnamic acid at 50 °C was completed (>99%) within 20 s. The reactor after depressurizing was also washed with acetone-d_6 for NMR analysis. No detectable amount of 4-methoxycinnamic acid was observed in the spectrum. In the absence of hydrogen gas or $PdCl_2$, NMR spectra of the control systems did not show any detectable 4-methoxyhydrocinnamic acid peaks.

Hydrogenation of another CO_2-soluble olefin *trans*-stilbene utilizing the Pd nanoparticles in the water-in-CO_2 microemulsion (eq 2) was also investigated in liquid CO_2 (20 °C and 200 atm).



(2)

In this case, UV−vis spectra cannot be used to monitor the reaction speed because both the reactant *trans*-stilbene and the product 1,2-diphenylethane absorb in the UV range that overlapped with the surfactants. Therefore, ^1H NMR spectroscopy was used for identification of the product. Two minutes after the injection of *trans*-stilbene and hydrogen in the microemulsion system, the product was collected into acetone using the RESS technique. The NMR spectrum of this solution indicates that almost all *trans*-stilbene (>95%) in the reactor was converted to 1,2-diphenylethane. Washing of the reactor with acetone after depressurizing showed no detectable amount of *trans*-stilbene. In the absence of hydrogen gas or $PdCl_2$, NMR peaks of 1,2-diphenylethane were not observed.



(3)

The water-in-CO_2 microemulsion system can dissolve ionic species and hydrophilic organic compounds in the water core. This property can be used to perform hydrogenation of water-soluble compounds in CO_2. To demonstrate this, maleic acid was chosen as a water-soluble starting material for this experiment (eq 3). After formation of the microemulsion ($W = 20$) with the water core containing 0.04 M $PdCl_2$ (total amount 2.2×10^{-3} mmol in the system) and 1.8 M maleic acid (9.6×10^{-2} mmol in the system), 10 atm of hydrogen in CO_2 (total pressure = 200 atm at 20 °C) was injected into the system. Two minutes after injection, the product was collected into acetone using the RESS technique. After evaporation of acetone, the product was dissolved in D_2O. The NMR spectra clearly indicated that only succinic acid was detected (>95% conversion based on the detection limit of the maleic acid peak). Washing of the reactor with acetone after depressurizing showed no detectable amount of maleic acid in NMR. In the absence of hydrogen gas or $PdCl_2$, only maleic acid NMR peaks were observed in this system.

Our results indicate that the Pd nanoparticles in the water-in-CO_2 microemulsion can also catalyze other hydrogenation processes such as the conversion of the nitro group (NO_2) to amine (NH_2). For example, the hydrogenation of nitrobenzene to aniline was completed (>99%) within 30 min in supercritical CO_2 at 50 °C and 200 atm. These and other hydrogenation examples will be detailed in a separate report.

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Supporting Information Available: NMR spectra (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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