

# Recycling Nanoparticles Stabilized in Water-in-CO<sub>2</sub> Microemulsions for Catalytic Hydrogenations

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Catalytic hydrogenations of olefins took place effectively in supercritical CO<sub>2</sub> with Pd<sup>0</sup> nanoparticles dispersed in the fluid phase using a water-in-CO<sub>2</sub> microemulsion consisting of water, sodium bis(2-ethylhexyl) sulfosuccinate (AOT) as a surfactant, and 1-octanol as a cosolvent. The hydrogenated products dissolved in supercritical CO<sub>2</sub> can be separated from the octanol solution containing AOT microemulsions with Pd<sup>0</sup> nanoparticles by phase separation (upper phase, supercritical CO<sub>2</sub> with hydrogenated products; lower phase, 1-octanol containing AOT microemulsions with Pd<sup>0</sup> nanoparticles) accompanied by reduction of CO<sub>2</sub> pressure. After collecting the hydrogenated products by flowing the upper CO<sub>2</sub> phase to a collection vessel, the Pd<sup>0</sup> nanoparticles remaining in the lower phase can be redispersed into supercritical CO<sub>2</sub> by pressurizing the system to a pressure where a homogeneous phase is attained. The redispersed nanoparticles can be reused as catalysts for the next runs of the hydrogenations. Triphenylethylene was hydrogenated to 1,1,2-triphenylethane at conversions of 100% (1st–3rd runs), >99% (4th run), and >96% (5th run) using the recycled Pd<sup>0</sup> nanoparticles. The feasibility of using other organic solvents as cosolvents is also studied in the present paper.

## Introduction

Nanometer-sized particles of metals and semiconductors have become of great interest over several decades,<sup>1–4</sup> because the nanoparticles have significant potential as catalysts with high activity and selectivity over conventional bulk metal catalysts.<sup>5,6</sup> The high catalytic activity of nanoparticles can be explained by their structural specificities such as the following: (1) nanoparticles have a large surface area per volume compared with that of bulk particles, (2) a nanoparticle has a relatively high ratio of active surface atoms to bulk atoms, and (3) a nanoparticle has a larger percentage of catalytically active surface sites (e.g., edge, corner, and kink) than those in a bulk particle. To apply nanoparticle catalysts to practical uses, both stability of nanoparticles and facile separation of reaction products from nanoparticles are considered to be important in the catalysis process. Also reuses of nanoparticle catalysts will become a critical issue when expensive noble metals such as Pt and Rh are chosen as catalysts. Since nanoparticles have a tendency to agglomerate, the nanoparticles need to be stabilized by an appropriate support such as porous solid supports (e.g., carbon and oxides),<sup>7,8</sup> polymers,<sup>9–11</sup> dendrimers,<sup>12</sup> chemical stabilizers (e.g., thiols and alkylammonium salts),<sup>13,14</sup> and

microemulsions.<sup>15–17</sup> A number of reports have appeared in the literature regarding catalytic hydrogenations utilizing metal nanoparticles stabilized in water-in-oil microemulsions.<sup>18–22</sup> Nagy et al. showed that Ni<sub>2</sub>B nanoparticles stabilized in water-in-oil microemulsions had a high catalytic capability for hydrogenation of 1-heptene. Boutonnet et al.,<sup>23</sup> Kishida et al.,<sup>24</sup> and Harelind Ingelsten et al.<sup>25</sup> showed that metal nanoparticles stabilized in water-in-oil microemulsions could be deposited on solid supports, and thus deposited nanoparticles could be used as catalysts. The deposited catalysts have advantages over the microemulsion-stabilized catalysts with respect to separation of reaction products and reuse of catalysts. However, the deposited nanoparticles do not have the dynamic reaction environment inherent in microemulsion systems.

Syntheses of metal and semiconductor nanoparticles utilizing water-in-CO<sub>2</sub> microemulsions have been reported in recent years.<sup>26–33</sup> The advantages associated with use

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of supercritical CO<sub>2</sub> as media for nanoparticle syntheses and catalytic reactions are not only related to its low environmental impact but also due to its chemical properties such as high diffusivity, miscibility with gaseous reagents, and tunable solubility with CO<sub>2</sub> density.<sup>34</sup> Because of these advantages, proper surfactants which dissolve in supercritical CO<sub>2</sub> and form a stable water-in-CO<sub>2</sub> microemulsion have been widely explored in the past decade.<sup>35–46</sup> We reported a mixed surfactant system consisting of AOT and perfluoropolyether phosphate (PFPE-PO<sub>4</sub>) for formation of water-in-CO<sub>2</sub> microemulsions.<sup>26,47</sup> Using the mixed surfactant system, palladium and rhodium nanoparticles stabilized in the water-in-CO<sub>2</sub> microemulsions could be synthesized, and catalytic hydrogenations using these nanoparticles were carried out in supercritical CO<sub>2</sub>.<sup>48,49</sup> The Pd<sup>0</sup> and Rh<sup>0</sup> nanoparticles stabilized in the water-in-CO<sub>2</sub> microemulsions showed high catalytic activities for hydrogenations of olefins and arenes, respectively. It was also found that mixtures of the hydrogenated products and the surfactants were easily removed from supercritical CO<sub>2</sub> by the rapid expansion of supercritical solution (RESS) technique.<sup>50</sup> However, separation of the products from the high-viscosity surfactants required a separate, conventional separation process such as column chromatography. In a previous study, Jacobson et al. used a water/CO<sub>2</sub> biphasic system containing an emulsion-forming surfactant for separation of products and recycling a water-soluble rhodium-phosphine catalyst by a change in phase behavior of the system at two different pressures.<sup>51</sup>

In the present study, metal and semiconductor nanoparticles were synthesized utilizing a water-in-CO<sub>2</sub> microemulsion formed with water, AOT, and a cosolvent, and catalytic hydrogenations of organic compounds with Pd<sup>0</sup> nanoparticles stabilized in the water-in-CO<sub>2</sub> micro-

emulsions were carried out in supercritical CO<sub>2</sub> at 50 °C and 200 atm. In the water-in-CO<sub>2</sub> microemulsion system, 2–20 vol % (relative to cell volume) of an organic solvent (e.g., 1-octanol) added in the system works as a cosolvent in supercritical CO<sub>2</sub> enabling dissolution of AOT at a high pressure such as 150 atm. The fluid separates into two phases (upper phase, supercritical CO<sub>2</sub>; lower phase, organic solvent containing AOT microemulsions with nanoparticles) at a low CO<sub>2</sub> pressure such as 100 atm. The present study takes advantage of the above phase behavior for both separation of hydrogenation products and recycling of Pd<sup>0</sup> nanoparticles for catalytic hydrogenations. The outline of the separation and recycling method is given as follows. First, an organic solution containing AOT microemulsions with PdCl<sub>2</sub> is prepared and a small amount (2–20 vol %) of the organic solution is placed in a high-pressure reactor. Suppose that the organic solution is miscible with supercritical CO<sub>2</sub> above 150 atm. Therefore, the AOT microemulsions with PdCl<sub>2</sub> can be dispersed in the homogeneous supercritical CO<sub>2</sub> phase as water-in-CO<sub>2</sub> microemulsions above 150 atm. By injecting hydrogen and a starting material for hydrogenation into the supercritical CO<sub>2</sub> phase, the hydrogen reduction of Pd<sup>2+</sup> takes place to form Pd<sup>0</sup> nanoparticles stabilized in the water-in-CO<sub>2</sub> microemulsions. The produced Pd<sup>0</sup> nanoparticles can be used as a catalyst for hydrogenation of the starting material. After the hydrogenation is completed, the CO<sub>2</sub> pressure is reduced to 100 atm, so that the supercritical CO<sub>2</sub> separates into two phases (upper phase, supercritical CO<sub>2</sub>; lower phase, the organic solvent). In the two-phase stage, parts of the hydrogenated products are expected to dissolve in the upper supercritical CO<sub>2</sub> phase. The lower organic solvent phase also contains some of the hydrogenated products and all of the AOT microemulsions with Pd<sup>0</sup> nanoparticles (AOT has little solubility in supercritical CO<sub>2</sub>). By continuous flow of supercritical CO<sub>2</sub> to a collection vessel through the reactor at the two-phase pressure, the hydrogenated products dissolving in the upper supercritical CO<sub>2</sub> phase can be collected in the vessel, and at the same time, the products dissolving in the lower organic phase can be extracted from the organic phase to the flowing supercritical CO<sub>2</sub> phase. On the other hand, the organic solvent remaining in the reactor becomes miscible with the supercritical CO<sub>2</sub> phase again by pressurizing the system to 150 atm, so that the Pd<sup>0</sup> nanoparticles stabilized in the AOT microemulsions can be redispersed in supercritical CO<sub>2</sub>. Therefore, if another starting material dissolving in supercritical CO<sub>2</sub> is introduced into the reactor, the redispersed Pd<sup>0</sup> nanoparticles can be used for the second catalytic hydrogenation.

In this paper, the above separation and recycling method is verified by dividing the whole process into five parts (processes 1–5 below) and by examining each process individually.

1. Formation of AOT microemulsions with PdCl<sub>2</sub> in 1-octanol.

2. Formation of Pd<sup>0</sup> nanoparticles with hydrogen reduction of Pd<sup>2+</sup> dissolved in water-in-CO<sub>2</sub> microemulsions.

3. Catalytic hydrogenations of organic compounds using the Pd<sup>0</sup> nanoparticles stabilized in the water-in-CO<sub>2</sub> microemulsions followed by separation of the products.

4. Redispersions of the AOT microemulsions with nanoparticles into supercritical CO<sub>2</sub>.

5. Repeated uses of the Pd<sup>0</sup> nanoparticles for catalytic hydrogenations of triphenylethylene.

1-Octanol was used as a cosolvent in these processes. In the fifth process, Pd<sup>0</sup> nanoparticles stabilized in the

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water-in-CO<sub>2</sub> microemulsions were successfully recycled for 5 times with negligible change in catalytic activity. In addition, uses of other organic solvents as cosolvents were examined to draw generalities for this separation and recycling method.

### Experimental Section

**Materials.** AOT (purity > 98%) was purchased from Aldrich. Precursors for syntheses of Ag<sup>0</sup>, AgI, CdS, and Pd<sup>0</sup> nanoparticles such as AgNO<sub>3</sub>, NaI, Cd(NO<sub>3</sub>)<sub>2</sub>, Na<sub>2</sub>S, and PdCl<sub>2</sub> were also obtained from Aldrich. Organic solvents used for this research were *n*-hexane (purity > 98.5%), *n*-heptane (purity > 99%), *n*-dodecane (purity 99%), 2,2,4-trimethylpentane (isooctane; purity 99.7%), methanol (purity 99.8%), 1-hexanol (purity 98%), 1-octanol (purity > 99%), and 1-nonanol (purity 98%). Chalcone (Alfa Aesar, purity 96%), nitrobenzene (Aldrich, purity > 99%), and triphenylethylene (Aldrich, purity 99%) were used as starting materials for catalytic hydrogenations. An instrument grade CO<sub>2</sub> tank and a technical grade H<sub>2</sub> tank were supplied by Oxarc, Spokane, WA.

**Analysis.** In situ measurements of UV-vis absorption spectrometry in supercritical CO<sub>2</sub> were carried out using a stainless steel, high-pressure cell equipped with fiber optics. A CCD array UV-vis spectrophotometer model SI-440 (Spectral Instruments, Inc., Tucson, AZ) was used for all UV-vis spectrometric measurements. The details of the stainless cell and the measurement procedure are described in our previous papers.<sup>27–29</sup> Reaction products from catalytic hydrogenations were analyzed by NMR spectrometry (Bruker AMX 300) and gas chromatography (5890 Hewlett-Packard).

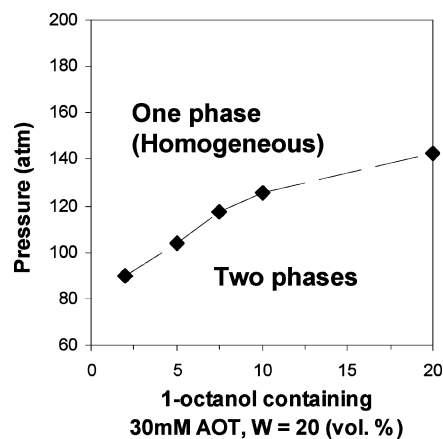
**Experimental Procedures.** The five processes for the separation and recycling method were studied individually using the experimental procedures described below.

1. *Formation of AOT Microemulsions with PdCl<sub>2</sub> in 1-Octanol.* AOT (106.6 mg, 30 mM) and 86.4  $\mu$ L of PdCl<sub>2</sub> aqueous solution (<0.1 M) ( $W = [\text{H}_2\text{O}]/[\text{AOT}] = 20$ ) were added in 8 mL of 1-octanol. The contents were stirred in the octanol solution for 40 min.

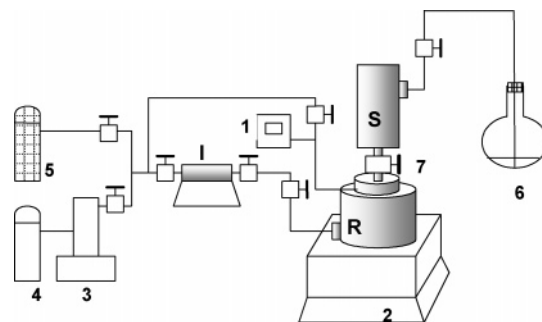
2. *Formation of Pd<sup>0</sup> Nanoparticles with Hydrogen Reduction of Pd<sup>2+</sup> Dissolved in Water-in-CO<sub>2</sub> Microemulsions.* The phase behavior of a system which consists of supercritical CO<sub>2</sub> and 1-octanol solution with AOT microemulsions (30 mM AOT,  $W = 20$ ) was studied in advance. The phase behavior was determined by visual observation using a stainless steel high-pressure cell with two sapphire windows (22 mL volume). The amount of the octanol solution was varied from 0.44 to 4.4 mL (2–20 vol % relative to the view cell). At less than 0.44 mL of the octanol solution, it was hard to identify the octanol solution spread on the cell bottom. After loading the octanol solution in the cell, the view cell was preheated to 50 °C and the system was pressurized with supercritical CO<sub>2</sub>. The pressure of CO<sub>2</sub> was varied from 78.5 to 200 atm. The temperature of the view cell was measured by J-type thermocouples. Before observation of the phase behavior, the system was stirred for 2 min and stood for 10 min to allow the system to reach an equilibrium state. The phase diagram showing the relation between amounts of the octanol solution and supercritical CO<sub>2</sub> pressure is shown in Figure 1.

In the pressure range above the dotted curve in Figure 1, a homogeneous, supercritical CO<sub>2</sub> solution with water-in-CO<sub>2</sub> microemulsions was obtained. Below the dotted curve, a two-phase system (upper phase, supercritical CO<sub>2</sub>; lower phase, 1-octanol with AOT microemulsions) was observed. The phase diagram indicates that the octanol added in supercritical CO<sub>2</sub> works as a cosolvent for dissolution of AOT microemulsions in supercritical CO<sub>2</sub> forming water-in-CO<sub>2</sub> microemulsions in the pressure range above the dotted curve. Therefore, syntheses of nanoparticles stabilized in the water-in-CO<sub>2</sub> microemulsions can be carried out in the pressure range.

Pd<sup>0</sup> nanoparticles stabilized in water-in-CO<sub>2</sub> microemulsions were synthesized by hydrogen reduction of Pd<sup>2+</sup> dissolved in the water-in-CO<sub>2</sub> microemulsions. A 4.3 mL (7.9 vol % relative to the cell volume) portion of the octanol solution prepared in process 1 was placed in a stainless steel cell (Cell-R, 54.3 mL) equipped with fiber optics for UV-vis absorption spectrometry. After preheating Cell-R to 50 °C, supercritical CO<sub>2</sub> at 150 atm was introduced into the cell to allow the AOT microemulsions to be



**Figure 1.** Phase diagram of the system consisting of supercritical CO<sub>2</sub> and 1-octanol solution containing AOT microemulsions at 50 °C.



**Figure 2.** Stainless steel, high-pressure system for hydrogenation of organic compounds catalyzed by Pd<sup>0</sup> nanoparticles stabilized in water-in-CO<sub>2</sub> microemulsions [1, pressure transducer; 2, stirring hot plate; 3, ISCO syringe pump; 4, CO<sub>2</sub> tank; 5, H<sub>2</sub> tank; 6, collection vessel with CDCl<sub>3</sub> solution; 7, high-pressure ball valve].

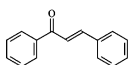
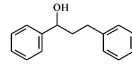



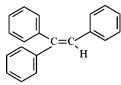
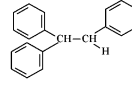
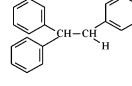
homogeneously dispersed in supercritical CO<sub>2</sub>. A separate, injection vessel (Cell-I, 5 mL) which was connected to Cell-R by 1/16 in. stainless tubing with an interconnecting valve was used for mixing hydrogen (10 atm) with supercritical CO<sub>2</sub> at a total pressure of 200 atm. By opening the interconnecting valve, the hydrogen in Cell-I was injected to Cell-R with the aid of the pressure difference. The hydrogen reduction of the Pd<sup>2+</sup> was carried out in supercritical CO<sub>2</sub> at 50 °C and 200 atm.

3. *Catalytic Hydrogenations of Organic Compounds Using the Pd<sup>0</sup> Nanoparticles Stabilized in the Water-in-CO<sub>2</sub> Microemulsions Followed by Separation of the Products.* A schematic diagram of the reactor system used for catalytic hydrogenations with Pd<sup>0</sup> nanoparticles stabilized in the water-in-CO<sub>2</sub> microemulsions is shown in Figure 2.

The starting material and the octanol solution prepared in process 1 (30 mM AOT,  $W = 20$ , PdCl<sub>2</sub> < 0.1 M) were placed in Cell-R (volumes: 11, 22, or 54 mL). The mixtures in the cell were stirred for 20 min in supercritical CO<sub>2</sub> at 50 °C and 85 atm. After the stirring, the fluid consisted of two phases (upper phase, supercritical CO<sub>2</sub>; lower phase, the octanol solution containing AOT microemulsions with PdCl<sub>2</sub>). The starting material is expected to dissolve mainly in the supercritical CO<sub>2</sub> phase, because of the small volume of the octanol solution relative to that of CO<sub>2</sub>. An injection vessel (Cell-I, 5 mL volume) was purged of ambient air with hydrogen gas for 2 min followed by pressurizing with 10 atm hydrogen, and then CO<sub>2</sub> was introduced into the cell to mix with the hydrogen at a total pressure of 200 atm. By opening the interconnecting valves between Cell-R and Cell-I, the supercritical CO<sub>2</sub> with hydrogen was injected into Cell-R to synthesize Pd<sup>0</sup> nanoparticles stabilized in water-in-CO<sub>2</sub> microemulsions and to allow catalytic hydrogenation of the starting material to occur in supercritical CO<sub>2</sub>. In this injection process, inlet valves between Cell-I and the syringe pump were also kept open so that the original CO<sub>2</sub> pressure in Cell-I (200



**Table 1. Catalytic Hydrogenations of Organic Compounds with Pd<sup>0</sup> Nanoparticles Stabilized in Water-in-CO<sub>2</sub> Microemulsions at 50 °C and 200 atm**

Entry	Substrate	Amount	Time (min.)	Catalyst <sup>a</sup> (%)	Product (Conversion, %)
1		30 mg	120	3	 (100)
2		10 μL	30	5	 (100)
3		50 μL	30	1	 (96)
4		10 mg	20	6	 (100)
5		20 mg	20	6	 (100)

Amounts of the octanol solution containing AOT microemulsions: 1–4 (20 vol.%) and 5 (7.9 vol.%). Volume of Cell-R: 1, 2 and 3 (22 mL), 4 (11 mL) and 5 (54 mL). <sup>a</sup> Percentage of catalyst to substrate.

atm) was kept constant. After the injection, Cell-R was isolated by closing the above interconnecting valves. The speeds of catalytic hydrogenations were estimated approximately by varying reaction time at intervals of every 10–30 min. After the reaction time of 20–120 min, the CO<sub>2</sub> pressure was reduced to 95 atm in order to separate the homogeneous fluid into two phases, so that the hydrogenated products dissolved in the supercritical CO<sub>2</sub> phase could be separated from the octanol phase containing the AOT microemulsions with Pd<sup>0</sup> nanoparticles. The depressurization to 95 atm was attained by opening an interconnecting ball valve (orifice, 4.8 mm) between Cell-R and another stainless steel, high-pressure vessel for phase separation (Cell-S, 18 mL). Since Cell-S was located vertically on Cell-R via the ball valve with the large orifice, the octanol solution which escaped from Cell-R during the depressurization could return to Cell-R with the aid of gravity. After the depressurization of CO<sub>2</sub>, the two-phase system was stirred for 10 min to reach a distribution equilibrium of hydrogenated products between the supercritical CO<sub>2</sub> phase and the octanol phase. The products dissolved in the supercritical CO<sub>2</sub> phase were removed by flowing the supercritical CO<sub>2</sub> to a collection vessel with CDCl<sub>3</sub> solution through both Cell-R and Cell-S at constant CO<sub>2</sub> pressure of 95 atm for 10 min. This constant flow process also allowed the products dissolved in the octanol phase to be extracted to the flowing supercritical CO<sub>2</sub> phase because all products listed in Table 1 were very soluble in supercritical CO<sub>2</sub>. The CDCl<sub>3</sub> solution was analyzed by NMR.

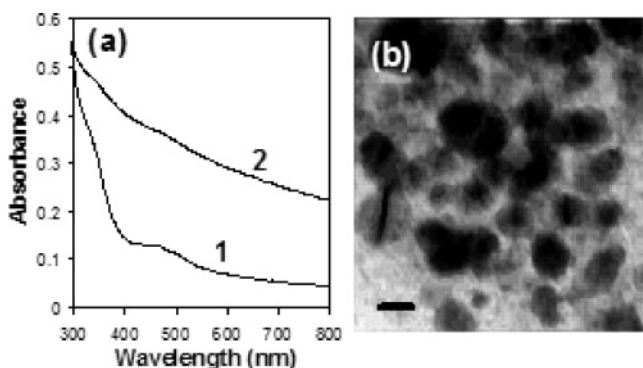
**4. Redispersion of the AOT Microemulsions with Nanoparticles into Supercritical CO<sub>2</sub>.** An octanol solution of AOT microemulsions with CdS nanoparticles was prepared by mixing an octanol solution of AOT microemulsion containing Cd(NO<sub>3</sub>)<sub>2</sub> aqueous solution [30 mM AOT, W = 12, 0.5 M Cd(NO<sub>3</sub>)<sub>2</sub>] with another one containing 0.5 M Na<sub>2</sub>S aqueous solution. The method for preparation of the octanol solutions of AOT microemulsions with Cd(NO<sub>3</sub>)<sub>2</sub> or Na<sub>2</sub>S was the same as that for the AOT microemulsion with PdCl<sub>2</sub> described in process 1. The synthesis of CdS nanoparticles using water-in-oil microemulsions as a template is well established by previous papers.<sup>30</sup> The redispersions of CdS nanoparticles stabilized in AOT microemulsions into supercritical CO<sub>2</sub> were observed using the view cell used in process 2. A 4.4 mL (20 vol % relative to the view cell) portion of the octanol solution with CdS nanoparticles was placed in the view cell, and the CdS nanoparticles were dispersed in a homogeneous, supercritical CO<sub>2</sub> phase by pressurizing the system to 200 atm.

**5. Repeated Uses of the Pd<sup>0</sup> Nanoparticles for Catalytic Hydrogenations of Triphenylethylene.** The high-pressure reactor system used in this experiment was the same with that used in process 3 (Figure 2). A 7.9 vol % [relative to Cell-R (54 mL)] portion of the octanol solution containing AOT microemulsions

with PdCl<sub>2</sub> was placed in Cell-R followed by pressurizing the cell to 85 atm with supercritical CO<sub>2</sub>. At this CO<sub>2</sub> pressure, the system was in the two-phase region. The starting materials for hydrogenation (20 mg of triphenylethylene and 10 atm H<sub>2</sub>) were placed in Cell-I) were dissolved in supercritical CO<sub>2</sub> at a total pressure of 240 atm. By opening the interconnecting valves between Cell-R and Cell-I, the starting materials were injected into Cell-R. Immediately after the injection, the two following reactions are supposed to take place: (1) formation of Pd<sup>0</sup> nanoparticles by hydrogen reduction of Pd<sup>2+</sup> dissolved in the water-in-CO<sub>2</sub> microemulsions and (2) hydrogenation of triphenylethylene catalyzed by the Pd<sup>0</sup> nanoparticles as described in process 3. The catalytic hydrogenation was carried out in supercritical CO<sub>2</sub> at 50 °C and 240 atm. All high-pressure valves connected to Cell-R were closed to isolate the cell from other vessels, and the fluid in Cell-R was stirred. After 20 min of reaction time, the fluid was depressurized to 100 atm to separate the system into two phases by opening the interconnecting ball valve between Cell-R and Cell-S, so that the hydrogenated product dissolved in the supercritical CO<sub>2</sub> phase was separated from the octanol solution containing the Pd<sup>0</sup> nanoparticles stabilized in AOT microemulsions. The products were collected by flowing the supercritical CO<sub>2</sub> phase into a CDCl<sub>3</sub> solution at a constant pressure of 100 atm. After the continuous flow of supercritical CO<sub>2</sub> for 10 min, all valves connected to Cell-R were closed, and both Cell-I and Cell-S were depressurized to ambient pressure. The starting materials for the second hydrogenation were placed in Cell-I and were dissolved in supercritical CO<sub>2</sub> at a total pressure of 240 atm. The second catalytic hydrogenation was started by injecting the starting materials into Cell-R by opening the interconnecting valves. As described in process 4, the nanoparticles segregated in the octanol phase can be redispersed into a homogeneous, supercritical CO<sub>2</sub> phase by pressurizing the system to the one-phase region. The above hydrogenation process using the redispersed Pd<sup>0</sup> nanoparticles was repeated 4 times.

## Results and Discussion

**Process 1.** AOT is a widely used surfactant for formation of water-in-oil and oil-in-water microemulsions in various solvents, because of the high stability of the AOT microemulsions. After stirring AOT and PdCl<sub>2</sub> aqueous solution in 1-octanol for 40 min, an optically transparent solution with light brown color indicative of formation of AOT microemulsions with PdCl<sub>2</sub> was formed. The octanol solution containing the AOT microemulsions was stable over several days.



**Figure 3.** Characterizations of Pd<sup>0</sup> nanoparticles stabilized in water-in-CO<sub>2</sub> microemulsions: (a) UV-vis spectra of (1) PdCl<sub>2</sub> dissolved in water-in-CO<sub>2</sub> microemulsions at 50 °C and 150 atm and (2) Pd<sup>0</sup> nanoparticles stabilized in water-in-CO<sub>2</sub> microemulsions at 50 °C and 200 atm; (b) a transmission electron micrograph of Pd<sup>0</sup> nanoparticles collected in octanol solution (scale = 5 nm).

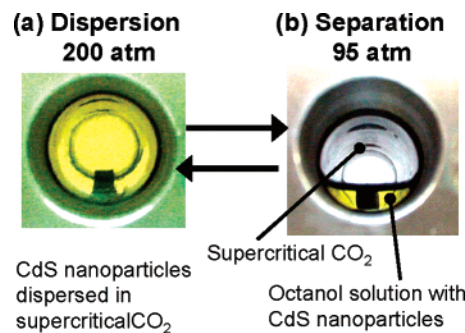
**Process 2.** Spectra 1 and 2 of Figure 3a show UV-vis absorption spectra of the water-in-CO<sub>2</sub> microemulsions with PdCl<sub>2</sub> before and after the H<sub>2</sub> injection, respectively.

The UV-vis absorption spectrum of Pd<sup>0</sup> nanoparticles does not have any characteristic peaks in the visible region.<sup>52</sup> The broad absorption which appeared in spectrum 2 was very similar to the reported spectra of Pd<sup>0</sup> nanoparticles.<sup>48</sup> Also spectrum 2 showed a small absorption peak due to PdCl<sub>2</sub> (<400 nm). Based on the decrease of the absorption peak intensity, the yield of Pd nanoparticles was estimated to be at least 90%. A transmission electron micrograph of the octanol solution collected after venting CO<sub>2</sub> from Cell-R confirmed the formation of Pd<sup>0</sup> nanoparticles as shown in Figure 3b. The Pd<sup>0</sup> nanoparticles in the octanol solution were about 2–10 nm in size.

**Process 3.** Table 1 shows the results of catalytic hydrogenations of organic compounds using the Pd<sup>0</sup> nanoparticles stabilized in the water-in-CO<sub>2</sub> microemulsions. The products collected in the CDCl<sub>3</sub> solution and remaining in the octanol solution were analyzed by NMR spectroscopy, respectively, and conversions in both phases were determined based on the ratios of substrate/product. In the hydrogenation systems listed in Table 1, the differences of the conversions between those in the CDCl<sub>3</sub> and in the octanol phase were negligible. Table 1 shows the conversions in the CDCl<sub>3</sub> solutions.

Chalcone (Table 1, entry 1), nitrobenzene (entries 2 and 3), and triphenylethylene (entries 4 and 5) were quantitatively hydrogenated to 1,3-diphenylpropane-1-ol, aniline, and 1,1,2-triphenylethane, respectively, under the experimental conditions. The results indicate that the Pd<sup>0</sup> nanoparticles have high catalytic activities in hydrogenations of the double bonds of olefins, nitro groups, and keto groups. Also the hydrogenations using the Pd<sup>0</sup> nanoparticles were selective toward the above groups. No hydrogenation of the benzene ring of these organic compounds took place under the experimental conditions.

**Process 4.** After the first catalytic hydrogenation and the separation of products as described in process 3, the octanol solution remaining in Cell-R can be remixed with supercritical CO<sub>2</sub> by pressurizing the system to 200 atm. The Pd<sup>0</sup> nanoparticles stabilized in AOT microemulsions can be redispersed in the supercritical CO<sub>2</sub> phase to allow the Pd<sup>0</sup> nanoparticles to be reused as the catalyst for the second hydrogenation. In the redispersion process, it is important to examine changes in size and amount of Pd<sup>0</sup>



**Figure 4.** Dispersion and separation of the CdS nanoparticles in supercritical CO<sub>2</sub>; 20 vol % octanol solution (relative to the view cell) containing AOT microemulsions (30 mM AOT and 360 mM H<sub>2</sub>O) with CdS nanoparticles in supercritical CO<sub>2</sub> at 50 °C.

nanoparticles during the redispersion process. However, the information on size and amount of Pd<sup>0</sup> nanoparticles cannot be obtained from the UV-vis absorbance spectrum, because there is no characteristic peak for Pd<sup>0</sup> nanoparticles as shown in Figure 3a. Cadmium sulfide (CdS) nanoparticles have a characteristic absorption in visible region, and the size and amount of CdS nanoparticles can be estimated from the absorption peak. Therefore, CdS nanoparticles can be utilized to study the changes in size and amount of nanoparticles accompanied by the redispersion process. Figure 4a shows an optical image of CdS nanoparticles dispersed in supercritical CO<sub>2</sub> at 200 atm.

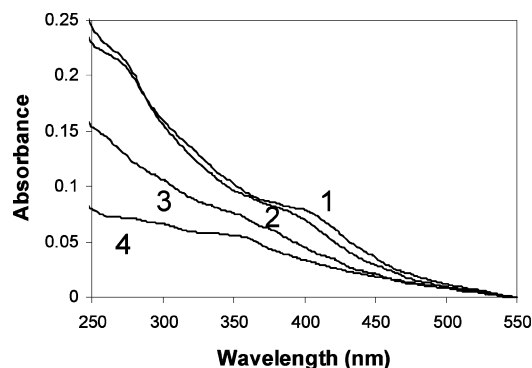
The fluid was transparent and yellowish, indicating that the CdS nanoparticles were uniformly dispersed in supercritical CO<sub>2</sub>. To separate the homogeneous fluid into two phases, the CO<sub>2</sub> pressure was reduced to 95 atm. Figure 4b shows an optical image of the two-phase system consisting of the supercritical CO<sub>2</sub> (upper phase) and the octanol solution (lower phase). The octanol phase was bright yellow, and the supercritical CO<sub>2</sub> was colorless. After the phase separation, the CO<sub>2</sub> pressure was increased to 200 atm again to redisperse the CdS nanoparticles in the supercritical CO<sub>2</sub> phase. The homogeneous fluid phase after the redispersion of CdS nanoparticles showed the same color as the first dispersion (Figure 4a). To evaluate changes in size and amount of CdS nanoparticles accompanied by repeated redispersions, UV-vis spectra of the CdS nanoparticles were measured after each redispersion process. Before describing the experimental results, some characteristics of the UV-vis absorption peak of CdS nanoparticles stabilized in a water-in-CO<sub>2</sub> microemulsion are briefly summarized below. We previously reported that the size of CdS nanoparticles stabilized in a water-in-CO<sub>2</sub> microemulsion could be controlled by the *W* value of the microemulsion.<sup>30</sup> This relationship between *W* value and size of CdS nanoparticles was also observed in the present system as shown in Figure 5.

The UV-vis absorption spectra of the CdS nanoparticles were measured using a reactor (44 mL volume) equipped with a fiber-optic UV-vis spectrophotometer. Theoretical<sup>53,54</sup> and experimental<sup>16</sup> studies on semiconductor particles have shown that the size of semiconductor particles can be estimated from the threshold wavelength of the UV-vis absorption spectrum of semiconductor particles. With reduction in particle size, the band gap of the semiconductor particle becomes larger, so that there is a concomitant blue shift in the spectrum. This is the

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(52) Teranishi, T.; Miyake, M. *Chem. Mater.* **1998**, *10*, 594.



**Figure 5.** UV-vis spectra of CdS nanoparticles stabilized in water-in-CO<sub>2</sub> microemulsions at 50 °C and 200 atm; 7.5 vol % of octanol solution (relative to the cell volume) containing AOT microemulsions with CdS nanoparticles [ $W = 18$  (1), 12 (2), 8 (3), and 6 (4)] dispersed in supercritical CO<sub>2</sub>.

so-called quantum size effect of semiconductor particles. As shown in Figure 5, blue shifts in the spectra were observed with reduction of the  $W$  value. Based on the theoretical calculation described in our previous paper,<sup>30</sup> the diameters of the CdS nanoparticles stabilized in the water-in-CO<sub>2</sub> microemulsions were estimated to be 3.8, 4.2, 5.3, and 6.6 nm at  $W = 6, 8, 12$ , and 18, respectively. The obvious shifts in the UV-vis spectra enable us to study possible changes in size of the CdS nanoparticles caused by the repeated redispersions. The absorbance of the CdS nanoparticles can be related to the concentration of the CdS nanoparticles dispersed in supercritical CO<sub>2</sub> by Lambert-Beer's law. Figure 6 shows UV-vis spectra of the CdS nanoparticles stabilized in the water-in-CO<sub>2</sub> microemulsions after redispersions. The amounts of the octanol solution added in the system were 4.4, 3.3, and 2.2 mL (10, 7.5, and 5 vol % relative to the cell) as shown in Figure 6a-c, respectively.

The particle diameters calculated using the threshold wavelengths and the absorbance were plotted against recycle time as shown in the insets of Figure 6. In the cases of 10 vol % (Figure 6a) and 7.5 vol % (Figure 6b) of the octanol solutions, the threshold wavelengths showed little change throughout the 5 redispersion processes. Also the absorbance after the 5 redispersions was still higher than 90% of that of the first dispersion. Figure 7 shows transmission electron micrographs of the octanol solutions before and after the experiment of Figure 6b. From the transmission electron micrographs, it is obvious that the sizes of CdS nanoparticles before the dispersion (1.5–3.5 nm) are almost the same as those after 5 redispersions (1.7–4.0 nm).

In the case of 5 vol % (Figure 6c) of the octanol solution, although the threshold wavelengths did not change significantly throughout the 5 redispersions, the absor-

**Table 2.** Hydrogenations of Triphenylethylene Catalyzed by Fresh and Recycled Pd<sup>0</sup> Nanoparticles Stabilized in Water-in-CO<sub>2</sub> Microemulsions at 50 °C and 240 atm

cycle	product	conversion (%)
1	1,1,2-triphenylethane	100
2	1,1,2-triphenylethane	100
3	1,1,2-triphenylethane	100
4	1,1,2-triphenylethane	>99
5	1,1,2-triphenylethane	>96

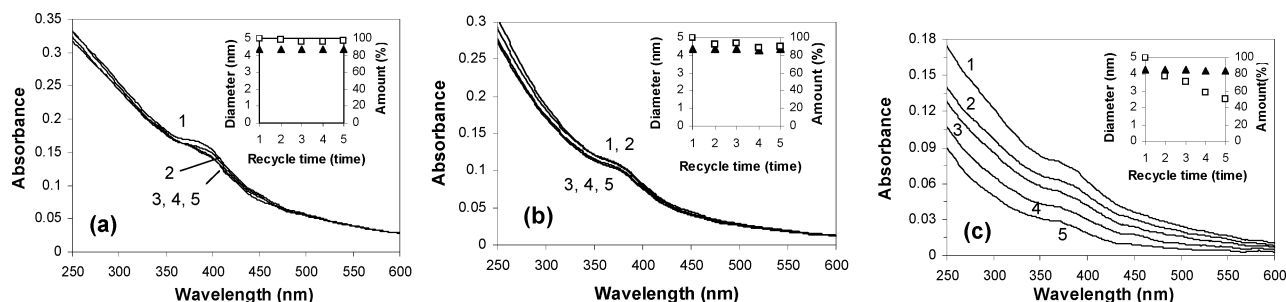
bance of the CdS nanoparticles was reduced to half. From the above results, it can be concluded that approximately above 7.5 vol % of the octanol solution is preferable for the present recycling process.

The amount of the octanol solution was somewhat reduced after the 5 redispersions. For example, the amount of octanol was reduced from 4.4 to 4.0 mL in the experiment of Figure 6a. One of the reasons for the decreases in absorbance observed in Figure 6 could be the loss of the octanol solution. The large decrease observed in 5 vol % of the octanol solution (Figure 6c) indicates instability of the water-in-CO<sub>2</sub> microemulsions under this condition causing other mechanisms such as aggregation of the CdS nanoparticles to occur during redispersions. However, the sizes of the CdS nanoparticles after 5 redispersions were found to be almost the same as those before dispersion by UV-vis spectrometry (Figure 6c) and transmission electron micrographs. Since a water-in-CO<sub>2</sub> microemulsion can be a stabilizer for nanoparticles with a certain size range ( $\approx 4$  nm CdS in this experiment), the aggregated CdS particles may end up as precipitates.

**Process 5.** The Pd<sup>0</sup> nanoparticles stabilized in the water-in-CO<sub>2</sub> microemulsions were repeatedly used for catalytic hydrogenation of triphenylethylene using the recycling process described above. The catalytic hydrogenation using the recycled Pd<sup>0</sup> nanoparticles was repeated 4 times. Table 2 shows the results of the catalytic hydrogenations of triphenylethylene using fresh (cycle 1) and recycled Pd<sup>0</sup> nanoparticles (cycles 2–5). The conversions in Table 2 were determined based on the ratios of triphenylethylene/triphenylethane in the CDCl<sub>3</sub> solution.

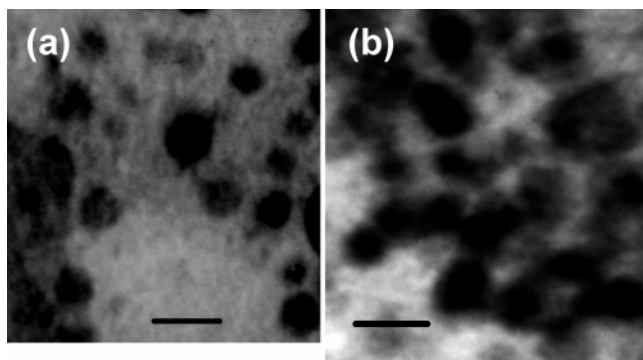
Using the above recycling process, the Pd<sup>0</sup> nanoparticles stabilized in the water-in-CO<sub>2</sub> microemulsions could be successfully redispersed into the supercritical CO<sub>2</sub> phase and reused for the hydrogenation without significantly losing catalytic activity.

**Uses of Other Organic Cosolvents for the Separation and Recycling Method.** The feasibility of using other organic solvents for recycling of microemulsion-stabilized nanoparticles is examined in this section. The organic solvents used as cosolvents were alkanes [ $n$ -hexane,  $n$ -heptane,  $n$ -dodecane, and isooctane] and alcohols [methanol, 1-hexanol, 1-octanol, and 1-nonanol]. Nanoparticles of silver (Ag), silver iodide (AgI), and CdS



**Figure 6.** UV-vis spectra after redispersions of CdS nanoparticles stabilized in water-in-CO<sub>2</sub> microemulsions at 50 °C and 200 atm: (a) 10 vol % of octanol solution with CdS nanoparticles stabilized by AOT microemulsions, (b) 7.5 vol % of the octanol solution, and (c) 5 vol % of the octanol solution [(▲) diameter of CdS nanoparticles (nm), (□) amount of CdS nanoparticles (%)].





**Figure 7.** Transmission electron micrographs of CdS nanoparticles: (a) before dispersion (scale = 5 nm) and (b) after 5 redispersions in supercritical CO<sub>2</sub> (scale = 5 nm).

**Table 3. Redispersions of Nanoparticles Stabilized by AOT Microemulsions in Various Organic Solvents**

cosolvent	nanoparticles	recycle <sup>a</sup>
	(1) Alkane	
<i>n</i> -hexane	Ag <sup>0</sup>	B
<i>n</i> -heptane	Ag <sup>0</sup> , CdS	A
<i>n</i> -dodecane	Ag <sup>0</sup>	B
isooctane	Ag <sup>0</sup>	B
	(2) Alcohol <sup>b</sup>	
1-methanol	AgI	B
1-hexanol	AgI	B
1-octanol	AgI, CdS	A
1-nonanol	Ag <sup>0</sup> , CdS	A

<sup>a</sup> (A) The nanoparticles can be redispersed in supercritical CO<sub>2</sub> at least 10 times. (B) The nanoparticles can be dispersed in supercritical CO<sub>2</sub> in the first dispersion but cannot be redispersed.

<sup>b</sup> Phase boundaries of the systems which consist of alcohols (20 vol %) and supercritical CO<sub>2</sub> at 50 °C: methanol (<80 atm), 1-hexanol (115 atm), 1-octanol (143 atm), and 1-nonanol (156 atm).

were synthesized in these organic solvents using AOT microemulsions and were dispersed in supercritical CO<sub>2</sub>. Both Ag and AgI nanoparticles have characteristic peaks, which can be used for estimation of size and amount of these nanoparticles. The syntheses of these nanoparticles are detailed in the Supporting Information. The redispersions of these nanoparticles in supercritical CO<sub>2</sub> were studied using the same procedure described in process 4. The results are summarized in Table 3.

The first dispersion of the nanoparticles stabilized by AOT microemulsions in supercritical CO<sub>2</sub> was attained using all of these organic solvents by pressurizing the systems to pressures where a homogeneous phase was obtained. After depressurization of these systems to certain CO<sub>2</sub> pressures as the fluid is separated into two phases, the systems were pressurized again for the second dispersions of these nanoparticles. The second dispersion

of the nanoparticles was not observed using the following organic solvents: methanol, 1-hexanol, *n*-hexane, *n*-dodecane, and isooctane. The fluids became colorless during the redispersion, and precipitates often appeared in the fluids. Using *n*-heptane, 1-nonanol, and 1-octanol, the nanoparticles dissolved in these organic solvents could be repeatedly redispersed in supercritical CO<sub>2</sub>. Based on the above results, alcohols and paraffin hydrocarbons with carbon number of 7–9 appear to be good cosolvents for the separation and recycling method. The relations between chemical structures of cosolvents and stability of nanoparticles in AOT microemulsions are currently under investigation.

## Conclusion

The recycling of nanoparticles for catalytic hydrogenations and separation of hydrogenated products by taking advantage of the phase behavior of supercritical CO<sub>2</sub> were successfully verified by dividing the whole process into five processes described in the Introduction and by studying each process individually. Pd<sup>0</sup> nanoparticles synthesized using water-in-CO<sub>2</sub> microemulsions which consisted of water, AOT, and 1-octanol showed high catalytic activities in hydrogenations of the double bonds of olefins, nitro groups, and keto groups. Based on our results of UV–vis absorption spectrometry and transmission electron micrographs, the nanoparticles showed little agglomeration during phase transitions above 7.5 vol % of the octanol solution. Also the Pd<sup>0</sup> nanoparticles could be reused at least 5 times for hydrogenation of triphenylethylene without significantly losing catalytic activity using the recycling method. In the present work, it can be concluded that nanoparticles stabilized in water-in-CO<sub>2</sub> microemulsions consisting of water, AOT, and a cosolvent have great capabilities in stability, reusability, and facile separation from reaction products. Although most conventional heterogeneous catalysts also have great capabilities in the above three aspects, the heterogeneous catalysts have a serious limitation in reaction speed compared with the “dynamic” microemulsion systems. The recycling method summarized in the present work may be applied to different types of catalysts including enzymes, organometallic compounds, and ionic species besides nanoparticles when these catalysts are solubilized in the water core of the water-in-CO<sub>2</sub> microemulsions.

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**Supporting Information Available:** Syntheses of Ag<sup>0</sup> and AgI nanoparticles in organic solvents. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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