



# Partial hydrogenation of 1,3-cyclooctadiene using dendrimer-encapsulated Pd–Rh bimetallic nanoparticles

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## Abstract

This article reports the first effort for the preparation of Pd–Rh bimetallic nanoparticles in the presence of poly(amidoamine) dendrimers with surface hydroxyl groups (fourth generation, PAMAM-OH). The resulting dendrimer-encapsulated Pd–Rh bimetallic nanoparticles show a promising catalytic activity in partial hydrogenation of 1,3-cyclooctadiene.

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## 1. Introduction

Nanoparticles, defined by a diameter of 1–10 nm, have created a new category of materials because they may show different characteristics compared to conventional bulk materials or to atoms, the smallest units of matter. Therefore, the preparation of narrowly distributed metal nanoparticles has been the subject of intense investigation and research is in progress from various points of view [1,2].

Metal nanoparticles have also provided new opportunities for catalysis and consequently research in this area has paved the way to new solid catalysts over the past decade. From the catalytic point of view, bimetallic nanoparticles composed of two different metal elements have drawn a greater interest than monometallic ones because bimetalization would make it possible not only to obtain an improved cat-

alytic activity but also to create a new property, which may not be achieved by monometallic catalysts [3]. To date, the preparation of bimetallic nanoparticles has been carried out mainly on a mineral support and the resulting inorganic oxide-supported bimetallic nanoparticles have already been used as effective catalysts for various reactions [3].

On the other hand, colloidal dispersions of bimetallic nanoparticles have not been well examined until recently. Metal nanoparticles without inorganic supports may have some advantages in comparison with the supported ones [4]; the intrinsic properties of metal nanoparticles can be elucidated without the effect of the metal–support interaction. In addition, more uniform particle sizes can be obtained in the dispersed systems than in the supported cases. The higher loading of metal on inorganic supports normally gives bigger particles with wider particle size distributions.

Dendrimers are highly branched macromolecules and they are generally described to have a structure of spherical shape with a high degree of symmetry [5–7]. By virtue of their three-dimensional structure having

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internal void spaces, dendrimers have been considered as new types of host for the accommodation of guest molecules [8,9].

In line with the prospect of dendrimer as a template for the formation of inorganic nanoparticles, various metal nanoparticles have been successfully prepared [10]. However, it is worth noting that most of the previous studies have been confined to the “monometallic” nanoparticles, and “bimetallic” nanoparticles have not been exploited yet, although there has been a preliminary attempt to prepare dendrimer/bimetal nanocomposite using two different metal precursors [11,12].

Recently, we have prepared Pt–Pd [13] and Ag–Pd [14] bimetallic nanoparticles in the presence of poly(amidoamine) dendrimers. In the case of the former, we found that the resulting Pt–Pd bimetallic nanoparticles effectively promote the partial hydrogenation of 1,3-cyclooctadiene. The Pt–Pd system has also been studied by Scott et al. [15]. These results suggest that the potential application of the dendrimer-encapsulated bimetallic nanoparticles is promising in the field of catalysis.

In line with our ongoing effort for the preparation of dendrimer-templated bimetallic nanoparticles, we have aimed here to demonstrate the preparation of Pd–Rh bimetallic nanoparticles in the presence of poly(amidoamine) dendrimers with surface hydroxyl groups (fourth generation, PAMAM-OH) and the application of these bimetallic nanoparticles as catalysts to the partial hydrogenation of 1,3-cyclooctadiene. To the best of our knowledge, this is the first effort for the preparation of dendrimer-encapsulated Pd–Rh bimetallic nanoparticles.

## 2. Experimental

### 2.1. Chemicals

Starburst poly(amidoamine) dendrimer with surface hydroxyl groups was obtained as 10 wt.% methanol solutions (Aldrich). Prior to use, methanol was removed by rotary evaporation at room temperature.  $K_2PdCl_4$  (98%),  $RhCl_3$  (98%),  $NaBH_4$  (99%), 1,3-cyclooctadiene (98%), and cyclooctene (95%) were supplied from Aldrich and used as received without further purification. All solutions, used for the preparation of samples for HRTEM and UV-Vis

spectra and for test reactions, were dialyzed against water for 24 h. Cellulose membranes (Pierce) having a molecular weight cutoff of 10,000 were soaked in water for 1 h and rinsed with deionized water thoroughly before dialysis.

### 2.2. Synthesis of dendrimer-encapsulated Pd–Rh bimetallic nanoparticles

Dendrimer-encapsulated Pd–Rh bimetallic nanoparticles were prepared by simultaneous co-complexation of two different metal ions, followed by a single reduction step. Complexation of metal ions with dendrimers were carried out by the addition of desired amounts of  $Pd^{2+}$  and  $Rh^{3+}$  (total metal concentration = 60 mM) to 12 mM PAMAM-OH dendrimer solution under vigorous stirring. After 1 h, 0.6 M sodium borohydride was slowly added under vigorous stirring.

### 2.3. Characterization

Absorption spectra were recorded on a Perkin-Elmer Lambda 35 UV-Vis spectrometer using deionized water as a reference for all measurements.

High-resolution transmission electron micrographs (HRTEM) were obtained using a JEOL JEM-3000F transmission electron microscope (TEM) equipped with an energy dispersive spectroscopy (EDS) detector (Oxford Co.). The specimens of various bimetallic nanoparticles were prepared by placing a drop of dilute, aqueous dendrimer solution on a carbon-coated copper TEM grid and allowing the water to evaporate in air. The HRTEM images were recorded digitally with a charge-coupled-device (CCD) camera (Gatan MSC-794 model). Average particle sizes and the size distribution of the nanoparticles were measured from enlarged photographs of TEM images using an image analysis software (Scion image).

### 2.4. Partial hydrogenation of 1,3-cyclooctadiene

Partial hydrogenation of 1,3-cyclooctadiene was carried out in ethanol/water mixture (v/v = 4/1) at 20 °C under hydrogen at atmospheric pressure. Ethanol (7 ml) and the colloidal dispersions of the dendrimer-encapsulated Pd–Rh bimetallic clusters (2 ml, total metal =  $2.75 \times 10^{-6}$  mol) were poured into a 50 ml three-necked round-bottomed flask reactor.

The mixture was stirred under hydrogen atmosphere. After the initial hydrogen uptake ceased, 1 ml solution of 1,3-cyclooctadiene (1 mmol) in ethanol was added to the flask to initiate the reaction. After the reaction was initiated by starting the magnetic stirrer, maintaining the total pressure of hydrogen at 1 atm, the hydrogen uptake was monitored using a constant-pressure manometric unit which was reported elsewhere [13,16]. After completion of the reaction, the reaction mixture was analyzed by Varian CP-3380 gas chromatography equipped with a Carbowax column. The turnover frequency (TOF) was calculated on the basis of hydrogen uptake.

### 3. Results and discussion

The preparation of Pd–Rh bimetallic nanoparticles within dendrimer nanoreactor was carried out by the method similar to those for monometallic nanopar-

ticles [17] except for the simultaneous use of two metal precursors,  $K_2PdCl_4$  and  $RhCl_3$ . By preloading a dendrimer “nanoreactor” with suitable metal ions and then chemically reducing this composite in situ, a dendrimer-encapsulated metal cluster was prepared.

For this, dilute aqueous solution of PAMAM-OH dendrimer was mixed with the aqueous solution of two metal ions at controlled stoichiometries. After stirring the solution for 1 h, aqueous solution of  $NaBH_4$  was slowly added and subsequently the two metal ions were simultaneously reduced to yield zero-valent metal particles. The light red dendrimer/metal ions solution immediately turned dark brown or black indicating the formation of colloidal nanoparticles. The resulting nanoparticles were very stable and there was no precipitation up to 3 months. Schematic illustration for the preparation of dendrimer-encapsulated bimetallic nanoparticles, which is similar to that for the Pt–Pd bimetallic system [13] is represented in Fig. 1.

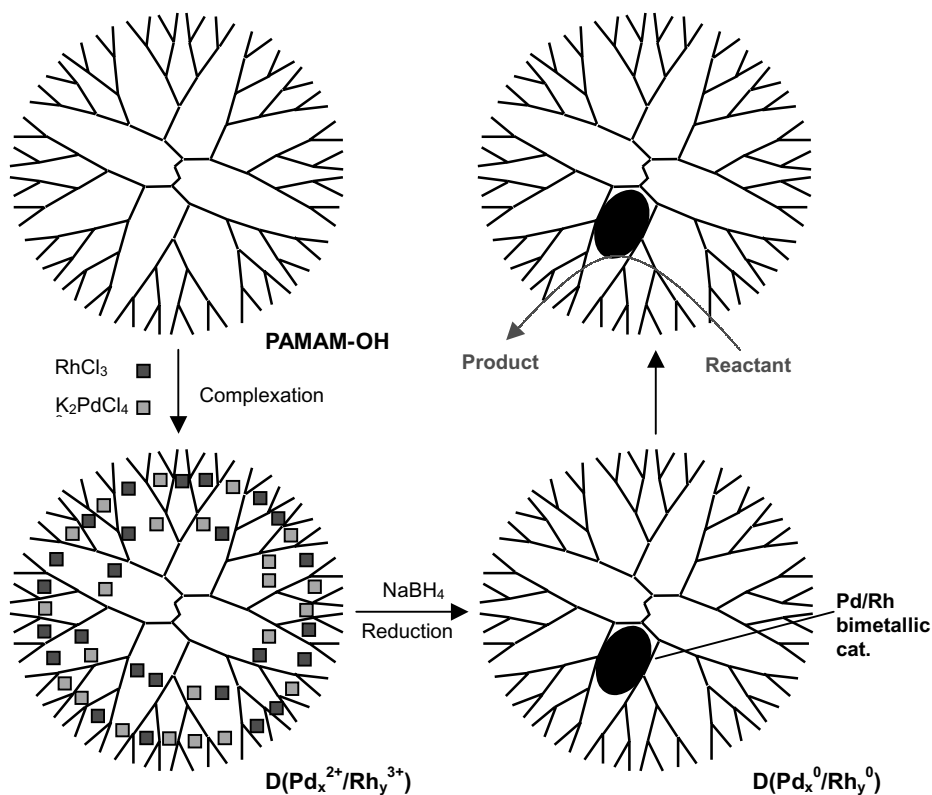


Fig. 1. Schematic diagram for the preparation of dendrimer-encapsulated Pd–Rh bimetallic nanoparticles.

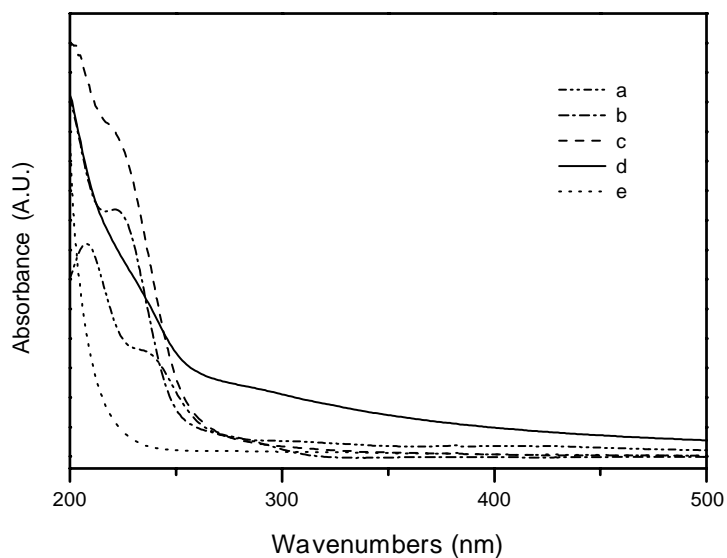


Fig. 2. Variations in the UV-Vis spectra of Pd and Rh metals during the course of the complexation and the subsequent reduction (Pd/Rh ratio = 1/2). (a) 60 mM  $K_2PdCl_4$ , (b) 60 mM  $RhCl_3$ , (c) complexation of metal mixture (24 mM  $K_2PdCl_4$  and 36 mM  $RhCl_3$ ) with 12 mM dendrimer, (d) reduction with 0.6 M  $NaBH_4$ , and (e) PAMAM-OH dendrimer (generation 4).

Fig. 2 shows the changes in the absorption spectra of Pd and Rh metals (Pd/Rh ratio = 1/2) during the course of the complexation with dendrimer and the subsequent reduction. In the case of the monometal ions, the characteristic absorption peaks arising from a ligand-to-metal charge-transfer (LMCT) are clearly

observed. After the addition of PAMAM-OH to the solution of the metal ions, however, an enhanced absorption band around 220 nm appears. This indicates that two metal ions are complexed with the internal functional groups of the dendrimer and are encapsulated in the dendrimer host. After reduction

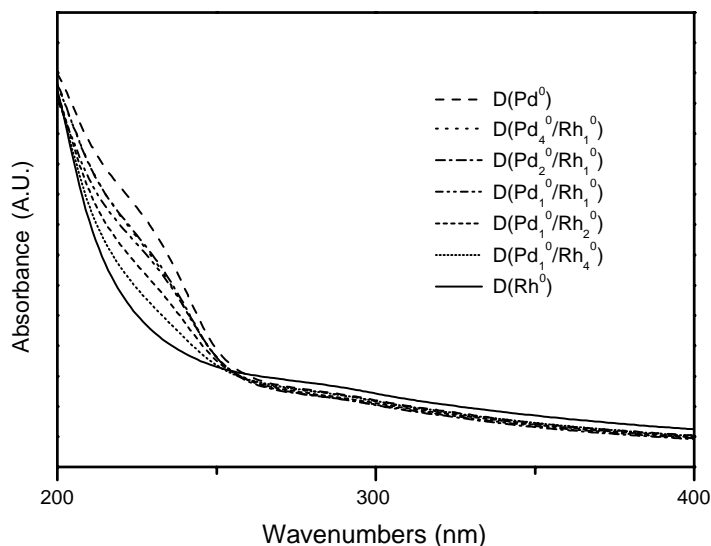


Fig. 3. UV-Vis spectra of dendrimer-encapsulated Pd-Rh bimetallic nanoparticles with various Pd/Rh ratios.

of the composite the spectrum changes significantly: there is now a much higher absorption intensity at low energy, which results from the interband transition of the encapsulated zero-valent metal particles [2].

Fig. 3 presents a series of UV-Vis spectra of the Pd–Rh bimetallic nanoparticles with various Pd/Rh ratios ( $D(\text{Pd}_x^0/\text{Rh}_y^0)$ , where  $x/y = \text{Pd/Rh mol ratio}$ ). Regardless of the Pd/Rh ratios, the absorption bands

are of nearly exponential shape and this indicates the complete reduction of metal ions. Moreover, it should be noted that the spectra of the resulting nanoparticles are different not only from those of the monometallic Pd or Rh nanoparticles but also from those of their physical mixtures. The change in the absorption spectra of the bimetallic nanoparticles from those of individual ones can be primarily attributed to the change in dielectric function caused by mixing the

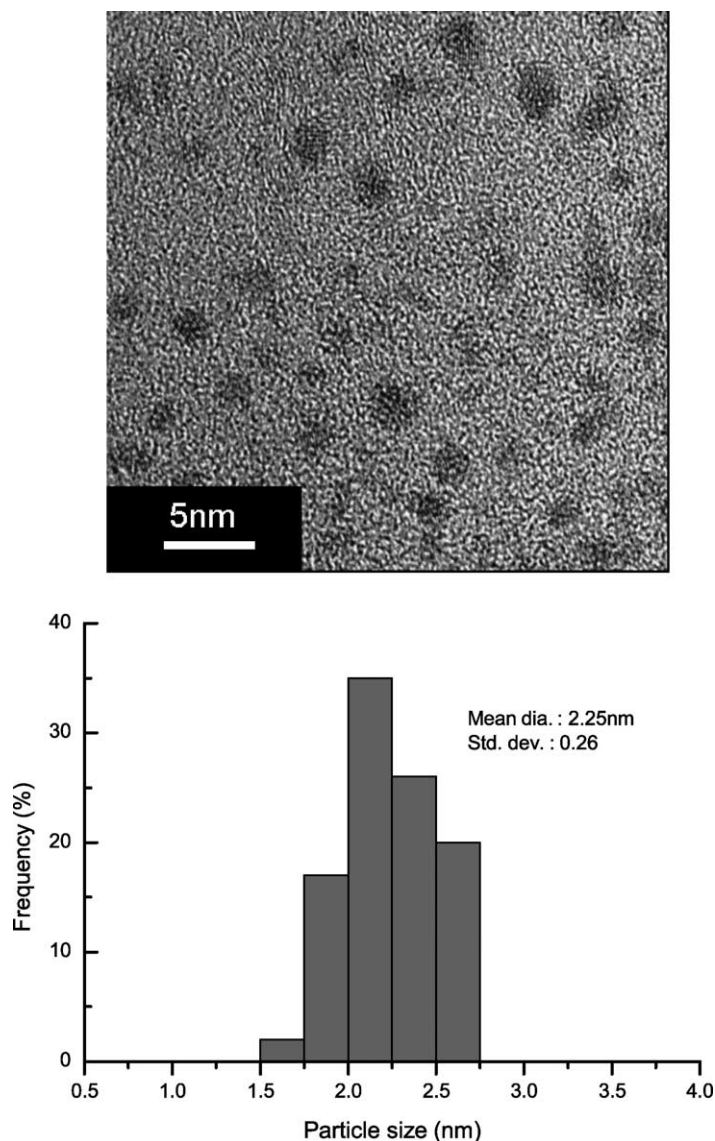


Fig. 4. HRTEM image and particle size distribution of Pd–Rh bimetallic nanoparticles with a Pd/Rh ratio of 1/2.





monometallic ones prepared by the same method. The enhanced catalytic activity of the bimetallic catalyst, which can be explained in terms of an ensemble and/or a ligand effect in catalysis [3,4], is hardly achievable in the case of physical mixtures of palladium and rhodium nanoparticles. It is worth noting, however, that there exist apparent differences between two systems. While bimetallic nanoparticles with a Pd content of 80% showed the highest activity in the case of Pt–Pd, the highest activity was achieved with a Pd/Rh ratio of 1/2 in Pd–Rh system as shown in Fig. 5. According to Toshima and Yonezawa [4], the electronic interaction between two different metals may provide an uneven distribution of electrons and thus make the electron density of one metal become poorer. This effect of one metal upon another may make bimetallic cluster more active than monometallic ones because the substrate having a double bond favors the electron-deficient surface. The results may be considered as another evidence for the formation of Pd–Rh bimetallic nanoparticles. Similar results have also been reported for the case when Pd–Rh bimetallic nanoparticles were protected by polymer [20]. The cyclooctene selectivity at the complete conversion of 1,3-cyclooctadiene was higher than 99%, which is as high as that of the palladium or rhodium nanoparticle catalyst.

In order to confirm the feasibility of catalyst recycling, after a reaction was completed, the catalyst was reused. It was found that the reaction performance was as good as that of the fresh one. This indicates that the dendrimer-encapsulated Pd–Rh bimetallic catalyst can be recycled and reused without a significant loss of catalytic activity.

On the basis of this result in conjunction with our previous Pt–Pd and Ag–Pd systems, it is clear that dendrimer template strategy is one of the most effective methods for the preparation of colloidal nanoparticle catalysts.

#### 4. Conclusions

Ultrafine and monodispersed dendrimer-encapsulated Pd–Rh bimetallic nanoparticles with various metal compositions have been successfully prepared. The resulting bimetallic nanoparticles effectively promote the partial hydrogenation of

1,3-cyclooctadiene and the highest activity was achieved with a Pd/Rh ratio of 1/2. This result suggests the effectiveness of dendrimer as a nanoreactor for the preparation of metal nanoparticle catalysts.

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