

Pt-Pd ,  
\_\_\_\_\_, \*  
,

### **Dendrimer-Encapsulated Pt-Pd Nanoparticles: Synthesis, Characterization, and Application to Catalysis**

Young-Min Chung and Hyun-Ku Rhee\*

*School of Chemical Engineering and Institute of Chemical Processes,  
Seoul National University  
Tel. +82-2-880-7405, Fax. +82-2-888-7295, E-mail: hkrhee@snu.ac.kr*

#### **Introduction**

Dendrimers are highly branched macromolecules and they are generally described to have a structure of spherical shape with a high degree of symmetry [1, 2]. By virtue of their three-dimensional structure having interior void spaces, dendrimers have been considered as new types of host for the accommodation of guest molecules [3]. The reasons why dendrimers are particularly well-suited for hosting metal nanoparticles are as follows: (1) the dendrimer templates themselves are of fairly uniform composition and structure, and therefore they yield well-defined nanoparticle replicas; (2) the nanoparticles are stabilized by encapsulation within the dendrimer, and therefore they do not agglomerate; (3) the encapsulated nanoparticles are confined primarily by steric effects, and therefore a substantial fraction of their surface is unpassivated and available to participate in catalytic reactions, (4) the dendrimer branches can be used as selective gates to control access of small molecules (substrates) to the encapsulated (catalytic) nanoparticles; (5) the terminal groups on the dendrimer periphery can be tailored to control solubility of the hybrid nanocomposite and used as handles for facilitating linking to surfaces and other polymers.

In line with the prospect of dendrimer as a template for the formation of inorganic nanoparticles, various metal nanoparticles have been successfully prepared. 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.

In this regard, we have aimed here to demonstrate the preparation of Pt-Pd bimetallic nanoparticles in the presence of poly(amidoamine) dendrimers with surface hydroxyl groups (4th generation, PAMAM-OH) and the application of these bimetallic nanoparticles as catalysts to the partial hydrogenation of 1,3-cyclooctadiene. To our knowledge, this is the first effort for the preparation of dendrimer-encapsulated bimetallic nanoparticles which exhibit a promising catalytic activity.

#### **Experimental**

Dendrimer-encapsulated Pt-Pd bimetallic nanoparticles are prepared by simultaneous co-complexation of two different metal ions, followed by a single reduction step. Complexation of metal ions with dendrimers are carried out by the addition of desired amounts of Pt<sup>2+</sup> and Pd<sup>2+</sup> (total metal concentration = 55mM) to 1mM PAMAM-OH dendrimer solution (4th generation) under vigorous stirring. After 1h, 0.55M sodium borohydride was slowly added under vigorous stirring.

Absorption spectra were recorded on a PERKIN-ELMER Lambda 35 UV-vis spectrometer using deionized water as a reference for all measurements.

Samples for XPS (X-ray Photoelectron Spectroscopy) analysis were prepared by soaking Si wafers in aqueous solution of dendrimers containing metal nanoparticles for 20h, followed by careful rinsing and drying. Before use, Si wafers were rinsed with ethanol, dried in nitrogen atmosphere.

XPS data were acquired using a PERKIN-ELMER PHI 558 spectrometer and employing a pass energy of 40eV, a step increment of 0.1eV, and an Al anode. XPS peak positions were referenced to

the carbon (1s) peak at 284.6eV.

High-resolution transmission electron micrographs (HRTEM) were obtained using a JEOL JEM-3000F transmission electron microscope equipped with an EDS (Energy Dispersive Spectroscopy) 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 (approximately 150 particles) were measured from enlarged photographs of TEM images using an image analysis software (Scion image).

Partial hydrogenation of 1, 3-cyclooctadiene was carried out in ethanol/water mixture (v/v=4) at 20 °C under hydrogen at atmospheric pressure. Ethanol (7ml) and the colloidal dispersions of the dendrimer-encapsulated Pt/Pd bimetallic clusters (2ml, total metal =  $5.5 \times 10^{-6}$  mol) were poured into a 50ml three-necked round-bottomed flask reactor. After the initial hydrogen uptake ceased, 1ml solution of 1, 3-cyclooctadiene (1mmol) 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 1atm, the hydrogen uptake was monitored using a constant-pressure manometric unit. 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.

### **Results and Discussion**

The preparation of Pt-Pd bimetallic nanoparticles within dendrimer templates was carried out by the method similar to those for monometallic nanoparticles except for the simultaneous use of two metal precursors,  $K_2PtCl_4$  and  $K_2PdCl_4$ . After reduction, the light yellow dendrimer/ $(PtCl_4^{2-} + PdCl_4^{2-})$  solution immediately turned dark brown indicating the formation of colloidal nanoparticles. The resulting nanoparticles were very stable and there was no precipitation up to three months.

Figure 1 shows the changes in the absorption spectra of Pt and Pd metals (Pt/Pd ratio = 1/4) in the course of the complexation with dendrimer and the following reduction. Concerning the monometal ions, the characteristic absorption peaks at 214 and 208nm arising from a ligand-to-metal charge-transfer (LMCT) are observed for  $PtCl_4^{2-}$  and  $PdCl_4^{2-}$ , respectively. In the absence of dendrimer, the mixture of  $PtCl_4^{2-}$  and  $PdCl_4^{2-}$  also exhibits the mixed absorption peaks of two metal ions. After the addition of PAMAM-OH to the solution of the  $PtCl_4^{2-}$  and  $PdCl_4^{2-}$ , however, a new band at 230nm appears at the expense of the decrease in the strong absorption peak at 205nm. 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, the band observed in the former case completely disappears and a new broad absorption band appears over a wide wavelength region.

Figure 2 presents a series of UV-vis spectra of the Pt-Pd bimetallic nanoparticles with various Pt/Pd ratios ( $D(Pt_x^0/Pd_y^0)$ , where x/y = Pt/Pd mol ratio). Regardless of the Pt/Pd 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 Pt or Pd 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 two different metal atoms. Therefore, the characteristic monotonic absorption spectra strongly suggest that bimetallic nanoparticles are formed in the cavity of the dendrimer.

The result of X-Ray photospectroscopy (XPS) analysis also supports that all the metal ions are completely reduced irrespective of the Pt/Pd ratios. In the case of Pt, the peaks corresponding to platinum  $4f_{7/2}$  and  $4f_{5/2}$  levels are observed at 72.5 and 75.7eV binding energies, respectively, and these peaks are assigned to  $Pt^{2+}$ . Upon reduction, the peaks are shifted to 71.3 and 74.4eV, respectively, which are assigned to  $Pt^0$ . Similarly, it is observed that the  $Pd(3d_{5/2})$  peak is shifted from 337.6 to 334.9eV and  $Pd(3d_{3/2})$  peak from 342.7 to 340.5eV upon reduction.

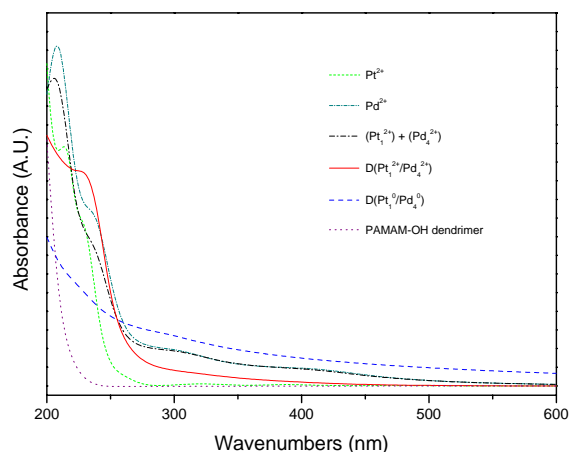


Fig. 1. Variations in the UV-vis spectra of Pt and Pd metals in the course of the complexation and the subsequent reduction (Pt/Pd ratio = 1/4).

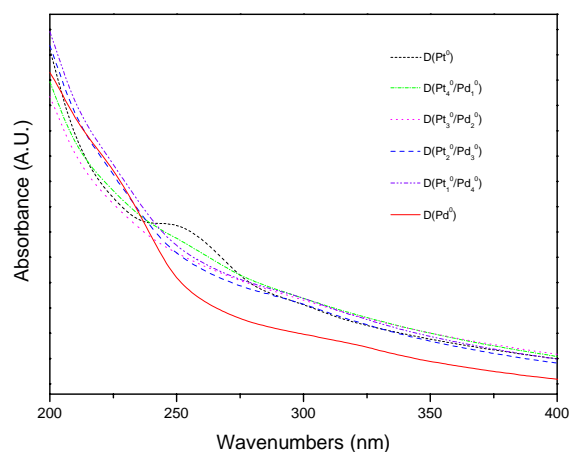


Fig. 2. UV-vis spectra of dendrimer-encapsulated Pt-Pd bimetallic nanoparticles with various Pt/Pd ratios.

The representative HRTEM image of  $D(\text{Pt}_1^0/\text{Pd}_4^0)$  is shown Figure 3. The microscopy demonstrates that the particle size is uniform and the shape is nearly spherical. Regardless of the metal composition, bimetallic nanoparticles with a diameter of  $\sim 2.3 \pm 0.2 \text{ nm}$  were observed. The formation of quite monodispersed nanoparticles suggests the effectiveness of dendrimers acting as both nanoreactors for the preparation of nanoparticles and nanoporous stabilizers for the prevention of aggregation.

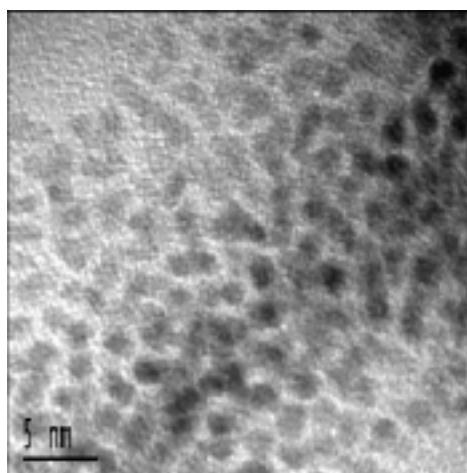


Fig. 3. HRTEM image of dendrimer-encapsulated Pt-Pd bimetallic nanoparticles (Pt/Pd ratio=1:4).

To confirm whether the nanoparticles are a mixture of Pt and Pd nanoparticles or bimetallic ones, EDS analysis was carried out and both Pt and Pd elements were detected. However, it was rather difficult to acquire the elements of one particle because the spatial resolution (ca. 5nm) was not high enough to detect the X-ray generated from a single particle. In the present study, therefore, only their average compositions are discussed. Although precipitation was expected due to the metal-induced

crosslinking of amine terminated dendrimers (PAMAM-NH<sub>2</sub>), we alternatively prepared another type of Pt-Pd bimetal/dendrimer nanocomposite using PAMAM-NH<sub>2</sub> to obtain nanoparticles large enough to detect the X-ray generated from a single particle. For these alternative samples, the two elements were detected in all the particles analyzed and this clearly indicates that they are bimetallic ones.

The dendrimer-encapsulated Pt-Pd bimetallic nanoparticles were applied as catalyst to the partial hydrogenation of 1, 3-cyclooctadiene in ethanol/water mixture (v/v=4/1). As shown in Figure 4, the catalytic activity of the bimetallic nanoparticles increased as the Pt/Pd ratio decreased and the catalytic activities of D(Pt<sub>2</sub><sup>0</sup>/Pd<sub>3</sub><sup>0</sup>) and D(Pt<sub>1</sub><sup>0</sup>/Pd<sub>4</sub><sup>0</sup>) were higher than that of the palladium nanoparticles prepared by the same method. It is worth noting that the enhanced catalytic activity of the bimetallic catalyst, which can be explained in terms of an ensemble and/or a ligand effect in catalysis, is hardly achievable in the case of physical mixtures of palladium and platinum nanoparticles.

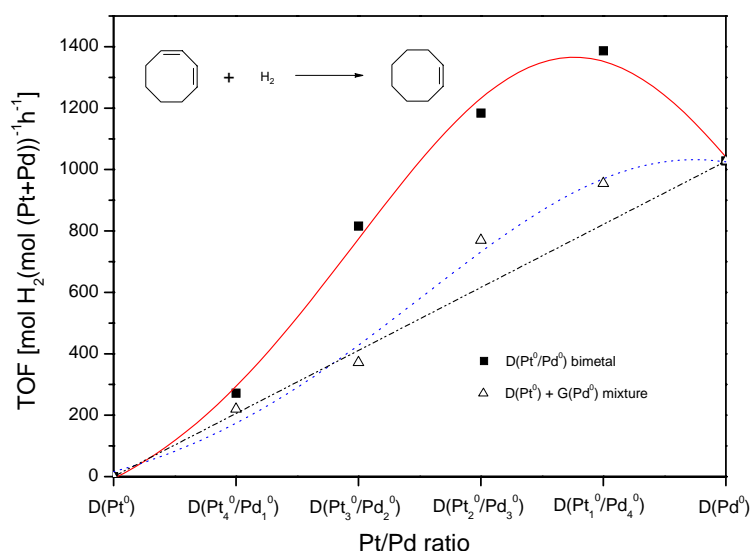


Fig. 4. The dependence of the catalytic activity of the dendrimer-encapsulated Pt-Pd bimetallic nanoparticles on its composition in partial hydrogenation of 1,3-cyclooctadiene.

In summary, ultrafine and monodispersed dendrimer-encapsulated Pt-Pd bimetallic nanoparticles with various metal compositions have been successfully prepared. The Pt-Pd bimetallic nanoparticles effectively promote the partial hydrogenation of 1, 3-cyclooctadiene and the highest activity was achieved with a Pt/Pd ratio of 1/4. This result suggests that the potential application of the dendrimer-encapsulated bimetallic nanoparticles is promising in the field of catalysis

### **Acknowledgement**

Financial aid from the Brain Korea 21 Program supported by the Ministry of Education is gratefully acknowledged.

### **References**

- [1] Chung, Y.-M. and Rhee, H.-K., *Chem. Commun.*, 238 (2002).
- [2] Chung, Y.-M. and Rhee, H.-K., *Catal. Lett.*, in press (2002).
- [3] Crooks, R. M., Zhao, M., Sun, L., Chechik, V., and Yeung, L. K., *Acc. Chem. Res.*, **34**(3), 181 (2001).