

Subnanoscale Size Effect of Dendrimer-encapsulated Pd Clusters on Catalytic Hydrogenation of Olefin

Zen Maeno,¹ Takayuki Kibata,¹ Takato Mitsudome,¹ Tomoo Mizugaki,¹ Koichiro Jitsukawa,¹ and Kiyotomi Kaneda^{*1,2}

¹Graduate School of Engineering Science, Osaka University, 1-3 Machikaneyama, Toyonaka, Osaka 560-8531

²Research Center for Solar Energy Chemistry, Osaka University, 1-3 Machikaneyama, Toyonaka, Osaka 560-8531

(Received November 15, 2010; CL-100954; E-mail: kaneda@cheng.es.osaka-u.ac.jp)

Dendrimer-encapsulated subnano Pd clusters catalyze selective hydrogenation of 1,3-cyclooctadiene to cyclooctene. The catalytic activity increases with the size of the subnano Pd clusters. The activity of the threefold hollow sites of the subnano Pd clusters plays an important role in the hydrogenation reaction.

Metal nanoparticles (NPs) have received much attention in various fields, including catalysis, optics, and electronics, due to the difference in their chemical and physical properties compared to mononuclear metal atoms and bulk metals.¹ Among NPs, small clusters of a range of diameters less than 1 nm, known as subnano metal clusters, are considered a new material since they bridge the gap between mononuclear metal atoms and NPs.² Subnano metal clusters have significant advantages in terms of efficiency because they possess extremely large surface-to-volume ratios, and also large numbers of coordinatively unsaturated surface atoms, which are expected to show unique catalytic properties. Several attractive methods for synthesizing subnano metal clusters have been developed using organic polymers^{3a–3c} and inorganic materials.^{3d–3g} However, size-selective synthesis of subnano metal clusters has been challenging due to their instability—they have a tendency to aggregate into larger NPs—and consequently, the catalysis of subnano metal clusters and the size effect are still unclear.⁴

We recently succeeded in the controlled synthesis of subnano-ordered Pd clusters consisting of a specific number of Pd atoms (Pd₄, Pd₈, and Pd₁₆) within fifth generation poly(propylene imine) (PPI) dendrimers (G₅-Pd⁰_y, y = 4, 8, and 16).⁵ Herein, we investigate the application of dendrimer-encapsulated subnano Pd clusters in the hydrogenation of 1,3-cyclooctadiene (1,3-COD) in order to reveal size-dependent catalysis.

Dendrimer-encapsulated subnano Pd clusters of G₅-Pd⁰₄, -Pd⁰₈, and -Pd⁰₁₆ were synthesized according to a previous paper from our laboratory.⁵ Briefly, an appropriate amount of aqueous solution of Na₂PdCl₄ was added to a chloroform solution of fifth generation triethoxybenzamide-terminated PPI dendrimer, G₅-TEBA (Figure 1A), giving dendrimer-encapsulated Pd²⁺ ions, G₅-Pd^{II}_y (y denotes the number of precursor Pd ions in one dendrimer; y = 4, 8, and 16), and these were reduced with an aqueous solution of KBH₄, with vigorous stirring, to form Pd⁰ clusters, G₅-Pd⁰_y. Curve-fitting analysis of inverse Fourier-transform (FT) of *k*³-weighted Pd K-edge extended X-ray absorption fine structure (EXAFS) (Figure 2) revealed that the coordination numbers (CNs) of the Pd–Pd shell of G₅-Pd⁰_y (y = 4, 8, and 16) were 3.2, 4.6, and 5.9, respectively (Table S2¹²). The nuclearities of the Pd clusters were estimated to be 4, 8, and 16, respectively, which match the number of preorganized Pd²⁺ ions within each dendrimer (Figure 1B).

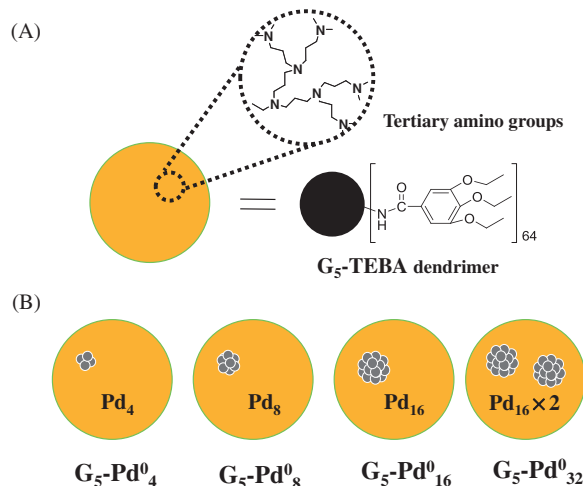


Figure 1. (A) Structure of G₅-TEBA dendrimers. (B) G₅-Pd⁰_y (y = 4, 8, 16, and 32) and subnano Pd clusters within G₅-TEBA.

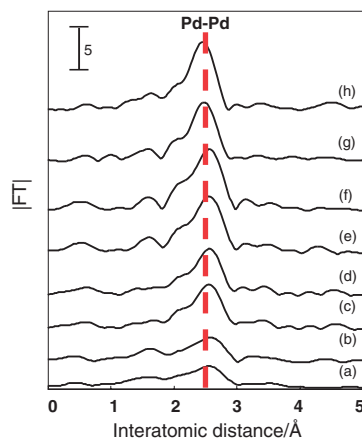


Figure 2. Fourier transforms of *k*³-weighted Pd K-edge EXAFS experimental data for (a) G₅-Pd⁰₄, (b) used G₅-Pd⁰₄, (c) G₅-Pd⁰₈, (d) used G₅-Pd⁰₈, (e) G₅-Pd⁰₁₆, (f) used G₅-Pd⁰₁₆, (g) G₅-Pd⁰₃₂, and (h) used G₅-Pd⁰₃₂.

The preparation of G₅-Pd⁰_y using larger amounts of Pd²⁺ ions was also examined. Notably, the CN of the Pd–Pd shell in G₅-Pd⁰₃₂ was close to that of G₅-Pd⁰₁₆, as confirmed by Pd K-edge EXAFS (Table S2¹²). This indicated that G₅-Pd⁰₃₂ might consist of two Pd₁₆ clusters encapsulated within one dendrimer (Figure 1B). The internal void spaces of the G₅-TEBA dendrimer may fit the size of the Pd₁₆ cluster.

The catalytic performances of the dendrimer-encapsulated subnano Pd clusters G₅-Pd⁰_y (y = 4, 8, 16, and 32) were

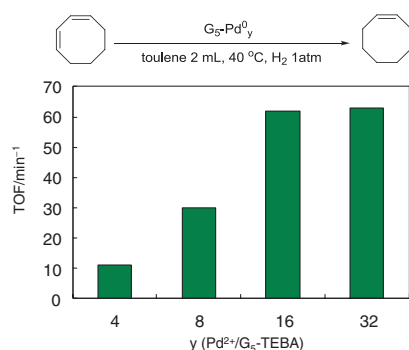


Figure 3. TOFs for hydrogenation of 1,3-cyclooctadiene using $G_5-Pd^0_y$.

examined in the hydrogenation of 1,3-COD.⁶ All $G_5-Pd^0_y$ tested promoted hydrogenation selectively, giving cyclooctene in over 99% yield. Interestingly, the initial turnover frequency (TOF/ min^{-1}), normalized to the total number of surface Pd atoms in the Pd clusters within $G_5-Pd^0_y$, increased with increasing Pd cluster size; the TOFs of $G_5-Pd^0_y$ ($y = 4, 8$, and 16) were 10, 31, and 62, respectively (Figure 3).⁷ Moreover, the TOF of $G_5-Pd^0_{32}$ (65) was similar to that of $G_5-Pd^0_{16}$ (62), which is consistent with the presence of two Pd_{16} clusters within one dendrimer (vide supra).

After the 1,3-COD hydrogenation reaction, FT of the k^3 -weighted Pd K-edge EXAFS spectra of $G_5-Pd^0_y$ ($y = 4, 8, 16$, and 32) gave similar peak intensities and CNs for the Pd–Pd shell to those of fresh clusters (Figure 2 and Table S2¹²). Furthermore, the TOFs of $G_5-Pd^0_y$ were maintained in repeated addition of 1,3-COD (Table S3¹²). These phenomena suggest that the original sizes of the Pd clusters remain unchanged during the hydrogenation reaction.

In order to investigate the size effect of the subnano Pd clusters, preliminary kinetic studies were carried out. The initial reaction rate of the 1,3-COD hydrogenation using $G_5-Pd^0_y$ ($y = 4, 8$, and 16) was dependent on the partial pressure of H_2 and independent of the concentration of 1,3-COD (Figure S2).^{8,12} The kinetic isotope effect was observed for the hydrogenation using D_2 ($k_H/k_D = 1.5$). From the above results, dissociative adsorption of H_2 is considered as the rate-determining step in the 1,3-COD hydrogenation.⁹ Zhi et al. and others reported that the density functional theory (DFT) calculations of dissociative adsorption of H_2 on small Pd clusters revealed that the configuration with H atoms adsorbed on Pd threefold hollow sites is the most stable structure.¹⁰ In our case, the TOF normalized to the total number of the threefold hollow sites in the Pd cluster also increased with increasing the size of subnano Pd clusters (see the Supporting Information).¹² Namely, the size effect on catalytic activity in the hydrogenation reaction was derived from the difference of activity of the threefold hollow sites of the Pd cluster.¹¹

In conclusion, investigation of the catalysis of dendrimer-encapsulated subnano Pd clusters in the 1,3-COD hydrogenation showed that the initial rate of the hydrogenation was dependent on the size of the Pd clusters, and the TOF of the hydrogenation reaction increased with the Pd cluster size. The activity of the threefold hollow sites of the subnano Pd clusters in dissociative adsorption of H_2 played an important role in the 1,3-COD

hydrogenation reaction. Furthermore, the preparation of $G_5-Pd^0_y$ using a larger number of Pd^{2+} ions succeeded in the formation of two Pd_{16} clusters within one dendrimer.

This work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology of Japan. The XAFS experiments were performed at the BL01B1 and BL14B2 in the SPring-8 with approval of the Japan Synchrotron Radiation Research Institute (Nos. 2009A1856, 2009A1860, 2009B1854, 2009B1506, 2010A1781, and 2010A1788). One of the authors T. K. expresses his special thanks for the Global COE (center of excellence) Program “Global Education and Research Center for Bio-Environmental Chemistry” of Osaka University.

References and Notes

- a) D. V. Talapin, J.-S. Lee, M. V. Kovalenko, E. V. Shevchenko, *Chem. Rev.* **2010**, *110*, 389. b) *Metal Nanoclusters in Catalysis and Materials Science: The Issue of Size Control*, 1st ed., ed. by B. Corain, G. Schmid, N. Toshima, Elsevier, Netherlands, **2008**.
- a) A. Roucoux, J. Schulz, H. Patin, *Chem. Rev.* **2002**, *102*, 3757. b) D. Astruc, F. Lu, J. R. Aranzas, *Angew. Chem., Int. Ed.* **2005**, *44*, 7852. c) A. W. Castleman, Jr., S. N. Khanna, *J. Phys. Chem. C* **2009**, *113*, 2664.
- Recent examples of the synthesis and catalysis of subnano metal clusters: a) K. Okamoto, R. Akiyama, H. Yoshida, T. Yoshida, S. Kobayashi, *J. Am. Chem. Soc.* **2005**, *127*, 2125. b) K. Yamamoto, T. Imaoka, W.-J. Chun, O. Enoki, H. Katoh, M. Takenaga, A. Sonoi, *Nat. Chem.* **2009**, *1*, 397. c) B. S. González, M. J. Rodríguez, C. Blanco, J. Rivas, M. A. López-Quintela, J. M. G. Martín, *Nano Lett.* **2010**, *10*, 4217. d) K. Okumura, K. Noto, K. Yoshida, M. Niwa, *J. Catal.* **2005**, *231*, 245. e) T. Mitsudome, K. Nose, K. Mori, T. Mizugaki, K. Ebitani, K. Jitsukawa, K. Kaneda, *Angew. Chem., Int. Ed.* **2007**, *46*, 3288. f) W. E. Kaden, T. Wu, W. A. Kunkel, S. L. Anderson, *Science* **2009**, *326*, 826. g) Y. Liu, H. Tsunoyama, T. Akita, T. Tsukuda, *J. Phys. Chem. C* **2009**, *113*, 13457.
- Although the chemical vapor method with quadrupole mass is applicable to size-selective synthesis of subnano metal clusters,^{3f} investigations of the catalytic activity of subnano metal clusters prepared by this method are limited to gas-phase reactions.
- T. Mizugaki, T. Kibata, K. Ota, T. Mitsudome, K. Ebitani, K. Jitsukawa, K. Kaneda, *Chem. Lett.* **2009**, *38*, 1118.
- The total amount of Pd (mol) used for each hydrogenation reaction was constant. See Supporting Information for the reaction conditions.¹²
- See Supporting Information for a definition of TOF.¹²
- In other Pd NP catalyst systems, the reaction rate for 1,3-COD hydrogenation shows similar dependence on H_2 pressure and 1,3-COD concentration. See: H. Arnold, S. Göbel, D. Reinig, J. Gaube, *Chem. Ing. Tech.* **1994**, *66*, 727.
- S. Naito, M. Tanimoto, *J. Chem. Soc., Faraday Trans. 1* **1988**, *84*, 4115.
- a) M. Ni, Z. Zeng, *THEOCHEM* **2009**, *910*, 14. b) E. D. German, I. Efremenko, M. Sheintuch, *J. Phys. Chem. A* **2001**, *105*, 11312. c) J. Roques, C. Lacaze-Dufaure, C. Mijoule, *J. Chem. Theory Comput.* **2007**, *3*, 878.
- The activation enthalpies ($\Delta H^\ddagger/\text{kJ mol}^{-1}$) for 1,3-COD hydrogenation using $G_5-Pd^0_y$ ($y = 4, 8$, and 16) at 313 K were 41.3, 38.1, and 34.3, respectively, while the activation entropies ($\Delta S^\ddagger/\text{kJ mol}^{-1} \text{K}^{-1}$) were -141 , -142 , and -149 , respectively.
- Supporting Information is available electronically on the CSJ-Journal Web site, <http://www.csj.jp/journals/chem-lett/index.html>.