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

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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 (Pd_4, Pd_8, and Pd_{16}) within fifth generation poly(propylene imine) (PPI) dendrimers (G_5-Pd^0_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 G_5-Pd^0_4, -Pd^0_8, and -Pd^0_{16} were synthesized according to a previous paper from our laboratory.[5] Briefly, an appropriate amount of aqueous solution of Na_2PdCl_4 was added to a chloroform solution of fifth generation triethoxybenzamide-terminated PPI dendrimer, G_5-TEBA (Figure 1A), giving dendrimer-encapsulated Pd^{2+} ions, G_5-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 KBH_4, with vigorous stirring, to form Pd^0 clusters, G_5-Pd^0_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 G_5-Pd^0_y ($y = 4$, 8, and 16) were 3.2, 4.6, and 5.9, respectively (Table S2[12]). The nuclearities of the Pd clusters were estimated to be 4, 8, and 16, respectively, which match the number of preorganized Pd^{2+} ions within each dendrimer (Figure 1B).

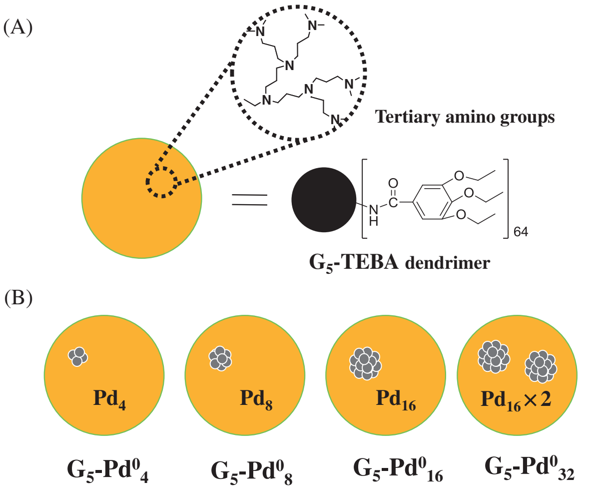

Figure 1. (A) Structure of G_5-TEBA dendrimers. (B) G_5-Pd^0_y ($y = 4$, 8, 16, and 32) and subnano Pd clusters within G_5-TEBA.

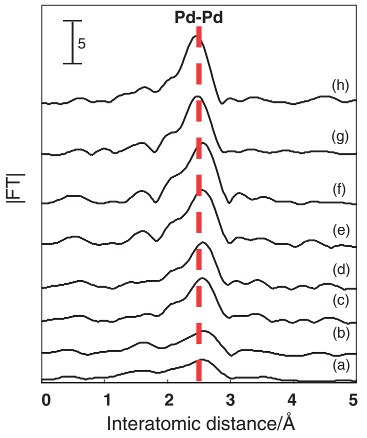

Figure 2. Fourier transforms of k^3-weighted Pd K-edge EXAFS experimental data for (a) G_5-Pd^0_4, (b) used G_5-Pd^0_4, (c) G_5-Pd^0_8, (d) used G_5-Pd^0_8, (e) G_5-Pd^0_{16}, (f) used G_5-Pd^0_{16}, (g) G_5-Pd^0_{32}, and (h) used G_5-Pd^0_{32}.

The preparation of G_5-Pd^0_y using larger amounts of Pd^{2+} ions was also examined. Notably, the CN of the Pd–Pd shell in G_5-Pd^0_{32} was close to that of G_5-Pd^0_{16}, as confirmed by Pd K-edge EXAFS (Table S2[12]). This indicated that G_5-Pd^0_{32} might consist of two Pd_{16} clusters encapsulated within one dendrimer (Figure 1B). The internal void spaces of the G_5-TEBA dendrimer may fit the size of the Pd_{16} cluster.

The catalytic performances of the dendrimer-encapsulated subnano Pd clusters G_5-Pd^0_y ($y = 4$, 8, 16, and 32) were

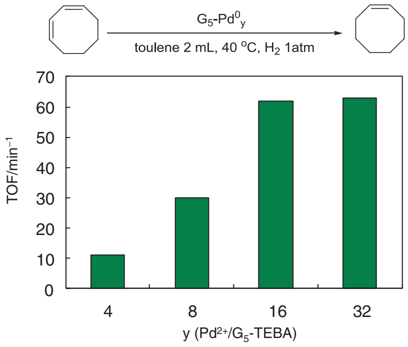

Figure 3. TOFs for hydrogenation of 1,3-cyclooctadiene using G_5-Pd^0_y.

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 S2[12]). Furthermore, the TOFs of G_5-Pd^0_y were maintained in repeated addition of 1,3-COD (Table S3[12]). 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.

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7 See Supporting Information for a definition of TOF.[12]

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11 The activation enthalpies ($\Delta H^{\ddagger}$/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 ($\Delta S^{\ddagger}$/kJ mol^{-1} K^{-1}) were −141, −142, and −149, respectively.

12 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.