

Investigation of size-dependent properties of sub-nanometer palladium clusters encapsulated within a polyamine dendrimer†

Cite this: *Chem. Commun.*, 2013, **49**, 167

Received 28th September 2012,
Accepted 9th November 2012

DOI: 10.1039/c2cc37038g

www.rsc.org/chemcomm

Takayuki Kibata,^a Takato Mitsudome,^a Tomoo Mizugaki,^a Koichiro Jitsukawa^a and Kiyotomi Kaneda^{*ab}

This study describes the first example of the investigation of electronic, geometric, and catalytic properties of Pd subnano metal clusters of Pd₄, Pd₈, and Pd₁₆ stabilized by poly(propylene imine) (PPI) dendrimers using XAFS and IR analyses. The relations among these properties are also discussed.

Chemical and physical properties of metal nanoparticles (MNPs) in diverse fields such as catalysis, optics, and electronics are strongly influenced by nanoparticle size due to electronic and geometric effects.¹ Recently, MNPs with sizes smaller than 1 nm, called subnano metal clusters (SNMCs), have attracted attention because they bridge the gap between mononuclear metal atoms and MNPs. In catalytic applications, SNMCs are expected to show different catalysis from MNPs, and to offer significant advantages of an extremely large surface-to-volume ratio, as well as large numbers of coordinatively unsaturated surface atoms, leading to unprecedented, high catalytic performance.² However, the precise synthesis of SNMCs possessing catalytic potential has been difficult because the use of strong stabilizers for SNMCs such as thiols poisons the catalytic active sites of SNMCs.³ In contrast, the low coordination of a weak stabilizer of CO causes easy aggregation.⁴ For example, subnano Pd carbonyl clusters can be size-selectively synthesized, but these clusters decompose easily to larger nanoparticles and metal precipitates during catalytic reactions.⁵ Therefore, few examples of successful SNMC catalysts have been reported.⁶

Dendrimers are spherical organic macromolecules that have well-regulated units branched from the core to the periphery. Their chemical and physical properties can be adjusted by changing the units. One of the main structural features of dendrimers is the nanovoids within their sterically confined branches. These voids can encapsulate various types of substances such as organic

molecules, metal complexes, and MNPs.⁷ Recently, we successfully synthesized subnano Pd clusters using the poly(propylene imine) (PPI) dendrimer functionalized with bulky substituents on the periphery.⁸ The PPI dendrimer functioned as a “macroligand” to maintain the catalytically active sites of the subnano Pd clusters while retaining its sub-nanometer size during hydrogenation reactions. This synthetic methodology using PPI dendrimers enabled the selective synthesis of specific sizes of subnano Pd clusters, such as Pd₄, Pd₈, and Pd₁₆ clusters, allowing the study of size-dependent catalysis of subnano Pd clusters.

As a continuation of studies on subnano Pd clusters, this report describes the size-dependent electronic, geometric, and catalytic properties of the subnano Pd clusters of Pd₄, Pd₈, and Pd₁₆. Results from spectroscopic analyses using X-ray absorption fine structure (XAFS) and IR revealed that the size-dependent electronic properties of the subnano Pd clusters were quite different from those of the nanocluster. Furthermore, size-dependent catalysis of the subnano Pd clusters also occurred in phosphine-free allylic substitution reactions. This finding also highlighted the relation between the catalytic and electronic or geometric properties of the subnano Pd clusters. This is the first example of the investigation of electronic, geometric, and catalytic properties of subnano Pd clusters, as well as the relations among properties.

Subnano Pd₄, Pd₈, and Pd₁₆ clusters were prepared using the fifth generation of the PPI dendrimer functionalized with triethoxybenzoyl chloride (G₅-TEBA) according to previous reports.⁸ The dendrimer-encapsulated Pd clusters were denoted G₅-Pd_n⁰ where *n* represents the number of Pd ions in one dendrimer (*n* = 4, 8, and 16). The G₅-Pd_n⁰ was characterized using Pd K-edge XAFS and the numbers of Pd atoms in the clusters were estimated to be 4, 8, and 16 within G₅-Pd₄⁰, G₅-Pd₈⁰, and G₅-Pd₁₆⁰, respectively, from the coordination number of the Pd–Pd bond. The TEM image of G₅-Pd₁₆⁰ also confirmed that the average diameter of the Pd cluster was ca. 1 nm, corresponding to the size of the Pd₁₆ cluster.^{8a} The Pd L₃-edge X-ray absorption near edge structure (XANES) spectra shown in Fig. 1 indicate that the intensity of the white lines increased with a decrease in the size of the subnano Pd clusters. The white line intensity is dependent on the number of holes in the 4d band; a more intense white line corresponds to a higher

^a Department of Materials Engineering Science, Graduate School of Engineering Science, Osaka University, 1-3 Machikaneyama, Toyonaka, Osaka 560-8531, Japan.

E-mail: kaneda@cheng.es.osaka-u.ac.jp; Fax: +81 6-6850-6260; Tel: +81 6-6850-6260

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

† Electronic supplementary information (ESI) available: Experimental details, XAFS analysis, TEM image, FT-IR spectra and kinetic studies. See DOI: 10.1039/c2cc37038g

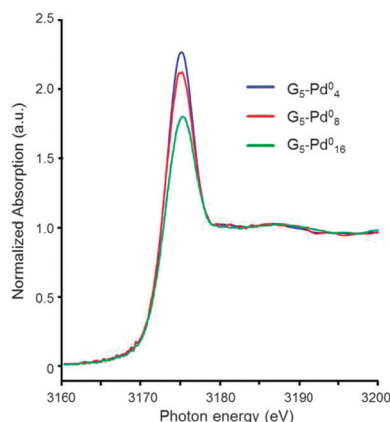


Fig. 1 Pd L₃-edge XANES spectra of dendrimer-encapsulated subnano Pd clusters and of G₅-Pd₄⁰ (blue), G₅-Pd₈⁰ (red), and G₅-Pd₁₆⁰ (green). The spectra were normalized to the absorption edge step height at 50 eV past the absorption edge.

unoccupied 4d band.⁹ Therefore, the size-dependent intensity of the white lines reveals that the larger subnano Pd clusters have a higher occupied 4d band. This size dependency is quite different from that of the nano Pd cluster; the d-electron counts of nano Pd clusters decrease as the cluster size increases.¹⁰

A CO adsorption FTIR experiment is also useful for obtaining detailed insights into the electronic and geometric properties of G₅-Pd_n⁰. The FTIR spectra of G₅-Pd_n⁰ treated with a CO atmosphere showed a red-shift of the CO stretching bands (ν_{CO}) with an increase in the size of the subnano Pd clusters; the main ν_{CO} bands were observed at 1843, 1837, and 1830 cm⁻¹ for G₅-Pd₄⁰, G₅-Pd₈⁰, and G₅-Pd₁₆⁰, respectively (Table 1).¹¹ These phenomena can be explained by an increase in the strength of π -back-donation from Pd to CO.¹² The subnano Pd cluster with the larger size has a higher energy level of the highest occupied orbitals (HOMO) of the Pd clusters, which enhances π -back-donation from Pd d π to the CO π^* orbital.^{13,14} Furthermore, the higher intensity of the ν_{CO} band with increasing cluster sizes was observed, indicating an increase in surface sites of Pd clusters where the π -back-donation from Pd to CO can occur. These XAFS and IR studies demonstrate conclusively that the number of 4d electrons, the energy level of the 4d band, and the number of surface sites increase with the size of the subnano Pd clusters.

Next, the catalytic ability of G₅-Pd_n⁰ was investigated in phosphine-free allylic substitution reactions. We have previously found high catalytic activity of subnano Pd clusters enwrapped by inorganic material (montmorillonite) in allylic substitution reactions.

Table 1 Characteristic data of CO adsorption based on the band deconvolution of diffuse reflectance infrared Fourier transform spectra

Sample	Signal position/cm ⁻¹	fwhm ^a /cm ⁻¹	Intensity
G ₅ -Pd ₄ ⁰	1899	52.2	0.04
	1843	43.8	0.03
	1884	67.6	0.06
G ₅ -Pd ₈ ⁰	1837	38.0	0.08
	1792	52.9	0.04
	1868	62.3	0.15
G ₅ -Pd ₁₆ ⁰	1830	87.2	0.27
	1769	93.3	0.11

^a fwhm = full width at half-maximum.

Table 2 Allylic substitution reactions using G₅-Pd_n⁰ in various solvents^a

Entry	Catalyst	Solvent	Cluster size/nm	Yield ^b /%
1	G ₅ -Pd ₁₆ ⁰	Toluene	0.97	91 (92) ^c
2		DMF		62
3		Ethyl acetate		49
4		DMSO		23
5	G ₅ -Pd ₄ ⁰	Toluene	0.50	35
6	G ₅ -Pd ₈ ⁰	Toluene	0.76	52

^a Reaction conditions: catalyst (Pd: 2.5 μmol), allyl methyl carbonate **1** = 0.1 mmol, benzoic acid **2** = 0.5 mmol, solvent 2 mL, 80 °C, Ar, 24 h.

^b Yields of products were determined by GC based on the amount of **1**. ^c Data in parentheses were obtained for the used catalyst.¹⁶

The stable subnano Pd clusters maintained coordinatively unsaturated active sites, which did not require phosphine ligands.^{6c} Initially, the catalytic activity of G₅-Pd₁₆⁰ was examined for the reaction of allyl methyl carbonate (**1**) with benzoic acid (**2**) in toluene solvent at 80 °C for 24 h. Interestingly, the phosphine-free allylic substitution proceeded efficiently to afford allyl benzoate (**3**) in 91% yield (Table 2, entry 1), where the size of the subnano Pd clusters was maintained during the allylic substitution.¹⁵ The G₅-Pd₁₆⁰ catalyst was reusable without any loss of its activity (entry 1, in parentheses).¹⁶ The catalytic activity and the stability of G₅-Pd₁₆⁰ were strongly influenced by solvents (Table 2, entries 1–4). The use of polar solvents, such as DMF, ethyl acetate, and DMSO, in place of toluene gave low yields of **3**, and black precipitates formed by aggregation of Pd species were observed during the reactions, showing that the G₅-TEBA dendrimer acted as a suitable macro-ligand for subnano Pd clusters in nonpolar solvents. The high stability of the subnano Pd clusters in nonpolar solvents may be due to the strong interaction of intramolecular hydrogen bonding between the amide groups of the periphery of the G₅-TEBA dendrimer,¹⁷ leading to rigid encapsulation of subnano Pd clusters within the dendrimer. In contrast, interaction of the amide groups with polar solvents weakened the intramolecular hydrogen bonds, resulting in leaching of the Pd clusters out of the dendrimer.

With optimized reaction conditions (toluene solvent, 80 °C, 24 h) in hand, the size-dependent catalytic properties of G₅-Pd₄⁰, G₅-Pd₈⁰, and G₅-Pd₁₆⁰ were examined in phosphine-free allylic substitution reactions. All of the G₅-Pd_n⁰ tested promoted the substitution reactions (Table 2, entries 1, 5, and 6). Note that the turnover frequencies (TOFs) of G₅-Pd₄⁰, G₅-Pd₈⁰, and G₅-Pd₁₆⁰ (0.7, 1.7,

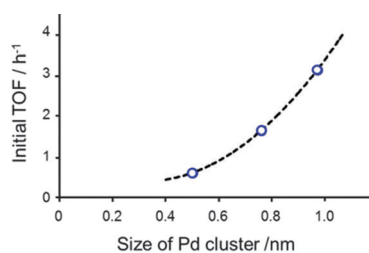


Fig. 2 Plot of initial TOF of G₅-Pd_n⁰ ($n = 4, 8$, and 16) for allylic substitution reaction. The initial TOF values were calculated from yields at the initial stage of the reaction (10% yield of **3**) and normalized by the number of surface Pd atoms.

and 3.1, respectively) increased with cluster size (Fig. 2). In a separate experiment, a preliminary kinetic study of $G_5\text{-Pd}_n^0$ -catalyzed allylic substitution reactions showed that the initial reaction rates were dependent on the concentration of **1** but were independent of the concentration of **2**.^{18,19} These results indicate that the oxidative addition of **1** to subnano Pd clusters to form π -allyl Pd clusters might be the rate-determining step.²⁰ The kinetic study combined with the electronic and geometric properties of the subnano Pd clusters revealed that the energy level of the 4d band and surface sites of Pd clusters increased with size of the subnano Pd cluster, which facilitates the rate-determining step, i.e., the formation of π -allyl Pd clusters through π -back-donation from the d-electron of Pd to the π^* orbital of C=C in **1**. The size-dependent catalysis of subnano Pd clusters in the allylic substitution reaction relied significantly on their electronic and geometric properties. These size-dependent properties were disclosed by successful encapsulation of the subnano Pd clusters in dendrimer-ligands while maintaining the size and catalytically active sites.

In summary, size-dependent electronic and geometric properties of subnano Pd clusters encapsulated within PPI dendrimers were determined. Spectroscopic analyses revealed that the number of 4d electrons, the energy level of the Pd 4d band, and the number of surface sites of the Pd clusters increased with Pd cluster size. Furthermore, PPI dendrimers acted efficiently as macroligands for subnano Pd clusters while retaining size and catalytically active sites during phosphine-free allylic substitution reactions. This finding permitted the study of the size-dependent catalysis of subnano Pd clusters and highlighted that increasing the size of the subnano Pd clusters increased the energy level of the Pd 4d band and the number of surface sites, which facilitated the rate-determining step of the formation of π -allyl Pd clusters.

This study was supported by JSPS KAKENHI (23656514, 23360357). The authors would like to thank Prof. Mitsutaka Okumura (Osaka University) for fruitful discussions and suggestions. We also thank Dr Tetsuo Honma, Dr Hironori Ofuchi, and Ms Sayaka Hirayama (JASRI) for Pd K-edge XAFS measurements, and Dr Koji Nakanishi (Ritsumeikan University) for the Pd L₃-edge XANES measurements. The TEM experiments were carried out at a facility of the Research Center for Ultrahigh Voltage Electron Microscopy, Osaka University.

Notes and references

- For books on MNPs, see: G. Schmid, *Nanoparticles - From Theory to Application*, Wiley-VCH Verlag GmbH & Co. KGaA, 2004. For the papers on MNPs, see: (a) G. C. Bond, *Surf. Sci.*, 1985, **156**, 966; (b) C. Burda, X. Chen, R. Narayanan and M. A. El-Sayed, *Chem. Rev.*, 2005, **105**, 1025; (c) Y. Yuan, N. Yan and P. J. Dyson, *ACS Catal.*, 2012, **2**, 1057; (d) K. M. Bratlie, H. Lee, K. Komvopoulos, P. Yang and G. A. Somorjai, *Nano Lett.*, 2007, **7**, 3097; (e) R. M. Rioux, B. B. Hsu, M. E. Grass, H. Song and G. A. Somorjai, *Catal. Lett.*, 2008, **126**, 10; (f) O. M. Wilson, M. R. Knecht, J. C. Garcia-Martinez and R. M. Crooks, *J. Am. Chem. Soc.*, 2006, **128**, 4510.
- (a) A. A. Herzing, C. J. Kiely, A. F. Carley, P. Landon and G. J. Hutchings, *Science*, 2008, **321**, 1331; (b) Y. Liu, H. Tsunoyama, T. Akita and T. Tsukuda, *ACS Catal.*, 2011, **1**, 2; (c) I. N. Remediakis, N. Lopez and J. K. Nørskov, *Angew. Chem., Int. Ed.*, 2005, **44**, 1824; (d) Y. Lei, F. Mehmood, S. Lee, J. Greeley, B. Lee, S. Seifert, R. E. Winans, J. W. Elam, R. J. Meyer, P. C. Redfern, D. Teschner, R. Schlögl, M. J. Pellin, L. A. Curtiss and S. Vajda, *Science*, 2010, **328**, 224; (e) W. E. Kaden, T. Wu, W. A. Kunkel and S. L. Anderson, *Science*, 2009, **326**, 826; (f) L. Alves, B. Ballesteros, M. Boronat, J. R. Cabrero-Antonino, P. Concepción, A. Corma, M. A. Correa-Duarte and E. Mendoza, *J. Am. Chem. Soc.*, 2011, **133**, 10251.
- (a) C. H. Bartholomew, *Appl. Catal., A*, 2001, **212**, 17; (b) Y. Negishi, Y. Takasugi, S. Sato, H. Yao, K. Kimura and T. Tsukuda, *J. Phys. Chem. B*, 2006, **110**, 12218.
- E. G. Mednikov and L. F. Dahl, *Philos. Trans. R. Soc., A*, 2010, **368**, 1301.
- Z. Zhang, F. A. P. Cawalcanti and W. M. H. Sachtler, *Catal. Lett.*, 1992, **12**, 157.
- (a) K. Okamoto, R. Akiyama, H. Yoshida, T. Yoshida and S. Kobayashi, *J. Am. Chem. Soc.*, 2005, **127**, 2125; (b) K. Okumura, K. Noto, K. Yoshida and M. Niwa, *J. Catal.*, 2005, **231**, 245; (c) T. Mitsudome, K. Nose, K. Mori, T. Mizugaki, K. Ebitani, K. Jitsukawa and K. Kaneda, *Angew. Chem., Int. Ed.*, 2007, **46**, 3288; (d) S. Vajda, M. J. Pellin, J. P. Greeley, C. L. Marshall, L. A. Curtiss, G. A. Ballentine, J. W. Elam, S. Catillon-Mucherie, P. C. Redfern, F. Mehmood and P. Zapol, *Nat. Mater.*, 2009, **8**, 213; (e) K. Yamamoto, T. Imaoka, W.-J. Chun, O. Enoki, H. Katoh, M. Takenaga and A. Sonoi, *Nat. Chem.*, 2009, **1**, 397; (f) A. Siani, O. S. Alexeev, D. S. Deutsch, J. R. Monnier, P. T. Fanson, H. Hirata, S. Matsumoto, C. T. Williams and M. D. Amiridis, *J. Catal.*, 2009, **266**, 331.
- (a) S. H. Medina and M. E. H. El-Sayed, *Chem. Rev.*, 2009, **109**, 3147; (b) M. Wang, X. Gong, J. Hu, Y. Yu, Q. Chen and Y. Cheng, *J. Phys. Chem. B*, 2011, **115**, 12728; (c) M. Ooe, M. Murata, T. Mizugaki, K. Ebitani and K. Kaneda, *J. Am. Chem. Soc.*, 2004, **126**, 1604; (d) M. Ooe, M. Murata, T. Mizugaki, K. Ebitani and K. Kaneda, *Nano Lett.*, 2002, **2**, 999; (e) E. Badetti, A.-M. Caminade, J.-P. Majoral, M. Moreno-Mañas and R. M. Sebastián, *Langmuir*, 2008, **24**, 2090; (f) M. V. Gomez, J. Guerra, A. H. Velders and R. M. Crooks, *J. Am. Chem. Soc.*, 2009, **131**, 341.
- (a) T. Mizugaki, T. Kibata, K. Ota, T. Mitsudome, K. Ebitani, K. Jitsukawa and K. Kaneda, *Chem. Lett.*, 2009, **38**, 1118; (b) Z. Maeno, T. Kibata, T. Mitsudome, T. Mizugaki, K. Jitsukawa and K. Kaneda, *Chem. Lett.*, 2011, **40**, 180.
- T. K. Sham, *Phys. Rev. B*, 1985, **31**, 1888.
- (a) S. C. Cook, J. D. Padmos and P. Zhang, *J. Chem. Phys.*, 2008, **128**, 154705; (b) J. A. van Bokhoven and J. T. Miller, *J. Phys. Chem. C*, 2007, **111**, 9245; (c) M. W. Tew, J. T. Miller and J. A. van Bokhoven, *J. Phys. Chem. C*, 2009, **113**, 15140.
- Diffuse reflectance infrared Fourier transform spectra were measured after CO adsorption on $G_5\text{-Pd}_n^0$ as shown in Fig. S4 in ESI†. The CO species adsorbed at 3-fold hollow sites on the Pd clusters was observed at about 1850 cm^{-1} . See: (a) I. V. Yudanov, R. Sahnoun, K. M. Neyman, N. Rösch, J. Hoffmann, S. Schauermaier, V. Johánek, H. Unterhalt, G. Rupprecht, J. Libuda and H.-J. Freund, *J. Phys. Chem. B*, 2003, **107**, 255; (b) T. Beutel, Z. Zhang, W. M. H. Sachtler and H. Knozinger, *J. Phys. Chem.*, 1993, **97**, 3539.
- (a) F. Zaera, *ChemCatChem*, 2012, **4**, 1525; (b) G. Pacchioni and J. Koutecky, *J. Phys. Chem.*, 1987, **91**, 2658; (c) R. Persaud and R. H. Prince, *Surf. Sci.*, 1993, **282**, 91; (d) Y. Y. Tong, C. Rice, A. Wieckowski and E. Oldfield, *J. Am. Chem. Soc.*, 2000, **122**, 1123.
- U. Heiz, A. Sanchez, S. Abbet and W.-D. Schneider, *J. Am. Chem. Soc.*, 1999, **121**, 3214.
- The energy of HOMO increased with cluster size, which is also supported by computational chemistry. See: R. M. Watwe, B. E. Spiewak, R. D. Cortright and J. A. Dumesic, *Catal. Lett.*, 1998, **51**, 139.
- In the FT spectra of the Pd K-edge XAFS of $G_5\text{-Pd}_{16}^0$, the intensity of the peak due to the Pd-Pd bond was not different before and after the reaction. See Fig. S1 and Table S1 in ESI†.
- Details of the reuse experiment of the $G_5\text{-Pd}_{16}^0$ catalyst are described in ESI†.
- (a) S. Stevelmans, J. C. M. van Hest, J. F. G. A. Jansen, D. A. F. J. van Bortel, E. M. M. de Brabander-van den Berg and E. W. Meijer, *J. Am. Chem. Soc.*, 1996, **118**, 7398; (b) J. G. Jang, S.-T. Noh and Y. C. Baek, *J. Phys. Chem. A*, 2000, **104**, 7404; (c) T. K.-K. Mong, A. Niu, H.-F. Chow, C. Wu, L. Li and R. Chen, *Chem.-Eur. J.*, 2001, **7**, 686.
- Dependency of reaction rates is shown in Fig. S5 in ESI†.
- Nucleophilicity of acid **2** was accommodated within the nanocavity of $G_5\text{-Pd}_n^0$ through the acid-base interaction, leading to a locally high concentration of **2** within the dendrimer. This is supported by ¹H-NMR studies; a downfield shift of the α -methylene protons of the tertiary amino groups was observed when **2** was added to the toluene-*d*₈ solution of $G_5\text{-TEBA}$.
- (a) C. Amatore, S. Gamez and A. Jutand, *Chem.-Eur. J.*, 2001, **7**, 1273; (b) R. Shintani, T. Tsuji, S. Park and T. Hayashi, *J. Am. Chem. Soc.*, 2010, **132**, 7508.