DOI: 10.1002/ange.201302860

Nanoclusters

Formation of a Pt_{12} Cluster by Single-Atom Control That Leads to Enhanced Reactivity: Hydrogenation of Unreactive Olefins

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Metal nanoparticles (NPs) have been applied to organic reactions as catalysts because of their large surface-to-volume ratio relative to those of bulk metals.[1] In contrast, subnanoclusters (SNCs) occasionally exhibit significantly different reactivities from those of the larger nanoparticles.[2] There are still few reports of the SNC catalysts in solution-phase reactions because their application requires two contradictory conditions: 1) suppression of the aggregation by a protection of the surface; and 2) enough surface accessibility for the reactants onto the catalytic active sites. An application of the SNCs as the catalyst is one of the most important challenges in current catalytic chemistry.[3] Although conventional stabilizers, such as surfactants, polymers, and dendrimers have been utilized for the size control of the NPs, the considerable size distribution still remains.[4]

During the course of our studies, we have reported excellent catalytic activity of precisely size-controlled monodisperse platinum NCs for oxygen reduction, and rhodium NCs for hydrogenation reactions utilizing the phenylazomethine dendrimer (Figure 1). This dendrimer can act as a template, which can define an exact number of metal atoms based on an intramolecular basicity gradient of the imines allowing their stepwise complexations with metal ions.[5,6]

Herein, we describe the preparation of platinum SNCs encapsulated in fourth-generation phenylazomethine dendrimers with a tetraphenylmethane core (TPM G4 dendrimer) loaded onto graphitized mesoporous carbon (GMC), which can provide both activity and further stability of the clusters together with the advantage of facile handling as a solid catalyst (Scheme 1).[7]

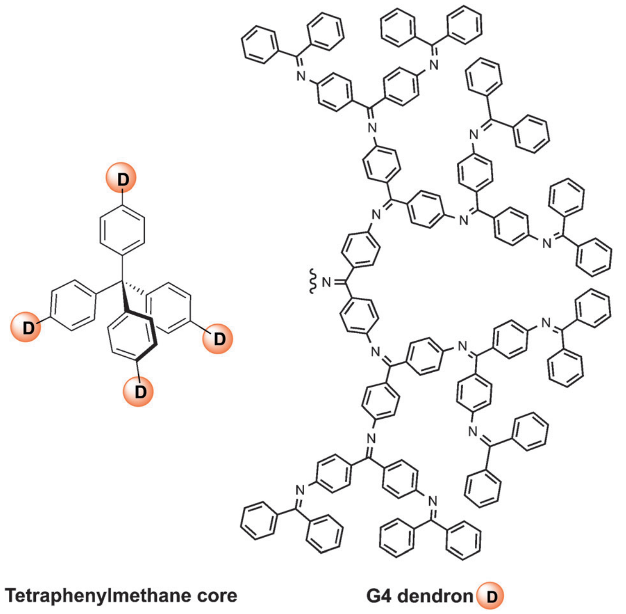
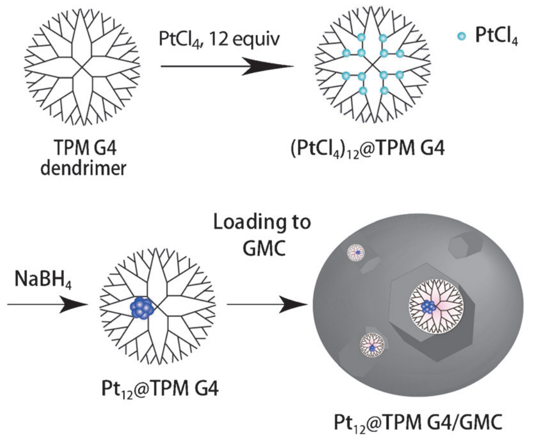


Figure 1. Structures of phenylazomethine core G4 dendrimers (TPM G4) used to control the number of platinum atoms of a cluster and to stabilize a cluster.



Scheme 1. Representation of Pt_{12}@TPM G4/GMC using a phenylazomethine dendrimer. GMC = graphitized mesoporous carbon.

$PtCl_4$ can quantitatively form complexes with imine groups of the phenylazomethine dendrimers. The number of metal atoms in one nanoparticle can be precisely controlled by the stoichiometry of the $PtCl_4$ to dendrimer ratio at 4, 12, 28, and 60 equiv, where each layer was filled up. The synthesis of SNCs is shown in Scheme 1. These clusters were prepared from the complex of $PtCl_4$ with TPM G4 dendrimer by a subsequent reduction using $NaBH_4$. It is noteworthy that the Pt_{12} cluster prepared by this method has one-atom level precision; it was characterized not only by TEM image (0.9 ± 0.1 nm) but also by ESI-TOF-MS spectrometry.[8] The SNCs could be promptly supported onto the GMC by just adding the GMC suspension to the solution of the dendrimer encapsulating Pt SNCs. The filtrate after the supporting became colorless (yellow or slight yellow in original color, respectively), indicating complete deposition of the dendri-

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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201302860.

mer-encapsulated Pt SNCs onto the GMC, of which pore size is 6.4 nm in the average diameter and this is suitable support for the dendrimer molecules having 2.1–2.9 nm of the diameter observed by TEM and AFM.[9]

A HAADF-STEM image of the catalyst in Figure 2a shows monodispers SNCs supported on the GMC surface. The resulting Pt_{12}@TPM G4/GMC was highly stable against their aggregation under air in a solution for over two weeks.

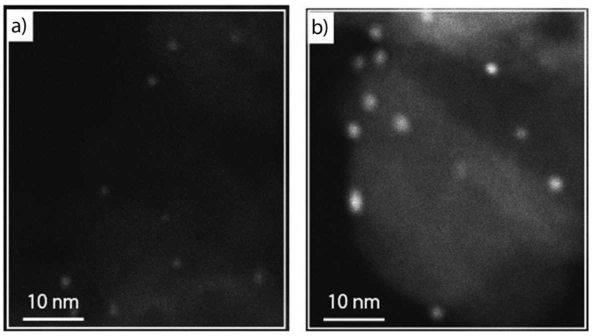
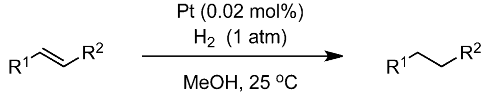
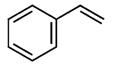
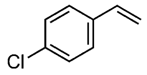
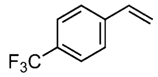
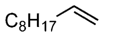
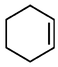
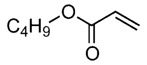


Figure 2. HAADF-STEM images of a) Pt_{12}@TPM G4/GMC and b) Pt (2.2 ± 0.8 nm) without dendrimer.

Table 1: Turnover frequencies of olefin hydrogenation in the presence of Pt_{12} or Pt (2.2 ± 0.8 nm) catalysts.



Entry	Substrate	Pt_{12}@TPM G4[a]/ GMC	Pt (2.2 ± 0.8 nm)[a]/ GMC
1		1.35×10^{3}	4.73×10^{2}
2		8.00×10^{2}	$1.80\times10^{[b]}$
3		$6.20\times10^{[b]}$	$0^{[b]}$
4		5.85×10^{3}	4.80×10^{3}
5		$2.03\times10^{2[b]}$	$1.30\times10^{[b]}$
6		1.69×10^{3}	8.89×10^{2}

[a] The turnover frequencies [atom $(Pt)^{-1}$ h^{-1}] were corrected for the total metal content and were determined by GC analysis using anisole as an internal standard. [b] The reaction was monitored after ten hours by GC analysis.

Despite such an excellent stability, the catalytic performance of SNCs for hydrogenations of olefinic substrates was still very high. The progress of the reaction under a hydrogen atmosphere (1 atm) at room temperature was monitored as a time-course of the conversion of the starting material based on NMR and gas chromatograph (GC) analyses. The initial activity of Pt_{12}@TPM G4/GMC in methanol was represented as the turnover frequency (TOF), which corresponds to the number of catalytic cycles within an hour. At initial investigation using the SNCs revealed a significantly higher turnover-frequency (TOF) values for a hydrogenation reaction of styrene to be 1350 atom$(Pt)^{-1}h^{-1}$ under atmospheric hydrogen pressure at room temperature (25 °C). To the best of our knowledge, this catalytic activity is better than any previously reported data under such mild conditions.[10] After the reaction, the catalyst is able to be separated from reaction mixture easily. TEM images of both as-prepared and used Pt_{12}@TPM G4/GMC catalysts displayed no obvious aggregation of the SNCs during the reaction (see the Supporting Information).

The scope of the reaction was extended to various olefins under the same condition. To evaluate the particle-size effect on the catalytic activities, NPs, of which average diameter is 2.2 ± 0.8 nm, were prepared at almost the same conditions without dendrimers (Figure 2b) and compared to the SNCs. The activities of the SNC catalyst are much higher than that of the larger Pt NP catalyst for all of the substrates.

Of particular interest is that even for substrates that are difficult to catalytically hydrogenate by larger NPs (entries 2, 3, and 5) owing to the electronic or steric reasons could be efficiently converted by the SNCs. For example, the TOF of hydrogenation of *p*-chlorostyrene by the Pt_{12} cluster was about 44 times higher than that of the larger Pt NPs. This acceleration is much higher than non-substituted styrene (Table 1, entries 1 and 2). Moreover, the hydrogenation of *p*-trifluoromethylstyrene was catalyzed only by Pt_{12}@TPM G4/GMC catalysts (Table 1, entry 3). The hydrogenation of cyclohexene, which is more difficult than 1-decene owing to steric effects, also increased significantly upon the decrease in particle size, while for the reaction of 1-decene it was not so significant (Table 1, entries 4 and 5).

Hydrogenations of alkenes by the metal NPs have been previously considered to be insensitive to the size of the catalysts, although none of the previous reports demonstrated the size effect on a subnanometer scale.[11,12] Our results revealed for the first time that the reactivities of hydrogenation of olefins by platinum cluster catalysts dramatically changed in the size of NCs below 2 nm into subnanometer scale, and SNCs can act as efficient catalysts even under mild conditions for low-reactivity substrates that have an electron-withdrawing group or steric hindrance.

In conclusion, we have developed an efficient SNC catalyst encapsulated by TPM G4 dendrimer for the hydrogenation of olefins. The catalytic activity of the SNC was highest among the previously reported Pt catalysts. In particular, this catalyst enabled the hydrogenations of low-reactive olefins that have an electron-withdrawing group or steric hindrance. These results demonstrate potential application of the SNCs in catalyst chemistry. Further studies of the origin of the size effect in hydrogenation reactions by platinum clusters and applications of the catalysts to other organic reactions are now undergoing.

Experimental Section

Preparation of Pt nanoclusters: Pt_{12}@TPM G4/GMC: The procedure was conducted under a dry nitrogen atmosphere. A solution of $PtCl_4$

in acetonitrile (3 mmol L^{-1}, 29 μL, 12 equiv for the TPMG4 dendrimer) was added to a solution of TPMG4 (2.4 mL, 3 μmol L^{-1}) in dichloromethane–acetonitrile (1:1). After stirring for 30 min, sodium borohydride solution in methanol (10 μL, 0.53 mol L^{-1}; 61 equiv relative to Pt) was added to the solution. Immediately after the addition, the solution was added to a stirred suspension of GMC (1 mL, 1.67 mg) in dichloromethane–acetonitrile (1:1) in a sample tube to afford a dispersion of Pt_{12}@TPMG4/GMC for the following hydrogenation reactions.

Pt(2.2±0.8 nm)/GMC: The procedure was conducted under a dry nitrogen atmosphere. A solution of $PtCl_4$ in acetonitrile (29 μL, 3 mmol L^{-1}) was added to a 0.45 mL solution of dichloromethane–acetonitrile (1:1). After stirring for 30 min, a solution of sodium borohydride in methanol (10 μL, 0.53 mol L^{-1}; 61 equiv relative to Pt) was added to the solution. After stirring for 1 hour, the solution was added to a stirred suspension of GMC (1 mL, 1.67 mg) in dichloromethane–acetonitrile (1:1) in a sample tube to afford a dispersion of Pt/GMC for the following hydrogenation reactions.

Typical procedure for Pt-catalyzed hydrogenation: The procedure was conducted at room temperature under atmospheric pressure. After removal of the solvent in the sample tube with the catalyst solution (Pt_{12}@TPMG4/GMC or Pt/GMC) under reduced pressure, the flask was charged with dry nitrogen. Styrene (45.5 mg, 0.433 mmol) in methanol (1.5 mL) was then added into the flask. Hydrogen gas was supplied from a balloon. The reaction progress was monitored by GC after an hour without 1-decene. Because the hydrogenation reaction of 1-decene is fast, the reaction was monitored after half an hour. The samples for the GC measurement were prepared by filtrations of the each reaction mixture in methanol sampled through a short silica gel column.

Received: April 6, 2013
Published online: May 31, 2013

Keywords: dendrimers · hydrogenation · nanoclusters · olefins · platinum

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[1] a) *Nanoparticles and Catalysis* (Ed.: D. Astruc), Wiley-VCH, Weinheim, **2008**; b) A. Molnár, *Chem. Rev.* **2011**, *111*, 2251–2320; c) Y. Zhang, X. Cui, F. Shi, Y. Deng, *Chem. Rev.* **2012**, *112*, 2467–2505; d) G. Kyriakou, M. B. Boucher, A. D. Jewell, E. A. Lewis, T. J. Lawton, A. E. Baber, H. L. Tierney, M. Flytzani-Stephanopoulos, E. C. H. Sykes, *Science* **2012**, *335*, 1209–1212; e) Y. Yamada, C.-K. Tsung, W. Huang, Z. Huo, E. S. Habas, T. Soejima, E. C. Aliaga, A. G. Somorjai, P. Yang, *Nat. Chem.* **2011**, *3*, 372–376; f) T. Yasukawa, H. Miyamura, S. Kobayashi, *J. Am. Chem. Soc.* **2012**, *134*, 16963–16966.

[2] a) N. Satoh, T. Nakashima, K. Kamikura, K. Yamamoto, *Nat. Nanotechnol.* **2008**, *3*, 106–111; b) D. E. Bergeron, P. J. Roach, A. W. Castleman, Jr., N. O. Jones, S. N. Khanna, *Science* **2005**, *307*, 231–235; c) S. Mostafa, F. Behafarid, J. R. Croy, L. K. Ono, L. Li, J. C. Yang, A. I. Frenkel, B. R. Cuenya, *J. Am. Chem. Soc.* **2010**, *132*, 15714–15719.

[3] a) G. C. Bond, *Chem. Soc. Rev.* **1991**, *20*, 441–475; b) 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, P. Zapol, *Nat. Mater.* **2009**, *8*, 213–216; c) Y. Liu, H. Tsunoyama, T. Akita, S. Xie, T. Tsukuda, *ACS Catal.* **2011**, *1*, 2–6; d) K. Shimizu, R. Sato, A. Satsuma, *Angew. Chem.* **2009**, *121*, 4042–4046; *Angew. Chem. Int. Ed.* **2009**, *48*, 3982–3986.

[4] a) O. Wilson, R. Scott, J. Gracia-Martinez, R. Crooks, *J. Am. Chem. Soc.* **2005**, *127*, 1015–1024; b) K. Gopidas, J. Whitesell, M. Fox, *J. Am. Chem. Soc.* **2003**, *125*, 6491–6502.

[5] a) K. Yamamoto, T. Imaoka, W.-J. Chun, O. Enoki, H. Katoh, M. Takenaga, A. Sonoi, *Nat. Chem.* **2009**, *1*, 397–402; b) I. Nakamula, Y. Yamanoi, T. Imaoka, K. Yamamoto, H. Nishihara, *Angew. Chem.* **2011**, *123*, 5952–5955; *Angew. Chem. Int. Ed.* **2011**, *50*, 5830–5833.

[6] Also see reports describing the phenylazomethine dendrimer: a) K. Yamamoto, Y. Kawana, M. Tsuji, M. Hayashi, T. Imaoka, *J. Am. Chem. Soc.* **2007**, *129*, 9256–9257; b) T. Imaoka, S. Tanaka, M. Arimoto, M. Sakai, M. Fujii, K. Yamamoto, *J. Am. Chem. Soc.* **2005**, *127*, 13896–13905; c) T. Imaoka, H. Horiguchi, K. Yamamoto, *J. Am. Chem. Soc.* **2003**, *125*, 340–341; d) K. Yamamoto, M. Higuchi, S. Shiki, M. Tsuruta, H. Chiba, *Nature* **2002**, *415*, 509–511.

[7] a) R. Liu, Y. Shi, Y. Wan, Y. Meng, F. Zhang, D. Gu, Z. Chen, B. Tu, D. Zhao, *J. Am. Chem. Soc.* **2006**, *128*, 11652–11662; b) W. Huang, J. N. Kuhn, C.-K. Tsung, Y. Zhang, S. E. Habas, P. Yang, G. A. Somorjai, *Nano Lett.* **2008**, *8*, 2027–2034.

[8] A TEM image (0.9 ± 0.1 nm) and XPS spectra are given in Reference [5a], and the ESI TOF MS peak of $[Pt_{12}(CO)_{16}]^{2-}$ is shown in the Supporting Information of Reference [5a].

[9] O. Enoki, H. Katoh, K. Yamamoto, *Org. Lett.* **2006**, *8*, 569–571.

[10] Z. Guo, L. Hu, H. Yu, X. Cao, H. Gu, *RSC Adv.* **2012**, *2*, 3477–3480. It was mentioned that, in styrene hydrogenation, the TOF value of their platinum catalysts calculated as 1333 h^{-1} at 40 °C is better than any previous reported data in mild condition. TOF value of our Pt_{12} catalyst is higher than that of their catalyst at room temperature (Table 1, entry 1).

[11] Platinum nanoparticle catalysts for hydrogenation reactions of olefins: a) S. Ikeda, S. Ishino, T. Harada, N. Okamoto, T. Sakata, H. Mori, S. Kuwabata, T. Torimoto, M. Matsumura, *Angew. Chem.* **2006**, *118*, 7221–7224; *Angew. Chem. Int. Ed.* **2006**, *45*, 7063–7066; b) C. W. Scheeren, G. Machado, J. Dupont, P. F. P. Fichtner, S. R. Texeira, *Inorg. Chem.* **2003**, *42*, 4738–4742.

[12] a) M. Boudart, *J. Mol. Catal.* **1985**, *30*, 27–38; b) R. K. McCrea, G. A. Somorjai, *J. Mol. Catal. A* **2000**, *163*, 43–53; c) N. J. Kuhn, W. Huang, C. Tsung, Y. Zhang, G. A. Somorjai, *J. Am. Chem. Soc.* **2008**, *130*, 14026–14027; d) A. M. Doyle, S. K. Shaikhutdinov, S. D. Jackson, H. Freund, *Angew. Chem.* **2003**, *115*, 5398–5401; *Angew. Chem. Int. Ed.* **2003**, *42*, 5240–5243.