Palladium–Platinum Bimetallic Nanoparticle Catalysts Using Dendron Assembly for Selective Hydrogenation of Dienes and Their Application to Thermomorphic System

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Self-assembly of dendrons allows a new approach for size control of bimetallic Pd–Pt nanoparticles, which affords reusable dendritic nanoreactors for selective hydrogenation of dienes and alkynes to monoenes in thermomorphic systems.

Metal nanoparticles composed of two metal elements are of interest in materials science, particularly in catalysis, because they afford the synergistic effect on the catalytic activity and selectivity.[1] Simultaneous and sequential reduction of two metal complexes results in corresponding bimetallic nanoparticles, such as Pd–Pt, Pd–Ni, and Pt–Au, in the presence of stabilizing agents.[2] Pd–Pt bimetallic nanoparticles were prepared by co-reduction of $PdCl_4^{2-}$ and $PtCl_4^{2-}$ with poly(*N*-vinyl-2-pyrrolidone) (PVP)[1] or unimolecular dendrimers.[2a] Here, we report a new approach for the preparation of Pd–Pt bimetallic nanoparticles via the self-assembly of dendrons, which was applied to a nanoreactor for highly selective hydrogenation of conjugated dienes and alkynes to monoenes. The recycling of the dendritic catalyst was also investigated using the thermoresponsive phase separation of solvents, called as thermomorphic systems.[3]

Alkylated amidoamine dendrons (Gn Py–C6; $n = 1, 2, 3$) were synthesized from 4-picolylamine with methyl acrylate and ethylenediamine using the divergent method. Terminal ester moieties of the branches were alkylated by *n*-hexylamine (Figure 1a)[4] and these products were characterized by NMR, IR, MS, dynamic light scattering (DLS), and TEM. Treatment of the dendrons with a solution of $[PdCl(C_3H_5)]_2$ and $PtCl_2(PhCN)_2$, followed by reduction using $LiB(C_2H_5)_3H$, led to a dark brown solution containing dendritic mixed metal nanoparticles (Gn Py–C6 Pd–Pt; $n = 1, 2, 3$).[5] Using a similar procedure, Gn Py–C6 Pd(0)[6] and Py–C6 Pt(0) were prepared from $[PdCl(C_3H_5)]_2$ and $PtCl_2(PhCN)_2$, respectively. Sequential reduction of the Pd complex after formation of Gn Py–C6 Pt(0) afforded Gn Py–C6 Pd–(Pt).

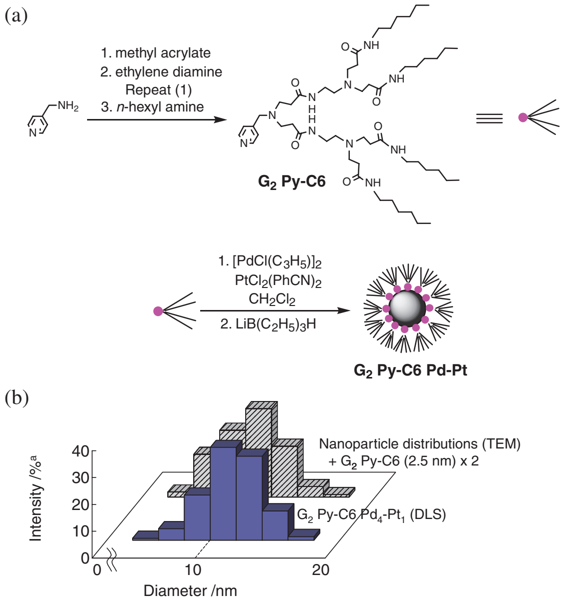


Figure 1. Structure of dendritic Pd-Pt nanoparticles (G_2 Py–C6 Pd–Pt) (a) and the size distributions by DLS and TEM measurements (b). [a]Intensity was based on the number of particles.

^{1}H NMR spectra of Gn Py–C6 exhibited broad, weak signals of internal methylene and pyridyl core protons, which implies a reversed micelle-like assembly of the dendrons.[7] DLS and TEM images provided information about the size of the dendritic Pd–Pt nanoparticles, as shown in Figure 1 and Table 1. DLS measurements of G_2 Py–C6 revealed the formation of globular assemblies with average diameters of 10.9 ± 2.0 nm (Entry 1). After co-reduction of the Pd and Pt complexes, size distributions for G_2 Py–C6 Pd_4–Pt_1 (Pd/Pt = 4) were similar to those for the parent dendron assemblies (Entry 2). TEM images revealed an average metal nanoparticle size of 5.3 ± 1.4 nm for G_2 Py–C6 Pd_4–Pt_1, and X-ray energy dispersive spectroscopy (EDS) analysis provided atom % of 79% and 21% for Pd and Pt, respectively, similar to those of the parent Pd and Pt mol ratios. In addition, average particle sizes of G_2 Py–C6 Pd(0), Py–C6 Pt(0), and Py–C6 Pd–(Pt) were 5.3 ± 1.7, 5.3 ± 1.3, and 5.4 ± 1.5 nm, respectively (Entries 3–5). As shown in Figure 1b, the size distribution of the dendron assemblies agreed well with a distribution derived from the combination of the mixed metal nanoparticle and dendron sizes.[8] These data suggest that the dendrons assemble to form monolayer capsules with polar voids, which act as useful templates for metal nanoparticles having ca. 5 nm diameter, which are generated within the voids of the assemblies.[6]

The catalytic ability of dendritic Pd–Pt bimetallic nanoparticles was investigated in the hydrogenation of 1,3-cyclooctadiene, which yielded cyclooctene exclusively without formation of an insoluble metal aggregate. G_2 Py–C6 Pd–Pt nanoparticles

Table 1. Average diameter of G_2 dendron assemblies and metal nanoparticles by DLS and TEM measurements

Entry		Avarage Diameter/nm		
		DLS[a]	Vold space[b]	TEM
1	Py–C6	10.9 ± 2.0	5.9	
2	Py–C6 Pd_4–Pt_1(0)	11.2 ± 1.6		5.3 ± 1.4
3	Py–C6 Pd(0)	11.0 ± 1.7		5.3 ± 1.7
4	Py–C6 Pt(0)	11.1 ± 1.7		5.3 ± 1.3
5	Py–C6 Pd–(Pt)	11.1 ± 1.7		5.4 ± 1.5

[a]Measured in CH_2Cl_2 at 25 °C. [b]Calculated by [DLS − G_2 dendron size (2.5) × 2].

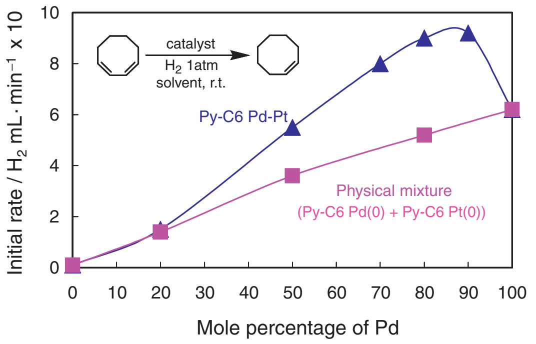
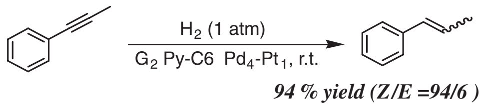


Figure 2. Hydrogenation of 1,3-cyclooctadiene using G_2 Py–C6 Pd–Pt. Reaction conditions: 1,3-cyclooctadiene 1.0 mmol, dendron 0.082 mmol, Pd (mmol) + Pt (mmol) 0.005 mmol, CH_2Cl_2 3 mL, rt., H_2 1 atm.

possessed higher catalytic activity than that found for a physical mixture of G_2 Py–C6 Pd(0) and Py–C6 Pt(0) (Figure 2). A significant bimetallic effect was observed with Pd–Pt dendrimers containing a Pd content of 80–90 mol %; a similar phenomenon was reported using polymer-stabilized mixed Pd–Pt bimetallic nanoparticles.[1] No synergistic effect was observed with Py–C6 Pd–(Pt) nanoparticles prepared by sequential reduction. Notably, the catalytic activity of G_3 Py–C6 Pd_4–Pt_1 was 1.9 times greater than that of G_2 Py–C6 Pd_4–Pt_1. This effect contrasts with the results reported for an unimolecular dendrimer-encapsulated Pd(0) nanoparticle catalyst.[9] An increase in dendron generation provides a less congested Pd surface, which facilitates substrate access to active sites.[6,10]

An extremely high selectivity for the monoene was also achieved in the hydrogenation of alkynes; e.g., 1-phenyl-1-propyne afforded 1-phenyl-1-propene in 94% yield (Z:E= 94:6) after complete conversion of the alkyne using G_2 Py–C6 Pd_4–Pt_1 catalyst (Scheme 1). This high monoene selectivity can be attributed to the coordination of the pyridyl core to the metal nanoparticles.[11]



Scheme 1. 1-phenyl-1-propyne 1.0 mmol, G_2 Py–C6 0.164 mmol, Pd (mmol) + Pt (mmol) 0.010 mmol CH_2Cl_2 3 mL, 42 min.

Recycling of dendritic catalysts has been attempted by solvent precipitation and membrane filtration,[12] which often results in loss of the catalytic activity during the reuse processes. G_2 Py–C6 dendron possessed high solubility in DMF, which allowed the transfer of the dendritic catalyst to DMF under the thermomorphic systems consisting of DMF and n-heptane (Figure 3).[3] In the hydrogenation of 1,3-cyclooctadiene, the two thermosensitive phases of DMF and heptane became homogeneous at 65 °C, but could be readily separated by cooling the reaction mixture to room temperature. The DMF phase containing the dendritic catalyst could be recycled after decanting the n-heptane phase. High catalytic activity was retained during reuse experiments; yields of cyclooctene in heptane phase were 61% (fresh), 99% (second), 99% (third), and 99% (fourth).[13]

In conclusion, we report the preparation and high catalytic performance of dendritic Pd–Pt bimetallic nanoparticles using dendron self-assembly. The dendron assemblies act as a template of bimetallic nanoparticles. The dendritic nanoparticles functioned as nanoreactors for the hydrogenation of olefins and acetylenes, and could be reused under thermosensitive biphasic conditions. These self-assembled dendrons can be applied widely for the development of a variety of mono and mixed metal nanoparticles for materials science.

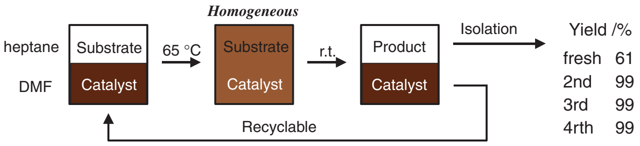


Figure 3. Thermomorphic system using dendritic catalyst.

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References and Notes

1 N. Toshima and T. Yonezawa, *New J. Chem.*, **1998**, 1179.
2 Recent examples of bimetallic nanoparticles, see: Pd–Pt: a) R. W. Scott, J. A. K. Datye, and R. M. Crooks, *J. Am. Chem. Soc.*, **125**, 3708 (2003). Pd–Ni: b) S. U. Son, Y. Jang, J. Park, H. B. Na, H. M. Park, H. J. Yun, J. Lee, and T. Hyeon, *J. Am. Chem. Soc.*, **126**, 5026 (2004). Pd–Au: c) R. Harpeness and A. Gedanken, *Langmuir*, **20**, 3431 (2004). Pt–Au: d) H. Lang, S. Maldonada, K. J. Stevenson, and B. D. Chandler, *J. Am. Chem. Soc.*, **126**, 12949 (2004).
3 a) D. E. Bergbreiter, *Chem. Rev.*, **102**, 3345 (2002). b) M. Ooe, M. Murata, T. Mizugaki, K. Ebitani, and K. Kaneda, *J. Am. Chem. Soc.*, **126**, 1604 (2004).
4 a) M. Murata, T. Hara, K. Mori, M. Ooe, T. Mizugaki, K. Ebitani, and K. Kaneda, *Tetrahedron Lett.*, **44**, 4981 (2003). b) K. Aoi, A. Motoda, M. Ohno, K. Tsutsumiuchi, M. Okada, and T. Imae, *Polym. J.*, **30**, 1071 (1999).
5 Typical procedures for the preparation of the dendritic Pd_4–Pt_1 bimetallic nanoparticles (Gn Py–C6 Pd_4–Pt_1; $n = 1, 2, 3$) are as follows. To a CH_2Cl_2 solution (5 mL) of Gn Py–C6 (0.164 mmol) was added a CH_2Cl_2 solution (1 mL) of $[PdCl(C_3H_5)]_2$ (0.004 mmol) and $PtCl_2(PhCN)_2$ (0.002 mmol), and stirred vigorously at room temperature for 1 h. The mixture was treated with $LiB(C_2H_5)_3H$ in THF (1M, 0.02 mL) and stirred at room temperature for 1 h.
6 M. Murata, Y. Tanaka, T. Mizugaki, K. Ebitani, and K. Kaneda, submitted.
7 I. Gitsov and J. M. J. Fréchet, *Macromolecules*, **26**, 6536 (1993).
8 The molecular size of G_2 Py–C6 dendron calculated by Chem 3D are 2.5 nm.
9 M. Ooe, M. Murata, T. Mizugaki, K. Ebitani, and K. Kaneda, *Nano Lett.*, **2**, 999 (2002).
10 A similar generation effect has been reported for nanoparticle-cored dendrimers, see: K. R. Gopidas, J. K. Whitesell, and M. A. Fox, *J. Am. Chem. Soc.*, **125**, 6491 (2003).
11 R. L. Augustine, "Heterogeneous Catalysis for the Synthetic Chemist," Marcel Dekker, Inc., New York (1996).
12 B. Yi, Q.-H. Fan, G.-J. Deng, Y.-M. Li, L.-Q. Qiu, and A. S. C. Chan, *Org. Lett.*, **6**, 1361 (2004).
13 The relatively low yield for the fresh run was due to the distribution of cyclooctene in the DMF phase.

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