

Palladium–Platinum Bimetallic Nanoparticle Catalysts Using Dendron Assembly for Selective Hydrogenation of Dienes and Their Application to Thermomorphing 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 thermomorphing 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 thermomorphing systems.³

Alkylated amidoamine dendrons ($\text{G}_n \text{Py-C6}$; $n = 1, 2, 3$) 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 $[\text{PdCl}(\text{C}_3\text{H}_5)]_2$ and $\text{PtCl}_2(\text{PhCN})_2$, followed by reduction using $\text{LiB}(\text{C}_2\text{H}_5)_3\text{H}$, led to a dark brown solution containing dendritic mixed metal nanoparticles ($\text{G}_n \text{Py-C6 Pd-Pt}$; $n = 1, 2, 3$).⁵ Using a similar procedure, $\text{G}_n \text{Py-C6 Pd(0)}$ ⁶ and Py-C6 Pt(0) were prepared from $[\text{PdCl}(\text{C}_3\text{H}_5)]_2$ and $\text{PtCl}_2(\text{PhCN})_2$, respectively. Sequential reduction of the Pd complex after formation of $\text{G}_n \text{Py-C6 Pt(0)}$ afforded $\text{G}_n \text{Py-C6 Pd-Pt}$.

¹H NMR spectra of $\text{G}_n \text{Py-C6}$ 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 $\text{G}_2 \text{Py-C6}$ revealed the formation of globular assemblies with average diameters of $10.9 \pm 2.0 \text{ nm}$ (Entry 1). After co-reduction of the Pd and Pt complexes, size distributions for $\text{G}_2 \text{Py-C6 Pd}_4\text{-Pt}_1$ (Pd/Pt = 4) were similar to those for the parent dendron assemblies (Entry 2). TEM images revealed an average metal nanoparticle size of $5.3 \pm 1.4 \text{ nm}$ for $\text{G}_2 \text{Py-C6 Pd}_4\text{-Pt}_1$, 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 $\text{G}_2 \text{Py-C6 Pd(0)}$, Py-C6 Pt(0) , and Py-C6 Pd-Pt were 5.3 ± 1.7 , 5.3 ± 1.3 , and $5.4 \pm 1.5 \text{ nm}$, 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. $\text{G}_2 \text{Py-C6 Pd-Pt}$ nanoparticles

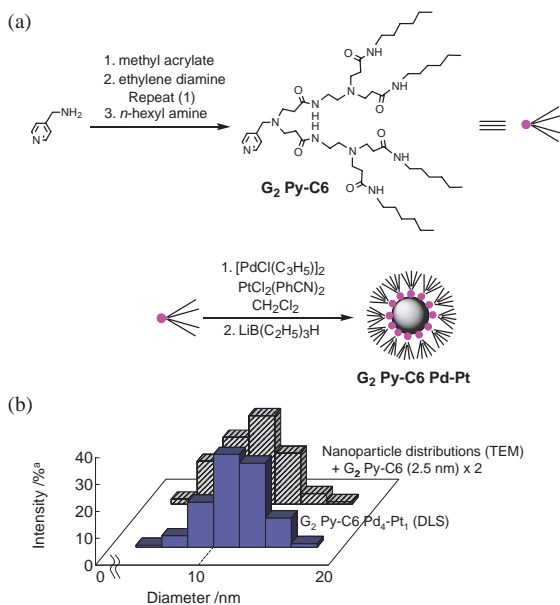


Figure 1. Structure of dendritic Pd–Pt nanoparticles ($\text{G}_2 \text{Py-C6 Pd-Pt}$) (a) and the size distributions by DLS and TEM measurements (b). ^aIntensity was based on the number of particles.

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

Entry		Average Diameter/nm		
		DLS ^a	Void 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

^aMeasured in CH_2Cl_2 at 25 °C. ^bCalculated by $[\text{DLS} - \text{G}_2 \text{ dendron size } (2.5) \times 2]$.

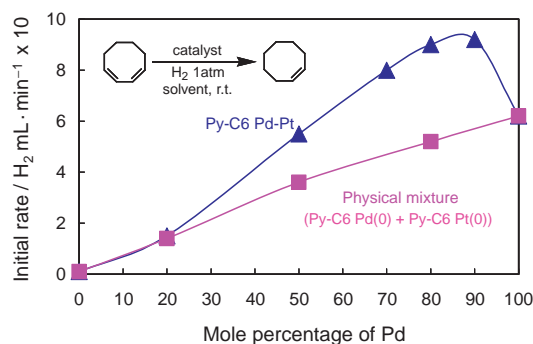
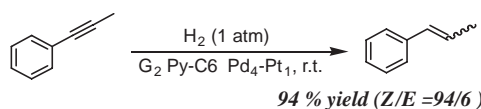


Figure 2. Hydrogenation of 1,3-cyclooctadiene using G₂ Py-C6 Pd-Pt. Reaction conditions: 1,3-cyclooctadiene 1.0 mmol, dendron 0.082 mmol, Pd (mmol) + Pt (mmol) 0.005 mmol, CH₂Cl₂ 3 mL, rt., H₂ 1 atm.

possessed higher catalytic activity than that found for a physical mixture of G₂ 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 G₃ Py-C6 Pd₄-Pt₁ was 1.9 times greater than that of G₂ Py-C6 Pd₄-Pt₁. 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 G₂ Py-C6 Pd₄-Pt₁ 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, G₂ Py-C6 0.164 mmol, Pd (mmol) + Pt (mmol) 0.010 mmol CH₂Cl₂ 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. G₂ 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

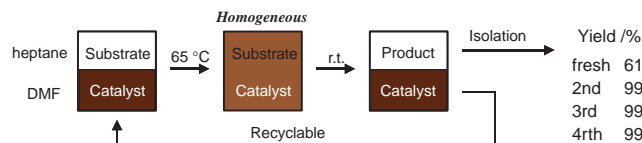


Figure 3. Thermomorphic system using dendritic catalyst.

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.

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