

Heterogeneous Hydrogenation Catalyses over Recyclable Pd(0) Nanoparticle Catalysts Stabilized by PAMAM-SBA-15 Organic–Inorganic Hybrid Composites

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Noble metal nanoparticles are attractive for catalyses because of their size effects.^{1–3} However, having very active surface atoms could often lead to aggregation of the naked nanoparticles and decreases in catalytic activity and selectivity. In particular, Pd(0) catalysts are known to aggregate easily and form Pd(0) black, although they realize a wide variety of useful reactions in organic syntheses.⁴ Recently, many stabilizing methods have been developed to solve the problem.^{5–9} Unfortunately, the strong absorption of the stabilizers on the active sites of the nanoparticles results in losses of the catalytic activity and selectivity. Polyamidoamine (PAMAM) dendrimers are highly branched, well-defined, synthetic macromolecules available in nanometer dimensions. The characteristic of the dendrimers is that they are soft adsorbents that permit passage of the substrates and products of the catalytic reactions. Recently, Crooks' group reported that the dendrimer-encapsulated noble metal clusters exhibited highly catalytic activity, and the dendrimers acted as both templates and porous nanoreactors.^{10–12} Although, as homogeneous catalysts, the dendrimer-encapsulated noble metal nanoparticles show uniquely catalytic characteristics, difficulties in separation and reuse limit the application of the materials. Immobilization of catalysts on solid supports may result in significant losses of catalytic activities.¹³ As a result, much effort has been put into finding new catalytic systems, which effectively combine the advantages of both heterogeneous and homogeneous catalyses.^{14,15}

During our preparation progress, two steps were followed (see the Supporting Information (SI) for details). First, the dendrimers (more accurate names should be hyperbranched polymers; see the SI description) up to generation 4 (G_n , $n = 1–4$) were constructed onto the surfaces of the channels of amine-functionalized SBA-15 (Scheme 1), using modified multistep procedures, based on the literature.^{16,17} A Michael-type addition reaction of the preexisting amino groups to the methyl acrylates forms the amino propionate esters. Subsequent amidation of the ester moieties with ethylenediamine completed the generation. Repetition of these two reactions produced the desired generation of the dendrimers. The structural characterizations of the dendrimers grafted on the surfaces of SBA-15 were carried out by cross-polarized magic-angle spinning (CPMAS) ¹³C NMR and infrared spectroscopy (Figures S1 and S2). The decrease of the surface areas, pore volumes, and pore sizes with the increase of generations confirmed that the dendrimers were constructed onto the channel surfaces of SBA-15, based on the nitrogen adsorption analyses (Figure S3 and Table S2). Overall yields of every generation of dendrimers were also calculated by thermogravimetric and elemental analyses (Figure S4 and Table S3). The above results proved that the dendrimers were successfully constructed onto the channel surfaces of SBA-15. Second, Pd(II) ions were introduced into the dendrimers in the tunnels of SBA-15, and they were subsequently reduced by BH_4^- , which resulted

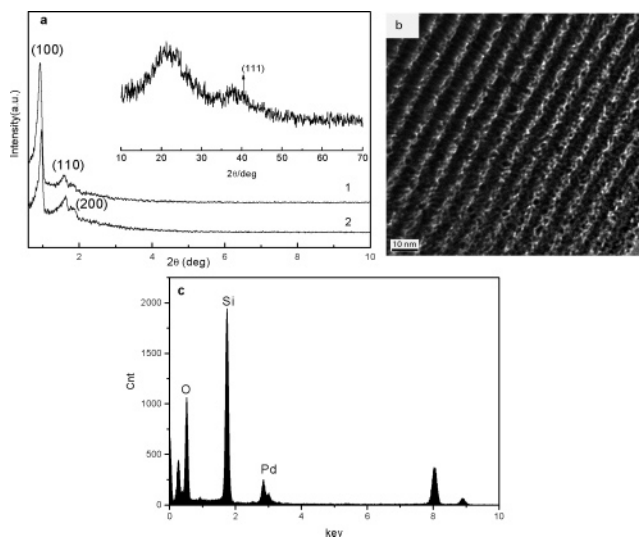
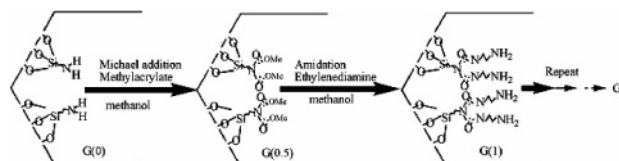
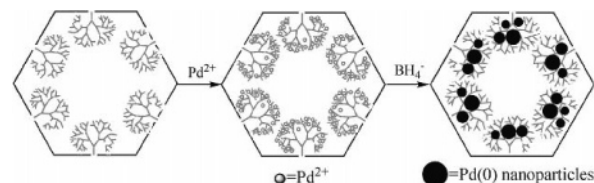


Figure 1. (a) The low-angle XRD patterns of G4-PAMAM-SBA-15 (1) and Pd(0)-G4-PAMAM-SBA-15 (2) with the insert of the wide-angle XRD pattern of Pd(0)-G4-PAMAM-SBA-15. (b) HRTEM image of Pd(0)-G4-PAMAM-SBA-15. (c) EDS spectrum of Pd(0)-G4-PAMAM-SBA-15.

Scheme 1. Preparation of SBA-15 Supported Dendrimers



Scheme 2. Formation of Nanoparticles



in the formation of dark brown powders of Pd(0)- G_n -PAMAM-SBA-15 (Scheme 2).

Low-angle X-ray diffraction (XRD) patterns (Figure 1a) of the G4-PAMAM-SBA-15 and Pd(0)-G4-PAMAM-SBA-15 powders show the peaks at 0.92, 1.57, and 1.84°, which correspond to the (100), (110), and (200) reflections of the mesoporous SBA-15, respectively,¹⁸ indicating that the structures of SBA-15 are well preserved. Wide-angle XRD pattern (insert in Figure 1a) of the Pd(0)-G4-PAMAM-SBA-15 powders shows a very weak peak at 40.2°, which is attributed to the (111) reflection of Pd(0) crystals,¹⁹ suggesting that the Pd(0) nanoparticles exist stably over the G4-

Table 1. Hydrogenation Activities and Selectivities of the Catalysts

	Pd(0)-G1-PAMAM-SBA-15	Pd(0)-G2-PAMAM-SBA-15	Pd(0)-G3-PAMAM-SBA-15	Pd(0)-G4-PAMAM-SBA-15
TOF ^a	2185/2150 ^b	2266/2288	711/705	739/734
selectivity ^c (%)	79.0/77.7	82.0/82.8	93.4/92.6	91.4/90.8
conversion(%)	>99.5%	>99.5%	>99.5%	>99.5%

^a The turnover frequencies (TOFs) were measured as moles hydrogenated allyl alcohol per molar Pd per hour. ^b Duplicate measurements were performed to illustrate the levels of run-to-run reproducibility. ^c The selectivities to the hydrogenated products of 1-propanol.

PAMAM-SBA-15 hosts. High-resolution transmission microscopy (HRTEM) image (Figure 1b) clearly shows that the Pd(0) particles are quite monodisperse in the channels of SBA-15. The elemental compositions of the nanoparticles were confirmed by the energy-dispersive spectroscopy (EDS) and ICP analyses (Table S1).

To evaluate the catalytic characteristics of the materials, we investigated the hydrogenation reactions of allyl alcohol over the different generation catalysts (Figures S6, S7, and S8) under similar conditions, which were adopted in the homogeneous hydrogenation over the dendrimer-encapsulated Pd(0) nanoparticles.¹⁰ The turnover frequencies (TOFs), selectivities to the 1-propanol, and conversions for the hydrogenation of allyl alcohol are summarized in Table 1, which suggest that all of the catalysts show highly catalytic activity for the hydrogenation of allyl alcohol. Notably, the activity of our Pd(0)-G4-PAMAM-SBA-15 catalyst is 1.5 times that of the fourth generation dendrimer-encapsulated Pd(0) homogeneous catalyst.¹⁰ Probably, the existence of the inorganic carrier may reduce the aggregation of the dendrimer-encapsulated Pd(0) nanoparticles relative to the homogeneous dendrimer-encapsulated Pd(0) catalysts.

Generally, substrate isomerization is a common but unwanted process in hydrogenation.²⁰ It is desirable to minimize the isomerization during the hydrogenation reaction. In our system, the selectivity to hydrogenation product (1-propanol) was improved when increasing the product generation. Under the same conditions, the selectivities were 79.0, 82.0% and 93.4, 91.4%, when using generations 1, 2 and 3, 4 catalysts, respectively. Selectivity of the isomerization byproduct of acetone over the generation 3 catalyst was 6.6%, which is much lower than that over the reported heterogeneous catalyst Pd/Al₂O₃ (25%).²⁰ These results indicate that the dendrimers may not only stabilize the nanoparticles but also modify both the environment of active sites and access to these sites.²¹

Interestingly, the hydrogenation reaction rates may be controlled by varying the generations. For example, the TOFs of the generations 1 and 2 catalysts were almost 3-fold compared with those of generations 3 and 4. To understand the determining factors that control the reaction rates, we studied the dependencies of reaction rates (r_0) on initial concentrations (C_0) of allyl alcohol with the generations 2 and 3 catalysts. As to the reaction over the generation 2 catalyst, the hydrogenation is zero order with respect to the initial concentration of the substrate. However, the one over the generation 3 catalyst agreed very well with Langmuir–Hinshelwood model ($r_0 = kKC_0/(1 + KC_0)$, Figure S9).²² At a low concentration, the first-order kinetics indicates that the rate-limiting step is the diffusion of the substrate to the active site or slow adsorption. At a high concentration, saturation of the catalyst surface occurred, and zero order was observed.

Finally, the reaction stopped when the catalyst was removed by filtration, suggesting that the hydrogenation is a heterogeneous

reaction. Generally, during the recycling and storage of the catalysts consisting of the supported Pd(0) nanoparticles, an increase in the size of the nanoparticles due to agglomeration and oxygenation in the air always leads to deactivation of the catalyst.²³ However, our Pd(0) nanoparticles stabilized by the organic–inorganic hybrid composites are stable enough to retain the activity when the catalyst was reused several times or stored under ambient condition for one month (Figure S10).

In summary, we have prepared heterogeneous Pd(0) nanoparticle catalysts stabilized by G_n-PAMAM-SBA-15 organic–inorganic hybrid composites. The catalysts show highly catalytic activity for the hydrogenation of allyl alcohol. Importantly, the hydrogenation rate and selectivity can be controlled by using different generation catalysts. Additionally, the catalysts are stable enough to be recycled multiple times and preserved for one month under ambient condition, while maintaining the catalytic activities.

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Supporting Information Available: Procedure for preparing Pd(0)-G_n-PAMAM-SBA-15 catalysts, hydrogenation reactions, data of catalyses, HRTEM of the G3-PAMAM-SBA-15 and Pd(0)-G3-PAMAM-SBA-15, N₂ adsorption data of the G_n-PAMAM-SBA-15, results of the ICP-AES, TGA, EA quantitative analyses, ¹³C CPMAS NMR, and FT-IR spectra of the materials (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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