Size-Selective Catalytic Activity of Pd Nanoparticles Encapsulated within End-Group Functionalized Dendrimers†

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The synthesis and size-selective catalytic activity of Pd nanoparticles encapsulated within dendrimers functionalized with different-sized end groups is described. We designed and synthesized a series of fourth-generation poly(amidoamine) dendrimers having various extents of steric crowding on their periphery. This was accomplished by reacting the terminal amine groups of these dendrimers with epoxyalkanes substituted with different-sized alkyl groups. The modified dendrimers were characterized by ^{1}H NMR, ^{13}C NMR, and matrix-assisted laser desorption ionization mass spectrometry. Nearly monodisperse (1.7 ± 0.2 nm) Pd nanoparticles were encapsulated within the interior of these dendrimers, and the resulting composite catalysts were used for the hydrogenation of three α-allylic alcohols having different sizes. The results showed a clear correlation between the extent of steric crowding on the dendrimer surface and the turnover frequencies (TOFs) for the substrates: more steric crowding on the dendrimer surface led to lower TOFs.

Introduction

Here we report that the catalytic selectivity of dendrimer-encapsulated nanoparticles (DENs) can be controlled by functionalizing the dendrimer periphery. Specifically, we have prepared nearly monodisperse Pd nanoparticles within the interior of fourth-generation poly(amidoamine) (PAMAM) dendrimers having end groups of various sizes appended onto their periphery. The catalytic activity of the encapsulated nanoparticles for the hydrogenation of a series of α-allylic alcohols was then examined as a function of the size of the peripheral functional groups. The results indicate that larger functional groups effectively select for smaller substrates, and, therefore, this approach provides a means for rendering an intrinsically nonselective catalyst, such as Pd, selective.

Since our first report showing that Cu^{2+} could be sequestered within PAMAM dendrimers and subsequently reduced to zerovalent nanoparticles, we and others have demonstrated the use of dendrimer templates for the synthesis of a variety of other metallic (Au, Ag, Pd, and Pt), bimetallic (PdPt, AuAg, PdAu, PdRh, and PtAu), and semiconducting (CdS) DENs.[1] DENs are prepared by mixing an appropriate dendrimer with a metal ion or complex. In favorable cases the ions are sequestered within the dendrimer through specific interactions with its interior functional groups. Subsequent reduction of the metal ions with BH_4^- or other reducing agents leads to a zerovalent, encapsulated metal nanoparticle. The size of the resulting DENs depends on the metal-ion-to-dendrimer ratio present within the dendrimer prior to reduction.

DENs can be effective homogeneous and heterogeneous catalysts.[1] For example, homogeneous reactions that have been catalyzed by DENs include hydrogenations,[2,3] as well as Suzuki,[4] Heck,[5−7] and Stille[8] carbon-coupling reactions. An interesting property of dendrimers is that their branches or peripheral groups can act as selective gates or filters that control substrate access to the dendrimer interior.[9,10] We have previously shown that it is possible to take advantage of this property to impart selectivity to intrinsically nonselective metal catalysts. For example, Pd DENs encapsulated within generation 4, 6, and 8 PAMAM dendrimers have different selectivities for the hydrogenation of olefins having slightly different sizes.[11] This is a consequence of the generation-dependent permeability of the dendrimers, which is itself a consequence of the increase in steric crowding on the dendrimer periphery that occurs as the generation increases. Kaneda and co-workers recently provided another example of DEN

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Scheme 1

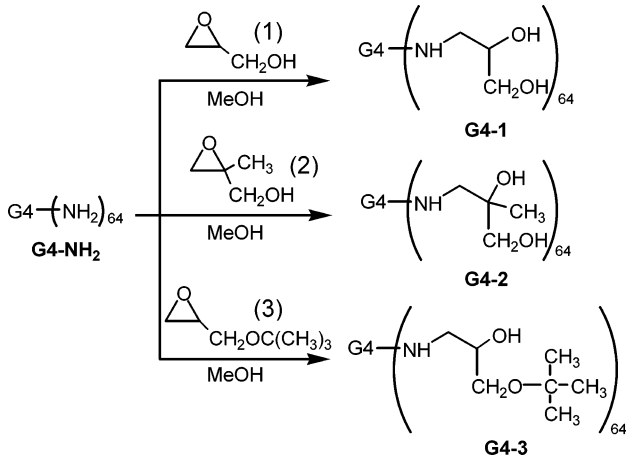
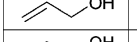
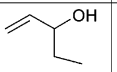
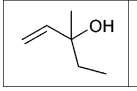


Table 1. TOF Values for the Hydrogenation of Allylic Alcohols Using G4-OH(Pd_{40}) and G4-X(Pd_{40}) (X = 1−3) Catalysts[a,b]

substrates	TOF[mol H_2(mol Pd)$^{-1}$ h^{-1}]			
	G4-OH(Pd_{40})	G4-1(Pd_{40})	G4-2(Pd_{40})	G4-3(Pd_{40})
	125	83/62	62/62	43
	105	62/56	60/56	53
	50	55/50	43/43	31

[a] Hydrogenation reactions were carried out at room temperature with 2×10^{-4} M Pd(0) composite catalysts in MeOH−H_2O (1:1, v/v) mixed solvents. [b] When two TOF values are listed, they represent independently performed reactions using independently prepared DENs. The TOFs were calculated on the basis of H_2 uptake (mol of H_2 per mol of Pd(0) per hour).

catalyst selectivity.[12] In this case Pd DENs exhibited hydrogenation selectivity for polar olefins as a consequence of their strong interactions with the dendrimer interior.

The objective of the present study is to better understand how steric crowding on the periphery of a dendrimer affects the selectivity of DENs. This objective was addressed by modifying the peripheral functional groups of fourth-generation, amine-terminated PAMAM dendrimers (G4-NH_2) with a series of epoxyalkanes. This results in the glycidol (G4-1), 2-methyl glycidol (G4-2), and *tert*-butyl glycidyl ether (G4-3) dendrimer derivatives shown in Scheme 1.[13] Forty-atom Pd DENs were prepared within these three surface-modified dendrimers, and within a fourth-generation, hydroxyl-terminated PAMAM dendrimer (G4-OH), using the previously described approach, and then the hydrogenation efficiency was determined for three allylic alcohol derivatives having slightly different sizes (Table 1). The results indicate that the turnover frequency (TOF) for dendrimers having the most sterically crowded peripheries was lower than for dendrimers modified with smaller functional groups. We conclude that the selectivity of DENs can be controlled by manipulation of the dendrimer periphery.

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Experimental Section

Materials. Fourth-generation PAMAM dendrimers having amine terminal groups (G4-NH_2) were obtained from Dendritech, Inc. (Midland, MI), as a solution in methanol. The methanol was removed under vacuum prior to use. The following chemicals were used as received from the Aldrich Chemical Co. (Milwaukee, WI): glycidol (96%), 2-methyl glycidol, *tert*-butyl glycidyl ether (99%), K_2PdCl_4 (99.99%), and $NaBH_4$ (99%). Methanol was used as received from EM Science. Cellulose dialysis sacks having a molecular weight cutoff of 1.2×10^4 were purchased from Sigma Diagnostics, Inc. (St. Louis, MO). 18 MΩ·cm water (Milli-Q, Millipore, Bedford, MA) was used to prepare aqueous solutions.

Synthesis of Dendrimers. Fourth-generation PAMAM dendrimers having end groups of various sizes (G4-X, X = 1−3, Scheme 1) were prepared by reacting G4-NH_2, which carries 64 terminal primary amines, with 64 equiv of glycidol (1), 2-methyl glycidol (2), or *tert*-butyl glycidyl ether (3; Scheme 1). The synthetic procedure followed that provided in our previous report.[13] For example, G4-1 was prepared by dissolving G4-NH_2 (0.20 g, 14 μmol) in 10 mL of methanol and then adding 67 mg (0.90 mmol) of glycidol dropwise with stirring. The reaction mixture was stirred for 2 days at 40 °C, and then the methanol was removed by rotary evaporation. The crude product was redissolved in 50 mL of water, and the solution was purified by dialysis against water for 24 h. The final product was dried in a vacuum to yield 0.25 g of G4-1 as a white sticky solid. Using the same synthetic procedure, G4-2 and G4-3 were prepared by reaction of G4-NH_2 with 2-methyl glycidol and *tert*-butyl glycidyl ether, respectively.

Characterization and Instrumentation. The chemical structures of G4-X (X = 1−3) were confirmed by ^1H and ^{13}C NMR and matrix-assisted laser desorption ionization mass spectrometry (MALDI-MS). ^1H and ^{13}C NMR spectra were collected on a Varian Inova 500 MHz spectrometer at 500.1 and 125.8 MHz, respectively. CD_3OD was used as an internal standard for the NMR analyses. MALDI-MS spectra were recorded on a Voyager Elite XL MALDI time-of-flight mass spectrometer outfitted with a 337 nm pulsed nitrogen laser. The MALDI matrix was 2′,4′,6′-trihydroxyacetophenone. Electron micrographs were obtained using a JEOL-2010 transmission electron microscope (TEM) having a point-to-point resolution of 0.19 nm. Samples were prepared by placing a drop of DEN solution on a carbon-coated Cu TEM grid (400 mesh, Electron Microscopy Science, Fort Washington, PA) and allowing the solvent to evaporate in air.

Preparation of DENs and Hydrogenation Reactions. The procedure used to prepare DENs containing an average of 40 Pd atoms per dendrimer was the same for all four dendrimers [G4-OH(Pd_{40}) and G4-X(Pd_{40}), X = 1−3].[13] For example, G4-1(Pd_{40}) was prepared by adding 100 μL of an aqueous 1.0 mM G4-1 solution to 9.82 mL of water and then combining this solution with 40.0 μL of aqueous 0.10 M K_2PdCl_4. After stirring for 30 min, 40.0 μL of an aqueous 1.0 M $NaBH_4$ solution was added. The resulting dark brown solution was purified by dialysis against water for 18 h to give a 5.0 μM G4-1(Pd_{40}) solution. To prepare the MeOH/H_2O (1:1, v/v) mixed solvent for carrying out catalytic reactions, 10.0 mL of methanol was added to the 10-mL aqueous nanoparticle solution. As described previously, hydrogenation reactions were carried out in a Schlenk flask fitted with an adapter that was connected to the top of a buret filled with H_2 gas.[11]

Results and Discussion

Synthesis of G4-1, G4-2, and G4-3 DENs. To modify the dendrimer periphery we selected the epoxide ring opening reaction for the following reasons. First, this reaction is nearly quantitative, and, therefore, it is possible to control the porosity of the dendrimer surface by controlling the size of the alkyl groups attached to the epoxides and the epoxide-to-dendrimer ratio. Second, this reaction introduces only alcohol and alkyl groups to the dendrimer periphery, and both of these are poor metal−ion ligands.[13] This is important, because it is essential that the peripheral groups not interfere with the templating ability of the dendrimer interior. Third, the hydroxyl groups introduced onto the surface of the

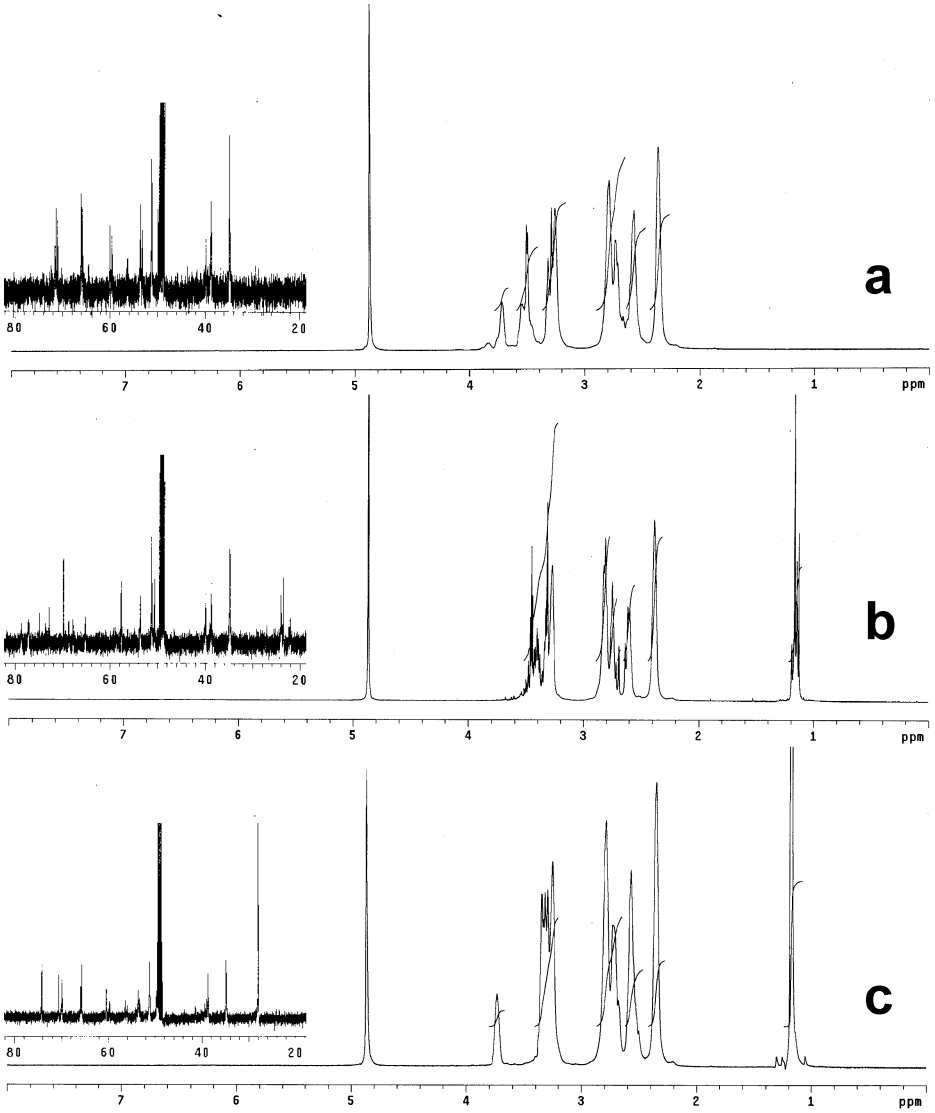

Figure 1. ^{1}H NMR (500 MHz, CD_3OD) spectra of (a) G4-1, (b) G4-2, and (c) G4-3. The inset is the ^{13}C NMR spectrum for each surface-modified dendrimer. ^{1}H chemical shift assignments for (a) G4-1 are δ 2.36, δ 2.57, δ 2.79, and δ 3.23 (protons within the dendrimer backbone), δ 2.73 (−NH−*CH*$_2$−CH(−OH)−, overlapped with protons within the dendrimer backbone), δ 3.72 (−NH−CH$_2$−*CH*(−OH)−); (b) G4-2 are δ 1.15 (−NH−CH$_2$−C*CH*$_3$(−OH)−CH$_3$), δ 2.39, δ 2.60, δ 2.81, δ 3.28 (protons within the dendrimer backbone), δ 2.75 (−NH−*CH*$_2$−CCH$_3$(−OH)−); and (c) G4-3 are δ 1.18 (−NH−CH$_2$−CH(−OH)(−C(*CH*$_3$))), δ 2.35, δ 2.57, δ 2.78, δ 3.25 (protons within the dendrimer backbone), δ 2.73 (−NH−*CH*$_2$−CH(−OH)−), δ 3.73 (−NH−CH$_2$−*CH*(−OH)−).

modified dendrimers help to ensure their solubility in water and alcohols. This makes it possible to compare the catalytic activities of the modified dendrimers with the activity of G4-OH, which we have studied previously and which is only soluble in polar solvents.[11]

The three surface-modified dendrimers (Scheme 1) were characterized by ^{1}H and ^{13}C NMR and MALDI-MS. The extent of surface modification was evaluated by integrating appropriate peaks in the ^{1}H NMR spectrum (Figure 1). For example, in the case of G4-1, comparison of the area of the methine proton (δ = 3.72 ppm) adjacent to the hydroxyl group with the area of the methylene protons (δ = 2.36 ppm) within the dendrimer backbone reveals that ~59 of the 64 primary amines on the surface of G4-NH_2 are modified with glycidol (92% surface modification). A similar analysis indicates that the extents of surface modification of G4-2 and G4-3 are 98 and 95%, respectively. Because the percentage surface modifications for all three dendrimers are similar, variation in steric crowding should depend only on the size of the alkyl groups attached to the epoxides (Scheme 1). The extent of surface modification was also confirmed by MALDI-MS (Supporting Information). Comparison of the measured molecular mass (molecular ion peak at 17 873 *m/z* for G4-1 and at 22 231 *m/z* for G4-3) with the calculated molecular mass of fully modified dendrimers (18 959 for G4-1 and 22 550 for G4-3) reveals that the percentage surface modifications for G4-1 and G4-3 are 94 and 99%, respectively. These values are in good agreement with the NMR data. It was not possible to obtain a meaningful MALDI spectrum for G4-2.

Pd nanoparticles were encapsulated within G4-OH and G4-X (X = 1−3) dendrimers by extraction of $PdCl_4^{2-}$ into the dendrimer interior, followed by chemical reduction [here, we denote the DENs containing 40 Pd atoms as G4-OH(Pd_{40}) and G4-X(Pd_{40}) (X = 1−3), respectively].[2,11,14] The presence of zerovalent Pd DENs was confirmed by UV−vis spectroscopy and TEM. The spectroscopic data were consistent with previously reported results,[9] and the TEM data are shown in Figure 2. The mean diameter for

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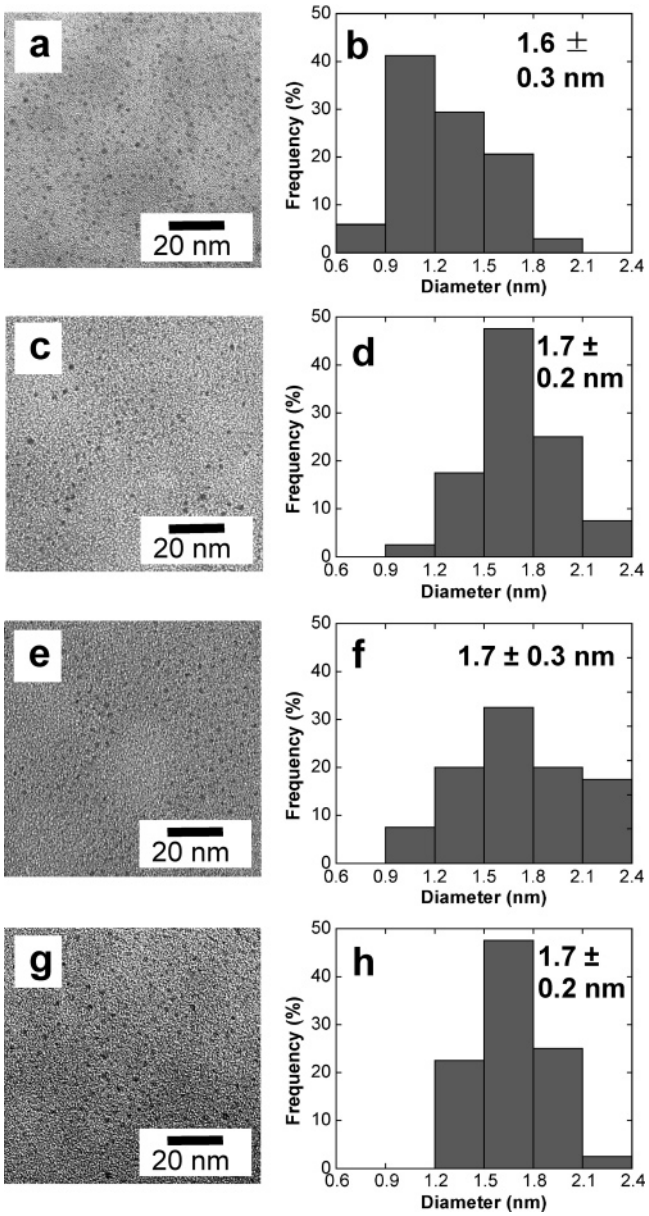

Figure 2. TEM micrographs of (a) G4-OH(Pd_{40}), (c) G4-1(Pd_{40}), (e) G4-2(Pd_{40}), and (g) G4-3(Pd_{40}) and the corresponding particle-size distributions (b, d, f, and h, respectively), obtained prior to the hydrogenation reactions. The average particle sizes and size distributions were determined by counting 100 randomly selected nanoparticles.

the G4-OH(Pd_{40}) DENs is 1.6 nm, and it is 1.7 nm for all three G4-X(Pd_{40}) DENs. The particle size distributions are very narrow, ranging from ±0.2 to ±0.3 nm. These data confirm that the Pd particle size is independent of the surface functionality of the dendrimer. Taken together with our earlier finding that the percentage of functional groups on the surface of the dendrimer is nearly independent of the identity of the functional group, this result means that only the size of the functional groups should affect catalytic activity. Thus, these four dendrimers provide an excellent model system for studying the effect of peripheral steric crowding on catalytic TOF.

Catalytic Activity of DENs as a Function of Steric Crowding on the Dendrimer Surface. The catalytic activity of G4-OH(Pd_{40}) and G4-X(Pd_{40}) DENS was investigated for the hydrogenation of allyl alcohol and two α-substituted allylic alcohols. TOFs were determined by H_2 uptake using a MeOH/H_2O (1:1, v/v) mixed solvent to ensure complete solubility of the DENs, the substrates, and the products.[11]

Table 1 summarizes TOF values for the catalytic hydrogenation of the three alkenes by the four different types of Pd DENs. It has been shown previously that the intrinsic TOFs of C3−C6 unsaturated alcohols, which are structurally similar to the allylic alcohols used here, differ only slightly.[15] Accordingly, it is appropriate to attribute differences in the TOFs shown in Table 1 to the presence of the dendrimer rather than to differences in the inherent hydrogenation rates of the substrates. It is also worth mentioning that the run-to-run variation in TOFs (Table 1) is sufficiently precise that trends in their numerical values as a function of dendrimer functionalization are meaningful. Specifically, half the reactions in Table 1 were carried out twice, and differences in the duplicate TOF values are smaller than the variation observed for different combinations of substrates and DEN catalysts.

There are three important conclusions that can be drawn from the data shown in Table 1. First, with one exception, the TOF values decrease as the substrates increase in size for all four catalysts. This observation is in agreement with our previous findings, which showed that TOFs decrease as the substrate size increases for different generation dendrimers having the same terminal groups.[11] Second, as the size of the peripheral groups on the dendrimer increases (G4-OH < G4-1 < G4-2 < G4-3), the TOF for a particular allylic alcohol generally decreases. For example, when the hydrogenation reaction is carried out using G4-3(Pd_{40}), which has the largest groups on its surface, the TOFs for all three substrates achieve their lowest values. In contrast, the highest TOFs (again, with one exception) are observed for G4-OH(Pd_{40}), which has the least sterically crowded surface. Third, the highest degree of size selectivity is observed for allyl alcohol, which is the smallest substrate. That is, the TOF for this substrate is 3 times lower for G4-3(Pd_{40}) compared to G4-OH(Pd_{40}). In contrast, the bulkiest substrate, 3-methyl-1-penten-3-ol, exhibited the lowest size selectivity (less than a factor of 2).

The largest linear dimensions perpendicular to the O−H bond for allyl alcohol, 1-penten-3-ol, and 3-methyl-1-penten-3-ol are 5.5, 7.5, and 8.0 Å, respectively.[11] Thus, the size of the bulkiest substrate (8.0 Å) is about the same as the average equilibrium distance between the terminal groups of the least sterically crowded dendrimer (G4-OH, 8.2 Å). Accordingly, it seems reasonable that the largest substrate will have difficulty accessing the interior of all four dendrimers, and it follows that in this case differences in the TOF values will be small and not too different from one another. In contrast, the smallest substrate, allyl alcohol (5.5 Å), should easily penetrate the least sterically crowded dendrimer (G4-OH, 8.2 Å between terminal groups) but not the more sterically crowded dendrimers. Therefore, the smallest substrate exhibits the highest degree of catalytic selectivity.

Summary and Conclusions

We have shown that the catalytic selectivity of DENs can be modulated in a logical way by controlling the terminal groups of the host dendrimers. This conclusion is based on the following observations. First, the size and size distributions of the encapsulated nanoparticles are independent of the dendrimer surface modification. Sec-

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ond, the intrinsic TOFs of the three substrates are about the same. Therefore, the differences in the TOFs shown in Table 1 primarily reflect the extent of steric crowding on the dendrimer periphery and, thus, the ease with which substrates are able to penetrate the dendrimer, encounter the encapsulated catalysts, and undergo reaction. Dendrimers that are more sterically crowded on their surface are poorer catalysts than more open dendrimers. This conclusion is in agreement with a previous report from our group, which showed that the catalytic selectivity of DENs could also be controlled by changing the dendrimer generation.[11] That is, just as increasing the size of the functional groups on the surface of a particular generation of dendrimer increases surface crowding and thereby reduces the TOF, so too does changing the generation of a family of dendrimers having the same surface functional groups. We anticipate that further developments in this line of research will lead to general rules for rendering intrinsically nonselective catalysts, such as Pd, selective by controlling the physical and chemical properties of the surrounding dendrimer scaffold.

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Supporting Information Available: MALDI mass spectra for G4-1 and G4-3. This information is available free of charge via the Internet at http://pubs.acs.org.

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