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Quantitative Analysis of the Stability of Pd Dendrimer-Encapsulated Nanoparticles

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The stability of Pd dendrimer-encapsulated nanoparticles (DENs) in air-, N_2-, and H_2-saturated aqueous solutions is reported. The DENs consisted of an average of 147 atoms per sixth-generation, poly(amidoamine) dendrimer. Elemental analysis and UV−vis spectroscopy indicate that there is substantial oxidation of the Pd DENs in the air-saturated solution, less oxidation in the N_2-saturated solution, and no detectable oxidation when the DENs are in contact with H_2. Additionally, the stability improves when the DEN solutions are purified by dialysis to remove Pd^{2+}-complexing ligands such as chloride. For the air- and N_2-saturated solutions, most of the oxidized Pd recomplexes to the interiors of the dendrimers, and a lesser percentage escapes into the surrounding solution. The propensity of Pd DENs to oxidize so easily is a likely consequence of their small size and high surface energy.

Introduction

Here, we report on the stability of aqueous solutions of Pd dendrimer-encapsulated nanoparticles (DENs) under oxidizing (air-saturated), inert (N_2-saturated), and reducing (H_2-saturated) conditions. The results indicate that Pd DENs are not fully stable in the presence of air or N_2 but that they do retain their integrity under reducing conditions. Additionally, the presence of coordinating anions, such as Cl^-, accelerate the oxidation of DENs. These findings are consistent with previous results indicating that Pd nanoparticles of many types degrade over time in oxidizing[1] and catalytic environments.[2−5] The presence of degradation products makes it difficult to identify the active species in nanoparticle-based catalytic reactions. For example, it has been found that metal atoms or ions dissociated from nanoparticles catalyze carbon−carbon coupling reactions.[3,4,6] Accordingly, this quantitative study of Pd DEN stability is significant.

An interesting aspect of the DEN architecture, which distinguishes it from other forms of stabilized Pd nanoparticles, is the ability of the dendrimer to retain Pd^{2+} resulting from oxidation of the metallic nanoparticle component.[1] Accordingly, we use the terms "retained" to refer to Pd^{2+} that remains within the dendrimer following DEN oxidation and "leached" to refer to Pd^{2+} that escapes from the dendrimer template into the solution. Unless otherwise indicated, all ionic forms of Pd are denoted here as Pd^{2+}, but it is understood that this includes various hydrolyzed and unhydrolyzed complexes of Pd^{2+} with Cl^-.

DENs are synthesized in a two-step process. First, metal ions are extracted from solution into the dendrimers via complexation with internal tertiary amines. Second, the metal ions are reduced, usually using BH_4^-, and subsequently coalesce to form zerovalent metallic nanoparticles within the dendrimer templates. Monometallic Au, Pt, Pd, Cu, Ni, and Fe as well as bimetallic AuAg, PdAu, PtCu, PtAu, PdPt, and CuPd DENs have been synthesized using this basic procedure.[1,7−20] DENs are stabilized by the dendrimer framework and therefore do not aggregate into larger particles. However, small molecules are able to penetrate the dendrimer and access the surfaces of the encapsulated nanoparticles, and therefore DENs are good models for homogeneous,[10,21,22] heterogeneous,[21] and electrochemical[9,14,18] catalysts. Specifically, DENs have been shown to be catalytically active for olefin hydrogenation,[22,23] oxygen reduction,[9,18] carbon monoxide oxidation,[14] and carbon-coupling reactions.[3,5,24]

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We have previously shown that aqueous solutions of Pd DENs oxidize in the presence of air when Pd^{2+}-coordinating ligands, such as Cl^-, are present.[1] However, UV−vis spectroscopic data indicated that the stability of Pd DENs improved when such ligands were removed by dialysis and DEN solutions were maintained under an inert gas atmosphere. The susceptibility of Pd DENs to oxidation was demonstrated by alternately bubbling aqueous DEN solutions with O_2 and H_2. In the presence of O_2, a ligand-to-metal charge-transfer (LMCT) band emerged in the UV−vis spectrum, indicating oxidation of the Pd DENs and complexation of the resulting Pd^{2+} ions with the tertiary amines of the dendrimer.[1] Subsequent exposure to H_2 gas eliminated the LMCT band, indicating re-reduction of the retained Pd^{2+}. We have also observed that the size of Pd DEN catalysts increases following the Stille coupling reaction.[5] This likely occurs because of oxidative degradation of the Pd DENs followed by redeposition of zerovalent Pd atoms, or very small clusters of atoms, onto other DEN catalysts present in solution. This result suggests that in at least some cases Pd^{2+} leaches from within the dendrimer host.

If a nanoparticle undergoes an undesirable reaction, such as oxidation, agglomeration, or precipitation, the lifetime of the catalyst is reduced. Hence, it is important to determine the stability of the catalyst during reaction.[3,4,21,25] For example, Astruc and co-workers used Pd DENs, Pd dendrimer-stabilized nanoparticles (DSNs), and Pd monolayer-protected clusters (MPCs) that were extracted from DENs to catalyze the Suzuki coupling reaction.[3] They found that the concentration of leached Pd increased when reaction kinetics were fast, and this finding correlated with the observation of an increased presence of aggregated Pd black. The other important finding in this study was that Suzuki coupling substrates add oxidatively to Pd nanoparticles during catalysis, resulting in leaching. These findings are important, because increased concentrations of leached Pd resulted in agglomeration and precipitation and this effectively quenched the active catalyst.

Rothenberg and co-workers have monitored leaching from tetraoctylammonium-glycolate-stabilized Pd nanoparticles during Heck and Suzuki coupling reactions in deoxygenated water.[4] For these studies, a reactor having two compartments separated by a nanoporous alumina membrane was used. Catalytic Pd nanoparticles, having diameters ranging from 11 to 20 nm, and the necessary reactants were placed into one of the chambers. If the nanoparticles were stable during reaction, then they would remain within this chamber. However, catalyst degradation would lead to formation of ions and perhaps smaller metal clusters, and these would be able to diffuse into the second chamber through the 5 nm membrane pores. Elemental analysis of the solution in the second chamber revealed that the concentration of Pd increased as a function of time, indicating poor catalyst stability. Indeed, even in the absence of the active reactants, the Pd nanoparticles oxidized and Pd was observed in the second chamber.

In the present study, Pd DENs consisting of an average of 147 atoms were prepared within sixth-generation, hydroxyl-terminated poly(amidoamine) (PAMAM) dendrimers (G6-OH(Pd_{147})), and their stability was evaluated in the presence of aqueous solutions saturated with air, N_2, and H_2. The results indicate that Pd DENs partially oxidize in air- and N_2-saturated solution but that the amount of oxidized Pd is small (usually less than 10% of the total zerovalent Pd initially present) after 12.0 h. Typically, about half of the oxidized Pd is retained within the dendrimer and half leaches into the solution. Oxidation is accelerated in the presence of coordinating ligands such as Cl^-. In H_2-saturated water, G6-OH(Pd_{147}) DENs are stable.

Experimental Section

Synthesis of Pd DENs. Sixth-generation, hydroxyl-terminated PAMAM dendrimers (G6-OH) were obtained from Sigma-Aldrich as a 4.49 wt % solution in methanol. Prior to use, the methanol was removed under vacuum and the dendrimers were redissolved in HPLC-grade, submicrometer-filtered water (Fisher Scientific) to make a 100 μM stock solution. K_2PdCl_4 and $NaBH_4$ were purchased from Sigma-Aldrich and used as received. Pd DENs were prepared by the chemical reduction of a precursor dendrimer−Pd ion complex, denoted as G6-OH(Pd^{2+})$_{147}$. A 2.00 μM solution of G6-OH(Pd^{2+})$_{147}$ was prepared by mixing 200 μL of a 100 μM G6-OH dendrimer solution in 9.48 mL of HPLC-grade water, followed by the slow addition of 294 μL of a 10.0 mM solution of K_2PdCl_4 while stirring. The solution was stirred for an additional 30 min, which is the time required for the Pd^{2+} ions to complex to the interior tertiary amines of the dendrimer.[1] The formation of the G6-OH(Pd^{2+})$_{147}$ complex was confirmed by UV−vis spectroscopy, which reveals a characteristic ligand-to-metal charge transfer (LMCT) band at 224 nm.[1] Next, 30.0 μL of a freshly prepared 1.00 M aqueous solution of $NaBH_4$ was added to the complex. The solution was stirred for 30 min, and then a second UV−vis spectrum was obtained to confirm that the precursor complex was completely reduced to form G6-OH(Pd_{147}) DENs.[1]

Purification. Purification of DENs was performed by dialysis. Dialysis sacks having a nominal molecular weight limit (NMWL) of 12 kDa were purchased from Sigma Diagnostics. A total of 40.0 mL of a 2.00 μM DEN solution was prepared and dialyzed for 24.0 h against 4.0 L of HPLC-grade water. To prevent oxidation of Pd DENs during purification, the dialysis water was purged with H_2 for 30 min prior to, and also during, dialysis. Additionally, the dialysis was carried out in a glovebag purged with H_2 gas. The dialysis water was exchanged for 4.0 L of fresh, H_2-saturated HPLC-grade water after 12.0 h.

Characterization. UV−vis absorbance spectra were obtained using a Hewlett-Packard HP 8453 UV−vis spectrometer. Quartz cuvettes having an optical path length of 0.20 cm were used. An aqueous 2.00 μM solution of G6-OH was used as a blank for all UV−vis measurements.

Transmission electron microscope (TEM) images were obtained using a JEOL 2010F TEM. Samples were prepared for analysis by dropwise addition of a G6-OH(Pd_{147}) solution onto 400 mesh Cu TEM grids coated with a thin layer of carbon (EM Sciences). Prior to analysis, the grids were allowed to dry overnight in a desiccator.

Separation of Leached Pd by Centrifugal Filtration. Leached Pd was quantitatively separated from solutions of DENs by centrifugal filtration through a membrane having a NMWL of 10 kDa. Amicon Ultra Centrifugal Filtration devices with an Ultracel 10 kDa NMWL membrane were purchased from Millipore (Billerica, MA). The membrane material is constructed from regenerated cellulose. Prior to use, the filters were rinsed with HPLC water and the lower vials used to collect the filtrate were cleaned in 4.0 M HNO_3. One hour was required for all of the solvent in 2.0 mL aliquots of aqueous 2.0 μM G6-OH(Pd_{147}) to pass through the filter when solutions were centrifuged at an acceleration of 5000g, where g is the free-fall acceleration in units of m s^{-2}. Centrifugation was carried using a Fisher Scientific AccuSpin 400 fixed-rotor centrifuge. Sample aliquots were removed by the procedure described in the next paragraph.

Elemental Analysis of Leached Samples. The amount of leached Pd was evaluated using inductively coupled plasma mass spectrometry (ICP-MS). Following centrifugal filtration, 900 μL of filtrate containing the leached Pd, along with an internal standard, was added to volumetric flasks and made to volume in a 1.00 wt % solution of UltraTrace HNO_3 (Fisher Scientific).

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All volumetric glassware was acid washed in a 4.0 M HNO_3 bath overnight and then rinsed with deionized water prior to sample preparation. Indium was used as the internal standard to correct for drift. An aliquot from a 100 ppm stock solution of indium in 2.00 wt % HNO_3 (Fisher Scientific) was added to all samples and calibration standards such that the final In concentration was 1.00 ppm. Quantitative analysis of leached Pd was performed on a GBC Optimass 8000 ICP-TOF-MS instrument, using a pneumatic nebulizer and cyclonic spray chamber, with a peristaltic pump sample uptake manifold. Calibration standards containing 5.00, 10.0, 25.0, 50.0, 100, 300, and 500 ppb Pd were prepared from a 110 μM K_2PdCl_4 stock solution. A 1.00 wt % solution of UltraTrace HNO_3 (Fisher Scientific) containing 1.00 ppm In served as a blank.

Results and Discussion

Synthesis and Characterization of Pd DENs. Pd DENs were synthesized in a two-step process. First, Pd^{2+} ions were complexed to the interior amines of G6-OH PAMAM dendrimers, and then the G6-OH$(Pd^{2+})_{147}$ complex was reduced with BH_4^- to yield G6-OH(Pd_{147}) DENs. Figure 1 provides UV−vis spectra of G6-OH$(Pd^{2+})_{147}$ and G6-OH(Pd_{147}) before and after dialysis. Prior to reduction, the G6-OH$(Pd^{2+})_{147}$ spectrum (black line) reveals a strong ligand-to-metal charge-transfer (LMCT) band centered at 224 nm, which confirms complexation of Pd^{2+} to G6-OH.[1] After reduction (G6-OH(Pd_{147}), red line), the sharp LMCT band is replaced by a broad absorbance characteristic of small metal nanoparticles.[26] TEM image analysis indicates that the Pd DENs are 1.5 ± 0.3 nm in diameter (Supporting Information, Figure S1), which is consistent with previous reports and the calculated size of 1.6 nm for cuboctahedral Pd clusters containing 147 atoms.[22] An X-ray photoelectron spectroscopy (XPS) spectrum was obtained from undialyzed G6-OH(Pd_{147}) (Supporting Information, Figure S2). The features present at 335.7 and 341.0 eV correspond to the $3d_{5/2}$ peaks of Pd(0), and the splitting between them (5.3 eV) is also consistent with zerovalent Pd (5.26 eV).[27,28] That only these two peaks are observed confirms that Pd is primarily in the reduced form following the reduction step.

Dialysis of G6-OH(Pd_{147}). The main point of this paper is to compare the stability of Pd DENs in air-, N_2-, and H_2-saturated aqueous solutions both before and after dialysis. However, this requires that the nanoparticles remain stable during dialysis. Therefore, to prevent oxidation of Pd DENs during dialysis, the dialysis water was purged with H_2 for 30 min prior to and during dialysis. Additionally, the dialysis was carried out in a glovebag purged with H_2 gas.

Figure 1 compares UV−vis spectra obtained before and after the dialysis of 2.00 μM G6-OH(Pd_{147}) in H_2-saturated water. That the red spectrum (before dialysis) and the green spectrum (after dialysis) are nearly identical indicates that the composition and concentration of the DENs are unchanged by the purification process. TEM size-distribution data (Supporting Information Figure S1) before and after dialysis are also consistent with this conclusion.

We confirmed that there is no detectable loss of Pd during dialysis by elemental analysis. Specifically, ICP-MS analysis of DEN solutions obtained before and after dialysis yielded Pd concentrations of 291.7 and 293.8 μM, respectively. These values can be compared to 294 μM, which is the expected concentration

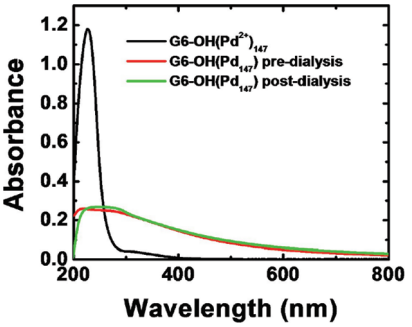

Figure 1. UV−vis absorbance spectra of aqueous 2.00 μM solutions of G6-OH(Pd_{147}) before and after reduction, and following dialysis. The prominent band at 224 nm in the spectrum of G6-OH$(Pd^{2+})_{147}$ corresponds to the LMCT band associated with complexation between Pd^{2+} and the tertiary amines of the dendrimer.

of Pd in a 2.00 μM DEN solution. The error in the expected concentration was calculated by propagation of errors and found to be 1.3%, or 3.3 μM.

To ensure that dialysis removes Cl^-, and presumably other ions introduced to the DENs solution during synthesis, a simple, qualitative test for the presence of Cl^- was carried out. Specifically, an excess of Ag^+ in the form of an aqueous $AgNO_3$ solution was added to an aqueous G6-OH(Pd_{147}) solution before and after dialysis. Figure S3 in the Supporting Information shows that an easily detectable quantity of AgCl precipitate forms in the DENs solution prior to dialysis but that no precipitate is observed after dialysis. If we assume that the maximum possible concentration of Cl^- initially present in solution is 1.18 mM (from K_2PdCl_4), then a simple equilibrium calculation suggests that the lowest concentration of Cl^- needed to generate a precipitate is 13.4 μM. This confirms that at least 98.7% of the Cl^- is removed by dialysis.

UV−vis Spectroscopic Analysis of DEN Stability. G6-OH(Pd_{147}) (2.00 μM) aqueous DEN solutions were placed in vials and immediately sealed with septum caps after completion of the reduction and dialysis steps described in the previous sections. Next, water-saturated air, N_2, or H_2 was bubbled into the vials via a syringe inserted through the septums for 12 h. Gas purging of the vials was performed with stirring and within a glovebag that was purged with N_2. Aliquots for spectroscopic analysis were periodically removed from the vials using a syringe.

Spectra of undialyzed G6-OH(Pd_{147}) DENs stirred in the presence of air are provided in Figure 2a. The initial spectrum (t = 0) is consistent with the red and green spectra in Figure 1 and confirms that the Pd DENs are initially completely reduced. After 1.0 h of exposure to air, peaks at 218 and 280 nm emerge. The sharp increase in the absorbance of the LMCT band at 218 nm indicates partial oxidation of the encapsulated Pd DENs and subsequent recomplexation of Pd^{2+} to the interior tertiary amines of the G6-OH dendrimers (note that the exact position of the LMCT peak ranges from 218 to 224 nm due to convolution of the peak with the baseline). UV−vis measurements of the undialyzed G6-OH(Pd_{147}) solution at times ranging from 2.0 to 12.0 h indicate that the absorbance of the LMCT band continues to increase while the continuum absorbance at longer wavelengths decreases. The latter is consistent with the presence of fewer or smaller DENs. Although it is difficult to judge the baseline underlying the LMCT peak, the percentage of oxidized Pd can be estimated from the spectroscopic data. For example, taking into account the rising baseline, the absorbance of the peak at 218 nm corresponding to 12.0 h of exposure to air is about 0.18. This can be compared to the absorbance of the same peak

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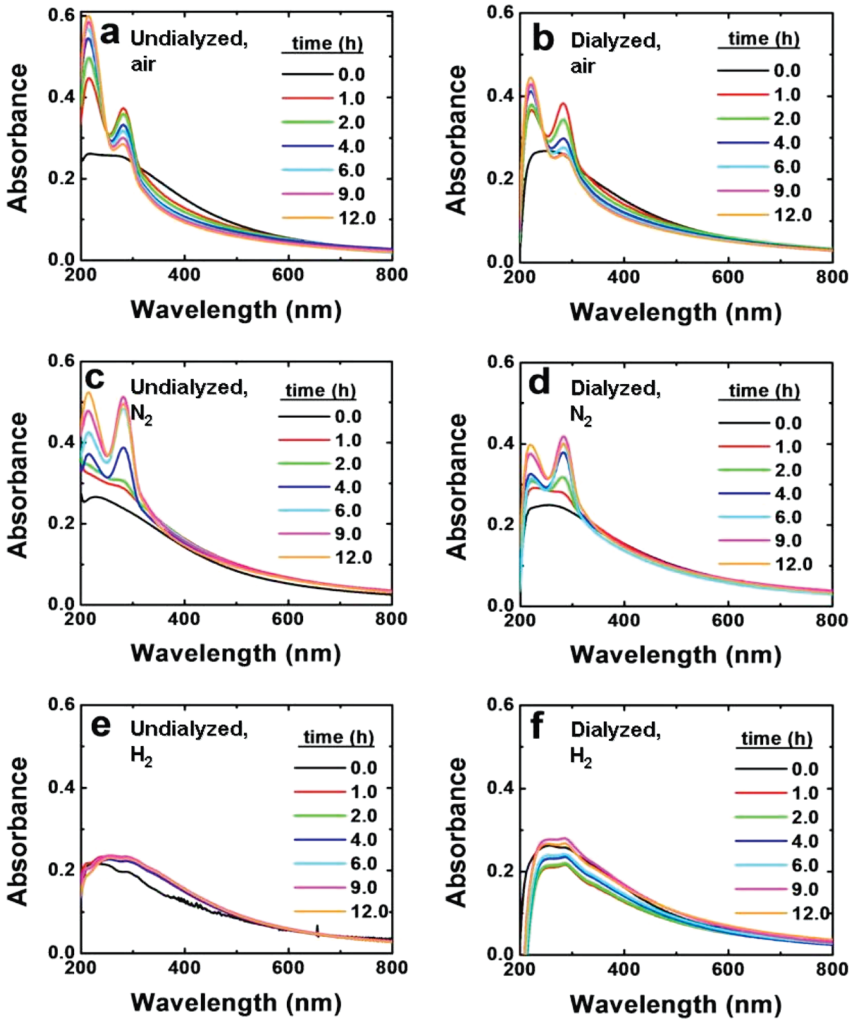

Figure 2. Time-resolved UV−vis absorbance spectra obtained before (left) and after (right) dialysis of G6-OH(Pd_{147}) DEN solutions. The aqueous DEN solutions were purged with (a,b) air; (c,d) N_2; and (e,f) H_2.

for the G6-OH(Pd^{2+})$_{147}$ precursor (black line, Figure 1) of 1.2, which corresponds to the absorbance when 100% of the Pd is complexed to the dendrimer. To a first approximation, therefore, the extent of oxidation is about 15%.

Figure 3a (red circles) is a plot of the absorbance of the LMCT band at λ_{max} = 218 nm versus time that corresponds to the spectra in Figure 2a. It is clear that a significant amount of oxidation takes place initially but that the rate slows at longer times. Two additional points merit mention. First, the origin of the peak at 280 nm is uncertain, but we[17] and others[29,30] have previously correlated it to partial degradation of PAMAM dendrimers. The presence of this peak is inconvenient because it complicates determination of the baseline for the LMCT band corresponding to the dendrimer−Pd complex, but otherwise it (and the species that it corresponds to) appears to be benign. Second, the LMCT band arises only from Pd^{2+} that is complexed to the dendrimer. However, it is possible that other Pd^{2+} species resulting from DEN oxidation, but which do not yield a distinct absorbance between 200 and 800 nm, are present in solution. This point will be discussed in more detail later, but for now it is only important to keep in mind that the LMCT peak corresponds to one particular type of Pd^{2+}.

Spectra of G6-OH(Pd_{147}) DENs dialyzed under H_2 and then exposed to air for times up to 12.0 h are provided in Figure 2b. This family of spectra is quite similar to that just discussed (Figure 2a). Specifically, a LMCT band corresponding to oxidation of Pd DENs and subsequent recomplexation to the dendrimers is present at λ_{max} = 222 nm. This peak increases in magnitude as a function of time (Figure 3a, black squares), and the absorbances at longer wavelengths decrease. This result indicates that removal of Cl^- and other complexing ligands from the aqueous DEN solution does not fully stabilize the DENs against air oxidation. Note, however, that the magnitude of the LMCT band is smaller after dialysis, which indicates that reformation of the G6-OH(Pd^{2+})$_n$ complex upon exposure to air is less extensive after the removal of coordinating anions. However, the presence of the dendrimer degradation peaks at 280 nm in parts a and b of Figure 2 makes it difficult to construct the baseline required to quantify the relative rates of G6-OH(Pd^{2+})$_n$ reformation.

Spectra of aqueous solutions of undialyzed and dialyzed G6-OH(Pd_{147}) stirred in the presence of N_2 are provided in Figure 2c and d, respectively. The trend is the same as that observed when the DENs are present in air-saturated water: growth of the LMCT band at λ_{max} = 218 and 223 nm for the undialyzed and dialyzed solutions, respectively. Because of the presence of the dendrimer degradation peak at 280 nm, it is not possible to quantitatively measure the rate of increase in these peaks and hence the rate of

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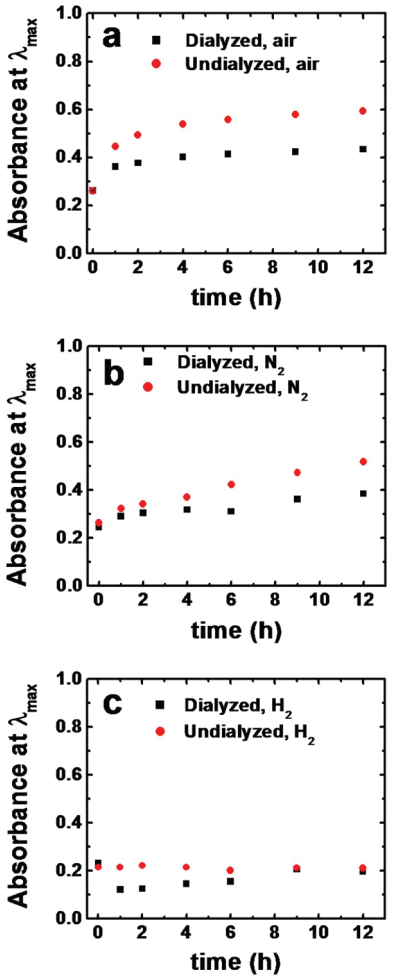

Figure 3. Absorbance of the LMCT band at λ_{max} versus time for G6-OH(Pd_{147}) DENs purged with (a) air; (b) N_2; and (c) H_2. Because of the convolution of this peak with the rising baseline, λ_{max} varied within the range 218−224 nm.

DEN oxidation. However, the growth rate of this peak in the N_2-saturated solutions (Figure 3b) appears qualitatively slower than that in air-saturated water (Figure 3a). We conclude that the presence of O_2 is a contributing factor to the oxidation of Pd DENs, but that either water or the dendrimer itself can also serve as a sufficiently powerful oxidant to convert Pd DENs to Pd^{2+} in the presence or absence of complexing ligands. Note, however, that unlike the spectroscopic results for air-saturated Pd DEN solutions there is no measurable decrease in the absorbance of the N_2-saturated DENs solutions at wavelengths > 350 nm. We will have more to say about the stability of Pd DENs exposed to N_2-saturated water later.

The spectra of undialyzed and dialyzed aqueous solutions of G6-OH(Pd_{147}) exposed to H_2 are shown in Figure 2e and f, respectively, and the evolution of the LMCT band at λ_{max} = 224 nm as a function of time is provided in Figure 3c. There are clear differences between these spectra and those obtained from Pd DENs in air- and N_2-saturated water. First, the LMCT band is absent in all of these spectra, indicating no detectable oxidation of Pd. Recall, however, that this band only correlates to Pd^{2+} that is complexed to the tertiary amines of the dendrimer. Pd that is oxidized, but not recomplexed to the dendrimer, will not be observed spectroscopically. However, we will show later that there is no evidence for any form of Pd in these solutions other than as Pd DENs. Also notice that the peak at 280 nm, which we tentatively assign to a degradation product of the dendrimer, is also absent in the presence of H_2. This observation suggests that the 280 nm peak might be correlated to an oxidizable intermediate species of Pd or to an unidentified byproduct. Taken together, the results shown in Figures 2 and 3 indicate that the presence of a reducing medium (H_2-saturated water) eliminates the conversion of G6-OH(Pd_{147}) to dendrimers encapsulating both zerovalent Pd and Pd^{2+} (G6-OH($Pd_{147-n}Pd_n^{2+}$)), but that the presence of O_2 and even N_2 leads to such mixed valence materials. In the next section, we explore the presence of forms of Pd^{2+} that might be present in the solution outside of the dendrimer, that is, forms of Pd^{2+} other than G6-OH($Pd_{147-n}Pd_n^{2+}$).

Centrifugal Filtration and Analysis of G6-OH(Pd^{2+})$_{147}$ Solutions. The just-discussed spectroscopic study indicates that a fraction of the atoms in Pd DENs oxidize and recomplex with the dendrimer unless they are maintained within a reducing environment. However, these data do not provide information about the fate of Pd species that escape from the dendrimer and into the solution, because they are transparent in the range of 200−800 nm. Accordingly, we devised the following experiment to separate and quantify leached Pd (in any form) from Pd^{2+} bound to the dendrimer. Specifically, centrifugal filtration membranes, which are designed to retain solutes having masses greater than 10 kDa, were used to separate the G6-OH dendrimers (MW = 58.3 kDa), and any forms of Pd they contain, from all forms of solution-phase Pd. The filtrates resulting from these experiments were then analyzed for Pd by ICP-MS.

The viability of this approach was confirmed by the following control experiment. We know from prior experience that air-saturated, aqueous G6-OH(Pd^{2+})$_{147}$ solutions are highly stable, even after long-term dialysis against pure water. Accordingly, we prepared a 2.00 μM solution of G6-OH(Pd^{2+})$_{147}$, immediately filtered a portion of it, and then analyzed the filtrate for Pd by ICP-MS. A second aliquot of this solution was stirred in air-saturated water for 12.0 h, filtered, and analyzed for Pd. These experiments were carried out in triplicate. The average concentration of Pd recovered from these six experiments was 5.5 ± 1.7 μM, which can be compared to the 294 μM initial concentration of Pd^{2+} present in the 2.00 μM solution of G6-OH(Pd^{2+})$_{147}$. We draw several conclusions from this experiment. First, because just under 2% of the Pd initially present in the G6-OH(Pd^{2+})$_{147}$ solution passes into the filtrate, it is clear that the dendrimer, and any Pd it carries, is retained by the filter. Second, the amount of Pd in the filtrates of the aged solutions was no higher than in those that were freshly prepared. Accordingly, it seems likely that the small amount of Pd found in the filtrate was not initially complexed by the dendrimer. Third, dendrimer fragments, resulting from degradation reactions of the type that might be responsible for the peak at 280 nm (Figure 2) and that are small enough to pass through the filter, are apparently not present to a significant degree. Fourth, Pd^{2+} that forms and recomplexes with the dendrimer after exposure of the DENs to air- or N_2-saturated water is strongly retained within the dendrimer. Fifth, the filtration process itself does not destabilize the dendrimers and cause them to release Pd.

Centrifugal Filtration and Analysis of G6-OH(Pd_{147}) Solutions. Experiments intended to quantify the extent of leaching from G6-OH(Pd_{147}) DENs were carried out as follows. First, triplicate 1.00 mL aliquots were obtained from the same dialyzed and undialyzed 2.00 μM G6-OH(Pd_{147}) solutions used to obtain the spectroscopic data shown in Figures 2 and 3. Second, these samples were filtered to separate the parent DENs from their solutions. Third, the filtrates were analyzed by ICP-MS to determine the extent of Pd leaching from the dendrimers.

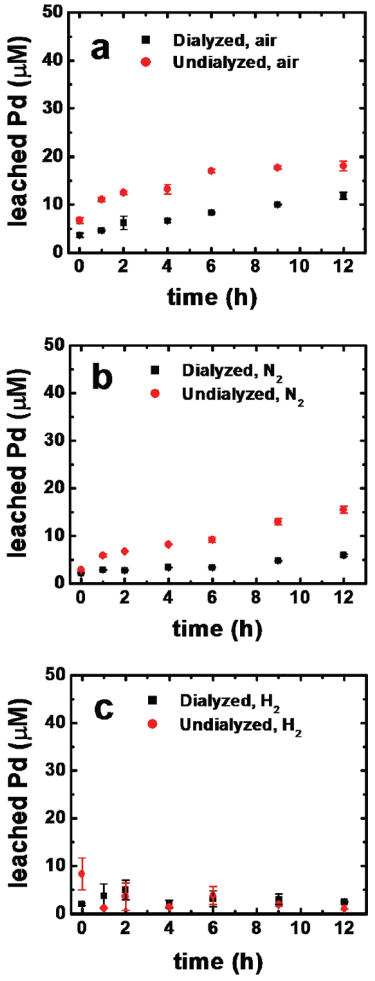

Figure 4. Plots of the concentration of leached Pd in filtered aqueous solutions versus time. The G6-OH(Pd_{147}) DENs solutions were purged with: (a) air; (b) N_2; and (c) H_2.

The results from these experiments are plotted in Figure 4. Figure 4a is a plot of the concentration of leached Pd found in the filtrates of dialyzed and undialyzed aqueous 2.00 μM G6-OH (Pd_{147}) solutions that were air-saturated for times ranging up to 12.0 h. The key points derived from these data are as follows. First, there is a higher extent of leaching in the undialyzed DEN solutions. Second, leaching is rather rapid initially and then it slows. However, it is not clear from these results whether the extent of leaching achieves equilibrium after 12.0 h. Third, the concentration of leached Pd is surprisingly small. After 12.0 h, the percentages of leached Pd are 6.2% and 4.0% for the undialyzed and dialyzed DENs, respectively. These values can be compared to ~2.0%, which is the percentage of Pd passing into the filtrate in the control experiments described in the previous section.

Similar conclusions can be drawn from the results presented for the Pd DENs exposed to N_2-saturated aqueous solutions (Figures 4b), except here the extent of leaching is lower: 5.3% and 2.0% for the undialyzed and dialyzed DENs, respectively. The results obtained for leaching in the H_2-saturated aqueous solutions are quite different, however. Whether the solutions were dialyzed, the amount of Pd found in the filtrates of these solutions was considerably less than 2.0% of the original concentration of Pd in the G6-OH(Pd_{147}) DENs. We conclude that Pd DENs kept under H_2 are fully stable.

Summary and Conclusions

This study was prompted by numerous recent findings suggesting that reactions thought to be catalyzed by Pd nanoparticles may actually be catalyzed by nanoparticle fragments or oxidation products.[3,4] Accordingly, we sought to learn more about the stability of Pd DENs in oxidizing (air), inert (N_2), and reducing (H_2) aqueous environments. The results indicate that in air- and N_2-saturated aqueous solutions DENs are not fully stable. In the worst case (undialyzed, air-saturated), about 15% of the Pd atoms in a 147-atom DEN oxidize and recomplex with the dendrimer after 12.0 h. A smaller percentage (up to ~6%) of Pd escapes from the dendrimer and is found in the surrounding aqueous solution. At present, we do not know the form of these extra-dendrimer species. In the best case (dialyzed, N_2-saturated), < ~4% of the Pd atoms oxidize and recomplex with the dendrimer after 12.0 h and about 2% is found in the aqueous solution. Pd DENs are fully stable in H_2-saturated aqueous solution.

The underlying reason for the oxidative instability of Pd nanoparticles likely relates to their oxidation potentials being shifted negative compared to bulk Pd. It seems likely that the observed decreased stability of Pd DENs in the presence of complexing ligands has the same origin: a ligand-induced negative shift in the oxidation potential of the metal. To the best of our knowledge these size-dependent redox potentials have not been determined, but clearly such measurements would be of tremendous value. Importantly, the redox potentials of nanoparticles are intrinsic, and therefore, these size-dependent shifts may provide a significant barrier to the use of DENs and related nanoparticles for certain types of catalyses.

We are now turning our attention to the stability of Pd DENs during catalytic reactions carried out under oxidizing and reducing conditions. The results of those experiments will be reported in due course.

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Supporting Information Available: TEM micrographs and size-distribution histograms, XPS spectra, and optical images related to the Cl^- analysis. This material is available free of charge via the Internet at http://pubs.acs.org.