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Low-Temperature Activation Conditions for PAMAM Dendrimer Templated Pt Nanoparticles

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Low-Temperature Activation Conditions for PAMAM Dendrimer Templated Pt Nanoparticles

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　　　Surface immobilized polyamidoamine (PAMAM) dendrimer templated Pt nanoparticles were employed as precursors to heterogeneous catalysts. CO oxidation catalysis and in situ infrared spectroscopy were used to evaluate conditions for dendrimer removal. Infrared spectroscopy showed that PAMAM dendrimer amide bonds begin decomposing at temperatures as low as 75 °C. Although the amide stretches are completely removed after 3 h of oxidation at 300 °C, 16 h were required to reach maximum catalytic activity. Further treatment under oxidizing or reducing atmospheres did not cause substantial changes in activity. Infrared spectroscopy of the activated materials indicated that organic residues, probably surface carboxylates, are formed during oxidation. These surface species passivate the Pt NPs, and their removal was required to fully activate the catalyst. Substantially less forcing activation conditions were possible by employing a CO/O$_2$/He oxidation treatment. At appropriate temperatures, CO acts as a protecting group for the Pt surface, helping to prevent fouling of the nanoparticle by organic residues. CO oxidation catalysis and infrared spectroscopy of adsorbed CO indicated that the low temperature activation treatment yielded supported nanoparticles that were substantially similar to those prepared with more forcing conditions.

Introduction

　　　Finely dispersed metal nanoparticles (NPs) supported on inorganic oxide carriers, a mainstay of commercial heterogeneous catalysts, are employed in numerous industrial reactions,[1] automotive catalytic converters,[2,3] and fuel cell technologies.[2,4] Industrial heterogeneous catalysts and laboratory-scale model catalysts are commonly prepared by first impregnating the pores of an oxide support with simple transition metal complexes such as metal chlorides. Catalytically active metal nanoparticles are subsequently prepared through a series of high-temperature calcination and/or reduction steps. These methods are relatively inexpensive and can be readily applied to numerous metals and supports. However, these methods prepare nanoparticles in situ on the support via processes that are not well-understood; consequently, there is only limited control over nanoparticle (and hence catalyst) properties. These problems, which are inherent to standard catalyst preparation techniques, are considerable drawbacks to studying and understanding reaction mechanisms on supported catalysts.[1]

　　　Recent advances in NP preparation techniques offer new opportunities for preparing supported catalysts. Polyamidoamine (PAMAM) dendrimers are particularly useful in this regard as they can be employed as nanoparticle templates and stabilizers for several catalytically important metal systems.[5,6] Through this method, mono- or bimetallic DENs can be prepared and purified in solution. After deposition onto a support, the organic

dendrimer shell can be thermally removed to yield supported NPs (Scheme 1) with known, characterizable, and reproducible synthetic histories. The dendrimer route also avoids the deposition of ions (e.g., K$^+$, Cl$^-$) that may affect the surface chemistry of the ultimate catalyst.

　　　DENs are active catalysts for a number of reactions in both aqueous and nonaqueous media.[6] Supported or immobilized DENs can also be active catalysts or electrocatalysts, provided an appropriate solvent is present.[6,7] In the absence of a solvent, however, supported, intact DENs are inactive catalysts and do not bind CO. Upon drying, the organic dendrimer apparently collapses onto the NP, poisoning the metal surface.[7–9]

　　　Several groups have now reported on using DENs to prepare supported Pt,[8–12] Pd,[13,14] Au,[10,14] Ru,[15] Fe,[16] Cu,[17] Pt–Au,[10] and Pd–Au[18] catalysts using a variety of activation protocols. The identification of appropriately mild activation conditions remains an important issue for these studies, particularly if catalytic properties of the resulting materials are to be correlated with solution

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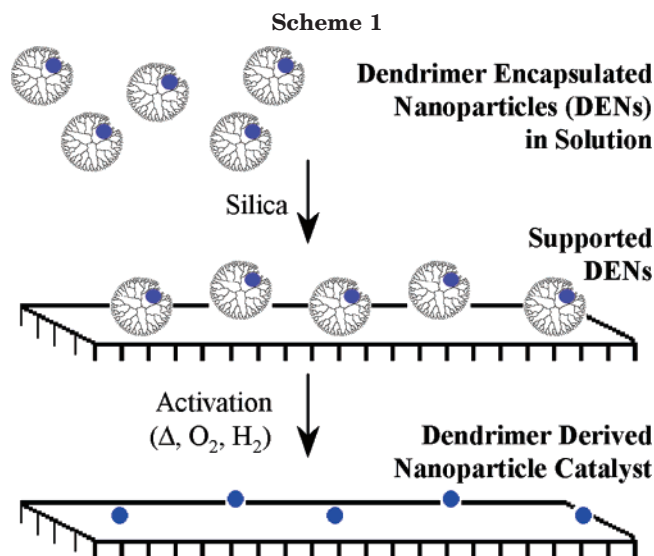　　　(14) Scott, R. W. J.; Wilson, O. M.; Crooks, R. M. *Chem. Mater.* **2004**, *16*, 5682–5688.
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Scheme 1

syntheses. Ideal activation conditions should be forcing enough to remove or passivate the organic material, yet mild enough not to induce particle agglomeration. Surface particle agglomeration or sintering processes are extremely temperature dependent,[19,20] so minimizing the activation temperature is an especially important consideration.

Previous Dendrimer Thermolysis Studies. Initial work with Pd DENs deposited onto mica highlights the importance of carefully determining decomposition protocols as even a short (10 min) treatment at high temperature (630 °C) caused widespread particle growth.[13] Further studies employed in situ infrared spectroscopy, thermogravimetric analysis (TGA), and mass spectrometry to follow dendrimer decomposition and to identify appropriate activation conditions. Crooks and co-workers used TGA to show that temperatures near 500 °C are required to completely remove organic material from Pd, Au, and Pd−Au DENs immobilized in porous sol−gel TiO$_2$.[14,18] This treatment resulted in substantial particle agglomeration, although pore templating by the dendrimer mitigated the particle growth.

In situ infrared spectroscopy has also been used to follow dendrimer decomposition and to evaluate activation conditions. Our initial studies followed the amide bond stretching frequencies while heating under various atmospheres; we subsequently evaluated metal availability with CO adsorption.[8,11] These studies showed that Pt DENs begin decomposing at relatively low temperatures (ca. 75 °C), but amide stretching frequencies were detectable after treatments with O$_2$ at 300 °C for several hours. A further treatment with H$_2$ at 300 °C was required to maximize CO adsorption for one of these samples. Elemental analysis showed no residual C or N in the resulting catalysts, although the detection limits were too high to rule out trace amounts of organic material.

More detailed studies into PAMAM dendrimer decomposition by supported Pt DENs have shown that the Pt nanoparticles play an important role in catalyzing dendrimer decomposition.[9,12] Notably, Chen and co-workers showed that, along with lower decomposition temperatures, the fragmentation patterns of organic material leaving the surface during thermolysis were substantially different when Pt particles are present in the dendrimer. Their TGA experiments showed that approximately 95%

of the organic material is removed from Pt DENs at 300 °C. Similar to results from the Crooks lab, treatments at temperatures between 300 and 500 °C were required to remove the residual organic material.

The studies described previously, including our own, generally followed some property of the dendrimer (amide stretch, mass) coupled with a subsequent probe for the metal (CO adsorption or IR of adsorbed CO, catalytic activity) to guide choices for activation conditions. In the present study, we monitored dendrimer removal by following catalytic activity as a function of pretreatment conditions. Although not generally applied as an analytical tool, catalysis is potentially useful in this regard because it directly probes the surface chemistry of metal nanoparticles and because catalytic activity is related to the number and types of exposed metal atoms. Catalysis may also be a relatively sensitive tool, requiring on the order of 10 μg of metal, depending on the efficiency of the catalyst, the temperature range studied, and the sensitivity of the monitoring equipment.

The purpose of this study was to further probe dendrimer activation with an eye toward keeping activation temperatures as low as possible. To accomplish this, we used generation 5 hydroxyl terminated (G5-OH) PAMAM dendrimers to prepare Pt nanoparticles with a 20:1 Pt/dendrimer ratio. This system represents a worst-case scenario for dendrimer thermolysis because the high dendrimer/Pt mass ratio will require the removal of a great deal of organic material by a relatively small metal surface area. We chose CO oxidation as a catalytic test reaction because Pt NPs are active for this reaction after both oxidation and reduction treatments.[8] Further, the interactions between Pt and CO can be directly probed with infrared spectroscopy, making comparisons between catalysis and characterization experiments straightforward.

Experimental Procedures

Preparation of Pt$_{20}$/SiO$_2$. Pt$_{20}$ DENs were prepared using Nanopure H$_2$O for all solutions, as previously described.[5,8] G5-OH (320 mL of 10 μM) was mixed with 27 mg of K$_2$PtCl$_4$ and stirred for 2 days. After 2 days, the flask was purged for 30 min with N$_2$, and 48 mg of NaBH$_4$ was added and stirred overnight. A total of 5 g of SiO$_2$ (DAVICAT SI-1403, 245 m²/g, supplied by W. R. Grace) was added the next day and stirred overnight. The resulting slurry was vacuum filtered using a fine frit. After drying, the Pt content was determined using AA spectroscopy.[8] The mass % Pt was determined to be 0.19, which corresponded to an overall yield of 76%.

Preparation of Pt(acac)$_2$/SiO$_2$. A total of 10 mg of Pt bis-acetonylacetonate (Aldrich) was dissolved in 1.4 mL of acetone with sonification. This solution was added dropwise to 2.5 g of DAVICAT SI-1403 silica. The impregnated silica was allowed to dry in a hood overnight, calcined at 300 °C for 4 h in flowing oxygen, and reduced at 300 °C in flowing hydrogen.

In Situ FT-IR Experiments. Spectra were collected using a Thermo Nicolet Nexus 470 spectrometer equipped with a DTGS detector with a resolution of 2 cm^{-1}. A water-cooled stainless steel IR flow cell with NaCl windows was used to hold the pressed catalyst wafer (18−20 mg). The optical bench and beam path (outside the flow cell) were continuously purged with N$_2$. A heating element wrapped around the cell with a thermocouple placed in close proximity to the catalyst sample allowed for in situ heating of samples and collection spectra at different temperatures. All gas spectra were collected with gases flowing at 60 mL/min. The gas composition was manipulated using the external manifold.

Dendrimer decomposition experiments were carried out with in situ oxidation, monitoring the 1450−1800 cm^{-1} region during heating. The catalyst wafer was dried overnight in a vacuum oven, loaded into the cell, and purged with He for 30 min. Dendrimer decomposition was monitored using two types of experiments. One experiment used the unoxidized wafer of the

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supported metal NPs pressed into a wafer as the background. Although this method is straightforward, the dendrimer decomposition corresponds to negative absorbance peaks in the spectra, and changes to the silica background at various temperatures affect the quality of the baseline. The other experiment used a pure silica wafer as the background. The pure wafer was subjected to the same in situ treatments as the catalysts, collecting background spectra at various temperatures. The clean wafer was then replaced with a fresh unoxidized supported nanoparticle wafer, and the decomposition experiments were repeated using the stored silica background files. For oxidation with O_2 or N_2O, the gas composition was 20% O_2 or N_2O, balance He. The gas composition for oxidation by CO was 1% CO, 20% O_2 (balance He).

For CO adsorption and desorption experiments, catalyst samples underwent in situ reduction (20% H_2 balance He at 300 °C for 2 h) followed by flushing with He for 1 h at 300 °C. The samples were then cooled under He flow, and a background spectrum was collected at room temperature. A 10% CO balance He mixture was then flowed over the sample for 15 min, followed by pure He. IR spectra of adsorbed CO on the surface were collected once the gas-phase CO had been removed from the cell. CO desorption was accomplished by heating the sample under flowing He.

CO Oxidation Catalysis. The feed and reactor effluent composition was monitored with a SRI 8610C gas chromatograph using a TCD detector, as described previously.[8] Catalyst samples were diluted 10:1 with α-Al_2O_3 and then activated in a tube furnace (Thermolyne) by oxidation with O_2 or CO + O_2. A total of 150 mg of the activated, diluted catalyst was then placed in a single pass plug flow microreactor. The feed composition in the reactor was 1.1% CO, 20% O_2 balance He, and the flow rate was kept constant at 27 mL/min. Conversion was measured as a function of temperature, and rate data were determined only when the conversion was below 10%.

Chemisorption. Platinum availability was determined by CO chemisorption using an Autosorb 1-C volumetric gas sorption system (AS1-C, Quantachrome Instruments). Approximately 300 mg of supported activated DENs was placed in a u-tube reactor and attached to AS1-C. The sample was placed under flowing H_2 while the sample temperature was ramped 10 °C/min to 300 °C and held at that temperature for 2 h. The sample was then evacuated at 300 °C for 1 h and cooled under vacuum to 30 °C. A CO adsorption isotherm was measured from 10 to 100 Torr. The monolayer coverage was determined by back extrapolating the linear portion of the isotherm to zero coverage. Pt dispersions ($Pt_{surface}/Pt_{total}$) were then calculated assuming a 1:1 CO/Pt stoichiometry.

Results and Discussion

Figure 1 shows activity for CO oxidation catalysis as a function of various O_2 treatments. In this experiment, the reactor was charged with catalyst, oxidized in 20% O_2 at 300 °C for 6 h, and tested for CO oxidation activity. The catalyst was then oxidized for a further 3 h at 300 °C, bringing the total oxidation time to 9 h, and again tested for CO activity. This process was repeated for total oxidation times of 6, 9, 16, 24, and 42 h. For clarity, only oxidation plots for 6, 16, and 42 h are shown in Figure 1 (an enlarged figure with all five oxidation times can be found in the Supporting Information). The reactivity data show that the catalyst activity increases until 16 h of oxidation at 300 °C. Further, even after oxidizing for 42 h, no decrease in activity was detected relative to the 16 h oxidation protocol.

In companion experiments to test the effects of reduction treatments on catalyst activation, the reactor was charged with catalyst and oxidized for 24 h at 300 °C in 20% O_2. The catalyst was then reduced in 20% H_2 at 100 °C for 1 h, tested for CO oxidation activity, rereduced in 20% H_2 at 150 °C for 1 h, and tested for CO oxidation activity. This process was repeated for 1 h reductions at 100, 150, 200, 250, and 300 °C, with a final additional reduction
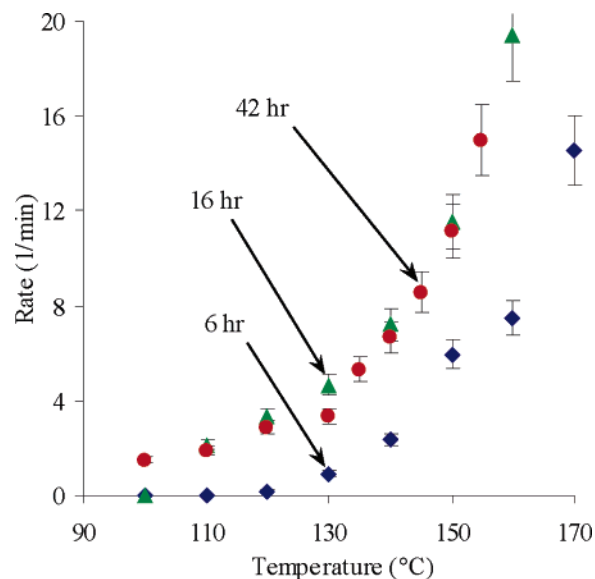

Figure 1. CO Oxidation catalysis as a function of oxidation treatments. A rate vs temperature graph following treatment with 20% O_2 at 300 °C for varying lengths of time.

time of 10 h at 300 °C (11 h total at 300 °C). CO oxidation catalysis results showed essentially no change in catalytic activity as a function of these H_2 treatments (see Supporting Information).

Figure 2a shows the disappearance of the PAMAM dendrimer amide I and II absorption bands from Pt_{20}/SiO_2 during heating in 20% O_2. The peaks appear with negative absorbance values because the unoxidized supported wafer was collected as the sample background. Experiments under an inert atmosphere (He) also show substantial loss of the amide bonds after treatment at 300 °C, although the amide bonds do not completely decompose after 4 h under He at this temperature. Experiments using a more strongly oxidizing atmosphere (20% N_2O/He) are qualitatively similar; we do not observe a significant enhancement in the decomposition rate when using this stronger oxidant.

The decomposition experiments with Pt_{20}/SiO_2 agree with IR decomposition experiments that we[8,11] and others[9,12] have reported for DENs with higher Pt/dendrimer ratios (40−100). In most of these studies, the amide peaks disappear after approximately 2 h at temperatures around 300 °C. Clearly, the amide bonds in the dendrimer backbone are relatively unstable and begin to break down at mildly elevated temperatures. The recent TGA and mass spectrometry study by Chen and co-workers using Pt DENs agrees with the IR data. Their TGA studies show that approximately 90% of the organic material is removed after treatment at 300 °C for 2 h; however, temperatures of at least 400 °C are required to remove the remaining residues.[12] They also clearly showed that Pt plays an important role in catalyzing dendrimer decomposition.[12] In studying Pd DENs immobilized in sol−gel materials, Crooks and co-workers similarly reported the onset of dendrimer mass loss at relatively low temperatures (ca. 150 °C) and that Pd helped to catalyze dendrimer decomposition. Temperatures of 500 °C or greater were required to completely remove organic residues from their materials.[14]

The catalytic activity studies reported here and previously reported dendrimer decomposition studies all point to a single conclusion: the dendrimer architecture is relatively unstable upon heating, regardless of the presence or absence of Pt and in oxidizing, reducing, or
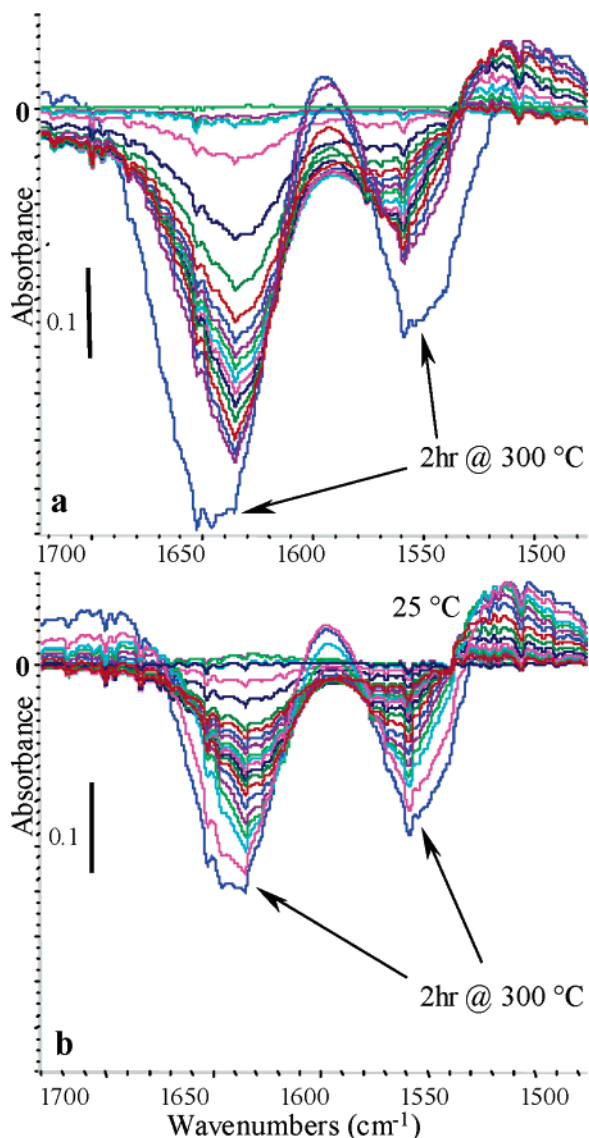
Figure 2. Dendrimer decomposition. (a) In 20% O_2 and (b) in 1% CO + 20% O_2. A wafer of the unoxidized supported DENs was collected as the background, and the temperature was increased at the same rate for each sample. Decreases in amide bands correlate with dendrimer backbone decomposition.

Figure 3. Dendrimer decomposition using a separate silica wafer as the background. As the amide bands decrease in intensity, a broad new absorption band grows in.

unreactive atmospheres. However, much more forcing conditions beyond those necessary to break down the amide bonds are required to completely activate DENs. The relative instability of PAMAM dendrimers is not surprising given the low temperatures and long reaction times generally used during dendrimer synthesis and modification.[21] Further, Bard and co-workers have shown that PAMAM dendrimers are susceptible to oxidation by molecular oxygen in solution, even in the absence of a NP catalyst.[22] The necessity of forcing activation conditions indicates that, during activation, PAMAM dendrimers are converted to other species that are difficult to remove from the surface.

Close examination of the spectra in Figure 2a shows that other changes to the surface are coincident with amide bond destruction. As the temperature increases, peaks associated with the dendrimer amide bonds (1635 and 1560 cm^{-1}) shift slightly (to ca. 1650 and 1550 cm^{-1},

respectively), and the valley between these peaks becomes deeper. These changes indicate the formation of new surface species during calcination. Repeating this experiment using silica backgrounds collected from a separate wafer, Figure 3 shows that as the amide bonds breakdown, a new broad absorption band appears at around 1650 cm^{-1}. The species associated with this band are extremely persistent and decompose slowly at 300 °C.

While activating supported Ru DENs under H_2, Williams, Amiridis, and co-workers observed the formation of surface bands at 1560 and 1480 cm^{-1}. These bands were not readily removed at 300 °C under a reducing atmosphere and were attributed to coke-type species.[15] The surface bands that we observe occur at substantially higher wavenumbers (ca. 1650 cm^{-1}) and are not likely due to coke. Catalyst coking is often removed by high temperature oxidation, and highly unsaturated hydrocarbons, the primary components in coke, are unlikely to form under oxidizing atmospheres. Consequently, it is unlikely that coke is formed during dendrimer removal under O_2. For activation under oxidative atmospheres, the observed species are more likely to be associated with surface carboxylates. Several previous reports assign peaks in the 1700–1600 cm^{-1} region to surface carboxylates on a variety of oxides.[23–28] We additionally deposited sodium acetate, sodium formate, and sodium bicarbonate onto our silica (see Supporting Information); all of these samples exhibit IR spectra characterized by broad absorbances in the 1700–1600 cm^{-1} region. The surface species observed during dendrimer oxidation could not be unequivocally attributed to a single compound, and the broad absorption band likely arises from several oxidized surface species, as well as water adsorbed on the surface, which appears at 1640 cm^{-1}.

Strongly bound surface carboxylates formed from reaction with liquid-phase carbonyl compounds have been implicated in the deactivation of Pt/Al_2O_3 catalysts,[24] and

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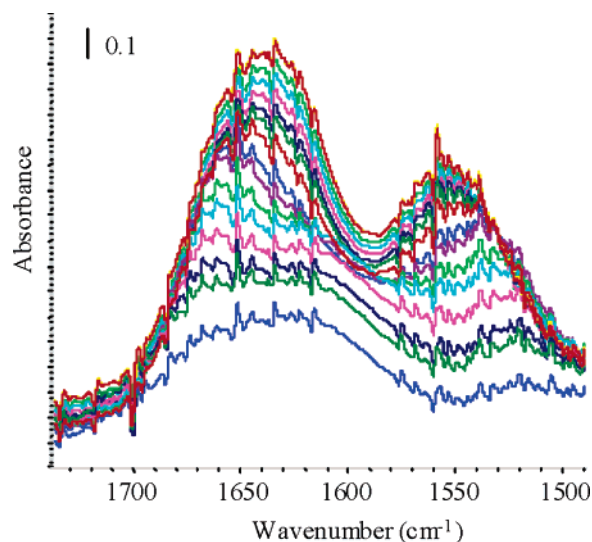(22) Lee, W. I.; Bae, Y.; Bard, A. J. *J. Am. Chem. Soc.* **2004**, *126*, 8358–8359.
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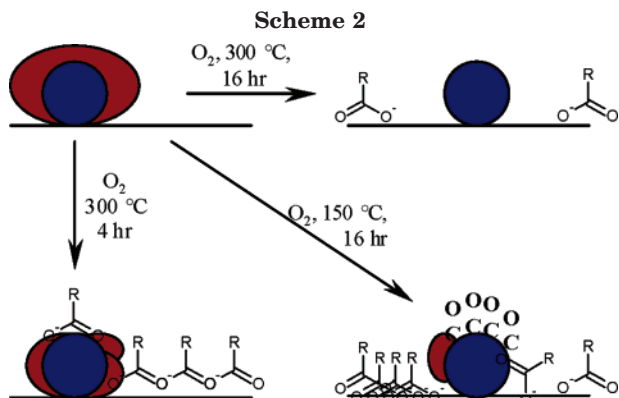(24) Marchi, A. J.; Grau, J. M.; Yori, J. C. *Appl. Catal., A* **2004**, *275*, 227–234.
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Scheme 2

Figure 4. CO oxidation catalysis as a function of oxidation treatments. A rate vs temperature graph following oxidation in 20% O_2 and in 1% CO + 20% O_2.

temperatures of 400 °C or greater are required to remove them from silica gels,[25] zeolites,[25] and Pt/Al$_2$O$_3$ catalysts.[24] The assignment of surface carboxylates is consistent with both the persistent organic species that we observe, as well as with the catalyst poisoning that coincides with those species. At the same time, the poisoning cannot be unambiguously attributed to carboxylates alone. Other surface species, possibly nitrogen containing dendrimer fragments, may be also be present, yet remain undetectable in IR experiments. Undetectable fragments might even be the dominant catalyst poisons, with the surface carboxylates predominately residing on the support. In this case, the surface carboxylates might only provide qualitative measures of the persistence of dendrimer decomposition products or of the completeness of dendrimer removal.

Using our results and the previous studies, we developed a working model for understanding the important factors involved in dendrimer thermolysis (see Scheme 2). The PAMAM dendrimer backbone reacts with oxygen (which may or may not be activated by a nanoparticle) in a relatively facile process to generate various carbonaceous species. For Pt DENs, the dendrimer decomposition products are strongly adsorbed onto the nanoparticle surface and poison catalytic activity. Complete activation of the nanoparticles requires removal of these carbonaceous species, either at a high temperature (≥ 400 °C) or possibly with extended treatment at more moderate (<300 °C) temperatures.

Given the persistence of dendrimer decomposition products, the question arises as to whether it is inherently necessary to remove all organic material to prepare clean, active supported nanoparticles. In a practical sense, carbon species from atmospheric sources are always present on oxide surfaces except when dealing with freshly calcined supports (e.g., treated overnight at 500 °C). Indeed, surface C−H stretching vibrations are readily observable in infrared spectra of supports taken directly from a manufacturer's container and appear rapidly after calcination if exposed to ambient air. The critical species are those directly adsorbed to the metal surface and in close proximity to the nanoparticles. On the basis of these insights, we thought that it might be possible to protect the metal surface during thermolysis by including strongly adsorbing small molecules in the activating atmosphere.

To test this hypothesis, we activated the supported DENs under CO oxidation catalysis conditions. Figure 2b shows the same dendrimer decomposition experiment as in Figure 2a, with the addition of 1% CO to the feed. Two differences between the experiments are readily apparent. First, the magnitude of the changes to the dendrimer amide bands is considerably smaller when CO is present, indicating that the dendrimer decomposition kinetics is
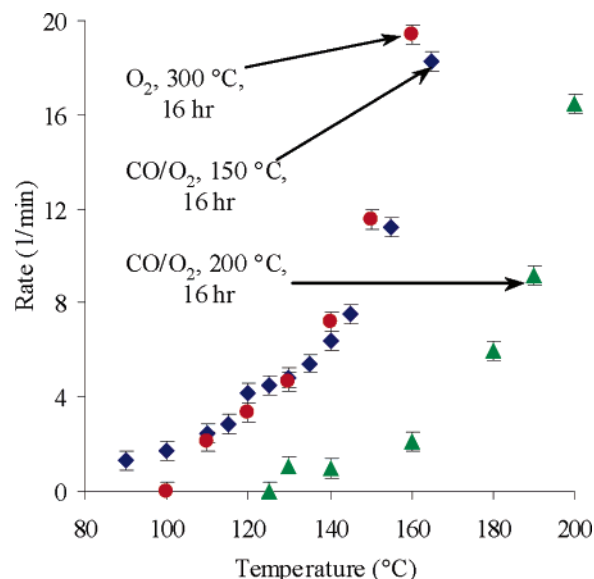
slowed by the presence of CO. This is consistent with the idea that CO binds and poisons/protects the Pt surface, simultaneously slowing or perhaps even preventing Pt from participating in dendrimer oxidation. Second, the shifts in peak maxima/minima associated with the formation of surface carboxylates are not substantially affected by the presence of CO. This indicates that carboxylates are still produced in the presence of CO and that they probably migrate onto the support.

CO oxidation catalysis results confirm the role of CO in protecting Pt nanoparticles from poisoning by dendrimer decomposition products. Figure 4 shows that the catalytic activity of Pt$_{20}$/SiO$_2$ after treatment in CO/O$_2$/He at 150 °C for 16 h (hereafter, the CO/O$_2$/150 protocol) is essentially the same as the catalyst treated at 300 °C for 16 h in 20% O$_2$/He (hereafter, the O$_2$/300 protocol). The CO/O$_2$ protocol also included an additional 2 h treatment at 300 °C with O$_2$/He to remove weakly adsorbed decomposition products. This treatment also partially dehydroxylates the silica and greatly improved reproducibility from run to run. Reduction of samples treated with the low-temperature protocol also did not increase their activity, further indicating that the majority of the surface sites was cleaned during thermolysis. The third data set in Figure 4 arises from supported DENs treated in CO/O$_2$/He at 200 °C for 16 h (+2 h at 300 °C). This catalyst is markedly less active than the other two and provides convincing evidence for the role of CO during dendrimer thermolysis at lower temperatures. At 200 °C, CO does not bind strongly to Pt surfaces and is therefore ineffective at shielding the metal from strongly adsorbing carboxylate species.

Characterization of the Activated Materials. Figure 5 shows infrared spectra of CO adsorbed on Pt$_{20}$/SiO$_2$ activated with each protocol. A spectrum of a supported Pt catalyst prepared by wetness impregnation of Pt-bis-acetonylacetonate (Pt(acac)$_2$) is also shown for comparison. This particular Pt precursor was chosen because it is a chloride free Pt source complexed only by organic ligands. The Pt(acac)$_2$ material is consistent with other Pt catalysts prepared in our labs and by others, and the full coverage stretching frequency of adsorbed CO (2085 cm^{-1}) is
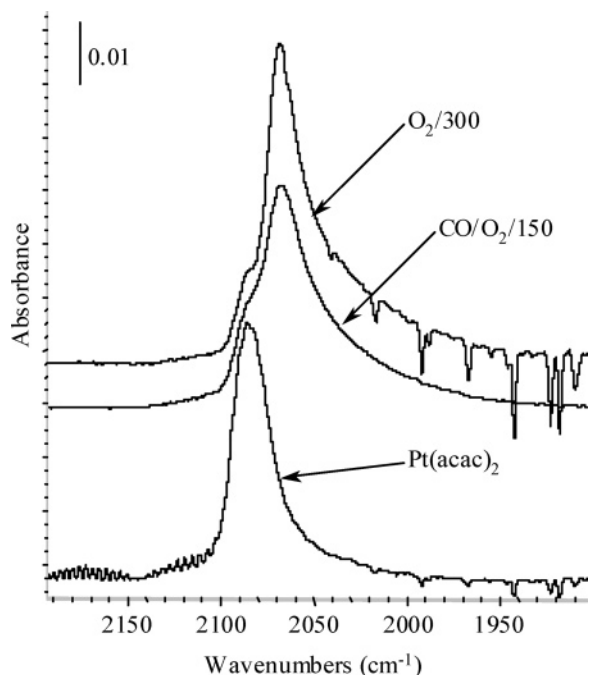
Figure 5. Infrared spectroscopy of adsorbed CO. A standard Pt(acac)$_2$ catalyst is compared to dendrimer templated catalysts activated at 300 °C in 20% O$_2$ and at 150 °C in 1% CO + 20% O$_2$.

consistent with CO adsorbed on supported Pt catalysts.[29,30] Both dendrimer templated catalysts show a primary CO absorption band at 2068 cm^{-1} with a small shoulder at 2085 cm^{-1}, although the peak for the CO/O$_2$/150 activated catalyst is somewhat smaller. Figure 6 shows CO desorption from the dendrimer templated catalysts as they were heated under flowing He. The CO desorption experiments are largely the same for both activation protocols, and both catalysts exhibit a red shift in the CO stretching frequency to 2058 cm^{-1} as CO desorbs. This 10 wavenumber shift is common for supported Pt catalysts and can be attributed to a reduction in dipole coupling as coverage decreases.[29,31]

The infrared data for the dendrimer templated materials is noteworthy in several respects. First, both dendrimer templated catalysts show slightly lower CO stretching frequencies than the traditionally prepared catalyst. Our previous results[8,10] and those reported by Williams and co-workers[9] show CO stretching frequencies between 2085 and 2075 cm^{-1} for dendrimer templated Pt catalysts. These values are comparable to the Pt(acac)$_2$ catalyst and to traditionally prepared Pt nanoparticle catalysts prepared from a variety of precursors.[29-31] The primary stretching frequency for Pt$_{20}$/SiO$_2$ occurs at 2068 cm^{-1}, with a distinguishable shoulder at 2085 cm^{-1}. The high coverage 2085 cm^{-1} band is consistent with previous assignments to terrace or face sites on extended surfaces.[29] Similarly, a number of studies loosely correlate lower CO stretching frequencies, such as the 2068 cm^{-1} band, with adsorption on the low coordination edge and corner sites that dominate small nanoparticles.[29] It is possible to roughly correlate the relative high intensity of lower energy adsorption bands to the presence of small (<2 nm) supported Pt particles;[29] however, the complexity of factors
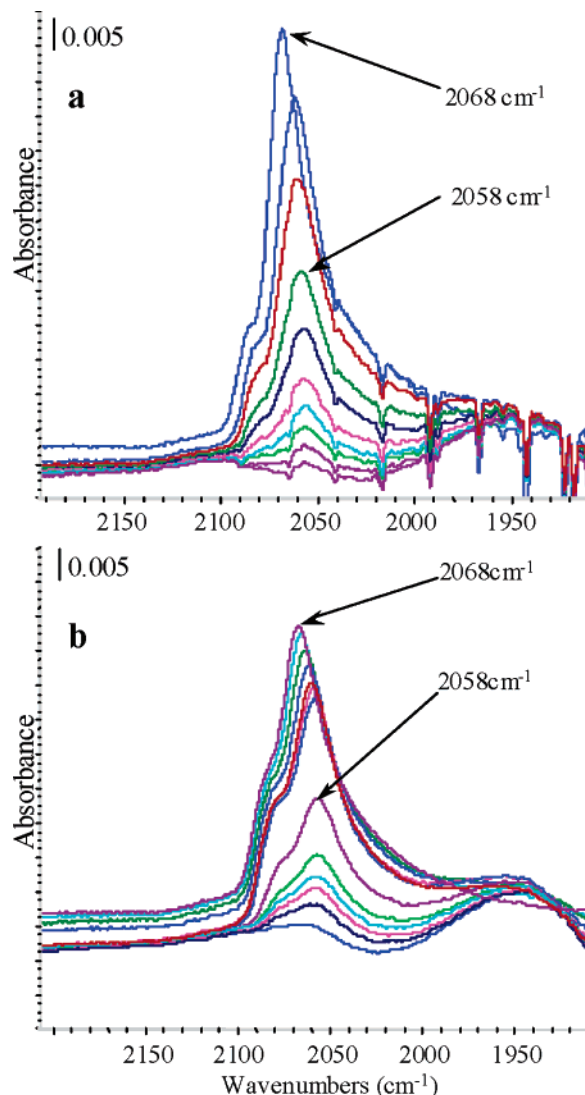
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Figure 6. CO desorption studies. Infrared spectra of adsorbed CO during heating in He atmosphere for Pt$_{20}$ activated (a) at 300 °C in 20% O$_2$ and (b) at 150 °C in 1% CO + 20% O$_2$. Temperature range shown is 20−150 °C.

affecting band intensity (intensity borrowing, dipole coupling, dephasing) makes quantitative interpretation of these bands unreliable.

Second, the peak for the CO/O$_2$/150 activated catalyst is slightly smaller than the O$_2$/300 activated catalyst. Although the CO/O$_2$/150 protocol yields a catalyst with activity similar to the O$_2$/300 protocol, the CO adsorption spectra indicate that there is slightly less available surface Pt using the CO/O$_2$/150 protocol. CO chemisorption experiments with the O$_2$/300 activated catalyst indicate a 0.51 Pt$_{surface}$/Pt$_{total}$ ratio. This value, which corresponds to an average particle diameter of 2.2 nm, is in good agreement with literature precedent for activated Pt catalysts derived from DENs.[8] CO chemisorption data for the CO/O$_2$/150 protocol is convoluted by a large reversible CO adsorption. The total CO uptake by this catalyst is comparable to the O$_2$/300 activated catalyst, but the large reversible adsorption makes quantitative interpretation of the adsorption data unreliable.

Transmission electron microscopy (TEM) studies of these samples are complicated by the difficulties in obtaining sufficient contrast with the support. This has limited our ability to reliably resolve individual particles smaller than approximately 2 nm, thus making TEM data

for these materials difficult to interpret. Qualitatively, we observe particles in the 2−4 nm range before activation, and the particle size distributions do not substantially change after either activation protocol (see Supporting Information). This is in good agreement with the chemisorption data, which inherently evaluate a much larger sample of particles than is possible through microscopy and is consistent with our studies using larger Pt/dendrimer ratios and comparable activations (O$_2$, 300 °C for 4 h followed by H$_2$ at 300 °C for 2 h).[8] The combination of chemisorption and TEM data definitively rule out the occurrence of widespread particle agglomeration during activation; however, we cannot rule out subtle changes in particle size distributions that might result from the activation procedures.

Although CO provides substantial protection for the nanoparticles during activation (treatment at temperatures where CO does not bind Pt yields inactive catalysts), the surface is apparently not as clean as the surface prepared with the more forcing oxidation. This is consistent with the difficulty in obtaining CO chemisorption data on the CO/O$_2$/150 activated catalyst, and future studies may help optimize the low temperature treatment. This result also has an important implication for the utility of CO oxidation catalysis as an analytical tool for evaluating nanoparticles. CO oxidation catalysis is useful for detecting or evaluating large differences in the availability of Pt nanoparticles and can be performed on small quantities of nanoparticles (these experiments utilized approximately 30 μg of Pt). At the same time, CO oxidation is somewhat insensitive to the more subtle differences between nanoparticle catalysts.

Conclusion

Infrared spectroscopy showed that PAMAM dendrimer architectures are unstable at temperatures as low as 75 °C. Although the amide bonds are effectively destroyed after oxidation for 2 h at 300 °C, 12−16 h of oxidation at 300 °C were required to reach maximum catalytic activity in the CO oxidation test reaction. Infrared spectroscopy also indicated that surface carboxylates (and possibly other dendrimer decomposition products) formed during dendrimer oxidation poison Pt NPs and must be removed to fully activate the catalyst. Carboxylate poisoning was substantially mitigated employing a CO/O$_2$/He treatment gas, effectively using CO as a protecting group for the Pt surface. Using this treatment gas, activation temperatures can be greatly lowered without substantially affecting the properties of the resulting nanoparticles.

Supporting Information Available: CO oxidation catalysis results as a function of reduction treatments; TEM particle size distributions; and infrared spectra of silica supported sodium formate, sodium acetate, and sodium carbonate. This material is available free of charge via the Internet at http://pubs.acs.org.

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