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Dendrimer templates for supported Au catalysts

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Abstract

Dendrimer templated thiol stabilized gold nanoparticles were evaluated as potential precursors for supported gold catalysts. Gold nanoparticles were prepared in hydroxyl- or alkyl-terminated polyamidoamine dendrimers. The nanoparticles were then extracted from the dendrimer interior with an appropriate hydrophilic or hydrophobic thiol. After deposition onto commercial titania, a variety of conditions were evaluated for removing the thiols. Desorption under nitrogen flows was most appropriate for alkyl thiols, whereas a hydrogen in nitrogen treatment gave the best results for amide containing thiols. CO oxidation catalysis by the resulting supported nanoparticles compared favorably with a standard gold test catalyst.

Keywords: Gold; Nanoparticle; Dendrimer

1. Introduction

Evidenced by the Au 2006 Conference and the preparation of this and other journal issues dedicated to the subject, catalysis by gold is an area of considerable scientific exploration. The science of Au catalysis has progressed substantially over the last 10 years, particularly with respect to developing preparation methods for synthesizing Au catalysts [1–5]. In spite of these advances, the preparation of supported gold catalysts remains a critical issue in the field. Catalyst activity strongly depends on details of the preparation method, and lab to lab reproducibility, although vastly improved over the past several years, remains a concern [1,2]. Even with the standard method for preparing supported Au catalysts (deposition–precipitation), it is not clear exactly what species are involved during the critical deposition procedure. Similarly, it remains unclear how the interactions between these species and the support may change from one oxide to the next [1–6]. Further, even ppm levels of chloride, which may remain after washing steps, act as severe poisons for Au catalysts [7].

One of the difficulties in studying catalysis by gold has been the lack of model catalysts that can be prepared under controlled conditions. Deposition–precipitation methods on high-surface area materials are not necessarily appropriate for low surface area model catalysts; similarly, UHV sputtering techniques cannot be readily applied to porous oxides. It is therefore desirable to develop new methods for preparing model Au catalysts. A variety of new solution nanoparticle preparation techniques offers opportunities for exploring preparative routes to supported Au nanoparticles. The Brust method, for example, reduces organic solutions of Au salts in the presence of an alkyl thiol [8,9]. This synthetic procedure, which can be used to prepare Au nanoparticles on the order of tens to hundreds of atoms, has been recently employed by Corma and coworkers to study the selective hydrogenation of nitroaromatics and selective alcohol oxidation [10,11]. An alternate means of preparing size-controlled Au nanoparticles utilizes polyamidoamine (PAMAM) dendrimers as nanoparticle templates [12,13].

Scheme 1 shows the general methodology for preparing heterogeneous catalysts from nanoparticle precursors. The primary advantage of using molecular or colloidal precursors is that particle preparation is separated from surface transport and mobility processes that are notoriously difficult to control. Beyond substantial potential advantages in reproducibility, this also allows for particles prepared by the same methods, or even in the same batch, to be deposited onto different substrates (e.g. various high-surface area oxide for studying support effects, or well defined substrates for surface science).

There are a number of important issues that must be addressed before nanoparticle precursors can be used to study

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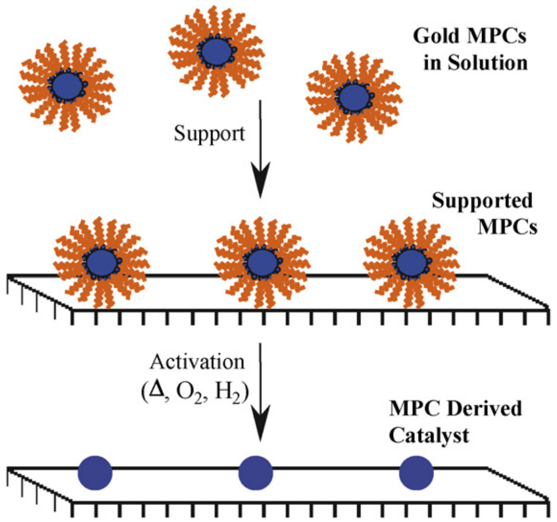


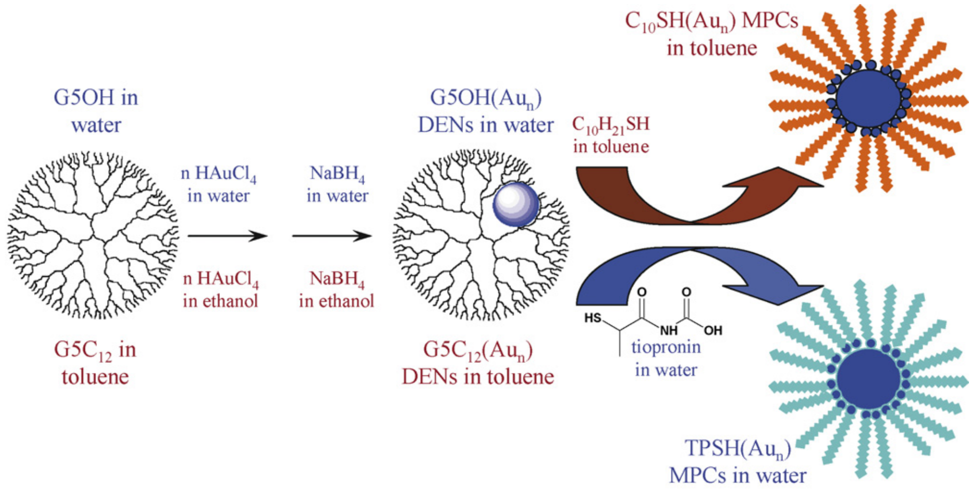
Scheme 1. Catalyst preparation.

heterogeneous catalysts. Primarily, appropriate activation conditions for removing the colloid stabilizers must be evaluated. Ideal activation protocols will be forcing enough to remove the organic stabilizers, yet not so forcing to cause widespread particle agglomeration. The following manuscript briefly reviews dendrimer-mediated synthetic routes to Au nanoparticles and reports on a proof of concept for applying this method to the preparation of highly active supported gold catalysts.

2. Dendrimer templates for gold nanoparticles: a brief review

Polyamidoamine (PAMAM) dendrimers, which are large, hyperbranched polymers that ramify from a single core [14,15], can also be used to template and stabilize metal nanoparticles in solution [12,13]. The macromolecular structure of the dendrimer consists of a closed but porous peripheral shell and a relatively open interior. This structural motif is well suited to trapping nanoparticles, which can be assembled within the interior cavity. The general synthetic protocol, shown in Scheme 2, involves intercalating metal complexes into the interior cavity of a PAMAM dendrimer, followed by reaction with a reducing agent such as H_2 or $NaBH_4$. The ability to precisely control metal:dendrimer stoichiometries allows for substantial control over critical nanoparticle properties such as particle size and composition. This synthetic procedure has been applied to a wide variety of mono- and bimetallic nanoparticles, including mixtures of: Au, Ag, Cu, Pt, Pd, Rh, and Ru [12,13]. These dendrimer encapsulated nanoparticles (DENs) can be active homogeneous catalysts and have been employed in a variety of hydrogenation and carbon–carbon coupling reactions [12,13].

Because they offer substantial control over particle size and composition for nanoparticles in the 1–5 nm range, DENs are attractive potential precursors for supported nanoparticle catalysts. We have been developing DEN precursors for supported Au [16,17], Pt [18–21], Au–Pt [16,22], and Cu–Pt [23] catalysts. Other groups have investigated heterogeneous Au [24], Pt [25–28], Pd [24,29], Ru [30,31], and Au–Pd [32], catalysts from DENs. Dry, supported DENs are inactive catalysts. In the absence of a solvent, the organic polymer collapses onto the nanoparticle, which prevents even small molecules such as CO from accessing the nanoparticle surface [18,27]. Consequently, the organic dendrimer must be thermally removed to prepare catalysts from DENs. Each dendrimer is essentially a single molecule weighing on the order of 30 kDa, so relatively forcing conditions (such as 6 h oxidation and reduction treatments at 300 °C) are required to remove this large mass of organic material [13]. PAMAM dendrimers are unstable under even moderate temperatures [18]; the difficulties involved in preparing active catalysts center around the decomposition by-products (carboxylates, etc.), which also serve as poisons for nanoparticle surfaces [20]. For platinum DENs, low temperature (150 °C) activation conditions are available when CO is used to protect the nanoparticle surface from non-volatile dendrimer decomposition products [20].



Scheme 2. Synthesis and extraction.

Previous studies with Au DENs have been less successful. When high temperature activation protocols have been applied to supported Au/silica DENs, widespread sintering has resulted [16]. Au/titania catalysts have also been prepared using a sol–gel synthesis in which the dendrimer helped template both the nanoparticle and the support pore structure. This helps to prevent Au sintering on titania, but has not been shown to yield highly active Au catalysts [24]. Sintering can be substantially prevented by employing bimetallic Au–Pt DENs, in which Pt helps to anchor Au to the oxide surface. These bimetallic catalysts show good ambient-temperature CO oxidation activity that was attributed to catalysis by gold or possibly gold-based bimetallic sites [16].

Comparable high temperature studies have not been employed with Au/titania catalysts, but the risks of sintering and possible strong metal–support interactions make it unlikely that such harsh treatments will be appropriate for monometallic Au catalysts. Low temperature activation protocols using CO/O_2 mixtures have also been used to activate Au DENs supported on P25 titania [17]. These results were initially encouraging as the catalysts showed excellent batch-to-batch reproducibility (Batch A versus Batch B in Fig. 1). However, aging of the supported DENs and even the activated catalysts (which still contain large amounts of organic material) led to loss of activity over time [17].

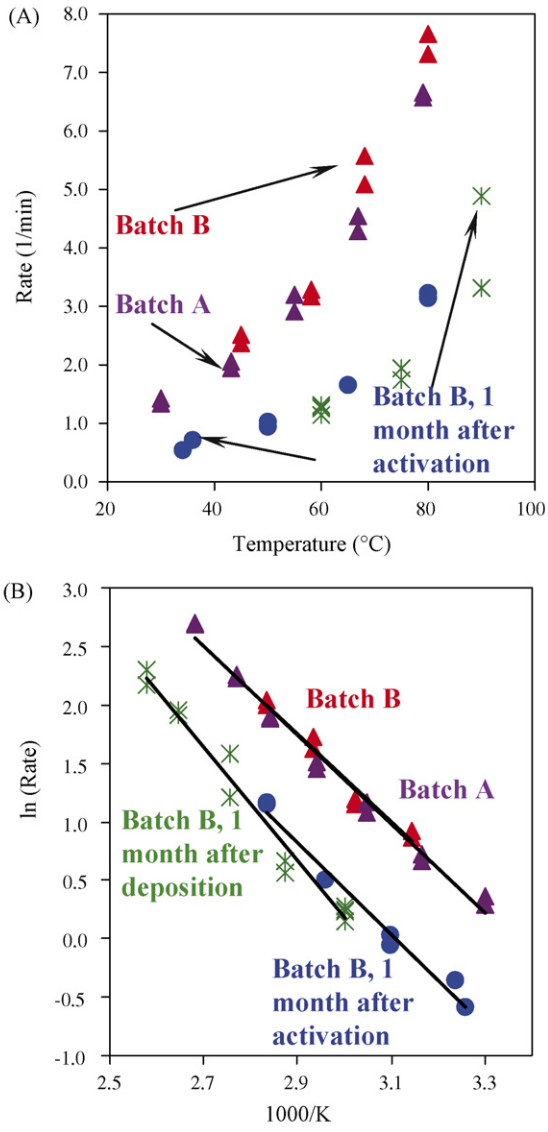


Fig. 1. (A) Rate vs. temperature plots and (B) Arrhenius plots for CO oxidation by Au/TiO_2 catalysts prepared from G5OH(Au_{55}) DENs. Catalysts were activated under $CO + O_2$ at 150 °C for 24 h. Reprinted from [40].

Based on these studies, the direct decomposition of Au DENs does not appear to be a suitable means of preparing supported Au catalysts. In 2004, however, Crooks and coworkers showed that Au nanoparticles could be extracted from aqueous hydroxyl-terminated PAMAM dendrimers into organic solution using long chain alkyl thiols (see Scheme 2) [33]. A subsequent report from Crooks' group showed that water soluble MPCs can be prepared in the same fashion using hydrophobic dendrimers and a water soluble thiol [34]. The resulting nanoparticles have been termed monolayer protected clusters (MPCs), as is the convention for nanoparticles prepared by the Brust method. Based on these reports, we set out to explore synthetic strategies for preparing supported Au catalysts from dendrimer templated MPCs.

3. Experimental

3.1. Aqueous DEN synthesis

Aqueous Au dendrimer encapsulated nanoparticles (DENs) were prepared according to the literature procedure [35]. Briefly, an aqueous solution of hydroxyl-terminated, fifth-generation polyamidoamine (PAMAM) dendrimer (G5OH, 35 mL, 2.11 μM) was mixed with an aqueous solution of $HAuCl_4$ (1.1 mL, 3.59 mM, 55:1 Au:G5OH molar ratio). After stirring for 2 min, excess $NaBH_4$ in 0.1 M NaOH was added to form G5OH(Au_{55}) DENs. G5OH(Au_{147}) DENs were prepared similarly adjusting the Au:G5OH to 147:1.

3.2. Synthesis and purification of hydrophobic MPCs

Nanoparticle extractions from aqueous DENs into toluene were carried out according to literature procedures using DEN volumes no greater than 60 mL [33]. An excess of $NaBH_4$ was added to the aqueous Au DEN solution to ensure the nanoparticles were fully reduced. An equal volume of toluene with a 125 M excess decanethiol was then added to the aqueous DENs solution and shaken in a separatory funnel for 5 min. The resulting microemulsion was allowed to settle until the phases completely separated. The $C_{10}S(Au_{55})$ or $C_{10}S(Au_{147})$ MPCs were purified by concentrating to 1 mL, precipitating with 15 mL ethanol, and centrifuging for 20 min. The ethanol was decanted and the remaining MPCs were redissolved in 5 mL hexanes, precipitated and centrifuged for a second time, and finally redissolved in hexanes or toluene.

3.3. Deposition of hydrophobic MPCs

The purified $C_{10}S(Au_{55})$ MPCs were redissolved in 0.16 mL hexanes and dropped on 100 mg TiO_2 to achieve a 0.4% weight loading. Likewise, the $C_{10}S(Au_{147})$ MPCs were redissolved in 0.8 mL hexanes and deposited on 500 mg TiO_2 to achieve a weight loading near 1.0% (actual loading determined by AA spectroscopy). These loadings were chosen to have a similar total number of nanoparticles on the support surface.

3.4. Organic DEN synthesis

Hydrophobic Au DENs were prepared according to the literature procedure [36]. Briefly, a toluene solution of dodecane-terminated, fifth-generation PAMAM dendrimer ($G5C_{12}$, 31 mL, 2.38 μM) was mixed with an ethanolic solution of $HAuCl_4$ (1.1 mL, 3.65 mM, 55:1 Au:$G5C_{12}$ molar ratio). The solution was stirred for 20 min, and reduced with an excess of $NaBH_4$ in methanol to form $G5C_{12}(Au_{55})$ DENs. $G5C_{12}(Au_{147})$ DENs were similarly adjusting the Au:G5OH to 147:1.

3.5. Synthesis and purification of aqueous MPCs

Aqueous MPCs were prepared from $G5C_{12}(Au_n)$ DENs using *N*-(2-mercaptopropionyl)glycine (tiopronin) [34]. A volume of tiopronin (125 mole excess) in 2 M HCl was mixed with an equal volume of freshly prepared $G5C_{12}(Au_n)$ DENs solution. The solutions were shaken in a separatory funnel for 5 min and the phases were allowed to separate. The subsequent aqueous phase with the $_{TP}S(Au_{55})$ or $_{TP}S(Au_{147})$ MPCs were dialyzed against 0.5 L of H_2O for 4 h with Spectra/Por Dialysis Membrane (MWCO: 6-8000). To deposit the $_{TP}S(Au_{55})$ MPCs, the dialyzed aqueous MPC solution was transferred to a beaker and stirred with 100 mg TiO_2 for 4–6 h to achieve a 0.4% weight loading. The $_{TP}S(Au_{147})$ MPCs were added to 100 mg TiO_2 to achieve a 1.0% weight loading.

3.6. Spectroscopy

UV–vis spectra were collected at ambient temperature with a Jasco-V-530 UV–vis spectrophotometer using quartz cuvettes with a path length of 1.00 cm. Infrared spectra were collected with a Thermo Nicolet Nexus 470 spectrometer equipped with a DTGS detector using a resolution of 4 cm^{-1}. The titania supporting the MPCs was pressed into a pellet (35–55 mg) and heated inside a stainless steel IR flow cell with NaCl windows, as described previously [16]. The cell has a heating unit and

Table 1
Nomenclature for gold dendrimer encapsulated nanoparticles (DENs) and extracted monolayer protected clusters (MPCs)

Dendrimer	Metal:dendrimer stoichiometry	DEN abbreviaton	Extraction thiol	MPC abbreviation
G5OH	55	$G5OH(Au_{55})$[a]	Decanethiol	$C_{10}(Au_{55})$[b]
G5OH	147	$G5OH(Au_{147})$[a]	Decanethiol	$C_{10}(Au_{55})$[b]
$G5C_{12}$	55	$G5C_{12}(Au_{55})$[b]	Tiopronin	$_{TP}S(Au_{55})$[a]
$G5C_{12}$	147	$G5C_{12}(Au_{147})$[b]	Tiopronin	$_{TP}S(Au_{147})$[a]

[a] Aqueous solution.
[b] Toluene solution.

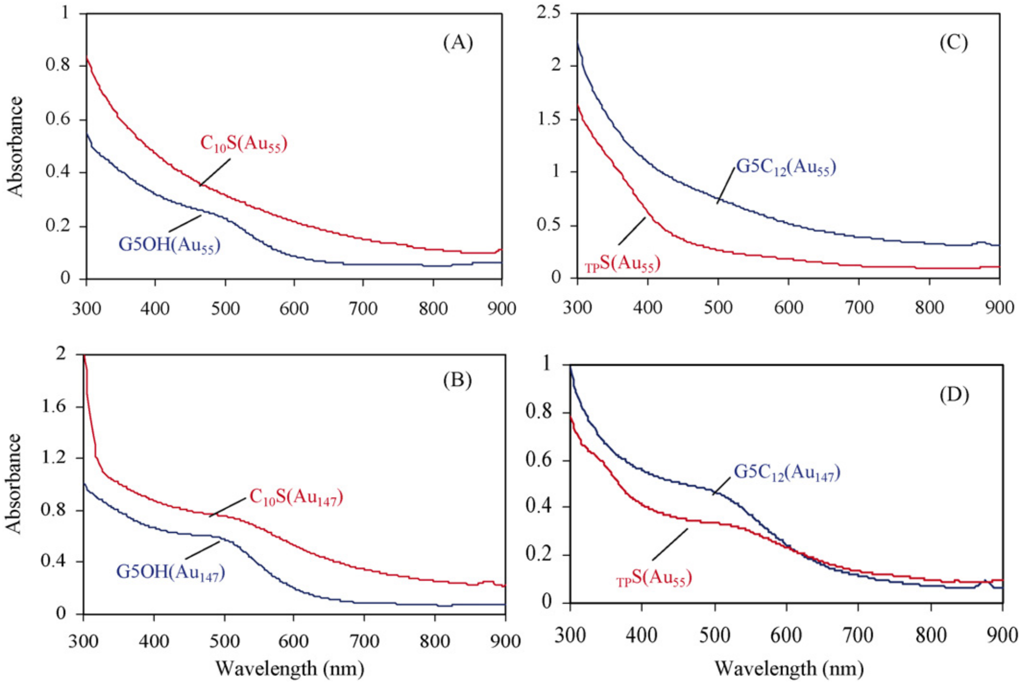


Fig. 2. UV–vis spectra of Au_{55} and Au_{147} DENs and MPCs.

thermocouple close to the pellet to monitor the temperature while collecting spectra.

3.7. CO oxidation catalysis

Details of the CO oxidation reactor system have been previously reported [18]. Catalysts were diluted with α-Al_2O_3 (1000:1 by mass) prior to catalysis experiments. Diluted catalyst masses were adjusted so that 5 μg Au were present for each experiment. Both catalysts were treated with 20% O_2/N_2 at 250 °C for 30 min immediately prior to catalyst testing; the MPC catalyst had previously been treated at 300 °C under flowing nitrogen for 2 h to desorb the alkyl thiol. The feed composition (1.1% CO, 27% O_2 balance He) and the total flow rate (20 mL/min) were kept constant during all experiments.

4. Results and discussion

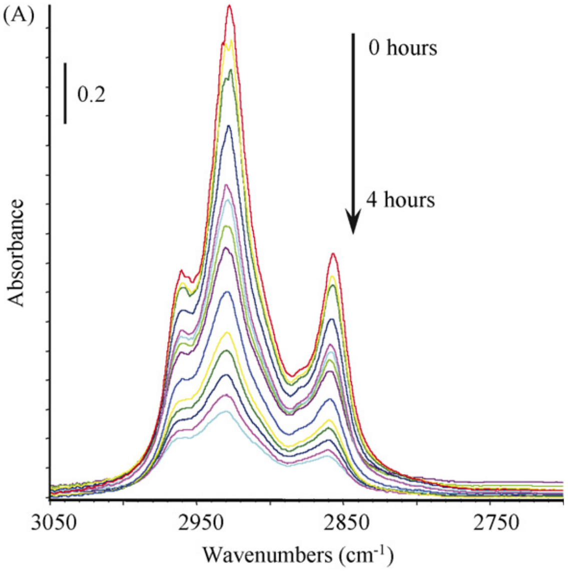
Using appropriate DENs and thiols, nanoparticles can be extracted from PAMAM dendrimers into either aqueous or organic solution as monolayer protected clusters (MPCs) without detectable agglomeration [37]. The synthetic procedures for preparing aqueous and hydrophobic DENs and MPCs are outlined in Scheme 2. $AuCl_4^-$ ions are first intercalated into the interior cavity of a PAMAM dendrimer and reduced with borohydride. Extraction with an appropriate thiol yields the MPCs and metal free dendrimer. These syntheses allow for substantial control over particle size while maintaining very narrow particle size distributions. For example, Au_{55} and Au_{147} DENs have been previously characterized to have 1.3 ± 0.3 and 1.6 ± 0.3 nm particles (errors are standard deviations from Gaussian distributions) [33,36]. Extracted MPC particle size distributions are not measurably different [33,34].

In this study, we evaluated the viability of both aqueous tiopronin-stabilized MPCs and hydrophobic alkane thiol stabilized MPCs as potential precursors for supported Au catalysts. We examined two nanoparticle sizes (Au_{55} and Au_{147}); the nomenclature system for all of the DENs and MPCs is summarized in Table 1. All of these DENs and MPCs have been previously characterized by UV–visible spectroscopy (UV–vis) and high resolution transmission electron spectroscopy (HRTEM) [33,34].

Fig. 2 shows representative UV–visible spectra of aqueous or toluene solutions of the DENs and MPCs in this study. All the spectra show the steady increase in absorbance with decreasing wavelength that is characteristic of Rayleigh scattering by nanoparticles in solution. An additional weak absorption band appears as a shoulder for the (Au_{147}) DENs and MPCs. This is the surface plasmon band that results from a concerted oscillation of Au electrons within the nanoparticle [38]. These bands are sensitive to the size, shape, and morphology of Au nanoparticles; they have high extinction coefficients, but do not arise on particles smaller than 2 nm in diameter. The absence of the plasmon band in the (Au_{55}) MPCs and the weak absorbance observed in the (Au_{147}) MPCs are consistent with published spectra for these materials.

Tiopronin-stabilized MPCs were readily deposited onto P-25 titania by stirring the MPC solution with the support for several hours. The alkyl thiol stabilized MPCs did not spontaneously adsorb onto the support after 24 h of stirring. A variety of organic solvents and solvent mixtures were evaluated (toluene, hexane, ethanol, ethyl acetate), but spontaneous adsorption of the hydrophobic MPCs was never observed. In order to prevent deposition of large quantities of thiol used in the extraction, the MPCs were then purified with two ethanol precipitation/centrifugation cycles. The hydrophobic alkyl thiol MPCs were then deposited via impregnation using a hexane solution.

A variety of conditions for removing the thiols were examined using transmission infrared spectroscopy. Fig. 3 shows IR spectra for titania supported $C_{10}S(Au_{55})$ MPCs heated to 160 °C in a 20% O_2/He atmosphere. The C–H stretching region, shown in the top portion of the figure, shows that the alkyl groups disappear over approximately 4 h. At the same



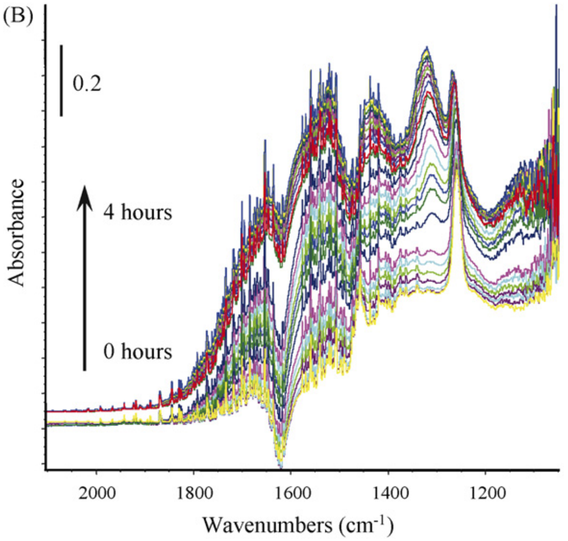


Fig. 3. Infrared spectra of titania supported $C_{10}S(Au_{55})$ MPCs heated to 160 °C for 4 h in a 20% O_2/He atmosphere.

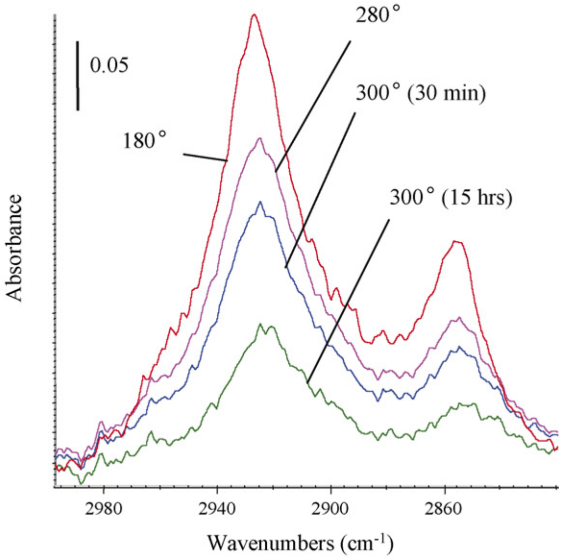


Fig. 4. Infrared spectra of the C–H stretching region for titania supported $C_{10}S(Au_{55})$ MPCs heated under hydrogen.

time, the bottom portion of the figure shows that a number of new bands grow in between 1800 and 1200 cm^{-1}. This experiment shows that the catalyst surface changes substantially during oxidation treatment. A variety of surface oxygenates (e.g. sulfates, carbonates, formates, etc.) have stretching frequencies in this region, so we do not attempt to make detailed assignments based on this data. Similarly, we did not further investigate thiol removal under oxidative atmospheres due to concerns over the appearance of these new surface species.

Figs. 4 and 5 show IR spectra of the C–H stretching region for titania supported $C_{10}S(Au_{55})$ MPCs heated under hydrogen and nitrogen, respectively. Both of these experiments indicate that thiol removal begins at or slightly below 300 °C, in good agreement with TGA experiments on MPCs monolayers [39]. Thiol removal was substantially faster under the heavier treatment gas, suggesting that thiol removal primarily occurs through a simple desorption. No significant changes were observed in the 1800–1200 cm^{-1} region during either activation protocol.

Fig. 6 shows IR spectra for titania supported $_{TP}S(Au_{55})$ MPCs heated under a nitrogen atmosphere. Both the C–H stretching vibrations shown in the top portion of the figure and the weak amide vibrations shown at the bottom have largely disappeared after approximately 4 h at 300 °C. At the same time, a broad band appears to grow in at around 1580 cm^{-1}. Studies with DENs indicate that amide bonds are relatively unstable at these temperatures, but that they decompose into relatively nonvolatile oxygenates that can poison nanoparticle catalysts [18,20]. Although the magnitude of the 1580 cm^{-1} band in Fig. 6 is substantially smaller than similar bands for supported DENs, its appearance suggests that the surface species may be of concern for MPC based catalysts activated under N_2.

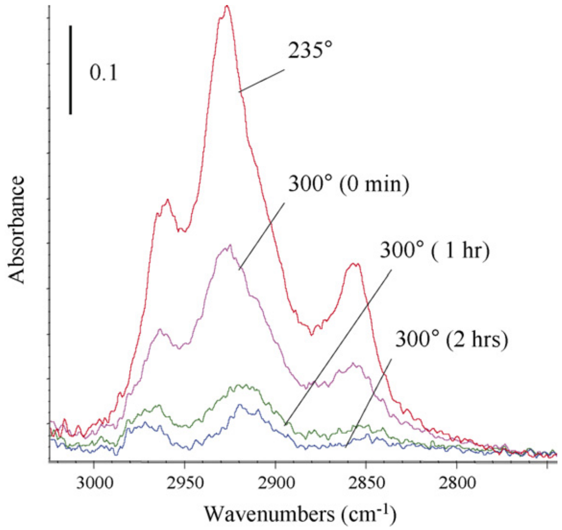


Fig. 5. Infrared spectra of the C–H stretching region for titania supported $C_{10}S(Au_{55})$ MPCs heated under nitrogen.

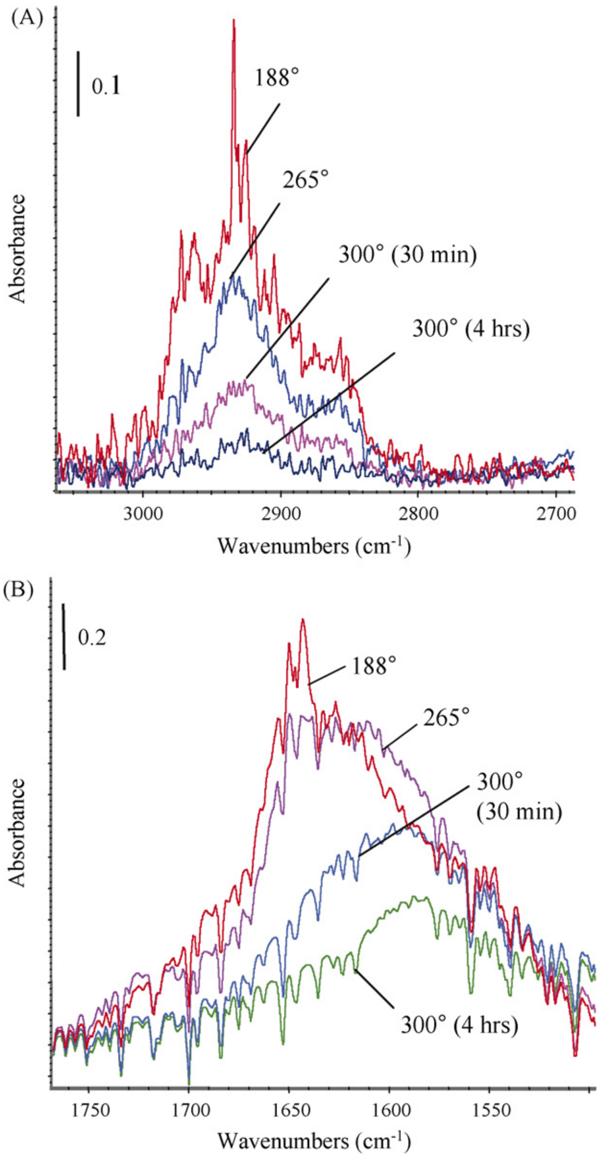


Fig. 6. Infrared spectra of titania supported $_{TP}S(Au_{55})$ MPCs heated under a nitrogen atmosphere.

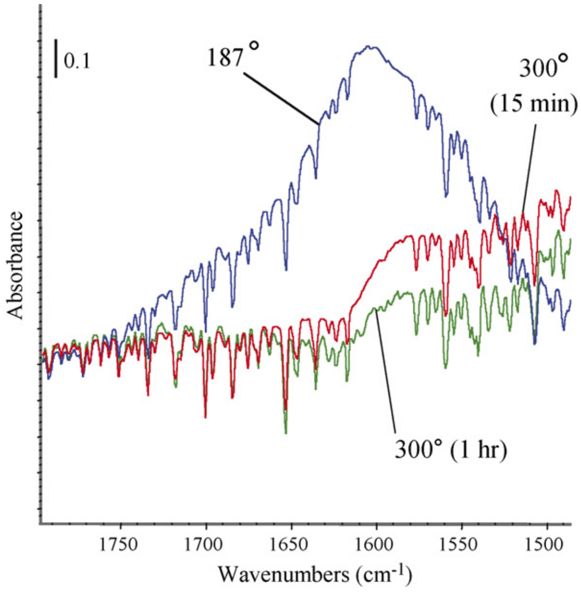


Fig. 7. Infrared spectra of the amide region for titania supported $_{\mathrm{TP}}\mathrm{S(Au_{55})}$ MPCs heated under 20% H_2/N_2.

To evaluate tiopronin removal under a reducing atmosphere, a 20% H_2/N_2 mixture was used. Nitrogen was used to dilute the reducing gas and to serve as a heavier carrier gas to facilitate desorption of the tiopronin or the reduced fragments originating from the thiol. As Fig. 7 shows, the amide region stretching frequencies diminish somewhat more quickly for the H_2/N_2 mixture than the pure N_2 treatment. More importantly, there is very little growth of additional bands in this region.

To show that the supported MPCs are potential precursors for supported catalysts, we compared a catalyst derived from $C_{10}S(Au_{55})$ MPCs to the World Gold Council Au/P25 titania test catalyst (WGC). The WGC catalyst was treated in 20% O_2/N_2 at 250 °C for 30 min, according to the procedure provided with the catalyst. The titania supported $C_{10}S(Au_{55})$ MPCs sample was treated at 300 °C under flowing nitrogen for 2 h to desorb the alkyl thiol. The resulting catalyst was then oxidized in 20% O_2/N_2 at 250 °C for 30 min in order to ensure that the two catalysts are compared under comparable conditions. As Fig. 8 shows, the MPC catalyst showed comparable or higher activity than the WGC catalyst at the moderate temperatures evaluated. We are currently pursuing a detailed study of activation conditions and kinetic characterization of the MPC catalysts, which will be communicated in a future publication.

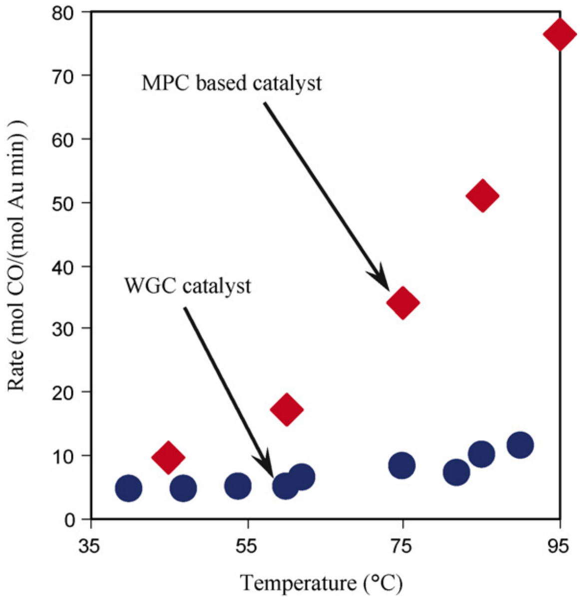


Fig. 8. CO oxidation catalysis by MPC derived catalysts compared to the World Gold Council standard catalyst.

5. Summary

Dendrimer templated nanoparticles, extracted thiol MPCs in particular, are potentially interesting precursors for supported gold catalysts. Tiopronin-stabilized clusters spontaneously adsorb onto titania supports; alkyl thiol stabilized clusters did not adsorb and were deposited via wetness impregnation from toluene solution. Alkyl thiols are readily removed at 300 °C with flowing nitrogen. For tiopronin, the addition of a small amount of hydrogen to the nitrogen feed produced the most favorable activation conditions. CO oxidation catalysis by the activated MPCs compared favorably with the World Gold Council test catalyst, indicating that the MPCs are viable precursors for studying catalysis by gold.

Acknowledgments

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