7

Dendrimer Templates for Supported Nanoparticle Catalysts

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7.1. INTRODUCTION

Catalysis has a tremendous impact on the national economy as one-third of material U.S. GNP involves a catalytic process somewhere in the production chain.[1] Catalytic technologies are well established throughout the economy, particularly in petroleum refining, emissions and pollution control (including energy production), polymers and plastics, pharmaceuticals and fine chemicals, and basic chemicals.[2] The utilization of heterogeneous catalysts in these areas of chemical industry is certain to increase as environmental and economic pressures drive the movement toward clean, selective chemical processes.[2] Similarly, developing new catalysts for more efficient, cost-effective processes will be especially important for growing industries involved in the potential development of a hydrogen economy.[3,4]

An important class of industrial catalysts consists of an active component dispersed in the form of very small particles over high surface area solids.[5] As the field of industrial heterogeneous catalysis has developed, catalyst formulations have evolved such that state-of-the-art catalysts often contain two or more metals and/or main group elements. The additives may promote a desired reaction, prevent undesirable side reactions, or enhance catalyst longevity.[5−7] Bimetallic nanoparticle catalysts in particular are widely

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employed in industry and will similarly be vital to the success and economic viability of hydrogen energy technologies,[8] particularly fuel cells and hydrogen production from photochemical and biorenewable resources.[3,4]

7.1.1. Traditional Routes to Supported Metal Nanoparticle Catalysts

In spite of the commercial importance of bimetallic catalysts, catalyst formulations, particularly the active sites or phases, are not necessarily well characterized or well understood. This is particularly true for bimetallic catalysts, largely due to the difficulties associated with preparing, characterizing, and proving the presence and activity of well-defined supported bimetallic nanoparticles. Traditional preparative routes involve impregnating metal salts (typically inexpensive chloride complexes) onto high surface area supports, followed by various thermal activation steps.[9] Most important industrial supports can also be employed as separation media; consequently, chromatographic separation of salt precursors as they pass through the support pore structure is unavoidable. Further, nanoparticle preparation via traditional routes depends on the surface and even gas phase mobility of the species present during the thermal treatments.[5,6] These processes vary widely for different metals and are poorly understood, at best.[5,6] Metal salt precursors also introduce ions (K^+, Cl^-) which may inadvertently affect catalyst properties or have deleterious effects on catalyst performance.[10−12]

These *in situ* particle preparation methods offer little control over critical catalyst properties such as particle size and composition. Because the properties of individual particles often vary widely within a given sample, the study of structure–activity relationships is difficult at best. The reliance on these methods also has significant drawbacks in terms of catalyst reproducibility. As pointed out by Ponec and Bond, the "lack of reproducibility of catalytic activity on a sample to sample basis using portions drawn from the same bottle is a humiliating reminder of the lack of control which we have over the complex chemistry involved" in catalyst preparation.[5] The inherent inhomogeneity in traditionally prepared bimetallic catalysts also dramatically complicates their characterization. This, in turn, poses a significant hurdle to evaluating the important features in the best catalysts, understanding how reactions occur over these materials, and learning how to control catalyst properties.

7.1.2. Molecular Clusters as Precursors to Supported Metal Catalysts

Ligand-stabilized inorganic and organometallic molecular clusters offer potential advantages over traditional methods for preparing supported bimetallic catalysts.[6] Using well-defined molecular precursors allows for the deposition of particles that are initially consistent in composition and limits the introduction of ions that may adversely affect catalyst performance. The potential for low thermolysis temperatures (e.g. for CO ligands) may also prevent particle agglomeration. Gates and coworkers have a number of excellent reviews detailing the cluster method, particularly as they pertain to preparing extremely well defined supported structures consisting of a few atoms.[6,13] Readers are directed to these reviews for details on the successes of this method; its limitations are outlined below.

Although the molecular cluster route has been known for decades, its potentials have only rarely been realized. A central problem is that under reaction conditions

a cluster is likely to lose its molecular integrity while undergoing a variety of fragmentation and agglomeration processes.[14] Although clusters have played an important role in understanding metallic bonding and selectivity in catalysis,[15] in general, they have not proven to be particularly good models for nanoparticle catalysts and are more appropriately considered as potential precursors to nanoparticle catalysts.[14] As precursors, their potential has been primarily in strict initial compositional control and the possibility of preparing nanoparticles with compositions that are not formed via traditional methods.[6]

Even as catalyst precursors, clusters have drawbacks due to inflexibility in metal stoichiometries. Metal ratios are set by cluster stoichiometry and cannot be systematically varied without an extensive cluster library. Cluster preparation is often time consuming and expensive, so such libraries are seldom available. Further, using clusters (nominally 4 to 12 atoms) to prepare nanoparticles (nominally 10 to 1000 atoms) relies on the same atom/particle mobility that plagues traditional routes, although perhaps to a lesser degree. Essentially, one must hope that cluster precursors stay intact long enough during activation to impart their precise stoichiometry to growing nanoparticles. In terms of understanding the properties of nanoparticles, this situation is less than desirable. Even worse, ligands that stabilize many noble metals often contain elements that can be severe poisons for catalysts (e.g. phosphines, arsines, S donors).[16]

7.1.3. Applying Nanotechnology to the Catalytic Sciences

Colloidal nanoparticles can be employed as heterogeneous catalyst precursors in the same fashion as molecular clusters. In many respects, colloidal nanoparticles offer opportunities to combine the best features of the traditional and cluster catalyst preparation routes to prepare uniform bimetallic catalysts with controlled particle properties. In general, colloidal metal ratios are reasonably variable and controllable. Further, the application of solution and surface characterization techniques may ultimately help correlate solution synthetic schemes to catalytic activity.

Until recently, the available colloidal nanoparticle syntheses generally prepared particles in size ranges (5+ nm) that are not of particular interest to many catalytic scientists. The recent explosion of interest in nanoparticles for nanotechnology applications has fueled the development of several new nanoparticle preparative techniques.[17−19] In some cases, careful syntheses allow control over nanoparticle size, composition, and even morphology. Several synthetic routes to colloidal nanoparticles in the 1 to 5 nm range are now becoming available. For large atoms like platinum, this size range is particularly important for catalysis as it corresponds to dispersions of 95 to 20%, respectively. This not only maximizes the fraction metal on particle surfaces, but also coincides with a transition from large particles with primarily metallic character to nanoparticles composed of tens of atoms that may have characteristics that are more molecular.

Three general preparative schemes are of particular interest due to their success in preparing nanoparticles on the order of 1 to 3 nm. The first, commonly known as the Brust method for preparing thiol stabilized Au nanoparticles, is discussed in detail in the chapter by Zhong *et al.* in Section IV of this book. The second method, which originates from Prof. El-Sayed's group, is noteworthy for preparing particles with extremely well-defined shapes (tetrahedra, cubes, etc).[20,21] The third method,

pioneered by Crooks and coworkers, involves using polyamidoamine dendrimers as nanoparticle templates and stabilizers.[19,22] The synthetic versatility of the dendrimer route to nanoparticle catalysts (see Scheme 7.1) offers substantial promise for the preparation of nanoparticles of interest to catalytic scientists and is the focus of the remainder of this chapter.

7.2. DENDRIMERS AND DENDRIMER ENCAPSULATED NANOPARTICLES (DENs)

Dendrimers are hyperbranched polymers that emanate from a single core and ramify outward with each subsequent branching unit (see Fig. 7.1).[23] They are generally prepared by sequential, alternating reactions of two smaller units, one of which has a point of bifurcation. Several classes of dendrimers are known, including polypropyleneimine (PPI), polyamidoamine (PAMAM), and Fréchet-type polyether dendrimers.[23] Starburst® PAMAM dendrimers (see Fig. 7.1) are a specific class of commercially available dendrimers that have repeating amine/amide branching units. These dendrimers are readily functionalized to terminate in a variety of moieties such as primary amines, carboxylates, hydroxyls, or hydrophobic alkyl chains. The presence of open spaces within the dendrimer interior and the synthetic control over their composition, architecture, and interior/exterior functionalities creates an environment to facilitate trapping guest species.[19,24]

These Dendrimer Encapsulated Nanoparticles (DENs) are prepared via a two-step synthesis (see Scheme 7.2): metal ions (e.g. Cu^{2+}, Pd^{2+}, Pt^{2+}) are complexed to the interior amine groups of a hydroxyl terminated PAMAM dendrimer and then chemically reduced to yield metal nanoparticles with narrow particle size distributions. Several reducing agents are available, depending on the metal and the synthetic conditions.[19,22] Purification is straightforward and reaction byproducts are readily removed with dialysis. DENs are stable for long periods and do not agglomerate because the nanoparticles (NPs) are trapped within the dendrimer framework. Some bimetallic DENs can be prepared via sequential or cocomplexation of metal cations followed by a variety of reduction procedures. Variations on these general schemes can also be used to prepare core-shell bimetallic nanoparticles.[22]

In the typical nomenclature for DENs,[22] the dendrimer is designated by Gx-R where x is the dendrimer generation and R is the surface group (typically –OH or –NH$_2$, see Fig. 7.1). The stoichiometry between the dendrimer and complexed ions or reduced encapsulated nanoparticles is denoted in parentheses after the dendrimer description, e.g. $(M^{c+})_n$ or (M_n). For bimetallic DENs, the metal:metal stoichiometry is typically included, e.g. G5-OH $(Pt_{16}Au_{16})$.

Synthetic methodologies for DEN preparation have been recently reviewed[19,22] and are only briefly described here. In a typical "direct metal loading" preparation, K_2PtCl_4 (5 mM, 4 ml) is added to an aqueous solution of G5-OH (0.01 mM, 20 ml) at room temperature and stirred for 3 days. The initial complexation time and metal:dendrimer stoichiometry vary widely with the metal precursor being used. After purging the solution with N_2 for 30 min, $NaBH_4$ (23 mg) is added and stirred overnight. Dialysis of the dark brown reaction product against water (pH 5.0–6.0, adjusted with HNO_3) over a period of 2 days yields a nanoparticle stock solution.
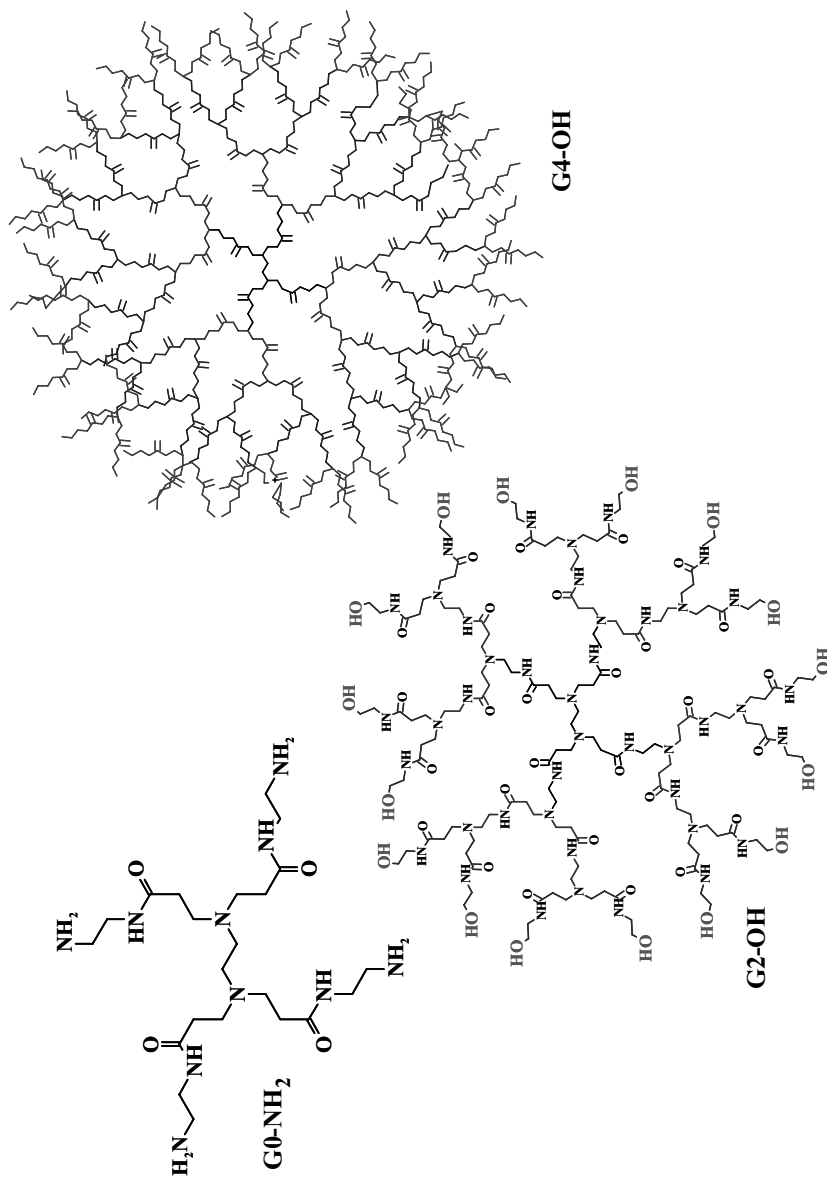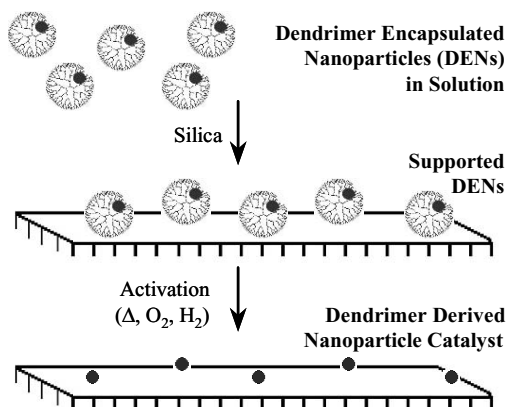
FIGURE 7.1. PAMAM dendrimers.

SCHEME 7.1.

Some metals, such as Ag and Au, do not readily form complexes with the interior amine groups of PAMAM dendrimers. However, DENs of these metals can be prepared by reacting the salt of a more noble metal (e.g. $AuCl_4^-$) with a nanoparticle of a less noble metal (e.g. Cu).[19,22] This "Cu displacement" method, pictured in Scheme 7.3, has been particularly useful in preparing bimetallic NPs where the metals are immiscible in the bulk or with substantially different reactivities toward reducing agents such as $NaBH_4$.[25] Cu displacement syntheses are somewhat more challenging than directly loading metal complexes into dendrimer interiors. Cu° nanoparticles are air-sensitive and will oxidize to Cu^{2+} in several hours,[26] so syntheses must be done under inert atmosphere with degassed solvents. Cu^{2+} also readily forms complexes with PAMAM dendrimers, making Cu removal an important consideration. For DENs in solution, dialysis at pH 4 is appropriate for removing residual copper.[27] The dialysis pH must be held low enough to protonate interior dendrimer amine groups[28] yet not so low that it causes dendrimer degradation, which may lead to particle agglomeration.

The Pt–Au system has been a valuable system to test DENs' potential for preparing NP systems of interest to the heterogeneous catalysis community. It is synthetically challenging, characterized by a wide bulk miscibility gap (18 to 98% Pt),[29,30] and bimetallic NPs within this gap are unavailable by traditional routes.[29,31−33] Nuzzo and coworkers have shown that bulk phase diagrams may not necessarily hold true for NPs[34] and results with the Pt–Au system support this conclusion provided appropriate syntheses are available.[25,33] Utilizing Cu displacement syntheses, these substantial
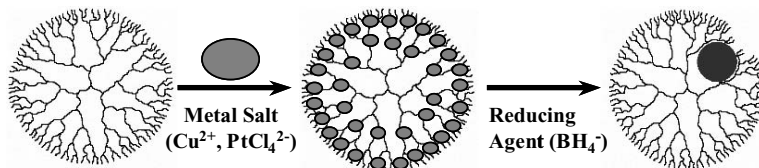
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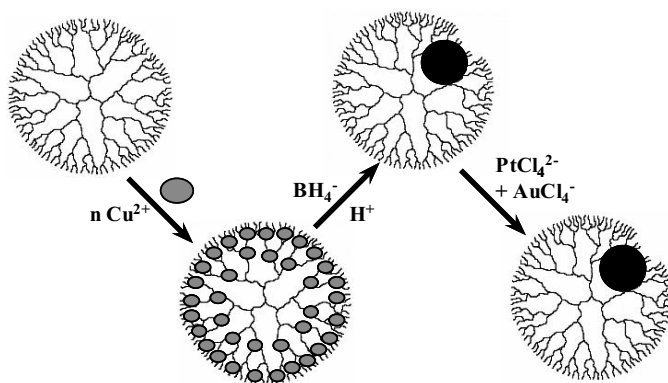
SCHEME 7.3.

synthetic challenges can be overcome to prepare Pt–Au DENs within the bulk misci-bility gap.

Cu displacement preparations of Pt–Au NPs are generally accomplished by ma-nipulations under inert atmosphere using standard Schlenk techniques. For example, 20 ml G5-OH (0.01 mM) can be mixed with 1.6 ml Cu(NO$_3$)$_2$ (5 mM) at pH 7.0 to 7.5 and degassed. A 3-fold molar excess of NaBH$_4$ is then added to prepare (G5-OH(Cu)$_{40}$) nanocomposites. After 30 min, the pH of the resulting brown solution is adjusted to 3.0 with HClO$_4$ and stirred for 1 h to destroy the excess NaBH$_4$. Solutions of K$_2$PtCl$_4$ (0.64 ml, 5 mM) and HAuCl$_4$ (1.6 ml, 2 mM) are degassed separately, mixed, and immediately added to the G5-OH(Cu)$_{40}$ nanocomposite solution via cannula transfer. The mixed solution is then stirred for an additional 1 to 2 h before deposition onto a suitable oxide support.

7.3. HOMOGENEOUS CATALYSIS BY DENs

The utilization of DENs in homogeneous catalysis has yielded several results of in-terest to the heterogeneous catalysis community. Homogeneous catalysis by DENs has been recently reviewed,[22] so only the most pertinent results are summarized here. As homogeneous hydrogenation catalysts, the PAMAM dendrimer surface functions as a size- and shape selective membrane for reactant molecules.[22,35−37] Polypropyleneimine DENs also impart substantial selectivity toward polar substrates in competitive hydro-genation reactions.[37] In a particularly elegant set of experiments, the size selectivity of Pd DENs for alkene hydrogenation, coupled with molecular "rulers" (alkenes teth-ered to large cyclodextrin "stoppers") has been used to estimate the distance of the Pd nanoparticle from the surface dendrimer surface.[22] This distance (0.7 ± 0.2 nm, on average) indicates that the nanoparticles are substantially displaced from the G4-OH dendrimer center (G4-OH radius ≈ 2.2 nm).[22,38]

The ability to functionalize DENs allows their use as homogeneous catalysts in a variety of reaction media including water, organic solvents, supercritical CO$_2$, and biphasic fluorous solvents.[22] Pd DENs have been the most widely studied homogeneous

catalysts, especially as carbon–carbon coupling catalysts. In Heck coupling reactions, Pd DENs show higher activities and selectivites relative to other colloidal Pd catalysts.[39] Pd DENs also compared favorably with polymer stabilized nanoparticles for stability in Suzuki couplings, although the DENs exhibited lower TOFs.[40]

Of particular interest to the heterogeneous catalysis community is the possibility of tuning nanoparticle properties by adjusting metal compositions. Homogeneous catalysis by bimetallic DENs has consistently provided control over reaction rates by modifying particle compositions. Better still, synergism between metallic components is a common theme in these studies. Allyl alcohol[41] and cyclohexene[42] hydrogenation by bimetallic Pt–Pd DENs, and 1,3-cyclooctadiene hydrogenation by bimetallic PdRh DENs[43] all exhibited higher intrinsic activities than physical mixtures of monometallic DENs with the same metal composition. Similarly, PdAu DENs prepared with a Au core and Pd shell show higher activity in allyl alcohol hydrogenation than monometallic Pd DENs.[44] The control experiments with physical mixtures of monometallic DENs are extremely important in these studies, and DENs offer the first real opportunities to do comparable control experiments for heterogeneous catalysts (see section 6.2).

7.4. IMMOBILIZATION & DEPOSITION OF DENs

7.4.1. *Deposition onto Preformed Supports*

For the dendrimer route to heterogeneous catalysts to realize its maximum potential, it is first necessary to prepare site-isolated NPs on a variety of oxide supports. Deposition and activation conditions are critical to preparing site-isolated nanoparticles, which are necessary if catalytic data is going to be meaningfully correlated with solution preparative techniques. DENs tend to agglomerate in solution unless low concentrations ($<50 \mu$M) are maintained, making solution concentration followed by wetness impregnation far from ideal.[19] Metal yields are typically ca. 70% so it may require 100 mL of solution or more to prepare a gram or two of supported catalysts with relatively low metal loadings.

Simply stirring hydroxyl-terminated DENs with oxides such as silica leads to a small degree of deposition onto the surface. Hydroxyl-terminated PAMAM dendrimers do not spontaneously adsorb onto silica without an encapsulated nanoparticle, suggesting that the adsorption is driven by the introduction of relatively strong metal–support interactions. To an extent, this process can be directed by carefully controlling the solution pH (presumably to maximize the number of deprotonated surface hydroxyl groups) and stirring for several hours. This "slow adsorption" technique has been applied to silica, alumina, and titania using mono or bimetallic Pt- and Au-based DENs and moderate (ca. 0.4 wt%) metal loadings can be achieved without condensing the solution.[45] The slow adsorption method also allows DENs to be deposited immediately after synthesis since the soluble byproducts of synthesis can be readily washed off the support. This allows for the elimination of the dialysis step, substantially reducing preparation time when rapid catalyst screening is a priority. Eliminating the purification step results in slightly broader particle size distributions, however, since dialysis also removes most large particles stabilized by several dendrimers (*inter*dendrimer colloids).

In a typical "slow adsorption" deposition onto silica, the pH of an as-prepared DENs solution is adjusted to 8.5 to 9, SiO_2 is added, and the suspension is stirred overnight. The resulting dark solid can be readily separated from the colorless mother liquor with a fine frit. If the DENs are prepared with the "Cu displacement" route, the wet solid catalysts should be stirred with saturated EDTA solution at pH 7.0 to 8.0 for 15 to 20 min, then filtered and washed with deionized water. This EDTA wash is typically repeated three times to remove any Cu(II) that might remain bound to the dendrimer. The catalyst is then washed several times with deionized water, and dried in a vacuum oven at 50°C overnight. The overall yields for Pt, Au, and Pt–Au DENs are generally about 70 to 75% and residual Cu is nearly always less than 0.01%. This same procedure is readily adapted to other oxide supports by adjusting the deposition pH and stirring time.[45]

7.4.2. Sol–Gel Immobilization

Immobilizing DENs within a sol–gel matrix is another potential method for preparing new supported catalysts. PAMAM and PPI dendrimers can be added to sol–gel preparations of silicas[46−48] and zinc arsenates[49] to template mesopores. In one early report, the dendrimer bound Cu^{2+} ions were added to sol–gel silica and calcined to yield supported copper oxide nanoparticles. Sol–gel chemistry can also be used to prepare titania supported Pd, Au, and Pd–Au nanoparticle catalysts.[50] Aqueous solutions of Pd and Au DENs were added to titanium isopropoxide to coprecipitate the DENs with TiO_2. Activation at 500°C resulted in particles approximately 4 nm in diameter. In this preparation, the PAMAM dendrimers served two roles, templating both nanoparticles and the pores of the titania support.

As prepared and purified G4-OH(Pt$_{50}$) DENs solutions (ca. 20 μM) can also be used to prepare high surface area sol–gel Pt/silica catalysts. This process can be used to carefully control metal loadings without condensing the solution provided the loadings remain low (less than 0.2 % Pt). The low concentrations do not allow the dendrimer to serve as a porosity template. Further, low loadings combined with delayed introduction of the DENs solution to a preformed sol likely lead to the occlusion of metal nanoparticles within the oxide matrix.[51]

Typical sol–gel silica immobilizations have been based on methods described by Lukehart and coworkers for immobilizing ligand stabilized molecular clusters.[52] In a typical preparation, tetramethoxysilane (TMOS, 2.5 mL) is added to a volume of up to 20 mL aqueous DENs solution in a 150 mL beaker along with a magnetic stir bar. Acetic acid (50 μL) is also added to 19.5 mL H_2O and combined with the first solution. The resulting solution is mixed thoroughly, covered, and stirred slowly for 3 days. The beaker is then placed in a muffle furnace to dry for 48 h at 80°C and resulting monoliths are ground in a mortar and pestle.[51]

7.5. ACTIVATION AND DENDRIMER REMOVAL

7.5.1. Immobilized In-tact DENs

DENs can be immobilized on electroactive substrates to prepare "heterogenized" homogeneous catalysts. Electrochemical grafting of hydroxyl-terminated Pt DENs

yields covalently linked DENs that are active (solution) electrocatalysts. These heterogenized systems are quite robust, withstanding numerous electrochemical cycles and sonification in 0.5 M H_2SO_4. Thiophene terminated PAMAM dendrimers can also be electrocopolymerized with 3-methylthiophene. Coordination of $PtCl_4^{2-}$ and reduction yields DENs within this matrix. Similarly, amine terminated Pt and Pd DENs have been immobilized on planar Au surfaces through self-assembled monolayer (SAM) chemistry. Neither of the latter two systems have proven to be catalytically or electrocatalytically active, although studies are ongoing.

In the absence of a solvent, supported, intact DENs are completely inactive as catalysts and do not bind CO. Presumably, upon drying, the organic dendrimer collapses onto the NP, poisoning the metal surface.[53,54] The activity of immobilized DEN electrocatalysts in water and a recent study by Williams and coworkers have provided the strongest evidence in support of dendrimer poisoning of supported, dried DENs. Using a solid-solution *in-situ* ATR-IR spectroscopy technique, Williams and coworkers have shown that alumina supported intact Pt DENs are capable of binding CO in the presence of water. Control experiments showed that the supported DENs do not migrate into the solution and stay adsorbed on the oxide. The supported DENs were active for CO oxidation in water and showed activity comparable to a Pt/alumina catalyst prepared via wetness impregnation of H_2PtCl_6. This study also showed that the presence of the Pt nanoparticle has a substantial effect on the stretching frequencies associated with the amide bonds that make up the dendrimer backbone.[54]

7.5.2. Activation Conditions

7.5.2.1. High Temperature Activation. Identifying appropriately mild activation conditions for supported DENs is a prerequisite for utilizing them as precursors to heterogeneous catalysts. 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,[55,56] so minimizing activation temperatures is critical for ultimately correlating supported catalyst properties with synthetic methodologies and particle properties.

Initial work with Pd DENs immobilized on mica showed the importance of carefully determining decomposition protocols as even a short (10 min) treatment at high temperature (630°C) caused substantial particle growth.[57] Thermogravimetric analysis (TGA) studies indicate that that, under the conditions of the TGA experiment, high temperatures (500°C) are required to completely remove organic matter from Pd and Au DENs immobilized in porous sol–gel TiO_2.[50] This treatment resulted in substantial particle agglomeration, although pore templating by the dendrimer mitigated the particle growth.

Similar to the TGA experiments, *in situ* Infrared Spectroscopy has been used to follow the amide bond stretching frequencies while heating under various atmospheres.[53,58−60] These experiments (see Fig. 7.2) suggest that dendrimer removal requires relatively forcing conditions to maximize CO adsorption on supported Pt catalysts prepared from DENs.[50,53,58−60] A variety of activation conditions have been chosen based on these experiments, generally involving some combination of oxygen and/or hydrogen treatments.[53,58−60]
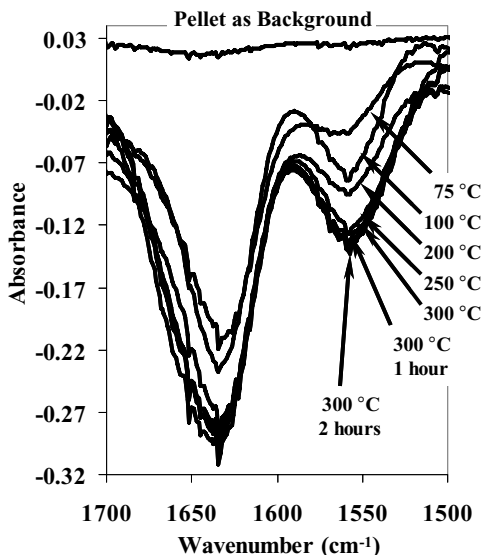
FIGURE 7.2. Typical in-situ dendrimer decomposition experiment in 20% O_2. The supported DENs were pressed into a self-supporting wafer, loaded into the IR cell, and temperature was increased at approximately 5°C/min. The first 5 spectra shown are at intervals of approximately 30°C; the bottom three spectra was collected after soaking at 300°C for 2 h.

The specific activation conditions required for an individual catalyst likely depend on the metal and support, but 300°C appears to be somewhat of a watershed temperature. Activation at temperatures above 300°C generally coincides with loss of Pt metal surface area due to sintering.[53,58,59] The metal loading, dendrimer loading, and metal:dendrimer ratios also impact activation conditions, suggesting that it may be necessary to optimize activation conditions for individual catalysts. Using temperatures at or near 300°C, supported Pt,[45,53,58,61] Au,[45] Pt–Au,[25,62] Pt–Cu,.[63] and Ru[60] nanoparticles have been prepared. In most cases, treatments at 300°C have resulted in little to no particle agglomeration and the ultimate supported nanoparticles have remained in the 1 to 3 nm range (see Fig. 7.3).

The differences in conclusions based on TGA and IR experiments are substantial; however, they are understandable based on conditions of each experiment. Although TGA provides explicit information regarding when removal of organic species is complete, it is most effective for monitoring rapid changes in mass as a function of temperature. Even at a relatively slow temperature ramp (e.g. 1°C/min), standard TGA experiments are ineffective in evaluating decomposition processes that take place over the course of several hours.

In-situ infrared spectroscopy has been used in much the same fashion at TGA, but temperature profiles have been combined with monitoring changes at constant temperature.[53,58−61] IR spectroscopy does not yield the same direct information about the complete removal of organic residues that TGA provides. On the other hand, CO adsorption experiments performed along with dendrimer decomposition experiments provide direct information regarding metal availability. Further, IR experiments provide
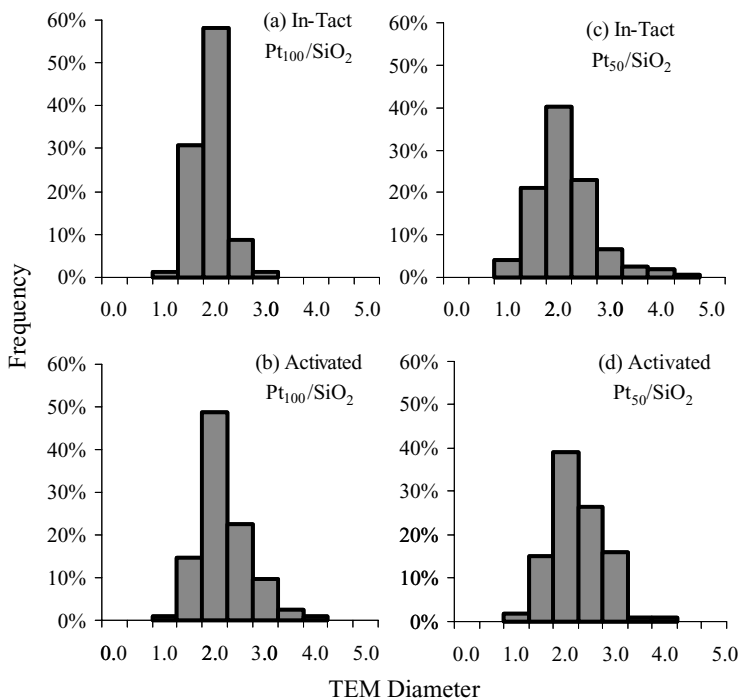
FIGURE 7.3. Transmission Electron Microscopy Data for in-tact (a & c) and activated (b & d) Pt/SiO₂ catalysts. Reprinted with permission from *J. Am. Chem. Soc.* **2003**, 125, 14832–14836. Copyright 2003 American Chemical Society.

important information regarding the dendrimer decomposition products and residues that can act as poisons for supported metal nanoparticle catalysts.

7.5.2.2. Activation Models and Low Temperature Activation. Both TGA and IR experiments show that the PAMAM dendrimer backbone begins decomposing at temperatures as low as 75°C, although more forcing conditions are required to fully activate the catalysts.[50,53,58−60] The low onset temperature of dendrimer decomposition is not surprising given that PAMAM dendrimers can undergo retro-Michael addition reactions at temperature above 100°C.[22] To avoid this, PAMAM dendrimer synthesis and modification are typically carried out at or near ambient temperature using reaction times as long as several days.[64] Further, Bard and coworkers have recently shown that, even in the absence of a nanoparticle catalyst, PAMAM dendrimers are susceptible to oxidation by molecular oxygen in aqueous solution at near ambient temperatures.[65]

Pt and Pd are good oxidation catalysts and have been clearly implicated in catalyzing dendrimer oxidation during decomposition.[50,59,66] Even in the absence of a metal nanoparticle, the dendrimer amide bonds degrade upon heating in He[59,66] Since the dendrimer architecture is relatively unstable upon heating, it is perhaps surprising that such forcing conditions were initially suggested for complete activation of DENs.

The necessity of forcing activation conditions has been attributed to the production of various carbonaceous species during activation. Under oxidizing atmospheres, the appearance of stretching frequencies consistent with the formation of surface carboxylates has been reported.[61] Similarly, several persistent surface bands consistent with coke-type species were identified when activating supported Ru DENs under H_2.[60]

A working model for dendrimer thermolysis during calcination involves the PAMAM dendrimer backbone initially reacting with oxygen (which may or may not be activated by a nanoparticle) in a relatively facile process to generate carboxylates and other surface species.[61] Removal of carbonaceous species closely associated with the nanoparticle is required for complete activation of the catalyst. For Pt DENs, the surface carboxylates may be strongly adsorbed to the nanoparticle surface and extended O_2 treatments are required for deep oxidation of the hydrocarbon to reach reasonably volatile species.[61] Once formed, however, it appears that they can be removed more readily with a hydrogen treatment than with further oxidation.[53]

Given that it may be difficult to remove surface carboxylates from supported DENs, 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, except when dealing with freshly calcined supports (e.g. treated overnight at 500°C), carbon species from atmospheric sources are always present on oxide surfaces and C–H stretching vibrations are readily observable in infrared spectra of supports taken directly from a manufacturer's container. The critical species are those directly adsorbed to the metal surface and in close proximity to the nanoparticles. Including strongly adsorbing small molecules such as CO in the treatment feed may effectively protect the metal surface from carboxylates, allowing them to migrate to the support.[61]

7.6. DENDRIMER TEMPLATED HETEROGENEOUS CATALYSTS

7.6.1. Catalysis by Platinum

Silica supported Pt catalysts have been examined in the most depth to identify appropriate activation conditions. The first study with these materials involved catalysts prepared from G5-OH(Pt_{50}) and G5-OH(Pt_{100}), calcined under O_2 at 300°C for four hours and reduced at 300°C for two hours.[53] The resulting catalysts are active for both oxidation and hydrogenation reactions. The turnover requencies (TOFs) for catalytic CO oxidation (see Fig. 7.4) and toluene hydrogenation (at 60°C) by the Pt_{100}/SiO_2 catalyst were indistinguishable from a traditionally prepared catalyst, as was the infrared spectrum of CO adsorbed to Pt_{100}/SiO_2. Beyond an important proof of concept, this study showed that dendrimer-derived catalysts can serve as good models for traditionally prepared or industrial catalysts.

Identifying appropriate deposition and activation conditions has remained a primary goal behind the study of Pt/silica catalysts prepared via the dendrimer route. For Pt/SiO_2 catalysts, calcination at 300°C for 4+ hours has proven to be the best activation protocol thus far. Figure 7.5 shows spectra of CO adsorbed on Pt_{50}/SiO_2 activated with O_2 compared a supported Pt catalyst prepared by wetness impregnation of H_2PtCl_6. The H_2PtCl_6 catalyst is consistent with standard Pt catalysts, and the full coverage CO stretching frequency (2085 cm^{-1}) is consistent with CO linearly adsorbed on Pt.[9,67]
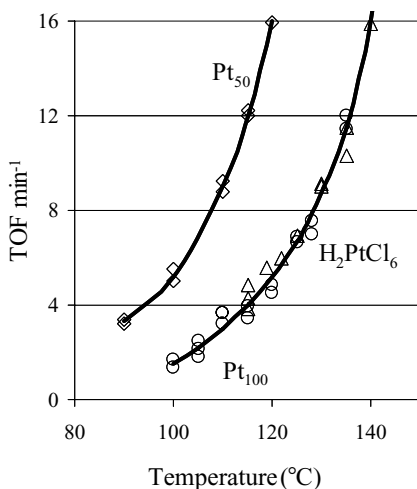
FIGURE 7.4. Co Oxidation by Catalysis by Dendrimer Templated Catalysts. Reprited with permission from *J. Am. Chem. Soc.* **2003**, *125*, 14832–14836. Copyright 2003 American Chemical Society.

Dendrimer derived catalysts have somewhat lower primary stretching frequencies. Fully activated Pt_{20}/SiO_2 catalysts, for example, have a primary stretching frequency near 2068 cm^{-1} with a distinguishable shoulder at 2085 cm^{-1}. These bands remain consistent after a number of activation protocols, including calcination at 300°C for up to 24 h.[61] A number of studies have loosely correlated lower CO stretching frequencies with adsorption onto low coordination edge and corner sites that dominate small nanoparticles.[67] Similarly, high coverage bands near 2085 cm^{-1} have been assigned
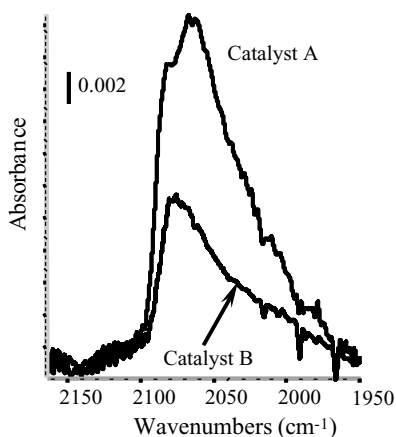

FIGURE 7.5. Infrared spectra of CO adsorbed on two sol–gel immobilized Pt_{50}/SiO_2 catalysts. Catalyst A was prepared by adding the DENs solution at the beginning of the sol–gel preparation. For catalyst B, the DENs solution was added after the sols were allowed to form for 24 hours, but before gellation. Both catalysts were oxidized at 300°C for 16 h and reduced at 300°C for 2 h. Reprinted with permission from *Appl. Catal. A.* **2005,** *292*, 124–129. Copyright 2005 Elsevier.

to terrace or face sites on extended surfaces.[67] The relative intensity of these adsorption bands has also been correlated to the presence of small (<2 nm) supported Pt particles; however, the complexity of factors affecting band intensity (intensity borrowing, dipole coupling, dephasing) makes quantitative interpretation of these bands unreliable.

The consistency of the high ($2068 \, \text{cm}^{-1}$) and low ($2058 \, \text{cm}^{-1}$) coverage values for the Pt_{20}/SiO_2 catalyst suggests this is a diagnostic band for fully activated dendrimer derived catalysts. The same $2068 \, \text{cm}^{-1}$ high coverage band also is found for a Pt_{50}/SiO_2 catalyst prepared with sol–gel chemistry (Fig. 7.5), along with the 10 wavenumber red shift during thermal desorption.[51] Dendrimer-derived catalysts that are not fully activated tend to have slightly blue shifted high coverage CO stretching frequencies. All of these catalysts have relatively similar activities for CO oxidation, indicating that this reaction is relatively fast, even on partially poisoned Pt surfaces. This is consistent with suggestions that the rate limiting step for CO oxidation by smaller nanoparticles involves desorption of a key surface intermediate.[68] In general, toluene hydrogenation appears to be a more sensitive probe reaction for dendrimer-derived catalysts as activity for this reaction is closely tied to the cleanliness of Pt nanoparticle surfaces.[51,53]

7.6.2. Bimetallic Catalysts

One of the most promising areas for dendrimer-derived catalysts is in the controlled preparation of bimetallic catalysts. This is particularly true for catalyst compositions that are unattainable by traditional routes. Using G5-OH, a $Pt_{16}Au_{16}/SiO_2$ catalyst has been prepared via the copper displacement synthesis and characterized. The dendrimer route allows for control experiments that are not available through traditional routes and are rarely available for molecular clusters. Using DENs, it is possible to prepare "cometallic" catalysts composed of monometallic DENS codeposited on a support. Although these catalysts certainly have two metals present, we describe them as "cometallic" to distinguish them from "bimetallic" dendrimer derived catalysts. Hence, "bimetallic" catalysts have been prepared with two metals in intimate contact in individual nanoparticles; "cometallic" catalysts have been prepared so that the two metals intentionally have no interactions prior to activation.

Figure 7.6 shows infrared spectra of adsorbed CO for $Pt_{16}Au_{16}/SiO_2$ compared to Pt_{32}/SiO_2 and a "cometallic" $Pt_{32}+Au_{32}/SiO_2$ catalyst. IR spectra of $Pt_{16}Au_{16}$ (Fig. 7.6b) show a high energy absorption band ($2113 \, \text{cm}^{-1}$), attributed to bound to Au surface sites. The lower energy band ($2063 \, \text{cm}^{-1}$) is attributable to Pt bound CO[53] and is red shifted $20 \, \text{cm}^{-1}$ relative to CO on monometallic Pt NPs. This result is also consistent with the presence of a bimetallic surface, where surface Pt atoms are diluted in Au.[31,33,69–71] The physical separation of diluted Pt–CO dipoles would reduce their ability to participate in dipole coupling, resulting in an apparent red shift relative to a pure Pt surface.[67]

During desorption experiments with $Pt_{16}Au_{16}$ (Fig. 7.7), the Au–CO band disappears quickly, and coincides with an increase in the Pt–CO band intensity. Closer inspection of the $Pt_{16}Au_{16}$ desorption experiment suggests that the broad room temperature Pt–CO band may be better described as two bands at 2065 and $2050 \, \text{cm}^{-1}$.
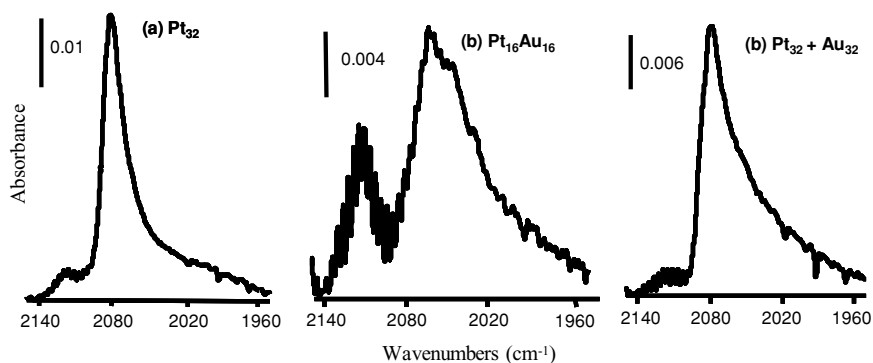
FIGURE 7.6. Infrared Spectroscopy of CO adsorbed at 30°C on (a) Pt_{32}/SiO$_2$, (b) Pt_{32}+Au$_{32}$/SiO$_2$ and (c) $Pt_{16}Au_{16}$/SiO$_2$. Reprinted with permission from *J. Am. Chem. Soc.* **2004**, 126, 12949–12956. Copyright 2004 American Chemical Society.

Changes in the Pt–CO band are due to a substantial increase in the intensity of the 2050 cm^{-1} band. Once CO completely desorbs from Au, the Pt–CO band becomes substantially more symmetric and the 2065 cm^{-1} band is no longer distinguishable. Complete desorption of the 2050 cm^{-1} band also occurs at a higher temperature than
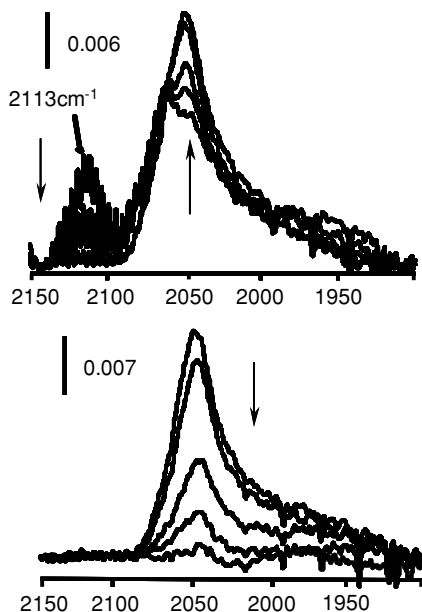

FIGURE 7.7. Infrared Spectroscopy during CO desorption from $Pt_{16}Au_{16}$/SiO$_2$ (a) 30 , 70, 90, &120°C and (b) 120 , 150, 170, 180 & 190°C. As the band at 2113 cm^{-1} decreases, the band at 2055 increases. Once the 2113 band disappears, the 2055 band decreases in intensity, but does not shift. Reprinted with permission from *J. Am. Chem. Soc.* **2004**, 126, 12949–12956. Copyright 2004 American Chemical Society.
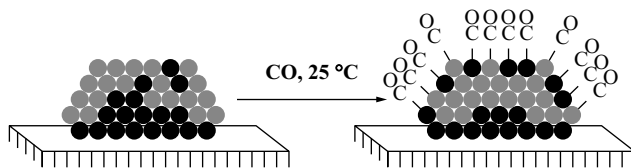
SCHEME 7.4.

with the Pt_{32} or $Pt_{32}+Au_{32}$ samples, suggesting that CO is more strongly bound to the intimately mixed bimetallic NPs.

These IR spectra were explained by a restructuring of the Pt–Au nanoparticles with CO providing a driving force for pulling Pt to the particle surface (see Scheme 7.4).[25,29,72] The mobility of Pt and Au within the bimetallic NPs also explains how the incorporation of Pt anchors Au to the support, preventing the severe particle agglomeration that is so prevalent in monometallic Au/SiO_2 catalysts.[10,31,32,70] TEM data for mono- and cometallic Au based catalysts always show widespread sintering as 100+ nm particles are nearly always observed after these catalysts have been activated. In contrast, Fig. 7.8 shows that bimetallic Pt–Au nanoparticles are primarily 2 to 3 nm in diameter after activation.

CO oxidation catalysis by $Pt_{16}Au_{16}$ also showed synergistic effects upon intimately mixing Pt and Au.[25] Supported Au NPs are well known to be highly active low temperature CO oxidation catalysts;[10,12,73] however, the most active catalysts utilize reducible oxide supports such as TiO_2.[10,73] Silica, being mildly acidic in water and having a low isoelectric point (IP $\approx$ 2), is unsuitable for deposition–precipitation methods because the surface is negatively charged at the pH values required to precipitate
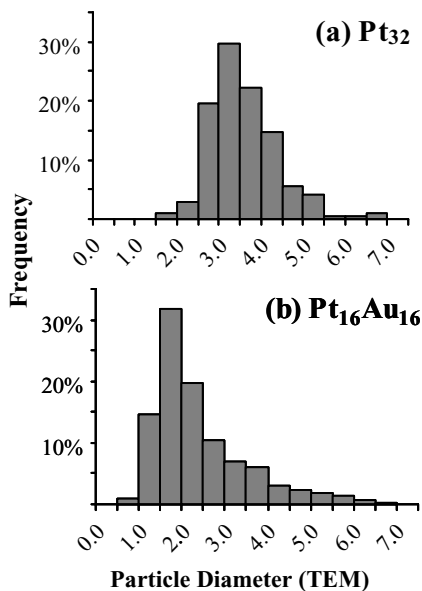

FIGURE 7.8. TEM particle size distributions for Pt_{32}/SiO_2 and $Pt_{16}Au_{16}/SiO_2$. Reprinted with permission from *J. Am. Chem. Soc.* **2004**, 126, 12949–12956. Copyright 2004 American Chemical Society.

FIGURE 7.9. CO Oxidation Catalysis by $Pt_{16}Au_{16}/SiO_2$. Reprinted with permission from *J. Am. Chem. Soc.* **2004**, 126, 12949-12956. Copyright 2004 American Chemical Society.

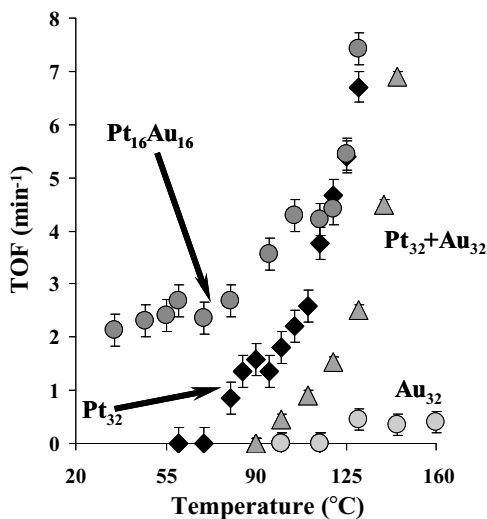$Au(OH)_x$. Additionally, silica does not stabilize gold NPs against agglomeration.[10] It appears that, on silica, one of the primary roles of Pt is to help stabilize small particles. Pt may also add additional functionality to the catalyst by binding O_2 and locating bound or activated O_2 near active Au sites. Alternately, the presence of Pt may affect the surface structure of Au, helping it to adopt a more active geometry.[74]

Dendrimer templated Pt–Au catalysts are also active for the selective catalytic reduction of NO by propylene in the presence of excess O_2. In addition to its commercial importance, this reaction is particularly interesting for the Pt–Au system. Previous work with cluster-derived Pt–Au catalysts has demonstrated that this reaction exhibits structure sensitivity, suggesting that it may be possible to use it as a structural probe for Pt based catalysts.[69,70]

Studies with traditionally prepared and cluster derived Pt_2Au_4 catalysts have shown that Pt is the active metal in this reaction. The primary role of Au appears to be that of a diluent, breaking up large Pt ensembles.[69,70] This mixing has two important results for the catalytic properties of these systems. First, catalytic activity is suppressed at lower temperatures, resulting in a delay in the "light-off curve" for NO and propylene conversion. This is a desirable result, as it allows for higher catalyst operating temperatures. Secondly, cluster derived catalysts show substantially higher selectivities for N_2 production over the undesirable N_2O product. Initial studies with the dendrimer derived Pt/SiO_2, Au/SiO_2, and $Pt_{16}Au_{16}/SiO_2$ catalysts, shown in Fig. 7.10, indicate that they behave similarly and support the conclusion that the dendrimer method is a viable means of templating bimetallic nanoparticles.

7.6.3. Evaluating Support Effects

Another potential advantage of the dendrimer route is the possibility of evaluating support effects. Because DENs are prepared *ex situ* from a support, it is possible to
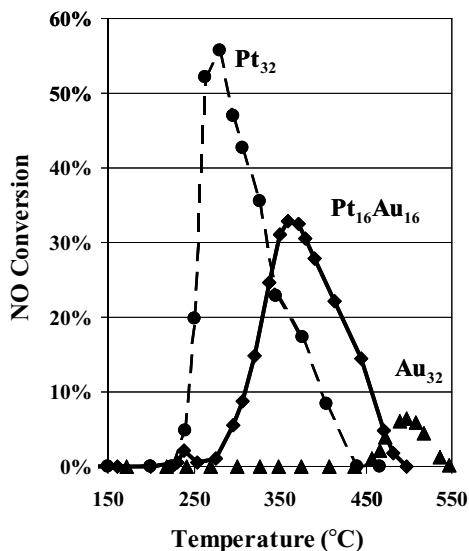
FIGURE 7.10. Selective catalytic reduction of NO with propylene by Pt_{32}/SiO_2, $Pt_{16}Au_{16}/SiO_2$, and Au_{32}/SiO_2.

deposit nanoparticles that, at least initially, are chemically identical on a variety of materials. Monitoring changes in particle size and catalyst properties may allow for eventually evaluating the nature of support effects for a variety of metal systems. Further, the dendrimer route allows for depositing the same set of nanoparticles on well-defined single crystal supports. Although there is only one current surface science study using dendrimer derived catalysts,[66] eventually this may allow for the comparison between catalytic properties of nanoparticles on high surface area and well-defined supports. This should both improve our understanding of dendrimer templated nanoparticles and aid in extrapolating UHV experiments to bench-scale catalysts.

Initial studies on support effects (silica, alumina, amorphous titania, Degussa P-25 titania) for Pt, Au, and Pt–Au bimetallic catalysts are currently underway.[45,62] For monometallic Pt catalysts, high coverage CO stretching frequencies range from 2081 to 2086 cm^{-1} and showed only a slight dependence on the support. Low coverage spectra vary more, from ca. 2053 cm^{-1} (silica and alumina) to 2075 (amorphous titania). CO bound to Au was only observed on Au/TiO_2 and Au/P-25 and occurs at 2119 cm^{-1} for both catalysts. All of the bimetallic $Pt_{16}Au_{16}$ catalysts showed CO bound to Au (2113 to 2119 cm^{-1}) at high coverage and lower Pt–CO stretching frequencies (ca. 2065 cm^{-1}). Additionally, all show an increase in the Pt band intensity during CO desorption from Au as shown in Fig. 7.8. Red shifts during CO desorption from Pt are all around 10 cm^{-1}.

CO oxidation catalysis showed that, for all the supports, the bimetallic catalyst was more active at low temperatures than the corresponding monometallic and cometallic catalysts. Apparent activation energies for monometallic Pt and Au catalysts were very consistent, near 32 and 80 kJ/mole, respectively. The synergism for $Pt_{16}Au_{16}$ catalysts also shows up in the apparent activation energies for these catalysts, which were consistently around 23 kJ/mole.

7.7. SUMMARY AND CONCLUSIONS

Dendrimer encapsulated nanoparticles (DENs) provide new opportunities for studying supported nanoparticle catalysts. A variety of synthetic methodologies now exist for the preparation of mono- and bimetallic DENs with controlled compositions and morphologies. Several methods are available for immobilizing DENs onto oxide and graphitic supports; in some cases, these supported (in-tact) DENs have proven to be active catalysts. The organic dendrimer template can be removed with a variety of thermal treatments, although details of individual treatments depend on the metal and support under study. The amide bonds in PAMAM dendrimers are thermally unstable but thermolysis yields products that are more difficult to remove. It may be possible, however, to protect some metals from the decomposition products by adding a strong ligand (such as CO) to the thermolysis feed. In general, treatement with O_2 at temperatures near 300°C has been required to prepare active catalysts.

Using the dendrimer route, it is possible to prepare supported catalysts not available via traditional routes. Dendrimer derived Pt–Au catalysts having compositions within the bulk miscibility gap can be prepared on several oxide supports. For all the supports studied, the bimetallic catalysts exhibited synergism with respect to mono- and cometallic catalysts for the CO oxidation and hydrocarbon NOx SCR reactions. The bimetallic Pt–Au catalysts also showed evidence of exchanging surface and subsurface atoms in response to strongly binding ligands such as CO.

ACKNOWLEDGMENTS

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