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**HYDROGEN (H₂) SENSING AND CATALYSIS WITH ORGANIC-STABILIZED
Pd AND Pd ALLOY NANOPARTICLES**

By

Monica Moreno

A Dissertation
Submitted to the Faculty of the
College of Arts and Sciences of the University of Louisville
in Partial Fulfillment of the Requirements
for the Degree of

Doctor of Philosophy

Department of Chemistry
University of Louisville
Louisville, Kentucky

May 2013

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Pd AND Pd ALLOY NANOPARTICLES**

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Monica Moreno

A Dissertation Approved on

March 25, 2013

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Dr. Richard P. Baldwin

Dr. Michael Nantz

Dr. Moises Carreon

DEDICATION

This dissertation is dedicated to my wonderful parents

Flor Alba Ruano and Nelson Moreno;

and my best friend Corey Carr

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Completing my PhD at University of Louisville is really a dream come true, and I would not have been able to complete this journey without the aid and support of countless people over the past five years. First of all, I want to express my gratitude toward my advisor, Dr. Francis P. Zamborini. His excellent mentoring, leadership, attention to detail, hard work, intelligence, and understanding have set an example I hope to match some day. I gratefully appreciate his encouragement during the time when I was feeling home sick and, thanks to his motivation and advice, I am here today finishing my PhD in chemistry, but most importantly believing in myself and confirming that with effort, dedication, and discipline we can conquer our dreams.

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ABSTRACT

HYDROGEN (H₂) SENSING AND CATALYSIS WITH ORGANIC-STABILIZED Pd AND Pd ALLOY NANOPARTICLES

Monica Moreno

March 25, 2013

This dissertation shows the hydrogen reactivity and stability of solid-state films and solutions of nanoparticles (NPs) for potential applications in hydrogen sensing and homogeneous catalysis of organic reactions. Mainly, this dissertation describes 1) the chemical synthesis of Pd and PdAg nanoparticles coated with various organic ligands and with different metal compositions, 2) the stability of solutions containing Pd and PdAg NPs in the presence of hydrogen, 3) the hydrogen sensing properties of films of NPs deposited onto Au microelectrodes, and 4) the evaluation of the catalytic activity of Pd and PdAg NPs for hydrogenation/isomerization of allyl alcohol.

We chemically synthesized Pd and Pd-containing alloy (PdAg) NPs stabilized with alkanethiolates (C_nS , $n = 4, 6, 8, 12, 16$, and 18), alkylamines (C_nNH_2 , $n = 8, 12$, and

16), and mixed C8NH₂/C6S ligands. All of the NPs were easily prepared and fully characterized by various analytical techniques to get their composition. By varying the initial mole ratio of Pd/CnNH₂ and the chain lengths of CnNH₂ and CnS, we were able to control the size, distribution, and stability of the NPs. When these NPs were exposed to 100% hydrogen, different stability was observed depending on the functionality and composition of Pd and PdAg NPs. While CnS Pd NPs ($n \geq 6$) had high stability against H₂-induced aggregation because of the strong Pd-S interaction and moderate-sized alkane chain, the 6x and 12x C16NH₂ Pd and Pd₉₁Ag₉ NPs exhibited the highest stability likely due to the formation of a bilayer of ligands on the Pd core that prevents the NP aggregation. For mixed ligand C8NH₂/C6S Pd NPs, the stability strongly depended on the C8NH₂/C6S ratio on the Pd NPs. The Pd NPs coated with ~3:1 or less C8NH₂/C6S ligands showed excellent stability against H₂-induced aggregation in solution.

In the area of hydrogen sensing, neither C6S Pd nor C8NH₂ Pd NPs displayed desirable sensing attributes. By synthesizing C8NH₂/C6S mixed Pd NPs with controlled ratios, we were able to prepare films of these NPs that displayed stable, reversible sensing behavior to H₂ gas down to 0.3%. In the area of catalysis, we synthesized a wide range of NPs with different composition and functionality. We discovered that the functionality plays a large role in the stability, selectivity, and reactivity of the catalysts. First, the NPs that are not stable showed very low turnover frequency (TOF) values since they were behaving as heterogeneous catalysts with lower surface area. For those that are stable, the strong thiolate ligands hindered the reaction rate, but provided a very interesting selectivity to form the aldehyde from allyl alcohol. In contrast, the very stable, but weak binding C16NH₂ ligands led to Pd NPs with high reactivity, but little

selectivity, forming both products. We learned that the long alkyl chain does not hinder the reaction very much as long as the ligand binds weakly. We also evaluated the catalytic properties of C6S and C16NH₂ Pd and PdAg NPs for the hydrogenation/isomerization of various allyl alcohols that differ only slightly in chemical structure. We observed that the more branched substrates have low TOF, likely due to the strong Pd-S interaction and to restricted diffusion and access to active sites through the packed multilayer of C16NH₂ ligands surrounding the Pd core. Interestingly, the C6S Pd NPs led to hydrogenation reaction when isomer formation is not possible. Importantly, by varying the H₂ flow rate, we could favor the isomerization or hydrogenation. In the case of Pd NPs coated with CnS ligands, we determined that these catalysts are highly selective for isomerization reactions and that the carbon chain length does not impede the reactivity of the NPs. C8S Pd NPs may be the optimal catalysts in terms of reactivity and stability. Our research has led to new fundamental insights about the reactivity between hydrogen and various Pd-containing NPs that may allow for rational design of metal NPs for specific sensing and catalysis applications.

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CHAPTER I

INTRODUCTION

1.1 Main Goal and Summary

The main goal of this research was to synthesize highly stable and reactive organic-stabilized Pd and Pd-containing alloy (PdAg) nanoparticles (NPs) for potential use in sensing and catalysis applications. This dissertation is divided into nine main parts. Chapter I contains the background information about all the topics related to this research, including the importance, synthesis, and main applications of metal NPs. Chapter II includes the chemicals, experimental procedures, and instrumentation that were used in this research. Chapter III describes the chemical synthesis of Pd and PdAg NPs stabilized with various organic ligands. The composition of all of the NPs is also given here by using various materials characterization techniques. In Chapter IV, we studied the stability of solutions containing metal NPs in the presence of H₂. We demonstrated that the metal and organic composition of the NPs play a fundamental role in the stability against H₂-induced aggregation in solution. Chapter V describes the H₂ sensing properties of films of Pd NPs coated with mixed monolayers of octylamine (C₈NH₂) and hexanethiolate (C₆S) ligands. We observed that C₈NH₂/C₆S Pd NPs exhibit significantly different reactivity with H₂ gas, depending on the relative amounts

of the two ligands coating the Pd NP surface, as determined by electronic measurements of films of Pd NPs as a function of exposure time to H₂. Chapters VI, VII, and VIII include the evaluation of the catalytic properties of Pd and PdAg NPs in the homogeneous catalysis of organic reactions in the presence of H₂. The results in Chapter VI show that all of the Pd and PdAg NPs can be used to catalyze the hydrogenation and isomerization of allyl alcohol with H₂ to give propanol and propanal, respectively. We demonstrate that the activity and selectivity of the catalysts can be controlled by simply modifying the ligand and metal composition of the NPs. These NPs can be reused at least for 5 cycles, although they maintain a high selectivity, reactivity, and stability for only 3 consecutive cycles. In Chapter VII, we continue with the use of Pd and PdAg NPs as homogeneous catalysts, but we alter the size and shape of allyl alcohols. In general, we observed that the activity and selectivity of the NPs are strongly correlated to the interactions between the organic stabilizers and substrates. This indicates that organic stabilizers, besides limiting the aggregation of Pd and PdAg NPs, also impart size- and product-based selectivity in the hydrogenation and isomerization of structurally related allyl alcohols. Here, we also discuss the effect of H₂ on the catalytic activity of Pd and PdAg NPs. We determine that the conversion, selectivity, and rate of hydrogenation/isomerization of allyl alcohol over Pd and PdAg NPs can be controlled by tuning H₂ flow rates. In Chapter VIII, we examine the reactivity of Pd NPs coated with alkanethiolate ligands of varied chain length in the presence of allyl alcohol and H₂. Although all of the C_nS Pd NPs favor the isomerization of allyl alcohol, their catalytic activity is strongly correlated to the Pd-ligand interaction, ligand surface coverage, and

NP stability, which all depend on the chain length. Finally, Chapter IX summarizes the results of this research and suggests future directions for it.

1.2 Motivation and Objective

The majority of this work was motivated by the need to chemically synthesize metal nanoparticles that are highly reactive with H₂ gas, but also highly stable against aggregation or morphology changes in solution or as films. Our approach was to use organic-stabilized Pd and PdAg NPs for H₂ sensing and catalysis applications. This is a tremendous challenge because, as the protecting ligand stabilizes the nanoparticle against irreversible aggregation, it also usually reduces the reactivity of the nanoparticle surface.

1.3 Importance of Metal Nanoparticles

Research on metal NPs has attracted a great deal of attention in recent years due to their interesting size- and shape-dependent properties and potential applications in a wide range of industrial,¹ catalysis,^{2,3} biomedical,^{4,5} sensing,^{6,7} and electronic applications.⁸ Metal NPs are metal materials with at least one dimension in the 1-100 nm range. This small size gives the NPs unique optical,⁹ catalytic,^{10,11} electrochemical,^{12,13} thermal,¹⁴ magnetic,¹⁵ and electrical properties,¹⁶ which are different from their bulk materials or from atoms or individual molecules.^{17,18}

1.4 Synthesis of Metal Nanoparticles

Nanoparticles can be prepared by both physical and chemical methods. Figure 1.1 shows a schematic illustration of preparative methods of metal NPs. The physical methods, which frequently involve vapor deposition, depend on the mechanical subdivision of bulk precursors into nanoparticles. The chemical approaches involve nucleation and growth of metallic atoms in the presence of stabilizers, followed by the controlled aggregation of atoms.^{17,18,19} The physical methods yield larger NPs (>10 nm) with broad distribution, while the chemical methods are the most convenient ways to control the size of the NPs. Therefore, in the latter methods, controlling the atomic aggregation is the most important challenge in controlling the size and uniformity of metal NPs.

A variety of techniques have been introduced to prepare metal NPs, including chemical reduction of transition metals,¹⁹ sonochemical reduction,²⁰ ligand reduction and displacement from organometallics,¹⁹ chemical liquid deposition,²¹ decomposition of organometallic precursors,²² and electrochemical deposition.²³ The reduction of transition metal salts in solution by borohydride (NaBH_4 or KBH_4) is the most widely used method of generating metal NP suspensions either in aqueous or organic phase. In general, the particles are formed by the reduction of metal ions in the presence of some stabilizers.

Typical coatings for stabilizing metal NPs include polymers,²⁴⁻²⁷ dendrimers,²⁸⁻³² surfactants,³³⁻³⁵ and ligands.³⁶⁻⁴² Mayer and co-workers have studied extensively the stabilizing polymer on the reduction of an aqueous suspension of Ag, Au, Pt, or Pd ions

Figure 1.1 Schematic illustration of preparative methods of metal nanoparticles.

by KBH_4 .⁴³⁻⁴⁶ They investigated cationic polyelectrolytes, polyacids, non-ionic polymers, and block copolymers. NaBH_4 has been used to obtain Au, Ag, Pt, Pd, or Cu NPs stabilized by dendrimers (polyamidoamine or PAMAM).^{28,31,47,48} These macromolecules lead to nearly monodispersed particles. Surfactants are generally used as stabilizers of aqueous NP suspensions of transition metals reduced by NaBH_4 or KBH_4 . Nakao and co-workers described the preparation of Ru, Rh, Pd, Pt, Ag, or Au NPs stabilized by quaternary ammonium, sulfates, or poly(ethylene glycol).⁴⁹ Ibañez and Zamborini synthesized tetraoctylammonium bromide (TOABr)-coated Au, Pd, AuAg, and PdAg NPs by the reduction of AuCl_4^- , PdCl_4^{2-} , Ag^+ , or some combination, with NaBH_4 in the presence of the surfactant in toluene solutions.⁵⁰ These surfactant-coated NPs were studied for vapor^{50,51} and gas sensing applications.⁵¹ Although all of these capping stabilizers are efficient for the preparation of small and uniform NPs, the metal NPs are often stable only as suspensions and tend to irreversibly aggregate over time or when removed from solvent, which limits their manipulation, characterization, solubility, and potential uses. In Chapter III we describe the synthesis of Pd and PdAg NPs coated with various organic ligands, specifically alkanethiolates, alkylamines, or mixtures of these two ligands, which can be repeatedly isolated from and re-dissolved in common organic solvents without irreversible aggregation or decomposition.

1.4.1 Metal Nanoparticles Coated with Organic Ligands

In 1994, Brust and co-workers reported, for the first time, an easy and reproducible synthesis for the preparation of Au NPs stabilized with dodecanethiolate

ligands.⁵² Figure 1.2 illustrates the synthesis of alkanethiolate-protected Au NPs by the two-phase Brust-Schiffrin method. The procedure involves the transfer of tetrachloroaurate anions from an aqueous phase to an organic phase (toluene) by using a phase-transferring agent (tetraoctylammonium bromide). The addition of a solution of alkanethiol in toluene to the organic solution causes the reduction of Au^{III} to Au^I and formation of the Au^I-thiolate polymer.⁵³ Subsequent reductive decomposition of the complex by NaBH₄ leads to the NP formation by nucleation and growth while the thiolate ligands adsorb onto the surface of the NP to form a single self assembled monolayer (SAM) coating.⁷ Figure 1.3 shows a metal NP surrounded by an organic monolayer. The figure also shows different types of stabilizers and the possibility to tailor the metal composition through the chemical synthesis. These NPs consist of roughly spherical metal cores surrounded by an organic monolayer.

Other reports have shown that a wide range of alkanethiolate chain lengths (C3-C24),⁵⁴ ω -functionalized alkanethiolates,⁵⁵ aromatic thiols,⁵⁵ and dialkyl disulfides⁵⁶ can be employed by using the Brust-Schiffrin approach. An example NP formula is Au₁₄₅(S(CH₂)₅CH₃)₅₀. Murray and co-workers have extensively studied the synthesis, reactivity, and electrochemistry of Au NPs.⁵⁷⁻⁵⁹ They demonstrated that the critical parameters responsible for the core dimensions and dispersity are the thiol/Au mole ratio, the temperature, and the rate of NaBH₄ addition. In particular, as the ratio increases, the NP size decreases and is in the general range of 2 to 5 nm in diameter for Au NPs protected with alkanethiolates.⁵⁴ Fast reductant addition and cooled solutions produce smaller, more monodisperse NPs. Some examples of alkanethiolate ligands used in nanoparticle synthesis include the commonly used hexanethiolate-coated (C6S) Au,⁵²

Figure 1.2 Scheme for alkanethiolate-protected Au nanoparticle by the Brust-Schiffrin two-phase approach.

Figure 1.3 Schematic representation of a metal nanoparticle surrounded by an organic monolayer.

Pd,⁶⁰ and Pt NPs,³⁸ octanethiolate-coated (C8S) Pt NPs,⁶¹ nonathiolate-coated (C9S) Ag NPs,⁶² and a mixture of alkanethiol and ω -carboxylate alkanethiol (i.e., 11-mercapto-undecanoic acid, MUA) NPs.⁶³ This procedure has been extended to other sulfur-containing organic compounds such as thioethers,⁶⁴ thiolated β -cyclodextrines,³⁶ sulfides, disulfides,⁵⁶ and Bunte salts ($\text{RSSO}_3^-\text{Na}^+$).⁶⁵ Some examples of organoamine ligands include octylamine-coated (C8NH₂), dodecylamine-coated (C12NH₂), and hexadecylamine-coated (C16NH₂) Au,⁶⁶ Pd, and PdAg alloy NPs,^{51,67-70} and dodecylamine-coated (C12NH₂) Pt,⁷¹ Au,⁷¹ and PdAu alloy NPs.⁵¹

1.4.2 Ligand Exchange Reactions

One of the most attractive features of metal NPs is the easy introduction of functional groups onto their surface by a simple ligand place-exchange reaction.⁵⁹ In ligand place-exchange reactions, a solution of thiolate-(SR) protected Au NPs is mixed with a solution of a different thiol (HS-R') by the reaction,

where x and m are the numbers of new and original ligands, respectively. Some of the HS-R' ligands replace the original SR thiolate ligands on the NPs, transferring the H from the incoming thiol to the replaced thiolate. Murray and co-workers determined that the rate and equilibrium stoichiometry (x) of reaction 1.1 are controlled by factors that

include the mole ratio of HS-R' to SR units, their relative steric bulk, and R versus R' chain lengths.⁵⁹

Studies of the mechanism of the place-exchange reaction are not still conclusive, however, it is always compared with ligand substitution reactions in metal complexes, whose mechanisms are well understood and accepted.⁷² There are associative, dissociative, and intermediate mechanisms. As associative mechanism is like the S_N2 reaction in organic chemistry, where one incoming ligand first interacts and adsorbs onto the Au NP and then desorption of one of the original ligands from the Au NP occurs, as illustrated in Figure 1.4A. In the S_N1-like dissociative mechanism, one of the original ligands first dissociates from the Au NP surface and leaves a vacant site for the incoming ligand to bind with the Au NP, as shown in Figure 1.4B. Figure 1.4C shows the intermediate mechanism, in which both incoming and outgoing ligands are incorporated into the Au NPs but they are not fully desorbed or adsorbed yet.

The presence of defect sites on the surface of NPs causes inhomogeneous coverage of the ligands.⁷³ These sites include vertices, edges, and grain boundaries on the NP surface. In these areas, the ligands are less crowded and less organized, giving the incoming ligands more opportunity to interact with the NPs. The exchange is very fast at the beginning, presumably when the reaction occurs at the defect-rich sites, like the corners and edges of the NPs. The reaction slows down dramatically later, due to steric hindrance along the terrace and smooth regions of the Au NP, where the ligands are well packed, organized, and crowded.^{59,73}

Figure 1.4 Schematic illustrations of the mechanism of the ligand place-exchange reaction on Au NPs. **(A)** Associative mechanism. The incoming ligand (R2, in red) interacts and adsorbs onto the NP surface, the one original ligand (R1, in black) becomes a thiol and desorbs from the NP. **(B)** Dissociative mechanism, in which one of the original ligands desorbs from the NP surface first, and then the incoming ligand fills the vacancy. **(C)** Intermediate mechanism. There is a reaction intermediate, where both R1 and R2 are not completely desorbed or adsorbed on the NP surface.

1.5 Applications of Metal Nanoparticles

The palladium-hydrogen (Pd-H) system was intensively investigated by Lewis 40 years ago.⁷⁴ Since then, the development of nanotechnology in the fabrication of Pd nanostructures including nanowires,^{75,76} nanochains,⁷⁷ nanoparticles,^{6,78} and nanotubes⁷⁹ has increased interest in the hydrogen related applications of the Pd-H system. In Chapter IV-VIII we study interactions of hydrogen with both solid-state films and solutions of Pd and PdAg NPs coated with various organic stabilizers for hydrogen sensing and homogeneous catalysis of olefins, respectively.

1.5.1 Importance of Hydrogen

Hydrogen is light, clean, abundant, sustainable,^{80,81} has many uses in the chemical, food,^{82,83} and glass processing industry, and is a byproduct of steel making.⁸⁴ There is tremendous interest in hydrogen as a chemical energy source.⁸⁵ Accordingly, it is important to produce hydrogen at a low cost and be able to separate, purify,⁸⁶ store,⁸⁷ and manipulate it efficiently and safely. However, hydrogen is highly explosive above 4% in air, requiring the development of low cost and effective hydrogen sensors for leak detection as a safety precaution.⁸⁸ Different Pd nanostructures have been widely explored for use as hydrogen storage, hydrogenation catalysts, and hydrogen gas sensors since the reaction between Pd and hydrogen is very selective and well known.

1.5.2 Pd-Hydrogen System

Solid-state hydrogen sensors based on pure Pd or Pd-containing alloys have been thoroughly explored due to the interaction of Pd with hydrogen to form PdH_x. When Pd is exposed to H₂ gas, Pd catalyzes the reaction where by H₂ is dissociated into atomic H. This atomic H adsorbs onto Pd surfaces and diffuses into the Pd lattice to form PdH_x. The reactions are given below.

When H diffuses into the Pd lattice, the Pd undergoes a phase transition from an α -phase to an α - to β -phase intermediate, and finally to the β -phase at different concentrations or partial pressures of H₂.⁸⁹ This results in an increased Pd-Pd atomic spacing in the material.⁸⁴ The phase transition and associated increase in lattice constant alters the volume,^{90,91} the resistance⁹²⁻⁹⁴ and the electrical⁹⁵⁻¹⁰² and optical^{83,103-105} properties of Pd and its alloys, forming the basis for hydrogen sensors. The diffusion of hydrogen into the Pd lattice provides large hydrogen storage capacity, and the dissociation of hydrogen into the more active atomic hydrogen leads to its desirable catalytic properties.

1.6 Hydrogen Sensing with Organic-Stabilized Pd Nanoparticles

Solid-state sensors containing Pd nanostructures allow the rapid and reproducible detection of hydrogen in all the environments.⁶⁰ In addition, they are less expensive and can be easily miniaturized using microfabrication technology. Most of the chemical sensors are fabricated by depositing thin films of metal nanostructures onto an appropriate transducer, which are then exposed to a liquid or gas phase analyte. For gas phase applications, mass sensitive sensors^{63,106} and, especially, chemiresistor devices have been highly investigated.^{7,107} Pd wires,^{75,76} nanotubes,⁷⁹ and nanoparticles^{6,7,51,60,78} have been widely utilized as resistor-based hydrogen sensors, where the resistance of the Pd nanostructured film changes upon exposure to hydrogen. In addition to lower cost, simplicity, reversibility, and portability, a major benefit of nanoscale sensors is their fast response times due to fast diffusion of H into these high surface-to-volume ratio materials.⁶⁰ Nanoscale sensors also often provide a lower limit of detection due to a large change in their electronic properties upon surface adsorption and overall greater adsorptive properties.⁶⁰ Chemiresistive sensors are the simplest type of electronic-based hydrogen sensors and the main focus of this dissertation. In Chapter V we describe the hydrogen sensing properties of films comprised of Pd NPs coated with alkanethiolates, alkylamines, and mixtures of these two ligands deposited onto electrode devices.

1.6.1 Chemiresistive Sensors

Two types of sensing mechanisms have been demonstrated previously for resistive based H₂ sensors using Pd nanostructures. Type I includes well-connected Pd

films. In this case, in the presence of H_2 , an increase in resistance is observed due to the formation of the more resistive PdH_x material.^{74,93} These are considered traditional chemiresistive H_2 sensors, and they have moderate sensitivity and slow response times (often several minutes), depending on the film dimensions.⁶⁰ Type II includes discontinuous Pd thin films or nanostructures containing break junctions. These Pd nanostructures exhibit poor conductivity initially due to the presence of break junctions.^{51,60,67,94,99-102} In the presence of H_2 , the resistance decreases due to the formation of PdH_x . This is because formation of PdH_x leads to a volume enhancement of the material and a more connected structure of the material with fewer high resistance junctions. Figure 1.5 shows the schematic representation of the two types of mechanisms involved in chemiresistive H_2 sensing. A benefit of the Type II sensing mechanism is the extremely low background currents and fast response times due to the nanoscale dimensions of the structures.^{60,78,81} Pd NPs coated with mixed alkylamine/hexanethiolate ligands discussed in Chapter V exhibit a Type II sensing mechanism.

1.6.2 Electronic Properties of Metal Nanoparticle Films

Metal NPs coated with organic stabilizers are usually deposited as films across electrodes by drop-coating,^{51,60,67} airbrushing,¹⁰⁸ spin-coating,¹⁰⁹ or stamping.¹¹⁰ These assemblies can be later interlinked by subsequent ligand-linker exchange. Linked multilayer assemblies can also be prepared by direct ligand-linker exchange reactions followed by precipitation or by layer-by-layer self-assembly procedure.^{71,111,112} Recently, NP films have also been deposited by microcontact printing,¹¹³ lithography techniques,¹¹⁴

A) Type I

Response

B) Type II

Figure 1.5 Schematic representation of Type I and Type II chemiresistive hydrogen sensing mechanism.

and microdispensing.¹¹⁵ In Chapter V we show that Pd NPs are drop-cast deposited onto Au electrodes, which lead to a very simple assembly of multilayers of NPs with film thicknesses well above the thickness of the electrodes.⁶⁷

Assembled films of organic modified metal NPs deposited between Au electrodes are initially conductive due to an electron transfer process, which is driven by a potential applied across the two electrodes. Conductivity of the film occurs by a core-to-core electron hopping mechanism,^{7,71} which is shown in Figure 1.6 and described in the following equation,

$$\sigma_{EL} = \sigma_0 \exp [-\beta_d \delta_{edge}] \exp [E_A/RT] \quad (1.4)$$

where, σ_{EL} is electronic conductivity ($\Omega^{-1} \text{ cm}^{-1}$), σ_0 is a pre-exponential constant, δ_{edge} the core edge-to-edge distance (cm), β_d is the electron tunneling coefficient ($\text{\AA}^{-1}$), E_A is activation energy (kJ/mol), R the gas constant, and T the temperature in Kelvin.

Figure 1.6 illustrates a schematic representation of a chemiresistive film comprised of metal NPs separated by interdigitated organic ligands through which electron hopping occurs. Equation 1.4 shows that conductivity is exponentially dependent on the distance between particles (δ_{edge}) and the tunneling coefficient (β_d). The value of δ_{edge} depends on the number of carbons in the alkyl chain of the ligands, which determines the distance between the metal cores. The tunneling coefficient is usually referred to as an attenuation factor that describes the exponential decay of

Figure 1.6 Schematic representation of a chemiresistive film comprised of metal NPs separated by interdigitated organic ligands. Electron hopping occurs from core to core when a voltage (V) is applied.

electron transfer as the distance between cores increases. In addition to the length of the alkyl chains, their structure and molecular composition plays an important role in the ability for electron tunneling. The second exponential term in Equation 1.4 correlates conductivity with temperature and energy of activation. For continuous metal films, conductivity decreases as the temperature increases. In contrast, films of separated metal NPs exhibit an increase in conductivity as the temperature increases. In summary, for sensing experiments at constant T , a change in β_d , δ_{edge} , and E_A will affect conductivity. Overall, σ_{EL} is controlled by β_d , δ_{edge} , E_A , and T .^{7,71}

1.7 Catalysis and Metal Nanoparticles

In catalysis, metal NPs can be used as heterogeneous catalysts, where they are attached to a solid support, or as homogeneous catalysts, where they are soluble in solution. Homogeneous catalysts are often more desirable as they are more reactive. A key issue in homogeneous catalysis with metal NPs is control of the size, shape, composition, solubility, and stability of the NPs.^{28,116-120} These parameters are controlled through synthesis and functionalization of the NPs with organic stabilizers such as polymers,²⁴⁻²⁷ dendrimers,^{28-32,121,122} surfactants,³³⁻³⁵ or ligands.^{36-42,51,67,68} A major challenge is to sufficiently protect the NP against irreversible aggregation or major morphology changes under the conditions of the reaction being catalyzed while retaining high catalytic activity of the NP surface.²⁵ This is difficult because the organic stabilizers that provide the necessary solubility and stability of the metal NPs also usually suppress the catalytic activity.

Several strategies have been reported for homogeneous catalysis with metallic nanostructures.¹¹⁷ Here we review those that focus on Pd NPs, since this is the subject in this dissertation. Crooks and co-workers used Pd NPs encapsulated in dendrimers for catalyzing the hydrogenation of unsaturated organic compounds^{123,124} and C-C coupling reactions such as Heck¹²⁵ and Stille⁴⁷ reactions. They studied the effect of NP size on hydrogenation reactions¹²³ and also developed a fluorous phase Pd-dendrimer catalyst that could be reused numerous times.⁴⁸ The benefit of dendrimers is that they stabilize the NPs, but allow molecules to access the NP surface and they can impart some selectivity into the reaction. El-Sayed and co-workers directly compared the catalytic activity and stability of polyvinylpyrrolidone (PVP)-stabilized Pd NPs in solution compared to those adsorbed onto carbon for catalyzing the Suzuki coupling reaction.¹²⁶ The carbon-supported Pd NPs were less catalytically active than the colloidal Pd NPs, but were highly recyclable. Sastry and co-workers synthesized Pd NPs immobilized on amine-functionalized zeolite.¹²⁷ The rate of hydrogenation and Heck reactions was significantly higher than those obtained using conventionally prepared catalysts.¹²⁷

A number of studies have been conducted using supported metal NPs as catalysts for a variety of organic and inorganic reactions. These heterogeneous systems suffer from low catalytic rates, limited lifetime, complex methods of preparation, and poor particle morphology control.^{126,127} Most of the homogeneous Pd catalysts described in the literature are stabilized with polymers (including dendrimers) or surfactants.^{19,117} They are used because they have fairly weak affinity to the metal NP enabling both catalytic activity and stability. One disadvantage is that the metal NPs in solution are unstable and undergo changes in their morphology. In addition, colloidal NPs are often

not stable in solvent-free form making separation, recovery, and regeneration of the catalyst difficult.^{19,126,127,128} Clearly, there is still a need to synthesize highly stable and reactive NPs with high recyclability for applications in homogeneous catalysis.

In this dissertation we focus on the use of organic ligand-stabilized Pd NPs as catalysts since they are highly stable, can be stored as solids, are easily characterized, and have the potential to be easily separated from reaction products.⁴² Au, Pd, and Pt NPs stabilized with thiols have drawn popular research interest,^{37,38,40-42,57,58,61,113,129} but have not been widely used in catalysis because the strongly bound stabilizing ligands greatly inhibit the catalytic activity.^{24,36,38,40,113} A few reports included the synthesis and catalytic activity of Pd and Pt NPs protected by a thiol monolayer for hydrogenation reactions^{36,38} and their electrocatalytic properties in methanol oxidation.^{37,41} Pd NPs coated with n-alkylamines have also been used for the electrochemical oxidation of methane.³⁹ Astruc and co-workers investigated C12S Pd NPs for catalysis of the Suzuki-Miyaura C-C coupling reaction under ambient conditions.⁴⁰ Fornasiero and co-workers reported an approach for the preparation of Pd NPs coated with thiols and their easy recycling/reuse in the Suzuki cross-coupling reaction.¹²⁹ Recently, Shon and co-workers showed that C12S Pd and PdAu NPs selectively catalyzed the isomerization of allyl alcohol over hydrogenation.¹³⁰⁻¹³³

1.7.1 Importance and Reactivity of Allyl Alcohol with Hydrogen

Catalytic selective hydrogenation of allyl alcohol to produce 1-propanol, which is a precursor in organic synthesis and the pharmaceutical industry, has been studied as a

function of particle size and shape of Pd NPs coated with polymers,^{134,135} biopolymers (collagen fiber),¹³⁶ surfactants,³⁵ or dendrimers^{29,30,32,123,124,137,138} either in solution or immobilized on solid supports such as alumina,^{35,134} composites,³² silica,¹³⁹ and magnetic NP cores.¹⁴⁰⁻¹⁴² However, the transformation of allyl alcohol to carbonyl compounds (isomerization reaction) has not been widely explored using Pd NPs as catalysts.¹⁴³ The isomerization reaction is an important and useful synthetic process because it leads to the formation of carbonyl compounds in a one-pot catalytic transformation, avoiding the two-step sequential oxidation and reduction reactions. Figure 1.7 shows a one-pot catalytic transformation of allyl alcohols into saturated carbonyl compounds.¹⁴³⁻¹⁴⁵ In particular, the isomerization of allyl alcohol is an attractive strategy that offers environmental and economical advantages because no byproducts are generated; therefore, only the corresponding saturated aldehydes or ketones are obtained, which are valuable and versatile synthetic intermediates for various pharmaceuticals, agrochemicals, and fine chemicals.¹⁴⁴⁻¹⁴⁹ In many cases the isomerization reaction requires relatively high quantities of catalyst, harsh reaction conditions, and expensive metals.¹⁴⁶ Although several transition metals have been used to perform this reaction, ruthenium, rhodium and iron have shown the best selectivity and activity.^{145,147-149}

1.7.2 Selective Isomerization of Allyl Alcohol by Pd Catalysts

Over the years, two classes of mechanisms shown in Figure 1.8 have been proposed to explain the Pd-based catalytic isomerization and hydrogenation of allyl alcohols.^{145,147,150} The main difference between these two mechanisms is that the former

Figure 1.7 Transformation of allyl alcohol into saturated carbonyl compounds.

A) Type I: Pd-alkyl Mechanism

B) Type II: π -allyl Hydride Mechanism

Figure 1.8 Proposed mechanisms for the isomerization of allyl alcohol.

is an *intermolecular* mechanism, while the latter is *intramolecular*.¹⁴⁵ The Type I mechanism in Frame A is known as the Pd-alkyl mechanism and requires the presence of the Pd-H species, either isolated or prepared in situ before the adsorption of allyl alcohol and the initiation of catalytic reaction. The insertion of Pd-H to the π bond of allyl alcohol is particularly important and most likely determines the selectivity of reaction. These reactions are usually reversible, and therefore, the abstraction of the hydrogen α to the OH group leads to formation of an enol complexed to the metal hydride. A final decomplexation gives back the catalyst and the enol, which then tautomerizes to the carbonyl derivative.¹⁴⁷ Shon and co-workers reported that the insertion of Pd-H to C=C should follow a Markovnikov addition pattern and produce a branched Pd-alkyl intermediate (route a). In comparison, the anti-Markovnikov addition of Pd-H to the π -bond produces a linear Pd-alkyl intermediate and increases the hydrogenation of allyl alcohol (route b).¹³³ A major difference of the π -allyl Pd hydride mechanism shown in Frame B is that the reaction does not require the presence of H₂ gas, because the Pd-H adduct is generated from the oxidative addition of Pd to the C-H bond α to the OH group. In both, Type I and II mechanisms, steric and electronic effects may play an important role in the formation of key intermediates such as the σ -bonded complexes or the π -allyl derivatives. Therefore, those factors could limit the isomerization reaction.¹⁴⁷ In Chapter VI-VIII we evaluate the catalytic properties of Pd and Pd-containing alloy NPs for hydrogenation and isomerization of various allyl alcohols. Since these reactions are performed in the presence of hydrogen gas, they follow the Type I mechanism.

Pietropaolo and co-workers reported the catalytic hydrogenation and isomerization of allyl alcohols over supported Pd catalysts.¹⁵¹ They found that the

reaction between α,β -unsaturated alcohols and H_2 over Pd/TiO₂ catalysts exhibited high activity and selectivity for the double bond migration leading to a high yield of the corresponding saturated aldehyde or ketones.¹⁵¹ Zharmagambetova and co-workers studied the route of the catalytic reaction of allyl alcohol with hydrogen on polymer-Pd(0) and Pd(II) complexes.¹⁵² They determined that catalytic activity and selectivity depends on the Pd valence state, structure of the polymer matrix, and functional groups.¹⁵² To our knowledge, there is only one report regarding the utilization of alkanethiolate-capped Pd NPs as homogeneous catalysts for the isomerization of allyl alcohols.¹³³ Shon and co-workers showed the isomerization of allyl alcohol to the corresponding carbonyl compound with a relatively high selectivity (95%) compared to other Pd-based catalysts (<75%).¹³⁰⁻¹³³ In our research we are the first to compare the catalytic activity of various alkylamine-, alkanethiolate-, and mixed ligand organic-protected Pd and PdAg NPs for the hydrogenation and isomerization of allyl alcohol in the presence of hydrogen gas.⁶⁸

CHAPTER II

EXPERIMENTAL

This chapter includes five main experimental parts.

- 1) Chemical synthesis of various Pd and PdAg nanoparticles (NPs).
- 2) Nanoparticle characterization.
- 3) Solution stability studies of NPs in the presence of H₂.
- 4) Hydrogen sensing experiments of NP films deposited onto Au microelectrodes.
- 5) Catalysis studies for the hydrogenation/isomerization of various olefins.

2.1 Synthesis of Pd and PdAg Nanoparticles (NPs)

2.1.1 Chemicals

Toluene (99.9%), 2-propanol (99.9%), acetone (99%), acetonitrile (99%), dichloromethane (99.5%), and ethanol (200 proof) were purchased from VWR Scientific Products and used as received. 1-butanethiol (99%), 1-hexanethiol (95%), 1-dodecanethiol (98%), 1-hexadecanethiol (92%), 1-octadecanethiol (98%), dodecylamine (98%), sodium borohydride (98%), potassium tetrachloropalladate (II) (98%), silver trifluoroacetate (98%), allyl alcohol (99%), propionaldehyde (99%), propyl alcohol

(99.7%), and chloroform-d (99.8%) were purchased from Aldrich Chemical Co. and used as received. Tetraoctylammonium bromide (98%), octylamine (99%), 1-hexadecylamine (90%) containing 1-octadecylamine, and 1-octanethiol (98%) were purchased from Alfa Aesar Co. and used as received. Ultra-high purity H₂ gas (99.999%) was used as received. Barnstead nanopure water (18.3 MΩ-cm) was employed for all aqueous solutions.

2.1.2 Synthesis of Alkanethiolate-Coated Pd NPs (C_nS Pd NPs)

Alkanethiolate-coated (C_nS) Pd NPs were synthesized as reported previously.^{42,51,60,67,68} Briefly, 0.50 g of K₂PdCl₄ in 10 mL of water was transferred into 100 mL toluene containing 1.25 g of TOABr as indicated by the colorless toluene layer becoming deep red after ~20 min of rigorous stirring. The colorless water layer was removed and the appropriate alkanethiolate ligand was added in a 1:2 thiol:Pd ratio. This ratio corresponds to 0.77 mmol of thiol, which is 76 μL for 1-butanethiol (C₄S), 110 μL for 1-hexanethiol (C₆S), 136 μL for 1-octanethiol (C₈S), 187 μL for 1-dodecanethiol (C₁₂S), 228 μL for 1-hexadecanethiol (C₁₆S), and 255 μL for 1-octadecanethiol (C₁₈S). The solution was cooled in an ice bath for 30 min and 0.60 g of NaBH₄ in 10 mL of water was added with stirring. The solution was removed from the ice bath after 15 min and stirred for 4 h at room temperature. The water layer was discarded, and the toluene removed by rotary evaporation. The black Pd NP product was suspended in 200 mL of acetonitrile by sonication and allowed to settle overnight before collection by vacuum filtration on a glass-fritted Büchner funnel. The NPs were washed with acetonitrile and ethanol successively two times before thoroughly drying and collecting. These NPs are referred to as ½x C_nS Pd NPs (n = 4, 6, 8, 12, 16, and 18). Figure 2.1 illustrates a metal

Typical Example for Pd NPs:

for 1:2 RSH:Pd mole ratio

Hexanethiol = $\text{CH}_3(\text{CH}_2)_5\text{SH}$

Composition = $\text{Pd}_{1112} (\text{C}_6\text{S})_{222}$

Ave. Core Diameter = 3.2 nm

Figure 2.1 Schematic representation of alkanethiolate-coated Pd NPs (C6S Pd NPs) obtained as a product of synthesis.

NP obtained as a product from the organic synthesis and an example of the chemical properties of C6S Pd NPs. Figure 2.2 shows a digital picture of C6S Pd NPs in solid state and dissolved in toluene.

2.1.3 Synthesis of Alkylamine-Coated Pd and PdAg NPs (C_nNH₂ Pd and C_nNH₂ PdAg NPs)

Alkylamine-coated Pd NPs were synthesized at room temperature according to our previous reports.^{51,67,68} Solutions of 0.50 g (1.53 mmol) of K₂PdCl₄ in 10 mL of water and 1.67 g (3.06 mmol) of TOABr in 70 mL of toluene were combined and stirred until all PdCl₄²⁻ transferred into the toluene phase. Then, the appropriate alkylamine ligand was added in a 12:1 alkylamine:Pd ratio and rapidly stirred for 45 min. This ratio corresponds to 18.4 mmol of alkylamine, which is 2.97 mL for octylamine (C₈NH₂), 3.34 g for dodecylamine (C₁₂NH₂), and 4.35 g for 1-hexadecylamine (C₁₆NH₂). These syntheses are referred to as 12x C₈NH₂ Pd, 12x C₁₂NH₂ Pd, and 12x C₁₆NH₂ Pd. The organic layer became light yellow whereas the aqueous layer turned cloudy white upon addition of the alkylamine. This could be due to complexation between the protonated amine and PdCl₄²⁻, but it is not certain since this precipitate has not been characterized.⁶⁹ Next, 0.87 g of NaBH₄ (23.0 mmol) in 10 mL of water was added to the two-phase solution while stirring. The organic phase quickly turned black and the cloudiness in the aqueous phase disappeared after about 2 min. The solution was stirred for 3 h, the clear and colorless water layer was separated, and the toluene layer was later removed by evaporation. The black Pd NP product was suspended in 100 mL of acetonitrile by sonication and allowed to settle overnight before collecting by vacuum filtration. The resulting NPs were washed with acetonitrile and ethanol to remove excess ligands and

Figure 2.2 Digital pictures of C6S Pd NPs in solid state (**A**) and dissolved in toluene (**B**).

other reaction byproducts before collecting. For 12x C12NH₂ Pd and 12x C16NH₂ Pd NPs, the solid was re-dissolved in toluene and the solvent reduced in volume again by rotary evaporation. The black NPs were precipitated in acetone overnight and the precipitate collected by vacuum filtration before washing with acetone and ethanol. Two other samples with C16NH₂:Pd of 6:1 (6x) and 3:1 (3x) were also synthesized. The five CnNH₂ Pd NPs were black powders and soluble in non-polar solvents.

Alkylamine-coated PdAg NPs were synthesized by adding the appropriate amount of K₂PdCl₄ and AgC₂F₃O₂ salts in a 10:1 ratio. AgC₂F₃O₂ was directly soluble in the toluene phase whereas PdCl₄²⁻ was phase transferred into toluene with TOABr. The amount of C8NH₂, C12NH₂, and C16NH₂ was 12:1 with respect to the total metal content. These syntheses are referred to as 12x C8NH₂, 12x C12NH₂, and 12x C16NH₂ PdAg NPs. A 15-fold excess of NaBH₄ with respect to total metal (Pd and Ag) was added to the solution. PdAg NPs were cleaned in the same way as the corresponding Pd NPs.

2.1.4 Synthesis of Pd NPs Coated with Mixed Octylamine and Hexanethiolate

Ligands (C8NH₂/C6S Pd NPs)

Approximately 0.01-0.05 g of C8NH₂ Pd NPs was dissolved in 5.0 mL of toluene or CH₂Cl₂ before addition of a variable amount of C6SH (0 to 5.0 μL).⁶⁷ The solution was stirred for 30-45 min for catalysis studies without further treatment, while for stability and sensing experiments the solution was stirred overnight (or 5 h for 5.0 μL C6SH) and the toluene layer removed by rotary evaporation. For optical measurements, the Pd NPs product was suspended in 50 mL of acetonitrile, collected by filtration with a

syringe filter using a 0.2 μm PTFE membrane, and washed with 20 mL of acetonitrile and 10 mL of ethanol. Finally, the Pd NPs were dissolved in 10 mL of toluene that was passed through the membrane. For sensing studies, the Pd NPs product was suspended in 50 mL of acetonitrile, collected by filtration, and washed with an additional 60 mL of acetonitrile and 20 mL of ethanol on a filter frit. The filter frit was then rinsed with toluene to dissolve the soluble NPs and the solution concentrated by evaporation.

Table 2.1 shows all the different types of synthesis performed in this dissertation. The table summarizes the metal salts used, type of stabilizer, metal/stabilizer ratios, reducing agent, and type of solvent in which particles are soluble.

2.2 Nanoparticle Characterization

2.2.1 Transmission Electron Microscopy (TEM)

TEM provided information about the size and morphology of the NPs. TEM images were obtained at different magnification using a FEI Tecani F20 field-emission (FE) TEM operating at an accelerating voltage of 200 keV. Samples were prepared by casting a single drop of a dilute toluene solution of NPs onto a copper grid-supported holey carbon film and allowing the solvent to evaporate. Particle sizes were determined manually from digital images.

2.2.2 Energy Dispersive X-Ray Analysis (EDX)

EDX analysis of the NPs was performed using an EDX spectrometer in the FEI Tecani F20 FEI-TEM. These measurements were done in the scanning TEM (STEM)

Table 2.1 Summary of the synthesis of the metal nanoparticles performed in this dissertation

Metal salt	Stabilizer	Metal:Stabilizer Ratio	Reducing agent	Solvent
K₂PdCl₄	Alkanethiol CnS (n = 4, 6, 8, 12, 16, 18)	2:1	NaBH ₄	Toluene
K₂PdCl₄	Alkylamine CnNH ₂ (n = 8, 12, 16)	1:12, 1:6, 1:3	NaBH ₄	Toluene
K₂PdCl₄	C8NH ₂ /C6S	1:12	NaBH ₄	Toluene
K₂PdCl₄/AgC₂F₃O₂ 10/1	Alkylamine CnNH ₂ (n = 8, 12, 16)	1:12	NaBH ₄	Toluene

mode using the nano-probe configuration with a probe size down to about 1 nm. EDX combined with TEM provided the means to accurately identify the metal composition.

2.2.3 Thermogravimetric Analysis (TGA)

TGA of the NPs were obtained over a temperature range of 25-800 °C at a heating rate of 20 °C/min on a 2950 TGA HR V5.4A instrument under nitrogen using sample sizes of 17.1-20.8 mg. TGA was used to examine the composition of the organic stabilizer attached to the metal core. TGA provides some insight on the stability of the NPs by analyzing the temperature at which the organic material desorbs from the metal and correlates with the strength of binding between different types of stabilizers and the metal core.

2.2.4 Nuclear Magnetic Resonance (NMR)

NMR data was used to confirm the attachment of the ligands to the metal core and also to characterize and monitor the organic molecules in solution after the ligand place-exchange or catalysis reactions. NMR analysis on all NPs was consistent with the successful synthesis of pure NPs. Since the peaks for the organic stabilizers are broadened in NMR due to association with the metal core, purity is determined by the absence of sharp peaks in the spectrum. NMR spectra were recorded on a 500 MHz INOVA spectrometer in CDCl₃ solutions internally referenced to CDCl₃ at δ 7.26 ppm.

2.2.5 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR is a spectroscopy technique that gives information about the monolayer shell surrounding the metal clusters. FTIR spectra were acquired on a Digilab FTS 7000

spectrometer (Varian, Cambridge, MA) in the wavenumber range of 500-4000 cm^{-1} . Samples were prepared by drop-casting a dilute toluene solution of NPs onto KBr salt plates and allowing the toluene to completely evaporate at room temperature before IR measurements.

2.3 Hydrogen Stability of Solution-Phase Pd and PdAg NPs

UV-vis spectroscopy and TEM imaging provide information about the stability of Pd and PdAg NPs in solution in the presence of H_2 for different amounts of time. The optical properties of NPs were evaluated over the range of 300-900 nm using a Varian Cary 50 Bio UV-visible spectrophotometer. At room temperature, two or three drops of a 10 mg/mL toluene solution of Pd or PdAg NPs were placed in a 1 cm path length quartz cuvette and diluted further with toluene. The baseline of each spectrum was corrected using the spectrum of toluene. The absorbance spectrum of the solutions was measured following exposure to pure H_2 bubbling through the solution at a flow rate of 8.0 ± 0.2 mL/min for 0, 5, 15, 30, and 60 min. After exposing to H_2 for 60 min, the solutions were sonicated for 2 min and drop-cast deposited onto a copper grid-supported holey carbon film for TEM measurements. Figure 2.3 shows the set-up used for H_2 stability of solutions of Pd and PdAg NPs.

Figure 2.3 Schematic illustration of H_2 stability set-up of NPs in solution.

2.4 Hydrogen Sensing Experiments of Solid-Phase Pd NPs

2.4.1 Microfabrication of Au Electrodes on Si/SiO_x

Two Au electrodes separated by 23 μm were used as substrates to deposit Pd NPs and fabricate electronic devices for sensing applications. Figure 2.4 shows a digital picture of the full electrode and an enlarged optical microscope image of the 23 μm gap area (indicated by the box). The Au electrodes were purchased from University of Louisville microfabrication facility. During the sputtering process an argon (Ar^+) ion source was used to eject Cr, Ti, or Ni targets as adhesion layers, followed by Au to form Au electrodes. The thickness of the adhesion layer was 10 $\text{\AA}$ and the Au layer was 100 nm.

2.4.2 Wiring and Cleaning of the Au Electrodes

First, the wires were attached to the electrode contact pads with Ag epoxy (Stan Rubinstein Assoc. Inc., Foxboro MA) and placed in an oven for ~ 12 h at 80 $^{\circ}\text{C}$ in order to cure the epoxy. The wires were further insulated with an overlayer of torr-seal epoxy and cured ~ 12 h at 80 $^{\circ}\text{C}$. The electrode was then cleaned by rinsing in acetonitrile, dichloromethane, acetone, ethanol, nanopure water and 2-propanol before drying under N_2 . The electrode was placed in a UV ozone cleaner (Jelight Company Inc., Irvine, CA, Model 4C442) for 10 min in order to remove organic impurities before MPC film deposition. Figure 2.5 shows a current-voltage (i-V) plot of an Au electrode device obtained in air from +0.3 to -0.3 V (started at 0.0 V) at a sweep rate of 100 mV/s. The background current of the plot indicates that the noise level of the instrument is 10-30 pA.

Figure 2.4 Digital picture of an electrode device (A) and optical microscope image of square region from frame A of the 23 μm gap between the Au electrodes (B).

Figure 2.5 Current-voltage (i-V) plot of an Au electrode device obtained in air from 0.3 to -0.3 V (started at 0.0 V) at a sweep rate of 100 mV/s. This shows a background current of a few pA.

2.4.3 Deposition of Films of NPs onto Au Electrodes

Films containing Pd NPs were drop-cast deposited onto the Au electrodes using 1-2 drops of a 10 mg/mL toluene solution, which leads to many multilayers of nanoparticles with film thicknesses well above the thickness of the electrodes.⁶⁷ The deposition of NPs was carried out by placing the drop(s) with a glass pipet onto a vertically hanging electrode device and allowing the solvent to evaporate under the fume hood. Figure 2.6 shows a digital picture of the electrode device after attachment of the wire leads and drop-casting of the NPs across the electrode gap.

2.4.4 Solid State Conductivity Measurements

Solid-state conductivity analysis was conducted on an electrochemical work station (CH Instruments, Inc., Model 660A) operating in cyclic voltammetry (CV) mode, which displays current-potential (I-V) curves. The samples were placed inside a picoamperometer booster (faraday cage) with three electrode terminals. These terminal refers to working, reference, and counter electrodes that are differentiated by green, white, and red colors; respectively. In the two electrode device, one electrode device lead was connected to the working electrode lead and the other electrode connected to both the counter and reference electrode leads.

2.4.5 Hydrogen Sensing Set-Up

For H₂ gas sensing experiments the electrochemical work station operated in chronoamperometry (CA) mode which plots current vs. time. The current was monitored with time at a constant potential of -0.3 V while the device was exposed to alternating

Figure 2.6 Digital picture of the electrode device after attachment of the wire leads and drop-casting of the NPs across the electrode gap.

flows of pure N₂ carrier gas and H₂ mixed with carrier gas. The H₂ concentration was varied by mixing H₂ and N₂ at different flow rates controlled by two flow meter (Cole-Parmer Instrument Co., Vernon Hills, IL) located between the sample and gas cylinders and operated by a 3-way valve. Figure 2.7 shows the set-up used for H₂ sensing. All samples were exposed to 100, 6.0, and 1.0% H₂ for 450 s to monitor the electronic response to H₂. Stable, reversible sensor devices were also tested in the presence of 9.6 to 0.3% H₂. The equation for calculating the percent flow mixture is described below:

$$\text{FM}_2 (\text{mL} \cdot \text{min}^{-1}) / [\text{FM}_1 (\text{mL} \cdot \text{min}^{-1}) + \text{FM}_2 (\text{mL} \cdot \text{min}^{-1})] \times 100 = \% \text{H}_2 \quad (2.1)$$

where; FM₂ denotes the variable flow of hydrogen (mL.min⁻¹) in flow meter #2, FM₁ corresponds to constant flow of nitrogen through flow meter #1. A sample calculation is shown in Table 2.2.

2.5 Catalysis with Pd and PdAg NPs

The catalysis experiments were performed by placing 3.5 mL of CH₂Cl₂ and ~1.5 mmol of allyl alcohol (100 µL) in a small glass reaction vessel. The solution was stirred for 10 min before adding ~3.0 mg of Pd or PdAg NP catalyst. The vessel was capped with a rubber septum and H₂ gas was allowed to bubble through the solution at a flow rate of 1.69 ± 0.02, 8.0 ± 0.2, 19.6 ± 0.2, and 39.0 ± 0.3 mL/min for the duration of the experiment. The total volume was kept constant by adding solvent to the vessel when

Figure 2.7 Schematic illustration of H_2 sensing set-up.

Table 2.2 Sample calculation for % H₂

Nitrogen Flow Meter 1 (FM₁)		Hydrogen Flow Meter 2 (FM₂)		Total flow FM₁ + FM₂ (mL.min⁻¹)	Percent Hydrogen (FM₂/Total flow)x100
Scale reading	mL.min ⁻¹	Scale reading	mL.min ⁻¹		
80	2826	150	300	3126	9.6%
150	4685	150	300	4985	6.0%
150	4685	100	148	4833	3.1%
150	4685	50	47.3	4732	1.0%
150	4685	40	37.4	4722	0.8%
150	4685	30	26.4	4711	0.6%
150	4685	20	18.6	4704	0.4%
150	4685	10	12.0	4697	0.3%

evaporation occurred. The reaction mixture was stirred at 500-600 rpm under atmospheric pressure and at room temperature.

2.5.1 Gas Chromatography

The progress of the reaction was followed by gas chromatography of samples before exposure to H₂ and after addition of NP catalyst and exposure to H₂ for different times. Gas chromatography data were recorded on a Buck Scientific model 910 gas chromatograph equipped with a 1/8 inch packed column (10% carbowax 20M on silica 80/100 mesh, 6 foot) using a flame ionization detector (FID) and helium as the carrier gas. The catalytic reaction was monitored using response factors that were determined with a standard mixture containing 10 mM of each reactant and products. Three structurally related allyl alcohols were studied: 2-propen-1-ol, 1-penten-3-ol, and 2-methyl-3-buten-2-ol, which give possibly the following hydrogenation and/or isomerization products in the presence of Pd and PdAg NP catalysts and H₂: propanol/propanal, 3-pentanol/3-pentanone, and 2-methyl-2-butanol, respectively. Figure 2.8 shows a gas chromatogram of a standard solution containing 2-propen-1-ol, 1-penten-3-ol, and 2-methyl-3-buten-2-ol as reactants with the corresponding products and retention times in Frames A, B, and C, respectively.

Figure 2.8 Gas chromatogram of a standard mixture containing 10 mM of (A) 2-propen-1-ol (reactant) and propanol/propanal (products), (B) 1-penten-3-ol (reactant) and 3-pentanone/3-pentanol (products), and (C) 2-methyl-3-buten-2-ol (reactant) and 2-methyl-2-butanol (product) in CH₂Cl₂. Integration was performed using instrument software. Injection volume = 1 μ L, initial temperature = 60 $^{\circ}$ C, final temperature = 135 $^{\circ}$ C, ramp = 15 $^{\circ}$ C/min, pressure = 20 PSI, detector = FID.

CHAPTER III

SYNTHESIS AND COMPOSITION OF VARIOUS Pd AND PdAg ORGANIC- PROTECTED NANOPARTICLES (NPs)

3.1 INTRODUCTION

Metal nanoparticles (NPs) have been a highly active area of research in recent years due to their unique optical, magnetic, and electrical properties, which are different from the bulk materials.¹⁷ In particular, their high surface area-to-volume ratio and size-dependent electronic structure have made them highly attractive tools for many applications, including sensing,^{6,18,50,113,153} imaging,¹⁵⁴ drug delivery,^{155,156} cancer diagnosis and therapy,^{157,158} hydrogen storage,¹⁵⁹⁻¹⁶¹ and catalysis.^{19,53,162-164} A key issue in the application of these materials is the control of the size, shape, composition, and stability of the nanoparticles,^{28,116-120} which can be accomplished through synthesis and functionalization of the nanoparticles with organic stabilizers such as polymers,²⁴⁻²⁷ dendrimers,²⁸⁻³² surfactants,³³⁻³⁵ or ligands.³⁶⁻⁴²

In 1994, Brust and co-workers reported, for the first time, an easy and reproducible synthesis for the preparation of Au NPs stabilized with self-assembled monolayers of dodecanethiolate ligands.⁵² These roughly spherical particles have a core of metallic atoms surrounded by an organic monolayer. Alkanethiolate-protected Au NPs

are highly stable, can be stored as solid, solvent-free powders, and characterized by the same analytical techniques used for the analysis of small molecules.⁴² Murray and co-workers have extensively studied the synthesis, reactivity, and electrochemistry of Au NPs.^{57,58} The ability to chemically modify the surface of Au NPs by ligand place-exchange^{73,165} and organic coupling reactions¹⁶⁶ has enhanced the potential use of these nanomaterials in technological applications. Other metal NPs (Ag,⁶² Pt,^{37,38,41} Pd,^{51,60,67} Ni,¹⁶⁷ and alloys^{51,68,168-170}) have also been synthesized by the Brust reaction and used for sensing and catalysis applications.^{38,39,67,68,123,131}

Here we describe the chemical synthesis of Pd and Pd-containing alloy (PdAg) NPs stabilized with CnNH₂, CnS, and mixed C8NH₂/C6S ligands.^{67,68} The NP size, distribution, and stability were controlled by varying the initial mole ratio of CnNH₂/Pd and carbon chain lengths of CnS and CnNH₂ including butanethiol (C4S), hexanethiol (C6S), octanethiol (C8S), dodecanethiol (C12S), hexadecanethiol (C16S), octadecanethiol (C18S), and octylamine (C8NH₂), dodecylamine (C12NH₂), and hexadecylamine (C16NH₂), respectively. In particular, we show how these Pd and PdAg NPs can be easily prepared by the modified Brust procedure and fully characterized by transmission electron microscopy (TEM), UV-visible absorption spectroscopy, infrared (IR) spectroscopy, proton nuclear magnetic resonance (¹H NMR), thermogravimetric analysis (TGA), and energy dispersive X-ray (EDX) analysis. The average NP size ranged from 2.5 to 3.5 nm. The Pd and PdAg NPs coated with a long alkyl chain and a high ligand/metal ratio used during the synthesis led to small, stable NPs.

The approach described here importantly leads to the synthesis of Pd and PdAg NPs with controlled functionality and composition. Chapter IV-VII describes their performance for applications in sensing and catalysis.

3.2 EXPERIMENTAL

The procedures of chemical synthesis, purification, and characterization of Pd and PdAg NPs using various analytical techniques are described in Chapter II.

3.3 RESULTS AND DISCUSSION

Figure 3.1 illustrates the various metal compositions (Pd and PdAg) and protecting ligands used in this study, which includes butanethiol (C4S), hexanethiol (C6S), octanethiol (C8S), dodecanethiol (C12S), hexadecanethiol (C16S), octadecanethiol (C18S), octylamine (C8NH₂), dodecylamine (C12NH₂), hexadecylamine (C16NH₂), and mixed C8NH₂/C6S.^{67,68} Nuclear magnetic resonance (NMR), Fourier Transform Infrared (FTIR) spectroscopy, and UV-vis spectroscopy measurements on Pd and PdAg NPs were consistent with the successful synthesis of pure NPs.

3.3.1 Synthesis and Composition of CnS and CnNH₂ Pd and PdAg NPs

The use of stabilizers with metal NPs plays a crucial role in controlling the particle size, shape, stability, and reactivity of the NPs.^{117,119} Table 3.1 shows the average diameter from TEM measurements, the organic weight percent from TGA, and the very roughly estimated compositions of Pd and PdAg NPs coated with different capping ligands. The number of Pd atoms was calculated from the TEM diameter and

Figure 3.1 Illustration of the NPs with different metal compositions and different ligand stabilizers used in this study.

Table 3.1 Characterization and Composition of CnS Pd and CnNH₂ Pd and PdAg NPs

Nanoparticles	TEM ^[a] diam. (nm)	TGA wt. % organic	Composition
½x C4S Pd*	3.4 ± 0.4	11.1	Pd ₁₃₃₄ (C4S) ₁₉₇
½x C6S Pd [#]	3.2 ± 0.4	18.8	Pd ₁₁₁₂ (C6S) ₂₂₂
½x C8S Pd [#]	3.0 ± 0.4	25.3	Pd ₉₁₆ (C8S) ₂₂₅
½x C12S Pd [#]	3.1 ± 0.4	30.5	Pd ₁₀₁₁ (C12S) ₂₃₄
½x C16S Pd [#]	2.8 ± 0.3	35.0	Pd ₇₄₅ (C16S) ₁₆₆
½x C18S Pd [#]	2.6 ± 0.4	37.0	Pd ₅₉₇ (C18S) ₁₃₀
12x C8NH ₂ Pd*	3.5 ± 0.4	18.9	Pd ₁₄₅₅ (C8NH ₂) ₂₈₀
12x C12NH ₂ Pd*	3.4 ± 0.6	22.0	Pd ₁₃₃₄ (C12NH ₂) ₂₁₇
12x C16NH ₂ Pd [#]	3.0 ± 0.5	83.6	Pd ₉₁₆ (C16NH ₂) ₂₀₅₇
6x C16NH ₂ Pd*	3.1 ± 0.4	57.9	Pd ₁₀₁₁ (C16NH ₂) ₆₁₄
3x C16NH ₂ Pd*	5.1 ± 1.0	14.4	Pd ₄₅₀₂ (C16NH ₂) ₃₃₄
12x C8NH ₂ Pd ₉₁ Ag ₉ *	2.8 ± 0.7	20.8	Pd ₆₇₂ Ag ₆₆ (C8NH ₂) ₁₆₁
12x C12NH ₂ Pd ₉₁ Ag ₉ *	2.5 ± 0.3	17.8	Pd ₄₇₈ Ag ₄₇ (C12NH ₂) ₆₅
12x C16NH ₂ Pd ₉₁ Ag ₉ [#]	2.9 ± 0.4	86.9	Pd ₇₄₆ Ag ₇₄ (C16NH ₂) ₂₃₉₈

These NPs were stable and appeared as well-isolated, individual structures.

* These NPs showed several aggregated structures in the TEM images and have the most uncertainty in the TEM measured diameter and overall composition.

^[a] The average particle sizes were obtained from counting only individual, well-isolated nanoparticles in the TEM images (see Figure 3.2 and 3.3). Larger, irregular shaped structures were not included because it was uncertain if those originally existed that way or became aggregated in solution or upon drying.

number of ligands was calculated from percent organic content given by TGA. Figure 3.2 and 3.3 present TEM images of the various CnS Pd and CnNH₂ Pd and PdAg NPs on carbon-coated copper grids, respectively. The average diameter of CnS Pd NPs was in the 3-nm range, similar to the core diameter reported for alkanethiolate-protected Pd NPs previously.^{51,60} Zamborini and co-workers determined that the core size of the C6S and C12S Pd NPs decreases with increasing thiol/Pd ratio.⁴² For the ½x, 1x, and 2x C6S Pd NP preparations, the average core diameter obtained was 3.0, 2.2, and 1.6 nm, respectively. However, they observed that Pd NPs synthesized with a 2:1 thiol/Pd ratio or larger led to some form of Pd (II) thiolate complexes rather than Pd (0) complexes as evidenced by UV-vis and NMR analysis.⁴² In this study we synthesized ½x CnS Pd NPs, which behave quite similar to Au NPs with metal-like cores. The average diameter of C4S, C6S, C8S, C12S, C16S, and C18S Pd NPs were 3.4, 3.2, 3.0, 3.1, 2.8, and 2.6 nm, respectively. Although the core sizes of the synthesized CnS Pd NPs are statistically similar to each other, TEM images revealed that an increase in carbon chain length leads to small and well-isolated NPs. For instance, Figure 3.2 shows that C4S Pd NPs appeared heavily aggregated (Frame A), while C6S and C8S Pd NPs were well-isolated and spherical (Frame B and C, respectively). Therefore, Pd NPs coated with shorter chain alkanethiols gives NPs with lower stability.

The average diameters of 12x C8NH₂, 12x C12NH₂, and 12x C16NH₂ Pd NPs were 3.5, 3.4, and 3.0 nm, respectively, statistically similar to each other and CnS Pd NPs. The average core diameters of 12x, 6x, and 3x C16NH₂ Pd NPs were 3.0, 3.1, and 5.1 nm, respectively, showing that a low alkylamine/Pd mole ratio used during the synthesis increased the size of the C16NH₂ Pd NPs.⁶⁸ The size of Pd NPs coated with

Figure 3.2 TEM images of drop-cast films of CnS Pd NPs synthesized with a 1:2 CnS:Pd ratio ($\frac{1}{2}x$): **(A)** C4S Pd, **(B)** C6S Pd, **(C)** C8S Pd, **(D)** C12S Pd, **(E)** C16S Pd, and **(F)** C18S Pd NPs. A few of the single individual nanoparticles are circled.

Figure 3.3 TEM images of drop-cast films of (A) 12x C8NH₂ Pd, (B) 12x C12NH₂ Pd, (C) 12x C16NH₂ Pd, (D) 6x C16NH₂ Pd, (E) 3x C16NH₂ Pd, (F) 12x C8NH₂ Pd₉₁Ag₉, (G) 12x C12NH₂ Pd₉₁Ag₉, and (H) 12x C16NH₂ Pd₉₁Ag₉ NPs. A few of the single individual nanoparticles are circled.

C16NH₂ did not differ statistically when the ratio was between 12:1 and 6:1 alkylamine/Pd. It is important to note that the average diameters reported in Table 3.1 are based on the counting of clearly isolated, individual NPs in the TEM images. Some of the NPs appeared larger, but it was not clear if that was the actual size of the NPs or if those were aggregates (Figure 3.3). In those examples, highlighted by an asterisk, we only counted clearly separated and individual NPs in the analysis and the size may not be very accurate. Images of 12x C16NH₂ Pd and PdAg NPs contained mostly well-isolated NPs while C8NH₂, C12NH₂, and 3x and 6x C16NH₂ Pd or PdAg NPs appeared slightly aggregated and irregular-shaped. This shows that Pd NPs coated with shorter chain alkylamines and a lower ratio of the C16NH₂ ligands used during the synthesis leads to NPs with lower stability against aggregation.

We also synthesized PdAg NPs coated with C_nNH₂, where the mole ratio was 10:1 (Pd:Ag). The mole ratio of C8NH₂, C12NH₂, and C16NH₂ was 12:1 with respect to the total metal content (12x). Energy Dispersive Analysis of X-rays (EDX) of PdAg NPs indicated that both Pd and Ag atoms are in each sample of nanoparticles. Figure 3.4 shows an EDX spectrum of Pd₉₁Ag₉ NPs coated with C8NH₂ ligands. Table 3.2 summarizes the final relative metal composition of Pd₉₁Ag₉ NPs prepared, where the Pd:Ag mole ratio was 10:1 during the synthesis. EDX confirmed that the final relative composition of Pd and Ag closely matched the relative metal salt concentrations of K₂PdCl₄ and AgC₂F₃O₂ used in the synthesis. 12x C8NH₂, 12x C12NH₂, and 12x C16NH₂ Pd₉₁Ag₉ NPs ranged in diameter from 2.5 to 2.9 nm (Figure 3.3 and Table 3.1).

TGA of Pd and PdAg NPs leads to thermal desorption of organic stabilizers leaving Pd as the residual mass. Thus, the attached C_nS or C_nNH₂ ligand component can

Figure 3.4 EDX spectrum of 12x C₈NH₂ Pd₉₁Ag₉ NPs.

Table 3.2 Atomic ratios of PdAg NPs as estimated by EDX measurements

Nanoparticles	Pd atomic %	Ag atomic %
12x C8NH ₂ Pd ₉₁ Ag ₉	89.95 ± 1.71	10.04 ± 0.84
12x C12NH ₂ Pd ₉₁ Ag ₉	89.30 ± 0.36	10.69 ± 0.15
12x C16NH ₂ Pd ₉₁ Ag ₉	85.29 ± 4.07	14.70 ± 1.94

be measured by the weight loss after desorption. Figure 3.5 displays the TGA analysis of $\frac{1}{2}\times$ C6S and $12\times$ C8NH₂ Pd NPs. Frame A exhibits the TGA of pure C6S Pd NPs with a fairly rapid 12.7% weight loss occurring between 100 and 200 °C and additional gradual weight loss up to 800 °C, resulting in a total weight loss of 18.8%. Frame B shows the thermal decomposition of the organic portion of C8NH₂ Pd NPs. The most rapid weight loss of about 12.3% occurs between 100 and 200 °C with an additional weight loss up to 800 °C for a total of 18.9%. The weight loss between 200 and 800 °C occurs in three fairly discrete steps with steep regions and plateaus in the TGA plot that is distinctly different compared to the gradual weight loss observed for C6S Pd NPs throughout the entire 200-800 °C range. Table 3.1 (column 3) shows the organic weight percent for Pd and PdAg NPs stabilized with various organic ligands. For $\frac{1}{2}\times$ C_nS Pd (n = 4, 6, 8, 12, 16, and 18), and $12\times$ C8NH₂ and $12\times$ C12NH₂ Pd and Pd₉₁Ag₉ NPs, the total organic content ranged from 11.1 to 39.3%. These values are consistent with monolayer coatings of the ligand.⁶⁸ As mentioned above, the nature of capping ligands plays a crucial role in controlling the particle size and composition of the nanoparticles. In fact, we observed from the TEM data that the particle size decreased with an increase in carbon chain length of C_nS; therefore, smaller Pd NPs have larger organic weight fractions, which is in agreement with the literature.^{39,42} This is also because a longer chain length has more mass. Among the C_nS Pd NPs used, C18S Pd NPs produced the smallest Pd NPs (2.6 nm) with a high organic weight percent (39.3%). It is interesting that an increase in chain length by only 2 carbons, from C4 to C6 of C_nS, allows a significant change in the morphology of the NPs, reducing the chance of collision between Pd atoms and their aggregation. This is due to the higher organic content for C6S Pd NPs compared to C4S

Figure 3.5 TGA measurements of (A) $\frac{1}{2}x$ C₆S Pd and (B) 12x C₈NH₂ Pd NPs.

Pd NPs. The organic content for 6x C16NH₂ Pd (57.9%), 12x C16NH₂ Pd (83.6%), and 12x C16NH₂ Pd₉₁Ag₉ NPs (86.9%) is too large for a single monolayer and is attributed to the formation of a full or partial bilayer of ligands on the Pd cores as reported previously by Shuang and co-workers for octadecylamine-coated Pd NPs.³⁹ The higher organic content for the larger alkylamine/Pd ratio for the C16NH₂ ligands is consistent with less aggregation in the TEM images for these NPs. In order to confirm that the increased stability of C16NH₂ Pd and PdAg NPs was due to the formation of a bilayer of ligands rather than the presence of excess ligands not fully rinsed, we also purified the NPs by 1) rinsing copiously with 500 mL of ethanol, 2) soaking in ethanol solution overnight and 3) sonicating in ethanol prior to filtration and collection. The TGA showed organic weight percents of 81.6, 81.4, and 68.4% for these treatments, respectively, showing that it is very difficult to remove the C16NH₂ ligands. Since the free ligand is highly soluble in ethanol, we believe all of the C16NH₂ ligands are associated with the Pd NPs and not just in excess. For some unknown reason the ligand structure around the Pd is very different for the 6x and 3x preps based on the very different organic weight percent. Further work is needed to better understand this.

The average core diameter from the TEM images and the organic weight percent from TGA measurements allowed us to roughly estimate the composition for the NPs listed in Table 3.1 (column 4). Our calculations were based on a spherical model of the Pd and PdAg core, although the metal cores likely have a truncated octahedral shape containing surface defect atoms (edges and vertices).^{38,42,54,73}

3.3.2 Synthesis and Composition of C8NH₂/C6S Pd NPs

As illustrated in Figure 3.6, we synthesized mixed ligand C8NH₂/C6S Pd NPs with varying ratios by a liquid-phase place-exchange reaction between 12x C8NH₂ Pd NPs and free C6SH ligands in solution.^{67,68} We propose that the exchange reaction proceeds as follows, although there is no direct evidence of the detailed mechanism, which is currently not fully understood.^{54,73}

Table 3.3 displays the estimated composition of Pd_n(C8NH₂)_{m-x}(C6S)_x, where n was 919 or 1455, m was 177 or 280, and x was varied to be 3, 10, 14, 16, 32, 46, 81, 95, 150, 217, 267, and 311. Nuclear magnetic resonance (NMR) spectroscopy confirmed that the C6SH ligands fully replace the C8NH₂ ligands on the Pd NP surface during the exchange reaction, which supports the fact that the Pd-S-R bond is much stronger compared to Pd-NH₂-R.⁶⁷ Overall, the compositions provided are rough estimates and, although Figure 3.6 shows a random mixture of C6S and C8NH₂ ligands, phase segregation¹⁷¹ of the ligands or preferential exchange at surface atom defects^{73,172,173} could occur. Figure 3.7 exhibits the UV-vis spectra of dilute toluene solutions containing C8NH₂ Pd, C6S Pd, and Pd₉₁₉(C8NH₂)_{177-x}(C6S)_x Pd NPs of varied ratio (x = 3, 10, 16, 32, and 81). The spectroscopic measurements of pure C8NH₂ Pd and C6S Pd NPs were performed immediately after the synthesis of the clusters. In the case of Pd NPs coated with mixed monolayers of C8NH₂/C6S, the optical properties were obtained in most

Figure 3.6 Illustration of the preparation of mixed monolayers of octylamine (C8NH₂) and hexanethiolate (C6S) Pd NPs by a liquid-phase place-exchange reaction.

Table 3.3 Quantities of reagents used and estimated composition for C8NH₂/C6S Pd NPs synthesized by liquid-phase place-exchange reaction

Starting NPs	mol C8NH ₂	μL C6SH	mol C6SH	Composition Pd/C8NH ₂ /C6S*
~50 mg Pd ₉₁₉ (C8NH ₂) ₁₇₇ Diam. 3.0 nm	7.45 x 10 ⁻⁵	0.2	1.42 x 10 ⁻⁶	919/174/3
	7.35 x 10 ⁻⁵	0.6	4.25 x 10 ⁻⁶	919/167/10
	7.30 x 10 ⁻⁵	1.0	7.09 x 10 ⁻⁶	919/161/16
	7.29 x 10 ⁻⁵	2.0	1.42 x 10 ⁻⁵	919/145/32
	7.33 x 10 ⁻⁵	5.0	3.54 x 10 ⁻⁵	919/96/81
~15 mg Pd ₁₄₅₅ (C8NH ₂) ₂₈₀ Diam. 3.5 nm	2.15 x 10 ⁻⁵	0.15	1.06 x 10 ⁻⁶	1455/266/14
	2.14 x 10 ⁻⁵	0.5	3.54 x 10 ⁻⁶	1455/234/46
	2.08 x 10 ⁻⁵	1.0	7.09 x 10 ⁻⁶	1455/185/95
	1.98 x 10 ⁻⁵	1.5	1.06 x 10 ⁻⁵	1455/130/150
	1.83 x 10 ⁻⁵	2.0	1.42 x 10 ⁻⁵	1455/63/217
	2.23 x 10 ⁻⁵	3.0	2.13 x 10 ⁻⁵	1455/13/267
	2.23 x 10 ⁻⁵	3.5	2.48 x 10 ⁻⁵	1455/0/311

* Composition of C8NH₂/Pd NPs based on full replacement of C8NH₂ with C6S on the Pd NP.

Figure 3.7 UV-vis spectra of dilute toluene solutions containing C8NH₂ Pd, C6S Pd, and mixed monolayers of C8NH₂/C6S Pd NPs.

cases after carrying out the liquid-phase place-exchange reaction for 24 hours. The UV-vis spectra exhibit an absorbance throughout the entire wavelength range that decays exponentially with increasing wavelength, which is expected for metallic Pd⁰ nanoparticles. One exception is the UV-vis spectrum of the 96/81 C8NH₂/C6S Pd NPs, which shows two small peaks at approximately 330 and 420 nm in the UV-vis spectrum after the 24 hour exchange reaction and very little absorbance greater than 500 nm. This is consistent with the presence of Pd^{II} species instead of Pd⁰.⁴² The larger quantity of C6S ligands in this case leads to the oxidation of Pd⁰ to Pd^{II}. To avoid this, we instead performed the place-exchange for only 5 hours, where the spectrum is again consistent with Pd⁰ NPs as shown in Figure 3.7.

3.4 CONCLUSIONS

In summary, we demonstrated the successful synthesis of Pd and PdAg NPs coated with various organic stabilizers such as CnS, CnNH₂, and mixed monolayers of C8NH₂/C6S. All of the NPs were in the 2.5 to 3.5 nm range. We showed how these particles can be easily prepared and confirmed the particle composition through various materials characterization techniques that include NMR, EDX, TEM, TGA, and UV-vis analysis. This extensive characterization leads to the following conclusions: 1) the Pd-S bond is much stronger compared to Pd-NH₂; 2) Pd and PdAg NPs coated with C16NH₂ ligands prepared in a 12:1 alkylamine:Pd ratio lead to small and stable NPs, which is attributed to the formation of multilayers of ligands on the Pd core; 3) longer chain CnS leads to smaller Pd NPs; 4) all CnS Pd NPs with $n \geq 6$ are stable.

CHAPTER IV

HYDROGEN STABILITY OF SOLUTION-PHASE Pd AND PdAg

NANOPARTICLES (NPs)

4.1 INTRODUCTION

It is well-known that hydrogen adsorbs and dissociates spontaneously onto group VIII transition metals.^{81,84} Among the many types of metals, the reaction between hydrogen and Pd or Pd alloys has attracted a great deal of attention due to its relevance in applications in hydrogen sensing, hydrogen storage, and catalysis.^{74,76} Figure 4.1 illustrates the reaction between Pd and hydrogen. The adsorption of hydrogen occurs in a two step process involving the reversible adsorption of hydrogen molecules at the Pd surface, followed by rapid dissociation and diffusion of atomic hydrogen into the metal lattice, where it occupies octahedral interstitial sites with an increase in the lattice constant.⁸⁴ At low hydrogen partial pressures α -phase PdH_x forms, which becomes β -phase PdH_x at higher pressures.⁸⁹ The phase transition and associated increase in lattice constant alters the physical,^{90,91} electrical,⁹⁵⁻¹⁰² and optical¹⁰³⁻¹⁰⁵ properties of Pd and its alloys, forming the basis for hydrogen sensors.^{75,78} The diffusion of hydrogen into the Pd lattice provides large hydrogen storage capacity and the dissociation of hydrogen into the more active atomic hydrogen leads to its desirable catalytic properties.

Figure 4.1 Illustration of the reaction between Pd and hydrogen.

For applications in sensing, storage, and catalysis, it is clearly of interest to synthesize nanomaterials that are highly reactive with hydrogen in a reversible manner and stable throughout many reaction cycles. Here we study the stability of CnS Pd (n = 4, 6, 8, 12, 16, and 18), CnNH₂ (n = 8, 12, and 16) Pd and PdAg (10:1), and C8NH₂/C6S Pd NPs in solutions of bubbling hydrogen gas by UV-vis spectroscopy and transmission electron microscopy (TEM) measurements of the NPs as a function of bubbling time.^{67,68} Out of the different NPs, C6S Pd, C8S Pd, C12S Pd, C16S Pd, C18S Pd, C16NH₂ Pd, C16NH₂ PdAg (10:1) and C8NH₂/C6S Pd (~1:1) NPs were stable in the presence of hydrogen for several hours. The others exhibited irreversible aggregation and precipitation within 1 hour. These studies provided interesting knowledge of hydrogen stability which is useful for the sensing and catalysis studies described in later chapters.

4.2 EXPERIMENTAL

The procedure for testing the stability of various solutions of Pd and PdAg NPs in the presence of H₂ is described in Chapter II.

4.3 RESULTS AND DISCUSSION

4.3.1 Hydrogen Stability of CnS and CnNH₂ Pd NPs

UV-vis spectroscopy and TEM imaging provided information about the stability of Pd NPs in solution in the presence of H₂ for different amounts of time. Figure 4.2

Figure 4.2 UV-vis spectra of a toluene solution of (A) C4S Pd, (B) C6S Pd, and (C) C8S Pd NPs synthesized with a 1:2 CnS:Pd ratio ($\frac{1}{2}x$) before and after exposure to 100% H_2 at a flow rate of 8.0 ± 0.2 mL/min for different times.

shows normalized UV-vis spectra of diluted toluene solutions containing $\frac{1}{2}\times$ C4S, $\frac{1}{2}\times$ C6S, and $\frac{1}{2}\times$ C8S Pd NPs, which were exposed to 100% H₂ at a constant flow of 8.0 ± 0.2 mL/min for 0, 5, 15, 30, and 60 minutes. UV-vis spectra of Pd NPs show no peaks since Pd has no surface plasmon band in this range; only an exponential rise in absorbance as wavelength decreases. Zamborini and co-workers reported that spectra of the 2x and 3x C12S Pd NP preparations exhibited two absorbance peaks at 350 and 400 nm, which correspond to S-containing Pd (II) complexes.⁴² The spectrum of the C4S Pd NPs did not show an exponential increase in absorbance. It is large at all wavelengths (Frame A), which is in agreement with the aggregation of these NPs, as also observed in the TEM images (Figure 3.2, Frame A). These NPs were not soluble in organic solvents and exhibited a dramatic absorbance decrease during H₂ exposure for 60 min due to further H₂-induced aggregation. These results show that C4S ligands are not good capping ligands for $\frac{1}{2}\times$ C4S Pd NPs. In contrast, the spectrum of the $\frac{1}{2}\times$ C6S and $\frac{1}{2}\times$ C8S Pd NPs (Frame B and C, respectively) did not change after H₂ exposure over time, indicating higher stability due to the longer chain length and larger organic content as determined by TGA measurements.

Figure 4.3 shows plots of the normalized absorbance at 310 nm of toluene solutions of CnS Pd NPs of varied chain length ($n = 4, 6, 8, 12, 16,$ and 18) as a function of exposure time to pure H₂ bubbling through the solution at a flow rate of 8.0 ± 0.2 mL/min. The points and curves represent the average of three samples prepared with the standard deviations shown. The absorbance of $\frac{1}{2}\times$ C4S Pd NPs decreased gradually with time, displaying a stable absorbance at $A \sim 0.4-0.5$. Although these NPs were insoluble in

Figure 4.3 Plots of the normalized absorbance at 310 nm of toluene solutions containing C4S Pd, C6S Pd, C8S Pd, C12S Pd, C16S Pd, and C18S Pd NPs synthesized with a 1:2 CnS:Pd ratio ($\frac{1}{2}x$) versus exposure time to 100% H₂ at a flow rate of 8.0 ± 0.2 mL/min.

toluene and unstable even before H₂ exposure, they showed some reactivity with H₂ gas as evidenced by the decrease in absorbance (Figure 4.2, Frame A). As the carbon chain length of the alkanethiolate ligands on the NPs increased, the overall stability against aggregation increased significantly. The normalized absorbance of the solutions of 1/2x C6S, C8S, C12S, C16S, and C18S Pd NPs was stable at A ~0.9-1 after 60 min, indicating high stability against aggregation in the presence of H₂. The high stability of CnS Pd NPs against H₂-induced aggregation is due to the strongly coordinated thiolates, preventing reactivity of Pd with H₂ or inhibiting aggregation of PdH_x NPs.^{60,67,68}

Figure 4.4 shows plots of the normalized absorbance at 310 nm of toluene solutions of CnNH₂ Pd NPs of varied chain length (Frame A) and C16NH₂ Pd NPs synthesized with different alkylamine/Pd ratio (Frame B) as a function of exposure time to 100% H₂. Frame A shows that the absorbance of 12x C16NH₂ Pd NPs is very stable over time (A ~0.8-0.9) while 12x C8NH₂ and 12x C12NH₂ Pd NPs are not stable as the absorbance decreases and the NPs visibly precipitate. This indicates that as the carbon chain length of the alkylamine ligands on the NPs increased, the stability against aggregation increased.⁶⁸ The high stability of 12x C16NH₂ Pd NPs is also attributed to the formation of a bilayer, which can reduce the chance of collisions and aggregation of the Pd NPs. In Frame B, the normalized absorbance of 3x C16NH₂ Pd NPs decreased dramatically with time, suggesting that the Pd NPs were not well protected by the C16NH₂ in this case. This was accompanied by the noticeable precipitation of the NPs. Figure 4.5 shows a digital picture of vials containing solutions of Pd NPs coated with C16NH₂ ligands in a 12:1 and 3:1 alkylamine: Pd ratio before and after H₂ bubbling for 60 min. Initially the two solutions of Pd NPs appeared dark brown in color (Frame A and

Figure 4.4 Plots of the normalized absorbance at 310 nm of toluene solutions containing (A) C_nNH₂ Pd NPs synthesized with a 12:1 C_nNH₂:Pd ratio (12x), and (B) C16NH₂ Pd NPs prepared at various ligand/metal ratios (12:1, 12x; 6:1, 6x; 3:1, 3x) versus exposure time to 100% H₂ at a flow rate of 8.0 ± 0.2 mL/min.

Figure 4.5 Dilute toluene solutions of (A, C) 12x C16NH₂ Pd and (B, D) 3x C16NH₂ Pd NPs before (A, B) and after (C, D) H₂ bubbling for 60 min at a constant flow rate of 8.0 ± 0.2 mL/min.

B). After H_2 exposure for 60 min, the color and appearance of the solution of 12x C16NH₂ Pd NPs did not change, confirming its great stability in the presence of H_2 (Frame C). In contrast, the dark color of the solution of 3x C16NH₂ Pd NPs changed to a colorless solution with a noticeably black solid precipitate of Pd NPs forming and settling to the bottom of the vial (Frame D). This is consistent with the low organic content determined by TGA (14.4%). As the number of C16NH₂ ligands on the Pd NPs increased, as determined by TGA, the rate of aggregation decreased. Accordingly, the 6x and 12x C16NH₂ Pd NPs were significantly more stable in the presence of H_2 . It is not clear why the 3x C16NH₂ Pd NPs had such a small organic content.

To further determine if the C16NH₂ ligands are associated with the Pd NPs in the 6x and 12x preps or if they are just excess ligands, we monitored the stability of C8NH₂ Pd NPs with excess C8NH₂ ligands intentionally added to the solution. Figure 4.6 shows a plot of the normalized absorbance at 310 nm of toluene solutions containing C8NH₂ Pd NPs with 66.4 and 82.0% excess C8NH₂ ligands. The C8NH₂ Pd NPs still precipitated by 60 min, but the rate of precipitation was decreased as the organic content increased. The fact that they were still not fully stable shows that the total organic content is not the only factor needed to stabilize the Pd NPs. There is something different about the C16NH₂ ligands, which we believe is the ability to form a fairly stable bilayer associated with the Pd NP surface.^{39,68} This experiment provides indirect evidence of that.

We used TEM to directly correlate the UV-vis data with the morphology of the Pd NPs. Figure 4.7 displays TEM images of Pd NPs prepared with C6S and C_nNH₂ ligands before and after H_2 exposure. Frame A, C, E, and G show TEM images of ½x C6S Pd, 12x C8NH₂ Pd, 12x C12NH₂ Pd, and 12x C16NH₂ Pd NPs before H_2 exposure,

Figure 4.6 Plot of the normalized absorbance at 310 nm of toluene solutions containing C8NH₂ Pd NPs with 66.4 and 82.0% excess C8NH₂ ligands versus exposure time to 100% H₂ at a flow rate of 8.0 ± 0.2 mL/min.

Figure 4.7 TEM images of drop-cast films of 1/2x C6S Pd, 12x C8NH₂ Pd, 12x C12NH₂ Pd, 12x C16NH₂ Pd, 6x C16NH₂ Pd, and 3x C16NH₂ Pd NPs before (**A, C, E, G, I, K**) and after exposure to 100% H₂ for 60 minutes (**B, D, F, H, J, L**).

respectively. All of the samples show the presence of metal NPs in the 3.0 to 3.4 nm diameter size range. All of the $\frac{1}{2}$ x C6S Pd (Frame A) and 12x C16NH₂ Pd NPs (Frame G) are well isolated and spherical. In contrast, several of the 12x C8NH₂ Pd (Frame C) and 12x C12NH₂ Pd NPs (Frame E) appear oddly shaped or slightly aggregated. Frame D and F show the images of the 12x C8NH₂ Pd and C12NH₂ Pd NPs, respectively, after exposure to 100% H₂ for 60 min at a constant flow of 8.0 ± 0.2 mL/min. These NPs aggregated into large superstructures and there was no evidence of individual, isolated NPs in the images. The images of the $\frac{1}{2}$ x C6S Pd (Frame B) and 12x C16NH₂ Pd NPs (Frame H) show several well-isolated NPs and a few that have undergone some slight enlargement. Frame I and K show TEM images of 6x and 3x C16NH₂ Pd NPs before H₂ exposure, respectively, while Frame J and L show images of the corresponding samples after exposure to H₂ for 60 min. As the C16NH₂:Pd ratio (6:1 and 3:1) decreased during the synthesis, the rate of aggregation increased and the Pd NPs exhibited significant morphology changes before and after H₂ exposure. In particular, the NPs synthesized with a 3:1 C16NH₂:Pd ratio were the largest and most heavily aggregated after H₂ exposure, forming structures with dimensions in the several hundred nanometer to micrometer size range, similar to those observed for 12x C8NH₂ and 12x C12NH₂ Pd NPs. In fact, these NPs even appeared aggregated after drying on the TEM grid without exposure to H₂ (Frame K), indicating lower stability. The images in Figure 4.7 are consistent with the UV-vis data.

4.3.2 Hydrogen Stability of C_nNH₂ PdAg NPs

We next studied the H₂ stability of PdAg NPs in solution. These alloys are significant because Ag has the ability to adsorb large amounts of H₂ into its lattice if Pd

atoms are present to catalyze the breaking of the H-H bond.^{103,174} Another added benefit of this alloy is that Ag is much cheaper than Pd, which could reduce the cost of catalysts based on these materials. Figure 4.8 shows the change in absorbance of toluene solutions of 12x C16NH₂, 12x C12NH₂, and 12x C8NH₂ PdAg NPs as a function of exposure time to 100% H₂ bubbling through the solution at 8.0 mL/min. The C16NH₂ Pd₉₁Ag₉ NPs displayed a minimal change in absorbance and high stability against aggregation in the presence of H₂ as shown for pure C16NH₂ Pd NPs (Figure 4.4). In the case of Pd₉₁Ag₉ NPs coated with C12NH₂ and C8NH₂, the absorbance decreased slowly with time, almost reaching A ~0.2-0.3 after 60 min of H₂ exposure. Interestingly, this decrease was more gradual than that observed for pure Pd alkylamine NP solutions in Figure 4.4 (Frame A), showing some enhanced stability by adding a small amount of Ag.⁶⁸ This is consistent with previous conductivity and IR data of these NPs in the presence of H₂.⁵¹

Figure 4.9 shows TEM images of PdAg NPs synthesized with 12x C16NH₂, 12x C12NH₂, and 12x C8NH₂ before (A-C) and after H₂ exposure (D-F). Frame A, B, and C show TEM images of Pd₉₁Ag₉ NPs coated with C16NH₂, C12NH₂, and C8NH₂ ligands, respectively, before H₂ exposure. These NPs were well-isolated and spherical, however, several of the C12NH₂ and C8NH₂ Pd₉₁Ag₉ NPs appeared slightly aggregated (Frame B and C) even without H₂ exposure. After exposure to 100% H₂ for 60 min, only the C16NH₂ Pd₉₁Ag₉ NPs remained well isolated and spherical with some minor evidence of aggregation, while the other two samples were heavily aggregated, consistent with the UV-vis data in Figure 4.8.

Figure 4.8 Plot of the normalized absorbance at 310 nm of toluene solutions containing CnNH₂ PdAg NPs versus exposure time to 100% H₂ at a flow rate of 8.0 ± 0.2 mL/min. The CnNH₂:PdAg mole ratio was 12:1 (12x). The mole ratio between Pd and Ag was 10:1.

Figure 4.9 TEM images of drop-cast films of 12x C16NH₂, 12x C12NH₂, and 12x C8NH₂ Pd₉₁Ag₉ NPs before (A, B, C) and after exposure to 100% H₂ for 60 minutes (D, E, F).

4.3.3 Hydrogen Stability of C8NH₂/C6S Mixed Ligand Pd NPs

The UV-vis and TEM data consistently show that C8NH₂ Pd NPs are much more reactive to H₂ compared to C6S Pd NPs. The reaction between C8NH₂ Pd NPs and H₂ presumably leads to the formation of PdH_x.^{67,68} The PdH_x formation leads to cluster aggregation as evidenced by the decrease in absorbance with time, noticeable precipitation, and presence of large aggregated structures in the TEM images as shown in Figure 4.4 and 4.7. Exposure to H₂ leads to strong Pd-H interactions, loss of the C8NH₂ ligands, and cluster aggregation in solution. The TEM images also reveal that there was a small degree of aggregation of the C8NH₂ Pd NPs even before H₂ exposure. This is again due to the weak Pd-NH₂ interactions, which leads to less stable clusters compared to those protected with C6S ligands. Further evidence of this is the fact that some C8NH₂ Pd NPs eventually precipitate when stored in solution for more than a week and they are generally not as stable when stored in solution or air compared to C6S Pd NPs.

The small changes in the UV-vis spectra of the C6S Pd NPs in the presence of H₂ shows that 1) these clusters are much less reactive to H₂ or 2) they react with H₂ in a manner that does not lead to as much aggregation or morphology changes compared to C8NH₂ Pd NPs (Figure 4.2). This is supported by the minimal change in the morphology of the NPs shown in the TEM images after H₂ exposure (Figure 4.7). Both the UV-vis and TEM data consistently show that there is a small degree of aggregation of Pd NPs resulting from the reaction between H₂ and C6S Pd NPs.

Figure 4.10 illustrates the differences between the reaction of H₂ with C6S Pd and C8NH₂ Pd NPs. Based on the data, C6S Pd NPs show little reactivity with H₂. Only a

A. C6S Pd NPs

B. C8NH₂ Pd NPs

Figure 4.10 Illustration of the stability of (A) C6S Pd and (B) C8NH₂ Pd NPs upon exposure to 100% H₂ at a flow rate of 8.0 ± 0.2 mL/min.

small amount of cluster aggregation or film morphology change occurs. In contrast, the C8NH₂ Pd NPs readily react with H₂, which leads to a larger degree of cluster aggregation and film morphology changes accompanied by a large loss of the C8NH₂ ligands from the cluster surface, as shown by our group previously.⁵¹ The H₂ does not readily react with C6S Pd NPs since they are coated with a strong binding thiolate ligand. The Pd-H bond is likely inhibited by the Pd-S bonds.^{175,176} PdH_x can readily form on the C8NH₂ Pd NPs because of the much weaker Pd-NH₂ interaction.

In summary, because alkanethiolates appear to inhibit Pd NP reactivity with H₂ and alkylamines do not stabilize the Pd NPs well, we synthesized Pd NPs stabilized with mixed monolayers of C8NH₂ and C6S ligands to determine if a certain ratio would lead to Pd NPs with high H₂ reactivity while maintaining the necessary structural stability for sensing and catalysis applications.^{67,68} Figure 4.11 shows plots of the normalized UV-vis spectra of diluted toluene solutions containing C8NH₂ Pd, C6S Pd, and C8NH₂/C6S Pd NPs of varied ratio that were exposed to 100% H₂ at a flow rate of 8.0 ± 0.2 mL/min for 60 min. Frame A displays the change in absorbance of solutions of Pd NPs coated with C8NH₂/C6S ratios of 174/3, 167/10, 161/16, 145/32, and 96/81. The absorbance of pure C8NH₂ Pd NPs decreased rapidly with time, almost reaching zero after 60 min as also shown in Figure 4.4. As the number of C6S ligands on the NPs increased, the rate of aggregation decreased and overall stability against aggregation increased. For C8NH₂/C6S ratios of 174/3, 167/10, and 161/16, the Pd NPs displayed a stable absorbance at A~0.2-0.4, showing that a little more than half of the Pd NPs became insoluble. The normalized absorbance of the solutions of 145/32, 96/81, and pure C6S-coated Pd NPs was stable at A ~0.8-0.9 after 60 min, indicating a small change in

Figure 4.11 Plots of the normalized absorbance at 310 nm of toluene solutions containing (A) C6S Pd, 96/81, 145/32, 161/16, 167/10, 174/3 C8NH₂/C6S Pd, and C8NH₂ Pd NPs, and (B) 0/311, 13/267, 63/217, 130/150, 185/95, 234/46, and 266/14 C8NH₂/C6S Pd NPs versus exposure time to 100% H₂ at a flow rate of 8.0 ± 0.2 mL/min.

absorbance and high stability against aggregation in the presence of H_2 . Assuming that the H_2 reactivity leads to aggregation, this suggests that less reactivity occurred. The same trend was observed for Pd NPs coated with C_8NH_2/C_6S ratios of 266/14, 234/46, 185/95, 130/150, 63/217, 13/267, and 0/311 (Frame B). For C_8NH_2/C_6S ratios of 266/14 and 234/46, the Pd NPs precipitated significantly, displaying a stable absorbance at $A \sim 0.1-0.3$ after 60 min. Pd NPs coated with ligand ratios of 130/150, 63/217, 13/267, and 0/311 remained much more stable for the entire 60 min time period ($A \sim 0.8-1.0$). For the 185/95 C_8NH_2/C_6S Pd NPs, the absorbance decreased by about 50% after 60 min of H_2 bubbling.

Figure 4.12 shows TEM images of Pd NPs coated with 174/3 and 96/81 C_6S/C_8NH_2 ligands before (A-B) and after H_2 exposure (C-D). 96/81 C_8NH_2/C_6S Pd NPs suffered minimal morphology changes after H_2 exposure with evidence of slight aggregation, while 174/3 C_8NH_2/C_6S Pd NPs appeared heavily aggregated before and after H_2 exposure as determined previously for pure C_8NH_2 Pd NPs.

The data in Figure 4.11 and 4.12 interestingly show that partial coverage with C_6S ligands (at least 32 out of 177 or 150 out 280) provides fairly good stability against H_2 -induced aggregation. It may be that there are only a limited number of reactive sites (edges and vertices, for example) on the Pd NPs and that these sites are protected with a low C_6S coverage. Others have shown that thiol place-exchange reactions occur preferentially at nanoparticle edge and vertex sites,^{73,172,173} which might also be the most reactive sites for H_2 adsorption and subsequent aggregation of the PdH_x NPs. A 3.0 nm diameter nanoparticle shaped as a truncated octahedron has about 31% defect surface atoms (edge and vertex).⁵⁴ Covering the edge and vertex atoms would require an

Figure 4.12 TEM images of drop-cast films of 174/3 and 96/81 C₈NH₂/C₆S Pd NPs before (A, B) and after exposure to 100% H₂ for 60 minutes (C, D).

estimated 55 ligands out of the 177. This is larger than the Pd NPs with 32 C6S ligands that showed high stability against H₂-induced aggregation, but within range considering that our composition is an estimate.

4.4 CONCLUSIONS

We studied the stability of solutions of chemically synthesized C_nS Pd ($n = 4, 6, 8, 12, 16$, and 18), C_nNH₂ ($n = 8, 12$, and 16) Pd and PdAg, and mixed C₈NH₂/C₆S Pd NPs in the presence of H₂ gas by UV-vis spectroscopy and TEM measurements. C_nS Pd NPs ($n \geq 6$) show high stability against H₂-induced aggregation because of the strong Pd-S interaction and long alkane chain, which inhibits either the reaction with H₂ gas or the aggregation step. The rate of aggregation for Pd and PdAg NPs coated with C_nNH₂ depends on the ligand and metal composition of the NPs. Among the C_nNH₂ Pd and PdAg NPs, the 6x and 12x C₁₆NH₂ Pd and Pd₉₁Ag₉ NPs exhibit the highest stability in the presence of H₂. This is attributed to the long carbon chain length and the high coverage of the alkylamine ligands on the NPs, which forms a full or partial bilayer that prevents the NP aggregation. For mixed ligand C₈NH₂/C₆S Pd NPs, the stability strongly depends on the C₈NH₂/C₆S ratio on the Pd NPs. The Pd NPs coated with ~3:1 or less C₈NH₂/C₆S ligands show excellent stability against H₂-induced aggregation in solution. In conclusion, in this study we were able to evaluate the stability of solutions containing metal NPs in the presence of H₂ by controlling the metal and ligand composition of the nanoparticles for possible hydrogen sensing, storage, and catalysis

applications. Chapter V describes sensing application, while Chapters VI – VII describe catalysis applications.

CHAPTER V

SOLID STATE FILMS OF OCTYLAMINE-, HEXANETHIOLATE-, AND MIXED MONOLAYER-STABILIZED Pd NANOPARTICLES FOR HYDROGEN SENSING

5.1 INTRODUCTION

Pd nanomaterials have been widely used as resistor-based hydrogen sensors,^{78,81} where the resistance of the Pd nanostructure or nanostructured film changes upon exposure to hydrogen. Sensors fabricated with well-connected Pd films show an increase in resistance in the presence of hydrogen due to the formation of the more resistive PdH_x material.^{74,78,93} In contrast, films or nanostructures that contain high resistance break junctions or discontinuities exhibit a decrease in resistance in the presence of hydrogen due to the volume-enhancement of the material, leading to improved connectivity.^{51,60,67,94,99-102} A third mechanism involves Schottky contacts formed by depositing Pd nanoparticles on n-type semiconductors (e.g., GaN,⁸¹ GaAs,⁹⁶ carbon nanotubes,⁷⁹ InP,¹⁷⁷ and DNA¹⁷⁸). The formation of PdH_x lowers the Schottky barrier height and increases the device current. Chemiresistive hydrogen sensors based on Pd nanostructures are promising due to their simplicity, high sensitivity, reversibility, high selectivity, low cost, and portability.^{60,78,81} Much of the previous work on Pd nanostructures involve expensive

lithography, high vacuum evaporation methods, or complicated fabrication procedures with sometimes poor reproducibility and low success rates. Our goal was to assemble the chemically synthesized Pd NPs onto electrode devices for resistive based hydrogen sensing. This would be a simple, low cost, all chemical benchtop approach that could provide hydrogen sensors based on the Pd expansion mechanism, which is desirable since it is a “turn on” sensing device.

In our previous research, Ibañez and co-workers studied the use of organic-stabilized Pd, PdAu (10:1), and PdAg (10:1) NPs for chemiresistive hydrogen sensing applications.⁵¹ The metal NPs were stabilized with hexanethiolate (C6S), octylamine (C8NH₂), dodecylamine (C12NH₂), hexadecylamine (C16NH₂), and the surfactant tetraoctylammonium bromide (TOABr).^{51,60} They discovered that the samples containing drop-cast films of C6S Pd NPs did not readily react well with H₂ without prior ozone or heat treatment.⁶⁰ They assumed that the strong metal-thiolate bond inhibited the reaction between Pd and hydrogen. In contrast, the alkylamine- and TOABr-coated Pd, PdAg, and PdAu NPs allowed the Pd-H reaction, avoiding the need for ozone or heat treatment.⁵¹ However, films of C16NH₂ Pd NPs were highly resistive because of the large Pd NP-Pd NP spacing (due to the long C16NH₂ ligands) and exhibited no change in the presence of hydrogen, which is also not desirable for sensing. In contrast, with C8NH₂-and C12NH₂-coated Pd and PdAu, the NP films reacted readily to the point of irreversible nanoparticle aggregation (i.e. unstable), which is associated with loss of the alkylamine monolayer as determined by Fourier transform infrared (FTIR) spectroscopy.⁵¹ Interestingly, C8NH₂-coated PdAg (10:1) NPs exhibited very little aggregation and loss of the C8NH₂ stabilizer, but were also reactive towards H₂. Ibañez

and co-workers concluded that the presence of <10% Ag in the NPs leads to more stable nanoparticles.⁵¹ This must be associated with a greater strength of the PdAg-NH₂ bond. TOABr-coated Pd NPs exhibited stable, reversible reactivity with H₂ without any pretreatment or film conditioning.⁵¹ The sensing mechanism for those films was not well understood, however.

Here we describe the H₂ sensing properties of films of Pd NPs coated with mixed monolayers of C8NH₂ and C6S ligands, believing that they would exhibit the benefit of both high reactivity and stability in the presence of hydrogen based on the H₂ reactivity studies discussed in Chapter IV. The C8NH₂/C6S Pd NPs exhibit significantly different reactivity with hydrogen gas, depending on the relative amounts of the two ligands coating the Pd NP surface, as determined by electronic measurements of films of Pd NPs as a function of exposure time to hydrogen.⁶⁷ The average estimated composition of the ~3.0 nm diameter Pd NPs was Pd₉₁₉(C6S)₁₉₂ or Pd₉₁₉(C8NH₂)_{177-x}(C6S)_x, where x was varied to be 0, 3, 10, 16, 32, or 81 by the synthesis of pure C8NH₂ Pd NPs and subsequent liquid-phase place-exchange with a varied amount of C6SH. When x = 0-10, the Pd NPs react strongly with H₂, leading to large irreversible changes in the morphology of films accompanied by an increase in film conductivity by 2-5 orders of magnitude. Pd₉₁₉(C6S)₁₉₂ NPs do not exhibit large film morphology changes, but they are also not highly reactive to H₂ as determined by the small, irreversible changes in the conductivity of films in the presence of H₂. Finally, when x = 32 and 81, the Pd NPs readily react with hydrogen based on the significant, reversible changes in film conductivity in the presence of hydrogen and they are stable.

5.2 EXPERIMENTAL

The procedures for the chemical synthesis of Pd NPs, wiring and cleaning of Au electrodes, deposition of films onto electrodes, and H₂ sensing experiments are described in Chapter II.

5.3 RESULTS AND DISCUSSION

5.3.1 Electronic Properties of C6S and C8NH₂ Pd NPs

Figure 5.1, Frame A and B, shows the current-voltage (i-V) curves for drop-cast deposited films of C6S and C8NH₂ Pd NPs, respectively. The current through the film of C6S Pd and C8NH₂ Pd NPs is 1.3×10^{-8} A and 1.7×10^{-7} A, respectively, as measured at -0.3 V in the i-V curve. It is well known that upon applying a potential across the electrode device, electronic current flows through the Pd NP films by an electron hopping mechanism, which depends on the cluster edge-to-edge distance (exponentially), the dielectric of the medium surrounding the clusters, and cluster size. The difference in initial current of the films of C8NH₂ Pd and C6S Pd NPs is consistent with the TEM images in Chapter IV, which shows that the C8NH₂ Pd NPs underwent some aggregation even before H₂ exposure. This likely led to the higher initial conductivity in the solid-state films. Frames C and D show current-time (i-t) plots in air of films of C6S Pd and C8NH₂ Pd NPs measured for 1000 s at -0.3 V. The magnitude of current is 1.36×10^{-8} A and 1.7×10^{-7} A for films of C6S Pd and C8NH₂ Pd NPs, respectively. For both films the current is fairly constant over time, consistent with ohmic behavior.

Figure 5.1 Current-voltage (i-V) curves of drop-cast deposited films of (A) C6S Pd and (B) C8NH₂ Pd NPs obtained in air from +0.3 to -0.3 V (started at 0.0 V) at a sweep rate of 100 mV/s. (C) and (D) Current-time plots of the same drop-cast films from (A) and (B), respectively, measured in air at -0.3 V for 1000 s.

5.3.2 Reactivity of Films of C6S and C8NH₂ Pd NPs to 100% H₂

Figure 5.2 shows current-time (i-t) plots of films of pure C6S Pd and C8NH₂ Pd NPs at a voltage of -0.3 V in 100% N₂ initially from 0 to 50 s, then exposed to 100% H₂ (●) for 450 s and then exposed back to 100 % N₂ (▼) for 100 s. The current was stable for both films during the initial 100% N₂ exposure from 0 to 50 s. In the presence of 100% H₂ at 50 s, the current passing through the film of C6S Pd NPs increased irreversibly from 1.36×10^{-8} to 1.64×10^{-8} A over the 450 s period. The plot appears flat in Figure 5.2 because of the large current scale, but there was a small increase in the current that did not return to baseline upon exposure back to N₂ at 500 s (see inset). The small conductivity increase for solid-state films of C6S Pd NPs after exposure to H₂ is consistent with some small reactivity with H₂. The irreversible conductivity increase could be due to the small degree of aggregation and morphology changes, as shown by TEM images and UV-vis spectra (see Chapter IV) or due to the inability of atomic H to combine and reform H₂ in the presence of the C6S ligands poisoning the Pd surface. Ibanez and co-workers previously determined that ozone- and heat-induced removal of C6S led to Pd NP films with much greater reactivity with H₂ and reversible sensing characteristics. In contrast to C6S Pd NPs, the conductivity of films of C8NH₂ Pd NPs changed much more appreciably in the presence of 100% H₂. The current passing through the film of C8NH₂ Pd NPs displayed a large irreversible 4 order of magnitude current increase from about 1.64×10^{-7} to 1.71×10^{-3} A upon exposure to 100% H₂ for 450 s. This reflects an irreversible film morphology change associated with Pd-H formation as shown by the TEM images in Chapter IV. The film morphology change leads to a more connected, lower resistance Pd film (see Figure 5.3). Because of the

Figure 5.2 Current-time plots of drop-cast deposited films of C6S Pd (green plot) and C8NH₂ Pd NPs (black plot) measured at -0.3 V during exposure to 100% H₂ (●) and 100% N₂ (▼) over a 450 s time period. (Inset) Expanded plot for the film of C6S Pd NPs.

Figure 5.3 Schematic representation of the mechanism involved with the C8NH₂ Pd NP film and H₂ gas.

irreversibility, films of C6S Pd and C8NH₂ Pd NPs are not useful for H₂ sensing applications.

5.3.3 Reactivity of Films of C8NH₂/C6S Pd NPs to 100% H₂.

Figure 5.4 displays current-time plots for films of C8NH₂/C6S Pd NPs with various ratios as indicated in the presence of N₂ initially from 0 to 50 s, followed by exposure to 100% H₂ (●) for 450 s, and finally exposed back to 100% N₂ (▼) for 100 s. Frame A shows that for a film of 174/3 C8NH₂/C6S Pd NPs, the current increased irreversibly from about 4.06×10^{-7} to 4.06×10^{-5} A. Similarly, the current through the film of 167/10 Pd NPs increased from 1.91×10^{-7} to 1.05×10^{-5} A upon exposure to 100% H₂. The current increase is due to irreversible aggregation of the Pd NPs upon PdH_x formation and removal. Interestingly, this is significantly smaller than the 4 order of magnitude increase observed for pure C8NH₂ Pd films in Figure 5.2. The presence of a low coverage of C6S ligands ($x = 3-10$) leads to a smaller current increase in the film following the 100% H₂ exposure, but it is still significant. This is consistent with a smaller amount of H₂-induced aggregation for Pd NPs with 3-10 C6S ligands compared to pure C8NH₂ Pd NPs as observed in the spectroscopy studies (Chapter IV). The irreversibility of these films is still undesirable.

Frame B shows the current-time plot of films of 161/16, 145/32, and 96/81 C8NH₂/C6S Pd NPs upon exposure to 100% H₂. The current increased by approximately 3 or 2 times (1.32×10^{-7} to 3.22×10^{-7} A, 1.02×10^{-7} to 1.63×10^{-7} A, and 2.46×10^{-8} to 4.17×10^{-8} A, respectively) following exposure to 100% H₂, which is dramatically less compared to the 2-4 order of magnitude current increase observed with $x = 0-10$ C6S

Figure 5.4 Current-time plots of drop-cast deposited films of (A) 174/3 and 167/10 and (B) 161/16, 145/32, and 96/81 C8NH₂/C6S Pd NPs measured at -0.3 V during exposure to 100% H₂ (●) and 100% N₂ (▼) over a 600 s time period.

ligands. Another major difference between the Pd NP films with 0-10 C6S ligands compared to those with 16-81 C6S ligands is that the current continued to increase in the presence of N₂ following the exposure to 100% H₂ for the former and the current decreased back towards the original baseline current for the latter. The morphology of the film continues to change in the presence of N₂ while H is removed from Pd for the films of Pd NPs with 0-10 C6S ligands. The films of Pd NPs with 16-81 ligands, in contrast, remain stable and exhibit more reversibility during H insertion and removal from Pd. Films of 96/81 C8NH₂/C6S Pd NPs, in particular, displayed a fairly stable current increase after the 450 s exposure to H₂ and then exhibited a decrease in current close to the baseline upon subsequent N₂ exposure.

We quantified the current change exhibited by films of Pd NPs coated with C8NH₂, C6S, and mixed C8NH₂/C6S upon initial exposure to different H₂ concentrations.⁶⁷ We calculated the relative change in current by the equation,

$$\Delta i_{relative} = (i_r - i_b)/i_b = \Delta i/i_b \quad (5.1)$$

where i_b is the initial baseline current in 100% N₂, i_r is the current in the presence of the H₂/N₂ mixture after 450 s, and $\Delta i = (i_r - i_b)$. Figure 5.5 shows the log of the relative change in current as a function of the varied composition of (C8NH₂/C6S)-coated Pd NPs after exposure to 1.0, 6.0, and 100% H₂ for a period of 450 s and subsequent exposure to 100% N₂ for 100 s. The points represent the average of several samples prepared for each ratio with the standard deviations also shown. When x = 0-10 C6S ligands, the Pd NPs were highly reactive to 1.0, 6.0, and 100% H₂ as indicated by the large irreversible 2-4 order of magnitude increase in current. Films of pure C6 Pd NPs (x = 192 C6S

Figure 5.5 The log of the relative change in current of Pd NPs exposed to different H₂ concentration for 450 s followed for N₂ for 100 s.

ligands) were not highly reactive to H₂ as determined by minimal changes in resistance in the presence of H₂ at different concentrations (log[response] $\sim$ -1). When x = 16-81 C6S ligands, the Pd NPs exhibited a slightly larger current response to H₂ compared to pure C6S Pd NPs, but not as large as those with fewer C6S ligands (x = 0-10). More importantly, the films of these Pd NPs were fairly stable and showed a somewhat reversible change in current in the presence of H₂.

5.3.4 Hydrogen Sensing with Films of C8NH₂/C6S Pd NPs

Figure 5.6 displays current-time plots for a film of 96/81 C8NH₂/C6S Pd NPs in the presence of 100% N₂ initially and then exposed to 1.0% H₂ (Frame A) and various concentrations of H₂ (Frame B). Frame A shows the high reversibility of a film of 96/81 C8NH₂/C6S Pd NPs following alternating exposure to 1.0% H₂ (●) and 100% N₂ (▼) for five cycles. The current through the film quickly increased by a factor of 1.2 (from about 5.46×10^{-8} to about 6.24×10^{-8} A) in the presence of H₂ and reversibly returned close to its original value upon exposure back to 100% N₂. This result indicates that films containing 96/81 C8NH₂/C6S Pd NPs are responsive reversibly to H₂. They are also highly stable against aggregation and large morphology changes as indicated by UV-vis and TEM data for solutions of the NPs.⁶⁷

Frame B shows a current-time plot for a film of 96/81 C8NH₂/C6S Pd NPs that was exposed to H₂ concentrations from 9.6% down 0.3% H₂. The film was initially exposed to 100% N₂ and then exposed to cycles of various concentrations of H₂ (●) and 100% N₂ (▼). The sensing experiment in Frame B occurred after some conditioning of the film until it displayed the reversible behavior shown in Frame A. Frame B shows that

Figure 5.6 Current-time plots of a drop-cast deposited film of 96/81 C₈NH₂/C₆S Pd NPs exposed to (A) 100% N₂ (▼) and 1.0% H₂ (●) for five cycles, and (B) 100% N₂ (▼) and varied concentrations of H₂ (●).

the film of 96/81 C8NH₂/C6S Pd NPs exhibited a reversible increase in current in the presence of 9.6-0.3% H₂. The increase in current was likely due to the volume enhancement of the Pd NPs upon PdH_x formation, which lowers the resistance between the Pd NPs in the film.^{74,93} The non-linear response between 1.0 and 3.1% H₂ is due to the well-know α - to β -phase-transition that occurs during PdH_x formation and above 9% the sensor approaches hydrogen saturation. Figure 5.7 shows three calibration curves plotting the percent response (y-axis) versus the H₂ concentration (x-axis) for the three different sensor devices containing 96/81 C8NH₂/C6S Pd NPs. Frame A and B show the percent response of the devices as a function of H₂ concentration from 0.3 to 9.6% and from 0.3 to 1.0% H₂, respectively. All the devices display fairly linear behavior below 1.0% H₂ (not forced through the origin) and detect H₂ below the explosive limit with a limit of detection of about $0.2 \pm 0.1\%$ (Table 5.1). The device-to-device reproducibility is also good. Because of the stability and relatively fast and reversible response to H₂ over a range of concentrations, these Pd NPs are not only potentially useful for H₂ sensing, but also excellent candidates for H₂ storage and catalysis studies involving H₂ as a reactant.

5.4 CONCLUSIONS

In this study we demonstrated that films of C6S Pd and C8NH₂ Pd NPs did not display desirable hydrogen sensing attributes. By synthesizing C8NH₂/C6S Pd NPs with controlled ratios by a liquid-phase place-exchange method, we were able to prepare films of these NPs that exhibited stable, reversible sensing behavior to hydrogen gas down to 0.3%. At high ratios ($x = 3$ -16 C6S ligands), the Pd NPs behave similarly to the pure

Figure 5.7 Calibration curves showing the percent response versus H₂ concentration from 0.3 to 9.6% (A) and 0.3 to 1.0% (B) for each sensor containing 96/81 C₈NH₂/C₆S Pd NPs. The percent response is defined as: % response = $(i_r - i_b)/i_b \times 100\%$, where i_r is the current in the presence of H₂/N₂ mixture and i_b is the initial base line current in 100% N₂.

Table 5.1 Percent response for three different H₂ sensor devices as a function of H₂ concentration along with the linear slope and limit of detection for each device

Sample	1	2	3	AVG	STD
% H₂	% Response	% Response	% Response		
0.3	1.05	0.81	1.39	1.08	0.29
0.4	1.71	1.80	3.10	2.20	0.78
0.6	4.10	3.69	5.07	4.29	0.71
0.8	5.70	5.30	7.41	6.14	1.12
1.0	8.51	10.0	9.19	9.23	0.75
3.1	20.2	25.7	21.3	22.4	2.91
6.0	29.2	33.4	29.9	30.8	2.25
9.6	37.1	40.8	35.5	37.8	2.72
Sample	1	2	3	AVEG	STD
Slope	10.6	12.3	11.0	11.3	0.9
Limit of detection (% H ₂)	0.11	0.19	0.32	0.20	0.11

C₈NH₂ Pd NPs, although they are slightly more stable. At medium ratios ($x = 32$ and 81 C₆S ligands), the Pd NPs show reversible reactivity to H₂ based on reversible increases in current for solid-state films in the presence of H₂. This was particularly evident for the 96/81 C₈NH₂/C₆S Pd NPs, which showed reversible electronic response to H₂ for at least 5 cycles and down to 0.3% H₂ as solid-state films. These are the most promising for sensing, storage, and catalysis applications.

CHAPTER VI

CATALYSIS STUDIES OF ORGANIC-STABILIZED Pd AND PdAg

NANOPARTICLES FOR HYDROGENATION/ISOMERIZATION OF ALLYL

ALCOHOL

6.1 INTRODUCTION

Here we studied the reaction of 2-propen-1-ol with hydrogen in the presence of various organic-stabilized Pd and PdAg NPs to investigate their catalytic properties. Because this allyl alcohol is the simplest α,β -unsaturated alcohol and has been used as a substrate in prior studies,^{29,30,32,35,123,124,134-142} it was a good starting point for this work. As illustrated in Figure 6.1, the reaction between allyl alcohol and hydrogen (g) using Pd catalysts results in the hydrogenation of the double bond to give propanol, but it may also lead to migration of the double bond (isomerization), yielding the corresponding saturated aldehyde.¹⁴³⁻¹⁴⁷ Although heterogeneous Pd catalysts, such as Pd/TiO₂,^{151,179} polymer-Pd(0) and Pd(II) complexes,¹⁵² and Pd NPs stabilized by polymers and immobilized on composites or embedded in polyelectrolyte films,^{134,180-182} have been used to study the activity and selectivity for hydrogenation and isomerization of allyl alcohols, the favored hydrogenation process prohibited formation of the isomer. An important challenge is to controllably obtain the alcohol, or the saturated carbonyl

Figure 6.1 Conversion of allyl alcohol to the saturated alcohol and aldehyde by catalytic reactions.

derivatives, which are essential compounds in organic synthesis.¹⁴⁴⁻¹⁴⁹ Therefore, our goal was to better understand the catalytic process with different Pd and Pd alloy NPs and to control the selectivity and improve the reaction rate by designing different, stable NPs.

In this study we compare the catalytic activity of various alkylamine, alkanethiolate, and mixed ligand Pd and PdAg NPs for hydrogenation and isomerization of 2-propen-1-ol in the presence of hydrogen.⁶⁸ All of the NPs catalyzed the reaction, but with different selectivity and different reactivity, or turnover frequencies (TOFs), depending on the metal (Pd or 10:1 PdAg) and the organic stabilizing ligand. C6S Pd NP catalysts are >95% selective toward the isomer, C8NH₂/C6S Pd NPs are 60-75% selective toward the isomer, depending on the ligand ratio, and CnNH₂ coated Pd NPs generally produce a 1:1 or 3:2 ratio of the hydrogenation:isomerization products, with a few exceptions. The catalytic turnover frequency (TOF) is low for C6S Pd NPs due to the strong thiolate-Pd bond. The TOF increases with increasing chain length in the order C16NH₂ Pd > C12NH₂ Pd > C8NH₂ Pd and increases for Pd₉₁Ag₉ alloys compared to pure Pd. The mixed ligand C8NH₂/C6S Pd NPs exhibit similar TOF as pure C8NH₂ Pd for low thiol content and similar to C6S Pd NPs for high thiol content. The 130/150 C8NH₂/C6S Pd exhibits the optimal TOF for the mixed monolayer Pd NPs. C16NH₂ Pd₉₁Ag₉ has the highest TOF of all the NPs studied due to the high stability afforded by the bilayer structure of the C16 chain and the high reactivity due to very little interference from the weak metal-amine interaction. Several of the Pd NPs that are stable in the presence of H₂ are not stable during the catalysis reaction (H₂ plus allyl alcohol), showing that the substrate also plays a role in NP stability. We also study the reusability of the

catalysts and determine that the Pd and PdAg NPs can be reused up to 5 times, but the reactivity decreases after the third use.

6.2 EXPERIMENTAL

The procedures for the catalysis experiments using Pd and PdAg NPs are described in Chapter II.

6.3 RESULTS AND DISCUSSION

As reported previously, the formation of a surface palladium hydride species (PdH_x), either isolated or generated in situ, is a fundamental requirement in the hydrogenation and isomerization of allyl alcohols.^{143,147,151,179} This was confirmed by the fact that we observed no reaction over our Pd and PdAg NPs in the absence of H_2 . We also observed no reaction with H_2 without the NP catalyst present. Pure H_2 was bubbled through a CH_2Cl_2 solution containing allyl alcohol and catalyst at a flow rate of 8.0 ± 0.2 mL/min and the reactions monitored by gas chromatography (GC). Figure 6.2 shows chromatograms obtained before and after 15, 30, 60, and 100 min of reaction with 1/2x C6S Pd and 12x C8NH₂ Pd NPs as catalysts in Frames A and B, respectively. With C6S Pd, the peak for allyl alcohol at 3.70 min decreased with time while a peak at 1.13 min corresponding to the aldehyde increased. C6S Pd NPs are clearly active catalysts and selective for the isomerization reaction (Figure 6.1, propanal). The small change in the

Figure 6.2 Gas chromatograms showing progress of catalytic reaction of allyl alcohol before and after exposure to 100% H_2 (8.0 ± 0.2 mL/min) at different reaction times. The reaction was catalyzed by ~ 3.0 mg of (A) $\frac{1}{2}x$ C6S Pd NPs and (B) 12x C8NH₂ Pd NPs in 4 mL of CH2Cl2 under atmospheric pressure and at room temperature. Integration was performed using instrument software. Injection volume = 1 μ L, initial temperature = 60 $^{\circ}$ C, final temperature = 135 $^{\circ}$ C, ramp = 15 $^{\circ}$ C/min, pressure = 20 PSI, detector = FID.

UV-vis, TEM, and previous conductivity studies suggested some reactivity with H_2 , but the GC data confirms that these NPs are active catalysts.^{51,67} Shon and co-workers recently described the same selectivity with alkanethiolate-capped Pd NPs prepared from Bunte salts.¹³⁰⁻¹³³ With 12x C8NH₂ Pd NPs, the peak for allyl alcohol also decreased (Frame B), but two peaks appeared at 1.26 and 3.12 min, corresponding to the aldehyde and alcohol, respectively, in about a 50:50 ratio. Figure 6.3 shows the percent hydrogenation, percent isomerization, and total conversion of allyl alcohol at different times when 12x C8NH₂ Pd NPs were used as catalysts. This shows that both isomerization and hydrogenation reactions took place with C8NH₂ Pd NP catalysts. Importantly, these NPs are active catalysts and the nature of the ligand strongly affects the reaction product.

6.3.1 Selectivity of C6S and CnNH₂ Pd and PdAg NPs

We conducted the experiment shown in Figure 6.2 on all of the Pd and PdAg NP catalysts synthesized. Figure 6.4 displays the selectivity toward hydrogenation and isomerization products after 100 min of reaction. The reaction went to 100% completion within this time using all of the catalysts, except for the C6S Pd NPs (91% completion) and the 3x C16NH₂ Pd NPs (98% completion). The results generally indicate that the selectivity depends on both ligand composition and metal composition of the NPs under the same conditions.

Figure 6.3 Plot of the % hydrogenation, % isomerization, and % conversion of allyl alcohol versus reaction time over 12x C₈NH₂ Pd NP catalysts in CH₂Cl₂.

Figure 6.4 Selectivity toward hydrogenation and isomerization products after 100 min of reaction between allyl alcohol and 100% H₂ (8.0 ± 0.2 mL/min) over (A) C6S Pd and C_nNH₂ Pd NP catalysts with different alkylamine: Pd ratio (12x, 6x, 3x), (B) PdAg NPs coated with C_nNH₂ (12:1 alkylamine: PdAg ratio, 12x), and (C) various C8NH₂/C6S ratios Pd NP catalysts.

Frame A shows a comparison between the selectivity of $\frac{1}{2}$ x C6S Pd, 12x C8NH₂ Pd, 12x C12NH₂ Pd, and 12x, 6x, and 3x C16NH₂ Pd NPs. The Pd NPs coated with C6S ligands selectively catalyzed the formation of the aldehyde (98%). In contrast, the reaction using C_nNH₂ Pd NPs gave both hydrogenation and isomerization products in about 5:5 or 6:4 ratio. This was true even after a prolonged reaction time of 5 h, showing that the aldehyde is not an intermediate to the alcohol product. Interestingly, the 3x C16NH₂ Pd NPs were slightly more selective to the aldehyde (73%) for reasons not understood.

We also compared the selectivity of 12x C_nNH₂ PdAg NPs as shown in Frame B. 12x C8NH₂ Pd₉₁Ag₉ NPs selectively catalyzed the alcohol (79%) over the aldehyde (21%). Interestingly, the addition of Ag to the Pd NP catalyst increased the selectivity toward the hydrogenation reaction. However, Pd₉₁Ag₉ NPs coated with 12x C12NH₂ and 12x C16NH₂ ligands showed both hydrogenation and isomerization products in about a 6:4 ratio, showing that the ligand chain length also plays an important role.

6.3.2 Selectivity of C8NH₂/C6S Mixed Ligand Pd NPs

Frame C shows the selectivity of the mixed ligand Pd NPs with C8NH₂/C6S ratios of approximately 266/14, 234/46, 185/95, 130/150, 63/217, 13/267, and 0/311. The reaction went to 100% completion within 100 min, and the selectivity favored the aldehyde (60-75%) over the alcohol (25-40%) in all cases. It is interesting that the incorporation of only 14 C6S ligands into the C8NH₂ Pd NPs altered the selectivity from 51% aldehyde for pure C8NH₂ to 75% aldehyde for a C8NH₂/C6S ratio of 266/14. This shows that a small amount of ligand additives could be a promising route to alter the

selectivity and stability of metal NP catalysts.

6.3.3 Catalytic Activity of C6S and CnNH₂ Pd and PdAg NPs

Figure 6.5 displays the linear portions of the plot of percent hydrogenation and percent isomerization versus time with the intercept of the line forced through zero for 12x C8NH₂ Pd NP catalysts. The turnover frequencies (TOFs, mol substrate/mol Pd/hour) were determined from the slopes of the plots when <60% allyl alcohol was converted to the isomer and hydrogenated alcohol.¹⁸⁰ The points and curves represent the average of three samples with the standard deviations shown. The TOF of the conversion of allyl alcohol to the corresponding hydrogenation and isomerization products (propanol and propanal, respectively) in the presence of H₂ and C6S Pd and CnNH₂ Pd and PdAg NPs are displayed in Table 6.1. The TOF values varied significantly depending on the ligand and metal composition of the NPs. It is useful to first note the difference between NPs that were stable (soluble) during the reaction (indicated by *) and those that were unstable (became insoluble) during the reaction (indicated by *NS*). Those that were unstable in H₂ only were also not stable during the catalysis reaction, which includes C8NH₂, C12NH₂, and 3x C16NH₂ Pd and PdAg NPs. It is interesting that 6x C16NH₂ Pd NPs were stable in H₂ only, but not stable during the catalysis reaction, showing that the reaction of allyl alcohol at the Pd NP surface can also contribute to NP instability. The clear trend in the CnNH₂ Pd and PdAg NPs is that the total TOF increased with increasing NP stability. The C12NH₂ Pd displayed a greater TOF compared to the C8NH₂ Pd due to greater stability imparted by the longer chain length. When comparing the same C8NH₂ or C12NH₂, the PdAg NPs displayed higher TOF values compared to the Pd NPs. This is also due to the greater stability of the PdAg NPs as shown by the

Figure 6.5 Plot of the % hydrogenation and % isomerization of allyl alcohol versus reaction time over 12x C8NH₂ Pd NP catalysts in CH₂Cl₂.

Table 6.1 Hydrogenation and isomerization rates of allyl alcohol by C6S Pd and CnNH₂ Pd and PdAg NPs

Nanoparticles	TOF (mol substrate/mol Pd/h) ^[a]		
	Hydrogenation	Isomerization	Total ^[b]
½x C6S Pd*	0	46.7 ± 12.0	46.7 ± 12.0
12x C8NH ₂ Pd ^{NS}	38.3 ± 4.1	81.4 ± 11.6	119.7 ± 12.3
12x C12NH ₂ Pd ^{NS}	61.2 ± 17.0	132.8 ± 5.1	194.0 ± 17.7
3x C16NH ₂ Pd ^{NS}	27.8 ± 10.5	85.7 ± 20.0	113.5 ± 22.6
6x C16NH ₂ Pd ^{NS}	99.0 ± 10.5	284.6 ± 0.9	383.6 ± 10.5
12x C16NH ₂ Pd*	158.4 ± 11.1	560.1 ± 85.9	718.5 ± 86.6
12x C8NH ₂ Pd ₉₁ Ag ₉ ^{NS}	63.2 ± 3.1	89.5 ± 1.8	152.7 ± 3.6
12x C12NH ₂ Pd ₉₁ Ag ₉ ^{NS}	61.1 ± 0.2	163.7 ± 4.2	224.8 ± 4.2
12x C16NH ₂ Pd ₉₁ Ag ₉ *	371.6 ± 9.3	605.3 ± 178.3	976.9 ± 178.5

^[a] The TOFs (mol substrate/mol Pd/h) are initial values determined at total conversion of less than 60%. (See Figure 6.5). The TOFs represent the average of three samples analyzed for each catalyst.

^[b] Total values represent the sum of TOF for hydrogenation and isomerization.

* These NPs were stable during the course of the reaction.

^{NS} (not stable) These NPs precipitated during the course of the reaction.

UV-vis data. The largest total TOF in this series was 384 from the most stable 6x C16NH₂ Pd NPs. Those eventually precipitated, but took the longest to do so. Low stability leads to low total TOF values because aggregated NPs have less surface area available and are less reactive. The stability provided by the longer chain length alkylamines is more beneficial compared to the possible negative effects of the larger barrier properties of the longer chain length alkylamines since the C12NH₂ Pd and PdAg NPs have larger TOF values compared to the C8NH₂ Pd and PdAg NPs.

The C6S Pd and 12x C16NH₂ Pd and PdAg NPs were stable in H₂ only and during the catalysis reaction (see Figures 6.6). In the case of the 12x C16NH₂ Pd NPs, the same trend holds that the 12x C16NH₂ Pd had a larger total TOF compared to the shorter 12x C12NH₂ and C8NH₂ Pd NPs due to the greater stability afforded by the longer chain. That is more important than the fact that the longer chain might inhibit access of allyl alcohol to the Pd surface, which is apparently not a problem. The C16NH₂ PdAg NPs were again more stable than the pure Pd NPs due to greater stability of the PdAg. These displayed the highest total TOF of all the Pd NPs at 977 mol substrate/mol Pd/h. While highly stable, the C6S Pd NPs displayed the lowest total TOF value because of the strong coordination of the thiolate to the Pd surface. Comparing this to the C16NH₂ Pd NPs shows that strong coordination to the metal surface is more detrimental to its catalytic activity compared to a long chain length. With a long chain length, but weak coordinating ligand like the amine, the allyl alcohol readily reacts with the Pd NPs, but with a short chain length, but strong coordinating thiol, the reactivity is greatly diminished by a factor of 20 down to a TOF value of 47 mol substrate/mol Pd/h. NP size is also an important factor,^{35,116,117,124,134} but was not controlled in this study.

Figure 6.6 UV-vis spectra of a solution of $\frac{1}{2}x$ C6S Pd, 12x C16NH₂ Pd, and 12x C16NH₂ Pd₉₁Ag₉ exposed to 100% H_2 (A, C, E) and to 100% H_2 plus allyl alcohol (B, D, E) for 60 min and then the solutions were sitting in air for 20 min and 3 h.

6.3.4 Catalytic Activity of Mixed Ligand C8NH₂/C6S Pd NPs

Table 6.2 shows the TOF values for the hydrogenation, isomerization, and total TOF using the different mixed C8NH₂/C6S Pd NPs as catalysts. It is important to note that while Pd NPs with C8NH₂/C6S ratios of 130/150, 63/217, 13/267, and 0/311 were all stable in the presence of H₂ only, only the 0/311 ratio was stable during the catalysis reaction. This again shows that the reaction of allyl alcohol at the Pd NP surface can lead to NP instability for reasons not understood. Figure 6.7 shows UV-vis spectra of the various mixed monolayer Pd NPs in H₂ only as compared to H₂ plus allyl alcohol to demonstrate this point. More work is needed to better understand all of the factors leading to NP instability.

When comparing the different C8NH₂/C6S Pd NPs, there is a trade-off between stability provided by the C6S ligands and inhibition of the reactivity from the strongly coordinated thiolate group. In terms of the total TOF value, the highest value of 145 mol substrate/mol Pd/h occurred for the C8NH₂/C6S ratio of 130/150. This may be optimal since there are enough C6S ligands to improve the stability of the Pd NPs relative to C8NH₂ only, and there are also enough C8NH₂ ligands on the Pd NP surface to allow reactivity with allyl alcohol. While this is the optimal ratio in terms of total TOF, the TOF is still much lower compared to C16NH₂ Pd and PdAg NPs and they precipitate during the reaction. Unfortunately, the mixed monolayer strategy did not lead to Pd NPs with both high reactivity and high stability as hoped. It seems that the thiol groups still inhibit the reactivity and the amines still lead to instability with only a minor improvement. The C8NH₂/C6S ratio of 0/311 should lead to Pd NPs completely coated with C6S ligands with some excess C6S also in solution. While these are highly stable,

Table 6.2 Hydrogenation and isomerization rates of allyl alcohol by mixed ligands C8NH₂/C6S Pd NPs

Nanoparticles	TOF (mol substrate/mol Pd/h) ^[a]		
	Hydrogenation	Isomerization	Total ^[b]
Pd (C8NH ₂) ₂₆₆ (C6S) ₁₄ ^{NS}	24.7 ± 5.5	79.5 ± 14.0	104.2 ± 15.0
Pd (C8NH ₂) ₂₃₄ (C6S) ₄₆ ^{NS}	36.5 ± 1.9	100.0 ± 5.4	136.5 ± 5.7
Pd (C8NH ₂) ₁₈₅ (C6S) ₉₅ ^{NS}	33.7 ± 0.3	92.1 ± 9.6	125.8 ± 9.6
Pd (C8NH ₂) ₁₃₀ (C6S) ₁₅₀ ^{NS}	38.2 ± 8.1	106.5 ± 8.9	144.7 ± 12.0
Pd (C8NH ₂) ₆₃ (C6S) ₂₁₇ ^{NS}	24.0 ± 3.5	83.1 ± 2.4	107.1 ± 4.2
Pd (C8NH ₂) ₁₃ (C6S) ₂₆₇ ^{NS}	15.5 ± 2.7	30.2 ± 5.9	45.7 ± 6.5
Pd (C8NH ₂) ₀ (C6S) ₃₁₁ *	10.8 ± 1.6	21.7 ± 1.1	32.5 ± 1.9

^[a] The TOFs (mol substrate/mol Pd/h) are initial values determined at total conversion of less than 60%. The TOFs represent the average of three samples analyzed for each catalyst.

^[b] Total values represent the sum of TOF for hydrogenation and isomerization.

* These NPs were stable during the course of the reaction.

^{NS} (not stable) These NPs precipitated during the course of the reaction.

Figure 6.7 UV-vis spectra of a solution of 130/150, 63/217, 13/267, and 0/311 C6S/C8NH₂ Pd NPs exposed to 100% H₂ (A, C, E, G) and to 100% H₂ plus allyl alcohol (B, D, F, H) for 60 min and then the solutions were sitting in air for 20 min and 3 h.

they are not highly reactive (similar to the as synthesized C6S Pd NPs) due to the strongly coordinated thiols. They are actually worse than the C6S Pd NPs, probably due to excess thiols in solution.

6.3.5 Comparison with Other Nanoparticle Catalysts

Bruening and co-workers reported the TOFs for the hydrogenation of allyl alcohol with Wilkinson's catalyst, which is a common homogeneous catalyst.¹⁸⁰ They determined that Wilkinson's catalyst had a minor selectivity toward the formation of the isomer of allyl alcohol. Although the rates of hydrogenation of allyl alcohol obtained with our synthesized Pd and PdAg NPs compares very well with Wilkinson's catalysts, the selectivity and activity toward the formation of the hydrogenation and isomerization products could be controlled by changing the ligand composition and metal composition of the NPs.⁶⁸ For instance, we observed that Pd NPs coated with C6S ligands favored the formation of the isomer, giving 98% propanal after 100 min of reaction (see Figure 6.4), but had low TOF (47 mol substrate/mol Pd/h). Shon and co-workers reported the same selectivity for dodecanethiolate-capped Pd NPs generated from thiosulfate in the isomerization of allyl alcohol, where the reaction was 80% complete after 1 hour.^{130,131} Zharmagambetova and co-workers reported 74% propanal when Pd-polymer complexes containing iminodithiol were used as catalysts.¹⁵² In the case of the homogeneous 12x C16NH₂ Pd and PdAg NP catalysts, the selectivity to the alcohol was 60% which is lower than that of the commercial hydrogenation catalysts with high surface area, such as Pd/C^{130,139} and Pd/Al₂O₃ (~75%).^{136,152} However, these NP catalysts exhibited higher activity (TOF = 700-1000), with C16NH₂ Pd₉₁Ag₉ NPs being the best, compared to the activity of other homogeneous systems previously investigated including Pd and Pt NPs

stabilized by dendrimers^{30,123} and alkanethiolate monolayers (TOF < 500).^{38,130-133} Other studies have reported TOF >> 1000 when hollow polystyrene nanospheres¹³⁵ and collagen fiber¹³⁶ coated with Pd NPs were used to catalyze the hydrogenation of allyl alcohol. The reactions were carried out under different conditions, but these are clearly promising strategies for Pd catalysis.

Our motivation for making Pd-containing alloy NPs was based not only on increasing the atom-economy of the catalyst, but also on the possibility of enhancing its selectivity and activity. Other groups have investigated the catalytic activity of bimetallic NPs (PdAu,¹³¹ PdPt,^{183,184} and AgPd¹⁸⁵) for the selective hydrogenation of allyl alcohols. For example, Crooks and co-workers demonstrated that Pd-Pt dendrimer-encapsulated NPs have higher catalytic activity than dendrimer-encapsulated Pd or Pt NPs for the hydrogenation of allyl alcohol.¹⁸³ We observed that when 12x C8NH₂ Pd₉₁Ag₉ NPs were used, the complete consumption of allyl alcohol required 100 min and 80% alcohol was obtained with a hydrogenation rate two times faster compared to the corresponding pure Pd NPs. Scott and co-workers determined that the presence of Ag on AgPd NP catalysts prepared by galvanic exchange dramatically improved the selectivity for hydrogenation over the isomerization product and the overall rate of hydrogenation was enhanced, which is in agreement with our results.¹⁸⁵

6.3.6 Reusability Experiments

To examine the reusability of the ½x C6S Pd and 12x C16NH₂ Pd and PdAg NPs, which were the most promising homogeneous catalysts for the hydrogenation/isomerization of allyl alcohol with H₂, we recovered these NPs after the

first catalytic reaction and re-dissolved prior to use in a second cycle. Figure 6.8 displays a comparison between the selectivity and total conversion of allyl alcohol when $\frac{1}{2}$ x C6S Pd and 12x C16NH₂ Pd and PdAg NPs were used as catalysts over 5 reaction cycles. Each reaction cycle was performed for 100 min. Frame A shows that the Pd NPs coated with C6S ligands led to 97% conversion of allyl alcohol after the first cycle, favoring the formation of the aldehyde (91%) as determined previously (Figure 6.4). After the second cycle the reaction went to 94% completion and produced 89% aldehyde. However, after three cycles the NPs started to become insoluble, but still maintaining their catalytic activity and selectivity as heterogeneous catalysts. It is noticeable that after five cycles only 54% of the allyl alcohol reacted and 85% of the aldehyde was formed. Shon and co-workers reported that Pd NPs generated from S-dodecylthiosulfate showed ~75% isomerization conversion after ten additional repeated heterogeneous cycles.¹³¹ Their higher stability is likely due to the longer carbon chain length.

We also compared the recycling efficiency of 12x C16NH₂ Pd and PdAg NPs as shown in Frame B and C, respectively. These catalysts were more active during the first three cycles compared to C6S Pd NPs, which is attributed to the more accessible metal surface imparted by the weakly bound C16NH₂ ligands. It is also interesting to note that during the first two reaction cycles, the C16NH₂ Pd and PdAg NPs gave both hydrogenation and isomerization products in a ~5:5 ratio, while after five cycles they were slightly more selective to the aldehyde (~63%) than the alcohol (37%) and became heterogeneous catalysts (Figure 6.9). Wu and co-workers showed that both Pd (0) immobilized on collagen fiber (CF) support and Pd/C exhibited a sharp loss in catalytic

Figure 6.8 Recycling experiments of the hydrogenation and isomerization of allyl alcohol with H₂ (8.0 ± 0.2 mL/min) catalyzed by (A) C6S Pd, (B) C16NH₂ Pd, and (C) C16NH₂ PdAg NPs. Reaction was performed for 100 min for each cycle.

Figure 6.9 Catalysis solutions of C16NH₂ Pd (**A**) and C16NH₂ PdAg NPs (**B**) after the first cycle reaction between allyl alcohol and H₂ (8.0 ± 0.2 mL/min) for 100 min in CH₂Cl₂. (**C**) and (**D**) solutions of the same NPs from (**A**) and (**B**) after recovery and use for five consecutive reaction cycles.

activity for hydrogenation of allyl alcohol after five cycles (from 75 to 15%) with an extensive leaching of Pd from the catalysts to reaction solution.¹³⁶

6.4 CONCLUSIONS

Here we demonstrated that the Pd and PdAg NPs could directly be used to catalyze the hydrogenation and isomerization of allyl alcohol with H₂ in solution to give propanol and propanal, respectively. C6S Pd NP catalysts show high selectivity to propanal, but low activity (TOFs) due to the strong Pd-S interaction, which inhibits the reaction. All alkylamine-coated Pd NPs lead to a mixture of propanol and propanal in about 5:5, 6:4, or 3:7 ratios, depending on the ligand composition. The 12x C16NH₂ Pd and Pd₉₁Ag₉ NPs have the highest TOFs, due to high stability and weakly coordinated alkylamines. C8NH₂ Pd₉₁Ag₉ NPs favor the formation of the saturated alcohol, but have low stability. The mixed ligand C8NH₂/C6S Pd NPs were stable in the presence of H₂ only for 150 C6S ligands or more, but not highly stable during the catalysis reaction. This led to selectivities similar to C6S Pd NPs, which favor the aldehyde, and TOF values similar, but slightly larger than C8NH₂ Pd NPs.

In summary, this study shows that the selectivity and catalytic activity of Pd and PdAg NP catalysts for hydrogenation or isomerization of allyl alcohol can be controlled by simply modifying the ligand and metal composition of the NPs. In general, strong coordination of the capping ligands and low NP stability inhibit reactivity far greater than a long alkyl chain surrounding the Pd NP. The alkyl chain of the stabilizer can be quite long and the NP a highly active catalyst provided that the NP is stable and the stabilizer is

weakly coordinated to the NP. It is also clear from this work that NPs that are stable in the presence of H_2 , one of the reactants, may still become unstable during the hydrogenation or isomerization reaction occurring at the NP surface. Finally, we demonstrated that C6S Pd and C8NH₂ Pd and PdAg NPs can be reused at least for 5 cycles; however, after the third cycle the NPs started to become insoluble, but still maintaining their catalytic activity and selectivity as heterogeneous catalysts. Better strategies for improving reusability will be needed for commercial applications.

CHAPTER VII

**SIZE- AND PRODUCT-BASED SELECTIVITY IN CATALYSIS OF ALLYL
ALCOHOLS AND HYDROGEN BY Pd AND PdAg NANOPARTICLES AND
EFFECT OF HYDROGEN FLOW RATE**

7.1 INTRODUCTION

Here we describe the catalytic activity of organic-stabilized Pd and PdAg NPs for hydrogenation and isomerization of three structurally related allyl alcohols in the presence of hydrogen. This work was inspired by Crooks and co-workers, who chemically prepared Pd NPs encapsulated within the interior of different generation dendrimers and studied their catalytic efficiency toward reduction of the double bond in differently shaped allyl alcohols.^{123,124} They observed that the activity of dendrimer-encapsulated Pd NPs for a particular substrate can be controlled by changing the packing density on the dendrimer periphery and hydrogenation reaction rates differ significantly depending on the size and shape of the substrate. Similarly, they have demonstrated that by controlling the pH of a solution, dendrimers can act as molecular-gates admitting molecules on the basis of overall charge.^{186,187} Bruening and co-workers have examined the size-based selectivity of Pd NPs embedded in multilayered polyelectrolyte films in hydrogenation of mono-, di-, and tri-substituted alkenes.¹⁸⁰⁻¹⁸² These catalysts showed

remarkable intramolecular selectivity in the hydrogenation of alkenes based on the degree of substitution of the double bond. Although these Pd NPs have high reaction rates and great stability, the main product of the olefin hydrogenation reactions was the corresponding saturated alcohol excluding formation of the isomer.¹⁸⁰ Therefore, our goal was to control both size- and product-based selectivity in the hydrogenation or isomerization of larger allyl alcohols.

In Chapter VI we studied the reaction between hydrogen and 2-propen-1-ol (**1**) catalyzed by various organic-stabilized Pd and PdAg NPs.⁶⁸ We found that among all the NPs tested, those coated with C6S and C16NH₂ ligands were the most promising for homogeneous catalysis of allyl alcohol due to the following characteristics: 1) the high surface area-to-volume ratio of the NPs, which is important for high efficiency; 2) the high stability of the NPs in H₂ only and during the catalysis reaction over time; and 3) the controlled selectivity and catalytic activity for hydrogenation or isomerization of allyl alcohol by changing the ligand or metal composition of the NPs. Here, we have taken advantage of all these properties to show that C6S and C16NH₂ Pd and PdAg NPs are also effective for the selective hydrogenation or isomerization of more branched organic substrates including 1-penten-3-ol (**2**) and 2-methyl-3-buten-2-ol (**3**), which differ from **1** in the alkyl substituents in the position α to the double bond. The reaction products for the three unsaturated alcohols are given in Figure 7.1.

C6S Pd and C16NH₂ Pd and PdAg NPs catalyzed the reactions, but with different selectivity and reactivity depending on the composition of NP catalysts (metal and ligand) and structure of the organic substrates. C6S Pd NPs were highly selective toward the isomerization reaction of **1** and **2**, giving the corresponding aldehyde and ketone

Figure 7.1 Conversion of 2-propen-1-ol (**1**), 1-penten-3-ol (**2**), and 2-methyl-3-buten-2-ol (**3**) to the saturated alcohol and/or isomer by catalytic reactions.

products (>95%), respectively, while C16NH₂ Pd and PdAg NPs gave a mixture of both hydrogenation and isomerization products (5:5). Interestingly, the C6S Pd NPs catalyzed the reaction of **3**, yielding only the saturated alcohol (60%). The catalytic turnover frequency (TOF) was high for all of the Pd and PdAg NPs when catalyzing the reaction of **1** with H₂. The TOF decreased with increasing size of the allyl alcohols, indicating that these catalysts allowed size-based selectivity in the hydrogenation and isomerization of structurally related allyl alcohols. In general, Pd and PdAg NPs coated with C6S and C16NH₂ ligands not only had great stability over the catalysis reaction, but also remarkable selectivity afforded by the physical and electronic interactions between organic stabilizers and substrates.

We also investigated the effect of H₂ on the catalytic activity of Pd and PdAg NPs. We determined that conversion and selectivity of C6S Pd and C16NH₂ Pd and PdAg NPs can be tuned by adjusting the flow rates of H₂ bubbled through the catalysis solution. In the catalysis of allyl alcohol by C16NH₂ Pd and PdAg NPs, a conversion of 100% and a selectivity of >80% in the isomerization product were reached at 1.69 ± 0.02 mL/min. Moreover the NPs remained stable all over the reaction. Although it was possible to switch the selectivity of these NPs toward the hydrogenation product (70%) at higher flow rates (>8.0 mL/min) with TOF >1500, the NPs lost their stability and became insoluble. In the case of C6S Pd NPs, the selectivity was not affected by any of the H₂ flow rates, however, the stability was lost at high flow rates. High conversion of allyl alcohol (TOF = 90), moderate stability, and 92% aldehyde were obtained at 19.6 ± 0.2 mL/min.

7.2 EXPERIMENTAL

The procedures for the catalysis experiments using Pd and PdAg NPs are described in Chapter II.

7.3 RESULTS AND DISCUSSION

7.3.1 Catalytic Activity of C6S Pd and C16NH₂ Pd and PdAg NPs as a Function of Organic Substrate

The catalytic activity of allyl alcohols with different substituent groups was evaluated by bubbling pure H₂ (8.0 ± 0.2 mL/min) through a CH₂Cl₂ solution containing substrate **2** or **3** and various stable catalysts including 1/2x C6S Pd and 12x C16NH₂ Pd and PdAg NPs. The reactions were monitored by gas chromatography (GC). Figure 7.2 shows chromatograms obtained after 30, 60, 90, 120, and 150 min of reaction between H₂ and **2** using 1/2x C6S Pd and 12x C16NH₂ Pd and PdAg NPs as catalysts in Frames A, B, and C, respectively. With C6S Pd NPs, the peak for 1-penten-3-ol at 3.40 min decreased with time while a peak at 1.88 min (ketone) gradually increased. There was also a small peak at 2.87 min. This indicates that the isomerization of **2** is accompanied by a minor formation of the hydrogenation product. However, we could claim that similarly to the catalysis reaction of 2-propen-1-ol (**1**), the reaction of 1-penten-3-ol (**2**) catalyzed by C6S Pd NPs resulted in a high selectivity for isomerization producing 3-pentanone as the main product. Although the presence of an ethyl group in the α -carbon of **2** slows the reaction down by about one additional hour compared to **1** (see Figure 6.2), the formation of more

Figure 7.2 Gas chromatograms showing progress of catalytic reaction of 1-penten-3-ol after exposure to 100% H₂ (8.0 ± 0.2 mL/min) at different reaction times. The reaction was catalyzed by ~ 3.0 mg of (A) $\frac{1}{2}$ x C6S Pd NPs, (B) 12x C16NH₂ Pd NPs, and (C) 12x C16NH₂ Pd₉₁Ag₉ NPs in 4 mL of CH₂Cl₂ under atmospheric pressure and at room temperature.

stable enol intermediate facilitates the isomerization reaction.^{130,147} With 12x C16NH₂ Pd and PdAg NPs, the peak for 1-penten-3-ol at 3.30 min also decreased (Frame B and C) over time and two well-defined peaks appeared and became larger at 1.88 and 2.87 min, corresponding to the ketone and alcohol, respectively, in about a 50:50 ratio. This shows that both isomerization and hydrogenation reactions took place with C16NH₂ Pd and PdAg NP catalysts.

Figure 7.3 displays the selectivity toward hydrogenation and isomerization products after 150 min of reaction between H₂ and 1-penten-3-ol (**2**). When the reaction was catalyzed using 12x C16NH₂ Pd and PdAg NPs, 100% of the allyl alcohol converted into the corresponding saturated alcohol and ketone, while with ½x C6S Pd NPs the reaction went to 97% completion within this time. It is evident that Pd NPs coated with C6S ligands selectively catalyzed the formation of the ketone (95%). In contrast, Pd and PdAg NPs coated with C16NH₂ ligands gave a mixture of both products in about a 5:5 ratio as previously observed for the catalysis reaction of 1-propen-2-ol (**1**).

As illustrated in Figure 7.1, the reaction between H₂ and substrates **1** and **2**, which contain at least one α hydrogen, generated not only the alcohol but also the saturated aldehyde or ketone, respectively, over our Pd and PdAg NPs. The formation of carbonyl compounds involves a double bond migration resulting in the corresponding enol intermediates, which then slowly tautomerize to aldehydes and ketones.^{145,147,150} This mechanism is known as the Pd-alkyl mechanism and requires the presence of the Pd-H species before the adsorption of allyl alcohol and the initiation of catalytic reactions.^{133,145,147} In the case of substrate **3**, the absence of an α hydrogen leads to its

Figure 7.3 Selectivity toward hydrogenation and isomerization products after 150 min of reaction between 1-penten-3-ol and 100% H₂ (8.0 ± 0.2 mL/min) over 1/2x C6S Pd and 12x C16NH₂ Pd and PdAg NP catalysts.

complete hydrogenation, yielding only the saturated alcohol without isomerization or any other byproducts yielding only the saturated alcohol without isomerization or any other byproducts.

Figure 7.4 shows gas chromatograms over time between H₂ and **3** using 1/2x C6S Pd and 12x C16NH₂ Pd and PdAg NPs as catalysts in Frames A, B, and C, respectively. Although C6S Pd NP catalysts have selectively favored the isomerization of **1** and **2** to the corresponding aldehyde (98%) and ketone (95%) within 100 and 150 min, respectively, we evaluated the catalytic activity of these NPs for the hydrogenation of substrate **3**. Interestingly, when Pd NPs coated with C6S ligands catalyzed the reaction between **3** and H₂ (Frame A), the peak at 3.55 min gradually decreased with time, while a peak at 3.13 min appeared and increased after 30 min of reaction. This indicates that C6S Pd NPs were able to convert more than half of 2-methyl-3-buten-2-ol to the saturated alcohol 2-methyl-2-butanol after 150 min. In the case of 12x C16NH₂ Pd and PdAg NPs, the reaction went to completion after 90 min as shown in Frames B and C, respectively.

Table 7.1 summarizes the total turnover frequency (TOF, mol substrate/mol Pd/hour) values for the hydrogenation and isomerization of **1**, **2**, and **3** using the 1/2x C6S Pd and 12x C16NH₂ Pd and PdAg NPs as catalysts. Overall, the reaction rates of the allyl alcohols decrease as the substrates become bulkier for each particular catalyst. For instance, the maximum TOF for the 12x C16NH₂ Pd and PdAg NP catalysts for the hydrogenation and isomerization of allyl alcohol (**1**) ranged from 700 to 1000, with PdAg NPs being the best. A substrate having one α ethyl group, 1-penten-3-ol (**2**), yielded lower TOF (29-400) for all the catalysts evaluated. When the ethyl group was changed to two methyl groups at the α position, 2-methyl-3-buten-2-ol (**3**), the reaction rate

Figure 7.4 Gas chromatograms showing progress of catalytic reaction of 2-methyl-3-buten-2-ol after exposure to 100% H_2 ($8.0 \pm 0.2 \text{ mL/min}$) at different reaction times. The reaction was catalyzed by $\sim 3.0 \text{ mg}$ of (A) $\frac{1}{2}\text{x}$ C_6S Pd NPs, (B) 12x C_{16}NH_2 Pd NPs, and (C) 12x C_{16}NH_2 $\text{Pd}_{91}\text{Ag}_9$ NPs in 4 mL of CH_2Cl_2 under atmospheric pressure and at room temperature.

Table 7.1 Total rates for the hydrogenation and isomerization of a series of structurally related allyl alcohols by Pd and PdAg NPs

Substrates	Total TOF (mol substrate/mol Pd/h) ^[a]		
	C6S Pd	C16NH ₂ Pd	C16NH ₂ PdAg
1	46.7 ± 12.0	718.5 ± 86.6	976.9 ± 178.5
2	29.2 ± 11.5	369.0 ± 31.9	397.1 ± 28.3
3	17.0 ± 3.4	203.9 ± 28.7	219.3 ± 67.4

^[a] Total TOF values represent the sum of TOF for hydrogenation and isomerization. These values are the average of three samples analyzed for each catalyst.

decreased further to TOF = 17-220. For Pd NPs coated with C6S and C16NH₂ ligands, the conversion rates for **1** were ~2- and ~3-fold higher than those for **2** and **3**, respectively. In the case of C16NH₂ PdAg NPs, the catalytic activity of **3** decreased by a factor of ~5 compared to **1**. This shows that the presence of additional alkyl groups at the α carbon significantly alter the reactivity. Crooks and co-workers determined that the selectivity of dendrimer-encapsulated Pd NP catalysts for **1/2** and **1/3** was 1.8 and 3.2, respectively; while Bruening and co-workers showed that for Pd NPs embedded in polyelectrolyte films, the selectivity ranged from 3.6 to 4.3, respectively, which is in reasonable agreement with the data mentioned above for our catalytic system.

Previously, it has been reported that commercially available 5%-Pd-on-alumina catalyst (Aldrich) allowed very high rates of conversion for the three unsaturated alcohols, but TOFs were also very close (**1/2** $\approx$ **1/3** = 0.8).^{181,182} A similar trend was observed for dodecanethiolate-capped Pd NPs in the isomerization of **1** and **2**, which had high TOF values but a **1/2** selectivity of ~0.9.¹³² Comparing these results with those obtained with the Pd and PdAg NPs, we can confirm that our catalysts led to selective conversion of structurally different allyl alcohols.

7.3.2 Factors Imparting Selectivity

We determined that 12x C16NH₂ Pd and PdAg NPs were the most stable catalysts afforded by the longer chain length and formation of a bilayer. Because the great stability and weak NH₂-Pd interaction, 1-propen-2-ol (**1**) was able to reach the active sites and convert to the corresponding alcohol and isomer with high TOF values. However, when comparing the catalytic rates of **1** and **3**, which differ only in size, there is a

significant decrease in TOF that could occur because of a slower penetration of substrates into the packed C16NH₂ ligands coating the Pd and PdAg NPs. Since **1** is a more linear molecule than **3**, the navigation through the organic ligands might be easier and faster than **3**. Thus, larger and branched substrate molecules may have fewer paths available to them, and thus they move more slowly through ligands and to active sites. Figure 7.5 illustrates “nanofilters” or “nanogates” made of Pd or PdAg NPs coated with C16NH₂ ligands. This shows that organic stabilizers besides limiting the aggregation of metal NPs, they can also impart catalytic selectivity by restricting access of substrates to active sites.

In addition to size issues, the stability of the NPs in the presence of the substrates may also limit their catalytic activity. Interestingly, when C6S Pd NPs catalyzed the hydrogenation/isomerization of **1**, the NPs were highly stable during the catalysis reaction (see Figure 6.6); however, the NPs became unstable and eventually precipitated when substrates **2** and **3** reacted with H₂ as shown by the decrease in absorbance over time in the UV-vis data in Figure 7.6 (Frame A). Therefore, this led to low total TOF values because aggregated NPs have less surface area available and are less reactive. In the case of C16NH₂ Pd and PdAg NPs, the higher affinity between the larger and more branched substrates with the longer-chain-length alkylamines allowed stable catalysts in H₂ only and during the catalysis reaction as evidenced by no change in absorbance in Frames B and C, respectively. Thus, the decrease in TOFs for **2** and **3** compared to **1** with C16NH₂ Pd and PdAg NP catalysts was due to steric effects.

Figure 7.7 shows a kinetic profile comparing the % hydrogenation of **3** versus reaction time over ½x C6S Pd and 12x C16NH₂ Pd and PdAg NPs. As discussed above,

Figure 7.5 Illustration of “nanofilters” or “nanogates” made of Pd or PdAg NPs coated with C16NH₂ ligands to be used for hydrogenation/isomerization reactions.

Figure 7.6 UV-vis spectra of a solution of $\frac{1}{2}\times$ C6S Pd and 12x C16NH₂ Pd and Pd₉₁Ag₉ NPs exposed to 100% H₂ at a flow rate of 8.0 ± 0.2 mL/min plus 1-penten-3-ol (A, C, E) and 2-methyl-3-buten-2-ol (B, D, F) for 1 and 2 h, then the solutions were sitting in air for 2 and 3 h.

Figure 7.7 The kinetic profile of the catalytic hydrogenation of 2-methyl-3-buten-2-ol using $\frac{1}{2}$ x C6S Pd and 12x C16NH₂ Pd and PdAg NP catalysts in CH₂Cl₂.

although C16NH₂ Pd NPs may limit access of substrates to the coated NPs based on their size, the catalysts were highly stable and active and completed the reaction after 90 min. On the other hand, with C6S Pd NPs the hydrogenation of **3** resulted in a lower yield even after 4 h. This is attributed to the higher activation energy and kinetic barrier from the bulkier structure of **3** and its interaction with C6S ligands.

7.3.3 Effect of Hydrogen Flow Rate in Selectivity of C6S Pd and C16NH₂ Pd and PdAg NPs

Table 7.2 shows different flow rates of H₂ bubbled through the catalysis solution including 1.69 ± 0.02 , 8.0 ± 0.2 , 19.6 ± 0.2 , and 39.0 ± 0.3 mL/min, in order to evaluate the activity and selectivity of the Pd and PdAg NPs for hydrogenation or isomerization of 2-propen-1-ol.

As discussed in Chapter VI, the catalytic properties of the Pd and PdAg NPs were first tested for the reaction between allyl alcohol and H₂ at a constant flow rate of 8.0 ± 0.2 mL/min.⁶⁸ Figure 7.8 shows conversion and selectivity of allyl alcohol versus reaction time over C6S Pd and C16NH₂ Pd and PdAg NPs. Under the test conditions the C16NH₂ Pd and PdAg NPs (Frames A and B) gave both hydrogenation and isomerization products in about 5:5 ratio at a H₂ flow rate of 8.0 ± 0.2 mL/min. These products were obtained during the first 60 min and the ratio did not change even after prolonged reaction time (5 h), demonstrating that the aldehyde is not an intermediate to the alcohol product. In the case of C6S Pd NPs, Frame C shows that they selectively catalyzed the formation of the aldehyde with a constant conversion of ~95% after 5 h.

Table 7.2 Calibration of a flow meter using 100% H₂ as a gas at different flow rates

Scale reading	mL.min ⁻¹	Scale reading	mL.min ⁻¹	Scale reading	mL.min ⁻¹	Scale reading	mL.min ⁻¹
10	1.69	50	7.7	100	19.7	150	39.0
	1.66		8.2		19.2		38.7
	1.66		8.0		19.4		39.2
	1.71		8.2		19.5		39.0
	1.70		8.0		19.7		38.7
	1.70		7.8		19.8		39.5
AVEG	1.69	AVEG	8.0	AVEG	19.6	AVEG	39.0
STD	0.02	STD	0.2	STD	0.2	STD	0.3

Figure 7.8 Conversion and selectivity of allyl alcohol versus reaction time over (A) 12x C16NH₂ Pd, (B) 12x C16NH₂ Pd₉₁Ag₉, and (C) 1/2x C6S Pd NPs exposed to 100% H₂ at a constant flow rate of 8.0 ± 0.2 mL/min.

Figure 7.9 displays conversion and selectivity of allyl alcohol at various flow rates of H₂ (1.69 ± 0.02 , 8.0 ± 0.2 , 19.6 ± 0.2 , and 39.0 ± 0.3 mL/min) using C6S Pd and C16NH₂ Pd and PdAg NP catalysts. The points and curves represent the average of three samples analyzed with the standard deviation shown. For Pd and PdAg NPs coated with C16NH₂ ligands (Frames A and B), the total level of conversion of allyl alcohol was 100% over all H₂ flow rates considered. The selectivity, however, varied dramatically and exhibited different patterns. These results suggest that the selectivity depends on the rate of H₂ bubbled through the solution. Overall, when the flow rate of H₂ increased from 8.0 ± 0.2 to 19.6 ± 0.2 and 39.0 ± 0.3 mL/min, the reaction went to 100% completion within 20-35 min and the selectivity favored the alcohol (65-71%) over the aldehyde (35-29%) in both cases. Interestingly, when H₂ was bubbled through the solution at a constant flow rate of 1.69 ± 0.02 mL/min, the C16NH₂ Pd and PdAg NPs exhibited higher selectivity toward the formation of the aldehyde (81-85%) after 120 min of reaction.

We also compared the selectivity and conversion of allyl alcohol at different H₂ flow rates using C6S Pd NP catalysts as shown in Frame C. One would expect that increasing H₂ flow rate increases the conversion of allyl alcohol since more H₂ would be in contact with the substrate and NP catalysts, however we observed that complete conversion of allyl alcohol was achieved at 19.6 ± 0.2 mL/min (99%) and not at 39.0 ± 0.3 mL/min (80%). This is possibly attributed to the loss in stability of NPs which is discussed later. Importantly, selectivity of C6S Pd NPs remained constant toward the formation of the aldehyde over all H₂ flow rates tested (92-98%).

Figure 7.9 Conversion and selectivity of allyl alcohol versus various H₂ flow rates: 1.69 ± 0.02 , 8.0 ± 0.2 , 19.6 ± 0.2 , and 39.0 ± 0.3 mL/min over (A) 12x C16NH₂ Pd, (B) 12x C16NH₂ Pd₉₁Ag₉, and (C) $\frac{1}{2}$ x C6S Pd NPs.

7.3.4 Effect of Hydrogen Flow Rate in Catalytic Activity of C6S Pd and C16NH₂ Pd and PdAg NPs

The total TOF of the conversion of allyl alcohol (hydrogenation + isomerization) in the presence of C6S Pd and C16NH₂ Pd and PdAg NPs and H₂ at different flow rates: 1.69 ± 0.02 , 8.0 ± 0.2 , 19.6 ± 0.2 , and 39.0 ± 0.3 mL/min are displayed in Table 7.3. The TOF values varied significantly depending on the rate of H₂ bubbled through the catalysis solution. It is useful to first note the difference between NPs that were stable (soluble) during the reaction (indicated by *) and those that were unstable (became insoluble) during the reaction (indicated by *NS*) over all H₂ flow rates. We observed that an increase in H₂ flow rate led to NP instability, which was evidenced by the noticeable precipitation of the NPs. Figure 7.10 shows UV-vis spectra of a solution of C6S Pd and C16NH₂ Pd and PdAg NPs and allyl alcohol exposed to 100% H₂ at constant flow rates of 19.6 ± 0.2 and 39.0 ± 0.3 mL/min for 60 min. The significant loss in absorbance over wavelength demonstrates the decrease in stability of the NPs. The Pd and PdAg NPs that were stable during the catalysis reaction at a H₂ flow rate of 8.0 ± 0.2 mL/min for 60 min (Chapter VI, Figure 6.6), were also at 1.69 ± 0.02 mL/min. Although C6S Pd NPs underwent some aggregation when H₂ was bubbled through the solution at flow rates >8 mL/min (Frames A and B), their stability was higher compared to that of Pd and PdAg NPs coated with C16NH₂ ligands (Frames C-F), which is attributed to the strong Pd-S interactions. Thus, the stability provided by the strongly coordinating thiol at higher H₂ flow rates is more important than the fact that C16NH₂ ligands might form a bilayer surrounding the NP core.

Table 7.3 Total rates for the hydrogenation and isomerization of allyl alcohol by C6S Pd and C16NH₂ Pd and PdAg NPs at different H₂ flow rates

Nanoparticles	Total TOF (mol substrate/mol Pd/h) ^[a]			
	1.69 ± 0.02 mL/min	8.0 ± 0.2 mL/min	19.6 ± 0.2 mL/min	39.0 ± 0.3 mL/min
½x C6S Pd	---	46.7 ± 12.0*	92.0 ± 2.2 ^{NS}	46.5 ± 2.4 ^{NS}
12x C16NH ₂ Pd	247.6 ± 60.0*	718.5 ± 86.6*	1213.9 ± 38.2 ^{NS}	1496.9 ± 82.6 ^{NS}
12x C16NH ₂ Pd ₉₁ Ag ₉	168.8 ± 14.1*	976.9 ± 178.5*	1364.5 ± 21.7 ^{NS}	1868.7 ± 70.6 ^{NS}

^[a] Total TOF values represent the sum of TOF for hydrogenation and isomerization. These values are the average of three samples analyzed for each catalyst.

* NPs were stable during the course of the reaction at this flow rate.

^{NS} (not stable) NPs precipitated during the course of the reaction at this flow rate.

Figure 7.10 UV-vis spectra of a solution of $\frac{1}{2}\times$ C6S Pd and 12x C16NH₂ Pd and Pd₉₁Ag₉ NPs exposed to allyl alcohol and 100% H₂ at flow rates of 19.6 ± 0.2 mL/min (A, C, E) and 39.0 ± 0.3 mL/min (B, D, F) for 60 min, then the solutions were sitting in air for 20 min and 3 h.

The clear trend in the Pd and PdAg NPs is that the total TOF increased with increasing the H₂ flow rates. When H₂ was bubbled through the solution at a flow rate of 1.69 ± 0.02 mL/min, the C16NH₂ Pd and PdAg NPs exhibited total TOF values ranging from 169 to 248, which are similar to other homogeneous systems previously investigated.^{30,38,123,130-133} By increasing the rate to 8.0 ± 0.2 mL/min, the total TOF increased by a factor of 3 and 6 for C16NH₂ Pd and PdAg NPs, respectively, both keeping their stability. Further increase in the H₂ flow rate led to a dramatic increase in the catalytic activity of the NPs. For instance, the total TOF values obtained at 39.0 ± 0.3 mL/min were 6- and 11-fold higher than those obtained at 1.69 ± 0.02 mL/min for C16NH₂ Pd and PdAg NPs, respectively. It is evident that the C16NH₂ PdAg NPs displayed the highest total TOF of all the NPs at 1869 mol substrate/mol Pd/h. This is attributed to their little greater stability imparted by the Ag atoms as shown by the UV-vis data and the ability to adsorb larger amounts of H₂.^{103,174} Although the rates of conversion of allyl alcohol obtained with our synthesized C16NH₂ Pd and PdAg NPs at a H₂ flow rate of 39.0 ± 0.3 mL/min compare very well with the commercially available Pd catalyst (TOF = 1300),¹⁸² our NPs precipitated, lost their stability, and became heterogeneous catalysts over time. In the case of C6S Pd NPs, the low total TOF values is due to the strong coordination of the thiolate to the Pd surface. Comparing the various H₂ flow rates over the C6S Pd NPs, we observed that the catalytic activity at 19.6 ± 0.2 mL/min was 2-fold higher than that at 8.0 ± 0.2 mL/min. However, these eventually precipitated, but took the longest to do so. At 39.0 ± 0.3 mL/min, the NPs precipitated faster (after 3 h sitting in air) and the reactivity was greatly diminished by a factor of 2

down to a TOF value of 47 mol substrate/mol Pd/H₂, as the value obtained at 8.0 ± 0.2 mL/min with the difference that the NPs were highly stable at the lower flow rate.

7.4 CONCLUSIONS

Here we demonstrated that C6S Pd and C16NH₂ Pd and PdAg NPs can be used to catalyze the reaction between H₂ and various allyl alcohols that differ only slightly in chemical structure to give the corresponding saturated alcohol or carbonyl derivative. C6S Pd NPs were efficient for the catalysis of primary (**1**) and secondary (**2**) alcohols with high selectivity toward the formation of propanal and 3-pentanone, respectively, but they showed low activity (TOF) due to the strong Pd-S interaction. On the other hand, C16NH₂ Pd and PdAg NPs had high TOFs due to the weakly bound alkylamines, but gave a mixture of both hydrogenation and isomerization products (5:5). Interestingly, when a quaternary alcohol (**3**) was evaluated, not only the C16NH₂ Pd and PdAg NPs led to the hydrogenation product, but also the C6S Pd NPs with a conversion of 60% after 150 min. In general, the total TOF values decreased when bulkier and larger allyl alcohols were tested, indicating that these catalysts allowed size-based selectivity in the hydrogenation and isomerization of all the three allyl alcohols.

In this study we were also able to determine that the conversion, selectivity, and rate of hydrogenation/isomerization of allyl alcohol over Pd and PdAg NPs can be controlled by tuning H₂ flow rates. For C16NH₂ Pd and PdAg NPs, the best compromise between conversion and selectivity toward the formation of the isomerization product was reached at a constant H₂ flow rate of 1.69 ± 0.02 mL/min giving 100% conversion,

81-85% aldehyde, and total TOF = 169-248 mol substrate/mol Pd/h. Additionally, the NPs were stable during the catalysis reaction. At intermediate and higher H₂ flow rates (8.0 ± 0.2 to 39.0 ± 0.3 mL/min), the initial high isomerization selectivity showed a gradual decline while the hydrogenation product was favored. Overall, the reaction went to full completion within 20-35 min and 70% alcohol was obtained. The total TOFs were >1500 mol substrate/mol Pd/h at 39.0 ± 0.3 mL/min, which was accompanied by the precipitation of the Pd and PdAg NPs. For C6S Pd NPs, the best conversion, selectivity, and stability of allyl alcohol occurred at a flow rate of 19.6 ± 0.2 mL/min. 100% allyl alcohol was converted to 92% aldehyde within 60 min with TOF = 92 mol substrate/mol Pd/h. Although the NPs were relatively stable during the catalysis reaction, they eventually precipitated over time. It should be noted that the selectivity of C6S Pd NP catalysts basically remained unchanged over all H₂ flow rates tested.

CHAPTER VIII

ALKANETHIOLATE-COATED Pd NANOPARTICLES WITH CONTROLLED ACTIVITY AND SELECTIVITY FOR ISOMERIZATION OF ALLYL ALCOHOL

8.1 INTRODUCTION

Here we show that alkanethiolate-coated Pd NPs are selective catalysts for isomerization reactions and their catalytic activity is ruled by the Pd-thiolate interaction, ligand surface coverage, and NP stability. This work was inspired by Shon and co-workers, who reported the catalytic activity of alkanethiolate-capped Pd NPs prepared from Bunte salts, in which sodium S-alkanethiosulfate ligands were employed rather than alkanethiolates.¹³⁰⁻¹³³ These Pd NPs were stable and highly selective toward the isomerization of allyl alcohol. In order to produce stable Pd NPs with different surface ligand densities and particle core sizes, they performed systematic variations in the synthesis of Pd NPs and observed that there is a strong correlation between the Pd NP composition and the rate of isomerization of allyl alcohol.¹³³ Eklund and co-workers examined the catalytic properties of Pt NPs protected by a thiol monolayer for the hydrogenation of allyl alcohol.³⁸ They determined that differences in the catalytic rates

among the various Pt NPs evaluated correlated to the type of ligand, packing density, and core size.

We previously showed the synthesis and characterization of alkylamine alkanethiolate-coated Pd NPs and studied their stability and reactivity in the presence of hydrogen for sensing and catalysis applications. Although C6S-coated Pd NPs possess good stability and do not aggregate appreciably in solution⁶⁷ and solid state,⁶⁷ their reactivity is inhibited by the hexanethiolates since they are strongly bound to the Pd surface. This is shown by their factor of 20 lower TOF compared to alkylamine stabilizer of C16 chain length.⁶⁸ It is known that alkanethiolates form well-packed ordered monolayers surrounding the NP core, which may also inhibit the reaction taking place on the surface of the catalyst. Our previous work showed that the Pd-thiolate interaction is the main reason for the lower TOF as opposed to the chain length.⁶⁸ Interestingly, the thiol ligands lead to selective isomerization over hydrogenation. This seems to be a consequence of the slow reaction rate as opposed to the Pd-thiolate chemistry, since isomerization was also favored for alkylamine-coated Pd NPs when the reaction was slowed down by reducing the H₂ flow rate. Our overall goal is to functionalize Pd NPs with stabilizers that allow us to tune the activity and selectivity of NP catalysts while providing the NPs with stability. Here we examined the reactivity of Pd NPs coated with alkanethiolate ligands of varied chain length in the presence of allyl alcohol and H₂. The results indicate that all of the C_nS Pd NPs favor the isomerization of allyl alcohol and the carbon chain length does not impede the reactivity of the NPs. Although C4S and C6S Pd NPs have the highest activity due to the low thiolate coverage, they are unstable during the catalysis reaction. In contrast, Pd NPs coated with C_nS ligands with $n \geq 8$ are

highly stable but the reactivity is significantly diminished by the large density of ligands strongly bound to Pd. In conclusion, C8S Pd NPs may be the optimal catalysts in terms of reactivity and stability.

8.2 EXPERIMENTAL

The procedures for the catalysis experiments using CnS Pd NPs are described in Chapter II.

8.3 RESULTS AND DISCUSSION

8.3.1 Composition and Ligand Surface Coverage of CnS Pd NPs

Table 8.1 shows the very roughly estimated compositions of Pd NPs coated with various CnS ligands, including C4S, C6S, C8S, C12S, C16S, and C18S used in this study to evaluate their performance in the selective catalysis of allyl alcohol in the presence of H₂. The ligand surface coverage was obtained by dividing the number of average ligands on the Pd NPs by the theoretical amount of surface Pd atoms in the nanoparticle model. These calculations were based on a spherical model of the Pd core coated with tightly packed alkanethiolates that can achieve a maximum coverage of 43%, although the metal core likely have a truncated octahedral shape containing surface defect atoms (edges and vertices).^{73,132}

Table 8.1 Composition and ligand surface coverage of CnS Pd NPs

Nanoparticles^[a]	TEM diam. (nm)	Composition	Ligand surface coverage (ligands/surface atoms)^[b]
C4S Pd	3.4 ± 0.4	Pd ₁₃₃₄ (C4S) ₁₉₇	0.34
C6S Pd	3.2 ± 0.4	Pd ₁₁₁₂ (C6S) ₂₂₂	0.46
C8S Pd	3.0 ± 0.4	Pd ₉₁₆ (C8S) ₂₂₅	0.57
C12S Pd	3.1 ± 0.4	Pd ₁₀₁₁ (C12S) ₂₃₄	0.54
C16S Pd	2.8 ± 0.3	Pd ₇₄₅ (C16S) ₁₆₆	0.52
C18S Pd	2.6 ± 0.4	Pd ₅₉₇ (C18S) ₁₃₀	0.51

^[a] NPs synthesized with a 1:2 CnS:Pd ratio (1/2x).

^[b] Ligand surface coverage was calculated by dividing the total ligands by surface Pd atoms of Pd NP.

As we discussed in Chapter III, an increase in the carbon chain length of CnS Pd NPs led to small and stable NPs with larger organic weight fractions due to the higher mass of longer alkanethiolates. Comparing C4S to C6S Pd NPs, which differ by only 2 carbons, the average diameter size of the NPs decreased from 3.4 to 3.2 nm with significant changes in their morphology and stability against aggregation in the presence of H₂. As displayed in Table 8.1 (column 3), the calculated ligand surface coverage for C6S Pd NPs was 0.46, which is ~1.3-fold higher than that for C4S Pd NPs. This indicates the formation of Pd NPs with higher ligand packing, but also Pd NPs less reactive to H₂ due to the larger amount of strongly coordinated thiolates as evidenced by the UV-vis, TEM, and conductivity studies in Chapter III-V. For CnS Pd NPs with $n \geq 8$, the ligand surface coverage values ranged from 0.57 to 0.51, with C8S Pd NPs having a slightly higher ligand coverage. This decrease in coverage as a function of n might be possibly attributed to steric interference undergone by longer chain length ligands. This is interesting because although C18S Pd NPs had the lowest thiolate coverage (0.51), they produced the smallest NPs among all of the CnS Pd NPs used (2.6 nm). In addition to steric effect issues, average size of NPs also seems to play an important role in the packing of thiolates on a spherical metal core.³⁸ One would expect smaller NPs to have a higher thiolate coverage since they have a large proportion of edge and vertex atoms with higher exposed surface area over the polyhedron faces. The results of increased coverage due to core size can be readily seen when comparing C4S- to C8S- and C16S-coated Pd NPs, where the ligand surface coverage went from 0.34 to >0.51 and the average diameter decreased from 3.4 to 2.6 nm.

8.3.2 Catalysis Experiments with CnS Pd NPs

The rates of conversion (TOFs, mol substrate/mol Pd/h) of 2-propen-1-ol to the corresponding hydrogenation and isomerization products (propanol and propanal, respectively) in the presence of C6S Pd NPs and 100% H₂ at different flow rates are displayed in Figure 8.1. The points and curves represent the average of three samples analyzed with the standard deviation shown. The total TOF of the conversion of allyl alcohol (hydrogenation + isomerization) at a H₂ flow rate of 8.0 ± 0.2 mL/min was 47 mol substrate/mol Pd/h. As the rate of H₂ bubbled through the catalysis solution increased, the rate of conversion also increased. At 19.6 ± 0.2 mL/min, the total TOF was 92 mol substrate/mol Pd/h, indicating that the catalytic activity of C6S Pd NPs increased by a factor of ~2 as shown in Figure 8.1. Interestingly, further increase in the H₂ flow rate slowed down the reaction noticeable (TOF = 47 mol substrate/mol Pd/h), but the C6S Pd NPs still maintained a very high selectivity for the isomerization reaction (98%). The decrease in the rate of conversion of allyl alcohol was likely due to a loss in stability of NPs in the presence of excess H₂ flow rate, which led to formation of aggregated NPs with less surface area available and low reactivity. The Pd NPs noticeably precipitated at high flow rates.

Eklund and co-workers reported the catalytic properties of Pt NPs coated with alkanethiolate ligands for the hydrogenation of allyl alcohol.³⁸ These NP catalysts exhibited low hydrogenation rates (TOF <13) and only 21% allyl alcohol was converted after 1 hour.³⁸ Comparing to our system, we determined that C6S Pd NPs allowed the selective conversion of allyl alcohol to aldehyde (92%) within 60 min with higher TOFs. These results were obtained when H₂ was bubbled through the catalysis solution at a

Figure 8.1 Hydrogenation and isomerization rates (TOFs) of allyl alcohol by C6S Pd NP catalysts over various flow rates of 100% H₂.

constant flow rate of 19.6 ± 0.2 mL/min. This may be the optimal flow rate since it 1) maintains selectivity toward the isomerization product and 2) increases reactivity of the C6S Pd NPs with H_2 without significantly affecting their stability against H_2 -induced aggregation. Here, we evaluate the catalytic activity of various CnS Pd NPs with different chain length for the isomerization of allyl alcohol in the presence of 100% H_2 at a constant flow rate of 19.6 ± 0.2 mL/min.

Figure 8.2 shows chromatograms obtained before and after 10, 20, 30, 40, and 60 min of reaction between 100% H_2 and allyl alcohol catalyzed by C4S and C6S Pd NP catalysts in Frames A and B, respectively. For both C4S- and C6S-coated Pd NPs, the peak for allyl alcohol at 3.50 min decreased with time while a peak at 1.07 min corresponding to the aldehyde increased. This indicates that these Pd NPs are clearly active catalysts and selective for the isomerization reaction. Although C4S Pd NPs had the lowest stability among all the CnS Pd NPs as evidenced by the large absorbance at all wavelengths and heavily aggregated NPs observed in the UV-vis spectra and TEM images, respectively, even before H_2 exposure (Chapter III-IV), the GC data confirms that these NPs are active catalysts, which we can consider homogeneous at the beginning, but heterogeneous at the end of the reaction. Figure 8.3 shows the percent hydrogenation, percent isomerization, and total conversion of allyl alcohol at different times when C6S Pd NPs were used as catalysts. Importantly, these NPs were much more heterogeneous at the end of the reaction.

Figure 8.2 Gas chromatograms showing progress of catalytic reaction of allyl alcohol after exposure to 100% H_2 (19.6 ± 0.2 mL/min) at different reaction times. The reaction was catalyzed by ~ 3.0 mg of (A) $\frac{1}{2}$ x C4S- and (B) $\frac{1}{2}$ x C6S-coated Pd NPs in 4 mL of CH_2Cl_2 under atmospheric pressure and at room temperature.

Figure 8.3 Plot of the % hydrogenation, % isomerization, and % conversion of allyl alcohol versus reaction time over $\frac{1}{2}\times$ C6S Pd NP catalysts in CH_2Cl_2 .

8.3.3 Selectivity and Catalytic Activity of CnS Pd NPs

We conducted the experiment shown in Figure 8.2 on all of the CnS Pd NPs. Figure 8.4 displays the selectivity toward hydrogenation and isomerization products after 60-120 min of reaction. The catalytic reaction went to 100% completion within 60 min and resulted in 91-93% aldehyde along with 9-7% alcohol when using C4S and C6S Pd NP catalysts, respectively. For C8S, C12S, C16S, and C18S Pd NPs, the conversion of allyl alcohol was slightly slower (95-98%) and required a longer reaction time (90-120 min). The results indicate that the favorable trend for isomerization remained the same over all of the CnS Pd NPs and therefore the ligand chain length did not alter selectivity. We believe a slow reaction rate favors isomerization, even with alkylamine stabilizers.

Table 8.2 shows the TOF values for the hydrogenation, isomerization, and total TOF using the various CnS Pd NPs as catalysts. It is useful to first note the difference between NPs that were stable (soluble) during the reaction (indicated by *) and those that were unstable and precipitated during the reaction (indicated by *NS*). C4S Pd NPs were unstable in H₂ only and also precipitated during the catalysis reaction. Figure 8.5 shows UV-vis spectra of a solution of C4S, C6S, C8S, C12S, C16S, and C18S Pd NPs in the presence of 100% H₂ plus allyl alcohol. The change in absorbance over wavelength in the UV-vis spectra is directly correlated with the stability of NPs. The absorbance of C4S Pd NPs decreased to almost zero following 60 min in H₂ and 1 h in air, indicating nearly complete precipitation. The C6S Pd NPs decreased minimally after 60 min in H₂ and a little more after 3 h more in air, indicating some precipitation, but overall decent stability. In the case of C8S, C12S, C16S, and C18S Pd NPs, they were all stable during H₂ and air treatments.

Figure 8.4 Selectivity toward hydrogenation and isomerization products after 60-120 min of reaction between allyl alcohol and 100% H₂ (19.6 ± 0.2 mL/min) over C_nS Pd NP catalysts of varied chain length ($n = 4, 6, 8, 12, 16$, and 18). C₄S and C₆S Pd NPs required 60 min, C₈S, C₁₂S, and C₁₆S Pd NPs required 90 min, and C₁₈S Pd NPs took 120 min to complete the reaction.

Table 8.2 Hydrogenation and isomerization rates of allyl alcohol by various CnS Pd NPs

Nanoparticles	TOF (mol substrate/mol Pd/h) ^[a]		
	Hydrogenation	Isomerization	Total ^[b]
C4S Pd ^{NS}	5.9 ± 1.7	101.6 ± 1.8	107.5 ± 2.5
C6S Pd ^{NS}	5.3 ± 0.8	86.7 ± 2.0	92.0 ± 2.2
C8S Pd*	6.1 ± 0.1	65.2 ± 7.5	71.3 ± 7.5
C12S Pd*	1.3 ± 0.4	43.1 ± 3.5	44.4 ± 3.5
C16S Pd*	1.9 ± 0.4	43.9 ± 8.8	45.8 ± 8.8
C18S Pd*	1.6 ± 0.4	40.1 ± 9.3	41.7 ± 9.3

^[a] The TOFs (mol substrate/mol Pd/h) are initial values determined at total conversion of less than 60%. The TOFs represent the average of three samples analyzed for each catalyst.

^[b] Total values represent the sum of TOF for hydrogenation and isomerization.

* These NPs were stable during the course of the reaction.

^{NS} (not stable) These NPs precipitated during the course of the reaction.

Figure 8.5 UV-vis spectra of a solution of C4S, C6S, C8S, C12S, C16S, and C18S Pd NPs (A, B, C, D, E, F) exposed to 100% H₂ plus allyl alcohol for 60 min and then the solutions were sitting in air for 1 and 3 h. H₂ flow rate = 19.6 ± 0.2 mL/min. CnS Pd NPs synthesized with a 1:2 CnS:Pd ratio ($\frac{1}{2}x$).

Based on our previous results, we hypothesized that chain length itself would not significantly impede the reaction since very high TOF was possible with C18NH₂ stabilizing ligands. Therefore, the metal-ligand interaction and NP stability are more important. Figure 8.6 displays the change in TOF versus carbon chain length of CnS ligands on the Pd NPs. The plot shows the highest TOF for C4S Pd NPs at 108 mol substrate/mol Pd/h among all the CnS Pd NPs, which allowed the full conversion of allyl alcohol to the isomer as the main product within 60 min. We attribute the high catalytic activity of C4S Pd NPs not to the short chain, but to the low thiolate coverage on the NP surface, which leaves more exposed Pd atoms that react with H₂ and allyl alcohol. While C4S Pd NPs are not as stable, they are stable enough at short time for the reaction to proceed. C6S Pd NPs show a TOF at 92 mol substrate/mol Pd/h. While they are more stable, the catalytic activity of C6S Pd NPs was slightly lower than that of C4S Pd NPs because of the higher thiolate coverage. The reactivity of C8S Pd NPs decreased to a TOF value of 71 mol substrate/mol Pd/h, requiring 90 min to complete the reaction. These Pd NPs are very stable, but have a reduced TOF again due to higher thiolate coverage compared to C6S and C4S Pd NPs. The C12S, C16S, and C18S Pd NPs displayed the lowest total TOF of all the Pd NPs at 42-46 mol substrate/mol Pd/h. These NPs are all highly stable and have similar thiolate coverages, which explains why they exhibit similar TOF. This is consistent with our previous conclusion that Pd-S interaction (and coverage) and stability are more important in determining reactivity than the length of the alkyl chain. The C8S Pd TOF compared to C12S, C16S, and C18S is not consistent since they are equally stable, but more active, even with higher thiolate

Figure 8.6 TOF as a function of carbon chain length for hydrogenation and isomerization of allyl alcohol over various CnS Pd NPs.

coverage. This could be due to inadequate cleaning of that sample or slightly large size of NP, although it is similar to C12S Pd NPs. It is also possible that penetration of allyl alcohol through C8 is slightly more favorable compared to C12 and anything larger than C12 is similar. This is not consistent with high TOF values on C18NH₂ Pd NPs, though. More work is needed to explore the difference between C8S and lower versus C12S and higher ligands. While lower in TOF, we expect C18S Pd NPs to be very stable and reusable for more cycles.

8.4 CONCLUSIONS

Here we evaluated the catalytic activity of Pd NPs coated with alkanethiolates of varied chain length including C4S, C6S, C8S, C12S, C16S, and C18S in the reaction between allyl alcohol and H₂. All of the C_nS Pd NPs favored the selective isomerization of allyl alcohol (>90%) over hydrogenation (<9). An increase in the carbon chain length leads not only to small and stable NPs, but also to reactive NPs to H₂. Therefore, carbon chain length itself likely does not impede the reaction. There is a strong correlation between the catalytic activity and the Pd-S interaction, ligand surface coverage, and NP stability. C4S and C6S Pd NPs have the highest activity due to the low thiolate coverage, but show low stability during the catalysis reaction. C8S Pd NPs are highly stable, but the reactivity is diminished because of the large density of ligands strongly bound to Pd. Although further increase in carbon chain length produces stable and small NPs with a large percent of defect atoms, the low catalytic activity is most probably due to large coverage of ligands on the surface occupying the most reactive sites, which inhibit the

reaction with H₂ and allyl alcohol. C8S Pd NPs may be the optimal catalysts in terms of TOF and stability; however, it is not clear why higher catalytic activity than C12S, C16S, and C18S Pd NPs even though thiolate coverage is higher. More work is needed to explain these differences. Overall, these results demonstrate that it is possible to design stable, selective, and highly efficient catalysts by simply controlling the metal-ligand interaction, ligand surface coverage, and stability of NPs.

CHAPTER IX

SUMMARY, CONCLUSIONS, AND FUTURE DIRECTIONS

In summary, this dissertation shows the chemical synthesis, characterization, stability, and reactivity of Pd and Pd-containing alloy (PdAg) nanoparticles (NPs) coated with various organic stabilizers. We focused on the interaction between hydrogen and Pd and PdAg NPs, since it is important for hydrogen sensing applications and for using the NPs as homogeneous catalysts for the hydrogenation/isomerization of olefins. Accordingly, we studied interactions of hydrogen with both solid-state films and solutions of the NPs for these two applications, respectively. We also explored the use of various Pd and PdAg NPs as homogeneous catalysts for the hydrogenation/isomerization of various allyl alcohols.

Chapter III shows the successful synthesis of Pd and PdAg NPs stabilized with alkanethiolates (C_nS , $n = 4, 6, 8, 12, 16$, and 18), alkylamines (C_nNH_2 , $n = 8, 12$, and 16), and mixed $\text{C}_8\text{NH}_2/\text{C}_6\text{S}$ ligands. We demonstrated that these NPs can be easily prepared and confirmed their composition by various analytical techniques. All of the NPs were in the 2.5 to 3.5 nm range. An increase in carbon chain length of C_nS in the C_nS -coated Pd NPs led to small and well-isolated NPs. While C_4S Pd NPs were large and appeared heavily aggregated with a few individual NPs, C_{18}S Pd NPs produced the

smallest (2.6 nm) and highly stable NPs. Interestingly, an increase in chain length by only 2 carbons, from C4S to C6S, gave a significant change in the morphology of the NPs. Therefore, all CnS Pd NPs with $n \geq 6$ were small and stable. The same trend was followed by the CnNH₂ Pd and PdAg (10:1) NPs, although the average diameters of these NPs were statistically similar to each other. However, variations in the initial mole ratio of CnNH₂/Pd led to significant changes in size, distribution, and stability of the NPs. Pd and Pd₉₁Ag₉ NPs coated with C16NH₂ ligands prepared in a 12:1 alkylamine:Pd ratio produced small and stable NPs, which was attributed to the formation of multilayers of ligands on the Pd core based on large percentage of organic content determined by TGA measurements. We also synthesized mixed ligand C8NH₂/C6S Pd NPs with varying ratios by a liquid-phase place-exchange reaction between pure C8NH₂ NPs and free C6SH ligands in solution. This confirmed that the Pd-S bond is much stronger compared to Pd-CnNH₂, since C6SH ligands fully replaced the C8NH₂ ligands on the Pd NP surface during the exchange reaction. The approach described here importantly led to the synthesis of Pd and PdAg NPs with controlled functionality and composition.

Since the use of Pd and PdAg NPs for applications in sensing and catalysis requires them to be in the presence of hydrogen gas, in Chapter IV we studied the stability of CnS Pd, CnNH₂ Pd and PdAg, and C8NH₂/C6S Pd NPs in solutions of bubbling hydrogen gas by UV-vis spectroscopy and transmission electron microscopy (TEM) measurements of the NPs as a function of bubbling time. CnS Pd NPs ($n \geq 6$) had high stability against H₂-induced aggregation because of the strong Pd-S interaction and long alkane chain. Among the CnNH₂ Pd and PdAg NPs, the 6x and 12x C16NH₂ Pd and Pd₉₁Ag₉ NPs exhibited the highest stability in the presence of hydrogen for several

hours. The others irreversibly aggregated and precipitated within 1 hour. This difference in stability for C_nNH_2 Pd and PdAg NPs was explained by the formation of a bilayer of ligands on the Pd core for the $C_{16}NH_2$ -coated NPs that prevented the NP aggregation. For mixed ligand C_8NH_2/C_6S Pd NPs, the stability strongly depended on the C_8NH_2/C_6S ratio on the Pd NPs. The Pd NPs coated with $\sim 3:1$ or less C_8NH_2/C_6S ligands showed excellent stability against H_2 -induced aggregation in solution. This shows that a full monolayer of C_6S is not required to protect the NPs from aggregation. There may be certain Pd NP sites responsible for the aggregation that are coated with a small number of C_6S ligands. This study provided interesting knowledge of hydrogen stability of solutions containing metal NPs for potential hydrogen sensing and catalysis applications.

In Chapter V we specifically studied interactions between hydrogen gas and Pd NPs coated with C_6S , C_8NH_2 , and mixed C_8NH_2/C_6S by monitoring the resistance of solid-state films in the presence of alternating flow of hydrogen and nitrogen. We found that the resistance of films of C_6S Pd NPs irreversibly increased by a small amount upon the first exposure to 100% hydrogen, while the resistance of films of C_8NH_2 Pd NPs increased by several orders of magnitude. Therefore, these films were not ultimately useful for hydrogen sensing applications. The reaction of Pd with hydrogen leads to PdH_x formation, which is reversible when removed from hydrogen. The films of C_8NH_2 Pd NPs restructured into continuous Pd films upon the first exposure to hydrogen (and formation of PdH_x) and then act as bulk, continuous Pd films in their hydrogen sensing response. This is not desirable as they lose their NP structure. Films of mixed C_8NH_2/C_6S ($\sim 1/1$) Pd NPs retained their NP structure in 100% hydrogen and exhibited a

reversible decrease in resistance in the presence of various hydrogen concentrations down to 0.3%. These NPs were optimal for retaining the NP structure and exhibiting fast, reversible responses to hydrogen in the solid state for sensing applications. They benefitted from the reactivity of C8NH₂ Pd NPs and stability of C6S Pd NPs.

In Chapter VI we explored the catalytic properties of the various NPs for the hydrogenation/isomerization of olefins. We studied 2-propen-1-ol, the simplest allyl alcohol, as a model substrate first. All of the NPs catalyzed either or both the hydrogenation and isomerization of allyl alcohol with hydrogen in solution to give propanol and/or propanal, respectively. However, the selectivity, reactivity, and turnover frequency (TOF) varied depending on the metal (Pd or 10:1 PdAg) and the organic stabilizing ligand. The C6S and C8NH₂/C6S (~1/1) Pd NPs were stable, but exhibited the lowest TOFs, which we attribute to the strong thiolate-Pd interaction slowing down the interaction with hydrogen by limiting the Pd atoms available for reactivity. Remarkably, C6S Pd NPs were highly selective toward the isomerization reaction, while C8NH₂/C6S slightly favored the isomerization. C8NH₂ and C12NH₂ Pd and PdAg NPs catalyzed the reaction, but precipitated within 1 hour and had low TOFs. Interestingly, C8NH₂ PdAg was highly selective to the hydrogenation product, while the others produced a ~1:1 or 2:3 mixture of the hydrogenation and isomerization products. C16NH₂ Pd and C16NH₂ PdAg NPs were highly stable and exhibited the highest TOF values, producing a ~1:1 or 2:3 mixture of the two products. Taken together, we found that C8NH₂ and C12NH₂ Pd and PdAg NPs produced low TOF values due to their instability. The formation of aggregates and precipitation lowers the available surface area and converts these NPs into heterogeneous catalysts, which lowers their reactivity.

These are not considered useful for catalysis of reactions involving hydrogen as a reactant. Comparing C16NH₂ to C6S or C8NH₂/C6S Pd NPs, it is clear that the weaker Pd-NH₂ interaction relative to the strong Pd-S interaction is favorable for high reactivity (high TOF). Also, the Pd-ligand interaction is more important than the alkyl chain in determining reactivity since the longer C16 chain with an amine does not impede reactivity compared to the thiolate with a short C6 chain. The nature of the ligand-Pd chemistry can control the selectivity of the reaction. These NPs can be reused at least for 5 cycles, although they maintain a high selectivity, reactivity, and stability for only 3 consecutive cycles.

Following this work, in Chapter VII we continued with the use of Pd and PdAg NPs as homogeneous catalysts for the hydrogenation/isomerization of various allyl alcohols that differ only slightly in chemical structure. While C6S Pd NPs catalyzed the reaction of primary and secondary alcohols with hydrogen in solution with high selectivity toward the formation of aldehyde and ketone (>95%), respectively; C16NH₂ Pd and PdAg NPs were 50%. Interestingly, when a quaternary alcohol was evaluated, not only the C16NH₂ Pd and PdAg NPs led to the hydrogenation product, but also the C6S Pd NPs with a conversion of 60%. The C16NH₂ Pd and PdAg NPs had the highest TOFs, due to high stability and weakly coordinated alkylamines. However, more branched substrates had low reaction rates, likely due to restricted diffusion and access to Pd through the packed multilayer of C16NH₂ ligands surrounding the Pd core. In the case of C6S Pd NPs, the strong Pd-S interaction and greater restriction of more branched substrates led to low TOFs. Here, we also discussed the effect of hydrogen on the catalytic activity of Pd and PdAg NPs. At low hydrogen flow rates, C16NH₂ Pd and

PdAg NPs exhibited higher selectivity toward the formation of the isomer (>80%) and remained stable during the reaction. This is another way to selectively form the isomer, by varying the reaction rate. At intermediate and higher hydrogen flow rates, the reaction went to completion in a shorter time and the selectivity favored the alcohol (>65%) over the isomer. Although this was accompanied by a significant increase in the rate of conversion, the NPs unfortunately became unstable during the reaction and precipitated. C6S Pd NPs also underwent some aggregation at higher hydrogen flow rates, but the selectivity of these catalysts basically remained unchanged over all hydrogen flow rates tested.

In Chapter VIII we examined the reactivity of Pd NPs coated with alkanethiolate ligands of varied chain length in the presence of allyl alcohol and hydrogen. Although all of the C_nS Pd NPs favored the isomerization of allyl alcohol, their catalytic activity was somewhat correlated to the ligand surface coverage. C4S Pd NPs had the highest activity due to the low thiolate coverage, but showed low stability during the catalysis reaction. On the other hand, C8S Pd NPs were highly stable, but the reactivity was diminished because of the large density of ligands strongly bound to Pd. For C_nS Pd NPs with $n > 8$, the catalytic activity decreased significantly. This could be due to NP size, C_nS coverage, or the longer chain length. We do not suspect chain length based on the similar reactivity between C12S, C16S, and C18S Pd NPs, and the results of C16NH₂ Pd NPs. More work is needed, but this study led to interesting insights regarding the effect of chain length on the catalysis of C_nS Pd NPs.

Overall, this work shows that metal nanoparticles can be easily synthesized and their functionality and composition can be tailored to impart useful properties for sensing

and catalysis applications. Variations in the chain length, type of ligand, and metal composition had drastic effects on stability, reactivity, and selectivity. The chemistry of these materials can be altered to optimize their performance by designing stable, reactive, and reversible hydrogen sensors, and highly active, selective, and efficient catalysts.

FUTURE DIRECTIONS:

Future research should focus on the reusability of the Pd and PdAg NPs. This should be explored further to design strategies that improve the efficiency and reactivity of the NPs over various consecutive cycles. It is also important to study the effect of temperature in the stability of the various NPs. This will lead to use of organic-stabilized Pd and PdAg NPs as catalysts for other organic reactions such as C-C coupling reactions, which are a very important class of organic reactions with industrial applications. It would be also interesting to explore different synthesis methods for increasing the Ag content of PdAg NPs while still maintaining high stability and catalytic activity.

The search for ligands allowing both high reactivity and stability will be an ongoing challenge.

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CURRICULUM VITAE

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PROFESSIONAL OBJECTIVE:

To use my knowledge, skills, training, and experience in Analytical Chemistry with emphasis on Nanotechnology, Materials Science, and Electrochemistry to enter a career in academia and/or a research center.

SUMMARY OF QUALIFICATIONS:

- Large and small-scale synthesis of metal nanoparticles (NPs) with potential use in sensing and catalysis applications.
- Characterization of NPs using various analytical techniques and electrochemical methods.
- Well-organized and efficient planner to complete projects timely.
- Strong verbal and written communication skills.
- Excellent analytical, problem solving, and logic building skills.
- Ability to handle multiple tasks, work in teams and collaborations, and generate ideas in a clear and concise way.

- Extensive knowledge in conducting analytical tests and experiment.
- Well-trained in testing, maintaining, and repairing laboratory equipments.
- Goal-oriented, good motivator, and ability to use different teaching methods.
- Proficient with Microsoft programs and with database compilation and execution.

EDUCATIONAL BACKGROUND:

University of Louisville (Louisville, KY, USA)

Ph.D. in Chemistry

2007 – 2013

Department of Chemistry (Dr. Francis P. Zamborini)

Universidad del Cauca (Popayán, Colombia)

B.S. in Chemistry

1998 – 2005

Departamento de Química (Dr. Olga Lucia Hoyos)

RESEARCH EXPERIENCE:

Graduate Research Assistant

2009 – 2013

University of Louisville, Louisville, KY

Synthesized and characterized Pd, Ag, Au, and Pd-alloy NPs coated with various organic ligands. Evaluated the reactivity between H₂ and the NPs by controlling the metal and ligand composition of the nanoparticles for possible H₂ sensing, storage, and catalysis applications. Explored the catalytic properties of these interesting materials for the hydrogenation and isomerization of various organic substrates. Recently, the research involves fundamental surface chemistry and the study of the electrochemical and electronic properties of metal-ligand complexes attached to NPs with potential use in catalysis, separations, sensing, nanoelectronics, and energy.

Undergraduate Research Mentor**2010 – 2011****University of Louisville, Louisville, KY**

Conducted research with undergraduate students on Analytical Chemistry. Taught laboratory techniques, instrumentation, and basic concepts of chemistry, synthesis, and characterization of metal nanostructures. Helped the students prepare oral presentations and posters for group meetings and undergraduate research symposia.

Graduate Research Mentor**2007 – 2013****University of Louisville, Louisville, KY**

Taught laboratory techniques, instrumentation, and synthesis of metal nanostructures and their characterization. Responsible for maintaining the laboratory, chemicals, apparatus, and equipment effectively and in ready-to-use manner.

Undergraduate Researcher**2004 – 2005****Universidad del Cauca, Popayan, Colombia**

Responsible for the standardization of electrochemical methods for the quantification of trace metals in environmental matrices.

RESEARCH JOURNAL PUBLICATIONS:

- Chauhan, R.; **Moreno, M.**; Grapperhaus, C. A.; Zamborini, F. P. “Metal-Stabilized Thiyl Radicals as Scaffolds for Ethylene Detection”. In preparation for publication.
- **Moreno, M.**; Zamborini, F. P. “Size and Product-Based Selectivity in Hydrogenation of Allyl Alcohol by Pd and PdAg Nanoparticles and Effect of Hydrogen Flow Rate”. Ready to be submitted for publication.
- **Moreno, M.**; Zamborini, F. P. “Alkanethiolate-Coated Pd Nanoparticles with Controlled Activity and Selectivity for Isomerization of Allyl Alcohol”. Ready to be submitted.
- **Moreno, M.**; Kissell, L. N.; Jasinski, J. B.; Zamborini, F. P. “Selectivity and Reactivity of Alkylamine- and Alkanethiolate-Stabilized Pd and PdAg Nanoparticles

for Hydrogenation and Isomerization of Allyl Alcohol”. *ACS Catal.* **2012**, 2, 2602-2613.

- **Moreno, M.**; Ibañez, F. J.; Jasinski, J. B.; Zamborini, F. P. “Hydrogen Reactivity of Palladium Nanoparticles Coated with Mixed Monolayers of Alkyl Thiols and Alkyl Amines for Sensing and Catalysis Applications”. *J. Am. Chem. Soc.* **2011**, 133, 4389-4397.
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PRESENTATIONS:

- Grapperhaus, C. A.; Chauhan, R.; **Moreno, M.**; Haddad, A.; Mashuta, M. S.; Zamborini, F. P. “Metal-Stabilized Thiyl Radicals as Scaffolds for Ethylene Sensing, Alkene Activation, and Proton Reduction”, **Inorganic Reaction Mechanisms - Gordon Research Conference, Galveston, TX, USA, March 3-8, 2013.** Poster.
- **Moreno, M.**; Zamborini, F. P. “Alkanethiolate- and Alkylamine-Stabilized Pd and PdAg Nanoparticles for Product-Selective Catalysis of Allyl Alcohol in Solution”, **Eighth Kentucky Innovation and Entrepreneurship Conference, Louisville, KY, USA, June 1, 2012.** Poster.
- **Moreno, M.**; Zamborini, F. P. “Selective Isomerization of Allyl Alcohols to Carbonyl Compounds by Pd and PdAg Nanoparticles”, **University of Louisville 4th Annual Graduate Research Symposium, Louisville, KY, USA, March 23, 2012.** Oral Presentation.
- Zamborini, F. P.; **Moreno, M.**; Kissell, L. N. “Hydrogenation and Isomerization Reactions of α,β -Unsaturated Alcohols by Pd and PdAg Monolayer Protected Clusters in Solution”, **Pittcon, Orlando, FL, USA, March 11-15, 2012.** Poster.

- Ibañez, F. J.; **Moreno, M.**; Fernando, K.; Dalfovo, M. C.; Zamborini, F. P.; Sumanasekera, G. U.; Salvarezza, R. C. “Graphene Used as a Chemiresistive Sensing Film”, **Pittcon**, *Orlando, FL, USA, March 11-15, 2012*. Oral Presentation.
- **Moreno, M.**; Ouch, K.; Grapperhaus, C. A.; Zamborini, F. P. “Electrochemically-Controlled Ethylene Binding Affinity of Surface-Immobilized Re-Thiolate Complexes”, **Electrochemistry Gordon Research Conference**, *Ventura, CA, USA, January 8-13, 2012*. Poster.
- **Moreno, M.**; Ouch, K.; Grapperhaus, C. A.; Zamborini, F. P. “Electrochemically-Controlled Ethylene Binding Affinity of Surface-Immobilized Re-Thiolate Complexes”, **Electrochemistry Gordon Research Seminar**, *Ventura, CA, USA, January 7-8, 2012*. Oral Presentation.
- **Moreno, M.**; Kissell, L. N.; Zamborini, F. P. “Hydrogenation and Isomerization of Allyl Alcohol in the Presence of Pd and PdAg Monolayer Protected Clusters”, **42nd Central Regional Meeting of the American Chemical Society**, *Indianapolis, IN, USA, June 8-10, 2011*. Oral Presentation.
- **Moreno, M.**; Kissell, L. N.; Zamborini, F. P. “Characterization and Catalytic Properties of Pd and PdAg Monolayer Protected Clusters”, **Seventh Kentucky Innovation and Entrepreneurship Conference and 16th Kentucky EPSCoR Joint Conference**, *Louisville, KY, USA, May 26, 2011*. Poster.
- Kissell, L. N.; **Moreno, M.**; Zamborini, F. P. “Characterization and Comparison of Hydrogen Reactivity and Catalytic Activity of Pd and PdAg Monolayer Protected Clusters”, **University of Louisville – Undergraduate Research Symposium 2011**, *Louisville, KY, USA, April 19, 2011*. Poster.
- Kissell, L. N.; **Moreno, M.**; Zamborini, F. P. “Characterization and Comparison of Hydrogen Reactivity and Catalytic Activity of Pd and PdAg Monolayer Protected Clusters”, **University of Kentucky – Regional Poster Competition – Undergraduate Research in Chemistry 2011**, *Lexington, KY, USA, April 15, 2011*. Poster.
- **Moreno, M.**; Kissell, L. N.; Zamborini, F. P. “Characterization and Catalytic Properties of Pd and PdAg Monolayer Protected Clusters”, **University of Louisville 3rd Graduate Research Symposium**, *Louisville, KY, USA, April 1, 2011*. Poster.

- **Moreno, M.;** Zamborini, F. P. “A Study of the Reactivity and Stability in the Presence of H₂ of Pd Nanoparticles Coated with Mixed Monolayers of Octylamines and Hexanethiolates”, **Central Regional Meeting of the American Chemical Society**, *Dayton, OH, USA, June 16-19, 2010*. Poster.
- **Moreno, M.;** Zamborini, F. P. “A Study of the Reactivity and Stability in the Presence of H₂ of Pd Nanoparticles Coated with Mixed Monolayers of Octylamines and Hexanethiolates”, **Electrochemistry Mini Symposium Sponsored by the Cleveland Section of the Electrochemistry Society and the Yeager Center for Electrochemical Sciences**, Case Western Reserve University, *Cleveland, OH, USA, May 27, 2010*. Poster.
- **Moreno, M.;** Zamborini, F. P. “Reactivity and Stability of Pd Nanoparticles Coated with Mixed Monolayers of Octylamines and Hexanethiolates for Sensing and Catalysis Applications”, **Sixth Kentucky Innovation and Entrepreneurship Conference**, *Lexington, KY, USA, April 6, 2010*. Poster.
- **Moreno, M.;** Zamborini, F. P. “A study of the Reactivity and Stability in the Presence of H₂ of Pd Nanoparticles Coated with Mixed Monolayers of Octylamines and Hexanethiolates”, **University of Louisville 2nd Graduate Research Symposium**, *Louisville, KY, USA, March 5, 2010*. Poster.
- **Moreno, M.;** Zamborini, F. P. “A Study of the Reactivity and Stability in the Presence of H₂ of Pd Nanoparticles Coated with Mixed Monolayers of Octylamines and Hexanethiolates”, **Pittcon**, *Orlando, FL, USA, February 28-March 5, 2010*. Oral Presentation.
- **Moreno, M.;** Zamborini, F. P. “H₂ Reactivity of Pd Nanoparticles Coated with Mixed Monolayers of Alkyl Thiols and Alkyl Amines for Sensing and Catalysis Applications”, **Central Regional Meeting of the American Chemical Society**, *Cleveland, OH, USA, May 20-23, 2009*. Oral Presentation.
- **Moreno, M.;** Zamborini, F. P. “H₂ Reactivity of Pd Nanoparticles Coated with Mixed Monolayers of Alkyl Thiols and Alkyl Amines for Sensing and Catalysis Applications”, **Fifth Kentucky Innovation and Entrepreneurship Conference**, *Louisville, KY, USA, April 7, 2009*. Poster.

- **Moreno, M.;** Zamborini, F. P. “H₂ Reactivity of Pd Nanoparticles Coated with Mixed Monolayers of Alkyl Thiols and Alkyl Amines for Sensing and Catalysis Applications”, **Pittcon, Chicago, IL, USA, March 7-13, 2009.** Poster.
- **Moreno, M.;** Zamborini, F. P. “Reactivity of Pd Nanoparticles Coated with Mixed Monolayers of Alkyl Thiols and Alkyl Amines for Sensing and Catalysis Applications”, **University of Louisville 1st Graduate Research Symposium, Louisville, KY, USA, March 6, 2009.** Poster.

PROFESSIONAL EXPERIENCE:

- **Part-time Lecturer** **2010 – 2011**
Seasonal Employment. Quality Leadership University, Republic of Panama
 Taught General Chemistry I (Chem 201) and Introduction to Chemical Analysis I (Chem 207). Responsible for planning, designing, developing, and using effective teaching materials as well as methods to assist students in meeting their goals. Handled the tasks of conducting regular lectures and chemical experiments in the classroom as well in laboratories. Graded exams and examined lab notebooks for proper scientific format.
- **Graduate Teaching Assistant** **2007 – 2013**
Full time. University of Louisville, Louisville, KY
 Taught General Chemistry (Chem 201) and provided out-of-class help to students having difficulties with course content. Proctored and graded for Introductory and General Chemistry I and II (Chem 101 and 201/202). Lectured, supervised, and graded pre-labs and lab reports for Introduction to Chemical Analysis I, II, III, and IV (Chem 207, 208, 209, and 210).
- **Professor** **2006**
Full time. Universidad del Cauca, Popayán, Colombia
 Taught Introductory, General, and Analytical Chemistry. Responsible for designing syllabus content and teaching the courses through effective lesson planning.

Maintained appropriate tools and equipment for practical work assignments of students. Gathered information and prepared best study materials for the students. Created student interest by organizing seminars, conferences, and special events. Handled the tasks of evaluating student performance constructively and provided timely feedback. Assisted with registration process and performed other tasks under the instruction of the Dean and Chairman of the Department of Chemistry.

▪ **Laboratory Analyst**

2003 – 2006

Full time. Department of Industrial Analysis, Universidad del Cauca, Popayan, Colombia

Responsible for the physicochemical analysis of food and water samples. Extensive experience in preparing the laboratory and maintaining stock of required chemicals and equipment necessary to perform the experiments successfully. Responsible for maintaining the laboratory, chemicals, and equipment effectively and in ready-to-use manner. Ensured that all of the experiments and functions performed within the laboratory adhered to the prescribed safety standards, methods, and protocols. Handled the task of maintaining efficient data management for the laboratory experiments.

AWARDS:

- Excellence in Safety in the Teaching Laboratory, University of Louisville, 2008 – 2009.
- Travel award from the Graduate Student Council (GSC), University of Louisville, for Pittcon 2009 and 2010, and Central Regional Meeting of the American Chemical Society 2009 and 2011.

LANGUAGES:

- English (fluent), Spanish (native).

INSTRUMENTATION:

- Electrochemistry: Cyclic Voltammetry, Anodic Stripping Voltammetry, Differential Pulse Voltammetry, and Chronoamperometry.
- Microscopic Techniques: Atomic Force Microscopy (AFM), Transmission Electron Microscopy (TEM), and Scanning Electron Microscopy (SEM).
- Spectroscopic Techniques: UV-vis Spectroscopy, Atomic Absorption Spectroscopy (AAS), Fourier Transform Infrared (FTIR) Spectroscopy, X-ray Photoelectron Spectroscopy (XPS), ^{13}C and ^1H Nuclear Magnetic Resonance (NMR) Spectroscopy.
- Separation Techniques: Gas Chromatography, Gas Chromatography-Mass Spectrometry (GC-MS), and Liquid Chromatography (HPLC).
- Other Techniques: Energy Dispersive X-ray (EDX) Analysis and Thermogravimetric Analysis (TGA).

MEMBERSHIP IN PROFESSIONAL ORGANIZATIONS:

- American Chemical Society (ACS), Student Member since April 2009.
- Society for Electroanalytical Chemistry (SEAC), Student Member since March 2012.

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