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# REGIO AND CHEMO SELECTIVE HYDROGENATION BY PALLADIUM NANOPARTICLES EMBEDDED IN POLYELECTROLYTE FILMS

By

Somnath Bhattacharjee

## A DISSERTATION

Submitted to Michigan State University in partial fulfillment of the requirements for the degree of

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#### ABSTRACT

# REGIO AND CHEMO SELECTIVE HYDROGENATION BY PALLADIUM NANOPARTICLES EMBEDDED IN THE POLYELECTROLYTE FILMS

By

#### Somnath Bhattacharjee

Transition-metal nanoparticles (NPs) are attractive catalytic materials because they possess a high surface area to volume ratio and electronic properties that are a function of particle size. Without a suitable support, however, aggregation of NPs tends to reduce their surface area and alter their electronic properties. This research examines the catalytic properties of NPs embedded in multilayer polyelectrolyte films. The polyelectrolyte matrix restricts NP aggregation, and layer-by-layer assembly on alumina supports yields a heterogeneous catalyst that can be easily recycled. Encapsulated NPs exhibit remarkable catalytic selectivities that are a strong function of NP diameter.

Pd NPs embedded in multilayer polyelectrolyte films can be easily prepared through layer-by-layer adsorption of poly(acrylic acid) (PAA) and poly(ethylenimine)- $Pd^{2+}$  (PEI-Pd(II)) complexes followed by chemical reduction of Pd(II) with NaBH<sub>4</sub>. Transmission electron microscopy confirms the formation of Pd particles with diameters of 1-3 nm. Remarkably, [PAA/PEI-Pd(0)]<sub>3</sub>PAA films catalyze the hydrogenation of monosubstituted alkenes with turnover frequencies (TOFs) that are as much as 100-fold higher than TOFs for hydrogenation of multiply substituted double bonds. These selectivities are higher than those of Wilkinson's catalyst. Regioselective hydrogenation of monosubstituted C=C bonds occurs when substrate molecules contain both mono and multiply substituted C=C bonds. The combination of the encapsulating polyelectrolyte film and small NPs likely hinders access of multiply substituted double bonds to catalytic sites.

NP-containing films can also be prepared through deposition of PAA-Pd(II)/PEI films and subsequent reduction of Pd(II). The use of different ratios of PAA to Pd(II) in deposition solutions gives a series of films with Pd NPs whose average diameters range from 2.2 to 3.4 nm, and the catalytic selectivities of these NPs vary dramatically with their size. TOFs for the hydrogenation of monosubstituted unsaturated alcohols increase with decreasing average NP size, whereas multisubstituted unsaturated alcohols show the opposite trend. Hence, the ratio of TOFs for the hydrogenation of allyl alcohol and crotyl alcohol is 39 with average particle diameters of 2.2 nm and only 1.3 with average particle diameters of 3.4 nm. Ratios of TOFs for hydrogenation of allyl alcohol and  $\beta$ -methallyl alcohol are as high as 240. Increasing selectivity with decreasing average particle size occurs with both films deposited on alumina powder and NPs stabilized by polyelectrolytes in solution. Presumably, the highest selectivities occur on the smallest NPs because hydrogenations of monosubstituted and multisubstituted double bonds take place on different types of atoms

[PAA-Pd(0)/PEI]<sub>3</sub> films also catalyze chemoselective hydrogenation of aromatic nitro compounds that contain other readily reducible functional groups. The resulting amines may serve as intermediates in the synthesis of a wide range of important organic compounds. In the reduction of 4-nitrobenzaldehyde to 4-aminobenzaldehyde, [PAA-Pd(0)/PEI]<sub>3</sub> films are more selective than either Pd/C or Pd/alumina. Chemoselective hydrogenation of aromatic nitroamides, nitroesters, nitroaldehydes, and nitronitriles is also possible with these catalysts. TO MY FAMILY

,

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## LIST OF ACRONYMS

LBL: Layer-by-layer

**PEI:** Poly(ethylenimine)

**PAA:** Poly(acrylic acid)

TEM: Transmission Electron Microscopy

**AES:** Atomic Emission Spectroscopy.

**NP:** Nanoparticles

**DMF:** Dimethylformamide

MSI: Metal-Support Interaction.

**TOF:** Turnover Frequencies

**PMHS:** Polymethylhydrosiloxane

EtOAc: Ethyl Acetate

EtOH: Ethanol

THF: Tetrahydrofuran

#### **CHAPTER 1**

### **BACK GROUND INFORMATION**

#### **1.1. Introduction**

During the last 15 years, the formation, characterization, and application of nanoparticles (NPs) have become one of the most prominent areas of chemical research. The yearly number of publications in this field has grown exponentially as shown in Figure 1.1. Much of the interest in NPs stems from the fact that they often manifest properties that are different from the properties of the bulk material of the same



**Figure 1.1.** Number of publications found in a search for the key word "nanoparticles" using SciFinder Scholar (Chemical Abstracts search tool). "Images in this dissertation are presented in color"

composition,<sup>1,2</sup> and classical laws of physics are sometimes not applicable to small NPs. By definition, NPs have diameters that range from 1 to 100 nm, so they contain between about 10 and 10<sup>6</sup> atoms or molecules per particle.<sup>3,4</sup> Because of their unique properties, NPs are being intensively studied for various applications in sensing,<sup>5-13</sup> optoelectronics,<sup>14-18</sup> tissue engineering,<sup>19-23</sup> biotechnology,<sup>24-29</sup> and catalysis.<sup>30-49</sup>

Because of their high surface area to volume ratio, perhaps the most natural application area for NPs is catalysis. Berzelius introduced the term catalysis in 1836 to classify certain types of chemical reactions whose progress is greatly affected by additional substances even though they are neither reactants nor products.<sup>50</sup> Since then, a molecular understanding of catalytic processes has been emerging, and catalytic reactions constitute about 90% of chemical processes.<sup>51</sup> Solid-state materials, including transition metals, are frequently the materials of choice for catalysis because they can be readily separated from a reaction mixture and frequently reused. One disadvantage of heterogeneous catalysts, however, is that typically only surface atoms serve as active sites for catalytic processes. The percentage of atoms that reside at the surface of a material increases with decreasing particle size, so small metal particles are highly reactive catalysts for many reactions. However, optimal use of metal atoms for catalysis requires extremely small particles. Even in a 20 nm-diameter particle, only 10% of the atoms reside at the particle surface. In contrast, in a 3 nm-diameter particle, 50% of the atoms are on the surface. The large surface areas of nanostructured metals allow efficient use of metal atoms in various catalytic reactions.

During the twentieth century, chemists made tremendous achievements in heterogeneous catalysis, which is responsible for the vast majority of chemical

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production.<sup>52-59</sup> Nevertheless, heterogeneous catalysts sometimes show relatively low selectivity, and it is often difficult to elucidate catalytic mechanisms. On the other hand, homogeneous catalysts, which have been primarily developed since the early 1970s,<sup>60-63</sup> can sometimes be tailored to selectively catalyze specific reactions. Still, homogeneous catalysts are not often used on a large scale because they cannot be easily recovered. Transition-metal NPs<sup>64,65</sup> might bridge the gap between homogeneous and heterogeneous catalysis because they can be either suspended in solution as homogeneous catalysts or fixed onto a support. Although by definition the diameters of NPs vary between one nm and 100 nm, the most active NPs in catalysis because there is a full continuum between small metal clusters and larger NPs. Moreover, NP catalysts are frequently selective, efficient, and recyclable, and thus they meet the modern requirements for green catalysts. Already, numerous applications of transition-metal NP catalysts are emerging.<sup>69-97</sup>

As discussed above, the high surface area of NPs is attractive for catalysis. However, the high fraction of active surface atoms also gives rise to a high surface energy that often causes metal NPs to aggregate. This aggregation yields larger, stable particles with less surface area and less catalytic activity and provides a serious challenge in catalysis where control over NP size is often vital for improving the reactivity and selectivity of a catalyst. Fortunately, several methods have been developed to stabilize metal NPs and prevent aggregation. Perhaps the most common of these is to cap the particles with ligands that reduce surface energy or provide repulsive interactions between particles.<sup>98-101</sup> However, the capping ligands may isolate the particle surface and decrease catalytic activity. Other methods of NP stabilization that may be appropriate for catalysis include immobilization on solid supports and in polymer films.<sup>102,103</sup>

This dissertation focuses on the layer-by-layer (LBL) assembly of polyanions and polycations to incorporate stable Pd NPs in a polyelectrolyte matrix. These NPs show remarkable regio and chemoselective hydrogenation, and selectivities vary dramatically with NP diameter. In this introduction I attempt to place my work in context by providing background on previous studies of NP catalysis and layer-by-layer deposition. Section 1.2 discusses the historical background of transition-metal NPs and their preliminary development for catalytic applications. Section 1.3 describes more recent work including stabilization of NPs using ligands, surfactants, dendrimers/polymers, and solid supports. Finally, the last section of this chapter (section 1.4) introduces the general procedure of layer-by-layer assembly, which can be implied to prepare stable and catalytically active homogeneous and heterogeneous metal NPs for catalytic applications.

### **1.2. Early Development of Catalytically Active Transition-Metal NPs**

In the mid-nineteenth century, Michael Faraday was the first to record the synthesis of NPs.<sup>82,104</sup> Faraday noted the formation of deep red solutions upon the reduction of aqueous NaAuCl<sub>4</sub> by phosphorous in CS<sub>2</sub>. Faraday believed that the particles formed via his method had diameters smaller than wavelength of visible light. Unfortunately, at the time there were no tools for determining the actual size of the gold particles. In the 1980s J. M. Thomas reproduced the formation of gold particles according to Faraday's method and generated NPs with diameters ranging from 3-30 nm.<sup>105</sup> However, these gold NPs were not used for catalytic applications.

The use of transition-metal NPs as catalysts started in the second half of the twentieth century. Initial studies included a small but important group of reactions including hydrogenation, hydrosilylation and hydration of unsaturated organic substrates. In the 1940s, Nord reported pioneering catalytic applications of NPs in the reduction of nitrobenze.<sup>106-108</sup> In 1970, Parravano used Au NP catalysts for hydrogen-atom transfer between benzene and cyclohexane, as well as oxygen-atom transfer between CO and CO<sub>2</sub>.<sup>109</sup> However, the real breakthrough in NP catalysis came in the 1980s when Haruta observed that oxide-supported Au NPs catalyze CO oxidation by O<sub>2</sub> at low temperatures and that the small size of gold is crucial for the transformation.<sup>110-113</sup> In the 1970s and 1980s, NP catalysts were also used in the fields of redox catalysis, photocatalysis including photo-water splitting and photo-hydrogenation of  $CO_2$  to methane, and hydrogenation and oxidation of unsaturated compounds.<sup>114-122</sup> In the 1990s, Reetz reported seminal studies of Pd NPs as catalysts for Heck coupling reactions between butyl acrylate and iodobenzene or aryl bromides and styrene.<sup>123-130</sup> Moreover, Figure 1.2 illustrates that in the first few years of the twenty-first century, there has been enormous growth in the number of publications concerning the application of metal NPs for catalysis. The fundamental goals of recent research on NP catalysts include preparation of stable NPs; improvement of catalyst activities and selectivities; and understanding the catalytic mechanisms which cause high activity and selectivity. The next section discusses studies in these specific areas.



Figure 1.2. Number of publications found for the key phrase "Nanoparticles for catalysis" in a SciFinder Scholar (American Chemical Society Search tool) search.

#### 1.3. Recent Developments in the Preparation of Stable, Catalytic Metal NPs

As mentioned in section 1.1, the preparation of catalytically active, stable metal NPs is challenging due to their tendency to aggregate. To prevent aggregation, metal NPs are immobilized on various solid supports such as carbon and metal oxides, or stabilized by surfactants, ligands, or polymers. Immobilization on a support physically prevents NP aggregation, whereas ligands, polymers, and surfactants typically surround particles to lower surface energy or provide repulsive forces between particles. NPs stabilized by surfactants, ligands, and small polymers can serve as homogeneous catalysts, whereas NPs on solid supports act as heterogeneous catalysts that can be readily recovered. The following subsections focus on the different techniques for preparing stable metal NPs and the catalytic applications of these particles.

#### 1.3.1. Immobilization of Metal NPs on Solid Supports

#### Carbon Supports

Charcoal is a common solid support for catalysts, and Pd on activated C (Pd/C) is an archetypical catalyst. Activated carbon is produced by treatment of charcoal with acid and elution to remove ash and other contaminants, and to prepare a highly porous material. Purified activated carbon often provides optimal interactions with the precious metal catalysts and ensures dispersibility in the reaction media. A recent report suggests that Pd NPs on single wall carbon nanotubes are more active than commercially available Pd on activated carbon for the Heck reaction of styrene and iodobenzene (Scheme 1.1). However, Pd on activated C is the more active catalyst in the case of oxidation of cinnamyl alcohol to cinnamaldehyde by molecular oxygen and the hydrogenation of cinnamaldehyde to 3-phenylpropionaldehyde (Schemes 1.2 and 1.3).<sup>131</sup> The average diameter of Pd NPs on single-wall carbon nanotubes is 5 nm, whereas the average diameter of Pd on activated carbon (1 wt %) is 14.5 nm. A number of studies show the high activity of metal NPs on carbon in a wide range of reactions.<sup>132-135</sup> Another report shows that catalytic activities of cobalt NPs on graphite, mesoporous carbon, and charcoal are almost same for the Pauson-Khand reaction. This suggests that in this case, the catalytic activity depends on the NPs and not on the nature of support <sup>136</sup>



Scheme 1.1. Heck reaction of styrene and iodobenzene catalyzed by Pd/C and Pd NPs on single-wall carbon nanotubes.



Scheme 1.2. Oxidation of cinnamyl alcohol by Pd/C and Pd NPs on single-wall carbon nanotubes.



Scheme 1.3. Hydrogenation of cinnamaldehyde by Pd/C and Pd NPs on single-wall carbon nanotubes.

#### Metal Oxide Supports

A large number of recent publications focus on catalysis with NPs supported on oxides of Si, <sup>137-152</sup> Al, <sup>69,150,153-155</sup> Ti, <sup>156-158</sup> Zr, <sup>159-168</sup> Ca, <sup>76</sup> Mg, <sup>69,155,169-173</sup> and Zn.<sup>174</sup> These supports are attractive because they are stable at high temperatures and easy to remove from the reaction medium. The performances of these supported catalysts were examined for various reactions such as hydrogenation of unsaturated substrates, <sup>175</sup> Heck, <sup>124-127,129,130,176-179</sup> Suzuki, <sup>93,126,137,140,161,177,180,181</sup> Sonogashira, <sup>165,166,182</sup> Stille, <sup>183</sup> Negishi, <sup>184</sup> and Kumada<sup>185,186</sup> coupling reactions, oxidation of CO using molecular oxygen, <sup>77,82,187-194</sup> Mannich reactions, <sup>74</sup> and Pauson–Khand reactions (Scheme 1.4). <sup>141,195</sup>



Scheme 1.4. Pauson-Khand reactions catalyzed by Co and Pd NPs supported on silica for a one-pot syntheses of bicyclicenones.

Catalyst particles are anchored to oxide supports through a metal-support interaction (MSI), which prevents NP aggregation and can potentially influence the activity of the catalyst.<sup>196,197</sup> Studies indicate that the strength of the MSI depends on both the support and the metal. For example, the extent of aggregation of supported silver NPs in a vacuum decreases in the order SiO<sub>2</sub>>Al<sub>2</sub>O<sub>3</sub>>C, while for Pt nanoparticles, the extent of interaction decreases in the order Al<sub>2</sub>O<sub>3</sub>> SiO<sub>2</sub>>C.<sup>198</sup> In particular, alumina powders have surface areas that range from 0.1 to 400 m<sup>2</sup>/g, pore volumes between 0.1 and 1.5 cm<sup>3</sup>/g, and average pore sizes between 2 nm and 170  $\mu$ m.<sup>199</sup> The large surface area seem to help keep prevent NP aggregation and increase NP loading.<sup>200,201</sup> Thus, aluminum oxide powder is perhaps the most attractive support material for NP catalysis. Additionally, alumina membranes can be used as a support to catalytic NPs.<sup>202,203</sup>

#### **1.3.2. Solution-based Metal NP Stabilizers**

#### **Surfactants**

Surfactants are common stabilizers of metal-NP suspensions. These molecules interact with small NPs to reduce their surface energy. A recent report indicates that suspensions of Pd NPs stabilized by N,N-dimethyl-N-cetyl-N-(2-hydroxyethyl) ammonium chloride successfully catalyze hydrogenation and dehalogenation of various halogenoarenes.<sup>204</sup> Cetyltrimethylammonium bromide also stabilizes Cu NPs on several metal oxides, and these supported Cu NPs were employed for the selective dehydrogenation of methanol to produce formaldehyde.<sup>205</sup> Metal oxide supports help to recover the catalyst at the end of the reaction.

#### Ligands

The use of ligands as NP stabilizers is especially interesting because variation of the ligand composition allows some optimization of the NP reactivity for use in specific catalytic reactions. Treatment of molecular Pd complexes with CO in DMF or toluene at room temperature produces Pd NPs that catalyze nucleophilic substitution/carbonylation/amination to afford isoindolinones at room temperature as shown in the scheme 1.5.<sup>206</sup> Pd NPs capped with special ligands such as cyclodextrins



Scheme 1.5. 3-component cascade process by palladium NPs generated in situ to form isoindolinone.

are active for the catalysis of the hydrogenation of unsaturated substrates and of the Suzuki, Heck, and Stille coupling reactions.<sup>94-96</sup> Dodecanethiolate-capped Pd NPs catalyze the Suzuki-Miyaura reaction of aryl halides, including, with phenylboronic acid at ambient temperature.<sup>93</sup> Another simple method of stabilization involves addition of



DMA = Dimethylacetamide

Scheme1.6. Regioselective silvlation of sugars through Pd NP-catalyzed silane alcoholysis.

silanes (R<sub>3</sub>SiH), such as *tert*-butyldimethylsilane, to PdCl<sub>2</sub> in N, N-dimethylacetamide. The black NP solution formed in this way catalyzes silane alcoholysis of sugars<sup>207</sup> (Scheme 1.6), and selective cross-coupling of the silane with phenyl and vinyl thioethers gives the corresponding thiosilanes and silthianes.<sup>208</sup>

#### Polymers

Polymers are particularly attractive stabilizers because they weakly bind metal nanoparticles via heteroatoms in the interior of the polymer and build a protective "shell" of polymer chains. In addition to stabilization, the steric bulk of the polymer framework may restrict access to metal NPs to impart selectivity. The polymer can be a soluble linear or branched macromolecule that "wraps" around the metal NP in solution to prevent metal aggregation and precipitation.

The most commonly encountered polymer stabilizers are commercially available poly(N-vinyl-2-pyrrolidone) (PVP),<sup>209-212</sup> polyurea,<sup>213</sup> polyacrylonitrile,<sup>214</sup> poly(acrylic acid),<sup>214</sup> polysiloxane,<sup>215</sup> oligosaccharides,<sup>145</sup> poly(4-vinylpyridine),<sup>216</sup> poly(N,N-dialkylcarbodiimide),<sup>217</sup> polyethylene glycol,<sup>218</sup> chitosan,<sup>219</sup> and a hyperbranched aromatic polyamide.<sup>220</sup> Metal NPs protected in these polymers are used as soluble catalysts, and they can also be immobilized in ionic liquids for various kinds of reactions. Hirai's pioneering work in the 1970s and 1980s is especially impressive. He generated Rh NPs using aqueous methanol or NaOH in methanol as a reducing agent for RhCl<sub>3</sub>·3H<sub>2</sub>O to produce polyvinyl alcohol (PVA)-stabilized Rh NPs.<sup>221,222</sup> Toshima pursued research on metal-NP catalysts in the early 1990s with polymer-stabilized bimetallic NPs generated by direct co-reduction of salts of two different metals (Pt and

Au for example), by sequential reduction (the initial NPs serve as seeds for the surface condensation of the second metal), or by galvanometric reduction of a metal salt by NPs of another more easily reduced metal.<sup>209,223,224</sup> In the late 1990s, Andres et al. synthesized PVP-stabilized Pt, Pd and Rh NPs by ethanolic reduction of the corresponding metal halide. These NPs were immobilized in an ionic liquid, 1-n-butyl-3-methylimidazolium hexafluorophosphate ([BMI][PF<sub>6</sub>]), and found to be very efficient catalysts for benzene hydrogenation at 40 °C.<sup>210</sup> The polymer-stabilized metal NPs could also be recycled without loss of activity. Additionally, Pd and bimetallic (PdAu, PdPt) NPs were stabilized in polystyrene-block-poly-4-vinylpyridine (PS-b-P4VP) micelles and studied in the selective hydrogenation of dehydrolinalool as shown in the scheme 1.7.<sup>225,226</sup> Cyclohexene hydrogenation was catalyzed with Pd NPs stabilized by highly branched amphiphilic polyglycerol.<sup>227</sup>



**Scheme 1.7.** Selective hydrogenation of Dehydrolinalool to linalool by PS-b-P4VP-Pd on alumina.

#### **Dendrimers**

Dendrimers are a unique class of polymeric materials that often find application as templates to stabilize metal NPs. The formation of NPs stabilized by dendrimers was reported in 1998 by the research groups of Crooks,<sup>228,229</sup> Tomalia<sup>230,231</sup> and Esumi.<sup>232-234</sup> Crooks pioneered the use of dendrimer-encapsulated metal NPs for catalysis. In his approach, metal cations such as  $Pd^{2+}$ ,  $Pt^{2+}$ , or  $Au^{3+}$  that are complexed with the nitrogen atoms of interior tertiary amines are reduced to NPs upon treatment with NaBH<sub>4</sub> as



Figure 1.3. Encapsulation of metal nanoparticles in a dendrimer matrix.<sup>235</sup>

illustrated in figure 1.3.<sup>228,235-240</sup> The procedure used by Crooks and Tomalia encapsulated metal NPs inside the dendrimers, whereas Esumi's process incorporated NPs at the dendrimer periphery. Dendrimer-encapsulated metal NPs are attractive for catalysis for several reasons. First, the dendrimer templates are fairly uniform structures, and they yield well-defined NPs.<sup>229,241,242</sup> Second, NPs are stabilized by encapsulation within the dendrimer through weak interactions with amines so they retain their reactivity but do not agglomerate.<sup>243,244</sup> Third, the dendrimer branches can be used as selective gates to limit the access of large substrates to the encapsulated nanoparticles.<sup>241,245</sup> Finally, the terminal groups on the dendrimer periphery can be tailored to control the solubility of the hybrid nanocomposite.<sup>246,249</sup>

#### 1.4. Layer-by-Layer Assembly of Oppositely Charged Polyelectrolytes

The previous sections described a number of ways to stabilize NPs, including Because this research specifically employs NPs in stabilization with polymers. multilayer polyelectrolyte films, this section discusses the layer-by-layer assembly of such films. In 1966, Iler reported the formation of layers of charged particles by In the early 1990's<sup>251,252</sup> Decher and coworkers adsorption from solutions.<sup>250</sup> rediscovered surface modification through layer-by-layer deposition, and greatly expanded the technique by using sequential assembly of oppositely charged polymers. This pioneering work spawned thousands of subsequent studies because of the simplicity and versatility of the approach. The stepwise growth of multilayer polyelectrolyte films (Figure 1.4) is an entropy driven process due to the release of salt counter ions that were originally neutralizing the polyelectrolytes in solution.<sup>253,254</sup> The stability of each polyanion/polycation "bilayer" is presumably maintained through the formation of multiple ion pairs between oppositely charged polyelectrolytes.<sup>255</sup> (Other interactions such as hydrogen bonding can also be employed for layer-by-layer deposition,<sup>256</sup> but this work focuses solely on electrostatic interactions.) The procedure for layer-by-layer deposition of polyelectrolyte films is very simple and begins with immersion of a charged substrate in a solution containing an oppositely charged polyelectrolyte. The polymer adsorbs on the surface, presumable due to a gain in entropy through the release of many counter ions, as mentioned above. The presence of the single-layer coating on the surface reverses the sign of the substrate charge. After rinsing to remove loosely attached polyelectrolyte, immersion of the substrate into a solution containing a polyelectrolyte of opposite charge gives a bilayer consisting of two oppositely charged polyelectrolytes, as
depicted schematically in the Figure 1.4.<sup>257</sup> Additional bilayers are added similarly (Figure 1.4).



Figure 1.4. Formation of bilayer on the substrate through layer-by-layer deposition of polyelectrolytes.<sup>257</sup>

Multilayer polyelectrolyte films should consist of stratified structures because they are formed via sequential adsorption of polycations and polyanions. However, layers are highly intertwined in most cases due to the loops and tails in polyions and interactions between polyelectrolytes in several different layers.<sup>257-259</sup> These tails and loops are partially responsible for the charge overcompensation at the film surface.<sup>260</sup> Additionally, the entanglement of neighboring layers also aids charge compensation within the multilayer films. Several studies did not detect any counter ions in the bulk of polyelectrolyte films, which suggested the complete compensation of opposite charge in the films.<sup>260,261</sup> However, more recent studies show that charge compensation depends on the compositions of the film as well as deposition and post-deposition treatments.<sup>262</sup>

The layer-by-layer deposition method has several attractive features. 1. It is an easy and convenient method that usually involves a simple dip and rinse procedure. 2. Film thickness can be controlled at the nm scale by varying the number of layers <sup>257,263</sup> and the ionic strength or the pH of the deposition solutions.<sup>263-266</sup> The pH controls the charge density of weak polyelectrolytes by changing the degree of protonation or deprotonation, and polyelectrolytes with high charge densities typically give thin films with polymer chains are highly extended. A high concentration of salt in the deposition solution usually increases the film thickness because it shields neighboring charges on the polyelectrolytes and allows the formation of loops and tails. 3. Films can form on any surface that will adsorb polyelectrolytes. This requirement is easily met because most common solid substrates are charged. Adsorption is also relatively independent of substrate geometry and can occurs on materials ranging from small particles<sup>267</sup> to test tubes<sup>268</sup> to spongy membranes<sup>203</sup>. **4.** Many different polyelectrolytes are available for deposition. This technique initially started primarily with polyamines and polysulfonates, but subsequent reports deomonstrated layer-by-layer deposition of electro-active polymers,<sup>269,270</sup> quantum dots,<sup>271-273</sup> DNA,<sup>274-276</sup> charged viruses,<sup>277,278</sup> inorganic sheets,  $^{269,279,280}$  proteins,  $^{281-284}$  and enzymes.  $^{285,286}$ . 5. Film formation is relatively environmentally friendly in that it typically uses water as the solvent. Due to the advantages of layer-by-layer assembly, these films are being examined for applications in areas such as sensors, electronics, tissue engineering, and biotechnology.

#### **1.5. Motivation and Research Goal**

Section 1.3 of this chapter indicates that a plethora of methods were developed to obtain stable metal NPs for use in catalysis. However, systematic studies of selective catalysis with a series of well-controlled, highly reactive NPs are lacking. There are two important challenges to prepare homogeneous/heterogeneous NPs for use as efficient catalysts. Firstly, to obtain maximum catalytic efficiency, the NPs must be stabilized to eliminate aggregation without blocking most of the active sites on the NP surfaces. Secondly, the stabilizer should afford control over NP size and reactivity to manipulate catalytic activity. We envisioned that the incorporation of metal NPs in thin polyelectrolyte multilayers prepared by layer-by-layer deposition could address these challenges quite effectively. To form NPs in these films, we first adsorb polyelectrolyte complexes of transition-metal ions and subsequently reduce these ions to form metal NPs. Variation of the concentration of metal ions in the film affords control over the NP size, and the polyelectrolyte film may also serve as a filter to enhance selectivity. Previous work in our group demonstrated the preparation of Pd NPs incorporated in poly(acrylic acid)(PAA)/polyethylenimine (PEI) films on alumina ([PAA/PEI-Pd(0)]<sub>3</sub>) and their catalytic activity (Figure 1.5). Those studies demonstrated moderate catalytic selectivity with allylic alcohols that had different substituents at the position  $\alpha$  to the double bond as shown in the figure 1.5. However, that research did not investigate the effect of NP size on selectivity or investigate a very wide range of hydrogenation reactions.



Figure 1.5. Intermolecularly selective hydrogenation of allyl alcohols by [PAA/PEI-Pd(0)]<sub>3</sub>PAA on alumina.

This research examines selective, NP-catalyzed hydrogenation of a much broader series of compounds including allylic alcohols with various substituents on the double bond, molecules with more than one double bond, and nitroaromatic compounds. The NP catalysts show selectivities >100 for hydrogenation of mono over disubstituted double bonds, and these selectivities vary dramatically with NP size. These studies are predicated on careful formation and characterization of films with controlled NP size. Both intramolecular and intermolecular selectivities can be achieved. Additionally, the NP films are chemoselective in the hydrogenation of nitroaromatic compounds. These studies certainly demonstrate the unique properties of NP catalysts in selective reactions.

#### 1.6. Outline of the Thesis

In this introduction, I have attempted to provide background on NP stabilization and catalysis with NPs to show how my work fits in the broader context of this field. Chapter 2 expands on our previous work with Pd NPs polyelectrolyte films and shows unprecedented selectivities in hydrogenation of mono and multisubstituted double bonds. Initially, the chapter shows that Pd NPs embedded in multilayer polyelectrolyte films can be easily prepared through layer-by-layer adsorption of poly(acrylic acid) (PAA) and poly(ethylenimine)-Pd(II) (PEI-Pd(II)) complexes followed by reduction of Pd(II) with NaBH<sub>4</sub>. Transmission electron microscopy confirms the formation of Pd particles with



Scheme 1.8. Regio selective hydrogenation of Linalool to dihydrolinalool by [PAA/PEI-Pd(0)]<sub>3</sub>PAA films on alumina

diameters of 1-3 nm. Remarkably, [PAA/PEI-Pd(0)]<sub>3</sub>PAA films catalyze the hydrogenation of allyl alcohols (monosubstituted unsaturated alcohols) with turnover frequencies (TOFs) that are as much as 100-fold higher than turnover frequencies for hydrogenation of 3-methyl-2-buten-1-ol (multisubstituted unsaturated alcohols).

Intramolecular selectivity for the hydrogenation of monosubstituted unsaturated alcohols also occurs when substrate molecules contain both mono and multiply substituted double bonds, and one example is illustrated in scheme 1.8. The combination of the encapsulating polyelectrolyte film and small NPs apparently results in hindered access of multiply substituted double bonds to catalytic sites.

Chapter 3 investigates selectivity in hydrogenation as a function of NP size, and shows that in the hydrogenation of mono and multisubstituted double bonds, selectivity increases dramatically as NP diameter decreases from 3.9 to 2.2 nm. The use of different ratios of poly(acrylic acid) to Pd(II) in deposition solutions for PAA-Pd(0)/PEI films gives a series of catalysts with Pd NPs whose average diameters range from 2.2 to 3.4 nm. Turnover frequencies (TOFs) for the hydrogenation of monosubstituted unsaturated



Scheme 1.9. Selectivity as a function of NP size in the catalytic hydrogenation of unsaturated alcohols.

alcohols increase with decreasing average NP size, whereas multisubstituted unsaturated alcohols show the opposite trend. Hence, the ratios of TOFs for hydrogenation of allyl alcohol and  $\beta$ -methallyl alcohol are as high as 240 with the smallest NPs as illustrated in Scheme 1.9. Presumably, high selectivities occur on the smallest NPs because hydrogenations of monosubstituted and multisubstituted double bonds take place on different types of atoms (e.g., terraces versus edges) on the Pd NPs.

Chapter 4 expands the scope of [PAA-Pd(0)/PEI]<sub>3</sub> catalysts and demonstrates chemoselective hydrogenation of aromatic nitro compounds. Chemoselective hydrogenation of nitroarenes is often challenging due to the formation of unwanted side products. The [PAA-Pd(0)/PEI]<sub>3</sub> catalysts allow hydrogenation of various nitroarenes to the corresponding amines with functional group tolerance in high yield (>90 %) and short reaction times (15 to 60 mins). Higher chemoselectivity is observed when the hydrogenation reaction is performed in a mixture of water and Ethanol than in pure Ethanol.

In chapter 5, I provide concluding remarks along with future prospects for these catalysts.

# 1.7. References

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#### **CHAPTER 2**

# SELECTIVE HYDROGENATION OF MONOSUBSTITUTED ALKENES BY Pd NANOPARTICLES EMBEDDED IN POLYELECTROLYTE FILMS

## **2.1. Introduction**

As shown in chapter 1, metal NPs are attractive catalytic materials because of their high surface area to volume ratio and their size-dependent, tunable electronic properties.<sup>1-6</sup> However, aggregation of metal NPs reduces surface area and restricts control over particle size. Thus, practical catalysts that rely on these materials generally contain a support, such as carbon,<sup>7-10</sup> metal oxides,<sup>11-15</sup> zeolites,<sup>16-18</sup> or polymers,<sup>19-38</sup> onto which the NPs are deposited to prevent particle aggregation and facilitate catalyst recovery. In particular, polymeric supports are attractive because they provide unique possibilities for modifying the environment around catalytic sites and controlling access Incorporation of NPs in multilayer polyelectrolyte films<sup>23,24</sup> or to these sites. dendrimers,<sup>25,26</sup> for example, allows size-based selectivity in the hydrogenation of olefins. This chapter demonstrates that catalytic NPs in multilayer polyelectrolyte films also show remarkable *intramolecular selectivity* in the hydrogenation of alkenes based on the degree of substitution of the double bond. Selectivity in the hydrogenation of monosubstituted double bonds over di or trisubstituted double bonds is equal to or greater than that of Wilkinson's catalyst, tris(triphenylphosphine)rhodium(I) chloride, which is the prototype homogenous catalyst for such reactions.<sup>39</sup> Additionally, alumina-supported NP/polyelectrolyte catalysts can be easily separated from the reaction mixture and recycled.

Several reports show that the layer-by-layer deposition of polyelectrolyte films provides a convenient method for synthesis or immobilization of nanoparticles.<sup>23,24,40-44</sup>

In the present case, we prepare selective catalysts using layer-by-layer adsorption of poly(acrylic acid) (PAA) and poly(ethylenimine)-Pd(II) (PEI-Pd(II)) complexes on alumina particles and subsequent reduction of Pd(II) by NaBH<sub>4</sub> to form NPs as illustrated schematically in scheme 2.1.<sup>23,24</sup> The resulting embedded NPs contain catalytic sites that show unusually high selectivities, partly because the polymer restricts access to catalytic sites.



Scheme 2.1. [PAA/PEI-Pd(0)]<sub>3</sub>PAA film formation on Alumina.

Our previous research reported that the size-based selectivity of these catalysts in hydrogenation of allyl alcohols containing different alkyl substituents in the position  $\alpha$  to the double bond.<sup>23,24</sup> Smaller molecules exhibited higher hydrogenation rates, presumably because of more rapid transport to catalytic sites. The work reported in this chapter shows that [PAA/PEI-Pd(0)]<sub>3</sub>PAA films on alumina also exhibit high selectivities based on the substitution on the double bond itself. Moreover, intramolecular selectivity demonstrates that specificity cannot be explained solely by differences in the rate of diffusion through the polyelectrolyte film to catalytic sites.

#### 2.2. Experimental

### 2.2.1. Materials

Poly(ethylenimine) (PEI,  $M_w = 25\ 000\ Da$ ), poly(acrylic acid) (PAA,  $M_w = 90\ 000\ Da$ ), palladium (5 wt % on alumina powder),  $\alpha$ -alumina (100 mesh, typical particle size 75-100 µm), allyl alcohol (99%), crotyl alcohol (97%, mixture of isomers), 2-methyl-2-propen-1-ol (98%), 3-methy-2-buten-1-ol (99%), propionaldehyde, 3-methyl-1-butanol (98.5+%), isovaleraldehyde (97%), 2-heptene-4-ol, 1,5-heptadien-4-ol, 3,7-dimethyl-1,6-octadien-3-ol (97%), potassium tetrachloropalladate(II) (99.99%), and sodium borohydride (98%) were purchased from Aldrich and used as received. 1-Butanol (J.T. Baker), n-propyl alcohol (Columbus Chemical), *iso*-butyl alcohol (Spectrum), ethanol (100%, Pharmco), and calcium hydride were also used as received. Benzene was purchased from EMD chemicals and distilled over calcium hydride. Aqueous solutions were prepared with deionized water (Milli-Q, 18.2 M $\Omega$  cm), and hydrogen (99.9%) was obtained from AGA gases.

# 2.2.2. Preparation of Pd NPs Encapsulated in Polyelectrolyte Multilayer Films

Preparation of  $[PAA/PEI-Pd(0)]_3PAA$  films on alumina began with vigorous stirring of 15 g of  $\alpha$ -alumina in 100 mL of 20 mM PAA (pH adjusted to 4.0 with 0.1 M NaOH, molarity of PAA is given with respect to the repeating unit) for 10 min. Subsequently, the alumina was allowed to settle, the supernatant was decanted, and the alumina was washed with three 100-mL aliquots of deionized water (stirring in water for 5 min each time) to remove excess PAA. The polycation layer was deposited by vigorous stirring of PAA-coated alumina in a 100-mL solution containing the PEI-Pd(II) complex (1 mg/mL PEI, 2 mM K<sub>2</sub>PdCl<sub>4</sub>, pH adjusted to 9.0 with 0.1 M HCl), followed by washing with three 100-mL aliquots of deionized water. This procedure was repeated until 3.5 bilayers were deposited on alumina. Reduction of Pd(II) was performed by stirring the [PAA/PEI-Pd(II)]<sub>3</sub>PAA films on alumina in 100 mL of freshly prepared 0.1 mM NaBH<sub>4</sub> for 30 min, followed by washing with three 100-mL aliquots of deionized water. The water was decanted, and the residual water was removed under reduced pressure to afford a catalytic powder.

#### 2.2.3. TEM of Pd NPs

For TEM imaging, films were deposited on carbon-coated copper grids that were treated in a UV/ozone cleaner for 1 min. [PAA/PEI-Pd(0)]<sub>3</sub>PAA films were deposited as described above, except the grid was simply immersed for 5 min in solutions without stirring, and rinsing between each step consisted of a 1-min washing with deionized water from a squirt bottle. Imaging was performed on a JEOL 100CX microscope using an accelerating voltage of 100 kV. Particle sizes were determined manually on digital images.

## 2.2.4. Determination of the Amount of Pd in Catalyst and Deposition Solutions

Calculation of turnover frequencies (TOFs), i.e., the moles of substrate that are hydrogenated per mole of Pd per hour, requires knowing the amount of Pd in the catalyst. To determine Pd content, Pd in the catalyst was dissolved using aqua regia, and atomic emission spectroscopy (Varian Spectra AA-200) was employed to analyze these solutions as described previously.<sup>23,24</sup>

## 2.2.5. Hydrogenation Reactions

Catalytic hydrogenation was performed in a 100-mL, three-neck, round-bottomed flask. During the reaction, hydrogen at a gauge pressure of 50 kPa was bubbled through a frit at the bottom of a solution that was vigorously stirred. Prior to the reaction, suspended catalyst (250 mg of [PAA/PEI-Pd(0)],PAA on alumina or 10 mg of commercial 5% Pd on alumina) in 25 mL of H<sub>2</sub>O was bubbled with H<sub>2</sub> for 30 min before adding 25 mL of a 50.0 mM solution of substrate in water or in a 1:1 (v:v) mixture of Much less mass of the commercial catalyst was used for ethanol and water. hydrogenation reactions because this material has a 36-fold higher Pd loading than [PAA/PEI-Pd(0)]<sub>3</sub>PAA films on alumina. (The amount of Pd in 10 mg commercial catalyst is about 1.42 times higher than that in 250 mg of [PAA/PEI-Pd(0)]<sub>3</sub>PAA on Gas chromatography (Shimadzu GC-17A equipped with an RTxalumina.) BAC1column) was employed to monitor reactions using response factors that were determined with a standard mixture containing 10 mM reactant, product, and isomer (if applicable), except for the case of 2-methyl-2-propen-1-ol, for which we did not have pure isomer. In this case only, the isomer response factor was assumed to be the same as the product, as these compounds have the same number of C and O atoms. <sup>1</sup>H NMR spectra obtained on 300 MHz or 500 MHz spectrometers and <sup>13</sup>C NMR spectra obtained on 75 MHz or 125 MHz spectrometers were plotted with chemical shift reported relative to the residue peaks of methanol ( $\delta$  3.30 for <sup>1</sup>H NMR and 49.0 for <sup>13</sup>C NMR). For molecules containing multiple double bonds, GC-MS (Hewlett Packard G1800B GCD system with a non-polar HP-5MS column) with appropriate response factors was used to determine TOF. TOFs were calculated from the slope of the linear portions of plots of percent hydrogenation versus time (conversion less than 50 %) with the intercept of the line forced through zero. Each experiment was repeated twice and the  $\pm$  values represent the difference between the average and the data points. Representative calculation of response factor and TOF are shown in appendix.

## **2.2.6. Recycling Experiment**

Catalytic hydrogenation was performed in 100% water as described above. Most of the solvent was decanted after the reaction, the catalyst was transferred to another flask, and the residual water was removed in vacuum for more than 4 hours prior to determination of the remaining catalyst mass. About 5 % of the catalyst was lost during the recycling process. The hydrogenation reaction was repeated with this catalyst prior to another recycling step and a third hydrogenation reaction.

### 2.2.7. Hydrogenation Reactions by Wilkinson's Catalyst

Catalytic hydrogenation was performed in a 100-mL oven dried three-neck, round-bottomed flask containing a condenser and a bubbler. N<sub>2</sub> was bubbled through the round-bottom flask for 10 min before the reaction. During the reaction, hydrogen at a gauge pressure of 50 kPa was bubbled through a frit at the bottom of a solution that was vigorously stirred with magnetic stir bar. Prior to the reaction, 23 mg (0.025 mmole) of RhCl(PPh<sub>3</sub>)<sub>3</sub>, Wilkinson's catalyst, was stirred in 18 mL of benzene with bubbling of H<sub>2</sub> for 20 min before adding 2.5 mmole substrate in 2 mL of benzene using a glass syringe. Sample was collected using a glass syringe at various time intervals that depended on the rate of the reaction. Gas chromatography was employed to monitor the reaction using response factors as described above.

### **2.2.8. Isolation of Products**

After 97% hydrogenation of compounds 5 (0.140 g, 50 mM solution in 25 mL 1:1 water and ethanol, later mixed with 25 mL water) and 7 (0.193 g, 50 mM solution in 25 mL 1:1 water and ethanol, later mixed with 25 mL water), the catalyst was removed from the solution by filtration through cotton, and about 1g of NaCl was added to the solution. Products (6 and 8) were extracted with 25 mL of anhydrous diethyl ether. The organic layer was collected and dried over anhydrous sodium sulfate, and solvent was removed under reduced pressure to afford crude compounds 6 and 8. Pure compound 8 was afforded in 81% yield (0.158 g) after column chromatography with 9:1 hexane and ethyl acetate. In the case of hydrogenation of compound 5, 0.120 g of crude product (84% yield) was isolated after extraction. GC/MS analysis showed that the ratio of 6 and 9 in crude 6 is 8:1. <sup>1</sup>H NMR indicated the presence of small amounts of impurities in the crude product as shown in the spectra, which are given in the appendix.

Compound **6**: <sup>1</sup>H NMR (500 MHz, CD<sub>3</sub>OD): δ 0.90 (t, 3H), 1.27-1.51 (m, 4H), 1.67 (dd, 3H), 3.95 (m, 1H), 5.41 (m, 1H), 5.61 (m, 1H), <sup>13</sup>C NMR (125 MHz, CD<sub>3</sub>OD): δ 14.3, 17.8, 19.7, 40.5, 73.4, 127.1 and 135.4. Spectral data were consistent with commercially available material.

Compound 8: <sup>1</sup>H NMR (300 MHz, CD<sub>3</sub>OD): δ 0.88 (t, 3H), 1.11 (s, 3H), 1.37-1.51 (m, 4H), 1.61 (s, 3H), 1.66 (s, 3H) 2.00 (m, 2H), 5.11 (m, 1H), <sup>13</sup>C NMR (75 MHz, CD<sub>3</sub>OD): δ 8.5, 17.6, 23.6, 25.9, 26.2, 34.9, 42.2, 73.4, 125.8 and 132.0

## **2.2.9. Transport Studies**

Diffusion dialysis experiments were performed using a home-built dialysis apparatus (shown in Figure 2.1) in which a porous alumina membrane (Whatman Anodisc,  $0.02 \mu$ m-diameter surface



**Figure 2.1.** Home-built diffusion dialysis set-up for transport experiments. (Figure courtesy of Dr. Jinhua Dai).

pores) coated with a [PAA/PEI]<sub>7</sub> film was sandwiched between two glass cells. (More layers were used in these experiments than in preparing catalysts to ensure complete coverage of the pores in the underlying alumina support.) The source cell was filled with 90 mL of a 20 mM aqueous solution of the desired unsaturated alcohol (allyl alcohol, crotyl alcohol, 2-methyl-2-propen-1-ol, or 3-methyl-2-buten-1-ol), while the receiving cell initially contained 90 mL of deionized water. Both the source and the receiving sides were stirred vigorously to minimize concentration polarization at the membrane

interface, and samples of the receiving phase were taken every 20 min and analyzed by gas chromatography using methanol as an internal standard.

#### 2.3. Results and Discussions

#### 2.3.1. NP Size

Figure 2.2 & 2.3 shows the TEM image of a [PAA/PEI-Pd(0)]<sub>3</sub>PAA film on a carbon-coated grid. Consistent with prior results,<sup>23</sup> the distribution of particle diameters ranged from 1-3 nm as shown in Figure 2.4. The estimated average particles size is 2.2 nm. The relatively impermeable PAA/PEI films likely inhibit ion and NP diffusion to give small particles.



Figure 2.2. TEM image of [PAA/PEI/Pd(0)]<sub>3</sub>PAA on carbon-coated cupper grid.



Figure 2.3. TEM image of a [PAA/PEI-Pd(0)]<sub>3</sub>PAA film on a carbon-coated copper grid. This image was taken at a lower magnification than Figure 2.2 in to better show the distribution of NPs.



Figure 2.4. Histogram of Pd NP diameters in several TEM images of [PAA/PEI-Pd(0)]<sub>3</sub>PAA film deposited on a TEM grid. The average particle size is 2.2 nm.

# 2.3.2. Intermolecular Selectivity

Using similar films on alumina particles, we initially compared the rates of hydrogenation of unsaturated alcohols with different substituents on the double bond and found very high selectivities (Table 2.1). With a [PAA/PEI-Pd(0)]<sub>3</sub>PAA-on-alumina catalyst in water, allyl alcohol (1) could be 82% hydrogenated in 15 min (formation of about 18% propionaldehyde isomer prohibits complete hydrogenation) with an initial turnover frequency (TOF) of 3500 moles hydrogenated/mole catalyst/h.<sup>45</sup> In contrast, 2-methyl-2-propen-1-ol (2), crotyl alcohol (3), and 3-methyl-2-buten-1-ol (4) exhibited TOFs that ranged from 14 to 100-fold lower (Table 2.1, column 4). By comparison, a commercially available 5% Pd on alumina catalyst facilitated hydrogenation of 1, 2, 3 and 4 with TOFs that varied by at most a factor of 2 when water was the solvent (Table 2.1, column 2).

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<u>** - , , +</u>	TOF (moles hydrogenated/ mol Pd/ h) <sup>a</sup>			
Substrates	5%Pd on	5%Pd on	[PAA/PEI-	[PAA/PEI-
	Alumina	Alumina	Pd(0)] <sub>3</sub> PAA	Pd(0)] <sub>3</sub> PAA
	(H <sub>2</sub> O) <sup>b</sup>	(H <sub>2</sub> O/EtOH) <sup>c</sup>	(H <sub>2</sub> O) <sup>b</sup>	(H <sub>2</sub> O/EtOH) <sup>c</sup>
1OH	1680±30	1160±120	3505±175	2700±100
	(2770±20)	(1700±170)	(5300±500)	(5590±50)
2 =<	835±65	415±45	120±5	75±5
	(2275±25)	(1270±130)	(365±35)	(230±20)
3 /=\OH	1705±15	1060±50	250±15	175±15
4 >	1220±190	850±80	35±5	25±5

**Table 2.1.** TOFs for the hydrogenation of a series of unsaturated alcohols by different Pd catalysts.

Interestingly, although the TOF for hydrogenation of allyl alcohol using the [PAA/PEI-Pd(0)]<sub>3</sub>PAA on alumina catalyst is higher than that of the commercially available 5% Pd on alumina, selectivity is still much higher for the Pd NPs in the polyelectrolyte multilayer. However, the commercial catalyst has a 36-fold higher wt % of Pd than [PAA/PEI-Pd-(0)]<sub>3</sub>PAA on alumina, as determined by atomic emission spectroscopy. To keep the amount of Pd in the different reactions about the same, 250 mg of [PAA/PEI-Pd(0)]<sub>3</sub>PAA on alumina was added to the reaction mixtures while only 10 mg of 5 wt % Pd on alumina was employed. Overall, the molar ratio of substrate to

<sup>[</sup>a] Values in parentheses represent TOFs where the isomer is included as part of the product, although it is not hydrogenated. Each experiment was repeated twice, and the  $\pm$  values represent the difference between the average and the data points. [b] 25 mM substrate was hydrogenated in water. [c] 25 mM substrate was hydrogenated in a 3:1 (v:v) mixture of water and ethanol.
Pd atoms was 400 for hydrogenation using [PAA/ PEI-Pd(0)]<sub>3</sub>PAA on alumina and 280 for hydrogenation using the commercial 5% Pd on alumina.

Hydrogenation was also performed in 3:1 mixtures of water and ethanol because of the relatively low solubility of the substituted unsaturated alcohols in water. For the [PAA/PEI-Pd(0)]<sub>3</sub>PAA on alumina catalyst, the TOF for allyl alcohol decreased by 23% in the less polar mixture, possibly because the reduced swelling of the polyelectrolyte films decreases the rate of substrate diffusion to the catalytic sites. However, TOFs also decreased for the commercial catalyst, suggesting that other factors influence the hydrogenation rate. Nevertheless, the observed selectivities are similar in the two solvent systems (compare columns 4 and 5 of Table 2.1), reaching 2 orders of magnitude (1/4) for the [PAA/PEI-Pd(0)]<sub>3</sub>PAA on alumina catalyst.

As a control experiment, hydrogenation of allyl alcohol and its isomer propionaldehyde was attempted in the absence of hydrogen gas using [PAA/PEI-Pd(0)]<sub>3</sub>PAA as a catalyst. No reaction occurred, which rules out the possibility of other reductants, such as trace amounts of residual NaBH<sub>4</sub>, driving the reaction.

The propionaldehyde and 2-methylpropionaldehyde isomers of 1 and 2, respectively, are not hydrogenated under the reaction conditions, so their formation results in a decreased rate of hydrogenation. Isomer formation was particularly extensive for 2 (ratio of the isomer to product was 1.5-2 with 50% of the reactant remaining) and also occurred for allyl alcohol (1) when using either the commercial 5% Pd on alumina or the  $[PAA/PEI-Pd(0)]_3PAA$  catalyst. Hence the TOFs of these molecules are somewhat lower than what might be expected, especially in the case of 2 (row 2, Table 2.1). The sum of TOFs for isomerization and hydrogenation are given in parentheses in Table 2.1 for cases where significant isomer formation occurred.

To examine the recylability of the [PAA/PEI-Pd(0)]<sub>3</sub>PAA on alumina, this catalyst was recovered after the hydrogenation of allyl alcohol in water and dried prior to use in a subsequent hydrogenation. Remarkably, the TOF was 3200±100 moles hydrogenated/mol Pd/h for three consecutive hydrogenations of allyl alcohol. Thus, unlike homogeneous catalysts such as tris-(triphenylphosphine)rhodium(I) chloride, [PAA/PEI-Pd(0)]<sub>3</sub>PAA on alumina can be readily recovered and reused.

The selectivity of the embedded Pd NPs compares very well with that of Wilkinson's catalyst, which previously showed a rate of hydrogenation for 1-hexene (monosubstituted unsaturated alcohols) in benzene that is 1.1 and 49 times higher than that for 2-methylpent-1-ene (a disubstituted unsaturated alcohol) and 1methylcyclohexene methylcyclohexene (a trisubstituted unsaturated alcohol).<sup>46</sup> respectively. To better compare the catalytic selectivity of [PAA/PEI-Pd(0)]<sub>3</sub>PAA films with that of Wilkinson's catalyst, we determined the TOFs for the hydrogenation of compounds 1, 2, and 4 with Wilkinson's catalyst (Table 2.2). (In this case, the reactions had to be performed in benzene rather than water because Wilkinson's catalyst is not soluble in aqueous solutions.) The selectivities of Wilkinson's catalyst for 1/2 and 1/4were 2.6 and 54, respectively, which is in reasonable agreement with the data mentioned above for 1-hexene, 2-methylpent-1-ene, and 1-methylcyclohexene. (The GC peak corresponding to 1-butanol, the hydrogenated product of 3, overlapped with that of benzene, so hydrogenation of this compound with Wilkinson's catalyst was not examined.) Wilkinson's catalyst shows only minor selectivity for mono versus disubstituted unsaturated alcohols, whereas the embedded NPs show selectivities ranging from 14 to 36 for allyl alcohol over 2 and 3. In the case of the trisubstituted unsaturated alcohol 4, the selectivity (1/4) of the embedded NPs is 2-fold higher than that of the Wilkinson's catalyst. However, unlike the  $[PAA/PEI-Pd(0)]_3PAA$  films, Wilkinson's catalyst showed minimal formation of the isomer of 1 and none of the isomer of 2. In contrast, Wilkinson's catalyst showed formation of the isomer of 4 (the amounts of isomer and hydrogenated product were the same although rates of formation of both were low), while the  $[PAA/PEI-Pd(0)]_3PAA$  film did not show any readily detectable isomer.

**Table 2.2.** TOFs for the hydrogenation of a series of unsaturated alcohols by Wilkinson's catalyst.

	Substrates	TOF (moles hydrogenated/ mol of catalyst/ h) <sup>a</sup>
1.	он	270±10 (290±10)
2.	=	105±25
4.	>он	5 (10)

[a] Values in parentheses represent the sum of TOFs for the hydrogenation and isomerization.

#### 2.3.3. Intramolecular Selectivity

We further examined the catalytic behavior of  $[PAA/PEI-Pd(0)]_3PAA$  films on alumina for intramolecularly selective hydrogenation of molecules containing a combination of mono and di or tri substituted double bond (Table 2.3). In this case, 1,5heptadien-4-ol (5) and 3,7-dimethyl-1,6-octadien-3-ol (7) were selectively hydrogenated into 2-hepten-4-ol (6) and 3,7-dimethyl-6-octen-3-ol (8), respectively, when hydrogenation was catalyzed by  $[PAA/PEI-Pd(0)]_3PAA$ . In a control experiment, the TOF for the hydrogenation of 2-hepten-4-ol (6) to 4-heptanol (9) was 3% of the TOF for reduction of 5 to 6, indicating much slower conversion for the disubstituted double bond. This is consistent with the fact that at 97% conversion of 5, the isolated product was an 8:1 mixture of 6 and 9 (84% overall yield). (Reactions are first order in substrate so product ratios cannot be calculated as simple ratios of TOFs.) No product with both hydrogenated double bonds was observed by GC-MS and NMR for compound 7 (81% yield of 8 after purification) because trisubstituted double bond are hydrogenated very slowly (Table 2.1).

The TOF for the hydrogenation of 5 to 6 is 2.6 times that for hydrogenation of 7 to 8, probably because the more bulky groups  $\alpha$  to the monosubstituted carbon-carbon double bond in 7 restrict access to catalytic sites and diminish the rate of the reaction. As a consequence, compounds 5 and 7 required 15 and 135 min, respectively, to achieve about 97% conversion to hydrogenated products. Control experiments with the 5% Pd on alumina also showed some intramolecular selectivity in the hydrogenation of 5 and 7, but much less than that for the [PAA/PEI-Pd(0)]<sub>3</sub>PAA catalyst. At about 99% hydrogenation of 5 by the commercial catalyst, the product distribution was 34% 6 and 65% 9. The TOF for the hydrogenation of compound 6 (550±130) was also 10-fold greater with the commercial catalyst than with [PAA/PEI-Pd(0)]<sub>3</sub>PAA. In the case of hydrogenation of 7 using the commercial catalyst, after 240 min, 95% of the mixture was the doubly hydrogenated product, but 25 min after starting, the mixture contained 94% 8 after only 25 min of reaction. In this case, the commercial catalyst may also be a viable choice for somewhat selective hydrogenation, but one would need to carefully monitor the reaction.

**Table 2.3.** TOFs (moles hydrogenated/ mole Pd/ h) for selective hydrogenation of monosubstituted double bonds in the presence of di and tri substituted double bonds in the same molecules. The reaction was catalyzed by  $[PAA/PEI-Pd(0)]_3PAA$  on alumina in a 3:1 mixture of water and ethanol.



[a] The reaction was catalyzed by [PAA/PEI-Pd(0)]<sub>3</sub>PAA on alumina in a 3:1 mixture of water and ethanol. TOF is expressed as moles/hydrogenated/mol Pd/h.

Our prior studies of diffusion of allyl alcohol derivatives through porous alumina membranes (0.02-µm surface pore size) coated with [PAA/PEI]<sub>7</sub> films suggested that different rates of diffusion to catalytic sites imparted selectivity.<sup>23,24</sup> Figure 2.5 presents analogous dialysis studies with compounds 1-4 and also shows selective transport through [PAA/PEI]<sub>7</sub> films on alumina. The ratios of transport rates (slopes in Figure 2.5) for 1/2, 1/3, and 1/4 were 2.2, 2.0 and 6.3, respectively. However, relative rates of hydrogenation in water are 25, 12 and 82 for 1/2, 1/3, and 1/4, respectively, suggesting that differences in transport rates are insufficient to account for the full hydrogenation selectivity among these compounds. Moreover, selective hydrogenation within molecules 5 and 7 shows that these compounds can diffuse through the film to reach catalytic sites and yet only one double bond is predominantly hydrogenated. Diffusion through the film cannot be limiting hydrogenation of the second double bond. On the other hand, compounds 1-4 are all hydrogenated at relatively similar rates (1/2=2.1, 1/3=0.95, and 1/4=1.2) with the commercial catalyst (5% Pd on Alumina) suggesting that selectivity cannot have a completely electronic basis (Table 2.1, column 2). We think that steric constraints for binding of multiply substituted double bonds to embedded NPs must be significantly greater than similar constraints in binding to the 5% Pd on alumina. I investigate the selectivity in the hydrogenation of unsaturated alcohols as a function of the NP size in chapter 3.



**Figure 2.5.** Time evolution of the receiving phase concentrations of allylic alcohols during diffusion dialysis of 1 (squares), 2 (triangles), 3 (diamonds), and 4 (circles) through porous alumina membranes coated with a [PAA/PEI]7 film. The source phase initially contained 20 mM of the allylic alcohols, and the receiving phase was initially deionized water.

# 2.4. Conclusion

Deposition of Pd (II) in polyelectrolyte films followed by reduction yields catalytic, NP-containing films that can be used as catalysts in inter and intramolecularly selective hydrogenation of unsaturated alcohols. Remarkably, the selectivity of these heterogeneous catalysts exceeds that of Wilkinson's homogenous catalyst. Intramolecular selectivity and studies of diffusion through PAA/PEI films suggest that selectivity stems from steric constraints for binding of multiply substituted double bonds to embedded NPs.

# 2.5. Appendix

**Calculation of TOFs From GC Data With Response Factors** 

# **Determination of Response Factors**

$$\frac{S_{P}}{S_{R}} = \frac{C_{P} k_{1}}{C_{R}}$$
$$\frac{S_{I}}{S_{R}} = \frac{C_{I} k_{2}}{C_{R}}$$

Where  $S_P = Peak$  area corresponding to product

- $S_I$  = Peak area corresponding to isomer
- $S_R$  = Peak area corresponding to Reactant
- $C_P$  = Concentration of product
- $C_R$  = Concentration of reactant
- $C_l = Concentration of isomer$
- $k_1$  = Response factor for product to reactant
- $k_2$  = Response factor for isomer to reactant

Response factors were calculated from the signals due to a solution containing 10 mM product, 10 mM reactant, and 10 mM isomer, and three chromatograms with three standard solutions were averaged to determine the value.

# **Calculation of % Hydrogenation**

1 mL samples were removed every few minutes (time intervals depended on the rate) from the hydrogenation mixture and placed in autosampler vials for GC analysis. Percent hydrogenation was determined as shown below.

% hydrogenation = 
$$\frac{C_P}{C_P + C_R + C_I} \times 100\% = \frac{S_P * k_2}{S_P * k_2 + S_R * k_1 * k_2 + S_I * k_1} \times 100\%$$

When the rates of hydrogenation and isomerization were added

% reaction = % of hydrogenation + % of isomerization:

% reaction = 
$$\frac{C_{P} + C_{I}}{C_{P} + C_{R} + C_{I}} \times 100\% = \frac{S_{P} * k_{2} + S_{I} * k_{1}}{S_{P} * k_{2} + S_{R} * k_{1} * k_{2} + S_{I} * k_{1}} \times 100\%$$

Table A-1 shows some sample data.

Table 2.	<b>A-1</b>	Time-dep	endent	percentage	of c	crotyl	alcohol	hydrogenation	catalyzed	i by
[PAA/PE	I-Pd(	<b>[0)]</b> 3PAA i	in water	r <b>.</b>						

Time (min)	% of hydrogenation		
0.0	0		
10.0	7.93		
20.0	24.3		
30.0	33.89		
40.0	45.3		



)

Figure 2. A-1 Example gas chromatograms of the reaction mixture from hydrogenation of crotyl alcohol (3) after 10 min (black line) and 40 min (red line) of reaction time. The reaction was catalyzed by  $[PAA/PEI-Pd(0)]_3PAA$  in water. Integration was performed using instrument software.

:



Figure 2. A-2. Plot of time-dependent percentage of crotyl alcohol hydrogenation catalyzed by [PAA/PEI-Pd(0)]<sub>3</sub>PAA in water.



Figure 2. A-3. <sup>1</sup>H NMR spectrum of isolated crude 2-heptene-4-ol (compound 6) in CD<sub>3</sub>OD. Impurity peaks are indicated with a \*.



Figure 2. A-4  $^{13}$ C NMR spectrum of isolated crude 2-heptene-4-ol (compound 6) in CD<sub>3</sub>OD. Impurity peaks are indicated with a \*.



**Figure 2. A-5**. <sup>1</sup>H NMR spectrum of purified 3,7-dimethyl-6-octen-3-ol (compound 8) in CD<sub>3</sub>OD. Impurity peaks are indicated with a \*



Figure 2. A-6. <sup>13</sup>C NMR spectrum of purified 3,7-dimethyl-6-octen-3-ol (compound 8, chapter 2) in CD<sub>3</sub>OD. Impurity peaks are indicated with a \*

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## CHAPTER 3

# SELECTIVITY AS A FUNCTION OF NANOPARTICLE SIZE IN THE CATALYTIC HYDROGENATION OF UNSATURATED ALCOHOLS

# **3.1. Introduction**

Control over particle size is essential in creating highly active NP catalysts for alkene hydrogenation,<sup>1-5</sup> alcohol oxidation,<sup>6,7</sup> Suzuki<sup>8</sup> and Heck<sup>9</sup> coupling, Norrish type II reactions,<sup>10</sup> reduction of aromatic nitro compounds,<sup>11</sup> CO oxidation,<sup>12,13</sup> and electrooxidation of formic acid<sup>14,15</sup> and methanol.<sup>16</sup> NP size is also a critical parameter for achieving partial hydrogenation in the conversion of alkynes to alkenes,<sup>17,18</sup>  $\alpha,\beta$  unsaturated aldehydes to unsaturated alcohols,<sup>19</sup> and conjugated alkenes to monoalkenes.<sup>20,21</sup> Moreover, NP catalysts show high intermolecular selectivities in the hydrogenation of alkynes<sup>22</sup> and allylic alcohols,<sup>23-27</sup> but selectivity has not been studied as a function of particle size. Examination of selectivities is particularly attractive for understanding the effect of particle size on reactivity because rate enhancements due solely to increases in surface area should cancel when calculating the ratios of reaction rates for structurally related compounds.

This chapter shows that both the rates and selectivities of hydrogenation reactions vary dramatically with the diameter of catalytic NPs. Remarkably, in the hydrogenation of mono and disubstituted double bonds, NPs with average diameters of 2.2 nm exhibit selectivities as high as 39 for allyl alcohol over crotyl alcohol, whereas NPs with average diameters of 3.4 nm show corresponding selectivities less than 1.3. Such variations in selectivity occur with polymer-encapsulated NPs immobilized on alumina as well as polymer-capped NPs in solution.

The first step in examining the effect of NP size on catalytic activity is development of a method to synthesize NP catalysts with several different average particle sizes and narrow size distributions. Among the methods for controlling NP size, a number of studies demonstrate that layer-by-layer deposition of polyelectrolyte films containing metal ions and subsequent reduction of these metal ions provide a straightforward technique for creating encapsulated NPs.<sup>23-25,28-32</sup> The amount of metal ion present during film deposition dictates the particle size, and layer-by-layer deposition on micron-sized alumina provides heterogeneous catalysts. Polyelectrolyte-NP catalysts can also form in solution, which allows comparison of particle-size effects in supported films and solution-based catalysts.

Palladium NPs in polyelectrolyte films are particularly attractive for investigating relationships between particle size and reactivity/selectivity because they show high selectivity in the hydrogenation of unsaturated alcohols.<sup>23,24</sup> In the previous chapter we described the preparation of Pd NPs encapsulated in multilayer polyelectrolyte films through layer-by-layer adsorption of poly(acrylic acid) (PAA) and poly(ethylenimine)-Pd(II) (PEI-Pd(II)) complexes and reduction of Pd(II) with NaBH<sub>4</sub>. Transmission electron microscopy confirmed the formation of Pd NPs, and the selectivities of [PAA/PEI-Pd(0)]<sub>3</sub>PAA films in the hydrogenation of monosubstituted over multisubstituted double bonds were as high as 100.<sup>23</sup> However, we employed only one average particle size. This work examines the hydrogenation of a series of unsaturated alcohols using NP/polyelectrolyte catalysts with several average NP sizes and shows that selectivity is an extremely sensitive function of particle diameter.

#### **3.2. Experimental Section**

#### 3.2.1. Materials

Poly(ethylenimine) (PEI,  $M_w = 25\ 000\ Da$ ), poly(acrylic acid) (PAA,  $M_w = 90\ 000\ Da$ ), α-alumina (100 mesh, typical particle size 75-100 µm), allyl alcohol (99.0%), crotyl alcohol (97.0%, mixture of isomers), 2-methyl-2-propen-1-ol (98.0%), 3-methyl-2-buten-1-ol (99.0%), propionaldehyde, 3-methyl-1-butanol (98.5+%), isovaleraldehyde (97.0%), isobutyraldehyde (98.0%), 3-methyl-1-penten-3-ol (99.0%), 3-methyl-3-pentanol (99.0%), cis-3-hepten-1-ol ( $\geq 95.0\%$ ) potassium tetrachloropalladate(II) (99.99%), and sodium borohydride (98%) were purchased from Aldrich. 1-Heptanol and 3-buten-1-ol were obtained from TCI, and butyraldehyde ( $\geq 99.0\%$ ) was purchased from Fluka. 1-Butanol (J.T. Baker), n-propyl alcohol (Columbus Chemical), iso-butyl alcohol (Spectrum) and ethanol (100%, Pharmco) were used as received. Aqueous solutions were prepared with deionized water (18.2 MΩ cm, Milli-Q purification system), and hydrogen (99.9%) was obtained from AGA gases.

# 3.2.2. Preparation of Pd NPs Encapsulated in Polyelectrolytes

#### 3.2.2.1. [PAA-Pd(0)/PEI]<sub>3</sub> on Alumina

Preparation of PAA/PEI-Pd(0) films on alumina was described previously,<sup>23,24</sup> and formation of PAA-Pd(0)/PEI films occurred similarly. Alumina was alternately suspended for 10 min in a solution that contained 20 mM PAA and 1, 4, 8, or 15 mM  $K_2PdCl_4$  and for 10 min in a solution that contained PEI (1 mg/mL). (The molarity of PAA is given with respect to the repeating unit.) Prior to their use in multilayer assembly, the PAA solution was adjusted to pH 4.0 with 0.1 M NaOH, and the PEI

solution was adjusted to 9.0 with 0.1 M HCl. After the deposition of each polyelectrolyte layer, the alumina was allowed to settle, the supernatant was decanted, and the solid was suspended similarly (vigorous stirring) in three 100-mL aliquots of deionized water for 5 min to remove excess polyelectrolyte. Overall, three PAA-Pd(II)/PEI bilayers were deposited. Reduction to Pd(0) was performed by stirring the [PAA-Pd(II)/PEI]<sub>3</sub> films on alumina in 100 mL of freshly prepared 0.1 mM NaBH<sub>4</sub> for 30 min, followed by washing with three 100-mL aliquots of deionized water for 5 min each. After decanting the final water rinse, the residual water was removed under reduced pressure overnight to afford a catalytic powder.

# 3.2.2.2. [Pd(0)/PEI] on Alumina

 $[Pd(0)/PEI]_3$  films on alumina were prepared as described previously.<sup>25</sup> In brief, 15 g of  $\alpha$ -alumina powder was stirred for 30 min in 100 mL of a solution that contained K<sub>2</sub>PdCl<sub>4</sub> (1 or 15 mM) and 0.1 M KCl. The alumina was washed as described above prior to suspension in PEI (2 mg/mL PEI, pH adjusted to 9.0 with 0.1 M HCl) for 10 min and additional washing. After deposition of three PdCl<sub>4</sub><sup>2-</sup>/PEI bilayers, the reduction of Pd(II) to Pd (0) was performed as described above.

# 3.2.2.3. PAA-Pd(0)/PEI in Solution

PAA-Pd(II) was prepared by mixing 20 mM PAA and  $K_2PdCl_4$  (1, 4, 8, or 15 mM) and adjusting the pH of the solution to 4 with 0.1 M NaOH. Five mL of this solution and 5 mL of PEI solution (1 mg/mL PEI, pH adjusted to 9.0 with 0.1 M HCl) were mixed together in a 20 mL glass vial at which point the solution became cloudy. Freshly prepared 0.1 M NaBH<sub>4</sub> (5 mL) was added to the cloudy PAA-Pd(II)/PEI, which

was then stirred vigorously for 3 h in a loosely capped vial. The resulting clear, brown solution was then immediately used for hydrogenation.

Crooks et al. previously reported that dendrimer-encapsulated Pd NPs, a homogeneous catalytic system, are unstable in the presence of oxygen.<sup>33</sup> We also observed that the brown color of the PAA-Pd(0)/PEI solution faded to pale yellow over 24 h if the solution was not capped tightly and refrigerated. This was especially apparent when the concentration of Pd(II) in the deposition solution was 1 mM.

#### 3.2.3. Characterization of Pd NPs

For TEM imaging, films were deposited on carbon-coated copper grids that were pretreated in a UV/ozone cleaner for 1 min. [PAA-Pd(0)]/PEI]<sub>3</sub> and reduced [PdCl<sub>4</sub><sup>2-</sup>/PEI]<sub>3</sub> films were formed as described above, except the grid was simply immersed for 5 min in deposition solutions without stirring, and rinsing between each step consisted of a 1-min washing with deionized water.

To characterize the PAA-Pd(0)/PEI solutions prepared with different initial concentrations of Pd(II) (1, 4, 8, 15 mM), we first diluted the reduced solutions with sufficient deionized water to obtain 0.33 mM Pd. We then spotted a drop of these solutions on separate carbon-coated copper grids that had been pretreated with UV/ozone for 1 min, and allowed the solutions to dry at room temperature overnight. Imaging was performed on a JEOL-2200FS microscope using an accelerating voltage of 200 kV. Diameters of at least 250 particles for each sample were measured manually on digital images, and uncertainties in average particle diameters represent standard deviations. The amounts of palladium in different catalysts were determined by atomic emission spectroscopy (AES). Standard solutions (0.1 to 0.5 mM) were prepared by dissolving

 $K_2PdCl_4$  in 0.1 M HNO<sub>3</sub>, and sample solutions were prepared by stirring the desired amount of alumina-supported catalyst (60 to 500 mg, depending on the Pd content) in 2 mL of aqua regia for 15 min. The aqua regia solutions were diluted to 12 mL with water and centrifuged (the  $\alpha$ -alumina support does not dissolve in aqua regia), and the supernatant was analyzed using its emission at 340.5 nm. Table 3.1 lists the amounts of Pd in each of the different catalysts. For the PAA-Pd(0)/PEI solutions, the amount of Pd(0) was calculated by assuming total conversion of Pd(II) to Pd(0).

Catalyst	Amount of Catalyst	Moles of Pd in the Catalyst
$[PAA-Pd(0)/PEI]_3$ on $Al_2O_3$ (Pd(II) = 1  mM), Catalyst A	500 mg	1.91
$[PAA-Pd(0)/PEI]_3$ on $Al_2O_3$ (Pd(II) = 4 mM), Catalyst <b>B</b>	250 mg	4.15
[PAA-Pd(0)/PEI] <sub>3</sub> on Al <sub>2</sub> O <sub>3</sub> (Pd(II)= 8 mM), Catalyst C	125 mg	7.66
$[PAA-Pd(0)/PEI]_3$ on $Al_2O_3$ (Pd(II) = 15 mM), Catalyst <b>D</b>	125 mg	12.8
$[PAA-Pd(0)/PEI]_3(PAA/PEI)_3 \text{ on } Al_2O_3$ $(Pd(II) = 1 \text{ mM}), \text{ Catalyst } \mathbf{E}$	500 mg	1.18
$[PAA-Pd(0)/PEI]_3 (PAA/PEI)_3 on Al_2O_3$ $(Pd(II) = 15 \text{ mM}), \text{ Catalyst } \mathbf{F}$	125 mg	11.2
Reduced $[PdCl_4^2/PEI]_3$ on $Al_2O_3$ (Pd(II) = 1 mM), Catalyst <b>G</b>	250 mg	3.71
Reduced $[PdCl_4^2/PEI]_3$ on $Al_2O_3$ (Pd(II)= 15 mM), Catalyst H	100 mg	11.0
PAA-Pd(0)/PEI solution (Pd(II)= 1 mM), Catalyst I	5.00 mL	1.67
PAA-Pd(0)/PEI solution (Pd(II) = 4 mM), Catalyst J	5.00 mL	6.65
PAA-Pd(0)/PEI solution (Pd(II)= 8 mM), Catalyst K	3.00 mL	8.00
PAA-Pd(0)/PEI solution (Pd(II) = 15 mM), Catalyst L	3.00 mL	15.00

**Table 3.1.** Amounts and Pd Content of Catalysts Used in Hydrogenation Reactions.

# **3.2.4. Hydrogenation Reactions**

Catalytic hydrogenation was performed in a 100-mL, three-neck, round-bottomed flask. Suspended alumina-supported catalyst in 25 mL of H<sub>2</sub>O (or 25 mL of diluted catalyst solution in the case of NPs stabilized by polyelectrolytes in solution) was bubbled with  $H_2$  for 30 min before adding 25 mL of a 50 mM solution of substrate in water or in a 1:1 (v:v) mixture of ethanol or methanol or THF and water. During the reaction, hydrogen at a gauge pressure of 50 kPa was bubbled through a frit at the bottom of a solution that was vigorously stirred. Different amounts of catalyst (Table 3.1) were used for hydrogenation reactions because each type of material had a different wt% of Pd. 0.5-mL aliquots were removed from the reaction vessel at specific times, filtered with cotton to remove the catalyst, and diluted by addition of 1-mL deionized water prior to analysis by gas chromatography (Shimadzu GC-17A equipped with an RTx-BAC1column). In the GC analysis of hydrogenation of 3, product and reactant peaks showed a small overlap, and one limit of integration was placed at the minimum between the peaks. Response factors were determined to calculate the turnover frequency (TOF) as described previously.<sup>23</sup> TOFs were calculated from the slope of the initial portion (total conversion of reactant to isomer and hydrogenated product <50%) of plots of percent hydrogenation versus time. In fitting the initial data, the intercept of the line was forced through zero. Each experiment was repeated twice and the  $\pm$  values represent the difference between the average and the data points.

#### **3.3. Result and Discussion**

#### 3.3.1. Catalyst Synthesis and Variation of Particles Size

The initial step in studying the effect of NP size on catalytic selectivity is to prepare a series of catalysts with different particle sizes. Previously, we made [PAA/PEI-Pd(II)]<sub>3</sub>PAA films using 2 mM Pd(II) in the PEI-Pd(II) deposition solution. Subsequent reduction of the Pd(II) gave [PAA/PEI-Pd(0)]<sub>3</sub>PAA coatings containing Pd NPs with diameters of 1-3 nm.<sup>23</sup> We tried to enhance NP size by increasing the concentration of Pd(II) in the PEI deposition solution, but at a Pd(II) concentration of 12 mM, the PEI solution became cloudy, perhaps because the Pd(II) serves as a cross- linking agent for PEI chains. To overcome this challenge, we add Pd(II) to the PAA, rather than PEI, deposition solution. The 20 mM PAA deposition solution (PAA concentration is given with respect to the repeating unit) remains clear at Pd(II) concentration as high as 15 mM. Prior studies demonstrated deposition of metal ions in PAA/protonated poly(allylamine) films and subsequent formation.

Most importantly, reduction of  $[PAA-Pd(II)/PEI]_3$  using NaBH<sub>4</sub> yields  $[PAA-Pd(0)/PEI]_3$  films, and the sizes of the resulting Pd NPs increase with increasing concentrations of Pd(II) in PAA deposition solutions. Figures 3.1, 3.2, 3.3, 3.4, and 3.5 present TEM images of films on carbon-coated grids and histograms of particle sizes.



Figure 3.1. (a) TEM image of a  $[PAA-Pd(0)/PEI]_3$  film on a carbon-coated copper grid. 1 mM Pd(II) was present in the PAA-K<sub>2</sub>PdCl<sub>4</sub> solution used for film deposition. A few of the NPs are circled. (b) Histogram of Pd NP diameters in several TEM images. The average particle size is 2.2±0.6 nm. The area-average particle size is 2.5±0.7 nm.



Figure 3.2. (a) TEM image of a [PAA-Pd(0)/PEI]<sub>3</sub> film on a carbon-coated copper grid. 4 mM Pd(II) was present in the PAA-K<sub>2</sub>PdCl<sub>4</sub> solution used for film deposition. A few NPs are circled. (b) Histogram of Pd NP diameters in several TEM images. The average particle size is  $3.0\pm0.5$  nm.



Figure 3.3. (a) TEM image of a [PAA-Pd(0)/PEI]<sub>3</sub> film on a carbon-coated copper grid. 8 mM Pd(II) was present in the PAA-K<sub>2</sub>PdCl<sub>4</sub> solution used for film deposition. (b) Histogram of Pd NP diameters in several TEM images. The average particle size is 3.2±0.6 nm. The area-average particle size is 3.5±0.7 nm.





Figure 3.4. (a) TEM image of a [PAA-Pd(0)/PEI]<sub>3</sub> film on a carbon-coated copper grid. 15 mM Pd(II) was present in the PAA-K<sub>2</sub>PdCl<sub>4</sub> solution used for film deposition. (b) Histogram of Pd NP diameters in several TEM images. The average particle size is 3.4±1.3 nm. The area-average particle size is 3.8±1.1 nm.

With Pd(II) concentrations of 1, 4, 8, or 15 mM in the PAA deposition solutions, the average particle diameters in [PAA-Pd(0)/PEI]<sub>3</sub> films on TEM grids are 2.2±0.6,  $2.9\pm0.5$ ,  $3.2\pm0.6$ , and  $3.4\pm0.9$  nm, respectively. Area-average particle sizes might be more representative of catalytic activities because larger particles make up a disproportionate share of the total catalyst surface area. We calculate the area-average diameters, D<sub>A</sub>, using equation 1, where D<sub>i</sub> represents the diameters of individual particles.

$$D_A = \frac{\sum_{i} D_i D_i^2}{\sum_{i} D_i^2} \tag{1}$$

Values of  $D_A$  are 2.5±0.7, 3.1±0.5, 3.5±0.7, and 3.8±1.1 nm for films prepared using 1, 4, 8, and 15 mM Pd(II), respectively, in the 20 mM PAA deposition solutions. Occasionally, TEM images of [PAA-Pd(0)/PEI]<sub>3</sub> films prepared with 15 mM Pd(II) in the PAA deposition solutions exhibit areas containing large particles with average diameters of 160±100 nm (Figures 3.5). We did not include these larger particles in the calculation of average particle diameters because they constitute only about 18 % of the total particle surface area (Table 3.2), and we are not sure whether they are representative of all samples. However, the absolute values of TOFs for catalysis with alumina-supported [PAA-Pd(0)/PEI]<sub>3</sub> films that are prepared using 15 mM Pd(II) should be viewed with caution.



Figure 3.5. Low-magnification TEM images of large particles and NPs in [PAA-Pd(0)/PEI]<sub>3</sub> films on carbon-coated copper grids. The films were prepared with 15 mM Pd(II) in the PAA deposition solution. (a) Image showing large particles with diameters of 160±100 nm, as determined from several TEM images. Such large particles appeared in ~30% of similar images. (b) Image of NPs. Larger spots are overlapping multiple particles. The dark spot in the center of low-magnification images is due to a defect in the lens where it was burned by the electron beam.

**Table 3.2.** Calculation of the relative surface area of large (ranging from ~50-300 nm) particles and NPs (< 5 nm) in [PAA-Pd(0)/PEI]<sub>3</sub> films and reduced [PdCl<sub>4</sub><sup>2-</sup>/PEI]<sub>3</sub> films on carbon-coated TEM grids. The initial concentration of Pd(II) was 15 mM in the solution containing PAA-PdCl<sub>4</sub><sup>2-</sup> or PdCl<sub>4</sub><sup>2-</sup>. Large particles were not prevalent when using lower concentrations of Pd(II).

Specific Descriptions	% occupy by big particles and NPs		
	[PAA- Pd(0)/PEI] <sub>3</sub>	[PdCl4 <sup>2-</sup> /PEI] <sub>3</sub>	
Average percentage of image area covered by large particles (when present)	~11%	~11%	
Percentage of low-magnification images containing large particles	~30%	~60%	
Percentage of image area covered by large particles in all low-magnification images (including images with and without large particles)	~3 %	~7 %	
Average percentage of image area covered by NPs (determined from high magnification images)	~14 %	~14 %	
Fraction of total Pd surface area due to small NPs (determined from the image areas covered by large and small NPs) <sup>a</sup>	0.82	0.67	

[a] Because both the surface area of a particle and the image area it covers are proportional to the square of the particle diameter, the fraction of the total Pd surface area due to NPs is equivalent to the image area covered by NPs divided by the sum of the image areas covered by NPs (< 5 nm) and larger particles (ranging from  $\sim$  50-300 nm).

Although we use films deposited on alumina particles for catalysis, we perform the TEM analyses with films on carbon-coated Cu grids because it is very difficult to visualize NPs on the rough alumina microparticles. The NPs likely have similar diameters on the TEM grids and on the alumina, but we cannot verify the diameters of particles on alumina. To address this problem, we also prepare polyelectrolyte/NP composites in water. These materials serve as catalysts and are amenable to TEM imaging, which allows a direct correlation between catalytic activity and particle size. A recent study showed that in many cases, NPs in water do not aggregate in the presence of polyelectrolytes.<sup>34</sup>

The preparation of the suspended polyelectrolyte/NP composites includes the addition of an aqueous solution of PEI (1 mg/ml, pH adjusted to 9) to a solution of PAA (20 mM, pH adjusted to 4) that contains various concentrations of K<sub>2</sub>PdCl<sub>4</sub> (1, 4, 8, or 15 mM). The yellow-colored PAA-Pd(II) solution becomes cloudy after addition of PEI and then turns to a clear brown color after addition of 0.1 M aqueous NaBH<sub>4</sub> and vigorous stirring. The pH of the PAA-Pd(II)/PEI mixture is about 5, but the addition of 0.1 M NaBH<sub>4</sub> gives a clear solution with a pH of ~9. Raising the pH of PAA-Pd(II)/PEI solutions by addition of 0.1 M NaOH also yields a clear solution, presumably because less protonation of PEI results in weaker PAA/PEI complexes. However, both polyelectrolytes are important for stabilizing the NPs. Addition of 0.1 M NaBH<sub>4</sub> to solutions containing either PAA and 8 mM Pd(II) or PEI and 8 mM Pd(II) produces a black precipitate.

To determine the sizes of NPs suspended in these solutions, we deposit a drop of solution on a carbon-coated copper grid and then image the NPs with TEM. These TEM images along with histograms of particle sizes (Figures 3.6, 3.7, 3.8, 3.9) indicate the formation of NPs whose size is a function of the concentration of Pd(II) in solution prior to reduction. In this case, the average particle diameters that result from the use of 1, 4, 8, and 15 mM Pd(II) to form NPs are  $2.6\pm0.8$ ,  $3.2\pm0.7$ ,  $3.5\pm0.7$  and  $5.1\pm1.3$  nm, respectively. Corresponding area-average diameters are  $3.1\pm0.8$ ,  $3.4\pm0.7$ ,  $3.7\pm0.7$  and  $5.8\pm1.4$  nm. We do not observe any large (>9 nm) particles in PAA-Pd(0)/PEI solutions

prepared with Pd(II) concentrations of 15 mM in the PAA deposition solutions (Figure 3.10).



**Figure 3.6.** (a) TEM image of a dried PAA-Pd(0)/PEI solution on a carbon-coated copper grid. 1 mM Pd(II) was initially present in the PAA solution. (b) Histogram of Pd NP diameters in several TEM images. The average particle size is  $2.6\pm0.8$  nm. The area-average particle size is  $3.1\pm0.8$  nm.



**Figure 3.7.** (a) TEM image of a [PAA-Pd(0)/PEI] solution on a carbon-coated copper grid. 4 mM Pd(II) was initially present in the PAA-PdCl<sub>4</sub><sup> $\circ$ </sup> solution. (b) Histogram of Pd NP diameters in several TEM images. The average particle size is 3.4±0.7 nm. The area-average particle size is 3.4±0.7 nm.


**Figure 3.8.** (a) TEM image of a dried PAA-Pd(0)/PEI solution on a carbon-coated copper grid. 8 mM Pd(II) was initially present in the PAA solution. (b) Histogram of Pd NP diameters in several TEM images. The average particle size is  $3.5\pm0.7$  nm. The areaaverage particle size is  $3.7\pm0.7$  nm.



**Figure 3.9.** (a) TEM image of a [PAA-Pd(0)/PEI] solution on a carbon-coated copper grid. 15 mM Pd(II) was initially present in the PAA-PdCL<sup>2</sup> solution. (b) Histogram of Pd NP diameters in several TEM images. The average particle size is  $5.1\pm1.3$  nm. The area-average particle size is  $5.8\pm1.4$  nm.



Figure.3.10. (a) TEM image of a dried PAA-Pd(0)/PEI solution on a carbon-coated copper grid. 15 mM Pd(II) was initially present in the PAA solution. This image was taken at a relatively low magnification to show the distribution of NPs and the absence of large particles on the TEM grid. The dark spot in the center of low-magnification images is due to a defect in the lens where it was burned by the electron beam.

#### 3.3.2. Selective Hydrogenation with Films on Alumina Particles

To investigate catalytic selectivity as a function of NP diameter, we first investigated hydrogenation of allyl alcohol (1, a monosubstituted unsaturated alcohol), 2methyl-2-propen-1-ol (2, a disubstituted unsaturated alcohol), and crotyl alcohol (3, a disubstituted unsaturated alcohol). TOFs (moles hydrogenated/mol Pd/h) at low substrate conversion provide a quantitative comparison of the reactivities and selectivities of the different catalysts. Unfortunately, interpretation of the TOFs is complicated by isomerization of the unsaturated alcohols to the corresponding aldehydes, which are not readily hydrogenated. Thus, Table 3.3 contains TOFs for initial hydrogenation along with values in parentheses that reflect the sum of the initial hydrogenation and initial isomerization TOFs. Isomerization is most extensive for 2, presumably because its isomer is a trisubstituted unsaturated alcohol that is more stable than 2 and readily tautomerizes to the corresponding aldehyde.

Table 3.3 shows that regardless of NP size, both the TOF for hydrogenation and the combined hydrogenation/isomerization TOF are higher for 1 than for 2 and 3, which contain disubstituted double bonds. In addition, selectivity varies dramatically with the particle size. The general trend in Table 3.3 is that the rate of hydrogenation of 1 (column 3) decreases with increasing NP size, while the corresponding TOFs for 2 (column 4) and 3 (column 5) increase with increasing NP size, even though the surface area to volume ratio for the catalyst is smaller for larger particles. Most remarkably, this trend yields selectivities (ratios of TOFs for different compounds, columns 6 and 7 of Table 3.3) that are as much as 90-fold larger with the smallest NPs than with the largest. These trends also hold when considering the sum of hydrogenation and isomerization. The selectivities for 1/2 and 1/3 with the smaller NPs are especially notable because Wilkinson's catalyst, the prototypical homogeneous catalyst for selective hydrogenation, shows essentially no selectivity in the hydrogenation of mono- and disubstituted double bonds.<sup>23,35</sup>

**Table 3.3.** TOFs and TOF ratios for unsaturated-alcohol hydrogenation catalyzed by  $[PAA-Pd(0)/PEI]_3$  films that contain Pd NPs with different diameters. The catalytic films were deposited on micron-sized alumina. Values in parentheses are the sums of TOFs for hydrogenation and isomerization.

	Average nano-	TOFs (moles	TOFs (moles hydrogenated/ mol Pd/ h) <sup>a</sup>			
Catalyst	particle diameter (nm)	= <sub>ОН</sub> 1	=< <sub>ОН</sub> 2	/— <sub>ОН</sub> 3	1/2	1/3
Catalyst A	2.2	2900±570	12±1	75±15	240	39
[Pd(II)]=1 mM <sup>b</sup>		(6200±2400)	(85±5)	(85±15)	(73)	(73)
Catalyst <b>B</b>	2.9	1700±830	160±10	450±80	11	3.8
[Pd(II)]=4 mM <sup>b</sup>		(4100±1800)	(730±20)	(620±130)	(5.6)	(6.6)
Catalyst C	3.2	1100±300	165±5	610±60	6.7	1.8
[Pd(II)]=8 mM <sup>b</sup>		(2400±800)	(895±15)	(760±80)	(2.7)	(3.2)
Catalyst <b>D</b>	3.4	760±40	290±70	580±100	2.6	1.3
[Pd(II)]=15 mM <sup>b</sup>		(2050±80)	(1400±100)	(790±160)	(1.5)	(2.6)

[a] 50 mL of 25 mM substrate was hydrogenated in water. TOFs are initial values determined at conversions less than 50%. [b] The initial concentration of  $K_2PdCl_4$  in the PAA deposition solutions.

Several studies show that polyelectrolyte multilayers provide a significant barrier to the diffusion of small compounds, and even molecules as small as glycerol and methanol show much slower transport than water in polyelectrolyte films.<sup>36</sup> Thus, one possible explanation for the high selectivities of NPs in polyelectrolyte films is that the polyelectrolytes decrease the rate at which bulkier molecules reach catalytic sites. To examine whether simple diffusion through polyelectrolyte films enhances selectivity, we coated films containing the smallest and largest NPs with additional layers of polyelectrolytes. Pd was reduced prior to the deposition of additional layers. As comparison of Table 3.3 and Table 3.4 shows, addition of three PAA/PEI bilayers on the

**Table 3.4.** TOFs and TOF ratios for unsaturated-alcohol hydrogenation catalyzed by  $[PAA-Pd(0)/PEI]_3/(PAA/PEI)_3$  films that contain Pd NPs with different diameters. The films were deposited on micron-sized alumina. Values in parentheses are the sums of TOFs for hydrogenation and isomerization.

	Average nano-	TOFs (moles h	Ratio of TOFs			
Catalyst	particle diameter (nm)	—_ <sub>ОН</sub> 1	=<он 2	/ОН 3	1/2	1/3
Catalyst E	2.2	1500±250	10±1	35±5	150	43
[Pd(II)]=1 mM <sup>b</sup>		(3000±1000)	(40±5)	(40±5)	(75)	(75)
Catalyst F [Pd(II)]=15 mM <sup>b</sup>	3.4	1200±90 (2600±600)	85±5 (370±15)	400±5 (540±35)	14 (7.0)	3.0 (4.8)

[a] 25 mM substrate was hydrogenated in water. TOFs are initial values determined at conversions less than 50%. [b] The initial concentration of  $K_2PdCl_4$  in the PAA deposition solutions.

top of a film containing 2.2 nm-diameter particles does not have a large effect on the relative TOFs of 1 and 2 or 1 and 3, although the magnitudes of TOF values decrease by a factor of  $\sim$ 2. Addition of three PAA/PEI bilayers to films containing NPs with a diameter of 3.4 nm increases selectivity as much as 6-fold, but the selectivity of these catalysts is still 11-(1/2) and 15-fold (1/3) lower than that with the 2.2-nm NPs (Table 3.4). These data suggest that the most important factor behind selectivity is NP size.

To further demonstrate that NP size is the primary factor behind selectivity, we studied catalysis with reduced  $[PdCl_4^{2^-}/PEI]_3$  coatings on alumina. (The nomenclature  $PdCl_4^{2^-}$  reflects deposition conditions and not the state of Pd in the films). These NP-containing films should be more permeable than [PAA-Pd(0)/PEI] coatings because they contain only one polyelectrolyte.<sup>25</sup> After reduction of the Pd(II) in these films, the average particle size is  $3.4\pm0.8$  nm when using 15 mM PdCl<sub>4</sub><sup>2-</sup> to prepare the films and





Figure 3.11. (a) TEM image of a  $[Pd(0)/PEI]_3$  film on a carbon-coated copper grid. The concentration of  $PdCl_4^{2*}/PEI]_3$  film was 1 mM. (b) Histogram of Pd NP diameters in several TEM images. The average particle size is 3.040.9 nm. The area-average particle size is 3.5±1.0 nm.





**Figure 3.12.** (a) TEM image of a [Pd(0)/PEI]<sub>3</sub> film on a carbon-coated copper grid. The concentration of PdCl<sub>4</sub><sup>2</sup> used in depositing the precursor [PdCl<sub>4</sub><sup>2</sup>/PEI]<sub>3</sub> films was 15 mM. (b) Histogram of Pd NP diameters in several TEM images. The average particle size is 3.4±0.8 m. The area-average particle size is 3.4±0.9 m.



Figure 3.13. (a) Low-magnification TEM image of a reduced [PdCl<sub>4</sub><sup>-2</sup>/PEI]<sub>3</sub> film on a carbon-coated copper grid. 15 mM PdCl<sub>4</sub><sup>-2</sup> was initially present in the deposition solution. The average size of these large particles in several TEM images is 170±110 nm. Large particles are visible in about 60% of these low-magnification images, but we estimate that the surface area of the large particles constitutes  $\sim$ 33% of the surface area in the film (Table 3.2).

 $3.0\pm0.9$  nm when using a 1 mM PdCl4<sup>2-</sup> solution (See Figures 3.11 and 3.12). Corresponding area-average diameters are  $3.8\pm0.9$  and  $3.5\pm1.0$  nm respectively. In this case, NP sizes are not very different because PdCl4<sup>2-</sup> does not bind to a polymer in solution before adsorbing to the film, but rather adsorbs directly to the polyelectrolyte film. Because the amount of adsorbed PdCl4<sup>2-</sup> in PdCl4<sup>2-</sup>/PEI films is somewhat self-limiting as the film becomes negatively charged, PdCl4<sup>2-</sup> concentration should not have a dramatic effect on the amount of Pd in the film. However, in some areas of reduced

 $[PdCl_4^{2-}/PEI]_3$  films prepared with 15 mM Pd(II), TEM images show the presence of large particles (average particle size 170±110 nm) as well as NPs (Figure 3.13). We estimate that the large particles represent ~33 % of the total Pd surface area. We did not include these larger particles in the calculation of average particle diameters because we are not sure whether they are representative of all samples. The absolute values of TOFs for catalysis with reduced  $[PdCl_4^{2-}/PEI]_3$  films that are prepared using 15 mM Pd(II) should, thus, be viewed with caution.

Table 3.5 summarizes the TOFs for the hydrogenation of 1, 2 and 3 using the two different reduced [PdCl<sub>4</sub><sup>2-</sup>/PEI] films on alumina. The smaller NPs in catalyst **G** give selectivities that are an order of magnitude higher than hydrogenation using catalyst **H**, even though the average NP diameters in the two catalysts differ by only 0.40 nm.

**Table 3.5.** TOFs and TOF ratios for unsaturated-alcohol hydrogenation catalyzed by reduced  $[PdCl_4^2/PEI]_3$  films that contain Pd NPs with different diameters. The films were deposited on micron-sized alumina. Values in parentheses are the sums of TOFs for hydrogenation and isomerization.

	•	TOFs (mole	Ratio of TOFs			
Catalyst	Avarage nano- particle diameter (nm)	= <sub>ОН</sub> 1	2_он	лана (С. 1996) З	1/2	1/3
Catalyst G	3.0	2230±70	25±5	220±40	89	10
$[Pd(II)]=1 mM^{b}$		(4600±38 0)	(150±40)	(250±40)	(30)	(19)
Catalyst H	3.4	880±110	380±110	580±80	2.3	1.5
$[Pd(II)]=15 \text{ mM}^{b}$		(2300±10 0)	(1700±350)	(750±100)	(1.4)	(3.1)

[a] 25 mM substrate was hydrogenated in water. TOFs are initial values determined at conversions less than 50%. [b] The initial concentration of  $K_2PdCl_4$  in the deposition solutions.

# 3.3.3. Hydrogenation with NP/Polyelectrolyte Complexes in Solution

Because we cannot effectively image NP catalysts on alumina, we also examined hydrogenation with suspended PAA-Pd(0)/PEI catalysts prepared by addition of a PEI (1 mg/mL) solution to 20 mM PAA solutions containing different concentrations of Pd(II). Reduction of the Pd(II) with NaBH<sub>4</sub> yields suspended PAA-Pd(0)/PEI catalysts with a variety of Pd NP sizes. One concern when using these NPs is that excess NaBH<sub>4</sub>, which is not removed from the NP solution, might promote side reactions. As a control experiment, we attempted reduction of allyl alcohol in the absence of hydrogen gas using the PAA-Pd(0)/PEI solution containing excess NaBH<sub>4</sub>. No reaction occurs, which rules out the possibility of NaBH<sub>4</sub> participating in side reactions.

Similar to catalysis by NP films on alumina, with the PAA-Pd(0)/PEI solution, the TOF for catalytic hydrogenation of 1 decreases with increasing particle size, whereas the TOFs for 2 and 3 either increase or remain approximately constant as particle size increases (Table 3.6). Thus, overall selectivity shows an order of magnitude decrease on going from an average NP diameter of 2.6 nm to 5.1 nm. Comparison of Tables 3.3, 3.4, 3.5 and 3.6 shows that selectivities are frequently higher for these suspended NPs than they are for [PAA-Pd(0)/PEI]<sub>3</sub> and reduced [PdCl<sub>4</sub><sup>2-</sup>/PEI]<sub>3</sub> films on alumina. The suspended NPs in solution may present a more uniform set of catalytic sites than the films on alumina powder, which might favor high selectivity. In general, supported catalysts are complex materials due to the presence of many types of potential active sites.

**Table 3.6.** TOFs and TOF ratios for unsaturated-alcohol hydrogenation catalyzed by solutions of PAA-Pd(0)/PEI that contain Pd NPs with different diameters. Values in parentheses are the sum of TOFs for hydrogenation and isomerization.

		Ratio	of TOFs			
Catalyst	Average nano- particle diameter (nm)		=<он	<u>з</u> -он	1/2	1/3
Catalyst I	2.6	3700±860	12	30±10	310	120
[Pd(II)]=1 mM <sup>b</sup>		(5800±1900)	(75±5)	(35±15)	(73)	(170)
Catalyst <b>J</b>	3.2	1600±190	12	45±5	130	35
[Pd(II)]=4 mM <sup>b</sup>		(2900±600)	(50±5)	(50±10)	(59)	(59)
Catalyst <b>K</b>	3.5	1100±560	12±4	35±5	95	33
[Pd(II)]=8 mM <sup>b</sup>		(2400±950)	(60±5)	(45±5)	(40)	(54)
Catalyst L	5.1	890±210	30±10	80±15	30	10
[Pd(II)]=15 mM <sup>b</sup>		(1700±350)	(100±15)	(100±15)	(16)	(18)

[a] 25 mM substrate was hydrogenated in water. TOFs are initial values determined at conversions less than 50%. [b] The initial concentration of  $K_2PdCl_4$  in the PAA deposition solutions.

#### **3.3.4.** Solvent Effects on Hydrogenation

Previous studies of catalytic hydrogenation showed that variations in solvent can lead to changes in reaction rates, differences in the extent of double-bond isomerization, or changes in selectivity.<sup>23,24,27,37,38</sup> Presumably, molecules of solvents such as MeOH, EtOH and THF adsorb to the catalyst to alter reactivities. Additionally, swelling of polyelectrolyte films in water may increase reaction rates.<sup>39</sup> We examined hydrogenation with catalysts A and D using solvents consisting of 3 parts water and 1 part of either MeOH or EtOH or THF. These two catalysts represent the widest range of particle diameters among the NPs deposited on alumina. Table 3.7 summarizes the TOFs for hydrogenation of **1**, **2**, and **3** in different mixed solvents. For catalyst **D** (average particle diameter of 3.4 nm), the rate of hydrogenation for all of the compounds decreases in the

	· · · · · · · · · · · · · · · · · · ·	TOFs (moles h	Ratio of TOFs			
Catalysts Solvent Mixtures				<u>з</u> -он	1/2	1/3
	Water & MeOH (3:1)	1400±100 (2500±250)	4 (30±10)	15±5 (20±5)	350 (83)	93 (125)
Catalyst A <sup>b</sup> [Pd(II)]=1 mM <sup>c</sup>	Water & EtOH (3:1)	1600±400 (2900±650)	6±1 (45±5)	40±5 (45±5)	267 (64)	40 (64)
	Water & THF (3:1)	600±200 (1050±50)	-	25±15 (-)	-	24 (-)
	Water & MeOH (3:1)	1200±350 (3900±1150)	280±5 (1400±200)	700±100 (1050±20 0)	4.3 (2.8)	1.7 (3.7)
Catalyst D <sup>b</sup> [Pd(II)]=15 mM <sup>c</sup>	Water & EtOH (3:1)	810±320 (2900±1100)	220±10 (1500±220)	400±100 (660±160)	3.7 (1.9)	2.0 (4.4)
111141	Water & THF (3:1)	300±60 (1300±390)	-	250±20 (-)	-	1.2 (-)

**Table 3.7.** TOFs and TOF ratios for unsaturated-alcohol hydrogenation catalyzed by  $[PAA-Pd(0)/PEI]_3$  films in different solvents. The films contain Pd NPs with different diameters and are deposited on micron-sized alumina. Values in parentheses are the sum of TOFs for hydrogenation and isomerization.

[a] Several TOFs could not be estimated because GC signals of the substrates, products, or isomers overlapped with the very large peaks corresponding to solvents. [b] Average nanoparticle sizes in catalysts A and D are 2.2 and 3.4 nm respectively. [c] The initial concentration of  $K_2PdCl_4$  in the PAA deposition solutions.

order water > water/methanol, water/ethanol > water/THF, which may reflect the degree of swelling of the polyelectrolyte. Higher swelling in more polar solvents should lead to higher reaction rates. With catalyst A, TOFs are higher in water (data in Table 3.3) than the mixed solvent systems (Table 3.7), but there is no clear trend in the different solvents. Table 6 shows that in most cases, selectivities are higher in 3:1 water/methanol than any of the other solvents. The small methanol molecules might more effectively compete for binding sites with 2 and 3 than with 1.

# 3.3.5. Hydrogenation of Other Unsaturated Alcohols

To examine the generality of these results, we studied the hydrogenation of several additional molecules using catalysts A and D, which have approximate NP diameters of 2.2 and 3.4 nm, respectively. As Table 3.8 shows, the rate of hydrogenation of compounds 4-7 decreases in the order monosubstituted double bonds>disubstituted double bond> trisubstituted double bonds. (These reactions occur in 3:1 water/ethanol to ensure substrate solubility.) Compounds 4 and 1 both contain a monosubstituted double bond, but in 3:1 water:ethanol, hydrogenation of 4 by catalyst A occurs at a slower rate than hydrogenation of 1 (compare Tables 3.7 and 3.8). Nevertheless, the TOF for the hydrogenation of 4 is still 11 times higher than that for 6, which contains a disubstituted double bond. Interestingly, using the smaller NPs, the TOF for hydrogenation of 5 is 11fold lower than that for hydrogenation of 1 in 3:1 water:ethanol. This suggests that when using the smaller NPs, rates are affected by the addition of a bulky substituent  $\alpha$  to the double bond, which is consistent with previous studies.<sup>24</sup> However, even with 5, hydrogenation using catalyst A is much faster than with the di and trisubstituted compounds 2, 3, 6 and 7. In contrast, catalyst D, which has much larger NPs, shows little difference in the TOFs among the molecules containing monosubstituted double bonds (1, 4, and 5). Furthermore, selectivities for hydrogenation of 4 and 5 vs di and trisubstituted double bonds (6 and 7, respectively) are much smaller when using the larger NPs in catalyst **D** than when using catalyst **A**.

**Table 3.8.** TOFs and TOF ratios for unsaturated-alcohol hydrogenation catalyzed by  $[PAA-Pd(0)/PEI]_3$  films that contain Pd NPs with different diameters. The catalytic films were deposited on micron-sized alumina. Values in parentheses are the sum of TOFs for hydrogenation and isomerization.

• 1929	TOFs (moles hydrogenated/ mol Pd/ h) <sup>a,b</sup>							
Catalysts	СОН	СН	он	OH				
	4	5	6	7				
Catalyst A <sup>c</sup> [Pd(II)]=1 mM <sup>d</sup>	290±10 (450±10)	150±30 (-)	27±3 (-)	8±2 (-)				
Catalyst <b>D<sup>c</sup></b> [Pd(II)]=15 mM <sup>d</sup>	895±45 (2175±65)	760±10 (-)	233±2 (-)	130±10 (150±5)				

[a] 25 mM substrate was hydrogenated in 3:1 water:ethanol. TOFs are initial values determined at conversions less than 50%. [b] In some cases, the TOF was not estimated because the amount of isomer detected was negligible. [c] Average nanoparticle sizes for catalysts A and D are 2.2 and 3.4 nm respectively. [d] The initial concentration of  $K_2PdCl_4$  in the PAA deposition solutions.

### 3.4. Possible Explanation of Selectivity

The above data demonstrate that selectivity in hydrogenation varies greatly with particle size, and related studies of NP reactivity imply that such trends arise from geometrical effects.<sup>40</sup> Doyle, et al. suggest that the sensitivity of catalytic hydrogenation rates to NP size occurs because the reaction takes place on specific types of atoms that are more (or less) prevalent on small particles.<sup>2</sup> Large particles mainly contain terraces with atoms of high coordination numbers, whereas small particles contain comparatively high numbers of surface atoms with low coordination numbers (edge and corner atoms). A recent study based on STM images shows that Pd NPs with diameters <4 nm are highly defective, whereas NPs with diameters >4 nm start to develop large and well defined facets.<sup>21,41</sup> Additionally, in some cases, if a TOF is calculated with respect to a



Scheme 3.1. Cuboctahedra Pd NP with different atoms.

defined type of atom (edge atoms, for example), the dependence of TOF on particle size disappears, and the reaction is deemed structure-sensitive but size-independent.<sup>8,17,21</sup>

Using the Van Hardeveld and Hartog statistics, we calculated the number of different types of surface atoms on cuboctahedra Pd NPs (Scheme 3.1) containing the same number of atoms as average NPs in catalysts I, J, K and L (NPs suspended in polyelectrolyte solutions) (Table 3.9).<sup>42</sup> Figure 3.14 presents the calculated percentage of surface, defect (edge and corner), and face atoms with respect to the total atoms for each average particle size and shows that the percentage of face atoms changes minimally (from 26% to 20%) as the average particle size increases from 2.6 to 5.1 nm. However, the percentage of defect atoms decreases from 18% to 5% as the average particles size increases from 2.6 to 5.1 nm. In general, the TOFs for hydrogenation of monosubstituted compounds decrease with increasing NP diameter, while the TOFs for di- and trisubstituted compounds increase slightly or are unaffected as NP size increases. One

Total no. of atoms	$(1/3)(2m-1)(5m^2-5m+3)$
No. of surface atoms	10m <sup>2</sup> -20m+12
Vertex atoms (5-coordinate)	12
Edge atoms (7-coordinate)	24(m-2)
Sq. face (8-coordinate)	$6(m-2)^2$
Triangular face (9-coordinate)	4(m-3)(m-2)

**Table 3.9.** Formula used to calculate m, the number of shells for NPs having cuboctahedron geometry, and the number of Pd atoms at the various positions available on NP surfaces.<sup>42</sup>

The total number of atoms (N) was calculated by the following equation<sup>1</sup> N =  $4\pi(r)^3/(3V_g)$ , where Vg = the volume of one Pd atom =15 Å<sup>3</sup>

explanation for this observation is that in the hydrogenation of monosubstituted double bonds, defect atoms are the primary active centers for catalysis, whereas hydrogenation of multisubstituted double bonds occurs on terraces. Hence, TOFs for the monosubstituted compounds increase as NP size decreases because of a larger fraction of defect atoms in the small NPs. Several recent studies show that interactions of alkenes with catalysts change with alkene size, and hydrogenation of higher alkenes such as *trans*-2-pentene takes place on face atoms.<sup>2,5,43</sup> Rates of hydrogenation on terrace sites should be much less dependent on particle size because the fraction of total atoms that are on terraces is relatively independent of the NP diameter. Thus, it is possible that preferential hydrogenation of monosubstituted double bonds on defect sites leads to high selectivities with small NPs.



Figure 3.14. Plot of the calculated percentage of surface, defect and face atoms with respect to the total atoms for each particle size.

#### 3.5. Conclusion

Selectivity in the hydrogenation of monosubstituted over disubstituted double bonds increases dramatically as the diameter of catalytic NPs decreases, and this sizedependent selectivity occurs with both suspended NPs and NPs deposited on micronsized alumina. High selectivities stem from the fact that TOFs for the hydrogenation of monosubstituted double bonds decrease as particle size increases, whereas the TOFs for the hydrogenation of multisubstituted double bonds show the opposite trend. When using the smallest NPs (average diameters 2.2 nm), these trends result in selectivities >100 for the hydrogenation of monosubstituted over disubstituted double bonds. Selectivities might occur because monosubstituted double bonds are hydrogenated on defect sites, while hydrogenation of multisubstituted double bonds takes place on terraces.

# 3.6. References

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#### **CHAPTER 4**

# CHEMOSELECTIVE NITROARENE HYDROGENATION CATALYZED BY PALLADIUM NPs EMBEDDED IN POLYELECTROLYTE MULTILAYERS

# 4.1. Introduction

Functionalized aniline derivatives are important synthetic intermediates in the production of dyes, herbicides, pesticides, and pharmaceuticals, and aromatic nitro compounds routinely serve as precursors to their corresponding anilines.<sup>1-7</sup> The transformation of nitrobenzene to aniline proceeds through intermediate nitroso and hydroxylamine compounds,<sup>8</sup> but slow conversion of hydroxylamine to aniline sometimes results in the accumulation of hydroxylamine,<sup>9-12</sup> as well as the formation of hydrazines,<sup>13,14</sup> azoarenes<sup>15</sup> or azoxyarenes.<sup>16-21</sup> Reduction of other functional groups in nitroaromatic compounds can also lead to undesired side products.<sup>22,23</sup>

Transformation of nitro compounds to aromatic amines is generally accomplished through catalytic reduction<sup>22,24-26</sup> or hydrogenation,<sup>1,23,27-33</sup> although electrochemical<sup>34</sup> or enzymatic reactions have also been used.<sup>35,36</sup> Stoichiometric reagent-based processes are selective towards the reduction of the nitro functional group, but such processes are frequently expensive and not environmentally friendly. The catalytic hydrogenation of nitroarenes using molecular hydrogen is both a clean and convenient method, but the chemoselective hydrogenation of a nitro group in the presence of other reducible groups is sometimes challenging. Catalytic hydrogenation by H<sub>2</sub> is typically less chemoselective than stoichiometric methods.<sup>2</sup> Thus, a number of recent studies aimed at developing new catalysts and protocols for chemoselective hydrogenation of nitroarenes with H<sub>2</sub>.

Several methods for chemoselective hydrogenation of nitroarenes catalyzed by supported Pd catalysts were reported.<sup>27,37-39</sup> Holy, et al. use polystyrene-supported anthranilic acid to anchor a Pd(II) complex for the hydrogenation of aromatic nitro compounds at temperatures ranging from 90-100°C and pressures ranging from 400-1000 psi.<sup>38</sup> The reaction times vary from 1 h to 15 h, but hydrogenation of nitrobenzene for 48 h affords only 60% aniline at room temperature and 60 psi pressure. Nitro compounds with different reducible functional groups were not tested in this study. Fréchet, et al.. described a polybenzimidazole-supported Pd(0) catalyst for hydrogenation of nitrobenzene at room temperature and under 45 psi H<sub>2</sub> pressure.<sup>39</sup> However, this catalyst was also not used for hydrogenation of various aromatic nitro compounds containing other reducible functional group. Choudary, et al. showed the use of a montmorillonitesilylpalladium (II) complex for chemoselective hydrogenation of nitro aromatic compounds at room temperature in EtOH, which is illustrated in Scheme 4.1. However, the preparation of the montmorillonitesilylpalladium (II) complex requires a long procedure as shown in scheme 4.2.<sup>37</sup>



**Scheme 4.1.** Chemoselective hydrogenation of aromatic nitro compounds by a montmorillonitesilylpalladium (II) complex.<sup>37</sup>



Scheme 4.2. Preparation of a montmorillonitesilylpalladium (II) complex.

As mentioned in previous chapters, metal NPs are frequently better catalytic materials than bulk metals because of their high surface area to volume ratio and their size-dependent electronic properties.<sup>40-42</sup> The use of metal NPs for the chemoselective reduction of nitroarene derivatives recently attracted tremendous interest.<sup>22-24,28,30,31,43,44</sup> Recent work by Serna, et al. published in *Science* shows that titania-supported gold NPs provide selectivity for nitro group hydrogenation in the presence of C=C, C=O, and C=N functional groups. However, these reactions occur under high temperature (110-140°C) and pressure (9-25 bar) with relatively long reaction times (0.03 to 9.5 h).<sup>31</sup> Ranu, et al. used Cu NPs and ammonium formate in ethylene glycol for reduction of aromatic nitro compounds with high chemoselectivity. However, these reactions take place under high temperature (120°C) and very long reaction times (8-12 h).<sup>24</sup>

Pd NPs, in particular, generated in situ<sup>22</sup> or supported on nanofibers<sup>23</sup> are used for reduction of nitro compounds. Maleczka, et al. prepared Pd NPs *in situ* using polymethylhydrosiloxane (PMHS), palladium (II) acetate, and aqueous potassium fluoride. Pd NPs generated in situ chemoselectively reduce aromatic nitro compounds in a high yield with short reaction times (30 min). However, in some cases either reduction of aromatic nitro compounds is not highly chemoselective (see scheme 4.3) or the reduction stops at an intermediate stage. Motoyama, et al. prepared Pd and Pt NPs supported on carbon nanofiber catalyst and used them for chemoselctive hydrogenation of several aromatic nitro compounds containing other reducible functional groups. However, the reactions took place under high pressure (10 atm) and required relatively long times (4 h) to complete. Additionally, in this case, hydrogenation of aromatic nitro compounds is not always highly chemoselective as shown in scheme 4.4. Therefore, an alternative efficient yet simple chemoselective procedure is highly desirable.



Scheme 4.3. Silicon hydride reduction of nitro benzaldehyde catalyzed by Pd NPs generated *in-situ*.<sup>22</sup>



Scheme 4.4. Chemoselective hydrogenation of p-nitrobenzonitrile catalyzed by Pd NPs on a carbon nanofiber.<sup>23</sup>

This chapter describes a very simple, room-temperature protocol for highly chemoselective hydrogenation of aromatic nitro compounds containing other readily reducible functional groups. The procedure uses the catalytic  $[PAA-Pd(0)/PEI]_3$  films described in previous chapters and a new catalyst prepared by reducing  $PdCl_4^{2-}$  impregnated in alumina. These catalysts show nearly complete selectivity for hydrogenation of nitro groups in the presence of aldehyde, nitrile, amide, ketone, and ester groups.

# 4.2. Experimental

# 4.2.1. Materials

Poly(ethylenimine) (PEI, Mw = 25 000 Da), poly(acrylic acid) (PAA, Mw = 90 000 Da), α-alumina (100 mesh, typical particle size 75-100 µm), potassium tetrachloropalladate(II) (99.99%), sodium borohydride (98%) and all nitro compounds were purchased from Aldrich and used as received. Ethanol (100%) was obtained from Pharmco. Aqueous solutions were prepared with deionized water (18.2 MΩ cm, Milli-Q purification system), and hydrogen (99.9%) was obtained from AGA gases. Flash chromatography was performed with silica gel 60, particle size 0.040-0.063 mm (230–400 mesh), which was purchased from EM science. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on a Varian spectrometer (300 MHz for <sup>1</sup>H and 75 MHz for <sup>13</sup>C, respectively), with chemical shifts reported relative to the residue peaks of solvent chloroform (δ 7.24 for <sup>1</sup>H and 77.0 for <sup>13</sup>C). Synthetic yields refer to chromatographically and spectroscopically pure compounds unless otherwise stated. GC-MS (Hewlett-Packard G1800B GCD system with a nonpolar HP-5 MS column) was used to analyze hydrogenation reactions. All reactions were carried out in clean glassware with magnetic

stirring and were monitored by thin-layer chromatography with precoated silica gel plates, unless otherwise noted.

# 4.2.2. Preparation of Pd NPs on Alumina

# 4.2.2.1. [PAA-Pd(0)/PEI]<sub>3</sub>

 $[PAA-Pd(0)/PEI]_3$  films on alumina were prepared following the procedure in Chapter 3. To form an initial PAA layer, alumina was vigorously stirred for 10 min in a pH 4 solution containing 20 mM PAA (molarity of PAA is given with respect to the repeating unit) and 15 mM K<sub>2</sub>PdCl<sub>4</sub>. After rinsing, the alumina coated with PAA was stirred in a pH 9 solution containing PEI (1 mg/mL) to form a PAA-Pd<sup>2+</sup>/PEI film. After the deposition of each layer, the coated alumina was allowed to settle, the supernatant was decanted, and the solid was washed through vigorous stirring in three 100-mL aliquots of deionized water (3 x 5 min) to remove excess polyelectrolyte. In total, three PAA-Pd(II)/PEI bilayers were deposited on the alumina in 100 mL of freshly prepared 0.1 mM NaBH<sub>4</sub> for 30 min, and the reduced films were washed with three 100-mL aliquots of deionized water (3 x 5 min). After decanting the final water rinse, the residual water was removed under reduced pressure overnight to afford a catalytic powder, which was stored in a clean dry vial until use.

# 4.2.2.2. Reduced PdCl<sub>4</sub><sup>2-</sup> on alumina

Fifteen mg of  $\alpha$ -alumina was stirred in a 100-mL solution containing 0.5 mM PdCl<sub>4</sub><sup>2-</sup> and 0.1 M KCl for 30 min. The powder was then washed with three 100-mL

aliquots of deionized water (3 x 5 min), and the Pd(II) was reduced to Pd(0) as described above to afford a catalytic powder.

#### 4.2.3. Characterization of Pd NPs

To obtain TEM images, [PAA-Pd(0)]/PEI]<sub>3</sub> films were deposited on carboncoated copper grids that were pretreated in a UV/ozone cleaner for 1 min. The deposition procedure on the TEM grid is similar to that described above, except that the grid was simply immersed for 5 min in solutions without stirring, and rinsing between each step consisted of a 1-min washing with deionized water. Imaging was performed on a JEOL 2200FS microscope using an accelerating voltage of 200 kV.

# 4.2.4. Determination of the Pd Content of Catalysts Used in Hydrogenation

The amounts of palladium in different catalysts were determined by atomic emission spectrophotometry (AES). Standard solutions (0.1 to 0.5 mM) were prepared by dissolving  $K_2PdCl_4$  in 0.1 M HNO<sub>3</sub>, and sample solutions were prepared by stirring 60 mg of catalyst in 2 mL of aqua regia for 15 min. The sample solutions were diluted to 12 mL with water and centrifuged (the  $\alpha$ -alumina support does not dissolve in aqua regia) to collect supernatant to analyze using its emission at 340.5 nm.

## 4.2.5. General Procedure for the Hydrogenation of Nitroaromatic Compounds

To determine catalyst turnover frequencies (TOFs), catalytic hydrogenation was performed in a 100-mL, three-neck, round-bottomed flask. 30 mg of catalyst was suspended in a 25-mL aliquot of deionized water and bubbled with  $H_2$  for 30 min.

Subsequently, a solution of nitrobenzene (2.5, 7.5, 15, 22.5, or 30 mM) in 25 mL of a 1:1 (v:v) mixture of ethanol or methanol or THF and water was prepared and added to the reaction vessels. During the reaction, hydrogen at a gauge pressure of 50 kPa was bubbled through a frit at the bottom of the solution, which was vigorously stirred. Sample aliquots (0.5 mL) were removed from the reaction vessel at specific times and diluted by addition of 1 mL of THF prior to analysis by GC-MS with appropriate response factors. The response factors were determined to calculate the TOF as described in chapter 2.<sup>45</sup> TOFs were calculated from the slope of the initial portion (total conversion of reactant to isomer and hydrogenated product <50%) of plots of percent hydrogenation versus time. In fitting the initial data, the intercept of the line was forced to be zero.

In reactions used for product isolation, 125 mg of catalyst (more catalyst was used to speed up the reaction) was suspended in 25 mL of EtOH or a mixture of 20 mL water and 5 mL of Ethanol and bubbled with  $H_2$  for 30 min. A 30 mM solution of substrate in 25 mL EtOH was added to the reaction vessels and the mixture was stirred until the hydrogenation was complete as judged by TLC. The reaction mixture was filtered through cotton with a top layer of Celite to remove the catalyst, and the solvent was evaporated under reduced pressure, dissolved in a minimum volume of solvent, and subjected to flash chromatography using hexanes/EtOAc.

4-Aminobenzaldehyde (2): Hydrogenation of 4-nitrobenzaldehyde (0.75 mmol, 0.113 g) in 3:2 EtOH and water for 15 min afforded >99% conversion. After collection of the crude product and flash chromatography (hexanes/EtOAc: 5:1), nitroarenes were

collected as a yellow liquid in the presence of solvent. Upon complete removal of the solvent, a yellow solid formed, which was insoluble in all solvents tested (presumably because of polymerization). Therefore, NMR in CDCl<sub>3</sub> was performed with a sample that contained residual EtOAc. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  9.64 (s, 1H), 7.60 (d, J = 6.59 Hz, 2H), 6.61 (d, J = 6.59 Hz, 2H), 4.50 (bs, 2H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  190.3, 152.8, 132.2, 126.9, 113.8.<sup>22</sup>

4-Aminobenzonitrile (3): 4-nitrobenzonitrile (0.75 mmol, 0.111 g) was subjected to the general procedure for reducing nitroarenes with stirring for 90 min followed by flash chromatography (hexanes/EtOAc: 5:1) to afford an inseparable mixture (0.084 g) of 4-aminobenzonitrile (95%) and 4-hydroxyaminobenzonitrile (5%) as a bright yellow solid. For 4-aminobenzonitrile: <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.36 (d, J = 8.79 Hz, 2H), 6.61 (d, J = 8.79 Hz, 2H), 4.23 (bs, 2H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  150.6, 133.6, 120.2, 114.3, 99.6.<sup>22</sup>

Methyl 4-aminobenzoate (4): Methyl 4-nitrobenzoate (0.75 mmol, 0.136 g) was subjected to the general procedure for reducing nitroarenes with stirring for 15 min followed by flash chromatography (hexanes/EtOAc: 5:1) to afford 0.11 g (97% yield) of methyl 4-aminobenzoate (14) as a yellow solid. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  7.83 (d, J = 8.14 Hz, 2H), 6.61 (d, J = 8.70 Hz, 2H), 4.06 (bs, 2H), 3.79 (s, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  167.1, 150.8, 131.6, 119.7, 113.7, 51.6.<sup>22</sup>

**4-Aminoacetophenone (5):** 4-nitroacetophenone (0.75 mmol, 0.124 g) was subjected to the general procedure for reducing nitroarenes with stirring for 15 min followed by flash chromatography (hexanes/EtOAc: 5:1) to afford 4-aminoacetophenone (5) 0.094 g (96% yield) as a yellow solid. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  7.78 (d, J = 6.15 Hz, 2H), 6.62

(d, J = 6.08 Hz, 2H), 4.06 (bs, 2H), 2.48 (s, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  196.5, 151.3, 130.7, 127.6, 113.6, 26.0.<sup>22</sup>

4-Aminobenzamide (6): 4-nitrobenzamide (0.75 mmol, 0.125 g) was subjected to the general procedure for reducing nitroarenes with stirring for 15 min followed by flash chromatography (EtOAc/MeOH, 100/0 then 9:1) to afford 0.096 g (94% yield) of 3-aminobenzamide (6) as a yellow solid. <sup>1</sup>H NMR (300 MHz, CD<sub>3</sub>OD):  $\delta$  7.63 (d, J = 7.58 Hz, 2H), 6.65 (d, J = 7.49 Hz, 2H), 4.87 (s, 4H); <sup>13</sup>C NMR (75 MHz, CD<sub>3</sub>OD):  $\delta$  172.8, 153.5, 130.5, 122.2, 114.6.<sup>22</sup>

**2-Aminotoluene** (7): 2-nitrotoluene (0.75 mmol, 0.088 mL) was subjected to the general procedure for reducing nitroarenes with 60 min of stirring followed by flash chromatography (hexanes/EtOAc: 5:1) to afford 0.77 g (95% yield) of 2-aminotoluene as a yellow oil. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  7.04 (m, 2H), 6.74-6.66 (m, 2H), 3.55 (bs, 2H), 2.17 (s, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  144.5, 130.4, 126.9, 122.3, 118.6, 114.9, 17.3.<sup>22</sup>

# 4.3. Result & Discussion

#### 4.3.1. Catalyst Preparation and Characterization

We prepared  $[PAA-Pd(0)/PEI]_3$  films on micron-size alumina particles using 15 mM Pd(II) in the PAA-Pd(II) deposition solution and reduction of Pd(II) to Pd(0) by NaBH<sub>4</sub>. Pd NPs embedded in these polyelectrolyte multilayers are stable and can be stored for months without losing their catalytic activity. Moreover, as shown in chapter 2, the catalytic activity of this material is not altered by recycling.<sup>45</sup> The average diameters of small NPs in these [PAA-Pd(0)/PEI]<sub>3</sub> films on TEM grids are 3.4±0.9 nm

(see chapter 3). Additionally, some big particles with average diameters of 160±100 nm appear in some images, but we roughly estimate that these particles constitute only 18% of the total particle surface area (see chapter 3). Figure 4.1 shows the TEM image of small particles in a [PAA-Pd(0)/PEI]<sub>3</sub> film on a TEM grid and as well as a histogram of the diameters of the small NPs.



**Figure 4.1.** (a) TEM image of a [PAA-Pd(0)/PEI]<sub>3</sub> film on a carbon-coated copper grid. 15 mM Pd(II) was present in the PAA-K<sub>2</sub>PdCl<sub>4</sub> solution used for film deposition.



Figure 4.1. (b) Histogram of Pd NP diameters in several TEM image based on their area.

# 4.3.2. Hydrogenation of nitrobenzene as a function of solvent and nitrobenzene concentration

To maximize TOFs, we initially evaluated the catalytic activity of [PAA-Pd(0)/PEI]<sub>3</sub> films on alumina for hydrogenation of nitrobenzene in several solvent systems. As Table 1 shows, hydrogenation in THF and a mixture of water and THF gives TOFs that are significantly lower than hydrogenation in pure EtOH or in a mixture of EtOH and water. Previous reports also showed that solvents affect the rate of the hydrogenation of aromatic nitro compounds,<sup>46</sup> and EtOH is commonly used to perform these transformations.<sup>27,30,37-39</sup> We further examined hydrogenation using different initial nitrobenzene concentrations. The data in Table 4.2 show that TOFs do not vary significantly with nitrobenzene concentrations ranging from 2.5 mM to 30 mM, which suggests that even at 2.5 mM nitrobenzene, the catalyst is essentially saturated with substrate. The calculated TOF for the hydrogenation of 15 mM nitrobenzene by Pd NPs

in  $[PAA-Pd(0)/PEI]_3$  films is about the same as the TOF with commercially available 5% Pd on alumina (Table 4.2), and films prepared by impregnation of the alumina with  $[PdCl_4^{2-}]$  and subsequent reduction of Pd(II) with NaBH<sub>4</sub> also show similar TOFs.

**Table 4.1.** TOFs for nitrobenzene hydrogenation catalyzed by alumina-supported [PAA-Pd(II)/PEI]<sub>3</sub> films in different solvents.



[a] 50 mL of 7.5 mM substrate was hydrogenated in different solvents. TOFs are initial values determined at conversions less than 50%.

**Table 4.2.** TOFs (moles hydrogenated/moles Pd/h) for nitrobenzene hydrogenation by different catalysts in EtOH.

TOFs (moles hydrogenated/ mol Pd/ h) <sup>a</sup>								
[PAA-Pd(II)/PEI]₃ film on alumina					5% Pd on alumina	Reduced PdCl₄ <sup>2-</sup> on alumina		
[nitrobenzene]	2.5 mM <sup>b</sup>	7.5 mM <sup>b</sup>	15 mM <sup>b</sup>	22.5 mM <sup>b</sup>	30 mM <sup>b</sup>	15 mM <sup>b</sup>	15 mM <sup>b</sup>	
TOF	1350	1460	1950	1690	1540	1430	1950	

[a] TOFs are initial values determined at conversions less than 50%. [b] Substrate's initial concentration in the reaction mixture.

### 4.3.3. Hydrogenation of nitrobenzaldehyde

In many synthetic reactions, aromatic nitro compounds must be selectively hydrogenated in the presence of other functional groups such as aldehydes and nitriles. Recent report indicate that aminals can be easily accessed from aminobenzaldehyde,<sup>47</sup> so we initially investigated whether [PAA-Pd(0)/PEI]<sub>3</sub> catalysts can facilitate chemoselective hydrogenation of 4-nitrobenzaldehyde, **2**, to 4-aminobenzaldehyde. Aminals are present in many natural product<sup>48,49</sup> and are also important building blocks in the preparation of many biological active compounds.<sup>50-55</sup> The chemoselective reduction of nitrobenzaldehyde to amino benzaldehyde is challenging due to the presence of the easily reducible carbonyl group (Scheme 4.5).

Using EtOH as a solvent, we carried out the hydrogenation of 2 in the presence of  $[PAA-Pd(0)/PEI]_3$  on alumina, reduced  $[PdCl_4^{2-}]$  on alumina, 5% Pd on alumina, or 10% Pd on carbon. Table 4.3 shows that in EtOH,  $[PAA-Pd(0)/PEI]_3$  films and reduced  $[PdCl_4^{2-}]$  on alumina are the most selective catalysts for the hydrogenation of 2 to 4-aminobenzaldehyde (2a). The use of  $[PAA-Pd(0)/PEI]_3$  films and reduced  $[PdCl_4^{2-}]$  on alumina gives only 2a and 4-aminobenzyl alcohol (2b) as hydrogenation products, and the ratio of these compounds in the product is about 17:1. The chemoselectivity with the commercial catalysts in EtOH is much lower than with the  $[PAA-Pd(0)/PEI]_3$  films, and the Pd on C shows much more reduction of the aldehyde than 5% Pd on alumina. The relatively small size of NPs in  $[PAA-Pd(0)/PEI]_3$  films may account for their high chemoselectivity in the hydrogenation of 2, but further studies are needed to confirm that this is the case. In contrast to a previous report (Scheme 4.3), we do not observe the formation of 4-nitrobenzyl alcohol (2d) with any catalyst.<sup>22</sup>


Scheme 4.5. Hydrogenation of 4-nitrobenzaldehyde to several possible products.

**Table 4.3.** Product distributions from 4-nitrobenzaldehyde hydrogenation (>99%conversion) using several catalysts and two solvent systems.

		% of Different Products			
Catalyst	Solvent	2a	2b	2c	2d
[PAA-Pd(0)/PEI] <sub>3</sub> on Alumina <sup>a</sup>	100% EtOH (15 min)	94	6	-	-
	(3:2) EtOH and water (20 min)	99.3	0.40	_	-
5% Pd on Alumina <sup>a</sup>	100% EtOH (15 min)	79.2	20.8	-	-
	(3:2) EtOH and water (30 min)	98.7	0.40	-	-
Reduced [PdCl4 <sup>2-</sup> ] on Alumina <sup>b</sup>	100% EtOH (15 min)	95	5	-	-
	(7:5) EtOH and water (20 min)	100	-	-	-
10% Pd on Carbon <sup>a</sup> (15 min)	100% EtOH (10 min)	39	50	10.5	-
	(3:2) EtOH and water (15 min)	94.5	3.5	2	-

[a] Substrate concentration was initially 15 mM in the reaction mixture. [b]Substrate concentration was initially 10 mM in the reaction mixture.

We also performed the hydrogenation reaction in a 3:2 (v:v) EtOH and water mixture. The limited solubility of 2 in water restricts the total water content for this reaction to about 40%. Water is a byproduct of the hydrogenation of aromatic nitro compounds. However, interestingly, we observe improved chemoselectivity in the presence of water for the hydrogenation of 2 to 2a with all of the catalysts. Further studies needs to be performed to understand the mechanistic reason why chemoselectivity increases in the presence of water.

### 4.3.4. Hydrogenation of Other Nitroarenes

To further explore the scope of hydrogenation with [PAA-Pd(0)/PEI]<sub>3</sub> films and reduced  $[PdCl_4^{2-}]$  on alumina, we examined the hydrogenation of the nitroarenes shown in Table 4.4. 4-nitrobenzonitrile (3) is an interesting example among them. Maleczka, et al. reported that the reduction of 3 by a hydride reducing agent PMHS, produced the corresponding N-hydroxylamine (3b), even when the reaction was performed for 12 h instead of 30 min<sup>22</sup> Cu and Au nanoparticles promoted the catalytic transformation of 3 to 4-aminobenzonitrile (3a) chemoselectively, but these reactions were run at 120°C and 110-140°C, respectively.<sup>24,30,31</sup> Corma, et al. reported that Pd/C and Pt/C catalysts are not chemoselective for the hydrogenation of 4-nitrobenzonitrile at high temperature and pressure (140°C, 25 bar).<sup>31</sup> Motovama, et al. recently showed that the hydrogenation of 3 catalyzed by nanofiber-supported Pd NPs produces 64 % 3a and 32% di(p-aminobenzyl) amine (see Scheme 4.4).<sup>23</sup> In our case, the hydrogenation of 4-nitrobenzonitrile by [PAA-Pd(0)/PEI]<sub>3</sub> films in pure EtOH produces 95% of the desired compound, **3a** and only 5% 3b. The ratio of 3a and 3b in the product did not change when the reaction was performed for 90 min instead of 15 mi

**Table 4.4.** Catalytic hydrogenation of various aromatic nitro compound by  $[PAA-Pd(0)/PEI]_3$  films and reduced  $[PdCl_4^{2-}]$  on alumina.

	Product	[PAA- Pd(0)/PEI] <sub>3</sub>	Reduced [PdCl4 <sup>2-</sup> ]
Substrates		Yield (%) <sup>b</sup> (Time, min)	Yield (%) <sup>b</sup> (Time, min)
	$NC - NH_2$ 3a	88 <sup>c</sup> (90)	90 <sup>d</sup> (40)
	$H_3CO_2C$ $ NH_2$ 4a	97 (15)	98 (10)
		92 (15)	98 (10)
	H <sub>2</sub> NOC- 6a	93 (15)	96 (10)
-NO <sub>2</sub>	<b>7a</b>	95 (60)	98 (120)

[a] 15 mM substrate was subjected to hydrogenation conditions in the presence of 125 mg of [PAA-Pd(0)/PEI]<sub>3</sub> on alumina in 50 mL of EtOH at room temperature. [b] >99% consumption (calculated by GC/MS) of the starting materials takes place. [c] The overall isolated yield is 93%, which consists of 95% **3a** and 5% **3b**. [d] The overall isolated yield is 96%, which consists of 94% **3a** and 6% **3b**.

A similar ratio of **3a** and **3b** (17:1) was obtained in the hydrogenation of **3** catalyzed by reduced  $PdCl_4^{2-}$  on alumina.

With both  $[PAA-Pd(0)/PEI]_3$  and reduced  $PdCl_4^{2-}$  on alumina catalysts, the hydrogenation of nitroarenes containing electron withdrawing substituents such as esters

(4), ketones (5) and amides (6) is 100% chemoselective and allow isolation of very high yields of the desired products 4a, 5a, and 6a after flash chromatography. Long reaction times are required for hydrogenation of 7 due to the steric hindrance caused by the methyl group at the ortho position, but >99% conversion can be achieved within a few hours.

Taken together, these studies demonstrate the high chemoselectivity of [PAA-Pd(0)/PEI]<sub>3</sub> and reduced PdCl4<sup>2-</sup> on alumina catalysts. The high selectivity of these catalysts relative to commercial Pd/C and 5% Pd on alumina may relate to the size of the Pd particles in the catalysts. Unfortunately, it is very difficult to image the Pd nanoparticles on the very rough supports, so we do not know their sizes at this time. Future studies of selectivity as a function of NP size, similar to those in chapter 3, may shed light on the mechanism of chemoselectivity.

### 4.4. Conclusion

In conclusion, NPs embedded in polyelectrolyte multilayer films on micron-size alumina powder provide highly active and chemoselective catalysts for the hydrogenation of nitroarenes to their corresponding amines. Reduced  $PdCl_4^{2-}$  on alumina is similarly active and selective. Reactions in ethanol proceed more rapidly than reactions in THF, and mixtures of water and ethanol give higher chemoselectivity than that pure ethanol in the case of hydrogenation of 4-nitrobenzaldehyde. Chemoselective hydrogenation of aromatic nitroamides, nitroesters, nitroaldehydes, and nitronitriles is also possible with these catalysts.

# 4.5. Appendix



Figure 4. A-1. <sup>1</sup>H NMR spectrum of purified 2-Aminotoluene (compound 7) in CDCl<sub>3</sub>.



Figure 4. A-2. <sup>13</sup>C NMR spectrum of purified 2-Aminotoluene (compound 7) in CDCl<sub>3</sub>.



**Figure 4. A-3**. <sup>1</sup>H NMR spectrum of purified Methyl-4-aminobenzoate (compound 4) in CDCl<sub>3</sub>.



**Figure 4. A-4.** <sup>13</sup>C NMR spectrum of purified Methyl-4-aminobenzoate (compound 4) in CDCl<sub>3</sub>.



Figure 4. A-5. <sup>1</sup>H NMR spectrum of purified 4-Aminobenzamide (compound 6) in  $CD_3OD$ .



Figure 4. A-6. <sup>13</sup>C NMR spectrum of purified 4-Aminobenzamide (compound 6) in CD<sub>3</sub>OD.



**Figure 4. A-7.** <sup>1</sup>H NMR spectrum of purified 4-Aminobenzaldehyde and residual AcOEt (compound 2) in CDCl<sub>3</sub>.



**Figure 4. A-8.** <sup>13</sup>C NMR spectrum of purified 4-Aminobenzaldehyde and residual AcOEt (compound 2) in CDCl<sub>3</sub>.



**Figure 4. A-9.** <sup>1</sup>H NMR spectrum of purified 4-Aminobenzonitrile (compound 3) in CDCl<sub>3</sub>.



**Figure 4. A-10.** <sup>13</sup>C NMR spectrum of purified 4-Aminobenzonitrile (compound 3) in CDCl<sub>3</sub>.



**Figure 4.A-11.** <sup>1</sup>H NMR spectrum of purified 4-Aminoacetophenone (compound 5) in CDCl<sub>3</sub>.



**Figure 4. A-12.** <sup>13</sup>C NMR spectrum of purified 4-Aminoacetophenone (compound 5) in CDCl<sub>3</sub>.

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#### **CHAPTER 5**

### **CONCLUSIONS AND FUTURE WORK**

This dissertation demonstrates that metal ions can be incorporated inside polyelectrolyte films and subsequently reduced by NaBH<sub>4</sub> to give polymer-encapsulated NPs. Most importantly, these NPs are highly selective in the hydrogenation of unsaturated alcohols and nitroarenes. However, this work has only begun to probe the potential of NPs to serve as highly selective catalysts. There are likely a number of reactions in which NP size plays a vital role in effecting catalytic selectivity. Below I briefly summarize the most important points of my research and suggest a number of directions in which this research could expand in scope and importance.

### 5.1. Selective Catalysis

Chapter 2 shows that the rate of hydrogenation of allyl alcohols containing methyl substituents on the double bond is order(s) of magnitude lower than the rate of hydrogenation of allyl alcohol. Such selectivity depends on both the number of substituents on the double bond and the size of these substituents. Polyelectrolyte-embedded Pd NPs also show intramolecular selectivity for the hydrogenation of molecules which contain mono and multisubstituted carbon-carbon double bonds. Additionally, chapter 2 indicates that the presence of the polyelectrolyte matrix restricts the access of larger substrates to the catalyst. However, size-based selective diffusion of substrates through the polyelectrolyte matrix only accounts for a small fraction of the

total inter and intramolecular selectivity in the hydrogenation of unsaturated alcohols catalyzed by polyelectrolyte-encapsulated Pd NPs.

### 5.2. Selective Hydrogenation of Unsaturated Alcohols as a Function of NP Diameter

Chapter 3 demonstrates that selectivity is a very strong function of Pd NP size in the hydrogenation of unsaturated alcohols. The rate of hydrogenation of allyl alcohol decreases as the NP size increases, but hydrogenation rates for crotyl alcohol and 2methyl-2-propen-1-ol increase as NP size increases. Chapter 3 further suggests that these different trends in reactivity for the hydrogenation of unsaturated alcohols are largely due to interactions with specific types of surface atoms on the catalytic NPs. Presumably the hydrogenation of allyl alcohol occurs primarily on defect atoms. Crotyl alcohol and 2methyl-2-propen-1-ol, on the other hand, might bind to face atoms during the hydrogenation reaction.

# 5.3. Chemoselective Hydrogenation of Aromatic Nitro Compounds by Pd NPs encapsulated in polyelectrolyte films

Chapter 4 extends the catalytic scope of polyelectrolyte-encapsulated Pd NPs to the chemoselective hydrogenation of aromatic nitro compounds that contain other readily reducible functional groups. The nanoparticles show higher selectivities than commercial catalysts such as Pd/C and Pd/alumina. This chapter also demonstrates that the addition of water improves chemoselectivity, even in case of commercially available Pd catalysts.

#### 5.4. Future Work

# 5.4.1. Effect of NP Size on the Chemoselective Hydrogenation of 4nitrobenzaldehyde

In chapter 4, I showed that [PAA-Pd(0)/PEI]<sub>3</sub> films are more chemoselective catalysts than commercially available Pd/C or 5% Pd on alumina for the hydrogenation of 4 nitrobenzaldehyde in ethanol. The [PAA-Pd(0)/PEI]<sub>3</sub> films in this case were prepared using 15 mM Pd(II) in the PAA deposition solution. Chapter 3 indicates that the average Pd NP diameter in this catalyst is 3.4 nm. It will be interesting to investigate the chemoslectivity for the hydrogenation of 4-nitrobenzaldehyde as a function of NP diameter. This may help to explain why the NP catalysts are more selective than Pd/C or Pd on alumina.

# 5.4.2. The Contribution of Size-Dependent Electronic Properties to Selective Hydrogenation

Chapter 3 suggests that the NP-size-dependent selectivity for hydrogenation of monosubstituted double bonds is primarily due to geometrical effects. However, several studies indicate that in some cases, differences in reaction rates as a function of NP size arise from either electronic or geometrical effects or both.<sup>1-3</sup> As the diameters of NPs decrease, in addition to changes in the fraction of different atom types (e.g., face versus edge), electronic properties of the NPs change due to the transition from metal to insulator to molecule.<sup>4,5</sup> This change might contribute to the selective catalytic properties of NPs because interactions of electron rich and poor substrates with NP surfaces may vary. Hydrogenation of nitrobenzene containing electron donating (-CHO, -COCH<sub>3</sub>),

withdrawing (-OH, -NH<sub>2</sub>), and sterically hindered (-CH<sub>3</sub>) groups would be an ideal set of reactions for investigating the contribution of changing NP electronic properties to selective hydrogenation

### 5.4.3. Synergistic Effects Using Bimetallic NPs

Bimetallic NPs manifest electronic properties that are uncommon in single-metal NPs, therefore these materials are attractive for developing new catalysts with unique reactivities and selectivities.<sup>6-8</sup> A recent report indicates that the rate of hydrogenation of allyl alcohol is enhanced in the presence of the bimetallic dendrimer-encapsulated PdPt NPs compared to only Pt or only Pd NPs supported by the dendrimer.<sup>6</sup> Additionally, the enhanced catalytic activity of dendrimer-supported PdAu catalysts in CO oxidation is indicative of a synergistic bimetallic interaction.<sup>7</sup>

Chemoselective hydrogenations of nitro compounds containing other reducible groups such as olefinic bonds are industrially important reactions. During the reduction of nitostyrene, transition-metal catalysts usually show poor chemoselectivity due to the hydrogenation of the olefinic bond to produce unwanted side products. Halogenated anilines are another industrially important class of compounds due to their presence in pharmaceuticals.<sup>9-11</sup> Halogenated aniline is often synthesized from halogenated nitro benzene, but dehydrohalogenation is a very common, unwanted side reaction.

Serna, et al. showed that titania-supported gold NPs provide selectivity for nitro group reduction in the presence of olefinic bonds or halogens. However, these reactions occur under high temperature and pressure with relatively long reaction times as

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discussed in chapter 4. Pd NPs show very poor chemoselectivity for the hydrogenation of these nitro compounds, but reactions are very fast at room temperature.

Preparation of bimetallic NPs encapsulated in a polyelectrolyte matrix can be easily performed by complexing two types of metal ions with polyelectrolytes during the deposition. Utilization of PdAu bimetallic NPs for chemoselective hydrogenation of nitro groups in the presence of olefinic bonds or other halogen groups under mild condition at short reaction times should again expand the scope of reactions available with NP catalysts.

### 5.5. Summary Statement

This dissertation showed that NPs encapsulated in a polyelectrolyte matrix can serve as highly selective catalysts. I envision that there is enormous potential for significant expansion to a wide range of catalytic reactions.

## 5.6. References

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