



LIBRARIES MICHIGAN STATE UNIVERSITY EAST LANSING, MICH 48824-1048

This is to certify that the thesis entitled

INVESTIGATIONS OF CATALYSIS BY Pd NANOPARTICLES EMBEDDED IN MULTILAYER POLYELECTROLYTE FILMS

presented by

Jin Li

has been accepted towards fulfillment of the requirements for the

Chemistry M.S. degree in Major Professor's Signature 12/09/04

Date

MSU is an Affirmative Action/Equal Opportunity Institution

PLACE IN RETURN BOX to remove this checkout from your record. TO AVOID FINES return on or before date due. MAY BE RECALLED with earlier due date if requested.

<u>DATE DUE</u>	<u>DATE DUE</u>	<u>DATE DUE</u>

6/01 c:/CIRC/DateDue.p65-p.15

· ---- ·

INVESTIGATIONS OF CATALYSIS BY Pd NANOPARTICLES EMBEDDED IN MULTILAYER POLYELECTROLYTE FILMS

By

Jin Li

A THESIS

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

MASTER OF SCIENCE

Department of Chemistry

2004

ABSTRACT

INVESTIGATIONS OF CATALYSIS BY Pd NANOPARTICLES EMBEDDED IN MULTILAYER POLYELECTROLYTE FILMS

By

Jin Li

Palladium nanoparticles immobilized in multilayer polyelectrolyte films were prepared by alternating adsorption of poly(acrylic acid) (PAA) and a poly(ethyleneimine)-Pd(II) (PEI-Pd(II)) complex on alumina followed by *in situ* reduction of Pd(II) by NaBH₄. These polymer-encapsulated nanoparticle catalysts showed order of magnitude selectivities in hydrogenation of substituted unsaturated alcohols of different sizes. Hydrogenation experiments with [PAA/PEI]₃PAA-coated commercial 5% Pd on alumina suggest that selectivity likely occurs due to differential rates of diffusion to embedded nanoparticles.

In Heck reactions, a [PAA/PEI-Pd(0)]₃PAA film on alumina allowed selective coupling of methyl acrylate to iodobenzene in the presence of di(ethylene glycol) ethyl ether acrylate (DEGA), but there was little selectivity between methyl acrylate and *tert*-butyl acrylate. The high temperature (95 °C) may limit selectivity. Pd nanoparticles were also prepared by alternating adsorption of PEI and PdCl₄²⁻ followed by reduction of Pd(II). Such films were nonselective in Heck coupling, probably because the active catalyst in these reactions was Pd that was leached from the film. Atomic emission spectroscopy confirmed the leaching of Pd.

To my family

ACKNOWLEDGMENTS

First, I need to give my warmest thanks to my advisor Prof. Merlin Bruening, a gentleman who always conveys his care with a sense of humor, always greets his students with "getting smarter" and helps them to achieve it. Thanks for his helpful advice, both academic and personal. I would never forget the patience and enthusiasm he demonstrated when he helped me prepare my first formal presentation in English.

Next, I would like to acknowledge all my committee members for their advice and support. Thanks to Prof. Gary Blanchard who always answered my questions with a "Cheers", thanks to Prof. Baker for his professional advice and encouraging words, and thanks to Prof. Borhan for allowing me to use the hood.

Special thanks also go to all the people working in Bruening's lab: Dan, Lei, Sri, Christin, Matt, Anagi, Brian, Xiaoyun, Jimmy, Jinhua, Yingda and Malai. I sincerely thank the group members for their suggestions and support on my project. I especially would like to thank Dan, Brian, and Matt. I dearly appreciate their help with training and advice on device set-up, nanofiltration, and use of the glovebox.

Thanks also to the amazing friends I made here, especially Yana, Ying, Ping and Yuening, those pleasant moments shared with you will always be shining in my memory.

Finally, I extend the most sincere gratitude to my family, my husband, Xiao, my daughter, Chuyue and my parents-in-law. Without your encouragement, I would not have landed on America. Without your unfailing support and love, I would not have been able to go through the over two years of research and study and finish this thesis.

TABLE OF CONTENTS

List of Tables		vi		
List of Figures		vii		
List of Abbrevia	ations	ix		
Chapter 1: Int	roduction	1		
1.1	Catalytic transition-metal nanoparticles	2		
1.2	Multilayer polyelectrolyte films	4		
1.3	Selective catalysis	7		
1.4	Heck reactions	8		
Chapter 2: Exp	perimental	14		
2.1	Materials	14		
2.2	Film deposition for diffusion dialysis studies 1			
2.3	Diffusion dialysis 1			
2.4	Nanofiltration 15			
2.5	Synthesis of Pd nanoparticles embedded in polyelectrolyte			
	multilayers	17		
2.6	Transmission electron microscopy (TEM)	19		
2.7	Determination of the amount of Pd in catalysts 2			
2.8	Catalytic hydrogenation 2			
2.9	Heck reactions	22		
Chapter 3: Res	ults and discussion	23		
3.1	Transport of acetophenone through MPFs	23		
3.2	Multilayer polyelectrolyte films containing Pd nanoparticles	26		
3.3	Catalytic hydrogenation	27		
3.4	Heck reactions catalyzed by bare and coated 5% Pd on Al_2O_3	30		
3.5	Heck reactions catalyzed by Pd nanoparticles embedded in MPFs	34		
3.6	Conclusions	39		
Bibliography		40		

LIST OF TABLES

Table 3.1	Normalized Fluxes (mol cm ⁻² s ⁻¹ / M) of acetophenone in diffusion dialysis through Bare Porous Alumina and Alumina Coated with a [PSS/PAH] ₇ film.	26
Table 3.2	Turnover frequencies (TOFs) for hydrogenation of structurally related unsaturated alcohols by several Pd catalysts.	29
Table 3.3	Turnover frequencies for the Heck reaction of methyl and ethyl acrylate with iodobenzene using bare or MPF-coated 5% Pd on Al ₂ O ₃ catalysts.	33
Table 3.4	Rates of HR conversion for structurally related substrates using bare 5% Pd on Al ₂ O ₃ or Pd nanoparticles embedded in MPFs	37

•

LIST OF FIGURES

Figure 1.1	High coordination ("terrace") and low coordination ("defect") sites present on a regular cuboctahedron particle.	3
Figure 1.2	Formation of an ultrathin film by alternating polyelectrolyte adsorption.	5
Figure 1.3	Schematic diagram of heat-induced cross-linking of PAA/PAH films. Cross-linking converts polyelectrolyte films into passivating coatings.	7
Figure 1.4	The Heck reaction.	9
Figure 1.5	Plausible mechanism for the supported-Pd ⁰ catalyzed Heck reaction.	11
Figure 1.6	A possible catalytic cycle for the Heck reaction with Pd metal catalysts.	13
Figure 2.1	Schematic diagram of the diffusion dialysis setup and a composite separation membrane with a selective skin layer on a porous support.	16
Figure 2.2	Synthesis of Pd-containing PEI/PAA films through alternating adsorption of PAA and PEI—Pd(II) followed by reduction	18
Figure 2.3	Synthesis of Pd-containing PEI films through alternating adsorption of PEI and PdCl ₄ ²⁻ followed by reduction	20
Figure 3.1	Normalized permeate-phase concentrations of acetophenone in diffusion dialysis through porous alumina before and after deposition of a 7-bilayer PSS/PAH membrane.	25
Figure 3.2	TEM image of a [PAA/PEI-Pd(0)] ₃ PAA film on a carbon-coated copper grid.	27

Figure 3.3	Percent of substrates hydrogenated vs time for allyl alcohol, 1- penten-3-ol, and 3-methyl-1-penten-3-ol on a [PAA/PEI- Pd(0)] ₃ PAA catalyst.	28
Figure 3.4	Percent of substrates converted vs time in the reaction of methyl acrylate and ethyl acrylate with iodobenzene using a bare 5% Pd on Al ₂ O ₃ catalyst and a 5% Pd on Al ₂ O ₃ catalyst coated with 3.5 bilayers of PAA/PEI.	32
Figure 3.5	Percent conversion of methyl acrylate and ethyl acrylate in HRs with iodobenzene using a PAA[PEI/Pd(0)] ₃ [PEI/PAA] ₂ film on alumina as a catalyst.	35
Figure 3.6	Percent of substrates converted vs reaction time for methyl acrylate and DEGA coupling to iodobenzene using a [PAA/PEI-Pd(0)] ₃ PAA film on alumina as a catalyst.	38

•

LIST OF ABBREVIATIONS

DEGA	di(ethylene glycol) ethyl ether acrylate			
DMF	N,N - dimethyl formamide			
Et	Ethyl			
EA	ethyl acrylate			
HR	Heck reaction			
MA	methyl acrylate			
MPF	multilayer polyelectrolyte film			
PAA	poly(acrylic acid)			
РАН	poly(allylamine hydrochloride)			
PEI	polyethyleneimine			
PSS	poly(sodium 4-styrenesulfonate)			
t-BA	tert-butyl acrylate			
TEM	Transmission electron microscopy			
TOF	turnover frequency			

Chapter 1

INTRODUCTION

Development of immobilized or insoluble metal catalysts that can be recycled is a major goal in the search for more environmentally benign organic syntheses.¹ Small. soluble catalysts are often very effective, but such catalysts are difficult to recycle, so homogeneous catalysis is often uneconomical on large scales.^{2,3} Because of this, certain organic reactions, such as the Heck coupling reaction, are attractive for bench-scale syntheses but less practical for industrial use.⁴ Heterogeneous catalysts present a promising alternative, but control over the structure and reactivity of these catalytic systems is often difficult to achieve.^{1,5} Taking this into consideration, we are investigating a novel methodology for creating catalytic Pd nanoparticles encapsulated in multilayer polyelectrolyte films (MPFs).⁶ Nanoparticles are attractive for catalysis because of their high surface area-to-volume ratio, and the polyelectrolyte matrix stabilizes the nanoparticles and modifies their reactivity and selectivity. The versatility of the layer-by-layer deposition of MPFs also makes them particularly attractive for varying catalyst properties. We initially demonstrated selective catalysis by using nanoparticles embedded in polyelectrolyte films for catalysis of hydrogenation reactions.⁷ This thesis briefly presents data on hydrogenation and then focuses on a more difficult reaction, Heck coupling. I chose to investigate the Heck reaction (HR) because it is thought to be a very sensitive probe of metal surface structure.⁸

To put this work in perspective, this introduction first discusses nanoparticles and challenges in their use as catalysts. Subsequently, I describe the properties of MPFs to illustrate why they are attractive for encapsulating catalytic particles. Section 1.3 mentions some previous work in the development of selective catalysts, and finally, section 1.4 discusses HRs and mentions the catalysts previously used in these reactions.

1.1 Catalytic transition-metal nanoparticles

Transition-metal nanoparticles have attracted a great deal of attention in the last decade because their properties often differ from those of the corresponding bulk metal. Additionally, the small size of such particles makes them attractive for nanoscale applications such as sensing and bioimaging. Most relevant to this thesis, nanoparticles are attractive for catalysis because of both their high surface area-to-mass ratio and their size-dependent properties.⁸⁻¹⁷

Nanoparticles are defined as having diameters of 1 to 50 nm, and the smaller the cluster of atoms, the higher the surface area-to-mass ratio will be. A nanoparticle with a diameter of 10 nm has about 10% of its atoms on the surface, but in a 1 nm particle, all atoms are on the surface.^{9,10,11} Several recent studies of the catalysis of Heck coupling by Pd nanoparticles revealed the importance of surface atoms. These studies demonstrated a direct relationship between the reaction rate and the quantity of low-coordination number or "defect" Pd surface atoms (see Figure 1.1).^{8,12,16,18}

A major challenge in utilizing nanoparticles is that they have a tendency to precipitate or aggregate. To overcome this challenge, stabilizers such as polymers, ligands, surfactants or dendrimers are used in nanoparticle preparations to provide enough electrostatic or steric stabilization to suppress the aggregation. However, the stabilizers must be carefully selected because strong adsorption on the active sites of nanoparticles can lead to a loss of catalytic activity.^{14,15}



Figure 1.1: High coordination ("terrace") and low coordination ("defect") sites present on a regular cuboctahedron particle.

Polymers containing functional groups with high affinities for metal ions, e.g., thiols, sulfides, amines, or phosphines,^{13, 14, 15, 17, 19} are often employed to stabilize metal nanoparticles. Frequently, the polymer first binds to metal ions in solution, and nanoparticles are generated using chemical, photo, or thermal reduction of the precursor metal-ion complexes. Such procedures often result in small nanoparticle sizes and narrow size distributions, and the protective polymer can also greatly influence the catalytic properties of the particles,^{14, 15, 16, 17, 19, 20} For instance, depending on the properties of the surrounding polymer, it can create hydrophobic, electrostatic, or asymmetric environments that influence the approach of the reactants to the catalyst surface.^{14, 15, 17, 20} Moreover, coordination of the nanoparticles by the protecting polymer can modify the electronic properties of the nanoparticle to alter its catalytic properties. Thus the polymers do much more than simply stabilize the nanoparticles.

1.2 Multilayer polyelectrolyte films

Although a variety of polymers have been utilized to create nanoparticlecontaining catalysts, cationic polyelectrolytes are particularly interesting in this regard for several reasons.²⁰ First, cationic, amine-containing polymers provide both steric and electrostatic stabilization of the metal particles to give very stable metal colloids.^{20,21} Second, there are often interactions between the polycation and various metal ioncontaining precursors, therefore, very small particle sizes and narrow size distributions frequently occur.^{20, 22} Finally, such systems surround the nanoparticle with a strong electrostatic environment that should influence catalytic properties.²⁰

Polycations are also potentially interesting for stabilizing nanoparticles because they are capable of forming multilayer polycation/polyanion films, and such films may provide an especially convenient and versatile matrix for encapsulating nanoparticles. Iler first reported the sequential adsorption of oppositely charged colloids,²³ and Decher and coworkers extended this concept of layer-by-layer growth to the preparation of multilayer films of polymeric polyelectrolytes.^{24, 25, 26} Figure 1.2 schematically portrays the principle of layer-by-layer deposition. A charged substrate is simply immersed in alternating solutions of polycations and polyanions, with rinsing between each adsorption step.



Figure 1.2: Formation of an ultrathin film by alternating polyelectrolyte adsorption.

Although deposition of these films proceeds in a layer-by-layer fashion, because of loops and tails in the polyions, the neighboring layers in the MPFs are highly intertwined in most cases and do not have a stratified structure. However, the polycations are often nearly completely charge-compensated by the neighboring polyanions, and vice versa.²³⁻²⁸

The thicknesses of MPFs are highly dependent on adsorption conditions. For a given substrate and polyelectrolyte system, the film thickness can be controlled by varying the pH and ionic strength of deposition solutions, the deposition time, rinsing and drying methods, and solvent composition.^{29, 30, 31, 32} The effects of pH on the thickness of films prepared from weak polyelectrolytes are particularly pronounced, because the charge density is affected by protonation/deprotonation,³⁰ which is a function of pH. Normally a high charge density results in relatively thin films because chains are in an extended configuration parallel to the substrate surface.

The simplicity and versatility of alternating polyelectrolyte deposition have stimulated investigations of possible applications of MPFs, and the inclusion of charged nanoparticles in these films further expands the spectrum of useful materials that can be prepared by layer-by-layer electrostatic adsorption. Nanoparticles are generally incorporated into polyelectrolyte films in one of two ways. In the first method, the charged nanoparticles serve as one of the polyelectrolytes,^{33, 34, 35} while in the second, metal ions are incorporated into the film and subsequently reduced to form nanoparticles.^{6, 36, 37, 38} Either way, the resulting films are nanoparticle-polymer hybrids, which sometimes combine the unique properties (e.g., electrical, optical, magnetic, and catalytic) of nanoparticles with the mechanical properties of polymers (e.g., flexibility and strength).

In applications of MPFs as protective shells for catalytic nanoparticles, film permeability will likely be important in governing both the rate and selectivity of catalysis. These coatings are usually semipermeable to small molecules in aqueous solutions because polyelectrolytes are hydrophilic and highly swollen in water.³⁹ However, the permeability may be reduced by cross-linking.^{37, 40} Harris and coworkers reported that heating of poly(acrylic acid) (PAA)/poly(allylamine hydrochloride) (PAH) films on gold results in the formation of amide cross-links by reaction of the –COO⁻ groups of PAA with the –NH₃⁺ groups of PAH (Figure 1.3).^{40, 41} Cross-linking of PAA/PAH films greatly reduces their permeability, as shown by the fact that the rate of Al corrosion decreases by 2-3 orders of magnitude after coating of the metal with a 10-nm thick, cross-linked film.⁴² Cross-linking could provide a means for increasing the

selectivity of catalysis by nanoparticles embedded in polyelectrolyte films, although it will likely also decrease rates.



Figure 1.3: Schematic diagram of heat-induced cross-linking of PAA/PAH films. Cross-linking converts polyelectrolyte films into passivating coatings.

1.3 Selective catalysis

There are a number of examples of modification of catalytic selectivity by immobilization of catalytic metal-ion complexes on polymers. Examples of selective reactions include hydrogenations of various olefins by Pd⁰-Ag⁰ bimetallic catalysts,⁴³ carbonylation of olefins by immobilized palladium complexes,⁴⁴ and hydrosilylation of alkenes using platinum and rhodium complexes.^{45,46} However, demonstrations of selective catalysis by polymer-immobilized colloids of zero-valent transition metals are much more limited. Vu and coworkers reported that palladium nanoparticles immobilized and protected by water-soluble polymers showed high geometric selectivity in hydrogenations of cyclic and noncyclic olefin molecules.¹⁴

selectivity depended on the hydrophilic/hydrophobic properties of the supporting polymer.⁴⁷ Crooks and coworkers encapsulated nonselective Pd nanoparticles within a dendrimer, and in hydrogenation reactions, such catalysts could distinguish between two substrates that differed only slightly in chemical structure. The dendrimer likely served as a nanoporous cage that controlled access to the nanoparticles.^{48,49}

In our preliminary studies of the transport of neutral organic molecules through MPFs, we found that even in poly(sodium styrenesulfonate) (PSS)/poly(allylamine hydrochloride) (PAH) films, methanol diffusion is ten times faster than glucose diffusion.⁵⁰ We therefore surmised that polyelectrolyte films might function as highly size-selective filters for nanoparticle catalysis.

1.4 Heck reactions

Catalytic coupling reactions that form new C-C bonds provide more strenuous measures of catalyst performance than hydrogenation reactions.⁸ One example of such couplings is the arylation and vinylation of alkenes with aryl or vinyl halides (Figure 1.4), which was discovered independently by Heck and Mizoroki.¹ This reaction, commonly known as the Heck reaction (HR), is usually homogeneously catalyzed by palladium species generated from either Pd(0) compounds or Pd(II) salts with ligands such as phosphines, amines or heterocyclic carbenes.⁸ Addition of base, e.g. tertiary amines, alkali acetates, carbonates, and phosphates, neutralizes the acid (HX) formed from the formal exchange of a hydrogen atom with an aryl or vinyl group.



Figure 1.4: The Heck reaction.

[Pd(PPh₃)₄] is one of the most popular HR homogeneous catalysts, and precatalysts such as PdX₂ are also commonly used with excess PPh₃ in solution.⁵⁰ The presence of excess phosphine could prolong the lifetime of the catalyst by stabilizing the homogeneous catalytic system and preventing the precipitation of palladium black, but large amounts of ligand inhibit the reaction.⁵¹ Moreover, the limitation of homogeneous catalysts (most frequently needed in the 0.1-1% mol/mol range) is that the catalyst cannot be recovered, which increases cost and environmental contamination.^{1, 50, 52} Hence, there is significant interest in developing a heterogeneous catalyst for the HR to afford easy separation of catalysts, products, and substrates in industrial reactions.⁵³ Supported metal catalysts are potential candidates for this role.⁵

However, there are limited concepts and contradictory ideas concerning the mechanism and structure-activity relationships in heterogeneous HRs. There are two divergent schools of thought as to how the Heck olefination reaction is mediated by heterogeneous catalysts. Reetz^{50, 54, 55} suggested that the reaction occurs at the heterogeneous surface and employs nanopalladium. Based on model reactions

(hydrogenations), a surface mechanism and the structure of the active centers were postulated to involve highly unsaturated Pd atoms on the surface of Pd particles.^{18, 55-58}

In related work, Choudary and coworkers reported the synthesis of a layered double hydroxide (LDH)-supported nanopalladium catalyst and its application in the HR. These LDH-supported catalysts as well as catalysts on Merrifield resin were prepared by anion exchange of PdCl4²⁻ onto the support followed by reduction. For the olefination of iodobenzene with styrene, TEM images of the fresh and used catalyst showed that the nanostructured palladium supported on LDH remained unchanged at the end of the reaction, while the XPS and evolved gas detection by TGA-MS of the used catalyst identified intermediate species (ArPdX) on the heterogeneous surface. Thus, Choudary concluded that the Heck Reaction occurs truly heterogeneously with aryl halide predominantly adsorbed at defect sites of the nanopalladium particles (Figure 1.5).⁸ The basic LDH surface likely increased the electron density of the Pd centers to promote the oxidative addition of aryl halide to Pd⁰ and increase activity.^{59, 60, 61, 62}



Figure 1.5: Plausible mechanism for the supported- Pd^{0} catalyzed Heck reaction. Adapted from reference 18.

In support of a second school of thought, Arai^{60, 61} and Biffis⁵² independently made detailed studies of supported palladium catalysts and found that the reactivity is proportional to the amount of leached palladium. This suggests that the heterogeneous palladium is the source of a homogeneous palladium species⁵² that actually performs catalytic homogeneous reactions. Thus, these reactions might not be truly heterogeneous.^{63, 64}

Sheldon also addressed the question of whether the use of heterogeneous catalysts under liquid-solid conditions really provides heterogeneous catalysis.⁵⁹ He illustrated "case histories" where heterogeneous catalysts were just reservoirs of soluble, active

species generated by the chemical interaction of the catalyst with one or more of the components of the liquid phase. He also suggested that recycling of a conventional heterogeneous catalyst without observing a significant loss of activity is not proof of heterogeneity, as the active species might still be released from the support and later redeposited on the catalyst prior to recycling. Zhao and other researchers suggested that the support can sometimes re-capture most of the dissolved metal, and recycling may well be possible if enough metal remains on the support or if the support is able to recapture leached metal species at the end of the reaction.^{59, 60, 61, 62} (Figure 1.6) The extent of re-precipitation of metal on the support depends on several factors, including the base employed, the reaction temperature, and the nature of the support.

Because catalyst stability is the key to realize the potential of heterogeneous catalysts for liquid-phase oxidations, Sheldon suggested that rigorous proof of true heterogeneity can be obtained only by filtering the catalysts at the reaction temperature and testing the filtrate for activity.⁵⁹ However, Arai et al. pointed out that re-precipitation can occur towards the end of the reaction, when the aryl halide concentration in solution is considerably decreased.^{60, 61} Thus, filtrate testing might not be a perfect proof for heterogeneity, as the quenching and re-heating procedure could bring about the deactivation of possibly active soluble species, and there also could be loss during the filtration. However, this is still the most popular method to test whether the catalysis is truly heterogeneous.



Figure 1.6: A possible catalytic cycle for the Heck reaction with Pd metal catalysts. Adapted from reference 60.

In summary, the mechanism for HRs is still not clear, and there is debate concerning the two mechanisms discussed above. However, if we can develop polymerimmobilized nanoparticles that serve as truly heterogeneous catalysts, then we would expect a catalytic selectivity in HRs that involve substrates with differing sizes or hydrophobicities. Such selectivity does occur in hydrogenation reactions.^{7,14, 47, 48, 49}

Chapter 2

EXPERIMENTAL

2.1 Materials

Polyethyleneimine (PEI) (Aldrich, M_w = 25,000), poly(sodium 4-styrenesulfonate) (PSS) (Aldrich, M_w = 70,000), poly(allylamine hydrochloride) (PAH) (Aldrich, M_w = 70,000), poly(acrylic acid) (PAA) (Aldrich, M_w = 90,000, 25 wt % solution), MnCl₂ (Mallinckrodt), NaBr (Aldrich), NaCl (Mallinckrodt), palladium (Aldrich, 5 wt% on alumina powder), α-alumina (Aldrich, 100 mesh), allyl alcohol (Aldrich, 99%), 1-penten-3-ol (Aldrich, 99%), 3-methyl-1-penten-3-ol (Aldrich, 99%), 3-methyl-2-buten-1-ol (Aldrich, 99%), methyl acrylate (Aldrich, 99%), ethyl acrylate (Aldrich, 99%), butyl acrylate (Aldrich , 99%), *tert*-butyl acrylate (Alfa Aesar, 99%), potassium acetate (Spectrum, 99%), N,N-Dimethyl-formamide (DMF) (Spectrum, 99.8%), acetophenone (Baker, 99%), methyl benzoate (Aldrich, 99%), di(ethylene glycol) ethyl ether acrylate (DEGA) (Aldrich, tech. 90⁺%), potassium tetrachloropalladate (II) (Alfa Aesar, 99.99%), bromobenzene (Aldrich, 99%), and iodobenzene (Aldrich, 98%) were used as received. All solutions were prepared with 18 MΩ cm deionized water from a Millipore water purification system.

2.2 Film deposition for diffusion dialysis studies

Porous alumina supports were cleaned in a UV/ozone cleaner (Boekel UV-Clean model 135500) for 10 minutes and placed in an O-ring holder so that only the top of

support would be exposed to polyelectrolyte solutions. Deposition of polyelectrolytes began with a 2-min immersion in 0.02 M PSS (pH 2.1, 0.5 M $MnCl_2$), and the substrate was rinsed with water for 1 min before a subsequent 5-min immersion in 0.02 M PAH (pH 2.3, 0.5 M NaBr) and another 1-min water rinse. (Polymer concentrations are always given with respect to the repeating unit.) Subsequent layers were deposited similarly. The film-coated support was dried with N₂ only after deposition of the entire film.

2.3 Diffusion dialysis

A home-built dialysis apparatus (Figure 2.1) was used to study the transport of neutral organic molecules. The apparatus consisted of two glass cells (100 mL) which were connected by a 2.5-cm-long neck, and a membrane was sandwiched between the source and receiving phases. The exposed membrane area was 2.3 cm², and both source and receiving phases were stirred vigorously in order to minimize the concentration polarization at the membrane interface. The receiving phase was initially filled with deionized water or ethanol, and the source phase contained 0.1 M acetophenone in deionized water or ethanol. Flux values were normalized by dividing by the concentration of the feed phase.

2.4 Nanofiltration

NF was performed using a cross-flow apparatus that was described previously.⁶³ The coated alumina membrane was placed in a stainless steel, O-ring-sealed cell, and the system was pressurized with Ar to 70 psi. A centrifugal pump circulated the analyte

15

solution through the system and across the membrane, and a flow meter was adjusted to achieve a cross-flow of 18 mL/min. The feed solutions (2 L) were pure water or ethanol.



Figure 2.1: Schematic diagram of the diffusion dialysis setup (a) and a composite separation membrane with a selective skin layer on a porous support (b).

2.5 Synthesis of Pd nanoparticles embedded in polyelectrolyte multilayers

Deposition of catalytic PAA/PEI-Pd(0) films on alumina followed the general layer-by-layer adsorption method shown in Figure 2.2. Specifically, 15 g of α -alumina (100 mesh) was mixed with 100 mL of 20.0 mM PAA (pH adjusted to 4.0 with 0.1 M NaOH, molarity of PAA given with respect to the repeating unit), and the suspension was stirred vigorously for 10 min. Subsequently, the alumina was allowed to settle, and the supernatant solution was decanted. The alumina particles were then washed with three 100-mL aliquots of deionized water to remove excess PAA. To deposit a polycation layer, 100 mL of a PEI-Pd(II) solution (1mg/mL PEI, 2.0 mM K₂PdCl₄, pH adjusted to 9.0 with 0.1 M HCl) was added to the PAA-coated alumina, and the particles were stirred and washed as described above. This procedure was repeated until 3.5 bilayers of PAA/PEI-Pd(II) were deposited. Reduction of the Pd(II) in the films by exposure to 100 mL of fresh 1.0 mM NaBH₄ for 30 min (with stirring) provided PAA/PEI-Pd(0)-coated alumina. The coated alumina was washed three times with water after exposure to NaBH₄.

Capped films were synthesized through deposition of a 3.5-bilayer PAA/PEI-Pd(0) film followed by deposition of PAH/PAA or PEI/PAA bilayers. The PAH deposition step involved a 10 min immersion in 0.02 M PAH (pH 4.5, 0.5 M NaCl) and three washes with deionized water. PAA deposition in the capping layers was slightly different than in the PAA/PEI-Pd(0) film. Specifically, PAA was deposited using a 10-min immersion in 0.02 M PAA (pH 4.5, 0.5 M NaCl). The slightly modified procedure was chosen in order to compare with a literature method.⁵¹



Figure 2.2: Synthesis of Pd-containing PEI/PAA films ([PAA/PEI-Pd(0)]_n) on alumina through alternating adsorption of PAA and PEI-Pd(11) followed by reduction.

Figure 2.3 shows the procedure used to prepare PAA/[PEI/Pd(0)]_n catalyst. First, fifteen g of alumina was coated with a bilayer of PAA/PEI by alternating immersion in a PAA (20.0 mM, pH 4.0) and a PEI solution (1mg/mL PEI, pH 9.0) for 10 min, with water rinses used after each deposition. Subsequently, the PAA/PEI-coated alumina was immersed in 100 mL of a 1 mM K₂PdCl₄ solution, washed 3 times with water, and immersed in 20 mM PEI (pH 9.0). Subsequent bilayers of PdCl₄²/PEI were deposited similarly, and finally capped with a PAA/PEI bilayer. Reduction of the Pd(II) occurred as described for PAA/PEI-Pd(0) films.

To prepare commercial 5% Pd on Al_2O_3 coated with MPFs, the 5% Pd on Al_2O_3 was immersed in 100 mL solutions containing 20.0 mM PAA (pH 4.0) and 20 mM PEI solution (pH 9.0), alternatively, and the powder was washed three times with water between each deposition. All coated powders were vacuum dried only after the deposition of all layers.

2.6 Transmission electron microscopy (TEM)

PAA/PEI-Pd(0) films (3.5 bilayers) were also deposited on carbon-coated copper grids for TEM. Before film deposition, the grids were cleaned in a UV/ozone cleaner for 1 min, and TEM was performed on a JEOL-2010F Field-Emission microscope operating at 200 kV. Films were prepared on the grid using alternating 5-min immersions in the PAA and PEI-Pd(II) solutions described above for coating of alumina, with 1-min water rinses between polycation and polyanion depositions. The reduction (10 min in 1.0 mM NaBH₄ solution), rinsing and drying with N₂ were done just before taking the TEM image.



Figure 2.3: Synthesis of Pd-containing PEI films $(PAA/[PEI/Pd(0)]_{\eta})$ on alumina through alternating adsorption of PEI and $PdCl_4^{2-}$ followed by reduction.

2.7 Determination of the amount of Pd in catalysts

For both the commercial and synthesized catalysts, the percentage of palladium in the material was determined by atomic emission spectroscopy. Standard solutions (0.1 to 0.5 mM) were prepared by dissolving K₂PdCl₄ in 0.1 M HNO₃, and sample solutions were prepared by stirring 250 mg of synthesized catalyst or 10 mg of commercial catalyst in 2 mL of *aqua regia* for 15 min. The solutions were diluted to 25 mL and centrifuged (the α -alumina support does not dissolve in *aqua regia*), and the supernatant was analyzed at a wavelength of 633 nm. For analysis of catalysts that were previously employed in reactions, powders were separated from the reaction mixture by filtration, washed with CH₂Cl₂ and water to remove adsorbed substances, and vacuum dried before being dissolved in *aqua regia* and treated as described above.

2.8 Catalytic hydrogenation

Hydrogenation reactions were run in a 100-mL, 3-necked flask. H_2 was bubbled through a frit at the bottom of the solution at a rate of 25 mL/min (atmospheric pressure, measured by volumetric method), and the solution was vigorously mechanically stirred. The hydrogenation solution initially contained 1.0 mM of substrate, or in competitive reactions, a total of 1 mM of substrates with eqimolar amounts of each component. Ten mg of commercial 5% Pd-on-alumina or 250 mg of alumina coated with PAA/PEI-Pd(0) multilayers was used as a catalyst. Suspensions of catalyst and solvent (25 mL of H₂O) were bubbled with H₂ for 15 min before adding the substrates (50 mL solutions). Gas chromatography (GC) (Shimadzu GC-17A equipped with a RTx-BAC1 column) was applied for reaction monitoring, and GC-MS was used to identify the products.

2.9 Heck reactions

Reactions were run under typical literature conditions.²⁹ Specifically, 2 mM of iodobenzene, 2 mM methyl acrylate, 2.5 mM KOAc, 1 mol% of Pd relative to iodobenze (relative to total acrylates for competitive reactions), and either 21 mg commercial 5% Pd on alumina or 780 mg alumina coated with Pd nanoparticles embedded in MPFs were introduced into a 25-mL, 3-neck round-bottom flask fitted with a condenser. Ten mL of solvent (DMF) was added, and 0.5 mL methyl benzoate was added as an internal standard. The mixture was deaerated by a N₂ flow for 15 min, and the reactor was placed in a preheated oil bath at 95 °C for 24 hours or longer with vigorous stirring.

For catalyst recycling studies, after cooling of the reaction mixture to room temperature, the catalyst was collected by decanting, washing with DMF and CH₂Cl₂ in order to remove adsorbed organic substrates, and drying at room temperature. This catalyst was reused without any further treatment. As a comparison, the catalyst was also separated from the reaction mixture at the reaction temperature (typically 95 °C), washed with hot DMF and then CH₂Cl₂, reduced with NaBH₄, washed with water, and vacuum dried before reuse. The catalyst was reduced again with NaBH₄ in case the Pd nanoparticles were air-oxidized at high temperature. For GC and GC-MS analysis, supernatant was removed from the reaction mixture after 15 min of air cooling to allow the reaction mixture to cool to room temperature, and these samples were diluted with EtOH and subsequently analyzed. The reaction mixture was returned to the hot oil bath after sampling.

Chapter 3

Results and Discussion

This section describes my efforts to develop nanoparticles embedded in polyelectrolyte films as selective catalysts for hydrogenation and, particularly, Heck reactions. Because catalysis by these materials depends on diffusion of the substrate through the film to the nanoparticles, I investigated transport of a typical organic substrate, acetophenone, through MPFs. Concurrently, I synthesized nanoparticles in polyelectrolyte films and demonstrated the presence of these particles using TEM. I performed a few hydrogenation reactions to show that catalysis by embedded nanoparticles can, indeed, be selective, and finally, I investigated the possibility of utilizing the nanoparticles to catalyze Heck reactions. The sections below describe the specific steps in this research.

3.1 Transport of acetophenone through MPFs

To better understand the permeability of MPFs, I investigated the diffusion dialysis of acetophenone through poly(sodium styrenesulfonate)/poly(allylamine hydrochloride) (PSS/PAH) membranes in different solvents (water and ethanol). The size of acetophenone is typical of reactants that may be involved in Heck reactions. In these diffusion dialysis experiments, a porous alumina membrane coated with a PSS/PAH film separated a source phase containing acetophenone from a receiving phase that was initially deionized water or ethanol. Acetophenone diffused across the membrane to the receiving phase, and by monitoring the concentration of acetophenone in the receiving phase as a function of time, I measured the rate of transport across the membrane. Because analyte concentrations in the permeate phase were negligible compared to those in the source phase, the concentration gradients across the membrane were essentially constant, and permeate-phase concentrations increased linearly with time.

Figure 3.1 shows permeate-phase concentrations as a function of time for the diffusion of acetophenone through porous alumina before and after coating with a 7-bilayer PSS/PAH film. In water, the flux of acetophenone across the bare alumina substrate is about 3-fold faster than that through a substrate coated with a 7-bilayer PSS/PAH film (Table 3.1). However, the decrease in transport rate due to the film is 6 fold greater when the experiment is run in ethanol. I suspect that the lower flux through the film in ethanol is due to decreased swelling of the film. This supposition is supported by the fact that water flux through the film in nanofiltration is 12-fold faster than ethanol flux. (In these nanofiltration experiments, a solution is pressurized to 70 psi and forced across the membrane.) The low ethanol flux (0.08 $m^3m^{-2}d^{-1}$) likely reflects a tight membrane that is not substantially swollen in this solvent, but the fact that ethanol is larger than water may also hinder its flux.

The low permeability of PSS/PAH to acetophenone in ethanol suggests that slow access to nanoparticles in similar films could greatly decrease rates of catalysis. However, slow transport could result in much higher selectivities. The relatively low diffusivity also restricts the number of layers that one should use in a catalytic film. Thus, most of our catalytic films contained less than 4 bilayers.



Figure 3.1: Normalized permeate-phase concentrations of acetophenone in diffusion dialysis through porous alumina before (triangles, ethanol; X's, water) and after (circles, ethanol; squares, water) deposition of a 7-bilayer PSS/PAH membrane.

Table 3.1: Normalized Fluxes (mol $\text{cm}^{-2} \text{ s}^{-1}/\text{ M}$)^a of acetophenone in diffusion dialysis through Bare Porous Alumina and Alumina Coated with a [PSS/PAH]₇ film.

Membrane	Feed solution - 0.	Feed solution - 0.1 M Acetophenone			
	In water	In ethanol			
Bare	3.5×10 ⁻⁷	3.3×10 ⁻⁷			
[PSS/PAH]7	0.7×10-8	1.7~10-8			
on Alumina	9.7~10	1./*10			

^a Flux was normalized by dividing by the source phase concentration, which was initially 0.1 M.

3.2 Multilayer polyelectrolyte films containing Pd nanoparticles.

We chose to prepare Pd nanoparticles using a poly(acrylic acid)/polyethyleneimine (PAA/PEI) system using the general scheme shown in Figure 2.2. Dai previously demonstrated that complexes of PEI with Ag⁺ and Pt²⁺ are capable of forming polyelectrolyte films and that reduction of the metal ions using NaBH₄ yields nanoparticles.^{23, 52} To show that PAA/PEI-Pd(II) films can also be reduced to form nanoparticles, we prepared such films on carbon-coated Cu TEM grids, exposed them to a NaBH₄ solution and obtained TEM images of the film. The TEM image in Figure 3.2 confirms that Pd nanoparticles are well distributed in a 3.5-bilayer PAA/PEI-Pd(0) film, and that particles are relatively uniform with a narrow size distribution of 1-3 nm.



Figure3.2: TEM image of a [PAA/PEI-Pd(0)]₃PAA film on a carbon-coated copper grid.

3.3 Catalytic hydrogenation

To show that selective catalysis can result from the encapsulation of Pd nanoparticles in polyelectrolyte films, a series of unsaturated alcohols were hydrogenated using catalytic 3.5-bilayer PAA/PEI-Pd(0) films on alumina. I also examined catalysis by 3.5-bilayer PAA/PEI-coated 5% Pd on Al₂O₃ to see if these PAA/PEI films could impart catalytic selectivity by controlling access to an *underlying* catalyst. As Figure 3.3 shows, hydrogenation rates for [PAA/PEI-Pd(0)]₃PAA films decrease with increasing substrate size. Pseudo zero-order kinetics were observed for all hydrogenations at low conversions, and turnover frequencies (TOFs) were calculated from the slopes in the linear range.



Figure 3.3: Percent of substrates hydrogenated vs time for reaction of allyl alcohol (triangles), 1-penten-3-ol (circles), and 3-methyl-1-penten-3-ol (X's) on a [PAA/PEI-Pd(0)]₃PAA catalyst. Percent hydrogenation was obtained from the integration of product and reactant peaks in a GC spectrum, and the initial substrate concentrations were 1 mM. Reactions of each substrate were run separately.

Table 3.2 shows the summary of the TOFs for aqueous hydrogenation of allyl alcohol (1), 1-penten-3-ol (2), and 3-methyl-1-penten-3-ol (3), which differ only in the substituents at the α -carbon of the double bond. For catalysis by bare 5% Pd on Al₂O₃ (Table 3.2, column 2), the hydrogenation reaction rates for 1, 2, and 3 were very close (1/2~1/3~0.87), showing that the presence of additional alkyl groups at the α -carbon does not have a significant effect on catalytic activity. When [PAA/PEI-Pd(0)]₃PAA on

alumina (3.5-bilayer film, Table 3.2) was used as a catalyst, the initial rate for hydrogenation of 1 was 3- and 7-fold faster than that for 2 and 3, respectively.

Table 3.2. Turnover Frequencies (TOFs) for Hydrogenation of Structurally RelatedUnsaturated Alcohols by Several Pd Catalysts.

TOF (moles converted per mol Pd per hour)					
Substrate	5% Pd on Al ₂ O ₃	3.5 bilayers of PAA/PEI-Pd(0) on Al ₂ O ₃	5% Pd on Al ₂ O ₃ Coated with 3.5 bilayers of PAA/PEI		
1 OH	1300	772	35		
2 OH	1500	291	12		
3 OH	1500	117	7		

To show that size-based selectivity comes from the protective polyelectrolyte multilayers, we coated the commercial 5% Pd on Al₂O₃ with 3.5 bilayers of PAA/PEI and characterized selective catalysis (Table 3.2). The initial rate for hydrogenation of **1** is 3- and 5-fold faster than that for **2** and **3**, and these ratios are close to the ones for catalysis by $[PAA/PEI-Pd(0)]_3PAA$, although the hydrogenation rate for all of the alcohols was lower for the coated 5% Pd on Al₂O₃. These results strongly suggest that selective catalysis occurs due to restricted diffusion to catalytic sites. I should note that Srividhya Kidambi recently performed these reactions multiple times and found similar trends.⁴⁹

The only significant difference between her work and that reported here was a 50% lower rate of hydrogenation for 3 by [PAA/PEI-Pd(0)]₃PAA.

3.4 Heck reactions catalyzed by bare and coated 5% Pd on Al₂O₃

To further understand the geometric selectivities of Pd nanoparticles embedded in MPFs, we studied their performance as catalysts for Heck coupling reactions. The Heck reaction is thought of as a sensitive probe of metal surface structure.⁵ First, we examined competitive Heck coupling of iodobenzene with methyl acrylate and ethyl acrylate on a commercial 5% Pd on Al₂O₃ catalyst, and found no selectivity between the two acrylates (Figure 3.4 (a)). To check if a MPF coating could impart selectivity to the 5% Pd on Al_2O_3 as it did in the hydrogenation, we coated the commercial catalyst with 3.5 bilayers of PAA/PEI, and utilized these coated catalysts in the competitive Heck reaction of iodobenzene with methyl acrylate and ethyl acrylate described above. Again, no significant selectivity was found (Figure 3.4, (b)). The [PAA/PEI]₃PAA-coated 5% Pd on Al₂O₃ catalyst was also recycled by hot filtration from the mixture. Use of the recycled catalyst in a second Heck reaction resulted in a significant decrease in conversion, indicating that there is probably leaching of the palladium species from the alumina support. Selectivity between ethyl and methyl acrylate is still minimal with the recycled catalyst.

Table 3.3 shows the summary of TOFs for reaction of methyl acrylate (4) and ethyl acrylate (5) with iodobenzene using several different PAA/PEI coatings on 5% Pd on Al_2O_3 . In no case is there a significant difference between methyl acrylate and ethyl acrylate, but the reaction rate (TOF) does decrease with the number of PAA/PEI layers

on the catalyst. The decrease in reaction rates could be due to the need for substrates to diffuse through the film, but it could also be due to protection of the catalyst by the MPF. This protection could help to decrease the leaching of Pd that leads to homogeneous catalysis. Such a mechanism would be in accord with the proposal of complexation of supported Pd with aryl halide and dissolution of Pd into solution.⁴¹ Homogeneous catalysis via leached material would be consistent with a lack of size-based selectivity as well as the lower activity of recycled catalyst.



Figure 3.4: Percent of substrates converted vs reaction time in the reaction of methyl acrylate (MA) and ethyl acrylate (EA) with iodobenzene using (a) a bare 5% Pd on Al_2O_3 catalyst and (b) 5% Pd on Al_2O_3 coated with 3.5 bilayers of PAA/PEI. In (b), the reaction was performed with fresh and recycled catalyst. (Catalyst was recycled by separating from the reaction mixture at the reaction temperature (typically 95 °C) and washing with hot DMF.)

Table 3.3. Turnover frequencies for the Heck reaction of methyl and ethyl acrylate with iodobenzene using bare or MPF-coated 5% Pd on Al₂O₃ catalysts.

TOF (moles converted per mol Pd per hour)						
Substrate	5% Pd on	5% Pd on	5% Pd on	5% Pd on		
	Al ₂ O ₃	Al ₂ O ₃ coated	Al_2O_3 coated Al_2O_3 coated			
		with 1.5	with 2.5	with 3.5		
		bilayers of	bilayers of	bilayers of		
		PAA/PEI	PAA/PEI	PAA/PEI		
O	184	186	114	78		
4 Ö						
	186	190	124	80		
5						

- a. Reaction conditions: 0.01mM commercial 5% Pd on Al₂O₃ catalyst, 1 mM iodobenzene, total of 1 mM of substrates with equimolar amounts, 1.5 mM KOAc, 0.5 mM methyl benzoate, 10 mL DMF; inert atmosphere (N₂), 95 °C.
- b. Reactions are run competitively. Turnover frequencies (TOFs) were calculated within the region of conversion between 20% and 40%.

3.5 Heck reactions catalyzed by Pd nanoparticles embedded in MPFs.

We also examined Pd nanoparticles embedded in MPFs as catalysts for the Heck reaction. In this case, we examined two types of MPFs. The first was prepared through alternating exposure of the alumina support to solutions of PEI and PdCl₄²⁻ as shown in Figure 2.3. We initially deposited a PAA layer to enhance adhesion to the substrate, and reduction of the Pd(II) using NaBH₄ yielded nanoparticles.²⁵ In some cases, we capped these films with PEI/PAA bilayers. We use the terminology $PAA/[PEI/Pd(0)]_n[PEI/PAA]_m$ to denominate these films.

Table 3.4, column 4 shows the TOFs for catalysis of HRs by PAA/[PEI/Pd(0)]₃PEI/PAA films on alumina, and the reaction rates for coupling of methyl acrylate and *tert*-butyl acrylate to iodobenzene are essentially the same. In an effort to achieve selectivity, I also capped a PAA/[PEI/Pd(0)]₃PEI/PAA film with a second bilayer of PEI/PAA. The extra bilayer should slow diffusion of substrates to nanoparticles, and we expected that methyl acrylate would diffuse more quickly than *tert*-butyl acrylate and, hence, couple at a faster rate. Coupling is, indeed, slowed an order of magnitude by the additional capping layer (Table 3.4, column 5), but the reaction rates for the two acrylates are very similar. There are two possible explanations for this result. One is that the acrylates diffuse through the film at slow, but nearly comparable rates. A second explanation, suggested above, is that the coupling is actually homogeneously catalyzed, and the capping layers simply decrease the amount of Pd leached into solution.

In an effort to distinguish between homogeneous and heterogeneous catalysis, we separated alumina coated with $PAA[PEI/Pd(0)]_3[PEI/PAA]_2$ from the reaction mixture by filtration at room temperature, and reused this catalyst for 5 subsequent HRs. (After each

reaction the catalyst was collected, washed with DMF, and used without further treatment.) No significant loss in catalytic activity was observed, even after 5 reactions (Figure 3.5). However, if the catalyst was collected without cooling prior to filtration, no catalytic activity was observed in subsequent reactions. I tried washing the deactivated catalyst with DMF and CH₂Cl₂ and re-reducing it with NaBH₄ (followed by vacuum drving), but the catalyst remained inactive.



Figure 3.5: Percent conversion of methyl acrylate and ethyl acrylate in HRs with iodobenzene using a $PAA[PEJPd(0)]_5[PEJPAA]_2$ film on alumina as a catalyst. The catalyst was recycled by separation at room temperature, and conversion was monitored by GC after 21 hours.

To quantify leaching, I collected 250 mg of hot-filtered, dried PAA[PEI/Pd(0)]₃[PEI/PAA]₂ on alumina and determined the amount of palladium remaining in this material. Atomic emission spectroscopy showed that the amount of palladium remaining on the alumina was 1.8×10^{-6} mol/g, compared with 2.8×10^{-6} mol/g for fresh catalyst. Thus, only 64% of the palladium in the nanoparticles remained immobilized in the MPFs. This result provides strong support for leaching and a homogeneously catalyzed HR.

The second catalytic nanoparticle system that we employed was prepared by alternating adorption of PAA and a PEI-Pd(II) complex and subsequent reduction of Pd(II) by NaBH₄ (Figure 2.2). This systems also showed minimal selectivity in the coupling of methyl acrylate and *tert*-butyl acrylate to iodobenze. However, we also investigated the coupling of 7 to iodobenzene using this catalysis and found an 18-fold decreased coupling rate compared to methyl acrylate. I repeated this experiment twice and found a similar results both times. In reactions catalyzed by commercial 5% Pd on alumina, coupling of 7 was as fast or faster than coupling of methyl acrylate. Thus, selective coupling of methyl acrylate in the presence of 7 is not a result of electronic effects. 5% Pd on alumina coated with 3.5 bilayers of PAA/PEI also did not couple methyl acrylate selectively over 7 (Table 3.4).

Selective coupling of methyl acrylate over 7 by [PAA/PEI-Pd(0)]₃/PAA films suggests that catalysis may truly be heterogeneous with this system. However, as shown in Figure 3.6, the coupling rate for 4 decreased substantially after 10 h of reaction, even though conversion was only 60%. The dramatic decrease in coupling rate suggests fouling of either the film or the nanoparticles.

 Table 3.4. Rates of Heck coupling for structurally related substrates using bare or Pd

 nanoparticles embedded in PMFs.

TOF (moles converted per mol Pd per hour)					
Substrate	5% Pd	5% Pd on	PAA/	PAA/	[PAA/
	on Al ₂ O ₃	Al ₂ O ₃	[PEI/Pd(0)]3	[PEI/Pd(0)]3	PEI-Pd(0)]3
		coated	PEI/PAA	[PEI/PAA] ₂	PAA on
		with 3.5	on Al ₂ O ₃	on Al ₂ O ₃	Al ₂ O ₃
		bilayers of			
		PAA/PEI			
	92ª/71 ^b	27ª/30 ^b	81	5ª/10 ^b	5ª/9 ^b
6 0 0	93	29	85	5	5
	°O 89	28	-	7	0.5°

Reaction conditions: 0.01mM commercial 5% Pd on Al_2O_3 catalyst, 1 mM iodobenzene, total of 1 mM of substrates with eqimolar amounts of each component, 1.5 mMKOAc, 0.5 mM methyl benzoate, 10 mL DMF; inert atmosphere (N₂), 95 °C. 3 or 4 was run competitively against 1, and turnover frequencies (TOFs) were calculated within the region of conversion between 20% and 40%.

- a. TOF of 1 in competition against 3.
- b. TOF of 1 in competition against 4.
- c. As the final conversion rate of 4 is below 20%, overall TOF was calculated instead of that between 20 and 40%.



Figure 3.6: Percent of substrates converted vs reaction time for methyl acrylate and DEGA coupling to iodobenzene using a $[PAA/PEI-Pd(0)]_3PAA$ film on alumina as a catalyst. Percent conversion was obtained from the integration of reactant and internal standard peaks in a GC spectrum.

3.6 Conclusions

Colloidal palladium nanocatalysts prepared by in situ reductions were immobilized and protected by multilayer polyelectrolyte films. These polymerencapsulated catalysts show order of magnitude selectivities in hydrogenations of some olefins with different sizes. Experiments with MPF-coated commercial 5% Pd on Al₂O₃ suggest that selectivity occurs due to differential rates of diffusion to embedded nanoparticles.

In HRs, $[PAA/PEI-Pd(0)]_3/PAA$ films on alumina allowed selective coupling of methyl acrylate in the presence of DEGA. Unfortunately, the rate of coupling was relatively slow, and fouling of the catalyst seemed to occur. Selectivies in HRs with more similar molecules such as methyl acrylate and *tert*-butyl acrylate were <1.5. In contrast to hydrogenation, coated 5% Pd on Al₂O₃ did not effect selective catalysis of HRs, and it appears that catalysis by this coated commercial catalyst occurs due to homogenous, leached Pd. Future work should aim at developing more stable and more selective catalysts for Heck reactions.

BIBLIOGRAPHY

Bibliography

- 1. a) Tundo, P Pure Appl. Chem. 2000, 72, 1207.
 - b) Shuttleworth, S Synthesis 2000, 8, 1035.
 - c) Loch, J Pure Appl. Chem. 2001, 73, 119.
 - d) Corain, B J. Mol. Catal A: Chem 2001, 173, 99.
- 2. Wagner, M.; Kohler, K.; Djakovitch, L.; Weinkauf, S.; Hagen, V.; Muhler, M. Topics in Catalysis 2000, 13, 319.
- 3. Yamada, Y.M.A.; Takeda, K.; Takahashi, H.; Ikegami, S. Tetrahedron, 2004, 4097.
- 4. Biffis, A.; Zecca, M.; Basato, M. Eur. J. Inorganic Chem. 2001, 5, 1131.
- 5. Yamada, Y.M.A.; Takeda, K.; Takahashi, H.; Ikegami, S. Tetrahedron Letters 2003, 44, 2379.
- 6. Dai, Jinhua; Ph.D. dissertation, Michigan State University, 2002.
- 7. Kidambi, S; Dai, J; Li, J; Bruening, M. J. Am. Chem. Soc., 2004, 126, 2658.
- 8. Bars, J; Specht, U; Bradley, J; Blackmond, D. Langmuir, 1999, 15, 7621.
- 9. Aiken III, J. D.; Finke, R. G. J. Mol. Catal. A 1999, 145, 1.
- 10. Bönnemann, H.; Richards, R. M. Eur. J. Inorg. Chem. 2001, 2455.
- 11. Roucoux, A.; Schulz, J.; Patin, H. Chem. Rev. 2002, 102, 3757.
- 12. Augustine, R. A.; O'Leary, S. T. J. Mol. Catal. A 1995, 95, 277.
- 13. Biffis, A. J. Mol. Catal. A 2001, 165, 303.
- 14. Vu, Y. T.; Mark, J. E. J. Colloid Polym. Sci., 2004, 282, 613.
- 15. Mayer, A; Mark, J; Hausner, S. J. Appl. Polym. Sci. 1998, 70, 1209.
- 16. Teranishi, T.; Miyake, M. Chem. Mater. 1998, 10, 594.
- 17. Gopidas, K; Whitesell, J; Fox, M. J. Am. Chem. Soc. 2003, 3, 1757.
- 18. Choudary, B.M; Madhi, S.; Chowdari, N.S.; Kantam, M.L; Sreedhar, B. J. Am. Chem. Soc., 2002, 124, 14127.

- 19. Moreno-Mañas, M; Pleixats, R. Acc. Chem. Res., 2003, 36, 638.
- 20. Mayer, A; Mark, J. J. Polym. Sci. A, 1997, 35, 3151.
- 21. Napper, D. H., in Polymeric Stabilization of Colloidal Dispersions, Academic Press, London, 1983.
- 22. Warshawsky, A.; Upson, D. A., J. Polym. Sci. A: Polym. Chem., 1989, 27, 2963.
- 23. Iler, R. K. J. Coll. Int. Sci. 1966, 21, 569.
- 24. Decher, G. Science 1997, 277, 1232.
- 25. Decher, G.; Hong, J. D. Macromol. Chem., Macromol. Symp. 1991, 46, 321.
- 26. Decher, G.; Hong, J. D. Ber. Bunsenges. Phys. Chem. 1991, 95, 1430.
- 27. Arys, X.; Jonas, A. M.; Laschewsky, A.; Legras, R. In Supramolecular Polymers; Ciferri, A., Ed.; Marcel Dekker: New York, 2000, 505.
- 28. Lowack, K.; Helm, C. A. Macromolecules 1998, 31, 823.
- 29. Bertrand, P.; Jonas, A.; Laschewsky, A.; Legras, R. Macromol. Rapid Commun. 2000, 21, 319.
- 30. Yoo, D.; Shiratori, S. S.; Rubner, M. F. Macromolecules 1998, 31, 4309.
- 31. Lvov, Y.; Munge, B.; Giraldo, O.; Ichinose, I.; Suib, S.L.; Rusling, J. F. Langmuir 2000, 16, 8850.
- 32. Krasemann, L.; Tieke, B. Langmuir 2000, 16, 287.
- 33. Cassagneau, T.; Mallk, T. E.; Fendler, J. H. J. Am. Chem. Soc., 1998, 120, 7848.
- 34. Schmitt, J.; Decher, G. Adv. Mater., 1997, 9, 61.
- 35. Mamedov, A. A.; Kotov, N. A. Langmuir, 2000, 16, 5530.
- 36. Dai, J.; Balachandra, A.; Lee, J.; Bruening, M. L. Macromolecules 2002, 35, 3164.
- 37. Dai, J.; Jensen, A.W.; Mohanty, D.K.; Erndt, J.; Bruening, M.L. Langmuir 2001, 17, 931.
- 38. Jiang, M.; Wang, E.; Kang, Z.; Lian, S.; Wu, A.; Li, Z. J. Mater. Chem., 2003, 13, 647.
- 39. Harris, J. J.; Bruening, M. L. Langmuir 2000, 16, 2006.
- 40. Harris, J.J.; DeRose, P.M.; Bruening, M.L. J. Am. Chem. Soc. 1999, 121, 1978.

- 41. Lee, B.-J.; Kunitake, T. Langmuir 1994, 10, 557.
- 42. Farhat, T. R.; Schlenoff, J. B. Electrochem. Solid-State Lett. 2002, 5, B13.
- 43. Jin, Y.; Datya A. K.; Righto E. R., Gulotty R.; Waterman W.; Smith M; Holbrook M; Maj J; Blackson J. J. Catal., 2001, 203, 292.
- 44. Marciniec, B.; Foltynowicz, Z.; Lewandowski, M.; Appl. Organometallic Chem. 1993, 7, 207.
- 45. Michalska, Z.M.; Strzelec, K. J. Mol. Catal. A: Chem, 2001, 177, 89
- 46. Ontaki, M.; Komiyama, M.; Hirai, H.; Toshima, N. Macromolecules, 1991, 24, 5567.
- 47. Zecca, M.; Fisera, R.; Palma, G.; Lora, S.; Hronec, M.; Kralik, M. Chem. Rur. J. 2000, 6, 1980.
- 48. Niu, Y.; Yeung, L.K.; Crooks, R.M. J. Am. Chem. Soc. 2001, 123, 6840.
- 49. Crooks, R. M.; Zhao, M.; Sun, L.; Chechik, V.; Yeung, L. K. Acc. Chem. Res. 2001, 34, 181.
- 50. Reetz, M. T.; Westermann, E. Angew. Chem. Int. Ed. 2000, 39, 165.
- 51. Dieck, H.; J. Am. Chem. Soc. 1974, 96, 1133.
- 52. Biffis, A.; Zecca, M.; Basato, M. J. Mol. Catal. A: Chem. 2001, 173, 249.
- 53. Bhanage, B; Catal. Rev. Sci. Eng. 2001, 43, 315.
- 54. Reetz, M. T.; Westermann, E. Angew Chem., Int. Ed. 2000, 39, 165.
- 55. Reetz, M. T.; Lohmer, G. Chem. Commun., 1996, 1921.
- 56. Le Bars, J.; Specht, U.; Bradley, J. S.; Blackmond, D. G. Langmuir 1999, 15, 7621.
- 57. Augustine, R.L; O'Leary, S.T. J. Mol. Catal. A: Chem. 1995, 95, 277.
- 58. Augustine, R.L.; O'Leary, S.T. J. Mol. Catal. A: Chem. 1992, 72, 229.
- 59. Sheldon, R.A.; Wallau, M. Acc. Chem. Res. 1998, 31, 485.
- 60. Zhao, F.; Shirai, M.; Arai, M. J. Mol. Catal. A: Chem 2000, 154(1-2), 39.
- 61. Zhao, F.; Bhanage, B.M.; Shirai, M; Arai, M. J. Mol. Catal. A: Chem. 1999, 142, 383.
- 62. Shmidt A.F; Mametova, L.V. Kinet. Catal. 1996, 37, 406.

- 63. Rylander, P.N.; Anderson, J.R.; Boudart M.(Eds.), Catalysis Science and Technology, Vol. IV, Akademie Verlag, Berlin, 1983, 1.
- 64. Bird, A.J.; Thomson, D.T.; Catalysis, in: Jones, W.H. (Ed.), Organic Synthesis, Academic Press, New York, 1980, 61.
- 65. Liu, X; Bruening, M. L. Chem. Mater. 2004, 16, 351.

