

**SUPPORTED AND UNSUPPORTED PALLADIUM NANOPARTICLES FOR
HETEROGENEOUS CATALYSIS**

by

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Abstract

The development of new methods to prepare Pd-containing nanomaterials for catalysis are reported. Monodisperse, catalytically active Pd⁰ nanoparticles were prepared using a one-pot procedure, and new insights into the mechanism of the formation of these catalytically active Pd⁰ nanoparticles were obtained. A number of key intermediates and byproducts were determined using NMR and IR spectroscopies. Furthermore, addition of Lewis bases such as TOPO and DMSO to the reaction mixture greatly reduced the temperature at which highly monodisperse nanoparticles were formed. This effect was shown to be applicable to other Pd precursors in preparing Pd⁰ nanoparticles.

Spherical Pd⁰@*m*-SiO₂ core-shell nanoparticles were prepared and characterized by a number of techniques, including TEM, PXRD, TGA, and XPS. These nanoparticles consist of a Pd⁰ core enclosed by a mesoporous silica shell and are prepared using a simple, scalable one-pot procedure. The reaction conditions were crucial in controlling the morphology and pore diameter of the nanoparticles synthesized. Acid treatment of the Pd⁰@*m*-SiO₂ nanoparticles was found to be the most suitable method in removing CTAB. The morphology, surface area, and pore diameter of the core-shell nanoparticles remained intact after removal of CTAB.

A new ceria-containing core-shell material, PdO@*m*-CeO₂, was prepared *via* templating from Pd⁰@*m*-SiO₂ and PdO@*m*-SiO₂ nanoparticles. The absence of Pd⁰ and presence of Pd²⁺ was explained by the possible formation of a solid solution composed of Ce_{1-x}Pd_xO_{2-δ} when Pd⁰ was the core. The catalytic activity of the nanoparticles was examined by performing the catalytic oxidation of methane. As well, the silica channels of the Pd⁰@*m*-SiO₂ nanoparticles were used as selector to separate molecules based on their size.

Size-selective hydrogenation was investigated using the porous silica shell of the Pd⁰@*m*-SiO₂ nanoparticles as a selector, where the porous shell controlled the selectivity by the size of the substrates. Hydrogenation of a small molecule, 1-hexene, in CDCl₃ using acid-treated Pd⁰@*m*-SiO₂ nanoparticles occurred quickly, while the hydrogenation of a larger substrate, *O*-allyl cholesterol proceeded more slowly. However, similar results were observed using commercially available Pd/C as the catalyst. Narrowing the pore diameter of Pd⁰@*m*-SiO₂ nanoparticles showed drastic difference in reaction rates between 1-hexene and *O*-allyl cholesterol.

Preface

Material in Chapter 2 has been previously published as a communication: Man, R. W. Y.; Brown, A. R. C.; Wolf, M. O. *Angew. Chem. Int. Ed.* **2012**, *51*, 11350-11353. I am the primary author and principal investigator under the supervision of Professor Michael O. Wolf.

Chapter 4 involved collaboration with the research group of Prof. Kevin Smith from the UBC Department of Chemical Engineering.

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List of Symbols and Abbreviations

Abbreviation	Description
Å	Angstrom; 10^{-10} m
AD	Anno Domini
a.u.	arbitrary units
acac	acetylacetonate
Anal	analysis
ATR	attenuated total reflection
APT	attached proton test
BET	Brunauer–Emmett–Teller
BJH	Barrett–Joyner–Halenda
br	broad (spectral)
calcd	calculated
cm^{-1}	wavenumbers
COSY	correlation spectroscopy (NMR)
CTAB	cetyltrimethylammonium bromide; $[\text{CH}_3(\text{CH}_2)_{15}\text{N}(\text{CH}_3)_3]\text{Br}$
δ	chemical shift in ppm
Δ	heat
d	doublet (spectral), day
DMF	<i>N,N</i> -dimethylformamide
DMHA	<i>N,N</i> -dimethylhexadecylamine; $\text{CH}_3(\text{CH}_2)_{15}\text{N}(\text{CH}_3)_2$
DMSO	dimethyl sulfoxide

dt	doublet of triplets (spectral)
EI	electron ionized
ESI	electrospray ionization
Et	ethyl group; CH ₂ CH ₃
eV	electron volt
fcc	face centered cubic
FT-IR	Fourier transform infrared
g	gram
h	hour
¹ H	hydrogen-1
Hacac	acetylacetone
HPLC	high-performance liquid chromatography
IPA	isopropyl alcohol; (CH ₃) ₂ CHOH
IR	infrared
IUPAC	International Union of Pure and Applied Chemistry
<i>J</i>	NMR coupling constant
JCPDS	Joint Committee on Powder Diffraction Standards
LED	light-emitting diode
<i>Ln</i>	ligand
LREI	low-resolution electron impact
M	molarity, mega
m	multiplet (spectral), meter
<i>m/z</i>	mass-to-charge ratio

mA	milliampere
MCM	Mobil Composition of Matter
Me	methyl group; CH ₃
min	minute
mmol	millimole
MS	mass spectrometry
nm	nanometer; 10 ⁻⁹ m
NMR	nuclear magnetic resonance
OAc	acetate; CH ₃ COO ⁻
<i>p</i>	para
³¹ P	phosphorus-31
PID	proportional-integral-derivative
pH	power of hydrogen
Ph	phenyl group; C ₆ H ₅
ppm	parts per million
PXRD	powder X-ray diffraction
r.t.	room temperature
R _f	retention factor
rpm	revolutions per minute
s	singlet (spectral), second
SBA	Santa Barbara Amorphous
SEM	scanning electron microscopy/microscope
STP	standard temperature and pressure

t	triplet (spectral)
TEM	transmission electron microscopy/microscope
TEOS	tetraethyl orthosilicate; $\text{Si}(\text{OCH}_2\text{CH}_3)_4$
TGA	thermogravimetric analysis
THF	tetrahydrofuran
TMOS	tetramethyl orthosilicate; $\text{Si}(\text{OCH}_3)_4$
TOPO	tri- <i>n</i> -octylphosphine oxide
tt	triplet of triplets (spectral)
UBC	University of British Columbia (Vancouver)
UV-vis	ultraviolet-visible
v	stretching frequency
v/v	volume-by-volume
wt. %	percent by weight
μL	microliter
μm	micrometer
xs.	excess
XPS	X-ray photoelectron spectroscopy
°	degrees

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*To my parents – Gabriel and Esther,
and my boyfriend – Jacky.*

Chapter 1: Introduction

1.1 Overview

Nanotechnology has been a highlight of research in chemistry for the past decade, following the coining of the term in 1981. Nanomaterials have been made and used far earlier than that, however, for example the Lycurgus Cup, dating from 290-325 AD, contains nanosized gold and silver which changes the color of the cup depending on whether light is reflected or scattered from the glass. Despite the early application of such materials, the field of nanotechnology expanded significantly after the invention of the scanning tunneling microscope, which allowed nanotubes and quantum dots to be prepared and characterized. With the development of additional nanoscale techniques, this area of research has attracted interest from many scientific fields, ranging from chemistry to physics to biology.

The manipulation of atoms and molecules to form nanoparticles is one important aspect of nanotechnology. Nanoparticles are defined as particles or colloidal dispersions with one dimension sized from 10 - 100 nm.¹ As an atom measures about 1 angstrom (10^{-10} m), nanoparticles are nanoclusters of a few to thousands of atoms. Compared to their bulk counterparts, nanoparticulate materials have high surface area-to-volume ratios which lead to improved electronic, optical, and chemical properties. One classic example is gold nanoparticles, which exhibit different colors in nanoscale than bulk gold (Figure 1-1). These colors are due to the interaction of surface plasmons of the nanoparticles with light, rendering the particles useful in applications from photovoltaics to biomedical applications.^{2, 3}

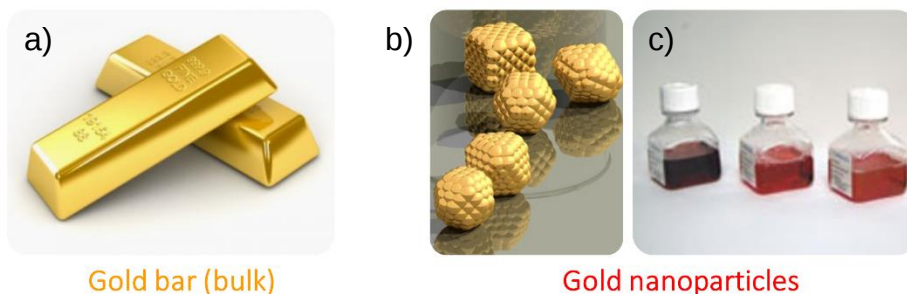


Figure 1-1. Comparison between different forms of gold. a) Gold in the bulk form. b) Representation of the atomic composition of gold nanoparticles. c) Samples of gold nanoparticles of various sizes in solution. Images reprinted from references.^{1, 4, 5}

Nanomaterials are suitable candidates for a vast number of applications, including organic photovoltaics, sensory applications, drug delivery, and biomedical applications.⁶ Semiconductor nanomaterials, such as quantum dots, exhibit unique fluorescence properties that have applications in solar cells,⁷ LEDs, and *in vivo* imaging.⁸⁻¹⁰ Porous nanoparticles of silica have been extensively studied for their uses in drug delivery¹¹ and water purification.¹² Because a large fraction of the metal atoms are exposed on the surface and due to the high surface-area-to-volume ratio, nanoparticles comprised of noble metals such as gold,^{13, 14} palladium,^{15, 16} and platinum^{17, 18} are excellent candidates as catalysts for a wide range of reactions.

Most nanoparticles are not naked: stabilizers are typically present on the surface of these nanoscale materials.¹⁹ Stabilizers serve as a protective layer, preventing agglomeration of the thermodynamically unstable particles using electrostatic forces, steric forces, or a combination of both. As illustrated in Figure 1-2, typical stabilizers are organic compounds such as ionic surfactants, polymers, and organic ligands that provide an accessible electron pair to stabilize the surface kinetically, hence they are also referred to as capping agents.²⁰ Ionic surfactants stabilize

nanoparticles kinetically by electrostatic interactions with a layer of anions, while polymers or ligands do so through the formation of relatively strong bonds with the surface atoms of the particles. These compounds present on the surface can render the nanoparticles soluble depending on the functionalities used.²¹⁻²⁴ As well, ligand exchange of the stabilizers is possible by sequential introduction of another stabilizer.²⁵ Typically stabilizing agents are introduced during the preparation of the nanoparticles, along with the metal precursors. The preparation of nanoparticles, specifically of palladium, will be discussed in Section 1.3.1.

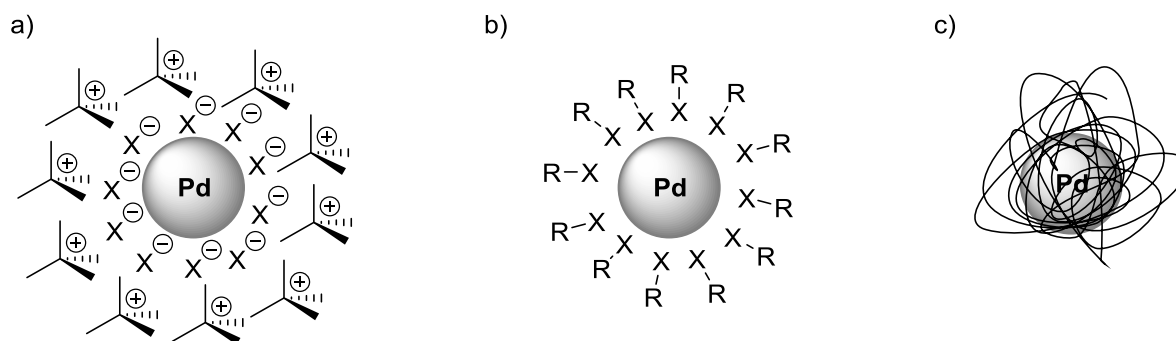


Figure 1-2. Schematic representation of the stabilization of Pd⁰ nanoparticles by a) ionic surfactants, b) ligands (X = heteroatom), c) polymers (illustrated by black lines). Redrawn from reference.²⁰

1.2 Palladium-Catalyzed Reactions

Amongst all the transition metals, palladium remains to be one of the most popular candidates for its high efficiency in a number of catalytic transformations.^{26, 27} Found in group 10 in the periodic table, palladium can catalyze a number of reactions, ranging from cross-coupling, hydrogenation, hydrogenolysis, carbonylation, to alcohol oxidation reactions. Of these reactions, the formation of new C–C bonds using Pd, including Suzuki-Miyaura,^{26, 28, 29} Heck,^{26, 29, 30} Stille,³¹ Negishi,^{29, 32} Corriu-Kumada,³³ Hiyama,³⁴ and Sonogashira³⁵ cross-coupling reactions, is a

powerful tool to synthesize organic scaffolds (Figure 1-3). This enables chemists to join organic fragments for the synthesis of new drugs, natural products, and industrially important starting materials.³⁶ Because of the importance of this transformation, Profs. Suzuki, Heck, and Negishi were jointly awarded the Nobel Prize in 2010 for their discovery and development of this novel methodology.^{26, 32}

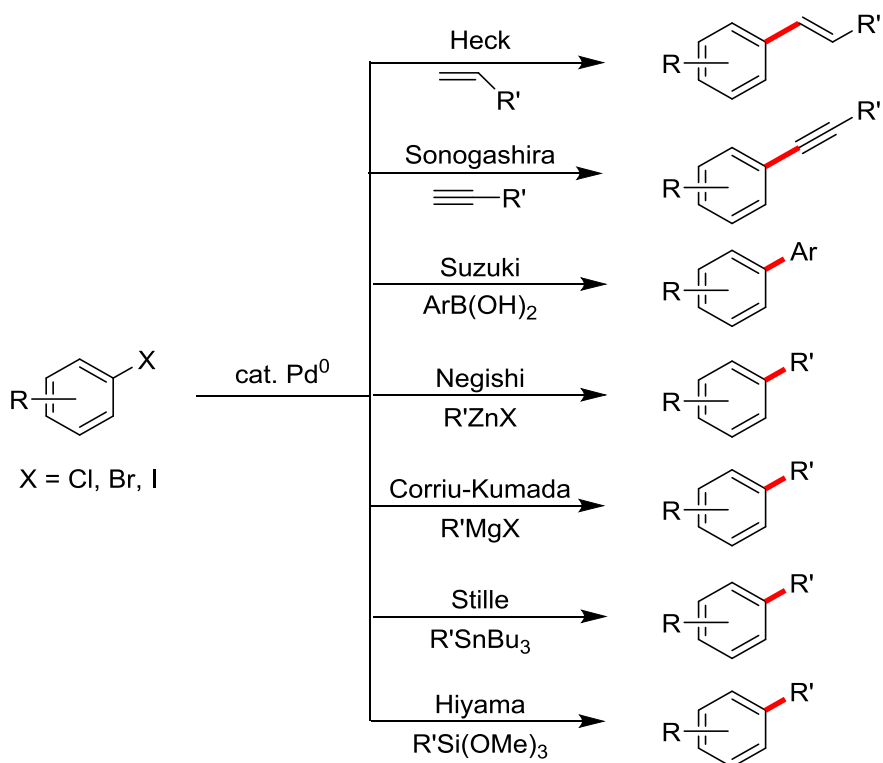
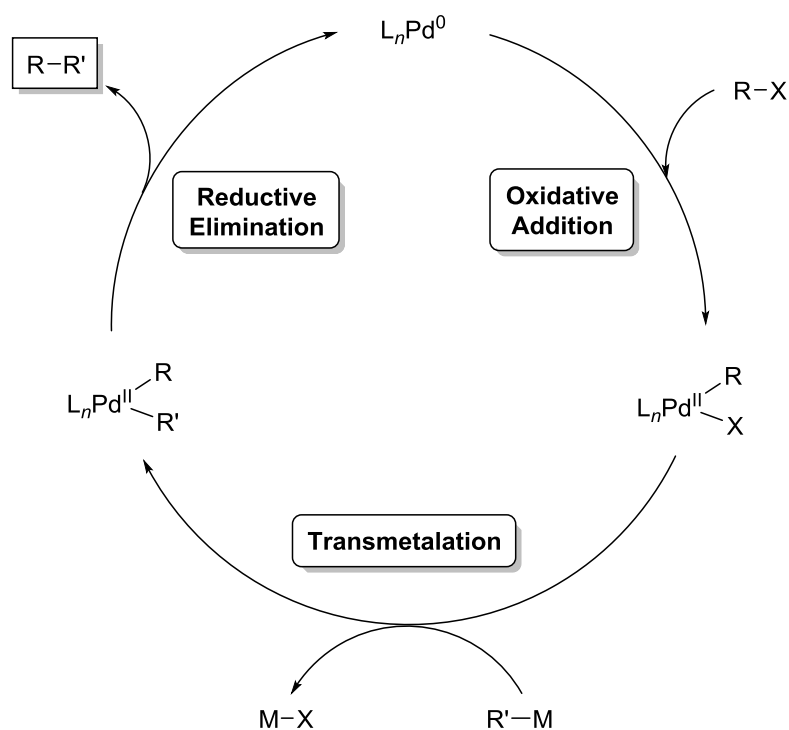


Figure 1-3. Palladium-catalyzed cross-coupling reactions. Redrawn from reference.³⁷

The generally accepted mechanism of palladium-catalyzed cross-coupling is illustrated in Scheme 1-1. A Pd^{II} complex is first introduced to the reaction and reduced to Pd^0 *in situ* (alternatively a Pd^0 complex may be directly introduced as the catalyst). The Pd^0 complex, denoted as L_nPd^0 , is the active species in the catalytic cycle. Oxidative addition of an aryl halide to the Pd^0

complex results in formation of Pd–C and Pd–X bond (X = halide), accompanied by the oxidation of Pd⁰ to Pd^{II}. Depending on the reaction, addition of the corresponding organometallic species generates a Pd^{II} intermediate with two organic fragments. Subsequent reductive elimination couples the two fragments together and forms the new C–C bond, while regenerating the active Pd⁰ species.



Scheme 1-1. General catalytic cycle of Pd⁰-catalyzed cross-coupling reactions. Redrawn from reference.³²

1.3 Palladium-Containing Heterogeneous Catalysts

Many Pd⁰-catalyzed reactions can be carried out using heterogeneous Pd⁰ catalysts, such as Pd/C and Pd⁰ nanoparticles. Homogeneous cross-coupling reactions have shortcomings such as the poor reusability of the catalyst, and undesired contamination of the organic product by residual catalyst.²³ This is crucial as the acceptable concentration limit of residual palladium in

pharmaceutical samples is on the ppm scale, and such low concentrations of Pd can be difficult and expensive to remove. Some of these problems may be resolved by using Pd nanoparticles in place of a Pd complex as the catalyst. However, the mechanism of this type of catalysis remains a subject of discussion, due to the possibility of Pd leaching and formation of catalytically active molecular species (Figure 1-4).^{15, 38, 39} For these reasons, the role of palladium in “homogeneous” catalysis by palladium remains under debate in the literature.^{40, 41}

Because of the size regime, nanoparticles have high surface area-to-volume ratios, providing a greater number of reaction sites on the surface. This translates to an increase in the number of reactive sites and increase in the catalytic activity. Furthermore, the increased number of Pd atoms available on the surface also enhances the adsorption of hydrogen, which opens up the possibility of using Pd nanoparticles for hydrogen storage and sensing applications.⁴² Using Pd nanoparticles for reactions is more convenient, as the catalysts are easy to handle, relatively more stable, and most importantly, the ease of separation of catalysts from the reaction is improved. As the nanoparticles are in the solid phase, they can be removed *via* filtration or centrifugation. This is important as much current research is geared towards “green” chemistry and applications for large-scale industrial processes, thus a simple separation procedure may provide a recyclable catalyst. Because these nanoparticles catalyze reactions in a separate phase, they are typically categorized as heterogeneous catalysts.

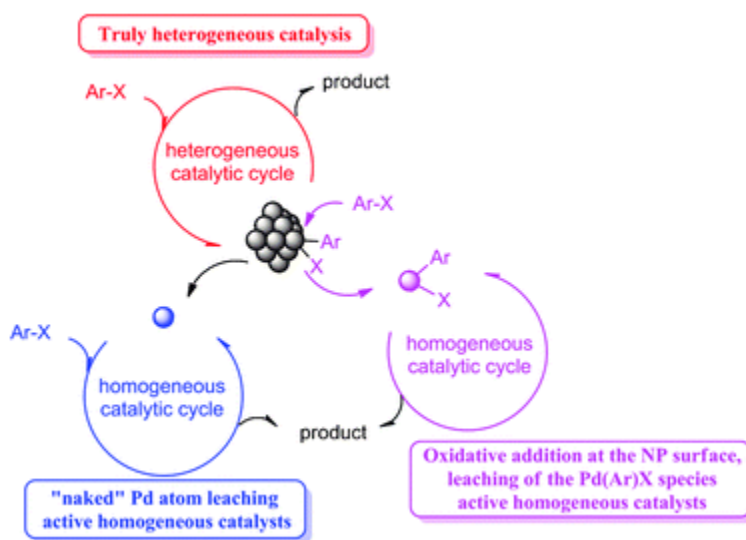


Figure 1-4. Proposed mechanisms for the C–C cross-coupling reactions catalyzed by Pd⁰ nanoparticles. Reprinted from reference with permission.¹⁵

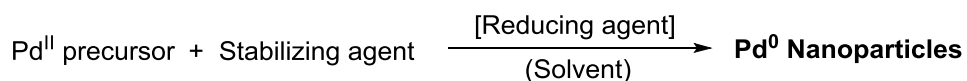
1.3.1 Unsupported Palladium Nanoparticles

Nanoparticles can be supported or unsupported. Unsupported nanoparticles are particles that are not immobilized on a substrate such as metal oxides, and are protected by stabilizing agents. Such nanoparticles are typically suspended in a suitable solvent when used for catalysis. Although Pd⁰ nanoparticles are extremely popular candidates for catalysis, questions such as how these unsupported nanoparticles are formed and what compounds are formed during synthesis remain unanswered. Nanoparticles of Pd prepared in water are better understood as the chemistry of the reductants used is better established.²⁸ New insight into the formation of Pd nanoparticles in organic media is reported in Chapter 2 of this thesis.

The preparation of Pd nanoparticles can be carried out in either aqueous or organic phases, as well as electrochemically.^{20, 24, 43} Preparation of these nanoparticles in the aqueous phase typically involves reduction of a palladium (II) precursor using a suitable reducing agent, in the

presence of a stabilizing agent (Scheme 1-2). The palladium (II) complex is first reduced by a reducing agent, such as sodium borohydride (NaBH₄) or ascorbic acid, to give Pd⁰ atoms. This is the nucleation step to the formation of crystalline Pd. As these Pd⁰ atoms are not stable on their own, the stabilizing agent in the solution prevents the agglomeration of Pd atoms to give insoluble Pd black precipitate *via* ionic interactions or coordination to the nanoparticle surface. Stabilizing agents such as amines,⁴⁴⁻⁴⁷ phosphines,^{25, 47, 48} thiols,^{49, 50} dendrimers^{51, 52} or polymers^{53, 54} have all been reported, and are responsible for the growth of the nanoparticles. Hence, each reagent used is crucial in controlling the size and morphology of the resulting Pd⁰ nanoparticles. Furthermore, size and shape can dramatically affect catalytic activity of nanoparticles. On the other hand, the preparation of nanoparticles in the organic phase often requires high temperatures (200 - 300 °C) and air-free conditions to initiate formation of nanoparticles in the absence of a reducing agent.^{46,}

55



Scheme 1-2. General scheme for the preparation of Pd⁰ nanoparticles.

With careful control of the reaction conditions, preparation of monodisperse nanoparticles of palladium is possible. Monodisperse nanoparticles refer to nanoparticles that are the same in size and shape, with diameter variation < 5% (Figure 1-5).⁵⁶ Control in the nucleation and growth of nanoparticles is crucial to prepare uniform particles.⁵⁷ Preparing monodisperse particles typically involves a trial-and-error approach, and very few examples have been reported.^{45, 48, 58-60} This was best demonstrated by Kim *et al.*, with their preparation of monodisperse Pd⁰

nanoparticles starting from palladium (II) acetylacetonate ($\text{Pd}(\text{acac})_2$) and tri-*n*-octylphosphine.⁴⁸ Heating the two compounds to 300 °C under inert atmosphere results in formation of a Pd-surfactant complex, which thermally decomposes into phosphine-stabilized Pd^0 nanoparticles with diameters of 3.5 nm (Figure 1-5a).⁴⁸ Using oleylamine along with $\text{Pd}(\text{acac})_2$ and tri-*n*-octylphosphine, as well as reduction of the preparation temperature to 250 °C results in formation of monodisperse Pd^0 nanoparticles with diameter of 5 nm (Figure 1-5b), and can be tuned to result in nanoparticles with diameters of 7 nm.

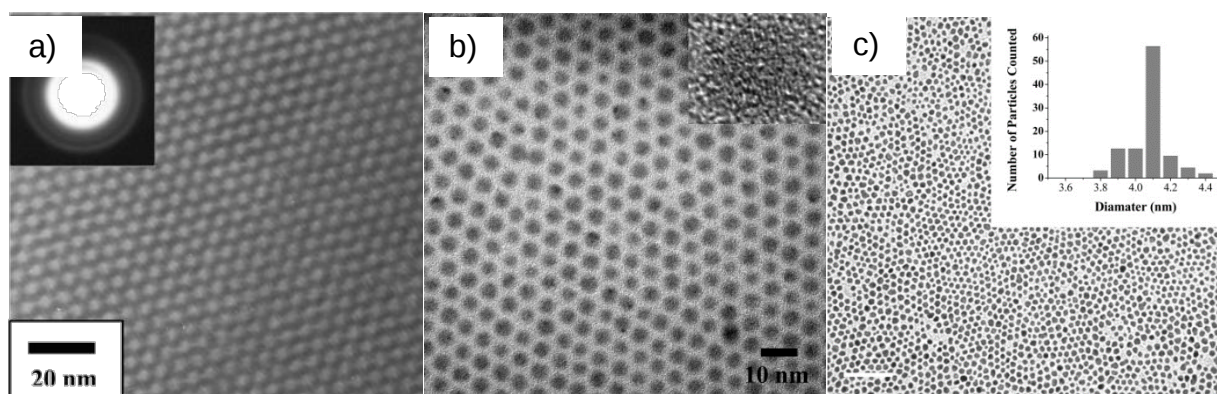


Figure 1-5. Examples of monodisperse Pd^0 nanoparticles prepared in the organic phase. a, b) Tri-*n*-octylphosphine stabilized Pd^0 nanoparticles with diameters 3.5 and 5 nm.⁴⁸ c) *n*-Dodecyl sulfide stabilized Pd^0 nanoparticles with diameters of 4.1 ± 0.1 nm.⁵⁸ Reprinted from references with permission.

In another study, Ganesan *et al.* also demonstrated the preparation of thioether-stabilized, monodisperse Pd^0 nanoparticles from a hot mixture of palladium (II) acetate ($\text{Pd}(\text{OAc})_2$) and *n*-dodecyl sulfide in toluene (Figure 1-5c).⁵⁸ The size and size distribution of the nanoparticles can be controlled by varying the solvent, reaction time, and the carbon chain length of the thioether used. Though the reaction is conducted at relatively low temperature, the morphology of the

particles is not uniform. Examples of the preparation of monodisperse Pd⁰ nanoparticles in organic solvents, especially those prepared at low temperature are rare.

1.3.2 Metal-Oxide Supported Palladium Nanoparticles

Heterogeneous catalysts containing palladium can also be employed in reactions involving gases at higher temperature (> 250 °C). Palladium-based catalysts are widely used in catalytic combustion systems, as well as CO oxidation,⁶¹ CH₄ oxidation,⁶²⁻⁶⁵ and NO_x reduction reactions.^{66,}
⁶⁷ Traditionally, these catalysts are prepared by combining a solution of palladium precursor with a metal oxide support. The resulting material is then dried and calcined at elevated temperature to decompose the metal precursor and form the nanoparticles, which are consequently immobilized on the surface of the support. This results in a material composed of PdO on a support, which typically is a different metal oxide.

Surface area is crucial in catalytic activity, as previously mentioned. Hence, a high surface area support may enhance catalytic activity by higher exposure of the reacting gases to the catalyst. This can be achieved using nanoporous metal oxides as the support. According to the IUPAC definition, nanoporous materials are classified in three groups, depending on the pore dimensions.⁶⁸ With pore dimension less than 2 nm, materials such as zeolites are considered microporous. Because these narrow pores allow diffusion of only small molecules and there are extensive interactions of the surface with the molecules, they are widely used in gas purifications and gas-storage applications.⁶⁹ On the other hand, pores with diameters exceeding 50 nm are called macropores. With these larger pores, guest molecules diffuse more quickly, and large polyaromatic molecules or small biological molecules can diffuse into the pores. Between the two extremes lies

mesopores, with pore dimensions between 2 and 50 nm, which have the perfect balance to allow larger molecules to enter the porous system, undergo reactions, and leave the pores.⁷⁰

Mesoporous materials are readily prepared using a bottom-up approach from a corresponding inorganic precursor and surfactant, where the pores are produced from self-assembly of the inorganic precursor or the condensation of the inorganic precursor around molecules (Figure 1-6). This is referred to as the sol–gel process, which involves two steps: hydrolysis of the metal oxide precursor (sol) and the condensation on self-assembled surfactant templates (gel). Removal of surfactant templates either by calcination or organic extraction results in the mesoporous metal oxide.

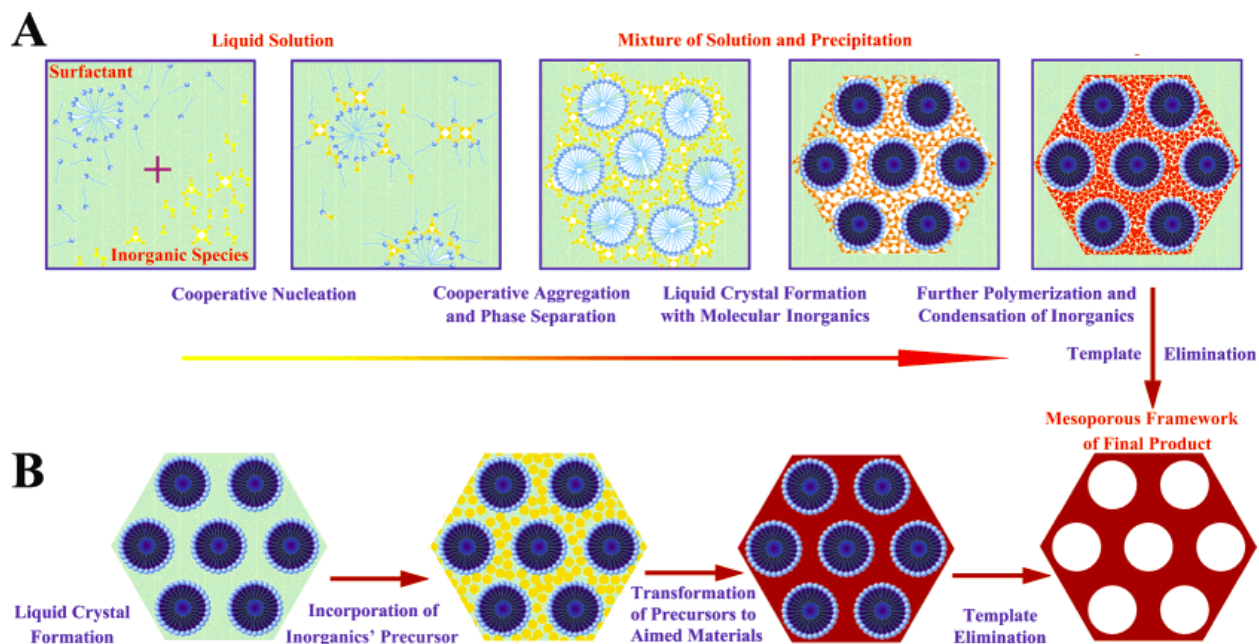
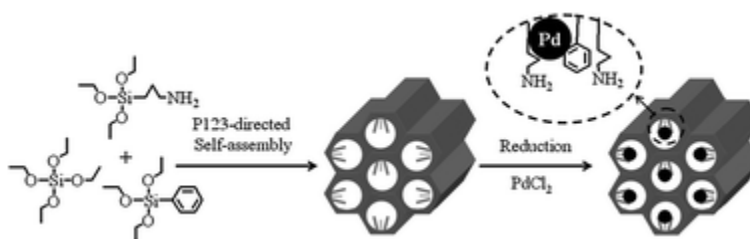


Figure 1-6. Two synthetic methodologies to forming mesoporous materials. a) Self-assembly of metal precursor; b) Liquid crystal templating process. Reprinted from reference with permission.⁷¹

Silica is the metal oxide of interest in this study due to its vast application, especially in templating, to result in materials of which morphology control is difficult.^{72, 73} MCM-41 is a common mesoporous silica material prepared using liquid crystals as the soft template, as illustrated in Figure 1-6. MCM-41 can be prepared from a basic aqueous solution of an alkylammonium salt as the surfactant and tetraethylorthosilicate (TEOS) or another silicate precursor as the silica source. In the process, the surfactant templates the formation of the mesopores while the silica precursor is hydrolyzed in the presence of a base as catalyst. The resulting silicates condense selectively around the self-assembled ionic surfactants, and form silica. This process of preparing solid material from small molecules is known as the sol-gel reaction. Removal of the surfactants results in a mesoporous material. Depending on the surfactants used in the preparation, the pore diameters of MCM-41 can be tuned from 1.5 to 10 nm.⁷¹

Incorporation of palladium nanoparticles into MCM-41, or other mesoporous silica materials has been demonstrated.^{16, 74} Typically, supported Pd⁰ catalysts are prepared by immobilizing palladium complexes to the support by surface-functionalized mesoporous silica, followed by reduction of the Pd^{II} complexes.¹⁶ Functionalization of mesoporous silica can be achieved by reacting with the corresponding organosilane to result in amine,⁷⁴⁻⁷⁶ phosphine,^{77, 78} thiol,^{79, 80} ether,⁸¹ ionic liquids,⁸² or *N*-heterocyclic carbene⁸³ groups on the surface. In some cases, supported Pd⁰ nanoparticles are prepared by a sol-gel route from palladium (II) complexes bearing organosilane-containing ligands⁸⁴ or addition of palladium complexes during the preparation of mesoporous silica.⁸⁵ Despite the higher surface area in such supported catalysts, a major problem is the irreversible, thermally-induced sintering on oxide supports, which often leads to loss of

activity. The preparation of catalysts with spatially separated active sites that remain stable during the reaction is a major area of current research.⁸⁶⁻⁸⁹



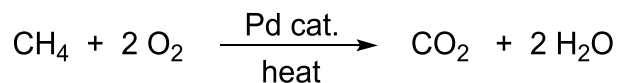
Scheme 1-3. Schematic illustrating the preparation of Pd⁰-containing catalyst supported on mesoporous silica (SBA-15) by functionalization of the surface of SBA-15, followed by immobilization of PdCl₂ and subsequent reduction to result in supported Pd⁰ nanoparticles. Reprinted from reference with permission.⁷⁴

One possible solution is the preparation of core-shell nanoparticles. Core-shell nanoparticles consisting of a nanoparticle core and porous oxide shell have the potential to impact many fields – from catalysis to spectroscopy.⁹⁰ Silica shells have been demonstrated to lead to enhanced nanoparticle catalyst stability at high temperatures, thus preventing sintering. More recently, Pt@m-SiO₂ nanoparticles have shown enhanced thermal stability for high temperature oxidation of CO.⁸⁸ Despite the large number of core-shell nanoparticle morphologies that have been reported, there are very few reports of silica shells on nanosized Pd catalysts.^{86, 87, 89} In these examples, the particles ripen and lose integrity upon heating to high temperature due to incomplete incorporation of the Pd nanoparticles. Pd nanoparticles that are individually encapsulated by silica were unknown prior to the work in this thesis.

1.3.2.1 Catalytic Oxidation of Methane Using Supported Palladium Catalysts

Development of new supported palladium-containing catalyst suitable for high temperature application is crucial, as concerns about the limited petroleum fuel supply is increasing daily. Alternative fuel resources are gaining global attention and are viewed as stepping stones towards a hydrogen economy. Natural gas is one promising candidate, as it is known for its abundance in the ocean (methane hydrates), its high octane value of 130, and its cleaner-burning capability compared to petroleum fuels such as diesel and gasoline. Currently, over 11.5 million natural gas vehicles are operating worldwide with the goal of meeting the emission regulations for vehicles to be enforced in the US by the Environmental Protection Agency, which requires significant reduction in the level of oxides of nitrogen (NO_x) and hydrocarbon emissions this decade.^{91, 92}

Despite the positive outlook in the implementation of natural gas fuel in internal combustion engines, unburned methane expelled into the environment contributes to pollution. With a potency more than 20 times that of carbon dioxide, methane gas in exhaust is a significant greenhouse gas contributor and remains in the atmosphere for a much longer time than carbon dioxide.⁴¹ As well, the strong C–H bonds of the molecule ($\sim 435 \text{ kJ mol}^{-1}$) render methane more stable and less reactive compared to other gases in the atmosphere. Conventional catalytic converters in automobiles are optimized for reducing NO_x , unburned long-chain hydrocarbons, and carbon monoxide, but are not suitable for oxidizing methane. This is due to the moderately low exhaust gas temperatures (150 to 500 °C) in natural gas-burning vehicles, which suggests that a catalyst is needed to transform methane gas into carbon dioxide, as the oxidation of methane does not occur efficiently under conditions (Scheme 1-4).



Scheme 1-4. Catalytic oxidation of methane into carbon dioxide.

Catalysts for methane oxidation are typically composed of Pd supported on alumina (Al_2O_3),^{93, 94} zirconia (ZrO_2),⁹⁵ or ceria (CeO_2).^{96, 97} Currently, very few catalysts can mediate methane oxidation at such low temperatures.⁹⁴ However, the synthetic procedure to make state-of-the-art catalysts involves a number of specialized techniques such as air-sensitive chemistry.⁹⁴ Thus, development of new palladium-containing catalysts that can oxidize methane at temperatures lower than 500 °C is critical. This is explored in Chapter 4 of the thesis.

1.4 Goals and Scope

The overarching aim of this thesis is the development of new methods to prepare Pd-containing nanomaterials for catalysis. The preparation of monodisperse Pd^0 nanoparticles in organic solvents typically requires high temperatures. As well, the mechanism of the formation of nanoparticles, the fate of organic compounds used, and the byproducts formed have not been elucidated prior to this study. The preparation of catalytically active, monodisperse Pd^0 nanoparticles prepared in a one-pot synthesis is explored in Chapter 2. The mechanism of the formation of these Pd^0 nanoparticles is discussed. A number of key intermediates are determined using a number of techniques, including NMR and IR spectroscopies.

Traditionally, supported Pd-containing nanomaterials suffer from loss of catalytic activity when used for catalytic reactions carried out at elevated temperatures (> 250 °C) due to the

thermally-induced sintering of the Pd nanoparticles. A small number of Pd-containing catalysts can mediate catalytic oxidation of methane at temperatures below 500 °C. For these reasons, spherical $\text{Pd}^0@m\text{-SiO}_2$ core-shell nanoparticles are developed; the physical and chemical properties of these particles are described in Chapter 3. These nanoparticles consist of a Pd core enclosed by a mesoporous silica shell and are prepared using a simple, scalable one-pot procedure. Different methods to remove the surfactant, cetyltrimethylammonium bromide (CTAB), and other organic components are explored. The factors that affect the morphology, composition, surface area, and pore diameter of the resulting core-shell nanoparticles are investigated. The applications of these core-shell nanoparticles in preparing other metal oxides and high-temperature catalytic reactions are then discussed in Chapter 4. $\text{PdO}@m\text{-CeO}_2$ can be prepared *via* templating with $\text{Pd}^0@m\text{-SiO}_2$ nanoparticles, and the effect of the Pd core is explored. The catalytic activity of the nanoparticles is examined by performing the catalytic oxidation of methane. As well, the silica channels of the $\text{Pd}^0@m\text{-SiO}_2$ nanoparticles can be used to separate molecules based on their size. Size-selective hydrogenation reactions evaluate the effectiveness of the pores, using a cholesterol derivative as one of the substrates. Kinetics of the hydrogenation reactions are studied.

Chapter 2: Mechanistic Study of the Preparation of Monodisperse Pd⁰ Nanoparticles at Lower Temperature

2.1 Introduction

Applications of metal nanoparticles that take advantage of the high surface area to volume ratio, high reactivity, size, shape and recyclability of these materials, continue to expand.^{98, 99} Palladium nanoparticles can serve as catalysts for Heck, Suzuki, and Sonagashira coupling, hydrogenation and oxidation reactions,^{24, 91, 92, 100} and their role in “homogeneous” Pd⁰ catalysis remains under debate.⁴¹ Pd⁰ nanoparticles are often prepared by reduction of Pd^{II} precursors in the presence of surface stabilizers such as amines,⁴⁴⁻⁴⁶ phosphines,^{25, 48} thiols,⁴⁹ dendrimers⁵² or polymers;^{53, 54} however the mechanism of nanoparticle formation is not known. In this chapter, the mechanism by which Pd⁰ nanoparticles are formed in the presence of amines is elucidated, and it is demonstrated that Lewis bases such as phosphine oxides or sulfoxides can act to significantly lower the temperature at which monodisperse nanoparticles form.

Preparation of organic-soluble Pd⁰ nanoparticles often involves thermolysis of a Pd^{II} precursor such as Pd(acac)₂ (acac = acetylacetonate) or sodium tetrachloropalladate^{45, 45, 45} in the presence of an amine such as oleylamine. High temperatures (200 - 300 °C) and air-free conditions are employed to initiate formation of nanoparticles, unless another reducing agent is introduced.^{46, 55} Some examples include preparation of Pd⁰ nanoparticles in the presence of a coordinating additive such as tri-*n*-octylphosphine,^{45, 48} or 1-dodecanethiol.⁴⁴ As higher temperatures and a trial-and-error approach are needed to prepare organic-soluble nanoparticles, very few examples of monodisperse nanoparticles have been reported.^{45, 48, 58} However, the mechanism of the formation

of nanoparticles has never been discussed fully in the literature; generally the starting materials form metal complexes, then with more heating, nanoparticles are formed. The fate of the ligands or formation of other by-products have not been previously explored fully. In this chapter, a new synthesis method of monodisperse Pd⁰ nanoparticles and a new proposed mechanism for the formation of Pd⁰ nanoparticles in the organic phase, are discussed.

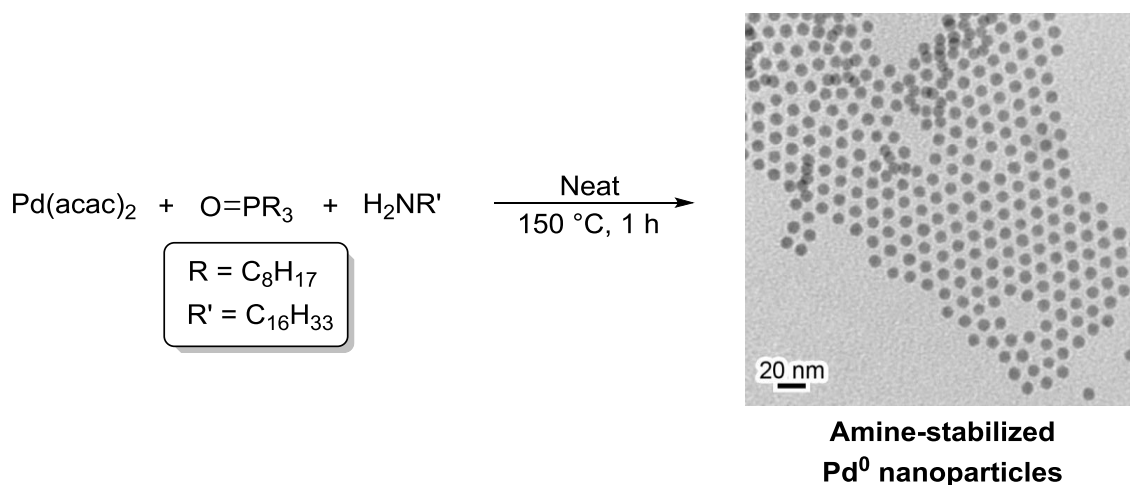
2.2 Preparation of Monodisperse Pd⁰ Nanoparticles with TOPO

Inspired by a method developed by Hyeon *et al.* involving an alkyl phosphine and an alkyl amine, an alkyl phosphine oxide was used to attempt preparation of Pd⁰ nanoparticles. Tri-*n*-octylphosphine (TOPO), 1-hexadecylamine, and palladium (II) acetylacetonate (Pd(acac)₂) were placed in a three necked round-bottom flask, and the solids were placed under a nitrogen atmosphere before heating at a rate of 3.3 °C min⁻¹ from room temperature to 150 °C. The heating rate of the reaction was carefully modulated using a temperature controller. As both the phosphine and the amine melt at ~44 °C, a pale yellow solution resulted after vigorous stirring. At *ca.* 85 °C, the solution started to turn black, and the mixture became dark black by 150 °C. This colour change is suggestive of the presence of Pd⁰. After cooling, a black precipitate, dispersible in organic solvents such as chloroform and hexanes, was isolated by centrifugation and washed numerous times with ethanol and acetone. This precipitate can be redispersed in suitable solvents and analyzed using a number of techniques outlined below.

2.2.1 Characterization of the Pd⁰ Nanoparticles

Transmission electron microscopy (TEM) was used to observe the morphology of the nanoparticles. Placing the purified precipitate in TEM revealed highly monodisperse spherical

nanoparticles, with an average diameter of 8.7 ± 0.7 nm (Scheme 2-1). The powder X-ray diffraction (PXRD) pattern of the nanoparticles shows broad signals corresponding to face center cubic (fcc) Pd^0 in the nanometer regime (JCPDS card #: 46-1043) (Figure 2-1). The broad signals are consistent with the small particle size visually observed in the TEM. No indication of the presence of other compounds of Pd, such as PdO, was observed in the PXRD pattern. As well, the nanoparticles do not change in size and shape when the samples were kept at room temperature for > 1 month. Heating the nanoparticles as a solid at 100 °C for 2 h in a muffle furnace resulted in aggregation of the nanoparticles, as observed by TEM.



Scheme 2-1. Synthesis of monodisperse Pd^0 nanoparticles in the presence of a phosphine oxide, showing TEM image of the Pd^0 nanoparticles isolated.

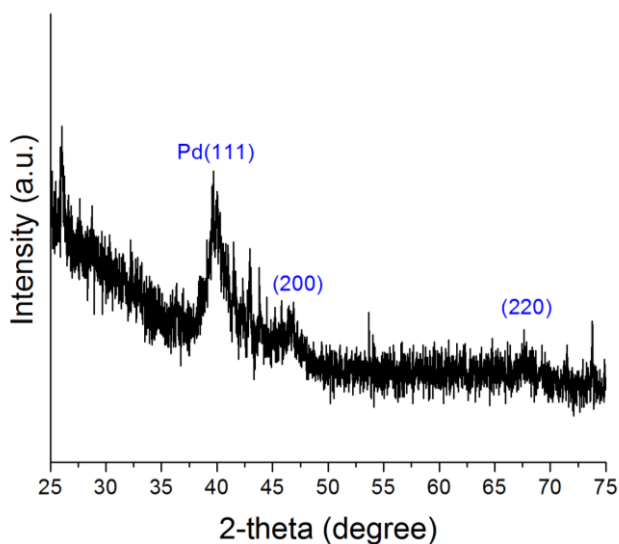


Figure 2-1. Powder X-ray diffraction pattern of the monodisperse Pd⁰ nanoparticles.

The dispersibility of the Pd⁰ nanoparticles in organic solvents suggests that it is likely that there are stabilizing agents present on the surface of the nanoparticles. This can be confirmed by FT-IR spectroscopy, where the FT-IR spectrum of the nanoparticles shows a broad N–H stretch at $\sim 3300\text{ cm}^{-1}$ and other bands close to those observed in the spectrum of 1-hexadecylamine (Figure 2-2). Surprisingly, no sign of the signature P=O stretch of the phosphine oxide was observed in the spectrum of the nanoparticles, suggesting that TOPO is not present on the nanoparticles. This is also consistent with the solution ^1H NMR spectrum of the nanoparticles, which shows C–H signals similar to that of 1-hexadecylamine but not those attributed to TOPO (Figure 2-3). The signal at δ 2.60 ppm, corresponding to the N–CH₂ protons in 1-hexadecylamine, has shifted upfield and peak broadening is observed due to interaction of the amine with the nanoparticle surface. No signals were observed in the ^{31}P NMR spectrum, which agrees with the FT-IR data indicating that negligible amounts of phosphine oxide are present on the nanoparticles. As the ^1H , ^{31}P NMR and

FT-IR spectra show no indication of the presence of TOPO on the nanoparticles, the stabilizing agent on the surface of the Pd⁰ nanoparticles is concluded to be 1-hexadecylamine.

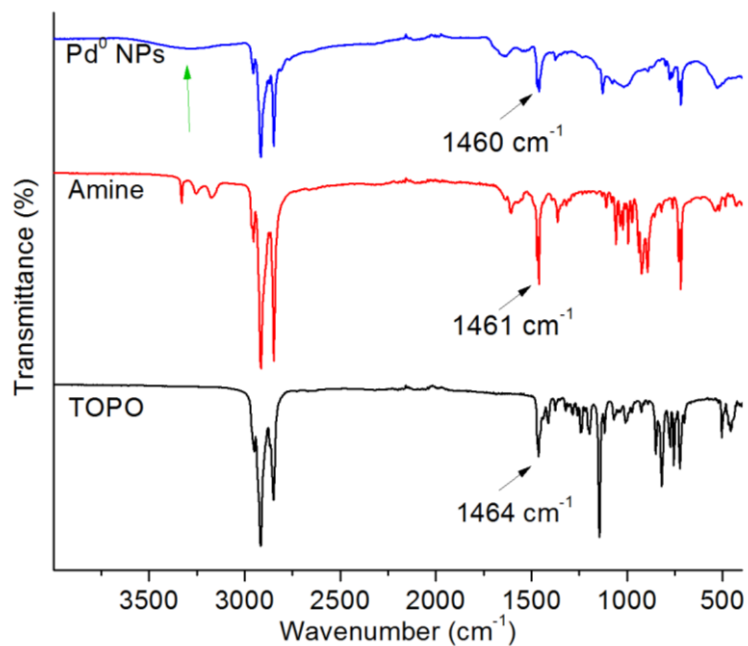


Figure 2-2. FT-IR spectra of the purified Pd⁰ nanoparticles, 1-hexadecylamine, and TOPO. Spectra collected at room temperature. The broad N–H stretch is indicated by the green arrow.

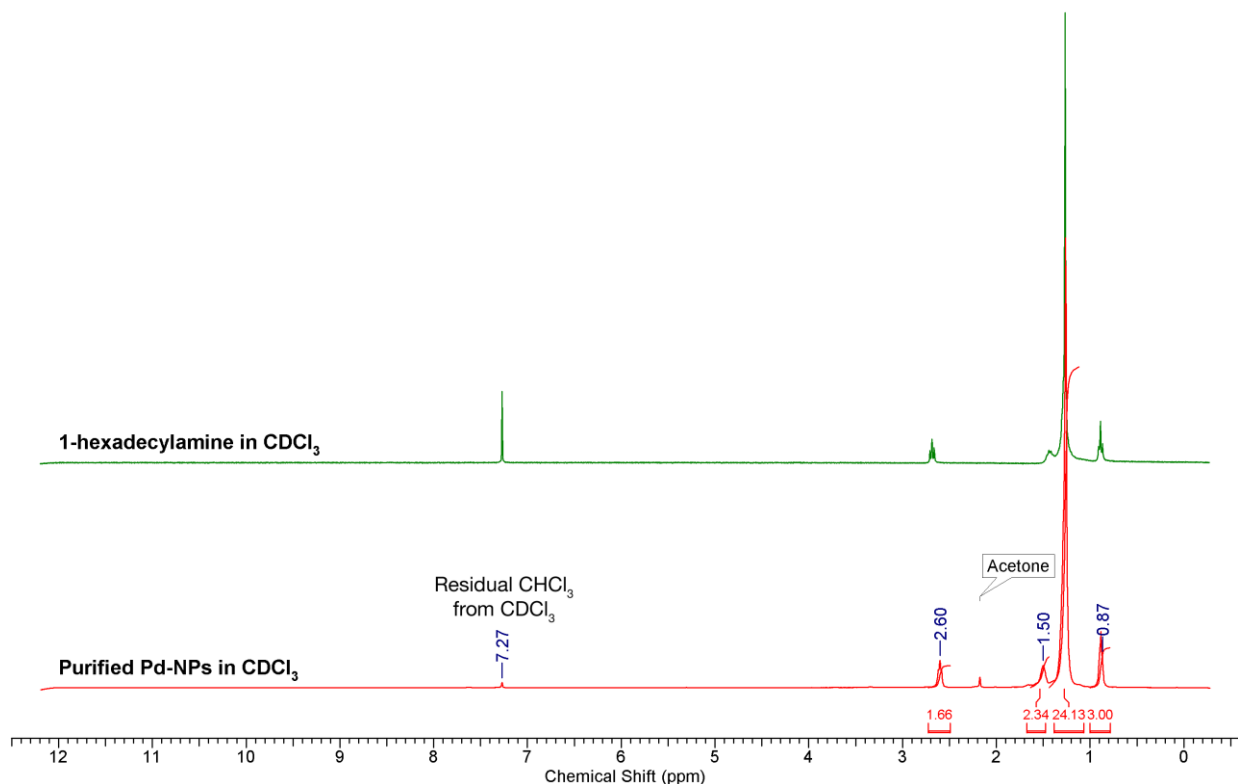
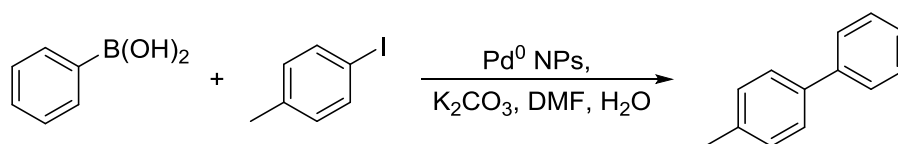


Figure 2-3. ^1H NMR spectra of the purified Pd^0 nanoparticles and 1-hexadecylamine in CDCl_3 (300 MHz, room temperature spectra).

Furthermore, the catalytic activity of the Pd^0 nanoparticles was tested by performing a prototypical Suzuki-Miyaura cross-coupling reaction (Table 2-1). Pd^0 nanoparticles are known to catalyze the cross-coupling reaction between boronic acids and aryl halides to form a new C–C bond. Phenylboronic acid and 4-iodotoluene were chosen as the substrates,¹⁰¹ and the product, 4-phenyltoluene, was purified by column chromatography and the identity was confirmed by ^1H NMR spectroscopy and EI-MS. As only 0.5 mol% Pd is needed for the reaction at moderate temperature, it can be concluded that the Pd^0 nanoparticles are highly catalytically active. The catalytic activity is comparable to other Pd^0 systems reported previously.^{91, 101}



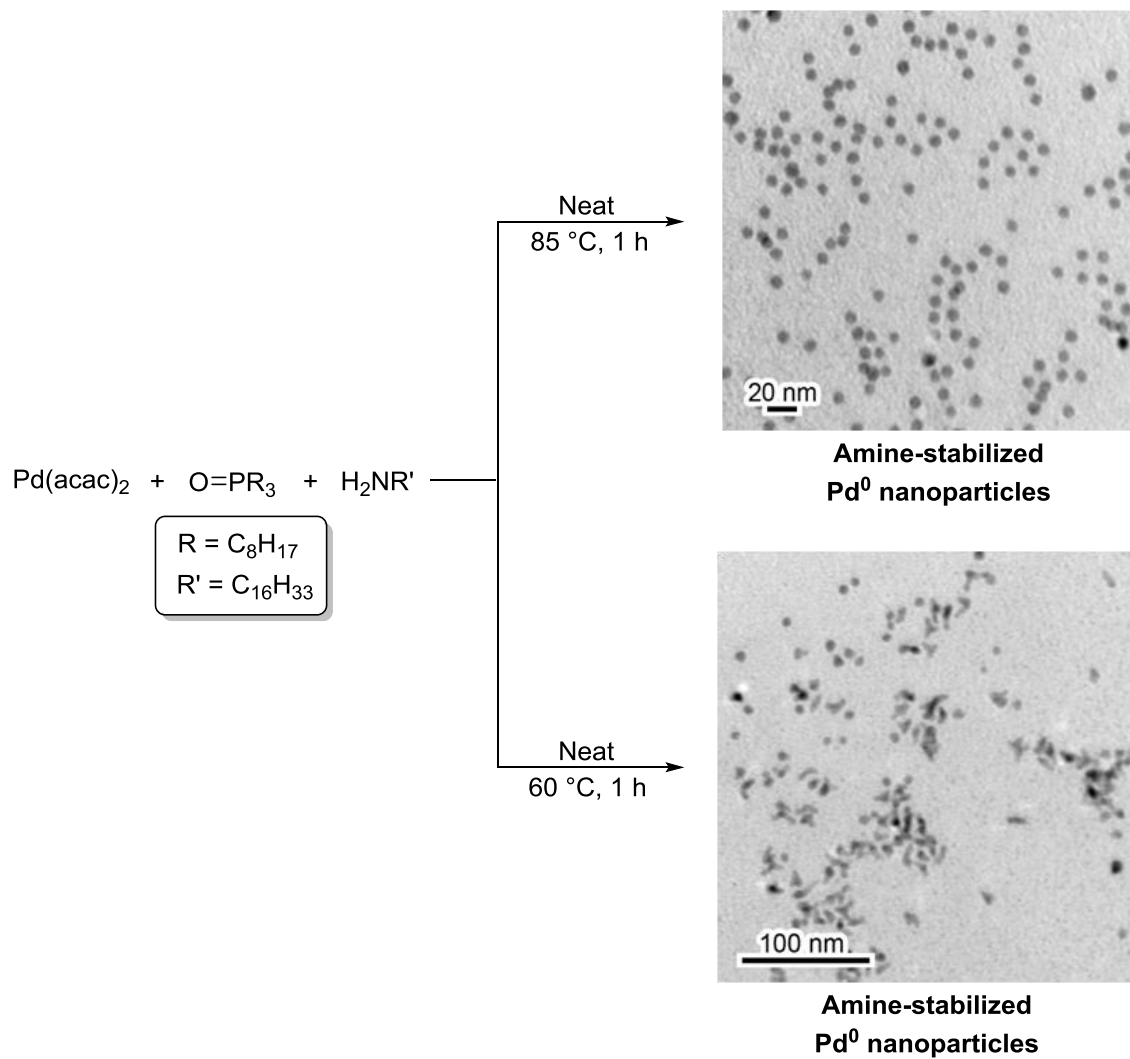
Entry	mol% Pd	Temperature (°C)	Time (h)	Isolated Yield (%)
1	0.5	60	5	68
2	0.5	60	42	78
3	0.5	100	5	83

Table 2-1. Suzuki-Miyaura cross-coupling reaction of phenylboronic acid and 4-iodotoluene catalyzed by Pd⁰ nanoparticles prepared in the presence of TOPO.

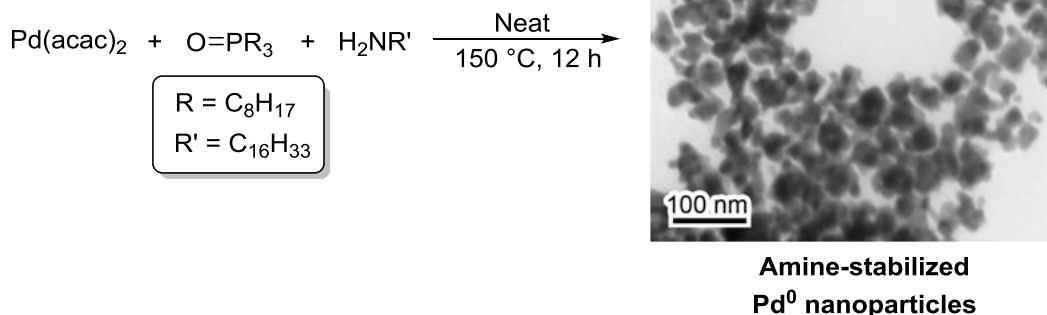
2.2.2 Preparation of the Pd⁰ Nanoparticles under Various Conditions

2.2.2.1 Effect of Temperature on the Preparation of Pd⁰ Nanoparticles

Modifying the reaction conditions has a large impact on the monodispersity, size, and morphology of the resulting nanoparticles. Temperature, time, heating rate, and ratio of the reactants were systematically changed, and the resulting nanoparticles studied by TEM. Lowering the reaction temperature from 150 °C to 85 °C did not greatly affect the results, as spherical, monodisperse Pd⁰ nanoparticles were still isolated (Scheme 2-2, top). The size of the nanoparticles are similar to those prepared at 150 °C. When the temperature is lowered to 60 °C, the colour change from yellow to black occurred more slowly, and the resulting nanoparticles were no longer monodisperse (Scheme 2-2, bottom). Particles formed at 60 °C appeared to be more rod-like, with some particles remaining spherical in shape. Allowing the reaction to proceed for 12 h at 150 °C appeared to initiate aggregation of the monodisperse Pd⁰ nanoparticles into larger, uneven nanoparticles (Scheme 2-3).



Scheme 2-2. Amine-stabilized Pd⁰ nanoparticles prepared by reacting Pd(acac)₂, 1-hexadecylamine and TOPO at 85 °C for 1 h (top) and 60 °C for 1 h (bottom).



Scheme 2-3. Pd⁰ nanoparticles isolated after allowing the reaction of Pd(acac)₂, 1-hexadecylamine, and TOPO to proceed for 12 h at 150 °C.

2.2.2.2 Effect of Heating Rate on the Preparation of Pd⁰ Nanoparticles

The heating rate of the reaction was varied using a temperature controller that modulated the heating rate. Because the temperature probe monitored the temperature of the reaction mixture directly, the heating rate could be carefully controlled. Increasing the heating rate from 3.3 °C min⁻¹ to 5.0 °C min⁻¹ without changing the amounts of reactants used resulted in spherical Pd⁰ nanoparticles with an average diameter of 9.9 ± 3.9 nm (Figure 2-4). Compared to the nanoparticles prepared at slower rate, the diameter increased slightly and the particles are less monodisperse (9.9 ± 3.9 nm as compared to 8.7 ± 0.7 nm). The reaction rate was further increased by heating the reaction mixture in a preheated sand bath. Using the sand bath for heating and a heating rate of 10 °C min⁻¹, the resulting particles were spherical but contained more large aggregates than those prepared at slower rates. This suggests that heating rate only slightly affects the growth of the nanoparticles, with a faster heating rate resulting in reduced monodispersity while preserving the general shape of the nanoparticles. The effect of a slower heating rate was not explored.

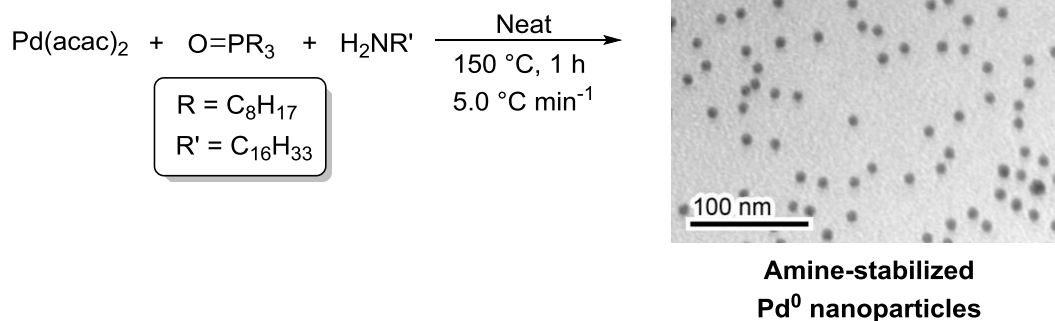


Figure 2-4. Amine-stabilized Pd⁰ nanoparticles prepared by reacting Pd(acac)₂, 1-hexadecylamine and TOPO at 150 °C for 1 h at a heating rate of 5.0 °C min⁻¹.

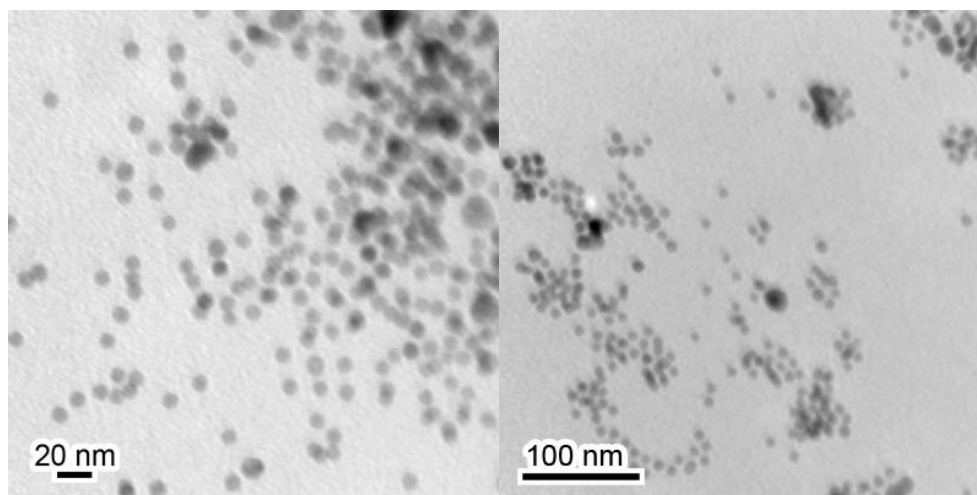


Figure 2-5. Amine-stabilized Pd⁰ nanoparticles prepared by reacting Pd(acac)₂, 1-hexadecylamine and TOPO at 150 °C for 1 h using a sand bath.

2.2.2.3 Effect of the Amount of Reagents Used in the Preparation of Pd⁰ Nanoparticles

The effect of varying the amounts of each reagent used in the on the monodispersity of the nanoparticles was probed. When the amount of TOPO used is lowered to 10 mol% relative to

amount of $\text{Pd}(\text{acac})_2$, nanoparticles were formed but the morphology of the particles became more branched (Figure 2-6). In addition, the nanoparticles appeared to be aggregate. Similar aggregates were observed when no TOPO is added to the reaction. This is interesting as TOPO does not serve as a stabilizing agent for the nanoparticles, yet appears to have an effect on the growth of the nanoparticles. The exact role TOPO plays in the reaction will be discussed in Section 2.3.

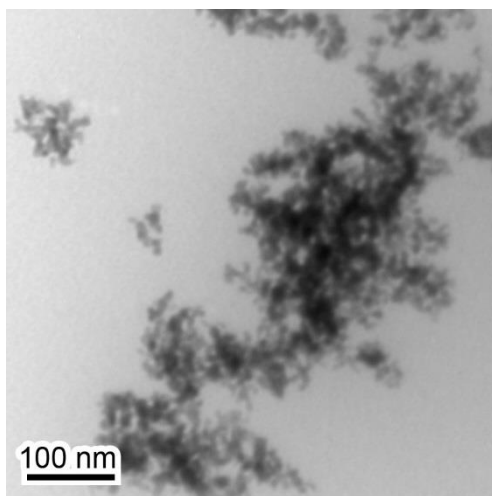
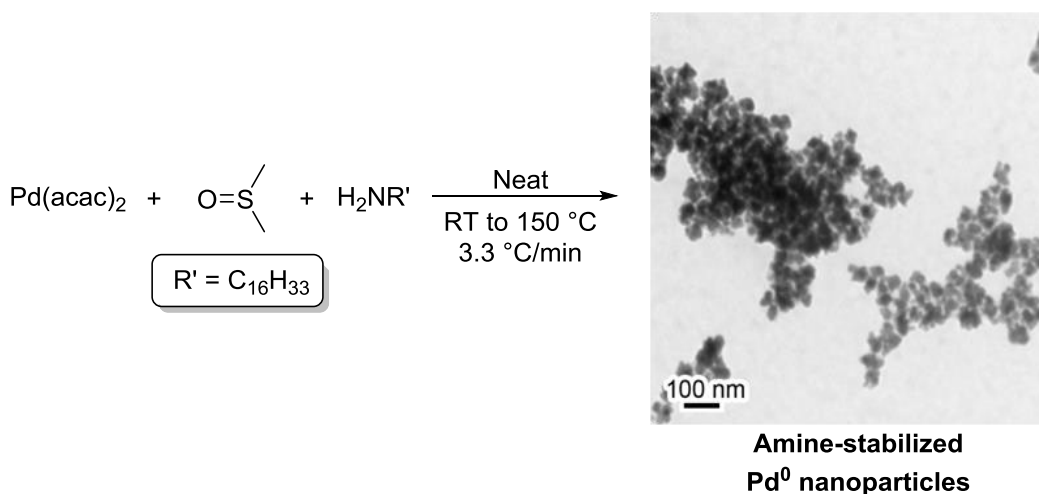


Figure 2-6. Transmission electron microscopy images of Pd^0 nanoparticles prepared using $\text{Pd}(\text{acac})_2$, 1-hexadecylamine, and TOPO (10 mol%) at 150 °C for 1 h at a heating rate of 3.3 °C min⁻¹.

Replacing TOPO with another oxides, dimethylsulfoxide (DMSO), also affected the quality of the nanoparticles produced. Similar to the results observed when modifying the amount of TOPO used, the nanoparticles prepared using an identical amount of DMSO as TOPO resulted in aggregates (Scheme 2-4). It is possible that with further fine-tuning of the conditions, monodisperse Pd^0 nanoparticles could also be prepared in the presence of DMSO.

On the other hand, replacing 1-hexadecylamine with an equal amount of another long chain amine did not greatly affect the monodispersity of the nanoparticles formed. When oleylamine was

used, spherical nanoparticles were isolated but with a slightly broader size distribution (Scheme 2-4). However, using a shorter chain length amine such as 1-dodecylamine resulted in Pd⁰ nanoparticles with various shapes, with a larger average diameter of 12.2 ± 8.7 nm (Figure 2-8), which is possibly due to the inability of the C12 chain of 1-dodecylamine to prevent aggregation of the nanoparticles during their growth. These two results suggest that chain length plays an important role in the preparation of nanoparticles, and the same dependence on chain length was observed in other studies.⁵⁸



Scheme 2-4. Pd⁰ nanoparticles prepared with Pd(acac)₂, 1-hexadecylamine, and DMSO at 150 °C for 1 h at a heating rate of 3.3 °C min⁻¹.

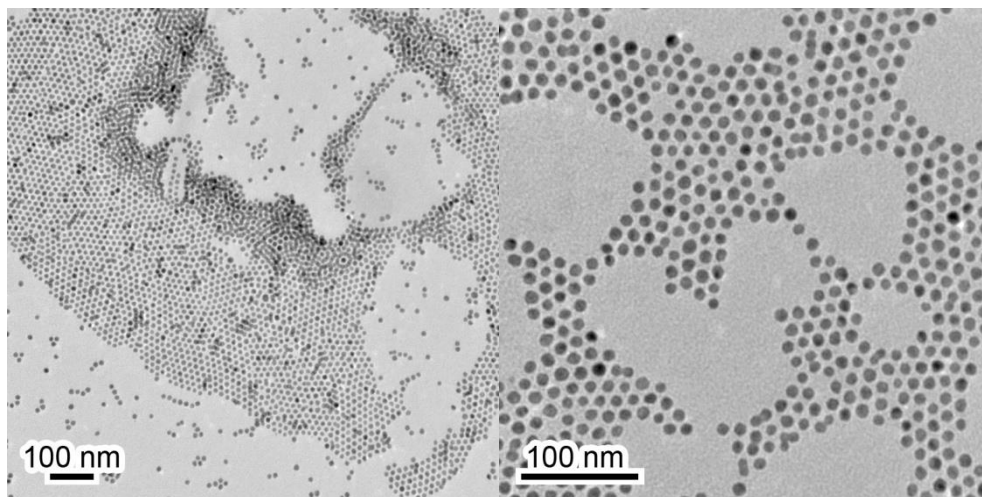
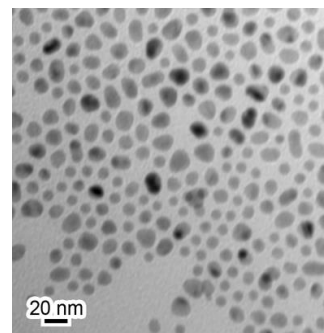
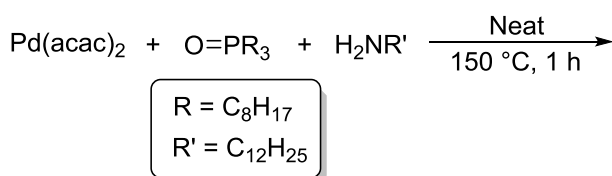


Figure 2-7. Transmission electron microscopy images of Pd⁰ nanoparticles prepared using Pd(acac)₂, oleylamine, and TOPO at 150 °C for 1 h at a heating rate of 3.3 °C min⁻¹.



**Amine-stabilized
Pd⁰ nanoparticles**

Figure 2-8. Pd⁰ nanoparticles prepared with Pd(acac)₂, 1-dodecylamine, and TOPO at 150 °C for 1 h at a heating rate of 3.3 °C min⁻¹.

2.3 Elucidation of the Mechanism of Formation of Monodisperse Pd⁰ Nanoparticles

¹H NMR spectroscopy was used to elucidate the identity of the intermediates involved in the preparation of nanoparticles from Pd(acac)₂ in the presence of excess 1-hexadecylamine. As the preparation of the Pd⁰ nanoparticles was conducted at a steady rate of heating, variable-

temperature ^1H and ^{31}P NMR spectra were deemed inadequate for this study due to the inconsistent heating rate within the NMR spectrometer and the need to equilibrate the temperature prior to collection of data, which could lead to poor reproducibility. This is especially true since heating a sample containing the precursors to 60 °C for 1 h can form Pd^0 nanoparticles, as discussed in the previous section. Instead, the reaction was conducted as before, and an aliquot of the reaction mixture was removed at 10 °C increments while the reaction mixture was heated. This approach prevents inconsistencies that might result from overheating the sample. Following removal of the aliquot, NMR samples were immediately prepared by addition of CDCl_3 and the spectral data were collected within a day (Figure 2-9). The growth of the nanoparticles does not occur at room temperature.

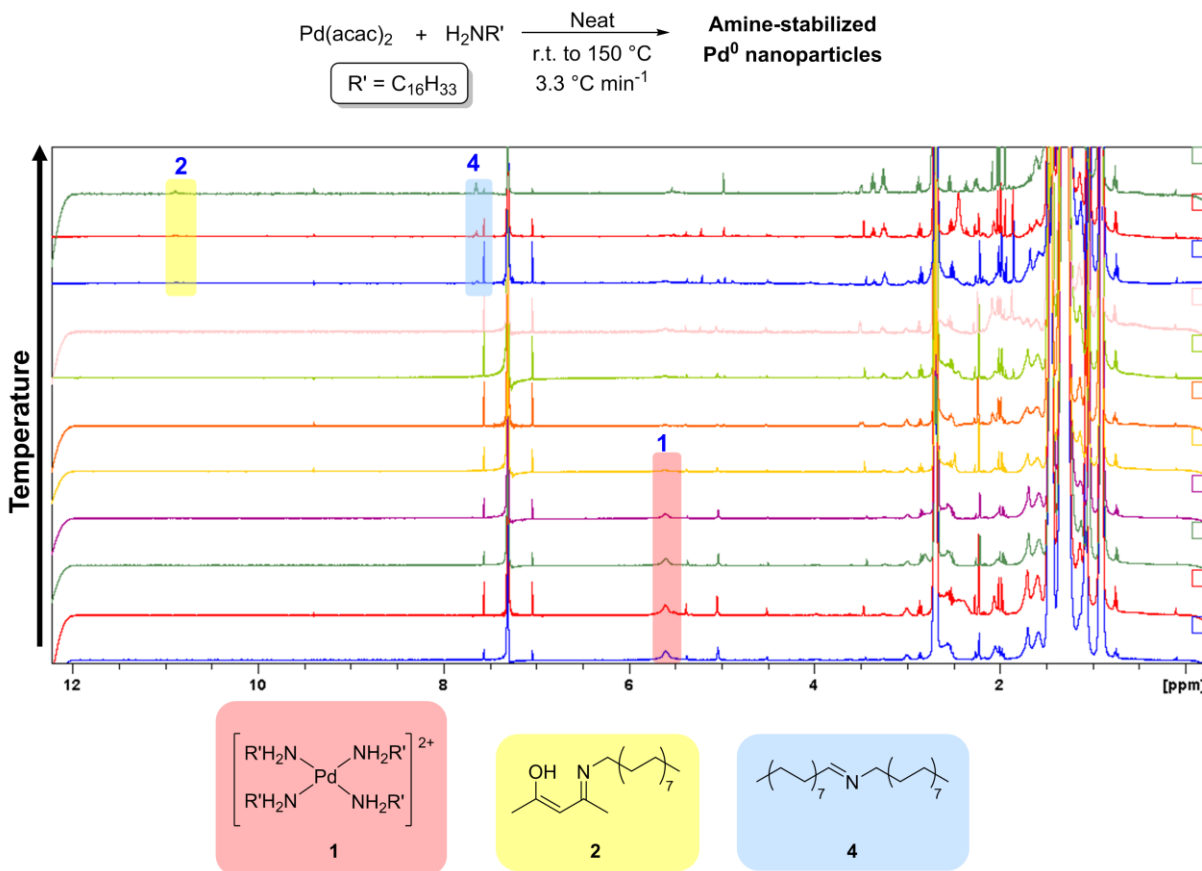


Figure 2-9. Stacked room-temperature ^1H NMR spectra of the $\text{Pd}(\text{acac})_2$ and 1-hexadecylamine reaction mixture from 50 to 150 $^\circ\text{C}$. Spectra were collected in CDCl_3 .

2.3.1 Identification of Intermediates Using NMR and UV-vis Spectroscopies

In order to elucidate the role TOPO was playing, the reaction between $\text{Pd}(\text{acac})_2$ and 1-hexadecylamine was first studied. At first glance, the ^1H NMR spectral data showed large signals corresponding to the excess amine present in the reaction mixture (Figure 2-9). Looking closely at the data, however, there are new signals due to various compounds that are formed and depleted during the course of the reaction. These compounds can be identified by comparison to data in literature, and all the identified compounds are summarized in Table 2-2. As the signal-to-noise

ratio was relatively weak, integration of the peaks were not reliable, hence the relative amounts of the various species were not quantified. Interestingly, species such as ketimines, diketimines, aldimines, as well as secondary amines were observed at different times. By identifying the various compounds present, and the order in which they are formed, a plausible mechanism for the formation of these Pd⁰ nanoparticles can be put forward.

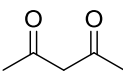
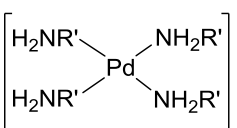
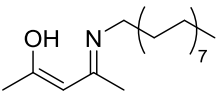
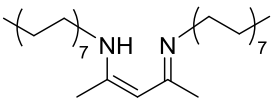
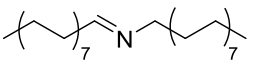
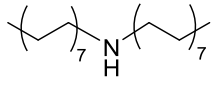
Compound	Diagnostic ¹ H NMR Chemical Shifts (ppm)	Temperature Observed (°C)	References for Similar Compounds
	3.61 (CH ₂) 2.24 (CH ₃)	50-60	
	5.6 (NH ₂)	60-130	R' = ⁿ Pr: <i>Bull. Chem. Soc. Jpn.</i> 1981 , 54, 1978-1994.
	10.82 (-OH) 4.91 (CH) 3.18 (NCH ₂) 1.95 (OCH ₃) 1.87 (N=CCH ₃)	50-150	ⁱ Pr analogue: <i>Organometallics</i> 2006 , 25, 5854-5862.
	ⁱ Pr analogue: 10.04 (NH) 4.47 (CH) 3.17 (NCH ₂) 1.87 (CCH ₃)	130-150	ⁱ Pr analogue: <i>Organometallics</i> 2006 , 25, 5854-5862.
	N-octylidenedodecylamine: 7.54 (N=CH) 3.26 (NCH ₂) 2.15 (CH ₂ CH)	90-150	N-octylidenedodecylamine: <i>Organometallics</i> 2011 , 30, 2468-2471.
	dihexylamine: 2.59 (NCH ₂)	140-150	dihexylamine: <i>Synthesis</i> 2009 , 24, 4110-4112.

Table 2-2. Summary of key ¹H NMR chemical shifts of compounds **1-5** or their analogues in CDCl₃.

At low temperatures ($\sim 50\text{ }^{\circ}\text{C}$), the reaction of $\text{Pd}(\text{acac})_2$ and 1-hexadecylamine results in the exclusive formation of tetraaminopalladium salt **1** (Scheme 2-5), evidenced by the diagnostic broad peak in the ^1H NMR spectrum corresponding to a Pd-bound $-\text{NH}_2$ group (δ 5.6 ppm).¹⁰² This complex can be formed by displacement of the acac ligands in the presence of excess amine. With 1-hexadecylamine present in large excess, other possible Pd complexes such as those shown in Figure 2-10 were not formed. The diagnostic ^1H NMR signal at ~ 4.5 ppm, which corresponds to the meso proton of the C-bound acac ligand in compound **6**, was not observed in any of the NMR spectra. As well, the diagnostic N–H signal of compound **7** at δ 5.20 ppm was not observed. Complexes **8** and **9** were ruled out by comparison of the chemical shifts of the C–H signal to the analogous isopropyl-substituted complexes, or in low, unobservable quantities.^{103, 104} These observations are consistent with other studies on the mechanism of nanoparticle formation, where metal complexes are also initially formed.¹⁰⁵

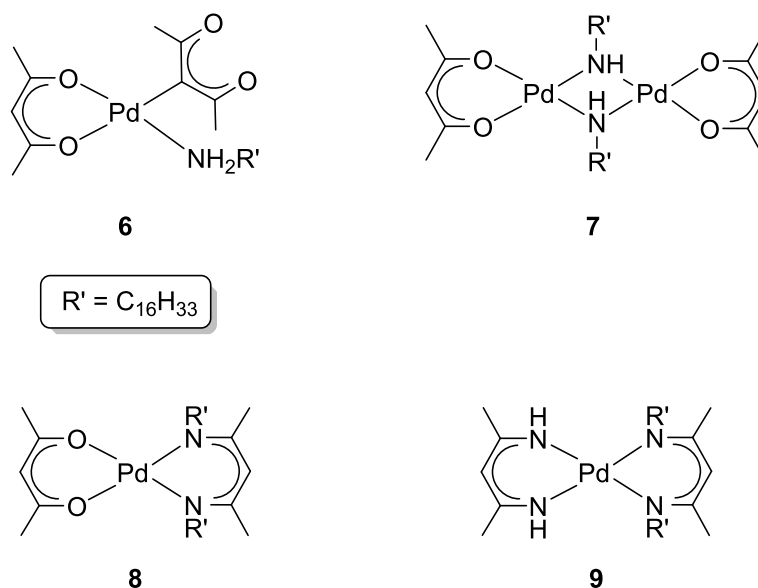
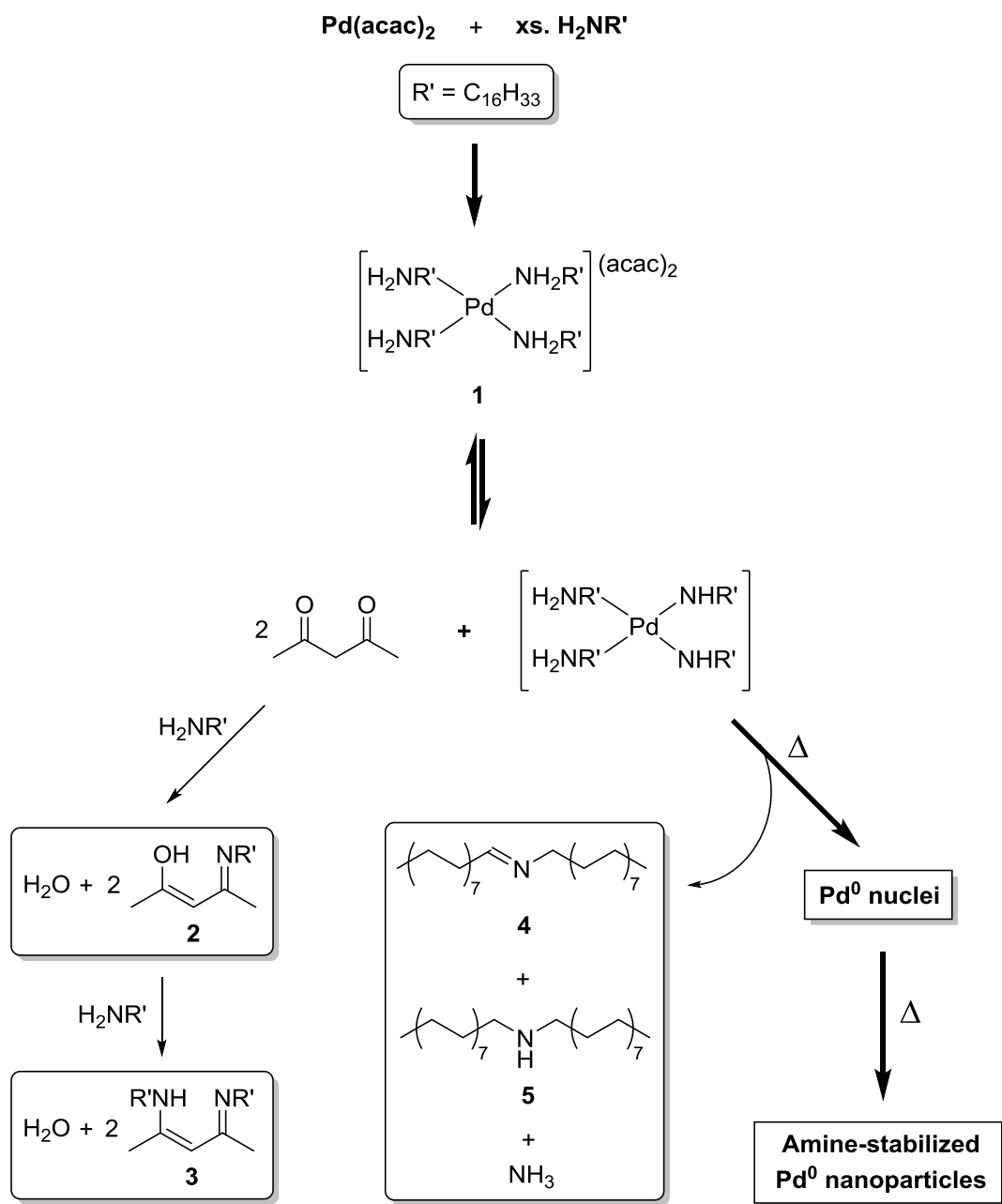


Figure 2-10. Other possible Pd^{II} complexes that were not observed in the ^1H NMR spectra.



Scheme 2-5. Proposed mechanism for the formation of Pd⁰ nanoparticles from Pd(acac)₂ and primary amine.

The displacement of the acac^- ligand by added amine can be further confirmed qualitatively by UV-vis spectroscopy, by monitoring changes in the absorption bands with the addition of 1-hexadecylamine, TOPO, and combinations of both compounds, in separate experiments. When amine is added to a dilute solution of $\text{Pd}(\text{acac})_2$ in hexanes, the absorption band at 328 nm depletes and a new band at 270 nm arises (Figure 2-11, red trace). The same peak can be observed when amine and TOPO are both added at the same time (green trace). These changes in the UV-vis spectrum are not observed when only TOPO is added to a solution of $\text{Pd}(\text{acac})_2$ (blue trace), suggesting amine plays an important role in the reaction, agreeing with the NMR studies, where the acac^- ligand is found to be displaced by added amine. Furthermore, the new band at 270 nm closely resembles the band observed in the UV-vis spectrum of $\text{Na}(\text{acac})$ (dotted line), which suggests possibility of the displacement of acac^- by amines, supporting the formation of complex

1.

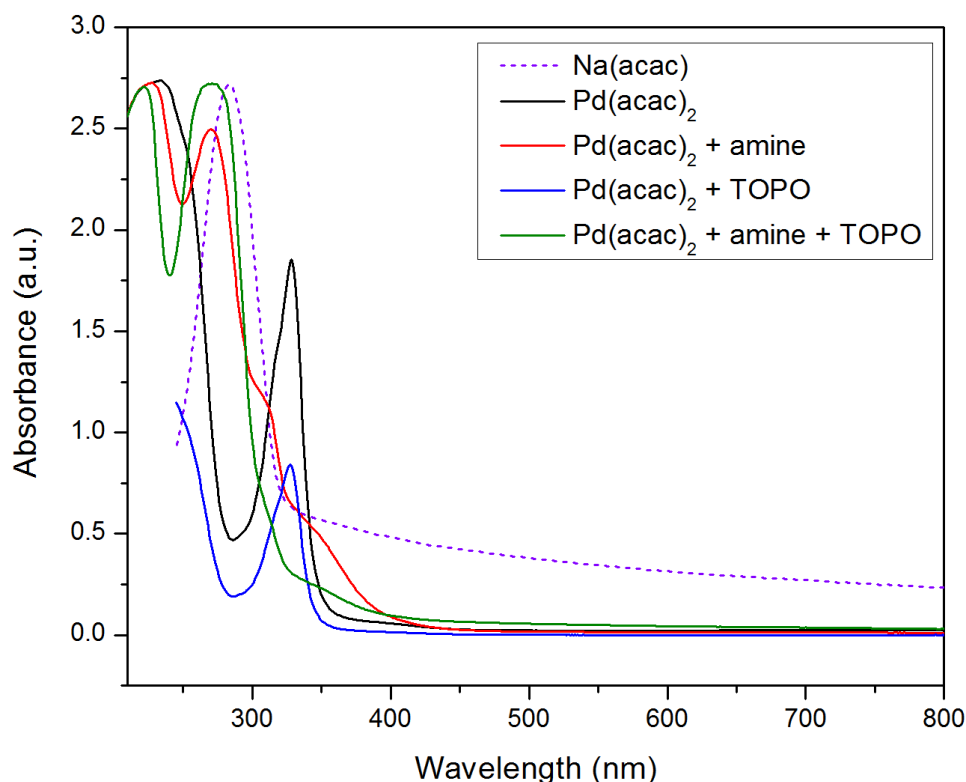
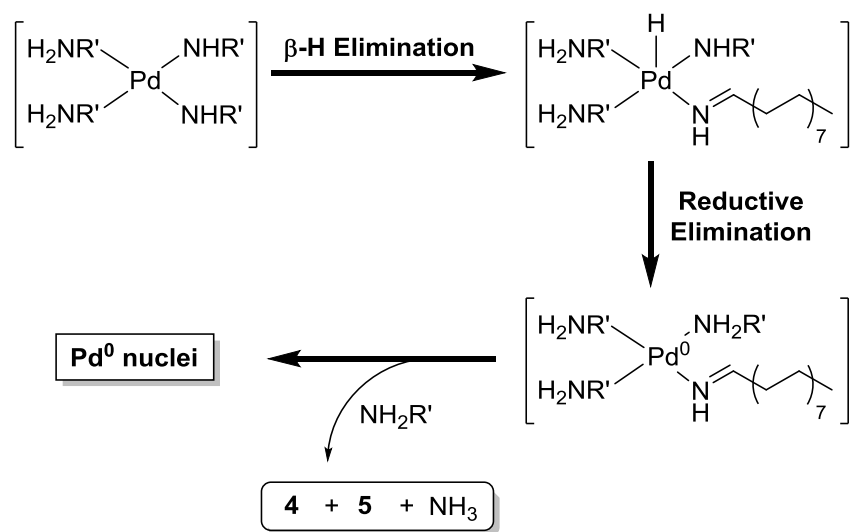


Figure 2-11. UV-vis spectra of the reaction between $\text{Pd}(\text{acac})_2$, 1-hexadecylamine, TOPO, and the combination thereof. Spectra were collected at room temperature.

At higher temperatures ($\sim 130^\circ\text{C}$), $\text{Pd}(\text{acac})_2$ was depleted and acetylacetone (Hacac) and ketimine **2** formed, accompanied by a darkening of the reaction mixture.¹⁰⁶ Ketimine **2** can form by condensation of Hacac with the amine.¹⁰⁷ The reaction of $\text{Na}(\text{acac})$ and 1-hexadecylamine does not result in the formation of any **2**, thus, protonation of the acac^- anion must first occur in order to form **2**. Here, Hacac can form from **1** *via* proton exchange between the Pd-bound amine ligands and the acac^- moiety in the outer coordination sphere, resulting in the formation of Hacac and a Pd-amido complex.^{102, 108} Hacac that is present at equilibrium can then react with amine to give **2** and water, driving the equilibrium to the right and resulting in formation of higher amounts of the putative amido complex. The Pd-amido complex was not directly observed by ^1H NMR

spectroscopy; it appears to be unstable and may form amido bridged Pd clusters.^{109, 110} Attempts to identifying either a Pd-amido complex or Pd cluster in the ^1H NMR spectra were unsuccessful. Similar results have been observed with an analogous Pt system, where a Pt-amido complex was identified using mass spectrometry.¹¹¹

It is known that Pd-alkylamido complexes readily undergo β -hydride elimination from the alkyl group to produce a Pd-hydride complex with a coordinated imine (Scheme 2-6).^{109, 112, 113} Indeed, when $\text{Pd}(\text{acac})_2$ and 1-hexadecylamine react at 80 °C, a peak is observed in the ^1H NMR spectrum of the mixture in toluene- d_8 at δ -0.83 ppm, which can be attributed to a Pd-hydride complex (Figure 2-13). This assignment was further confirmed using ^1H - ^1H COSY NMR spectroscopy, where a correlation was observed between the signal at δ = -0.84 ppm and a multiplet at 2.3 ppm, attributed to a N-CH bond (Figure 2-12). The coupling is due to the presence of two diastereotopic protons on the α -position of the nitrogen atom. Complexes of this type with a coordinated imine are unstable and generate Pd^0 upon heating, possibly by reductive elimination of hydride and an amide ligand to regenerate primary amine.¹¹⁴ Generation of nascent Pd^0 nuclei then allows further growth to form Pd^0 nanoparticles. This is consistent with the growth of a broad triplet at δ 7.62 ppm in the ^1H NMR spectra, which can be assigned to a proton in the α -position of an aldimine. Furthermore, this triplet is observed starting at ~ 80 °C, near the temperature where the reaction mixture begins to turn black, indicating formation of Pd^0 as discussed earlier.



Scheme 2-6. Formation of Pd^0 by β -hydride elimination and hydrogen transfer, illustrating formation of compounds 4 and 5.

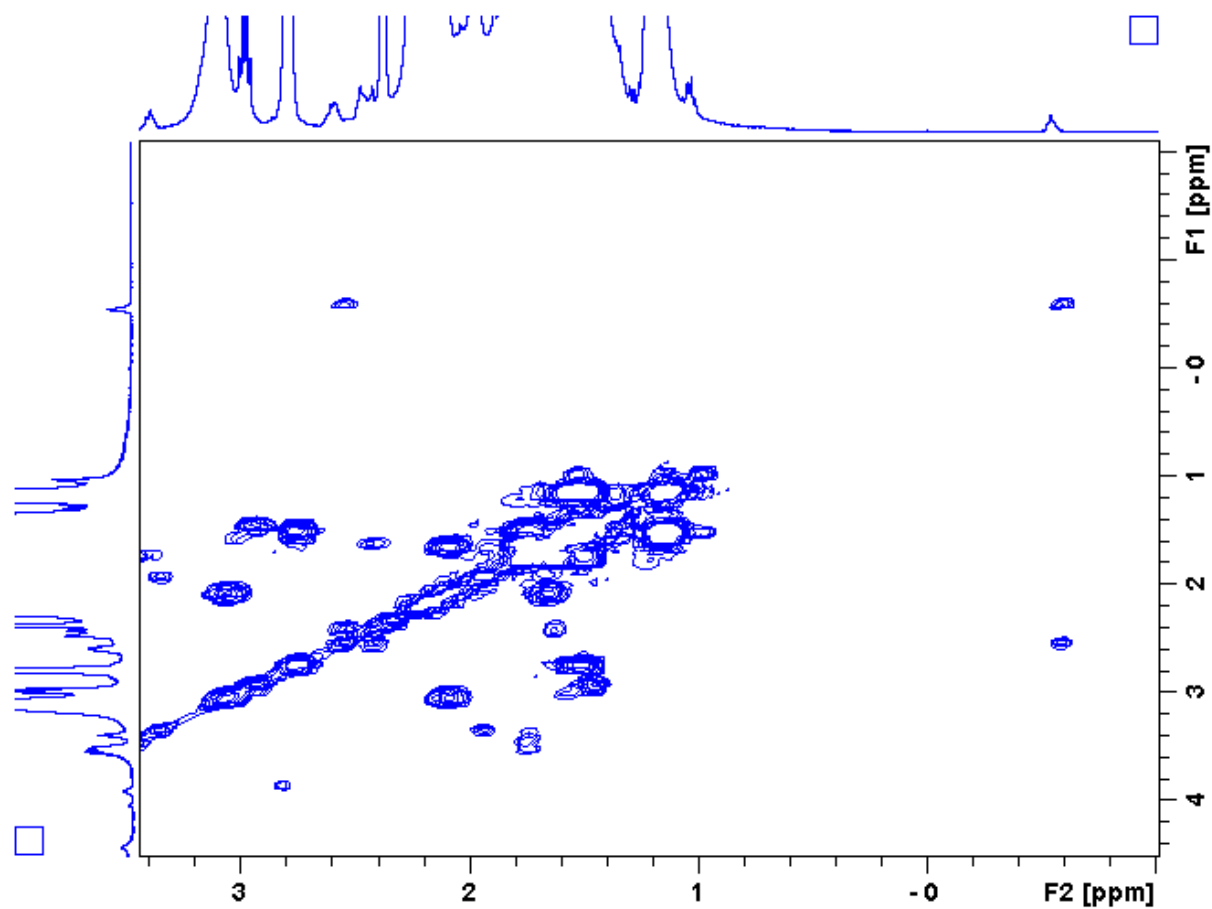


Figure 2-12. Partial ^1H - ^1H COSY NMR spectrum of the reaction mixture containing the Pd hydride, showing the correlation between the signals corresponding to N-CH (δ 2.3 ppm) and Pd-H (δ -0.83 ppm).

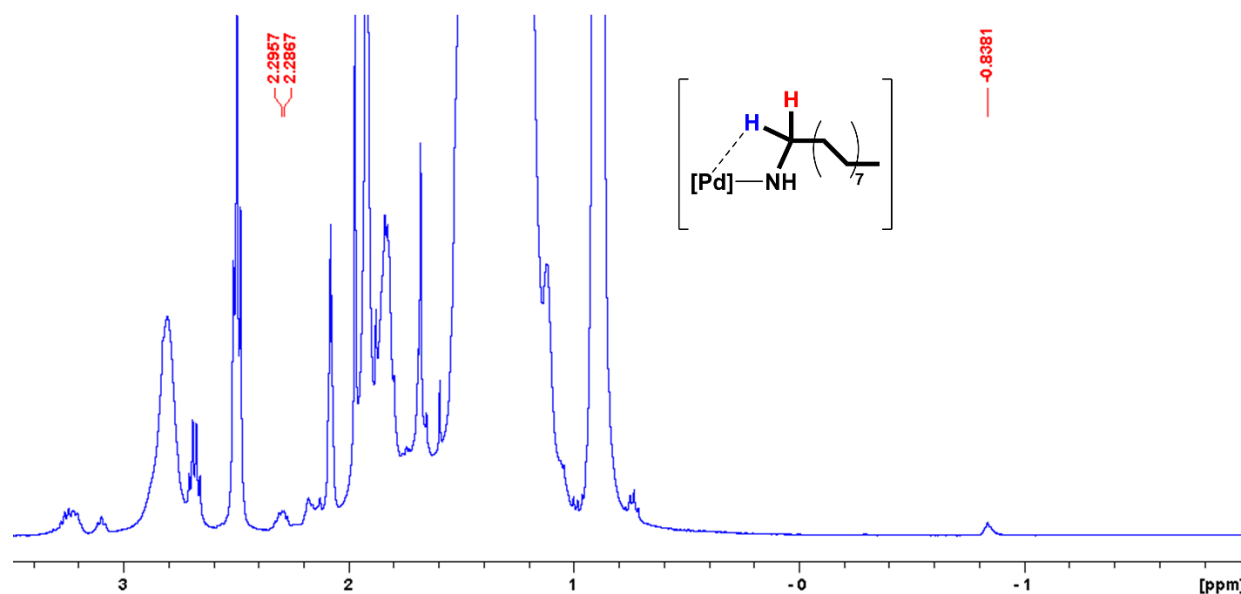
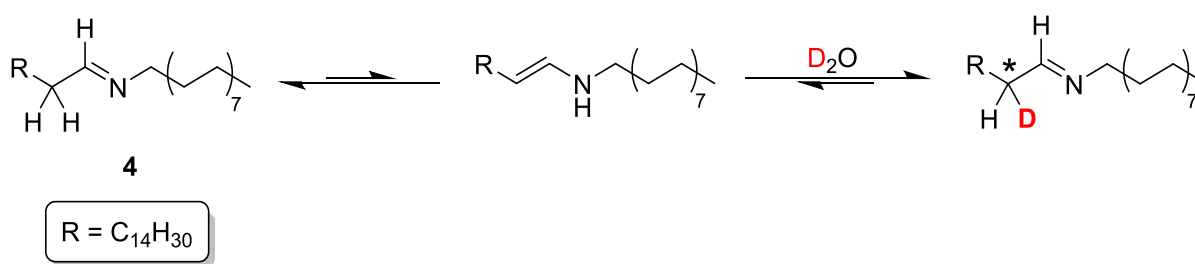


Figure 2-13. Partial ^1H NMR spectrum of reaction between $\text{Pd}(\text{acac})_2$ and 1-hexadecylamine in the presence of TOPO at 80 $^\circ\text{C}$, showing the peak at δ -0.84 ppm.

Furthermore, additional organic compounds are formed during the formation of the nanoparticles. Aldimine **4** is observed by ^1H NMR spectroscopy at the same temperature that Pd nanoparticles begin to form.¹¹⁵ Aldimines are known intermediates in the Pd^0 -catalyzed condensation of primary amines to form secondary amines.¹¹⁶ However, aldimines are known to undergo tautomerization to give enamines, although the aldimine species is favored (Scheme 2-7).¹¹⁷ Because of the tautomerization, D_2O can be added to incorporate deuterium atoms into the aldimine, and the changes can be observed in the ^1H NMR spectrum. As shown in Figure 2-14, addition of D_2O to the Pd^0 nanoparticles, which still contains aldimine **4**, broadens the signals at δ 2.16 and 7.57 ppm. These signals correspond to the NCHCH_2 and N-CH protons respectively. The NCH_2 signal at δ 3.30 ppm remains intact as these protons do not participate in the tautomerization.

A plausible explanation for the broadening is the generation of a new stereocenter by the addition of a deuterium atom, which complicates the couplings as there are now diastereotopic protons that have similar chemical shifts.



Scheme 2-7. Tautomerization of aldimine **4** to an enamine, and the incorporation of deuterium atoms into **4** by addition of D₂O.

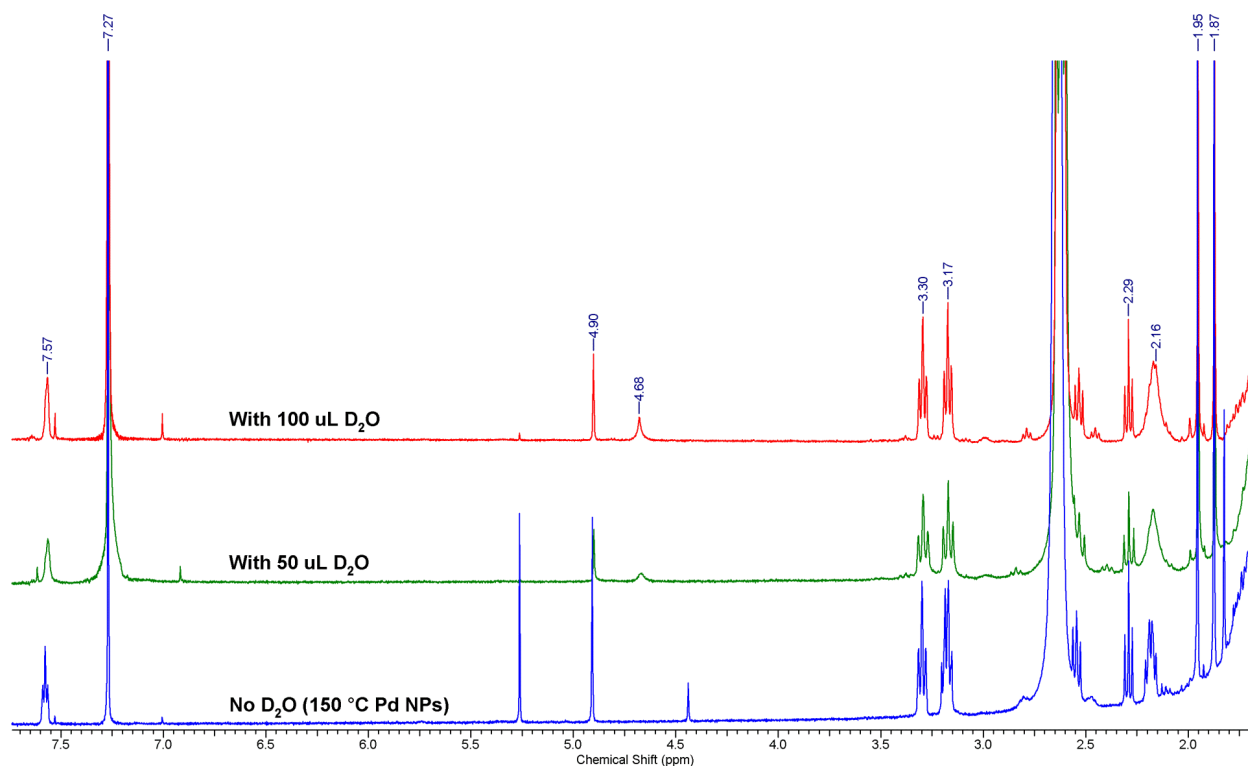
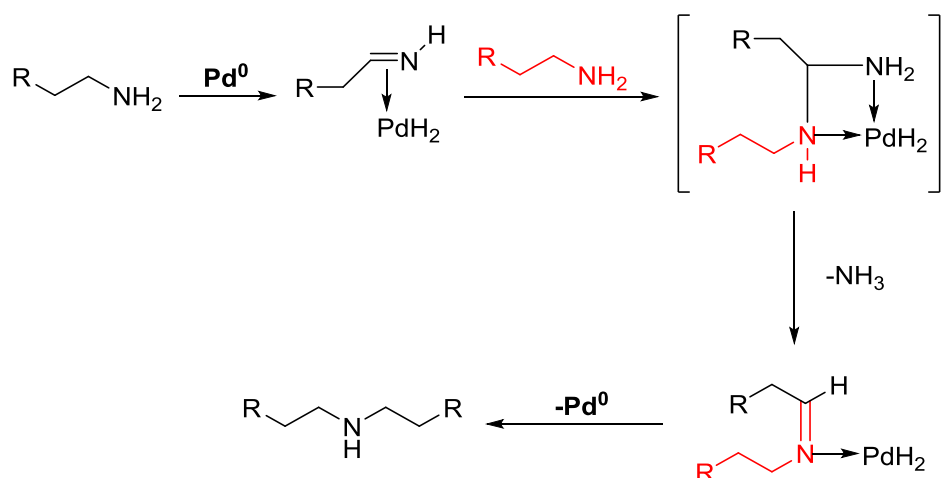


Figure 2-14. Stacked partial ^1H NMR spectra showing the changes that occurs with the addition of D_2O to the purified Pd^0 nanoparticles at room temperature. The broad singlet at δ 4.68 ppm corresponds to HDO .¹¹⁸

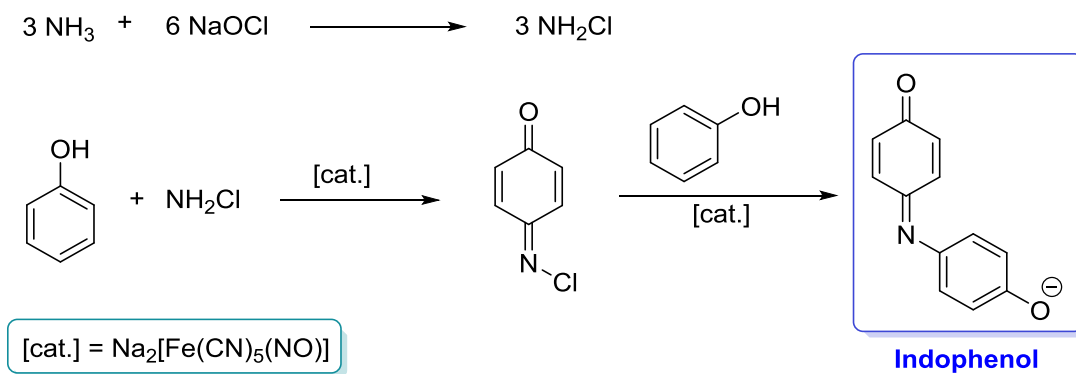
Dialkylamine **5**, was also observed in the ^1H NMR spectrum of the reaction mixture,¹¹⁹ however, this compound was not observed on the nanoparticles as a stabilizer as excess amount of primary amine is present. It is likely that the coordinated imine resulting from β -hydride elimination undergoes nucleophilic attack by primary amine to give aldimine **4**, dialkylamine **5**, and NH_3 (Scheme 2-8). Indeed, when extracting aliquots from the reaction mixture for the ^1H NMR spectroscopic analyses, vapor with an ammonia-like odor evolved from the reaction vessel. If the proposed mechanism is correct, NH_3 gas is expected to be produced during the course of the reaction, consistent with this observation.



Scheme 2-8. Generation of secondary amine and ammonia from 2 equivalents of primary amine. Redrawn from reference.¹⁰²

2.3.2 Detection of Ammonia Using Berthelot's Method

Ammonia can be detected directly using Berthelot's method, which involves generation of indophenol, a vibrant blue coloured compound that can be easily detected using UV-vis spectroscopy. Ammonia is first collected as an ammonium salt, and then reacted with sodium hypochlorite ($NaOCl$) to give chloroamine (NH_2Cl), as outlined in Scheme 2-9. Using sodium nitroprusside ($Na_2[Fe(CO)_5NO]$) as a catalyst, chloroamine can then further react with 2 equivalents of phenol to give indophenol. The amount of indophenol, and consequently the amount of ammonia, can then be determined colorimetrically.



Scheme 2-9. Detection of ammonia using phenol to quantitatively generate indophenol, a highly coloured compound.

This colorimetric method was applied to quantify the amount of ammonia formed in the reaction. Samples of the exhaust gas from the reaction were passed into a reservoir of dilute H_2SO_4 to give an aqueous solution. A standard solution is made, and further reacted with NaOCl and phenol solutions to allow formation of indophenol. The samples can be compared against previously prepared standards. As seen in the UV-vis spectra (Figure 2-15), a band at $\sim 640 \text{ nm}$ can be observed for samples containing the ammonium ion.

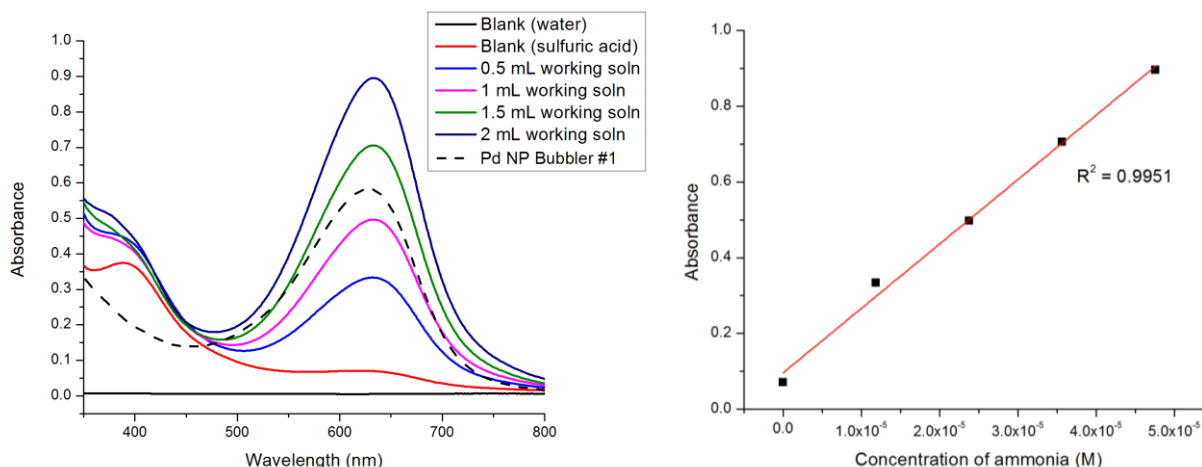


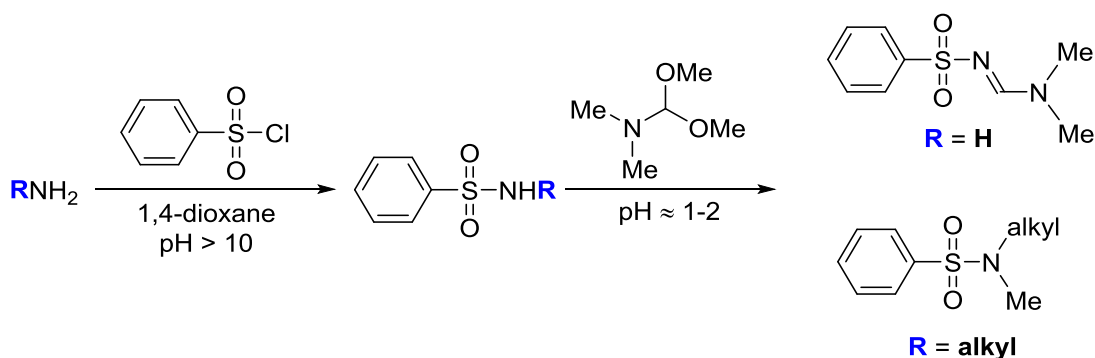
Figure 2-15. a) Stacked absorption spectra of indophenol generated from the. b) Calibration curve of the standard solutions prepared.

Despite the success in detecting amine-containing species, this method suffers from interference from other amine vapors. Aside from ammonia, other amines can also react with NaOCl to result in formation of indophenol as the final product, hence any vapor containing amine (not just ammonia) lead to positive response. Attempts to sublime any residual amine from the reaction were not successful in completely removing the amine. Hence, any numerical values obtained from the measurements were not reliable. However, the Berthelot reaction does confirm that a volatile amine species is indeed present.

2.3.3 Detection of Ammonia by Derivatizations

A more definitive method of detecting ammonia gas involves derivatization of ammonia into other isolable organic compounds (Scheme 2-10). It has been shown that ammonia can quantitatively react with benzenesulfonyl chloride under basic conditions to result in a

sulfonamide.^{120, 121} Subsequent reaction with *N,N*-dimethylformamide dimethyl acetal under acidic conditions results in the formation of different products, depending on the amine introduced initially. Specifically, reaction between ammonia and *N,N*-dimethylformamide dimethyl acetal results in formation of a sulfonyl amidine, while reactions using primary amines simply result in another sulfonamide. As the formation of *N,N*-dimethyl-*N'*-(phenylsulfonyl)formimidamide is exclusive to ammonia and is nearly quantitative, this is a highly selective reaction to detect ammonia formation.



Scheme 2-10. Derivatization of ammonia into sulfonyl amidines for isolation.

As in the case of Berthelot's method, the exhaust gas was first collected into sulfuric acid, and the ammonium ion-containing solution was then reacted with the two reagents, and the isolated products were analyzed. The ^1H NMR spectrum of the final product shows two inequivalent singlets at δ 3.03 and 3.14 ppm each integrating to 3 protons, indicative of the presence of two CH_3 groups (Figure 2-16). The diagnostic singlet at δ 8.15 ppm due to a N-CH proton reveals that the signal corresponds to the sulfonyl amidine. The NMR data was also consistent with that in the literature.^{122, 123} The absence of signals at δ 2.3, 3.3, and 4.4 ppm suggests *N,N*-dimethylformamide

dimethyl acetal was not present in the product. The purity of the compound was confirmed using HPLC, where only one signal for the ammonia derivative was observed. Small traces of methylene protons can be observed in the ^1H NMR spectrum (not shown) but the majority of the product appears to be the sulfonyl amidine. This conclusively indicates that ammonia is indeed produced from the reaction and the proposed mechanism is plausible.

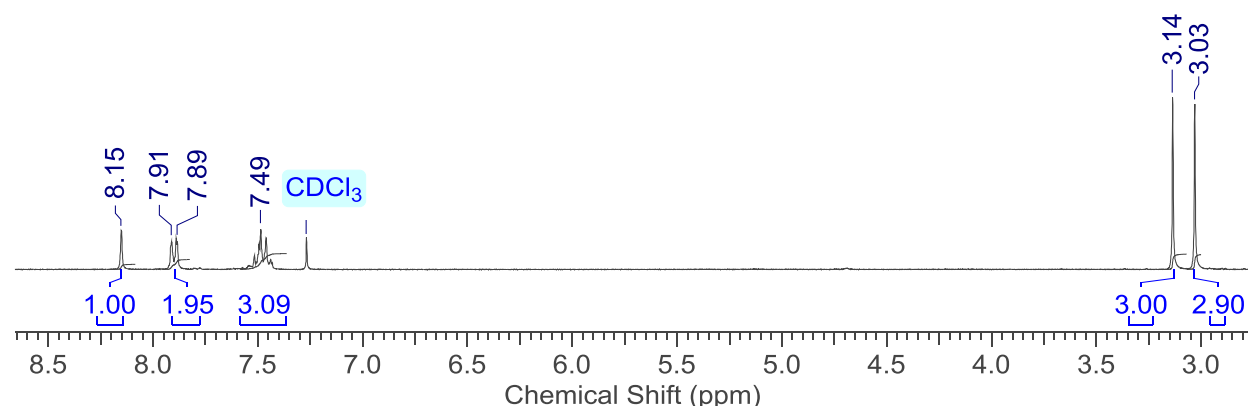
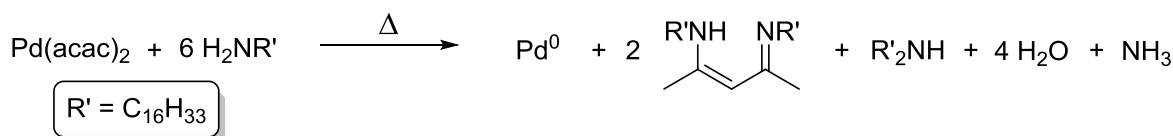


Figure 2-16. ^1H NMR spectrum of *N,N*-dimethyl-*N'*-(phenylsulfonyl)formimidamide derived from ammonia.

Detection of ammonia as ammonia borane was also attempted, but was unsuccessful. If ammonia were present, bubbling the vapor from the reaction mixture into a solution of $\text{BH}_3\cdot\text{THF}$ in THF should result in formation of ammonia borane (BH_3NH_3). This Lewis acid-base adduct can be detected using ^{11}B NMR spectroscopy, where a quartet located at δ -22.5 ppm would be observed if the compound were present. However, only a broad singlet at δ 17.9 ppm was observed (Figure A-4). This can be explained by the rapid hydrolysis of $\text{BH}_3\cdot\text{THF}$, as water is produced as one of the by-products generated from the synthesis of Pd^0 nanoparticles. As the amount of water generated from the reaction is much greater than the amount of ammonia generated (Scheme 2-5), it is not surprising that no ammonia borane was obtained.

With this new understanding of the mechanism, an overall reaction scheme can be assembled (Scheme 2-11). Four equivalents of amine are consumed to give ketimine **2** and diketimine **3** from the two Hacac species generated. In the later step, the reaction between aldimine **4** and another equivalent of amine gives the secondary amine, as well as generation of ammonia in the later step. This accounts for the amine consumed during the course of the reaction and does not include the excess amine that is needed to stabilize the Pd⁰ nanoparticles formed.



Scheme 2-11. Proposed overall reaction scheme for the preparation of Pd⁰ nanoparticles from Pd(acac)₂ and 1-hexadecylamine.

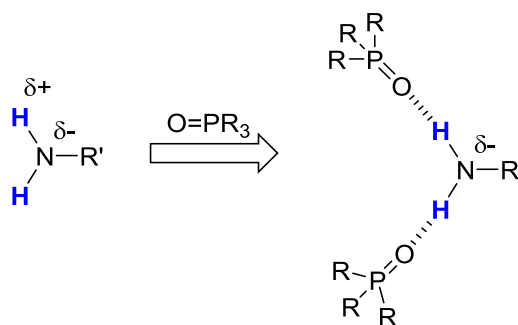
2.4 Elucidating the Role of TOPO in the Formation of Monodisperse Pd⁰ Nanoparticles

With an understanding of the underlying mechanism of nanoparticle formation in hand, the role of TOPO in the mechanism was explored. Phosphine oxides coordinate weakly to late transition metals and have been used only rarely to stabilize metal nanoparticles;¹²⁴ however, they have been used extensively to prepare quantum dots¹²⁵ and metal oxide nanoparticles.¹²⁶ As previously mentioned, TOPO does not serve as a stabilizing agent for the Pd⁰ nanoparticles prepared using this method, yet the preparation of monodisperse nanoparticles cannot occur without TOPO. This suggests that TOPO plays an important role in the mechanism.

The effect of the addition of TOPO was explored using NMR spectroscopic studies analogous to those described in Section 2.3. Upon addition of TOPO to a mixture of Pd(acac)₂ and

1-hexadecylamine, darkening of the solution occurred at a significantly lower temperature than in the absence of TOPO (Figure 2-17).

Lewis bases, such as phosphine oxides are known to increase the nucleophilicity of amines.¹²⁷ This can be achieved by hydrogen-bonding of the amine protons to the Lewis basic oxygen sites of phosphine oxide, such that the nucleophilicity of the amine is increased (Scheme 2-12). Considering the mechanism of nanoparticle formation, addition of a Lewis base is expected to increase the rate of formation of **2** by driving the equilibrium to the product side. This suggests the possibility that formation of nanoparticles can be facilitated by increasing the amount of amido complex present at equilibrium.



Scheme 2-12. Enhancement of the nucleophilicity of an amine by hydrogen-bonding interaction.

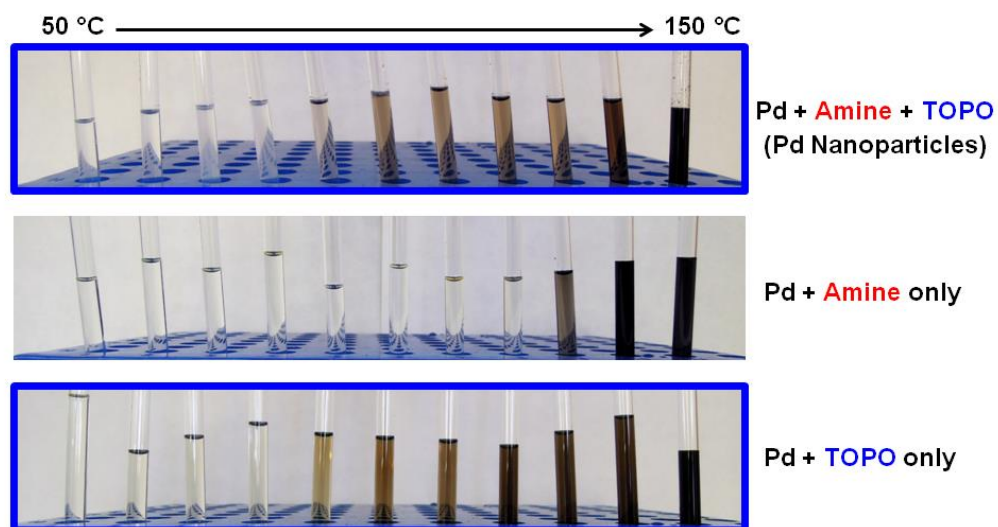


Figure 2-17. Photographs of samples of the reaction mixtures taken every 10 °C from 50 °C to 150 °C for NMR analyses.

When the reaction mixture containing Pd(acac)₂, 1-hexadecylamine and TOPO is slowly heated, formation of ketimine **2** is observed at temperatures as low as 50 °C, in contrast with the reaction performed without TOPO (Figure 2-18). New peaks in the ¹H NMR spectrum attributed to the formation of a diketimine **3** can be observed when the reaction mixture is heated to > 130 °C. Diketimine **3** is formed by condensation of **2** with another equivalent of the amine, possibly with TOPO as catalyst. Compound **3** appears to be the final destination of the acac ligand, as no further acac-derived compounds can be identified in the temperature range studied.

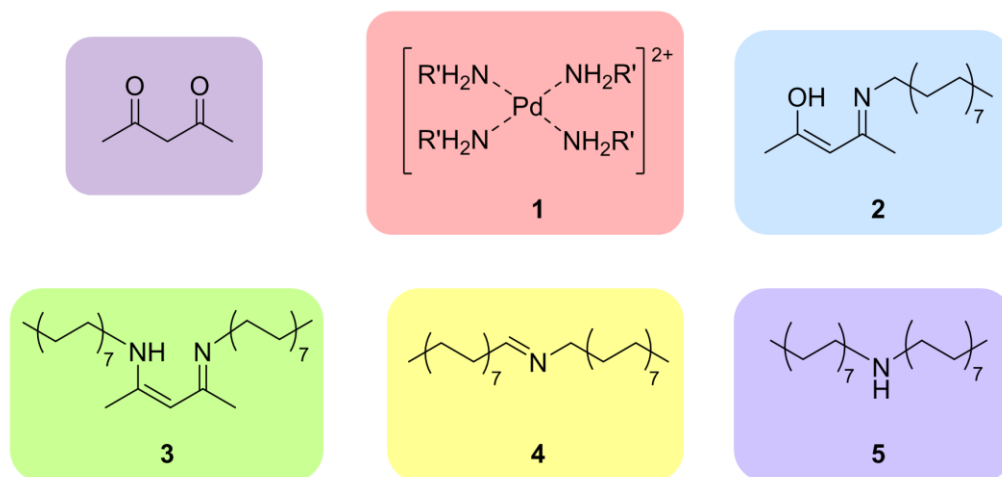
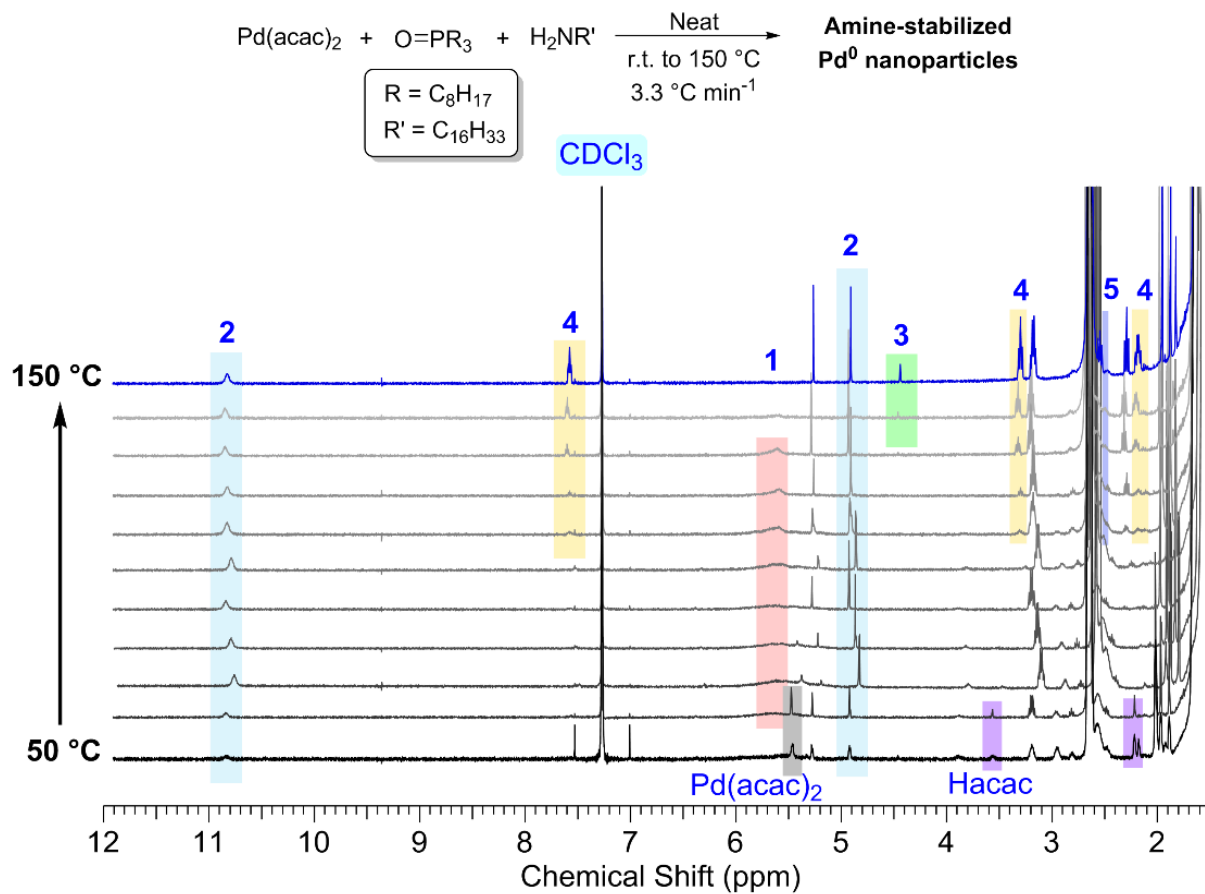


Figure 2-18. Stacked room-temperature ^1H NMR spectra of the nanoparticle reaction mixture ($\text{Pd}(\text{acac})_2 + 1$ -hexadecylamine + TOPO) from $50\text{ }^\circ\text{C}$ to $150\text{ }^\circ\text{C}$ collected in CDCl_3 . Compounds assigned to different signals are identified by different colors.

The formation of ketimine **2** of Pd(acac)₂ and 1-hexadecylamine was monitored at 80 °C in toluene-*d*₈. Addition of TOPO to the reaction mixture results in more rapid formation of ketimine **2** (Figure 2-19 and Figure 2-20). The signals at δ 4.8 and 11.1 ppm in the ¹H NMR spectra, which correspond to C–H and O–H of **2** respectively, increase in intensity as the reaction progresses. These signals match with the ¹H NMR signal corresponding to compound **2**, which was prepared in a separate experiment as confirmation (Figure A-1). These signals grow much faster when TOPO is added to the reaction (Figure 2-20), as is evident by plotting the relative integrations of the two experiments vs. time (Figure 2-21). TOPO also affects the rate of formation of **2** from Hacac (Figure 2-22), supporting the conclusion that the phosphine oxide acts to increase the nucleophilicity of the amine towards Hacac. Under these conditions, diketimine **3** was not observed in the NMR spectra collected. Because of the differences in the shape of the curves in Figure 2-21 and Figure 2-22, TOPO may also have some effect in speeding the proton transfer; however, this was not explored further and is therefore inconclusive.

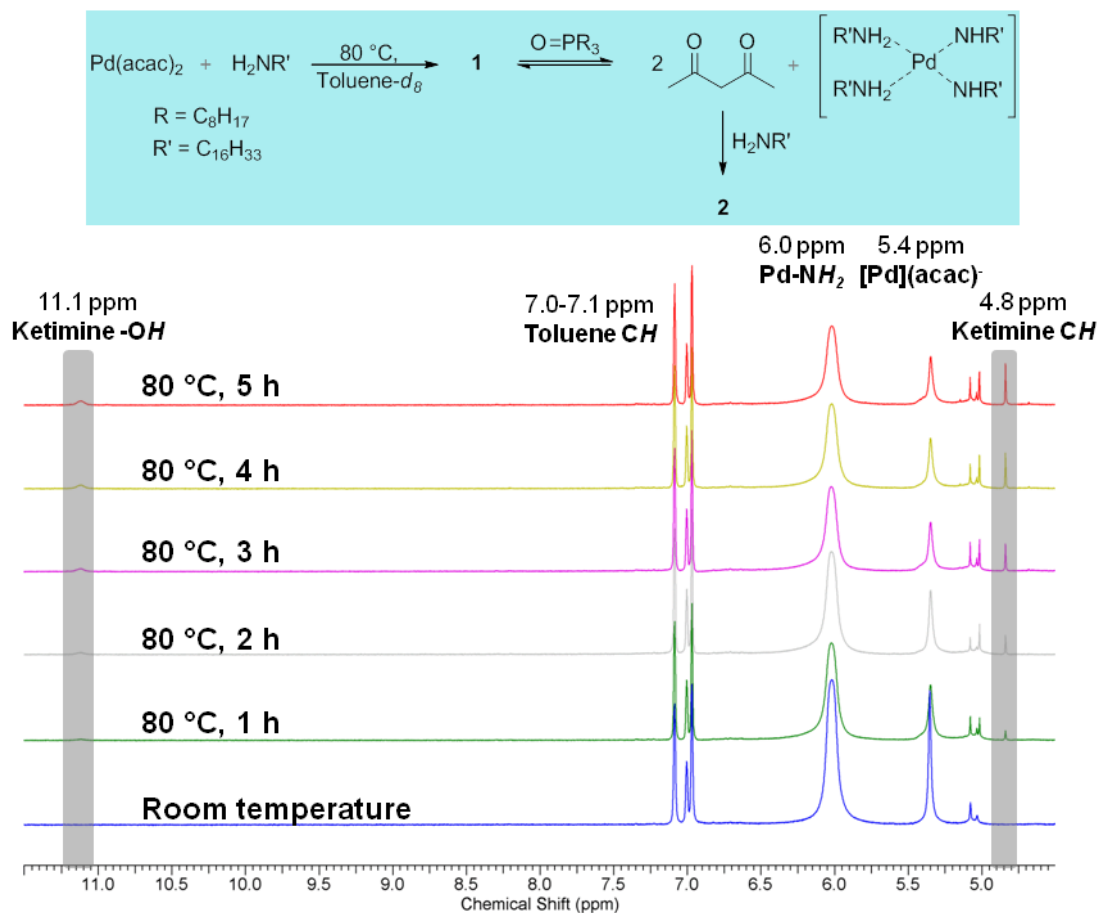


Figure 2-19. Stacked partial ^1H NMR spectra of reaction between $\text{Pd}(\text{acac})_2$, hexadecylamine and TOPO at 80 °C conducted in toluene- d_8 , showing the formation of **2** and decrease in amount of **1**. Spectra were collected at room temperature (300 MHz, room temperature).

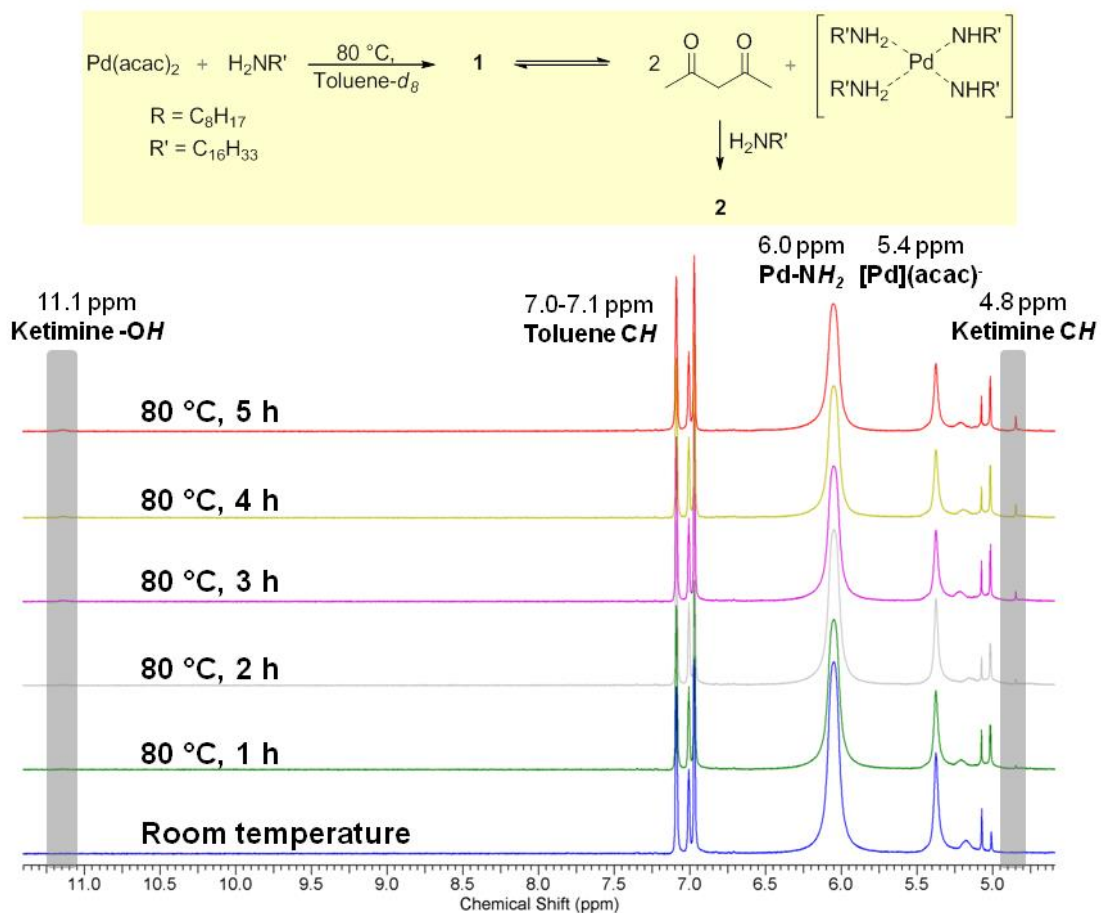


Figure 2-20. Stacked partial ^1H NMR spectra of reaction between $\text{Pd}(\text{acac})_2$ and 1-hexadecylamine conducted at 80 $^\circ\text{C}$ in toluene- d_8 , showing slower formation of **2** in the absence of TOPO. Spectra were collected at room temperature (300 MHz, room temperature).

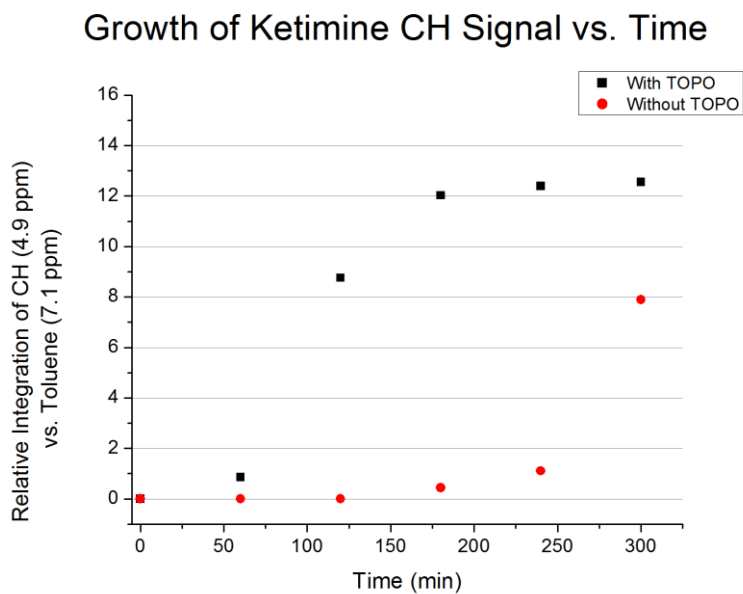


Figure 2-21. Plot of the integrated ketimine signal at δ 4.9 ppm as a function of time, of the reaction between $\text{Pd}(\text{acac})_2$ and 1-hexadecylamine, with and without TOPO at 80 °C. The signal at δ 4.9 ppm was integrated against the singlet at δ 7.1 ppm of toluene. (See Figure 2-19 and Figure 2-20 for the ^1H NMR spectra)

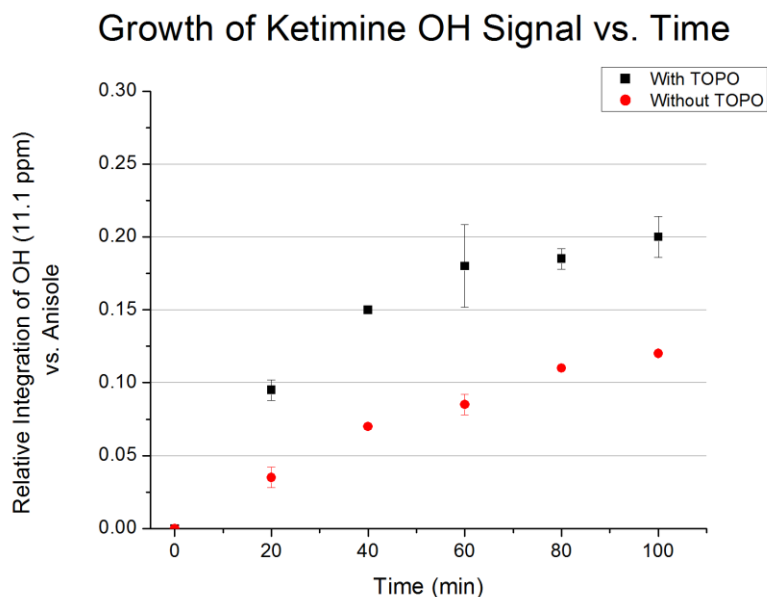


Figure 2-22. Plot of the integrated ketimine signal as a function of time, of the reaction between acetylacetone (Hacac) and 1-hexadecylamine, with and without TOPO at 50 °C. The signal at δ 11.1 ppm was integrated against the signal at δ 3.8 ppm of anisole (internal standard).

Given that the formation of **2** is enhanced in the presence of TOPO, it is logical that faster depletion of Hacac in the presence of TOPO would shift the equilibrium to the right, generating more Pd-amido complex and lowering the temperature of nanoparticle formation. The formation of Pd⁰ can be observed at < 95 °C with the addition of 10 mol% of TOPO, consistent with this compound acting in a catalytic role, although the nanoparticles prepared under these conditions were not monodisperse (Figure 2-6). This result suggests that the amount of TOPO present is important in controlling the monodispersity of the nanoparticles, possibly by affecting the rate of the side reactions TOPO participates in and influencing the nucleation of Pd⁰. It is possible that TOPO also acts in other ways, for example the possibility that TOPO facilitates the proton transfer from **1** to outer sphere acac⁻ cannot be eliminated. Monitoring the ³¹P NMR spectra during these

reactions shows only a signal corresponding to TOPO, with no additional signals observed, confirming that TOPO does not serve as a capping agent and does not coordinate to form stable complexes with Pd (Figure 2-23). The small signals at δ 43 and 54 ppm were observed in the ^1H NMR spectrum of TOPO in CDCl_3 .

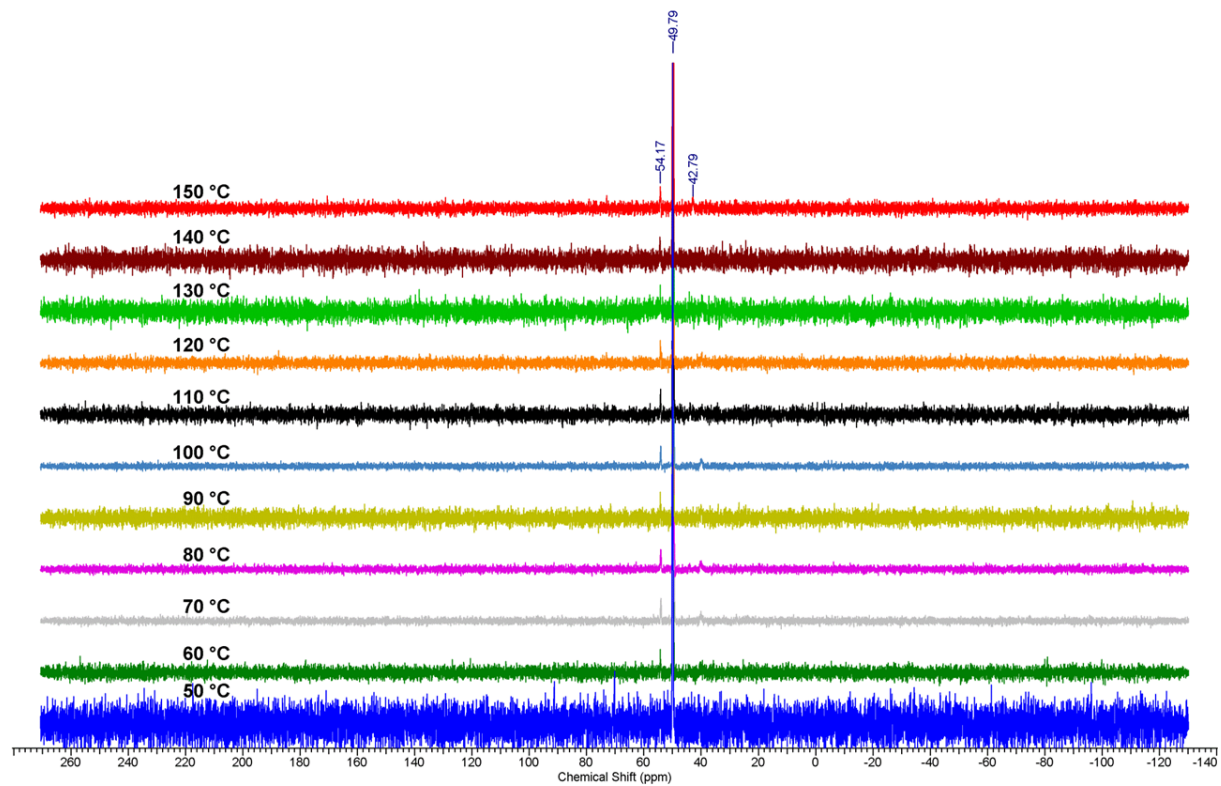


Figure 2-23. Stacked room-temperature ^{31}P NMR spectra of the nanoparticle-containing reaction mixture ($\text{Pd}(\text{acac})_2$ + 1-hexadecylamine + TOPO) from 50 °C to 150 °C collected in CDCl_3 (300 MHz).

When the reaction is conducted without 1-hexadecylamine ($\text{Pd}(\text{acac})_2$ and TOPO only), Hacac is formed but does not react further (Figure 2-24). As 1-hexadecylamine is not present, no signals of any amine-containing compounds were observed. A relatively unstable Pd complex

results and is reduced at lower temperature than when amine is present; however monodisperse nanoparticles are not formed under these conditions, in the absence of a stabilizing group (amine).

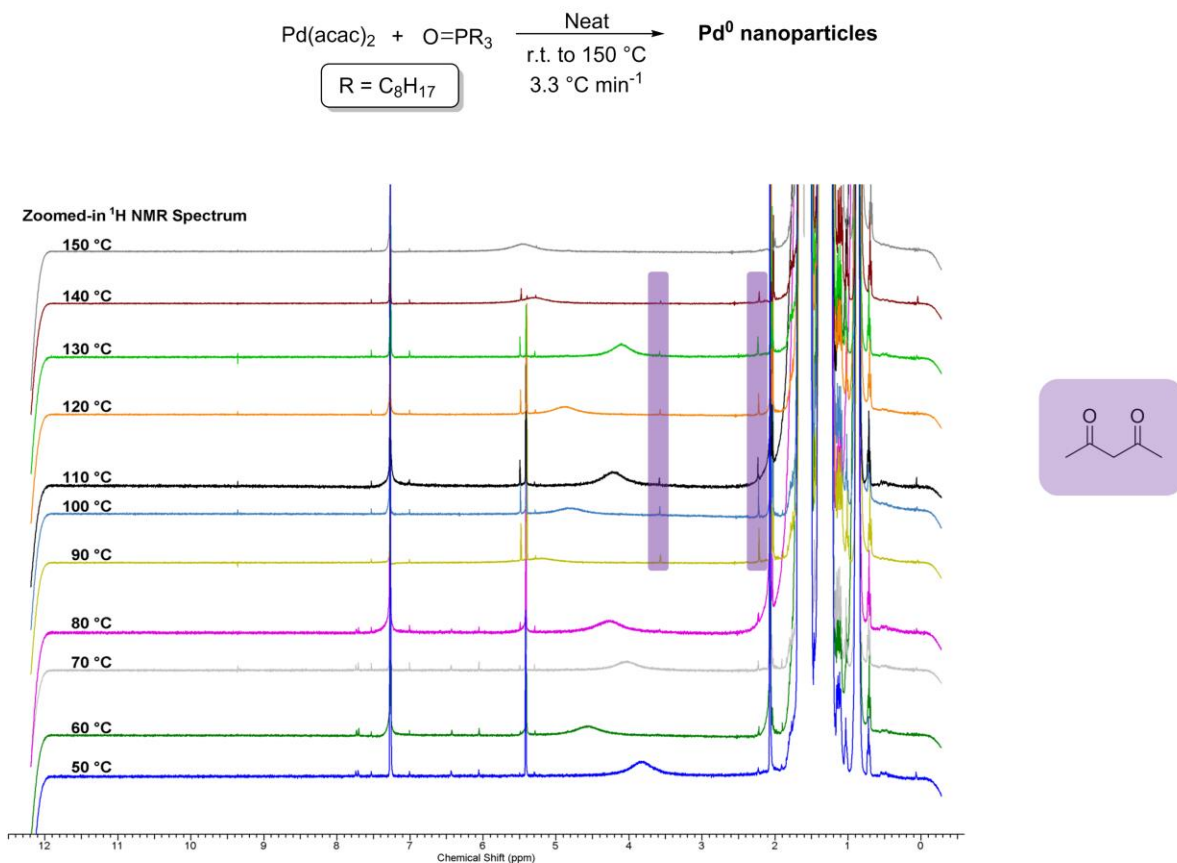


Figure 2-24. Stacked room-temperature ^1H NMR spectra of the $\text{Pd}(\text{acac})_2$ and TOPO reaction mixture from 50 to 150 $^\circ\text{C}$ collected in CDCl_3 (300 MHz).

As previously explored in Section 2.2, other Lewis bases can also act to facilitate Pd nanoparticle formation. When dimethylsulfoxide (DMSO) was used in place of TOPO with $\text{Pd}(\text{acac})_2$ and 1-hexadecylamine, nanoparticles were formed starting at $\sim 100\text{ }^\circ\text{C}$; however these particles were not as monodisperse as when TOPO was used (Scheme 2-4). It is possible that the

less Lewis basic DMSO is not as effective at increasing the nucleophilicity of the amine, thus resulting in a higher temperature for formation of Pd⁰.

2.4.1 Extending the Effect of TOPO to Other Pd Precursors

The effect of TOPO is not limited to only one particular Pd precursor: Replacing Pd(acac)₂ with palladium acetate (Pd(OAc)₂) also resulted in formation of Pd⁰ nanoparticles. The reaction between Pd(OAc)₂, 1-hexadecylamine, and TOPO was monitored using ¹H NMR spectroscopy. A color change from yellow to black was observed at *ca.* 105 °C and spherical nanoparticles with some branching particles were observed (Figure 2-25). Without TOPO, the indicative color change does not occur until 150 °C, which confirms the effect of TOPO on promoting the formation of Pd⁰. However, unlike the reaction using Pd(acac)₂ as the precursor, some crystalline white solid was found to have sublimed onto the sides of the reaction flask and the condenser. Analyses of this white solid by ¹H NMR spectroscopy, ESI-MS and melting point analysis showed the product to be an amine salt, [CH₃(CH₂)₁₅NH₃⁺][OAc⁻]. In order for this salt to be formed, the acetate ligand (OAc⁻) must be protonated to give acetic acid (HOAc) prior to its formation, as the reaction between OAc⁻ and amine does not proceed without acidic conditions. The presence of a likely side product, *N*-hexadecylacetamide, was not observed in the NMR spectra (Figure A-5). As well, additional signals other than the one due to TOPO were never observed in all of the ³¹P NMR spectra collected. These observations confirm that TOPO play a role in facilitating the formation of Pd⁰ nanoparticles. Detailed mechanistic study of the formation of Pd⁰ nanoparticles from Pd(OAc)₂ and 1-hexadecylamine was not performed.

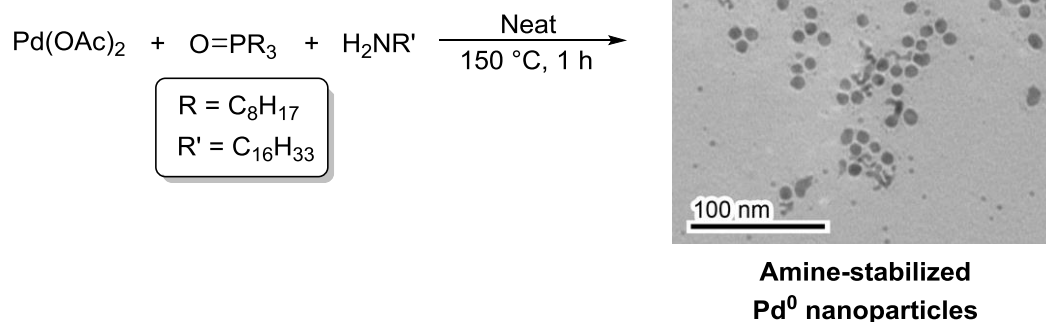


Figure 2-25. Amine-stabilized Pd⁰ nanoparticles prepared by reacting Pd(OAc)₂, 1-hexadecylamine and TOPO at 150 °C for 1 h.

2.5 Conclusions

Monodisperse Pd⁰ nanoparticles were prepared from Pd(acac)₂, 1-hexadecylamine, and TOPO at a lower temperature than other reported procedures. ¹H NMR, ³¹P NMR, and IR spectroscopy confirmed that the nanoparticles are stabilized by 1-hexadecylamine, with no indication of TOPO present. Powder XRD confirms that the nanoparticles are composed of Pd⁰. The monodispersity and shape of the nanoparticles are very sensitive to reaction condition changes, including the amount of reactants present and the chain length of the amine used. Heating rate and temperature was found to affect the size and morphology of the Pd⁰ nanoparticles synthesized. The monodisperse Pd⁰ nanoparticles were shown to be highly catalytically active by performing a prototypical Suzuki-Miyaura cross-coupling reaction with very low catalyst loading.

The mechanism of formation of Pd⁰ nanoparticles was explored using NMR spectroscopy. Through comparison with known compounds, the intermediates present in the reaction mixture were identified, allowing a plausible mechanism for the formation of Pd⁰ nanoparticles to be

proposed. Starting with $\text{Pd}(\text{acac})_2$, Pd^0 nanoparticles are formed from $\text{Pd}(\text{acac})_2$ *via* proton transfer from an initially formed tetraaminopalladium salt (**1**) to acac^- to yield a putative amido complex. This complex reacts further *via* β -hydride elimination and hydrogen transfer to give Pd^0 species by eliminating aldimine **4** and dialkylamine **5**. As well, organic compounds such as **2** and **3** were identified in the NMR spectra. No changes were observed in all of the ^{31}P NMR spectra collected.

The gaseous by-product, ammonia, was not directly observed by NMR spectroscopy but its presence was confirmed definitively using ^1H NMR spectroscopy and ESI-MS by derivatization into *N,N*-dimethyl-*N'*-(phenylsulfonyl)formimidamide. Attempts to quantify ammonia using other methods such as Berthelot's method or trapping the gas as ammonia borane were unsuccessful.

Addition of Lewis bases such as TOPO and DMSO was found to greatly reduce the temperature at which highly monodisperse nanoparticles are formed. TOPO greatly enhances the nucleophilicity of amines through hydrogen-bonding interactions, which leads to faster formation of compounds **2** and **3** as a nucleophilic attack of amine occurs. This was confirmed through ^1H NMR kinetic studies of the effect of TOPO on the reaction between Hacac and 1-hexadecylamine. As well, this effect is not restricted to one precursor; nanoparticles can also be prepared at lower temperature when $\text{Pd}(\text{OAc})_2$ is used as the Pd precursor. TOPO may also facilitate formation of the Pd -amido complex, but the effect was not confirmed.

In conclusion, this mechanism shows that Pd^0 nanoparticles can readily form at low temperatures from a Pd^{II} precursor, suggesting that caution is warranted in interpretation of homogeneous catalysis studies involving amines or Lewis bases as reagents. In addition to providing insight into the mechanism, the identification of organic byproducts **2-5** is important as these compounds may be present when $\text{Pd}(\text{acac})_2$ or $\text{Pd}(\text{OAc})_2$ is used as a catalyst, or when Pd^0 nanoparticles are formed in the presence of amines.

2.6 Experimental

2.6.1 General.

Palladium (II) acetylacetonate was purchased from Strem Chemicals. 1-Hexadecylamine, *p*-toluenesulfonic acid monohydrate, benzenesulfonyl chloride, *N,N*-dimethylformamide dimethyl acetal, 1-iodotoluene, and phenylboronic acid were purchased from Sigma-Aldrich. Tri-*n*-octylphosphine oxide (TOPO) and sodium nitroprusside dihydrate were purchased from Alfa-Aesar. Dimethyl sulfoxide (DMSO) and 1,4-dioxane were purchased from Fisher Scientific. All chemicals were used as received. Na(acac) was prepared using an established procedure.¹²⁸

All reactions were performed using standard Schlenk-line techniques. Reactions involving controlled heating rate were performed using a custom-made programmable controller, connected to a thermocouple. NMR spectra were recorded at room temperature on Bruker AV-300, AV-400, and AV-600 spectrometers and referenced to residual solvent or external 85% H₃PO₄. All chemical shifts are reported in Hz. FT-IR spectra were recorded on a Nicolet 4700 spectrometer (Thermo Electron Corporation). Low-resolution and high-resolution mass spectra (EI) were recorded by the staff of the UBC mass spectrometry facility using a Kratos MS-50 spectrometer. Electrospray ionization mass spectrometry (ESI-MS) data were obtained on a Bruker Esquire LC ion trap mass spectrometer. Powder X-ray diffraction data were recorded on a 60 Bruker D8 Advance X-ray diffractometer in the Bragg-Brentano configuration, using copper K α radiation at 40 kV, 40 mA. Transmission electron microscopy (TEM) samples were prepared by drop-casting ~3 μ L of the dilute solution in hexanes or EtOH onto a carbon-coated 400-mesh copper TEM grid, then dried in air under ambient conditions. Microscopy was carried out on a Hitachi H-7600 transmission electron microscope. An accelerating voltage of 100.0 kV was applied. The diameters of the

nanoparticles were measured using ImageJ, and measurements reported were averaged from over 100 nanoparticles.

2.6.2 Preparation of Hexadecylamine-Stabilized Pd⁰ Nanoparticles Assisted by TOPO.

A 50 mL, three-necked round-bottom flask was charged with Pd(acac)₂ (0.021 g, 0.067 mmol), 1-hexadecylamine (0.79 g, 3.3 mmol), and tri-*n*-octylphosphine oxide (0.88 g, 2.3 mmol). A thermocouple was inserted *via* the side-arm of the round-bottom flask, and the solids were subjected to three vacuum/nitrogen cycles. After backfilling the system with nitrogen, the reaction mixture was heated at a controlled rate of 3.3 °C min⁻¹ to 150 °C, and held at this temperature for 1 h. The reaction mixture melted in the course of the reaction to form a light yellow oil, and turned into a black solution at ~85 °C. After cooling, the nanoparticles were rinsed three times with EtOH (20 mL) and isolated as a black solid *via* centrifugation. The nanoparticles can be redispersed in suitable organic solvents by sonication.

2.6.3 Preparation of Hexadecylamine-Stabilized Pd⁰ Nanoparticles Assisted by TOPO

Using a Sand Bath.

The Pd⁰ nanoparticles were prepared in the same manner as with the case of TOPO (Section 2.6.2), except a preheated sand bath (~150 °C) was used as the source of heat. The reaction mixture melted in the course of the reaction to form a light yellow oil, and turned black within 5 min. After cooling, the nanoparticles was isolated by centrifugation three times against EtOH (20 mL).

2.6.4 Preparation of Dodecylamine-Stabilized Pd⁰ Nanoparticles Assisted by TOPO.

The Pd⁰ nanoparticles were prepared in the same manner as with the case of 1-hexadecylamine (Section 2.6.2), except 1-dodecylamine (0.60 g, 3.2 mmol) was used in place of 1-hexadecylamine. The reaction mixture melted in the course of the reaction to form a light yellow oil, and turned black at ~85 °C. After cooling, the nanoparticles were isolated by centrifugation three times against EtOH (20 mL).

2.6.5 Preparation of Hexadecylamine-Stabilized Pd⁰ Nanoparticles Assisted by DMSO.

The Pd⁰ nanoparticles were prepared in the same manner in with the case of TOPO (Section 2.6.2), except DMSO (162 μ L, 2.3 mmol) was used in place of TOPO. The reaction mixture melted in the course of the reaction to form a light yellow oil, and turned black at ~100 °C. After cooling, the nanoparticles were isolated by centrifugation three times against EtOH (20 mL).

2.6.6 Preparation of Hexadecylamine-Stabilized Pd⁰ Nanoparticles Starting with Pd(OAc)₂.

The Pd⁰ nanoparticles were prepared in the same manner as with the case of TOPO (Section 2.6.2), except Pd(OAc)₂ (0.022 g, 0.10 mmol) was used in place of Pd(acac)₂. The reaction mixture melted in the course of the reaction to form a light yellow oil, and turned black at ~105 °C. After cooling, the nanoparticles were isolated by centrifugation three times against EtOH (20 mL).

2.6.7 Monitoring Experiments Using ¹H and ³¹P NMR Spectroscopy.

Upon heating the reaction mixture to specific temperatures (between 50 - 150 °C), an aliquot was removed from the reaction mixture using a syringe under N₂ protection, and dissolved

in CDCl₃ to a total volume of ~0.5 mL in an NMR sample tube. The ¹H and ³¹P NMR spectra of these samples were collected within 6 h of preparation at room temperature.

2.6.8 ¹H NMR Kinetic Studies of Ketimine Formation from Pd(acac)₂ and 1-Hexadecylamine.

Pd(acac)₂ (0.020 g, 0.066 mmol), 1-hexadecylamine (0.098 g, 0.041 mmol), and TOPO (0.058 g, 0.015 mmol) were dissolved in toluene-*d*₈ (1 mL) and transferred to a NMR tube. Another sample was prepared without the addition of TOPO. The two samples were simultaneously placed in a preheated 80 °C oil bath, and the progress of the reaction was monitored by ¹H NMR spectroscopy. All NMR spectra were collected at room temperature. The signal at δ 4.9 ppm was integrated against the signal at δ 7.1 ppm of toluene.

2.6.9 ¹H NMR Kinetic Studies of Ketimine Formation from Acetylacetone (Hacac) and 1-Hexadecylamine.

Acetylacetone (0.013 g, 0.13 mmol), 1-hexadecylamine (0.031 g, 0.13 mmol), TOPO (0.018 g, 0.047 mmol), and anisole (0.014 g, 0.13 mmol, internal standard) were dissolved in toluene-*d*₈ (1 mL) and transferred to a NMR tube. Another sample was prepared without the addition of TOPO. The two samples were simultaneously placed in a preheated 50 °C silicone oil bath, and the progress of the reaction was monitored by ¹H NMR spectroscopy. All NMR spectra were collected at room temperature. The signal at δ 4.9 ppm was integrated against the singlet at δ 3.3 ppm of anisole.

2.6.10 Preparation of 4-Hexadecylimino-2-penten-2-ol (2).

This compound was prepared using a procedure adapted from He *et al.*¹⁰⁷ Acetylacetonate (105 μ L, 1.03 mmol), a spatula-tip-ful of *p*-toluenesulfonic acid, and toluene (1 mL) were added to a 50 mL round-bottom flask. 1-Hexadecylamine (0.24 g, 1.0 mmol) was added while stirring. The reaction mixture was heated to 120 °C for 2 h to give a yellow solution. Removal of the volatiles in *vacuo* gave a yellow oil (67 %).

Characterization Data for 2: ^1H NMR (300 MHz, CDCl_3) δ 0.84 (s, 3H, alkyl CH_3), 1.22 (br s, 26H, CH_2), 1.53 (m, 2H, NCH_2CH_2), 1.87 (s, 3H, $\text{N}=\text{CCH}_3$), 1.95 (s, 3H, OCCH_3), 3.18 (m, 2H, $\text{N}-\text{CH}_2$), 4.91 (s, 1H, CH), 10.82 (br s, 1H, $-\text{OH}$); ^{13}C APT NMR (151 MHz, CDCl_3) δ 14.10, 18.80 (alkyl CH_3), 22.67, 26.85 (alkyl CH_2), 28.71 (alkyl CH_3), 29.29, 29.34, 29.47, 29.56, 29.61, 29.63, 29.65, 29.66, 29.67, 29.68, 30.09, 31.90 (alkyl CH_2), 43.04 (NCH_2), 94.95 (meso CH), 163.11 (ipso C), 194.58 (ipso C); MS (LREI, m/z , probe temperature 150 °C) 323 [M^+]. HRMS-EI (m/z) [M^+] calcd for $\text{C}_{21}\text{H}_{41}\text{NO}$: 323.31882, found: 323.31887.

2.6.11 Preparation of $[\text{Pd}(\text{CH}_3(\text{CH}_2)_{14}\text{CH}_2\text{NH})(\text{acac})]_2$ (7).

This compound was prepared using a procedure adapted from Okeya *et al.*¹²⁹ $\text{Pd}(\text{acac})_2$ (0.16 g, 0.50 mmol), 1-hexadecylamine (0.12 g, 0.50 mmol) and toluene (8.5 mL) were added to a 100 mL round-bottom flask. The yellow-orange solution was heated to reflux for 5 h using an oil bath, during which the reaction mixture turned into a golden-orange color. After cooling to room temperature, the volatiles were removed by rotary evaporation, and the residue was subsequently recrystallized in CH_2Cl_2 (10 mL). Fine, light yellow-colored crystals were isolated by suction filtration (23 %).

Characterization Data for 7: ^1H NMR (300 MHz, CDCl_3) δ 0.89 (t, 3H, alkyl CH_3), 1.26 (br s, 28H, CH_2), 1.84 (s, 6H, OCCH_3), 2.04 (m, 2H, NCH_2), 2.15 (m, 2H, NCH_2), 5.20 (s, 1H, CH); MS (LREI, m/z , probe temperature 150 $^\circ\text{C}$) 892 [M^+].

2.6.12 Pd^0 -Amine Nanoparticles-Catalyzed Suzuki-Miyaura Cross-Coupling Reaction.

The reaction was performed using a procedure modified from Hyotanishi *et al.*¹⁰¹ A 10 mL round-bottom flask was charged with phenylboronic acid (0.18 g, 1.5 mmol), 4-iodotoluene (0.22 g, 1.0 mmol), K_2CO_3 (0.21 g, 1.5 mmol), and distilled water (2.0 mL). The purified Pd^0 -amine nanoparticles prepared using TOPO were suspended in *N,N*-dimethylformamide (DMF, 10 mL). An aliquot (2.0 mL) of this suspension was added to the round-bottom flask. The reaction mixture was then heated to the desired temperature for 5 h under nitrogen. The reaction mixture was cooled to room temperature, and diethylether (20 mL) was added. The organic layer was washed successively with water (5×20 mL) and was dried with anhydrous MgSO_4 . Removal of volatiles in *vacuo* resulted in a yellow or brown oil. The final product was then isolated by column chromatography (230 - 400 mesh silica gel, hexanes as eluent, $R_f = 0.39$) as a white solid. The isolated yields are reported in Table 2-1.

2.6.13 Detection of Ammonia Using Berthelot's Method.

Prior to the experiment, 3 different solutions were freshly prepared and used within 12 h. A Na_3PO_4 buffer was prepared from addition of aqueous NaOH (6.75 M, 3.7 mL) to Na_3PO_4 (2.51 g, 15.3 mmol), then dissolved with H_2O (50 mL) *via* sonication. The “working phenol” solution was made by dissolving phenol (5.01 g, 53.2 mmol) in MeOH (10 mL) and transferred to a 50 mL volumetric flask. Aqueous solution of $\text{Na}_2[\text{Fe}(\text{CN})_5(\text{NO})]$ (0.19 M, 500 μL) was then added to the

flask and diluted to the mark to result in a pale orange solution. The “working hypochlorite” solution was prepared by adding NaOCl (3 mL) and NaOH (6.75 M, 3 mL) into a 10 mL volumetric flask and diluted to the mark.

The typical preparation of Pd⁰ nanoparticles was conducted as per usual, except the vapour of the reaction was passed through two condensers before reaching to two bubblers, each containing H₂SO₄ (0.55 M, 40 mL and 5 mL in each bubbler). The gas flow was maintained to ~1 bubble per second during the course of the reaction. Once the reaction was cooled, the content of the bubblers were transferred quantitatively to a 25 mL volumetric flask. Subsequent addition of the Na₃PO₄ buffer solution (2 mL), the “working phenol” solution (5 mL), and the “working hypochlorite” solution (2.5 mL) allows formation of indophenol. The flask was diluted to the mark and was mixed in the dark, during which a color change from yellow to deep blue occurs in less than 10 s. The solution was allowed to stand for 1 h to further develop. The same developing procedure was conducted for the second bubbler, which resulted in a less intense blue color. The solutions were analyzed *via* UV-vis spectroscopy within 12 h as the blue color degrades after a day.

2.6.14 Derivation of Ammonia to *N,N*-dimethyl-*N'*-(phenylsulfonyl)formimidamide.

Ammonia was trapped as (NH₄)₂(SO₄) using the same bubbler setup as in the Berthelot’s method, and diluted to 100 mL with H₂O. The content of the bubbler (30 mL) and 1,4-dioxane (5 mL) were added to a separatory funnel. The solution was basified using aqueous Na₂CO₃ (2.5 wt.%, 8 mL) prior to addition of a solution of benzenesulfonyl chloride in 1,4-dioxane (20% v/v, 0.67 mL). The solution was shaken for 5 min, then extracted using hexanes (2 × 30 mL) to remove excess starting material. The aqueous layer was then acidified using 3 M HCl (1 mL) and was

extracted with Et₂O (2 × 30 mL). To the organic layer, *N,N*-dimethylformamide dimethyl acetal (320 μL) was added and the solution was mixed. Removal of the volatiles by rotary evaporation resulted in a clear, colorless oil. After drying *in vacuo* overnight, the final product was isolated by column chromatography (230 - 400 mesh silica gel, EtOAc as eluent, R_f = 0.38) as a white precipitate (4 mg).

Characterization Data of N,N-dimethyl-N'-(phenylsulfonyl)formimidamide: ¹H NMR (300 MHz, CDCl₃) δ 3.03 (s, 3H, NCH₃), 3.14 (s, 3H, NCH₃), 7.43 (m, 3H, ArH), 7.90 (d, 2H, ArH), 8.15 (s, 1H, N=CH). ESI-MS: 235.3 [M+Na].

2.6.15 Attempted Derivation of Ammonia to Ammonia Borane.

The procedure was adopted from Shore *et al.*¹³⁰ The typical preparation of Pd⁰ nanoparticles was conducted as per usual, except the vapor of the reaction was bubbled into a Schlenk tube containing BH₃•THF (2 mL, 1.0 M in THF). The Schlenk tube was vigorously stirred under N₂ atmosphere in a -78 °C cooling bath. Once the reaction was completed and cooled, the volatiles were removed from the Schlenk flask *in vacuo* to result in a clear, colorless liquid. A sample was immediately prepared for NMR analyses.

Chapter 3: Preparation of Pd⁰@*m*-SiO₂ Core-Shell Nanoparticles

3.1 Introduction

Heterogeneous Pd catalysts are critical for many important chemical processes including hydrogenation,¹³¹⁻¹³³ dehydrogenation,¹³⁴ CO oxidation,⁶¹ NO_x reduction reactions,^{66, 67} and conversion of organic compounds.^{135, 136} In these processes, the active catalyst is dispersed as small particles on a suitable oxide support, often silica or alumina.¹³¹ Despite the high surface area of such supported catalysts, a major problem is irreversible, thermally-induced sintering on oxide supports, which often leads to loss of activity. The preparation of catalysts with spatially separated active sites that remain stable under reaction conditions is a major area of current research.⁸⁶⁻⁸⁹

Core-shell nanoparticles consisting of a nanoparticle core and porous oxide shell have the potential to impact many fields – from catalysis to spectroscopy.⁹⁰ Silica shells have been demonstrated to lead to enhanced nanoparticle catalyst stability at high temperatures, thus preventing sintering. Recently, Pt@m-SiO₂ nanoparticles have been shown to have enhanced thermal stability for high temperature oxidation of CO.⁸⁸ Despite the large number of core-shell nanoparticle morphologies that have been reported, there are very few reports of silica shells on nanosized Pd catalysts.^{86, 87, 89} In the known examples, the particles ripen and lose integrity upon heating to high temperature due to incomplete incorporation of the Pd nanoparticles. Pd nanoparticles individually encapsulated by silica were unknown previous to this work. In this chapter, a simple, scalable one-pot synthesis of Pd⁰-silica core-shell nanoparticles will be discussed. These Pd nanoparticles are spatially separated from each other by a permeable shell of mesoporous silica. The physical properties, thermal stability and various synthetic modifications will be discussed in detail.

3.2 Preparation of Pd⁰@m-SiO₂ Core-Shell Nanoparticles

3.2.1 Overview of the One-Pot Synthesis of Pd⁰@m-SiO₂ Core-Shell Nanoparticles

Core-shell structured nanomaterials are not uncommon in the current literature. However, most methods used for the preparation of core-shell nanoparticles are not high-yielding, and require long reaction times or tedious workup procedures. Hence, a better preparation method for core-shell nanoparticles was needed. Instead of treating the preparation of the Pd⁰ core nanoparticle and the formation of the silica layer as two separate steps, a one-pot procedure to generate the nanostructure in a sequential manner would be more beneficial in reducing the amount of time and solvents used throughout the procedure. The details of this approach will be discussed in the coming subsections.

The Pd⁰-silica core-shell nanoparticles were prepared using a one-pot, sequential synthesis as outlined in Figure 3-1. First, Pd⁰ nanoparticles stabilized by cetyltrimethylammonium bromide (CTAB) were prepared following a modified procedure from Shen *et al.*²² Addition of palladium nitrate hydrate (Pd(NO₃)₂) to a hot solution containing CTAB and sodium ascorbate generated a black suspension. Next, the reduction of Pd^{II} by sodium ascorbate in the presence of CTAB under slight heating generated cube-shaped Pd⁰-CTAB nanoparticles.¹³⁷ As these nanoparticles are stabilized by CTAB molecules, the nanoparticles readily disperse in water as a black suspension. Without workup, the next step proceeded in the same reaction flask, following a modified procedure from Hyeon *et al.*¹³⁸ The pH of the suspension containing the Pd⁰-CTAB nanoparticles was adjusted to ~10 using aqueous NH₄OH solution prior to addition of tetraethoxy orthosilicate (TEOS). The basic condition and heat promotes formation of silica through a sol-gel process, which is selectively condensed on the particle surfaces due to the presence of CTAB.¹³⁸ This results in Pd⁰@m-SiO₂ core-shell nanoparticles, where CTAB are still present in the nanoparticles.

Stirring the nanoparticles in dilute acid dissolved in ethanol at room-temperature for 1 h removed the organics, resulting in the acid-treated $\text{Pd}^0@m\text{-SiO}_2$ core-shell nanoparticles. The silica-coated nanoparticles were then isolated as a grey-black powder from the solution by centrifugation and washed with multiple rinses of ethanol until neutral pH was reached, then dried in *vacuo*.

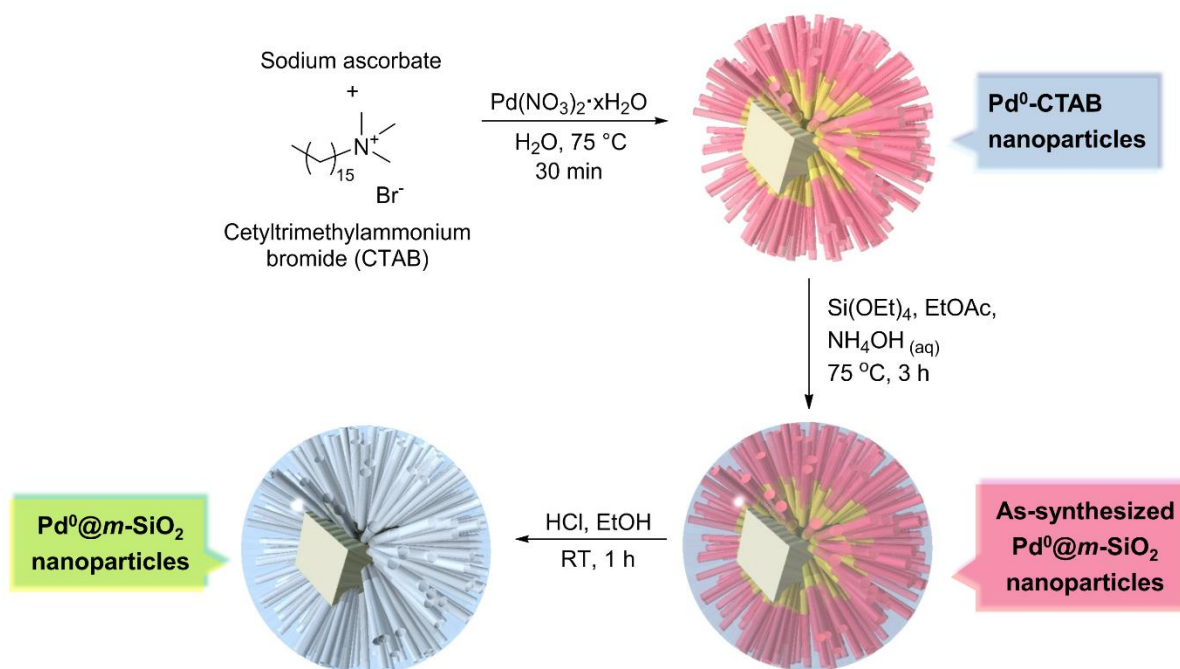
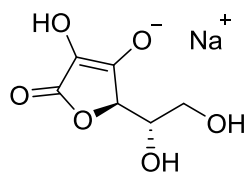


Figure 3-1. Schematic showing the procedure used to prepare $\text{Pd}^0@m\text{-SiO}_2$ core-shell nanoparticles. Pd^0 nanoparticles are represented by yellow cube, CTAB micelles by pink-shaded rods, and silica shell by the light blue shaded sphere. The blue cylinders of $\text{Pd}^0@m\text{-SiO}_2$ nanoparticles represent the porous channels, but do not represent the actual pore structure.

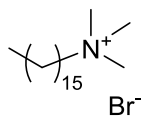
3.2.2 Characterization of Pd⁰-CTAB and Pd⁰@m-SiO₂ Nanoparticles

The nanoparticles were characterized using a number of techniques for analyzing solid materials at each step of the synthetic procedure. In the first step, the Pd⁰-CTAB nanoparticles were analyzed using transmission electron microscopy to identify the morphology of the particles. As shown in Figure 3-2, the TEM images of the material reveal the formation of cubic-shaped Pd⁰ nanoparticles with edges roughly 50 nm in length. The shape of the nanoparticles are predominately cube-shaped, with a few defects such as nanorods, prisms, or triangles present. The formation of cubes over other shapes has been shown previously to be an effect of the bromide ion in promoting the growth of the {100} facets of Pd⁰.¹³⁹ Nanoparticles in this size domain are not as effective for catalysis as their smaller counterparts. Interestingly, performing the same reaction at elevated temperature (75 °C) resulted in smaller Pd⁰-CTAB nanoparticles with roughly 15 nm diameter (Figure 3-3). Increasing the reaction temperature to 100 °C did not, however, further reduce the diameter of the Pd⁰-CTAB nanoparticles. In all cases, the solubility of the particles in water is consistent with the presence of a CTAB bilayer coating on the surface.

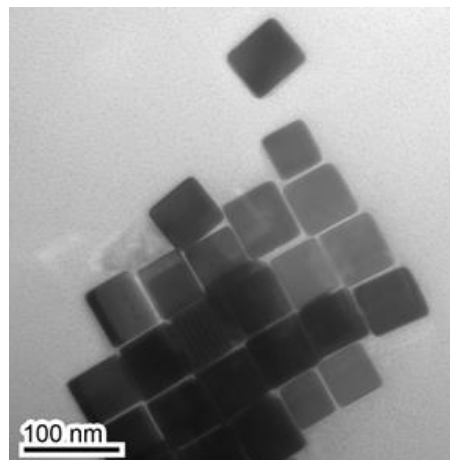
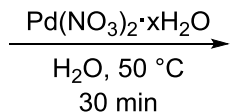


Sodium ascorbate

+

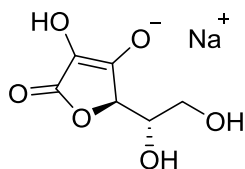


CTAB



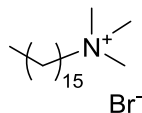
50 nm Pd⁰-CTAB nanoparticles

Figure 3-2. Preparation of 50 nm Pd⁰-CTAB nanoparticles in the aqueous phase.

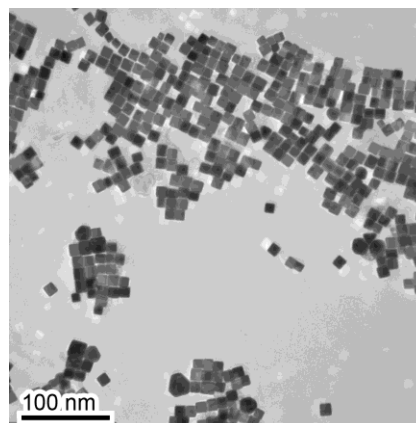
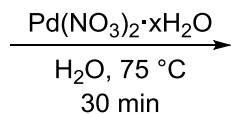


Sodium ascorbate

+



CTAB



15 nm Pd⁰-CTAB nanoparticles

Figure 3-3. Preparation of 15 nm Pd⁰-CTAB nanoparticles in the aqueous phase.

All attempts to isolate the Pd⁰-CTAB nanoparticles to remove excess CTAB molecules and other organic compounds were unsuccessful. Centrifugation of the nanoparticles at 12000 rpm for 1 h in order to isolate the nanoparticles resulted in only a small amount of precipitate containing the Pd⁰-CTAB nanoparticles. The precipitate dispersed easily, and so some precipitate was always lost during workup, resulting in variable isolated yields of Pd⁰-CTAB nanoparticles. This greatly

affected the next step of the procedure as substantial batch-to-batch variations resulted. Attempts to purify by addition of ethanol resulted in precipitation of the nanoparticles, generating black powder that could not be dispersed, and could not be used in later steps. This could be due to CTAB forming only a micelle around the nanoparticles, unlike other Lewis basic stabilizers that can better stabilize the nanoparticles in solution. Furthermore, precipitation of CTAB occurs when the nanoparticles are left at room temperature, since the CTAB micelles are only stable at higher temperature. As the purification of the Pd⁰-CTAB particles was difficult and troublesome, the nanoparticles were used in the next step as a suspension without any workup.

The silica layer was condensed from TEOS using the sol-gel process as outlined above to give “as-synthesized” Pd⁰@*m*-SiO₂ nanoparticles. TEM images of the Pd⁰@*m*-SiO₂ core-shell nanoparticles revealed that the Pd⁰-CTAB nanoparticles were encapsulated in a ~50 nm lighter-shaded, porous-looking layer of silica (Figure 3-4), resulting in spherical nanoparticles 130-150 nm in diameter. The presence of excess CTAB does not appear to adversely influence the formation of the core-shell Pd⁰@*m*-SiO₂ particles. The mesopores are visible in a low-resolution TEM image (Figure 3-4), and do not appear as straight channels as compared to those observed in spherical MCM-41 spheres.¹⁴⁰

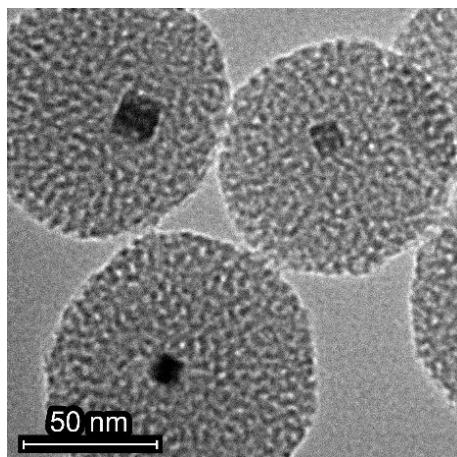


Figure 3-4. Transmission electron microscope image of “as-synthesized” Pd⁰@*m*-SiO₂ core-shell nanoparticles.

The amount of TEOS used during the synthesis was found to be crucial, as the quality of the nanoparticles were greatly affected by the amount of this reagent. In the presence of excess TEOS (mol Pd : TEOS = 1 : 57), the number of silica spheres that formed without a Pd core increases (Figure 3-5a). Reducing the amount of TEOS used in the synthesis (mol Pd : TEOS = 1 : 5) resulted in fewer core-shell particles being formed, while leaving some Pd nanoparticles unencapsulated (Figure 3-5b). This suggests a right balance in the amount of Pd and TEOS was used in the original preparation of the Pd⁰@*m*-SiO₂ nanoparticles (mol Pd : TEOS = 6).

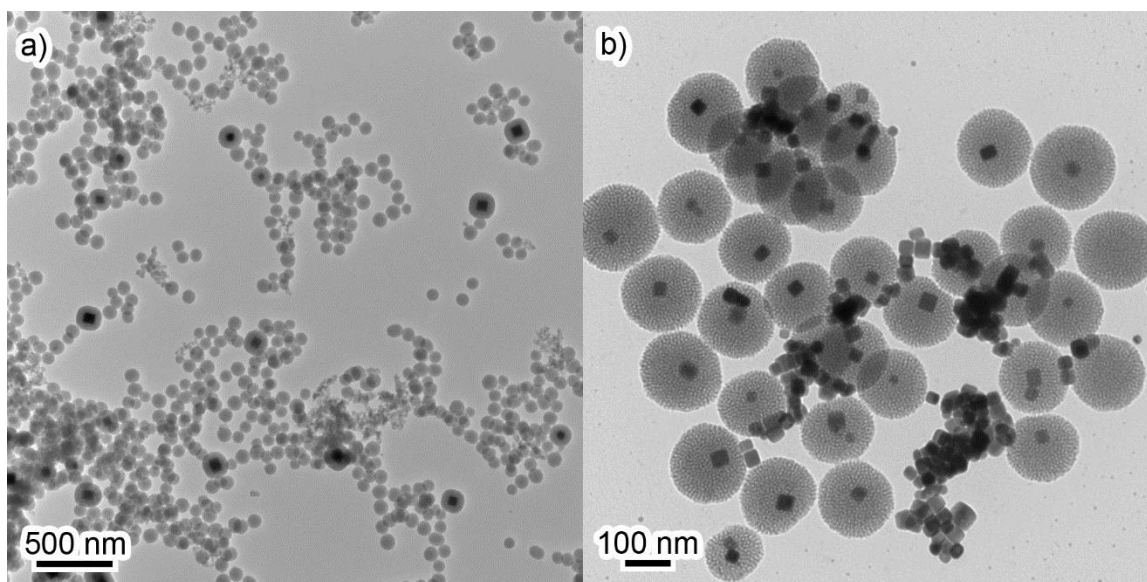


Figure 3-5. TEM images of the as-synthesized Pd⁰@*m*-SiO₂ core-shell nanoparticles formed with varying amounts of TEOS. a) mol Pd : TEOS = 1 : 57. b) mol Pd : TEOS = 1 : 5.

It is important to note that previously, high speed centrifugation (> 8000 rpm) has been used to remove excess CTAB from nanoparticles prior to condensation of the silica shell.^{88, 141} Here, initiating the silica condensation *in situ* immediately after the formation of Pd⁰-CTAB nanoparticles at elevated temperature was found to be more effective. This procedure eliminates repeated tedious centrifugation cycles, substantially simplifying the preparation. Consequently, larger scale preparations of the nanoparticles are possible because no dilution is required during the synthesis.

3.2.2.1 Removal of CTAB from Pd⁰@*m*-SiO₂ Nanoparticles

Removal of organic residues, such as CTAB, from the nanoparticles can be carried out in a number of ways. The straight-forward approach is through calcination, which involves treatment of the material with heat under gas flow in order to burn away volatile organic compounds. The

effects of calcination under oxygen and nitrogen gases, and the removal of CTAB using mild acid treatment were explored. Thermogravimetric analysis (TGA) and IR were used to determine the presence of CTAB in the samples.

3.2.2.1.1 Thermogravimetric Analysis of the Pd⁰@*m*-SiO₂ Nanoparticles

Thermogravimetric analysis (TGA) was used to determine the appropriate temperature for calcination. In TGA, a sample is heated under a gas flow, and its weight loss is monitored and plotted versus temperature. This reveals the temperature at which organic components are decomposed into CO₂, allowing an appropriate calcination temperature to be determined. Heating CTAB alone from room temperature to 800 °C under an air flow shows a decrease in the percent weight to nearly zero starting at 250 °C (Figure 3-6, red trace). Analyzing the as-synthesized Pd⁰@*m*-SiO₂ nanoparticles under the same conditions resulted in a curve with more weight loss features (Figure 3-6, black trace). The first decrease in weight just below 100 °C is assigned to loss of water adsorbed to the silica. The second weight decrease occurs at ~250 °C, which matches the TGA curve of CTAB. At elevated temperature 80% weight of the sample, indicating most of the sample is composed of non-volatile materials (Pd and SiO₂ only). From the TGA curves, temperatures above 350 °C are most suitable temperature for calcination.

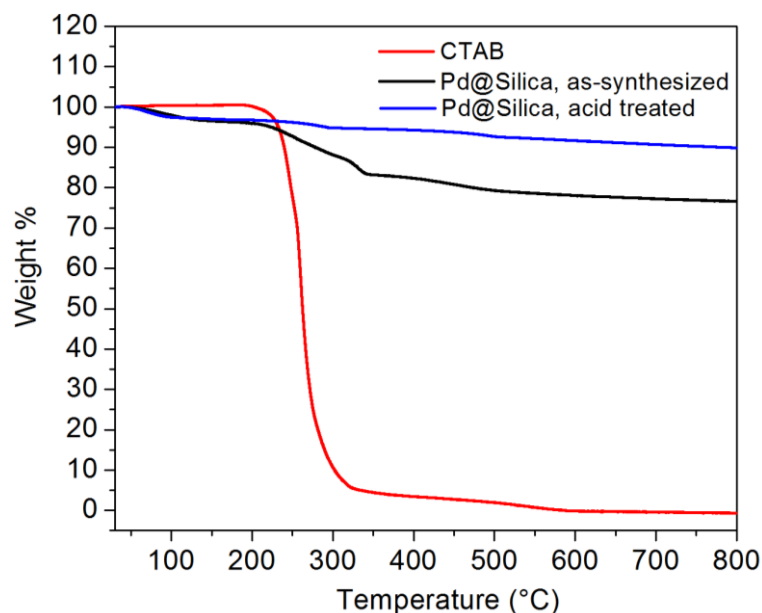


Figure 3-6. TGA curves of CTAB, as-synthesized Pd⁰@*m*-SiO₂ nanoparticles and acid-treated Pd⁰@*m*-SiO₂ nanoparticles. The samples were heated from room temperature to 800 °C at a heating rate of 10 °C min⁻¹.

3.2.2.1.2 FT-IR Study of the As-synthesized and Calcined Pd⁰@*m*-SiO₂ Nanoparticles

Calcination of the as-synthesized Pd⁰@*m*-SiO₂ nanoparticles at 400 °C for 4 h in air resulted in the formation of a brown powder (Figure 3-7). Fourier transform infrared spectroscopy (FT-IR) was used to verify the removal of the CTAB after calcination. The infrared spectrum of the as-synthesized Pd⁰@*m*-SiO₂ nanoparticles contains a broad band attributed to the Si–O bond stretching at ~1050 cm⁻¹, C–H stretching bands at 2923 and 2852 cm⁻¹ due to CTAB, as well as an O–H stretching band at 3000–3500 cm⁻¹ corresponding to water adsorbed on the silica surface (Figure 3-12). After calcination at temperatures as low as 350 °C, the disappearance of the C–H stretching bands in the 3000–3200 cm⁻¹ region in the FT-IR spectrum indicates loss of CTAB in the sample. The stretching bands of Si–O bonds remain in all samples.

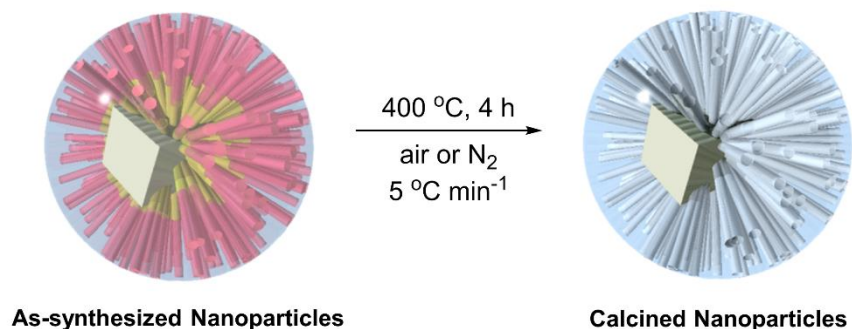


Figure 3-7. Schematic drawing illustrating the calcination procedure used for the Pd⁰@*m*-SiO₂ core-shell nanoparticles. Pd⁰ nanoparticles are represented by the grey cube, CTAB micelles by pink-shaded rods, and silica shell by the light blue shaded sphere.

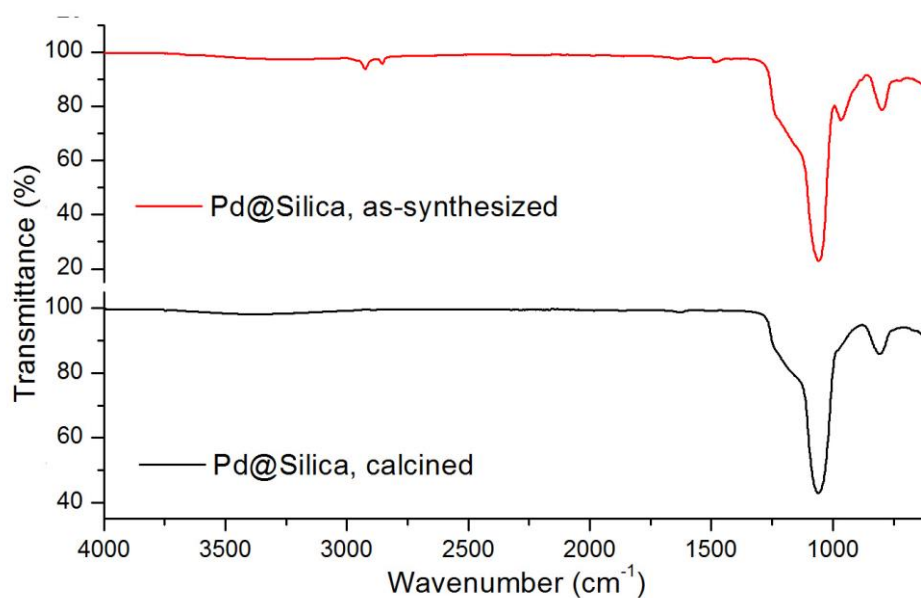


Figure 3-8. FT-IR spectra of the as-synthesized and calcined Pd⁰@*m*-SiO₂ nanoparticles.

3.2.2.1.3 Powder XRD Studies of the Calcined Pd⁰@*m*-SiO₂ Nanoparticles

While infrared spectroscopy provide information regarding the functional groups present in the material, the identity of the material can be established with powder X-ray diffraction

(PXRD). Treatment of the as-synthesized Pd⁰@*m*-SiO₂ nanoparticles to calcination at 400 °C for 4 h results in a brown powder. The PXRD pattern of the material shows no signals corresponding to face-centered cubic (fcc) Pd (Figure 3-9). Instead, the reflections can be assigned to tetragonal palladium oxide (JCPDS card no. 41-1107), formed by oxidation of the Pd core in air at elevated temperatures.¹⁴² This suggests that the final product that is obtained is PdO@*m*-SiO₂ nanoparticles. Calcination of as-synthesized Pd⁰@*m*-SiO₂ nanoparticles containing either 15 nm or 45 nm Pd cores did not result in any shifts in the PXRD patterns. The only difference between the two spectra is the intensities of the PdO reflections, which is due to the size differences between the nanoparticles. Larger nanoparticles tend to be more crystalline, hence their PXRD patterns exhibit sharper signals.

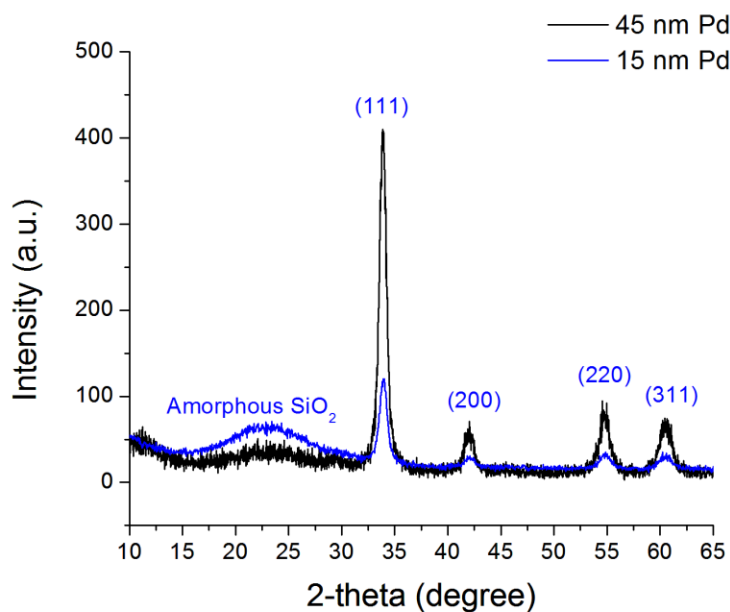


Figure 3-9. Overlaid PXRD patterns of the samples prepared from calcination of 15 and 45 nm Pd⁰@*m*-SiO₂ core-shell nanoparticles. The peaks are indexed to the known diffraction pattern of tetragonal PdO.

As palladium oxide was not the desired product, N_2 (g) was chosen as the gas flow source to prevent oxidation of the Pd^0 core. Calcination of the as-synthesized 50 nm $Pd^0@m-SiO_2$ nanoparticles under nitrogen at 400 °C for 4 h resulted in a black powder. The wide-angle PXRD pattern of the calcined core-shell nanoparticles (Figure 3-10) exhibits the characteristic reflections of fcc crystalline Pd ($a = 0.3890$ nm from JCPDS card no. 46-1043). The highly crystalline Pd core phase was preserved after calcination. A broad signal at $2\theta = 22.2^\circ$ is attributed to amorphous silica, further confirming the composition of the shell. The low-angle PXRD pattern shows a peak at $d(100) = 48.2$ Å, consistent with a hexagonal or worm-hole mesostructure (Figure 3-10a). Calcination results in a slight shift of the peak to a lower d -spacing of 45.3 Å and an increase in the peak intensity, as has been previously observed in mesoporous silica.¹⁴³⁻¹⁴⁵ The FT-IR spectrum shows no differences to that of the sample calcined in air. Elemental analysis of the nanoparticles, however, suggested the presence of 1.57% of carbon on the sample. This is attributed to the calcination condition, where nitrogen is used for gas flow. Incomplete combustion of the volatile organics under aerobic conditions leave residual carbon in the sample. As samples with minimal impurities are ideal for catalytic applications, a method for removal of CTAB under milder conditions and less impurities is desired.

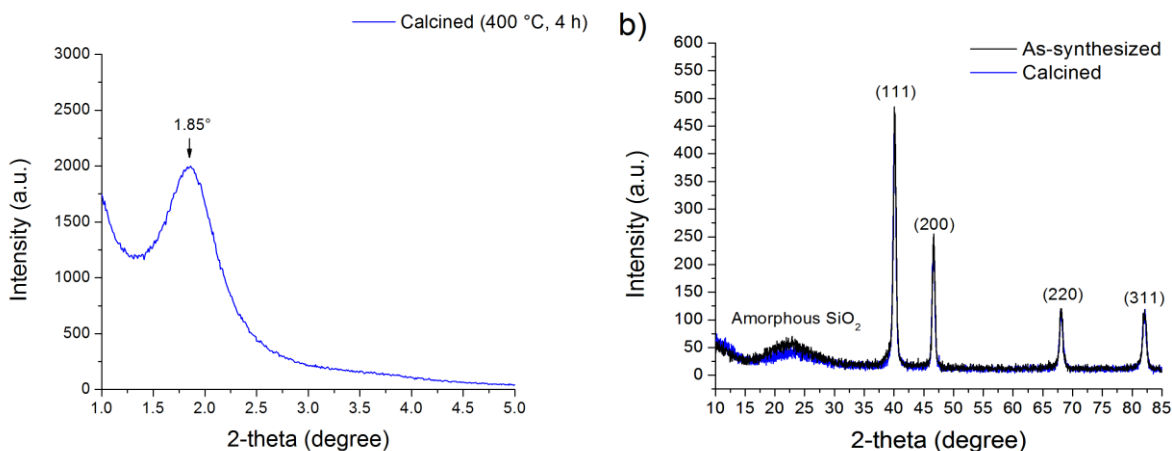


Figure 3-10. a) Low-angle and b) wide-angle PXRD patterns of the as-synthesized and calcined Pd⁰@*m*-SiO₂ core-shell nanoparticles. The peaks are indexed to the known diffraction pattern of fcc Pd.

3.2.2.1.4 Removal of CTAB Using Dilute Solution of HCl in Ethanol

One method to mildly remove CTAB from the as-synthesized Pd⁰@*m*-SiO₂ core-shell nanoparticles is using weak acids.^{146, 147} Previously it has been shown that 1% v/v of hydrochloric acid (HCl) in ethanol is an efficient solution for removal of CTAB from MCM-41.¹⁴⁶ This same treatment was used on the as-synthesized Pd⁰@*m*-SiO₂ nanoparticles: stirring a slurry of the Pd⁰@*m*-SiO₂ nanoparticles in a dilute solution of HCl in ethanol resulted in no color changes of the nanoparticles. After stirring at room temperature for 1 h, the nanoparticles can be easily isolated and cleaned by centrifugation to result in a grey-black powder that is denoted as acid-treated Pd⁰@*m*-SiO₂ nanoparticles.

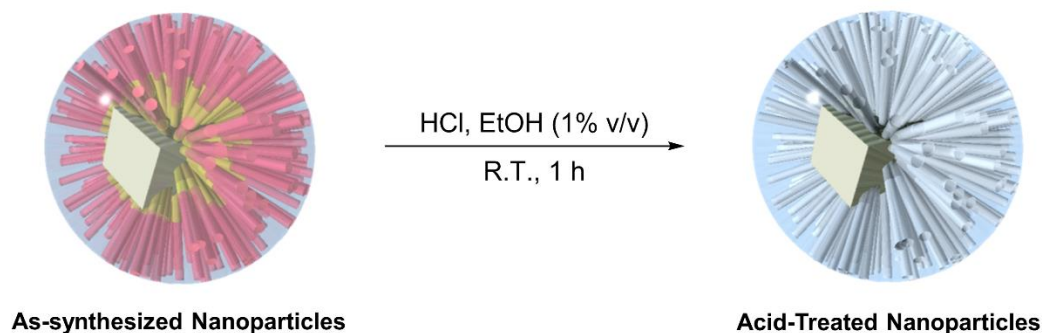


Figure 3-11. Schematic drawing showing the acid treatment procedure of the $\text{Pd}^0@m\text{-SiO}_2$ core-shell nanoparticles. Pd^0 nanoparticles are represented by yellow cube, CTAB micelles by pink-shaded rods, and silica shell by the light blue shaded sphere.

The removal of CTAB can be confirmed by TGA and IR spectroscopy techniques as previously discussed. The TGA curve of the acid-treated $\text{Pd}^0@m\text{-SiO}_2$ nanoparticles shows barely any weight losses, with most of the weight loss coming from loss of water just before 100 °C (Figure 3-6, blue trace). Very minimal CTAB is found as only an extremely small weight loss is seen at around 300 °C. The acid-treated nanoparticles exhibit Si–O stretches in the FT-IR spectrum consistent with the presence of SiO_2 , while no C–H stretches are found in the 2900-3200 cm^{-1} region (Figure 3-12). The small peak at 1634 cm^{-1} corresponds to water adsorbed on the surface of the silica shell. The peaks at 796 and 956 cm^{-1} will be discussed in the next section. Both TGA and IR suggest CTAB was successfully removed from the nanoparticles using this facile workup procedure. However, it is unknown whether the dilute HCl etched trace amounts of Pd from the nanoparticles during treatment.

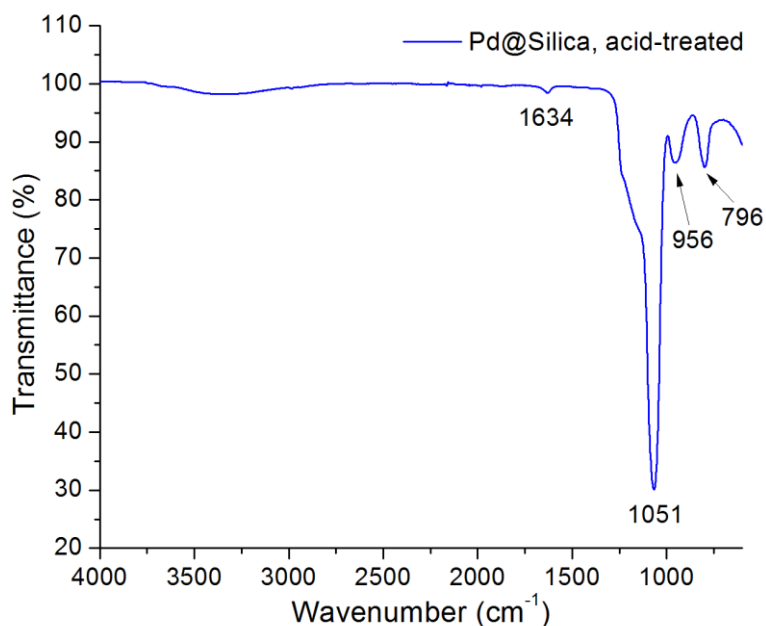


Figure 3-12. FT-IR spectrum of the acid-treated Pd⁰@*m*-SiO₂ nanoparticles.

The oxidation state of the Pd core was confirmed using powder XRD. The PXRD pattern of the acid-treated sample shows characteristic reflections of fcc Pd and amorphous SiO₂ (Figure 3-13). This is expected as Pd is not easily removed by dilute HCl, and the lack of heating does not induce oxidation of Pd⁰ to PdO. As the acid treatment does not require excessive heating, this method is suitable in removal of CTAB from the as-synthesized Pd⁰@*m*-SiO₂ nanoparticles.

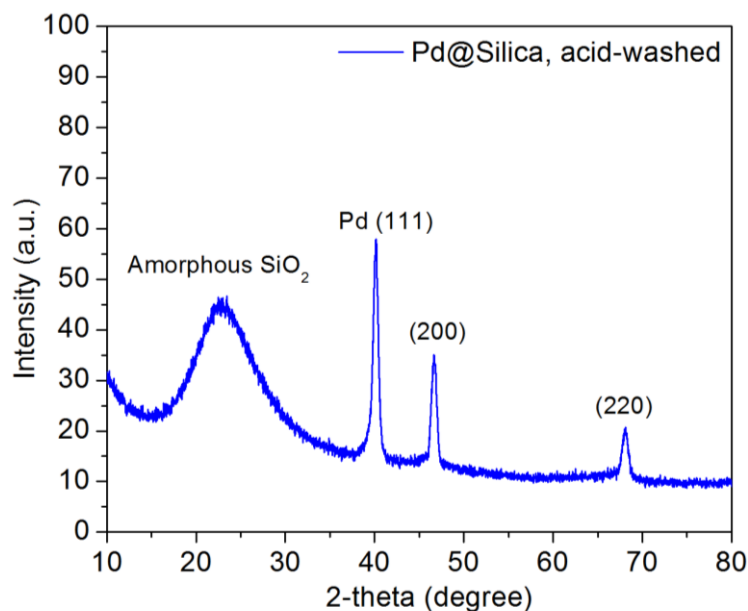


Figure 3-13. PXRD patterns of the acid-treated Pd⁰@*m*-SiO₂ core-shell nanoparticles. The peaks are indexed to the known diffraction pattern of fcc Pd.

3.2.2.2 Comparisons Between the Calcined and Acid-Treated Pd⁰@*m*-SiO₂ Nanoparticles

3.2.2.2.1 TEM Studies

In addition to the chemical composition of the nanomaterial, the morphology of nanomaterials is equally important as the core-shell structure may be destroyed during workup procedures. TEM images of the Pd⁰@*m*-SiO₂ nanoparticles calcined at 400 °C for 4 h in air reveal that the morphology of the particles, including the cube-shaped Pd⁰, was maintained after calcination (Figure 3-14, top). Scanning electron microscopy (SEM) images of the calcined nanoparticles also show spherical silica nanoparticles are present (Figure 3-14, bottom). The Pd⁰ core is also visible in the SEM images when higher accelerating voltage is used, demonstrating that the Pd is indeed found in the core of the nanoparticles and not on the outside of the silica shell. As well, calcination at 400 °C for 4 h under nitrogen does not affect the morphology of the

nanoparticles (Figure 3-15).

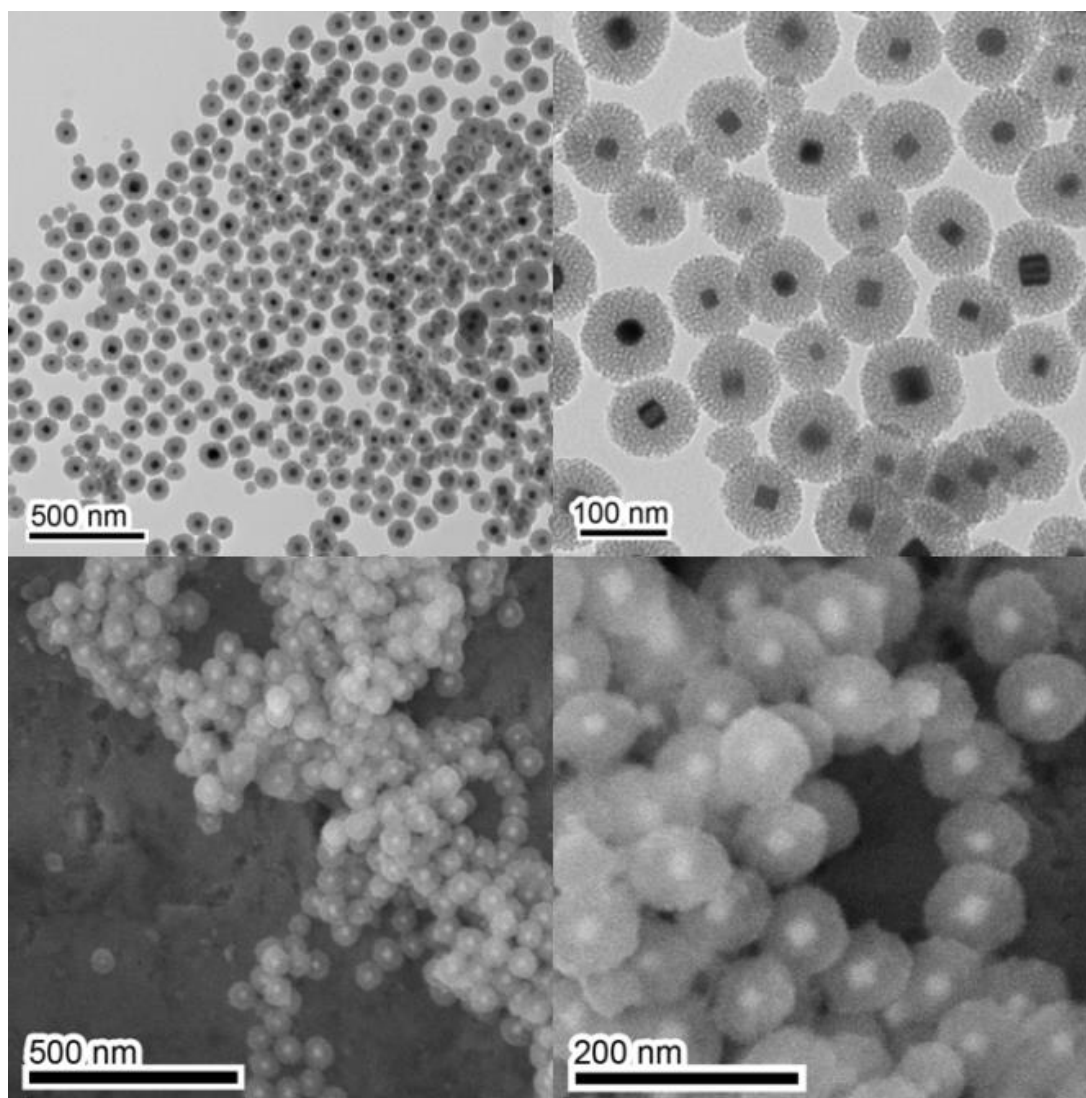


Figure 3-14. TEM (top) and SEM (bottom) images of the Pd⁰@*m*-SiO₂ core-shell nanoparticles calcined at 400 °C for 4 h in air.

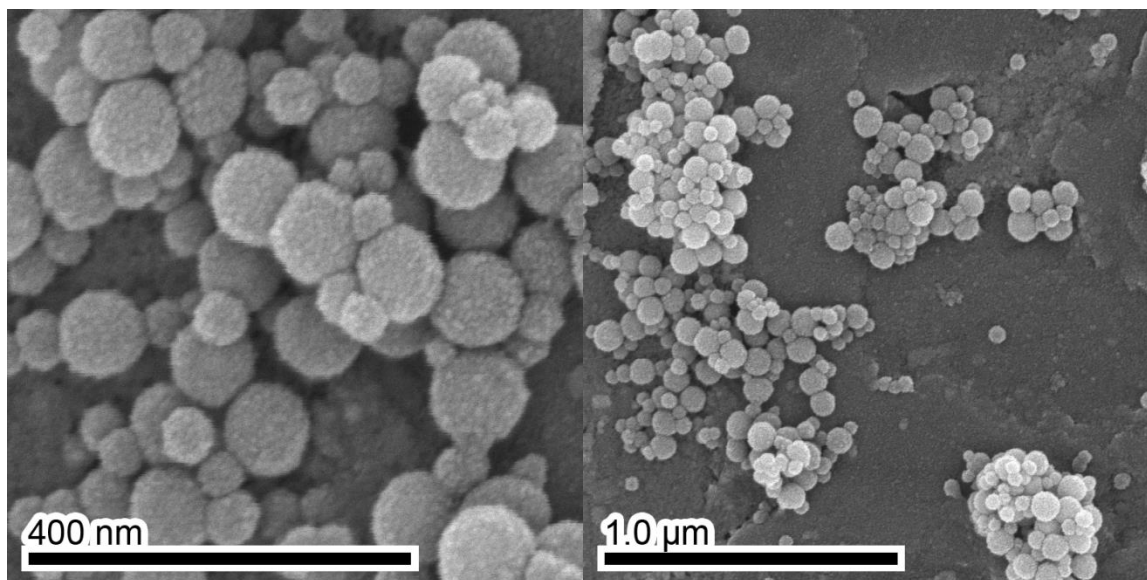


Figure 3-15. SEM images of the Pd⁰@*m*-SiO₂ core-shell nanoparticles after calcination at 400 °C for 4 h under N₂. The nanoparticles were sputter coated with 5 nm of Au/Pd (60:40) under vacuum prior to imaging.

Calcination at higher temperature was also performed. Heating the nanoparticles at 750 °C for 4 h under N₂ did not change the overall structure of the core-shell nanoparticles, while the Pd core became more spherical in shape (Figure 3-16). Only after heating the particles to 870 °C is disintegration of the particles observed, with some Pd that has melted from the silica appearing outside of the core-shell structure (Figure 3-17). This supports that there is a path through the silica channels to the Pd center, and that the channels do not appear to be straight as they are in MCM-41. The acid treatment method appears to be the best CTAB-removal method which leaves the Pd⁰ core intact and is the mildest and least energy-intensive method to remove CTAB from the nanoparticles.

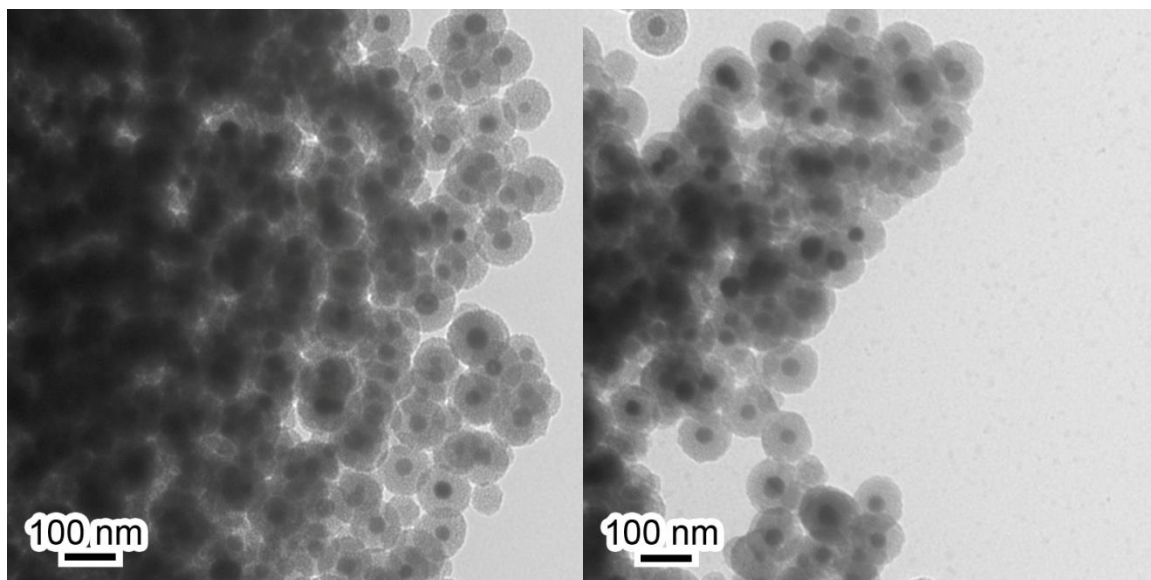


Figure 3-16. TEM images of the Pd⁰@*m*-SiO₂ core-shell nanoparticles after calcination at 750 °C for 4 h under N₂.

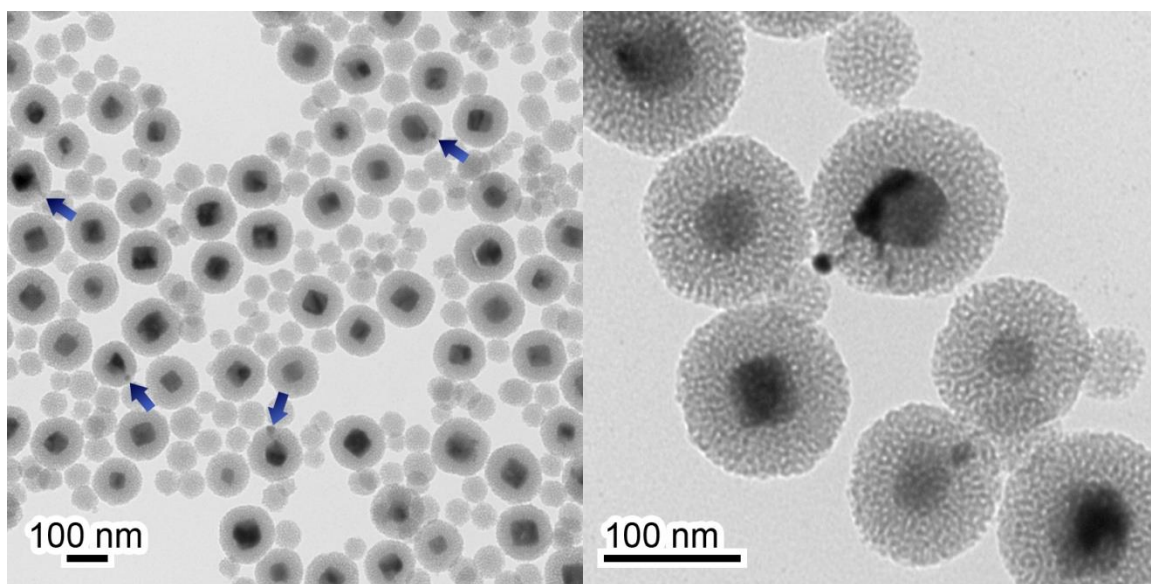
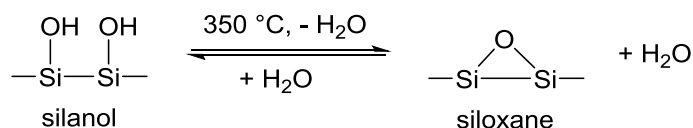


Figure 3-17. TEM images of the Pd⁰@*m*-SiO₂ core-shell nanoparticles after heating at 870 °C. The arrows indicate Pd that was melted from the core.

3.2.2.2.2 Comparison of the FT-IR Spectra

The difference between the calcined and acid-treated nanoparticles is not only the chemical composition of the Pd core: subtle differences are found when comparing the FT-IR spectra of the as-synthesized, calcined, and acid-treated Pd⁰@*m*-SiO₂ nanoparticles. As previously discussed, no C–H stretches are found in the 2900–3200 cm^{−1} region of the spectra of the calcined and acid-treated samples, confirming the absence of CTAB (Figure 3-18). The band at 956 cm^{−1} appear in lower intensity only in the calcined sample. In addition, in the acid-treated nanoparticles, there is a hint of a weak band at 3600 cm^{−1} (Figure 3-12). Bands at 3600 and 956 cm^{−1} are attributed to the O–H and Si–O stretches of silanols (Si–OH) respectively.¹⁴⁸ The presence of silanols on the nanoparticles suggests hydrophilicity on the silica shell in both the as-synthesized and acid-treated samples. The lower amount of silanol groups in the calcined sample is likely a consequence of the calcination step, as heating above 100 °C can result in dehydroxylation of some silanol groups on silica, generating siloxanes (Scheme 3-1).¹⁴⁸ Since heating above 1200 °C is required to remove all silanol groups, it is reasonable that a small shoulder corresponding to the Si–OH stretch is observed in the FT-IR spectrum of the calcined Pd⁰@*m*-SiO₂ nanoparticles.



Scheme 3-1. Formation of siloxane from dehydroxylation of silanols. Scheme reproduced from reference.¹⁴⁸

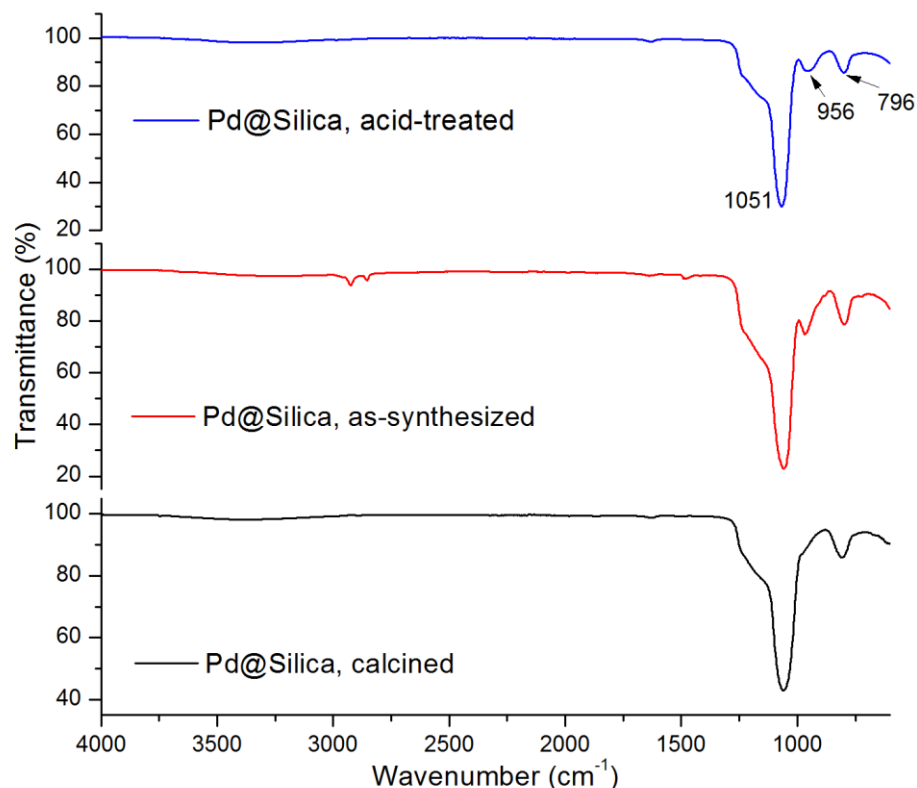


Figure 3-18. Stacked FT-IR spectra of the acid-treated, as-synthesized, and calcined Pd⁰@*m*-SiO₂ nanoparticles.

3.2.2.3 Analysis of Pd⁰@*m*-SiO₂ Nanoparticles Using X-ray Photoelectron Spectroscopy

As the materials prepared here are intended for application as catalysts, ideally most of the Pd⁰ nanoparticles should be encapsulated by mesoporous silica. The techniques used here do not confirm the presence of Pd outside of the core-shell nanoparticles, as they analyze the bulk materials only. TEM cannot confirm whether sub-nanometer scale particles or compounds of Pd are present on the outside of the core-shell nanoparticles. For these reasons, X-ray photoelectron spectroscopy (XPS) was used to validate that most of the Pd nanoparticles are encapsulated in the silica shell, as XPS is a surface-sensitive technique. The XPS spectrum of the calcined core-shell nanoparticles (Figure 3-19a) contains only peaks due to Si and O, with no peaks in the Pd 3d region

(Figure 3-19). This suggests the absence of Pd on the surface of the nanoparticles. Since XPS is surface sensitive with a probe depth of 10 nm,¹⁴⁹ and the silica shell is roughly 50 nm thick, none of the Pd in the core of the nanoparticles was detected. The lack of a significant Pd signal confirms that the majority of the metal nanoparticles are completely encapsulated by the silica shell.

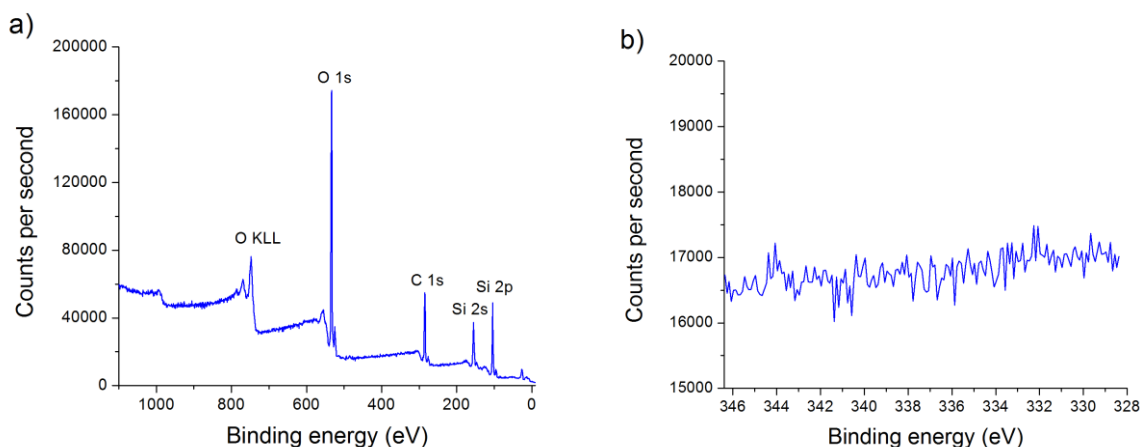


Figure 3-19. XPS spectrum of the Pd⁰@*m*-SiO₂ nanoparticles, referenced to the carbon 1s peak at 285.0 eV. a) Complete spectrum. b) Palladium 3d region of the XPS spectrum.

3.2.2.4 Nitrogen Physisorption Studies on the Pd⁰@*m*-SiO₂ Nanoparticles

Nitrogen physisorption studies were used to confirm the mesoporosity of the Pd⁰@*m*-SiO₂ nanoparticles after calcination and acid treatment. The experiment, which was conducted at liquid nitrogen temperature, measures the amount of nitrogen adsorbed and desorbed from the surface. From this data, the pore dimensions can be determined. Nitrogen adsorption-desorption analysis shows a type IV isotherm, with a Brunauer-Emmett-Teller (BET) surface area of 572 m² g⁻¹ for the 45 nm core Pd⁰@*m*-SiO₂ core-shell nanoparticles calcined at 400 °C for 4 h in air (Figure 3-20). The adsorption at $p/p_0 = 0.3$ is attributed to the reversible capillary condensation within

uniform pores, as observed in isotherms of mesoporous silica MCM-41.¹⁵⁰⁻¹⁵² The pore size distribution curve shown in Figure 3-20b has a maximum at 3 nm, similar to that observed for Pt⁰@*m*-SiO₂ nanoparticles.⁸⁸ Calcination of the nanoparticles at 400 °C for 4 h under nitrogen resulted in similar properties, with a BET surface area of the resulting Pd⁰@*m*-SiO₂ nanoparticles of 605 m² g⁻¹, and average pore diameters of 3.0 nm. Increasing the calcination temperature to 750 °C for 4 h in air does not appear to have dramatic effect on the BET surface area ($S_{\text{BET}} = 559 \text{ m}^2 \text{ g}^{-1}$, pore diameter = 3 nm). In all cases, the t-plot collected from the measurement shows a negative y-intercept, indicating the absence of micropores in the sample.¹⁵³

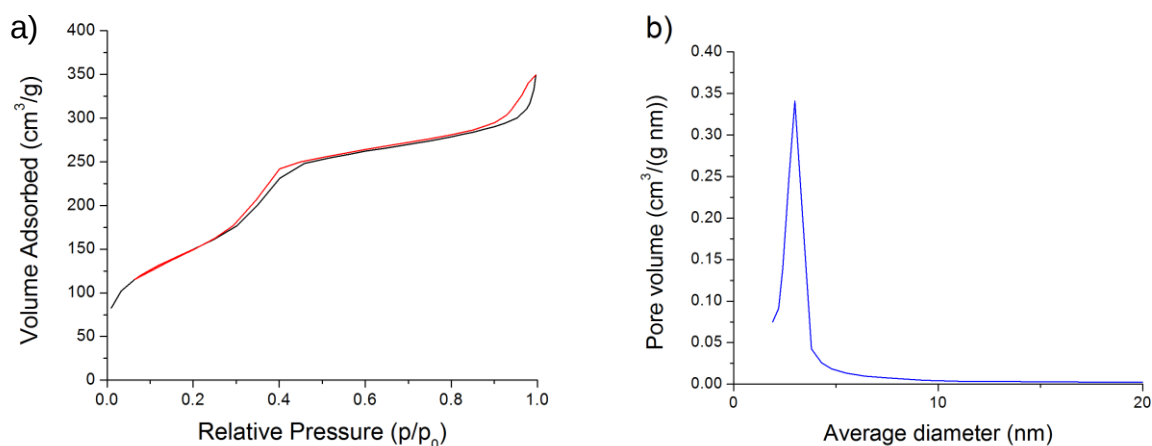


Figure 3-20. a) Nitrogen adsorption-desorption isotherms of Pd⁰@*m*-SiO₂ nanoparticles consist of 45 nm Pd cores. The black and red curves show the adsorption and desorption isotherms, respectively. b) Pore size distribution of the calcined core-shell nanoparticles as determined by BJH desorption.

The surface area of the Pd⁰@*m*-SiO₂ nanoparticles with smaller core diameter was also determined. With a decrease in the Pd core diameter, the surface area is expected to increase as more of the mesoporous silica shell occupy the same volume of space. This is observed as the BET

surface area measured for the Pd⁰@*m*-SiO₂ nanoparticles with a 15 nm core increased to 798 m² g⁻¹. Despite the surface area increase, the pore diameter remained 3 nm on average, with no micropores present.

As confirmed by FT-IR spectroscopy, acid treatment had no effect on the silica structure, hence drastic differences are not expected in the measured BET surface area. Nitrogen adsorption/desorption measurements on the acid-treated samples agree with this, as the BET surface area was found to be 747 m² g⁻¹, with an average pore diameter of 3.0 nm and pore volume of 1.43 cm³ g⁻¹. Comparing the adsorption and desorption curves, and the pore diameter distribution curves of the calcined and acid-treated samples, there appears to be no drastic differences (Figure 3-21). The high surface area serves as another confirmation that CTAB is removed from the particles.

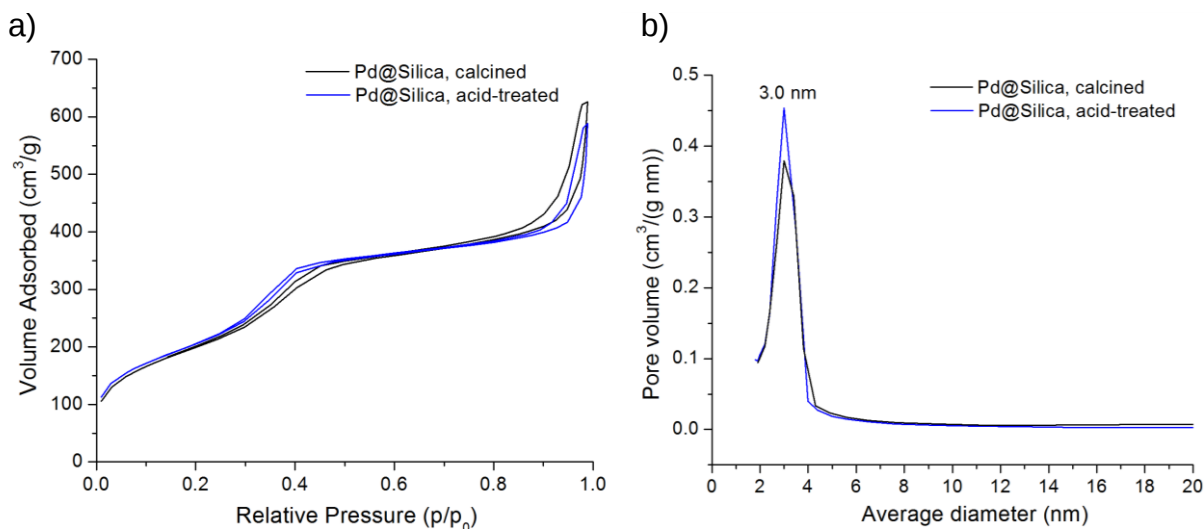


Figure 3-21. a) Stacked nitrogen adsorption-desorption isotherms of calcined (black trace) and acid-treated (blue trace) Pd⁰@*m*-SiO₂ nanoparticles. b) Pore size distribution of the two samples as determined by BJH desorption.

For comparison, mesoporous silica prepared without the Pd⁰ core was also analyzed. Without the Pd core, the BET surface area is 1114 m² g⁻¹, higher than that of either the calcined or acid-treated core-shell nanoparticles. The difference in BET surface areas is attributed to the slight difference in the reaction conditions, which greatly affects the size of silica nanoparticles generated, as well as the presence of Pd in the center of the core-shell nanoparticles which takes up some volume.

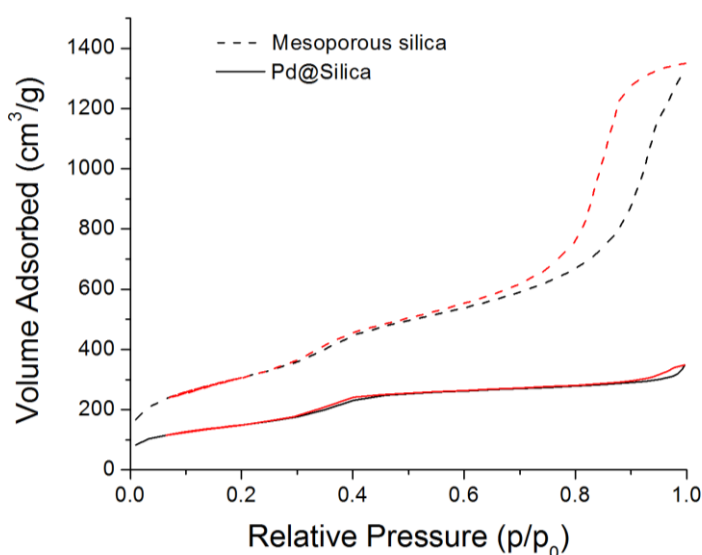


Figure 3-22. Nitrogen adsorption-desorption isotherms of mesoporous silica nanoparticles and Pd⁰@m-SiO₂ nanoparticles synthesized under identical conditions. The black and red curves show the adsorption and desorption isotherms, respectively.

3.2.3 Modifications to the Pore Diameters of Pd⁰@m-SiO₂ Nanoparticles

In the previous section the focus was on the removal of CTAB and the size effect of the core. Aside from the core diameter of the Pd⁰ nanoparticles, the pore diameter of the silica shell can be modified during or after the preparation of the Pd⁰@m-SiO₂ nanoparticles. As demonstrated below, this change can affect the morphology and physical properties of the nanoparticles

prepared.

3.2.3.1 Pore-Expansion of the Silica Channels of Pd⁰@*m*-SiO₂ Nanoparticles

Sayari *et al.* showed that the pore diameter of the channels of MCM-41 can be increased by the incorporation of *N,N*-dimethylhexadecylamine (DMHA) prior to condensation of silica.¹⁵⁴ Addition of a long chain alkylamine such as DMHA expands the CTAB micelles.¹⁵⁴ Since CTAB is responsible for generation of the mesopores, the micelle expansion gives rise to larger pores when silica is condensed. Using this method, the pore diameter of the particles can be expanded from 3 nm to 9 nm (Figure 3-23). The amount of DMHA added is proportional to the diameter increase of the pores. Incorporating this small modification to the preparation of the Pd⁰@*m*-SiO₂ nanoparticles, DMHA was added to the suspension of the as-synthesized Pd⁰@*m*-SiO₂ nanoparticles prior to addition of the TEOS/ethyl acetate mixture, resulting in a slightly cloudier reaction mixture than in the absence of DMHA. Following the reaction condition used by Sayari *et al.*, the reaction mixture was stirred at 75 °C for 3 d, instead of the typical 3 h.

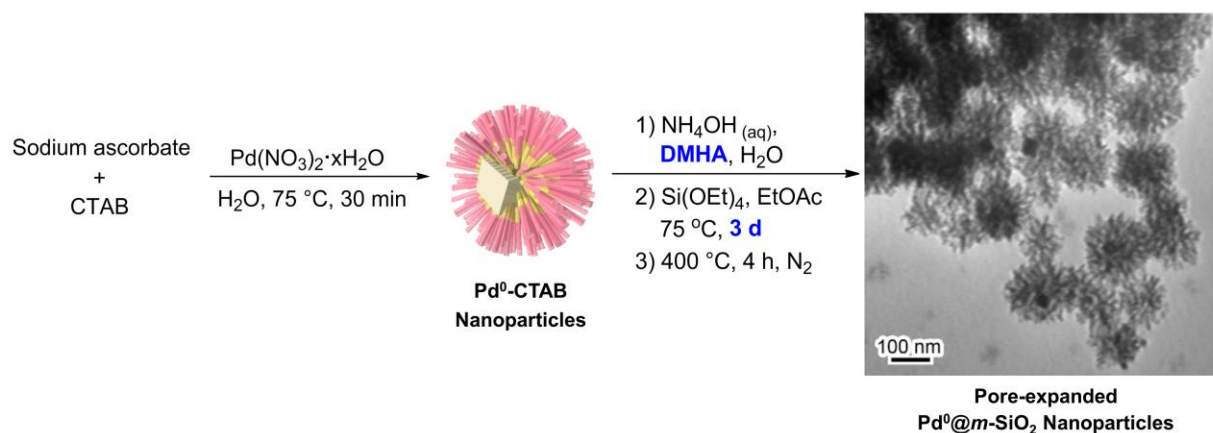


Figure 3-23. Schematic drawing showing the pore diameter expansion procedure of the Pd⁰@m-SiO₂ core-shell nanoparticles. Pd⁰ nanoparticles are represented by grey cube, CTAB micelles by yellow and pink-shaded rods. DMHA = *N,N*-dimethylhexadecylamine, CH₃(CH₂)₁₅N(CH₃)₂.

In TEM images, aggregates of spherical-looking particles are observed, with the Pd core remaining visible (Figure 3-23). Comparing to other TEM images of the other samples, the channels throughout the silica shell are visibly larger. However, the morphology of the nanoparticles do not appear as spherical and are distorted compared to the samples prepared without the pore-expanding procedure. This could be the consequence of the use of longer reaction times which results in the formation of aggregates, and insufficient silica condensed around the Pd⁰ nanoparticles as the pore diameter was increased, forming a less rigid-looking structure.

Nitrogen adsorption-desorption isotherms confirms the success in expanding the pore diameter of the Pd⁰@m-SiO₂ nanoparticles. The BET surface area of the material was found to be 631 m² g⁻¹, which is lower than that of the 15 nm core nanoparticles with 3 nm pore diameter. The blue trace in Figure 3-24a shows the adsorption and desorption isotherms of the pore-expanded nanoparticles, with the hysteresis loop shifted towards higher relative pressure. This is indicative

of a larger pore diameter, which was confirmed upon examination of the pore size distribution of the nanoparticles, showing a larger size distribution, centered at approximately 9 nm.

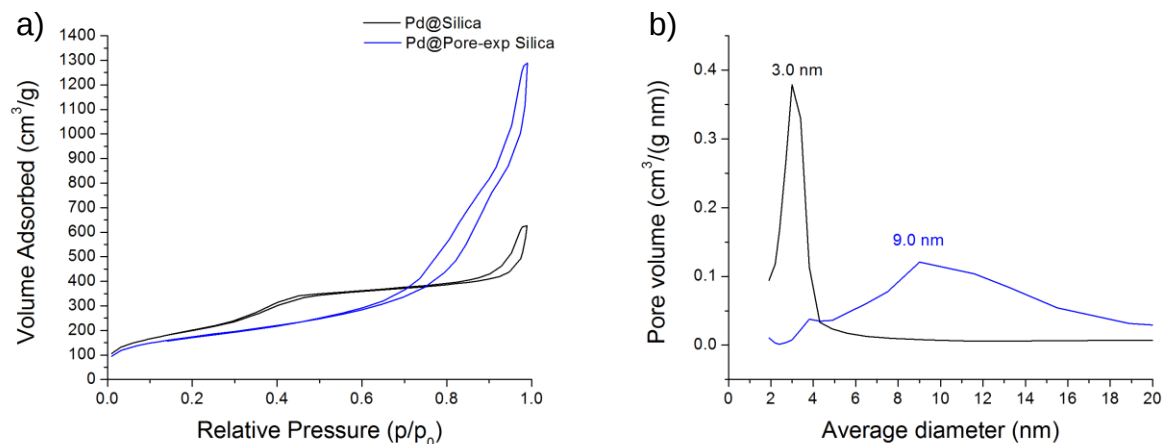


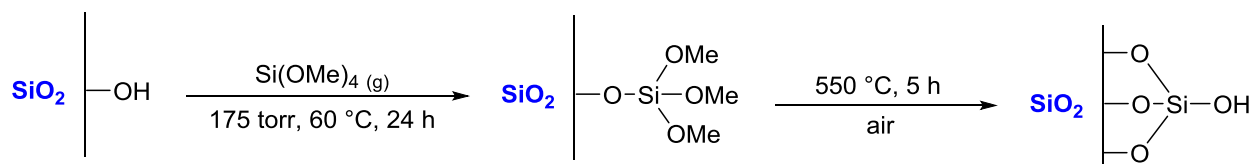
Figure 3-24. a) Stacked nitrogen adsorption-desorption isotherms of the pore (black trace) and acid-treated (blue trace) Pd⁰@*m*-SiO₂ nanoparticles. b) Pore size distribution of the two samples as determined by BJH desorption.

3.2.3.2 Pore-Narrowing of the Silica Channels of Pd⁰@*m*-SiO₂ Nanoparticles

Unlike the pore expansion of the silica channels, the pore diameter of the nanoparticles could not be easily narrowed through addition of reagents. Efforts to tune the pore diameter during the synthesis, including increasing the amount of CTAB used, were unsuccessful as the average pore diameter remained at 3 nm in all experiments. Variations in temperature appear successful in reducing the pore diameter to less than 2 nm. However, this result was not reproducible as temperature fluctuations of the oil bath greatly affected the reproducibility. Hence, another method was needed in order to reduce the pore diameter of the nanoparticles. The application of these pore-narrowed Pd⁰@*m*-SiO₂ nanoparticles will be discussed in detail in Chapter 4.

Jambhrunkar *et al.* reported a method to narrow the pore diameter of silica channels using post-synthesis modifications in a controlled manner.¹⁵⁵ In their method, mesoporous silica such as

SBA-15 and MCM-41 was subjected to a vacuum-assisted vapor deposition step, where silica precursors such as tetramethoxy orthosilicate (TMOS) and TEOS were introduced as vapor to the nanoparticles. The silanol groups on the pore surface of the silica nanoparticles react with the vapor, resulting in TMOS anchored to the pore surface (Scheme 3-2). Calcination of the nanoparticles at 550 °C in air for 5 h results in removal of the remaining methoxy groups to regenerate surface silanol groups. Repeating this process allows controlled adjustments of the pore diameter, hence the pore diameter is systematically reduced.



Scheme 3-2. Pore diameter narrowing by vapor diffusion of TMOS (tetramethyl orthosilicate, Si(OMe)_4) into the pores of mesoporous silica nanoparticles, followed by calcination of the particles to give the surface silanol group.

Scheme reproduced from reference.¹⁵⁵

The same methodology was applied to narrow the silica pores of $\text{Pd}^0@m\text{-SiO}_2$ nanoparticles. Following the protocol from Jambhrunkar *et al.*, acid-treated $\text{Pd}^0@m\text{-SiO}_2$ nanoparticles were subjected to vacuum-assisted vapor deposition of TMOS under static vacuum, while heating at 60 °C for 24 h in an oven, then calcined at 500 °C for 5 h in air. Although static vacuum was used in place of the dynamic vacuum system used in the literature, the compromise appears to be sufficient as long as the static vacuum was maintained during the heating process.

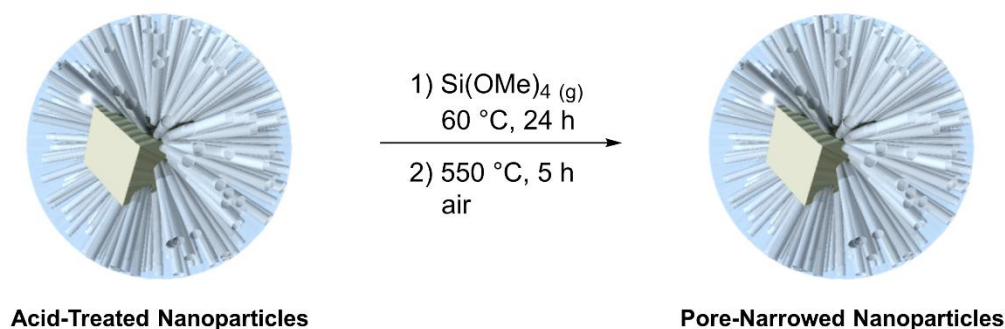


Figure 3-25. Schematic drawing showing the pore-narrowing procedure starting with $\text{Pd}^0@m\text{-SiO}_2$ core-shell nanoparticles. Pd and PdO nanoparticles are represented by grey cube, and the silica shell by the light blue shaded sphere.

As before, the calcination procedure completely oxidizes the Pd^0 core to PdO and resulted in $\text{PdO}@m\text{-SiO}_2$ nanoparticles with narrower pores, and as confirmed by PXRD (Figure 3-26). To reduce the PdO back to Pd^0 , the nanoparticles were suspended in ethanol and stirred with sodium borohydride (NaBH_4) for 1 h, after the pore-narrowing process (Figure 3-27). Within 10 seconds of adding NaBH_4 , the brown nanoparticles immediately turn black, suggesting reduction of PdO to Pd^0 . As shown in Figure 3-27, the core-shell morphology of the nanoparticles remain intact before and after reduction. No Pd particles are found on the outside of the core-shell nanoparticles. The observation was confirmed by PXRD, where the peaks due to PdO completely disappear, and peaks for Pd^0 appear (Figure 3-28). It is noteworthy that the Pd^0 signal appears rather weak and broad, likely due to formation of small nanoparticles of Pd^0 , suggesting the possibility of a cluster of small Pd^0 nanoparticles in the particle core. This result also indirectly confirms that even after the deposition of silica, the Pd center remains accessible through the silica channels.

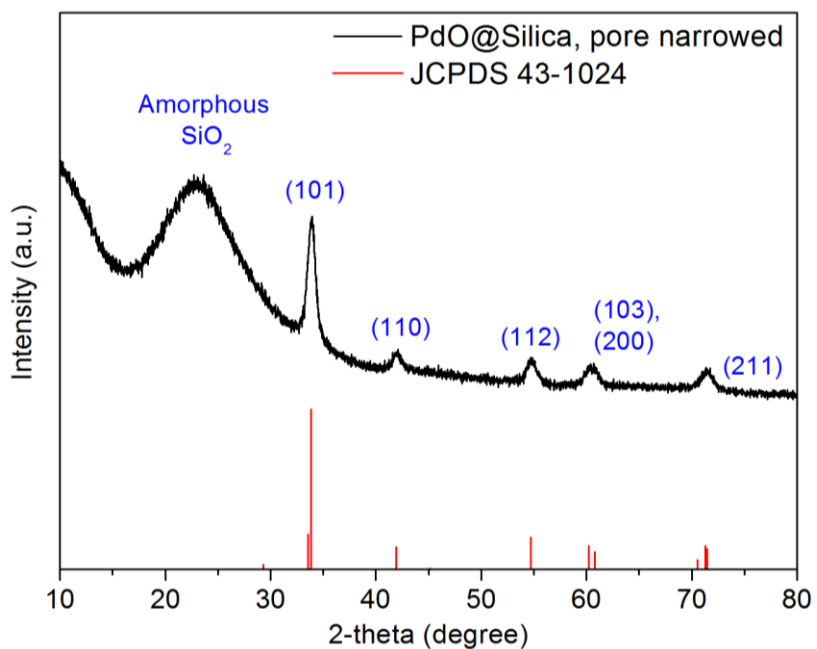


Figure 3-26. PXRD patterns of the pore-narrowed PdO@*m*-SiO₂ core-shell nanoparticles. The peaks are indexed to the known diffraction pattern of tetragonal PdO.

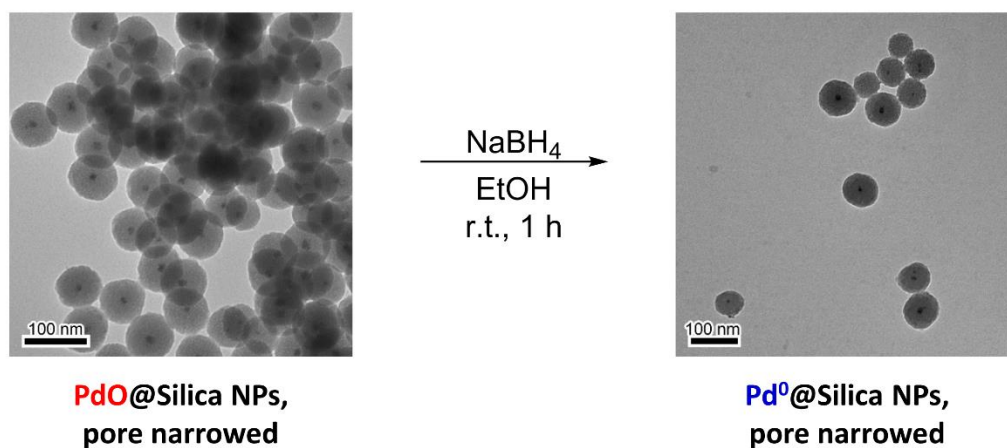


Figure 3-27. TEM images showing the reduction of PdO to Pd⁰ after pore-narrowing of the Pd⁰@*m*-SiO₂ core-shell nanoparticles.

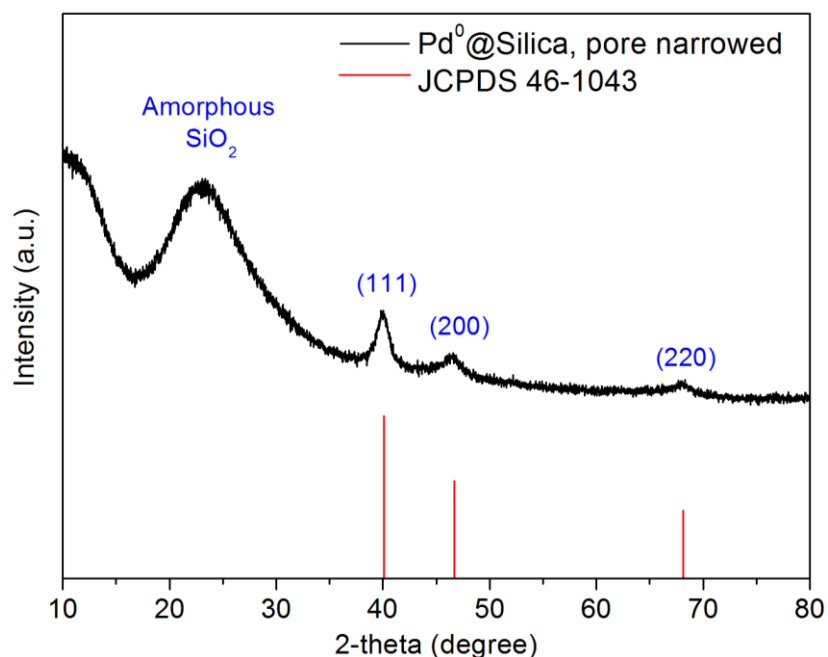


Figure 3-28. PXRD patterns of the pore-narrowed Pd⁰@*m*-SiO₂ core-shell nanoparticles. The peaks are indexed to the known diffraction pattern of fcc Pd.

Nitrogen adsorption-desorption measurements of these calcined nanoparticles, after 1 cycle of condensation, shows a similar curve to the core-shell nanoparticles, except with a lower BET surface area of 626 m² g⁻¹ and an average pore diameter of 2.61 nm (Figure 3-29). As anticipated, performing a second cycle of vapor condensation further reduces the pore diameter to less than 2 nm. TEM images of the nanoparticles revealed that the core-shell morphology of the nanoparticles remains after 2 cycles of the vapor deposition process, with mesopores not visible. In all cases, the silica channels are not blocked completely as the PdO core was successfully reduced to Pd⁰.

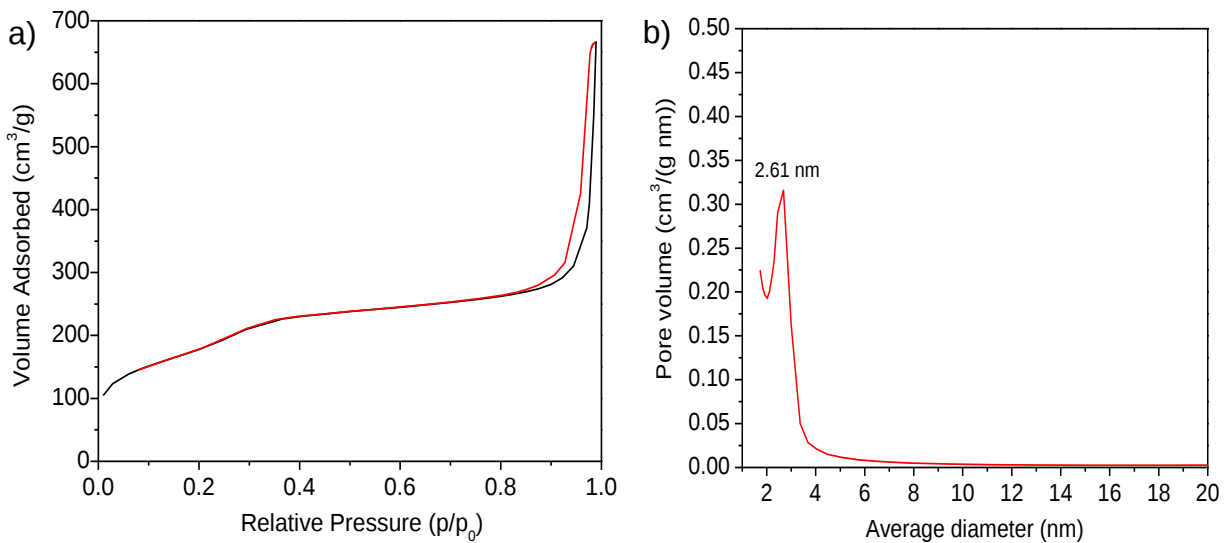


Figure 3-29. a) Nitrogen adsorption-desorption isotherms of the pore-narrowed PdO@m-SiO₂ nanoparticles after 1 cycle of vapor deposition process. b) Pore size distribution of the same sample as determined by BJH desorption.

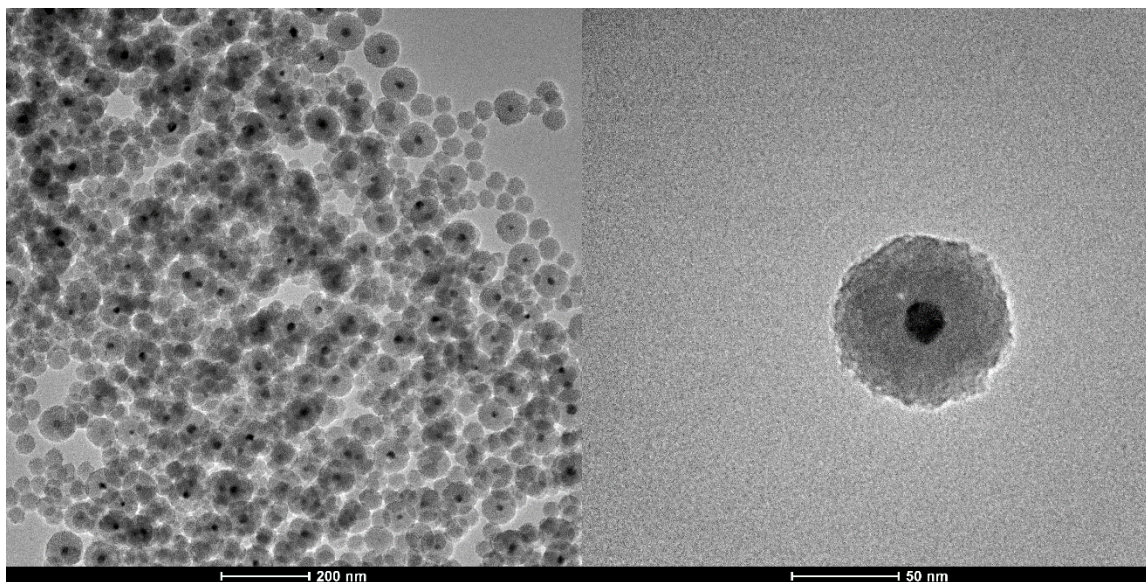


Figure 3-30. TEM image of the pore-narrowed Pd⁰@m-SiO₂ nanoparticles after 2 cycles of vapor deposition process and calcination. The presence of excess silica was due to the use of more TEOS in the formation of silica prior to the vapor deposition step.

3.3 Conclusions

In summary, spherical Pd⁰@*m*-SiO₂ core-shell nanoparticles were prepared using a simple, scalable one-pot procedure. Compared to conventional techniques, the nanoparticles are prepared more rapidly, on a larger scale and under more environmentally-friendly reaction conditions.

The morphology of the nanoparticles was confirmed using both TEM and SEM, showing that the cube-shaped Pd nanoparticles are found in the center of the nanoparticles. TGA curves of the as-synthesized nanoparticles showed that removal of organics, notably CTAB, can be achieved by heating the samples to temperatures above 350 °C under either air or nitrogen flow. Calcination at 400 °C for 4 h in air resulted in calcined PdO@*m*-SiO₂ nanoparticles as a consequence of the oxidation of Pd⁰ to PdO at elevated temperatures. Changes in the Pd oxidation states was confirmed using powder XRD. Changing the gas to nitrogen prevented the oxidation of Pd⁰ during calcination, resulting in calcined Pd⁰@*m*-SiO₂ nanoparticles. However, trace amounts of carbon were found on the sample by elemental analysis. In order to maintain the Pd⁰ core, an acid treatment was performed on the nanoparticles. Stirring the nanoparticles with a solution of dilute HCl in ethanol was sufficient in removing CTAB at room temperature. In performing the acid-treatment, the surface silanol groups on the nanoparticles were preserved as indicated by FT-IR, maintaining the hydrophilicity of the nanoparticles. With all methods used to remove CTAB, the morphology, surface area, and pore diameter of the core-shell nanoparticles remained intact.

Furthermore, increasing the preparation temperature of the Pd⁰-CTAB nanoparticles from 55 to 75 °C was found to result in a decrease in the diameter of the Pd⁰-CTAB nanoparticles. Further increasing the temperature to 100 °C did not result in a reduction in the size of the particles. As well, the amount of TEOS used in the reaction greatly affects the quality of the nanoparticles produced. With excess TEOS, more core-less silica nanoparticles were observed in the TEM

images, while un-encapsulated Pd nanoparticles were found when less TEOS was used.

The pore diameter of the nanoparticles can be expanded or narrowed using two different processes. To expand the pore diameter of the silica channels to 9 nm, DMHA was introduced to the reaction mixture prior to the condensation of silica around the Pd⁰-CTAB nanoparticles. However, expanding the pore diameter appears to destroy the morphology of the nanoparticles, as observed under TEM. Narrowing the pore diameter can be achieved by post-synthesis modification, where vacuum-assisted vapor deposition of TMOS precisely added layers of silica using the surface silanol groups, then calcination regenerates the surface silanols while oxidizing the Pd⁰ core to PdO. Regeneration of the Pd⁰ core was accomplished by addition of NaBH₄ to a suspension of the nanoparticles in ethanol, and the changes in the oxidation states of Pd were confirmed using PXRD. TEM confirms that the overall core-shell morphology of the particles was not affected using this procedure.

3.4 Experimental

3.4.1 General.

Palladium (II) nitrate hydrate (99.9% Pd) was purchased from Strem Chemicals. Cetyltrimethylammonium bromide (CTAB), tetraethyl orthosilicate (TEOS), and *N,N*-dimethylhexadecylamine (DMHA) were purchased from Sigma-Aldrich. Sodium ascorbate was purchased from Acros Organics. Ammonium hydroxide (28 wt. %) was purchased from Fisher Scientific. All chemicals were used as received.

FT-IR spectra were recorded on powdered solid samples on a Nicolet 4700 spectrometer (Thermo Scientific). Thermogravimetric analysis (TGA) was performed on a Pyris 6 analyzer. Powder X-ray diffraction (PXRD) data were recorded on a 60 Bruker D8 Advance X-ray

diffractometer in the Bragg-Brentano configuration, using copper K α radiation at 40 kV, 40 mA. Gas adsorption studies were performed using a Micromeritics ASAP 2000 system. X-ray photoelectron spectroscopy (XPS) analyses were carried out on a Leybold Max200 spectrometer using an aluminum K α X-ray source (Al K α = 1486.6 eV) and operating at a base pressure of 1×10^{-9} Torr. Initial survey scans were acquired with a pass energy of 192 eV, while higher resolution scans were acquired with a pass energy of 48 eV. Spectra were referenced to the C 1s peak at 285.0 eV. Samples were prepared for transmission electron microscopy (TEM) by drop-casting $\sim 3 \mu\text{L}$ of the dilute suspension in ethanol onto a carbon-coated 400-mesh copper TEM grid and drying in air under ambient conditions. Microscopy was carried out on a Hitachi H-7600 transmission electron microscope. An accelerating voltage of 100.0 kV was used. Samples for scanning electron microscopy (SEM) were prepared by drop-casting a suspension of the nanoparticles in ethanol onto an aluminum stub. Microscopy was carried out on a Hitachi S-4700 scanning electron microscope equipped with a cold field-emission electron gun and pinhole objective lens. An accelerating voltage of 5.0 kV was chosen in order to provide a balance between image resolution, charging effects, and surface penetration. Elemental analyses were performed by Derek Smith from the UBC mass spectrometry/microanalysis lab on a Carlo Erba Elemental Analyzer EA 1108.

3.4.2 Preparation of As-synthesized Pd⁰@m-SiO₂ Core-Shell Nanoparticles with Core Diameter of 15 nm.

The preparation of Pd⁰-CTAB nanoparticles was adapted from Shen *et al.*²² The procedure for adding the silica coating was modified from Hyeon's method.¹³⁸ A single-neck 500 mL round-bottom flask was charged with cetyltrimethylammonium bromide (CTAB, 1.81 g, 4.97 mmol), sodium ascorbate (0.10 g, 0.51 mmol), and distilled water (150 mL). The cloudy suspension was

placed in a preheated 75 °C oil bath until a clear solution was obtained. A golden-yellow solution of $\text{Pd}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$ (0.11 g, 0.47 mmol) in distilled water (50 mL) was then added to the reaction mixture quickly to initiate formation of Pd^0 -CTAB nanoparticles.

After 30 min, distilled water (100 mL) and NH_4OH (28 wt. %, 0.4 mL) were added to adjust the pH to approximately 10 while temperature was maintained at 75 °C. The solution was vigorously stirred for another 15 min prior to dropwise addition of a mixture of TEOS (4.8 mL, mol Pd : TEOS = 1 : 6) and ethyl acetate (4.8 mL). The black suspension was heated to 75 °C for 3 h. Ethanol (100 mL) was added to precipitate the core-shell nanoparticles, which were then isolated *via* centrifugation, washed with ethanol, and dried in *vacuo* overnight to result in a dark grey powder.

3.4.3 Preparation of As-synthesized $\text{Pd}^0@m\text{-SiO}_2$ Core-Shell Nanoparticles with Core Diameter of 45 nm.

The procedure for the preparation of $\text{Pd}^0@m\text{-SiO}_2$ nanoparticles with Pd core of 45 nm was analogous to that of the 15 nm Pd core (Section 3.4.2), except the formation of the Pd^0 -CTAB nanoparticles was conducted at 55 °C. After stirring for 30 min, the temperature was increased to 75 °C for the formation of the silica shell. Similar workup procedure was performed to result in a black powder.

3.4.4 Procedure for Calcination of $\text{Pd}^0@m\text{-SiO}_2$ Nanoparticles in Air or Nitrogen.

Calcination of the nanoparticles was done using a tube furnace. Calcination was performed at 400 °C under N_2 flow for 4 h, at a heating rate of 5.0 °C min^{-1} . The flow was measured using an

oil bubbler at ~1 bubble per second. After cooling, a brown powder was obtained if calcined in air, or a black powder if the calcination was performed under nitrogen.

3.4.5 Removal of CTAB from Pd⁰@*m*-SiO₂ Nanoparticles by Acid Treatment.

As-synthesized Pd⁰@*m*-SiO₂ nanoparticles were used as a slurry, without drying under vacuum. The black sludge was transferred to a 500 mL Erlenmeyer flask, after which ethanol (198 mL) and concentrated HCl (2 mL) were added. The black suspension was stirred at room temperature for 1 h, during which the nanoparticles become partially suspended in ethanol and formed a brown-black suspension. The nanoparticles were then isolated by centrifugation, and washed numerous times with ethanol until neutral pH is reached. The resulting black powder, designated as acid-treated Pd⁰@*m*-SiO₂ nanoparticles, was dried in *vacuo* overnight.

3.4.6 Preparation of Mesoporous Silica Nanoparticles in the Absence of Pd.

CTAB (0.91 g, 2.5 mmol), NH₄OH (28 wt. %, 200 µL), and 100 mL H₂O was added to a single-neck, 250 mL round-bottom flask. The mixture was heated to 75 °C until the temperature stabilized. A mixture of ethyl acetate (2.4 mL) and TEOS (300 µL) was then added dropwise while the reaction mixture was vigorously stirred. The reaction was allowed to proceed at 75 °C for 3 h, after which time ethanol (100 mL) was added to quench the reaction and precipitate the silica. The resulting clear gel was separated by centrifugation, washed with ethanol, and dried in *vacuo* overnight. Calcination was performed at 400 °C under N₂ for 4 h, then 400 °C in air for 2 h.

3.4.7 Pore-Expansion of the Silica Shell of Pd⁰@*m*-SiO₂ Nanoparticles.

The procedure for the pore-expansion of the silica shell was modified from Sayari *et al.*¹⁵⁴ Pd⁰-CTAB nanoparticles were prepared as in the first part of Section 3.4.2. Distilled water (100

mL) and NH_4OH (28 wt. %, 0.4 mL) were added to adjust the pH to approximately 10 while temperature was maintained at 75 °C, then DMHA (6.0 mL, 4.8 mmol) was added for pore-expansion. The solution was vigorously stirred for another 15 min prior to dropwise addition of a mixture of TEOS (4.8 mL, mol Pd : TEOS = 1 : 6) and ethyl acetate (4.8 mL). The black suspension was heated to 75 °C for 3 d. Ethanol (100 mL) was added to precipitate the core-shell nanoparticles, which were then isolated *via* centrifugation, washed with ethanol, and dried in *vacuo* overnight to result in a grey powder.

3.4.8 Pore-Narrowing of the Silica Shell of $\text{Pd}^0@m\text{-SiO}_2$ Nanoparticles.

The procedure for the pore-expansion of the silica shell was modified from Jambhrunkar *et al.*¹⁵⁵ Acid-treated $\text{Pd}^0@m\text{-SiO}_2$ nanoparticles (0.4071 g) was added to a custom-made glass crucible with porous sintered glass disc. The crucible was then attached to a 10 mL round-bottom flask containing TMOS (3.0 mL, 2.8 mmol). Kimwipes[®] was secured by elastic band to cover the top of the crucible. The setup was placed in a large Schlenk tube and was placed under vacuum for ~10 s, prior to heating in an oven at 60 °C for 24 h. After the setup was cooled, the resulting black powder was calcined at 550 °C for 4 h under an air flow to obtain the pore-narrowed $\text{PdO}@m\text{-SiO}_2$ nanoparticles.

3.4.9 Reduction of PdO to Pd^0 of Pore-Narrowed $\text{PdO}@m\text{-SiO}_2$ Nanoparticles.

Acid-treated $\text{Pd}^0@m\text{-SiO}_2$ nanoparticles (0.201 g) was suspended in ethanol (10 mL) in a 50 mL centrifuge tube. While vigorously stirring, a solution of NaBH_4 in warm ethanol (1.0 M, 5 mL) was added to the suspension, the brown reaction mixture immediately turned black. The reaction mixture was stirred for 30 min at room temperature, after which the nanoparticles were

washed numerous times with ethanol (20 mL), isolated by centrifugation, and dried in *vacuo* to result in a black powder.

Chapter 4: Applications of Pd⁰@*m*-SiO₂ Core-Shell Nanoparticles

4.1 Introduction

Hybrid materials containing both Pd and silica are common in nanoscience, especially in the field of catalysis because Pd is a well-established catalyst for a number of industrially relevant processes. As discussed in Chapter 3, examples of important transformations include hydrogenation,^{131-133, 135} dehydrogenation,¹³⁴ CO oxidation,⁶¹ NO_x reduction reactions,^{66, 67} and C–C coupling reactions.¹⁵⁶ Often the active catalyst is dispersed as small particles on a suitable oxide support such as silica in these processes.¹³¹ Most literature reports focus on preparing more efficient, environmentally friendly, or stable Pd catalysts, but rarely on other possible applications of Pd-containing nanoparticles.

In Chapter 3, the preparation of Pd⁰@*m*-SiO₂ core-shell nanoparticles was described. These nanoparticles are composed of a Pd⁰ core and silica shell, and are unique as no core-shell nanoparticles of this type have been prepared on a large scale previously. Due to their unique morphology, these modified nanoparticles may exhibit unique applications and catalytic activities that have not been explored previously. In this chapter, the utility of these novel core-shell nanoparticles as templates and catalysts will be demonstrated.

4.2 Templating of Other Core-Shell Structures Using Pd⁰@*m*-SiO₂ Nanoparticles

One method to utilize the unique core-shell morphology of these materials is to use the mesoporous silica as a template for other materials. Mesoporous silica has been widely used as a hard template to control the morphology of polymers or metal oxides, especially for materials with morphology that cannot be easily controlled in other ways.^{72, 73} Typically, metal precursors are

first dissolved in a suitable solvent and added to mesoporous silica, where the liquid solution is taken up into the pores by capillary action. After pore-filling, the particles are treated to generate the desired material within the pores. Treatment of the composite material with aqueous base results in removal of the silica template to yield the desired material. Since the new material is a replica of the pore structure of the mesoporous silica, the resulting material is also porous with higher surface area than bulk material.

This methodology may be applied to the $\text{Pd}^0@m\text{-SiO}_2$ nanoparticles developed in this study. Filling the pores of the $\text{Pd}^0@m\text{-SiO}_2$ nanoparticles and removing the silica template may result in a Pd core sheathed by a porous shell of the new material. Effectively, this is a transformation of one core-shell nanoparticle to another. Interestingly, there are no examples of such a transformation in the literature. This approach may open up a new avenue for the preparation of alternative core-shell nanoparticles.

4.2.1 Preparation of $\text{PdO}@m\text{-CeO}_2$ Nanoparticles by Templating

Ceria (CeO_2) was selected as a suitable metal oxide to replicate. Preparation of mesoporous CeO_2 is challenging as the typical sol-gel route requires handling air-sensitive compounds¹⁵⁷ and other methods often generate materials with no morphology control.¹⁵⁸⁻¹⁶⁰ Materials consisting of combinations of Pd and CeO_2 are known to be effective catalysts for the oxidation of methane (CH_4) to carbon dioxide (CO_2), as CeO_2 has an accessible $\text{Ce}^{3+}/\text{Ce}^{4+}$ redox cycle, giving rise to high oxygen storage capacity and high oxygen mobility, both of which can stabilize Pd or Pt on ceria and enhance catalytic activity.^{157, 161-163} As well, porous, high surface area CeO_2 may further enhance the catalytic activity of the nanoparticles.^{94, 164} Catalysts for methane oxidation are typically composed of Pd supported on alumina (Al_2O_3),^{93, 94} zirconia (ZrO_2),⁹⁵ or ceria (CeO_2).^{96,}

⁹⁷ Currently, very few catalysts can undergo methane oxidation at temperatures below 500 °C, the temperature suitable for oxidizing methane in automobile exhaust.⁹⁴ Using Pd⁰@*m*-SiO₂ nanoparticles as a template, it should be possible to prepare a new material consisting of a Pd core and mesoporous ceria shell, suitable for catalytically oxidizing methane at low temperature.

The procedure for the pore-filling of the core-shell nanoparticles was adapted from Yen *et al*, and is outlined in Figure 4-1.⁷³ This procedure was chosen as it allows a complete replica of the nanostructure to be obtained in one step, which cannot be achieved by other reported methods. Acid-treated Pd⁰@*m*-SiO₂ nanoparticles and cerium nitrate hexahydrate (Ce(NO₃)₃·6H₂O) were ground in the presence of hexanes to obtain a dark solid, which was then heated to reflux for 20 h. Heating the solution results in melted Ce(NO₃)₃, which enters the pores due to the polarity differences between Ce(NO₃)₃ and hexanes, and because the silica pores are relatively hydrophilic due to the presence of surface silanol groups. After heating to reflux, the Ce(NO₃)₃ was converted to CeO₂ by calcination at 600 °C for 4 h in air to result in a PdO@CeO₂/SiO₂ composite material, where the channels contained CeO₂. After calcination, the nanoparticles were treated with 2 M NaOH_(aq) to remove the silica template, resulting in the PdO@*m*-CeO₂ nanoparticles. For comparison, PdO@*m*-CeO₂ was also prepared starting with calcined Pd⁰@*m*-SiO₂ nanoparticles (denoted as PdO@*m*-SiO₂ nanoparticles), which have a lower amount of surface silanol groups as determined in Chapter 3.

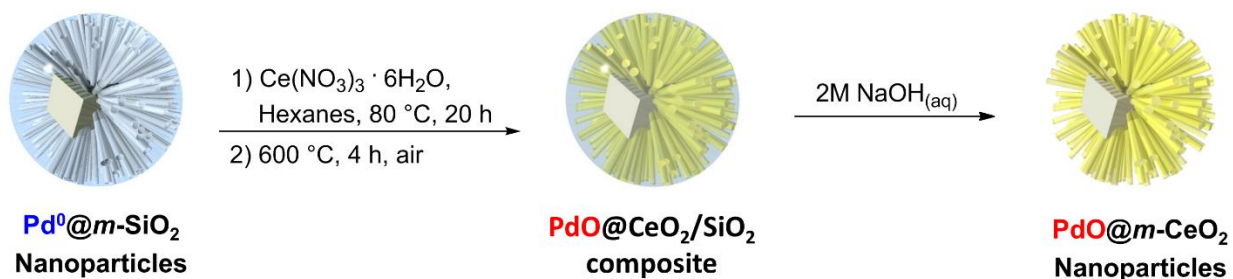


Figure 4-1. Schematic drawing showing the procedure for the preparation of $\text{PdO}@m\text{-CeO}_2$ nanoparticles using the pore-filling procedure, starting from $\text{Pd}^0@m\text{-SiO}_2$ core-shell nanoparticles. Pd^0 nanoparticles are represented by grey cube, CeO_2 by yellow-shaded rods, and silica shell by the light blue shaded sphere.

As shown in photographs of the $\text{PdO}@m\text{-CeO}_2$ nanoparticles, the color of the material obtained depends on the specific core-shell nanoparticles used as starting material (Figure 4-2). When the $\text{PdO}@m\text{-CeO}_2$ nanoparticles were prepared from the core-shell nanoparticles with a Pd^0 core, a yellow-orange colored solid was obtained. Starting with $\text{PdO}@m\text{-SiO}_2$ nanoparticles, however, resulted in a brown colored powder. As the procedure used to prepare CeO_2 is identical, the difference in the Pd core must play a role in the color variation.

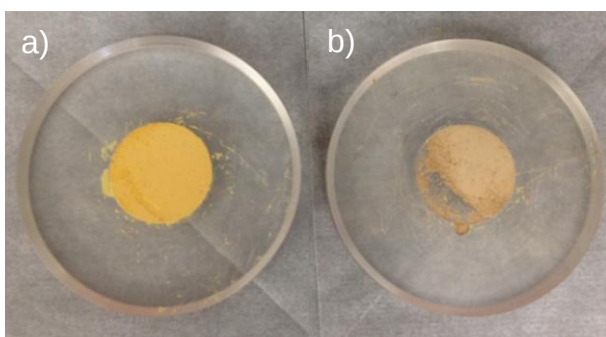


Figure 4-2. Photographs of a) $\text{PdO}@m\text{-CeO}_2$ prepared from acid-treated $\text{Pd}^0@m\text{-SiO}_2$ nanoparticles and b) $\text{PdO}@m\text{-CeO}_2$ prepared from $\text{PdO}@m\text{-SiO}_2$ nanoparticles.

TEM images revealed morphology differences between the materials prepared using the two different routes. The $\text{PdO}@m\text{-CeO}_2$ nanoparticles prepared from the $\text{Pd}^0@m\text{-SiO}_2$ nanoparticles appear porous, with spheres aggregated, possibly due to the excess $\text{Ce}(\text{NO}_3)_3$ used in the preparation (Figure 4-3). Although many of the nanoparticles appeared aggregated, some individual spherical particles were also observed using TEM (Figure 4-3, right). On the other hand, starting with $\text{PdO}@m\text{-SiO}_2$ nanoparticles resulted in porous aggregates of varying size and geometry. In this case, less spherical nanoparticles were found in the TEM images. The difference in morphology can be attributed to differences in the polarity of the silica surface, as the $\text{PdO}@m\text{-SiO}_2$ nanoparticles may be expected to have lower amounts of surface silanol groups. Increased hydrophobicity may reduce the amount of $\text{Ce}(\text{NO}_3)_3$ remaining in the pores, hence the resulting morphologies vary more greatly due to incomplete filling.

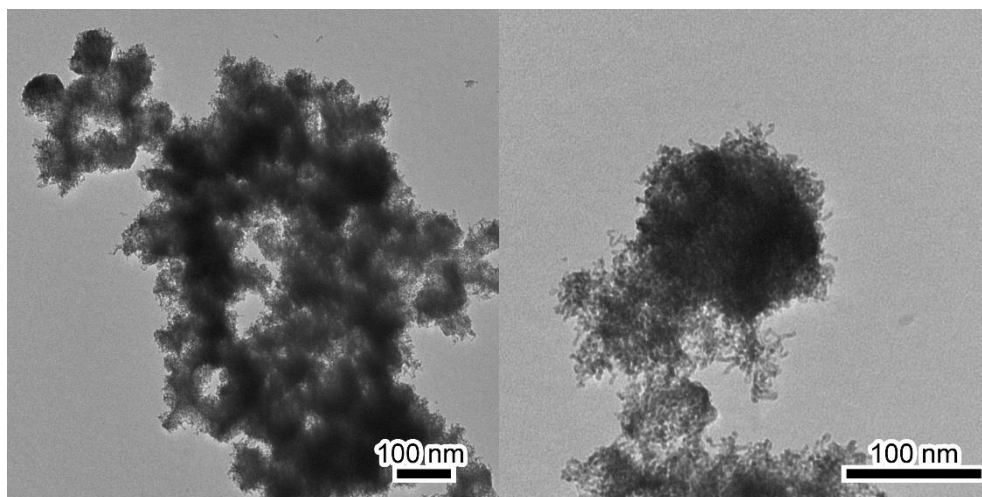


Figure 4-3. TEM image of $\text{PdO}@m\text{-CeO}_2$ nanoparticles prepared from $\text{Pd}^0@m\text{-SiO}_2$ nanoparticles.

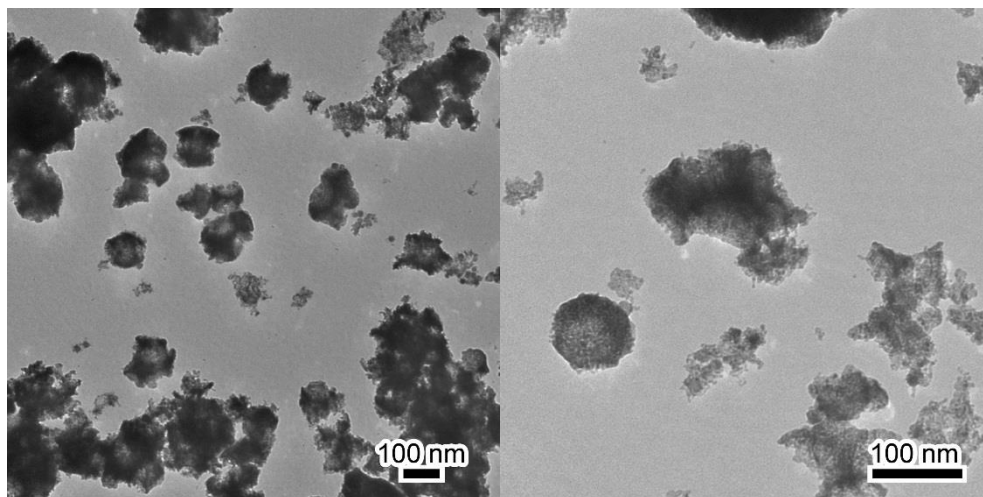


Figure 4-4. TEM image of PdO@m-CeO₂ nanoparticles prepared from PdO@m-SiO₂ nanoparticles.

The porosities of the nanoparticles were measured by nitrogen adsorption/desorption experiments. PdO@m-CeO₂ nanoparticles derived from Pd⁰@m-SiO₂ nanoparticles were found to have a relatively high BET surface area of 130 m² g⁻¹, with an average pore diameter of 2.4 nm (Figure 4-5). The surface areas obtained are in the range of other mesoporous CeO₂ materials prepared in the literature, where surface areas ranging from 100 - 250 m² g⁻¹ have been reported.^{165,}
¹⁶⁶ When PdO@m-CeO₂ was prepared from PdO@m-SiO₂, the surface area decreased to 88 m² g⁻¹, with an average pore diameter of 2-3 nm. This drop in surface area is consistent with the observations in the TEM images, where fewer porous structures were observed.

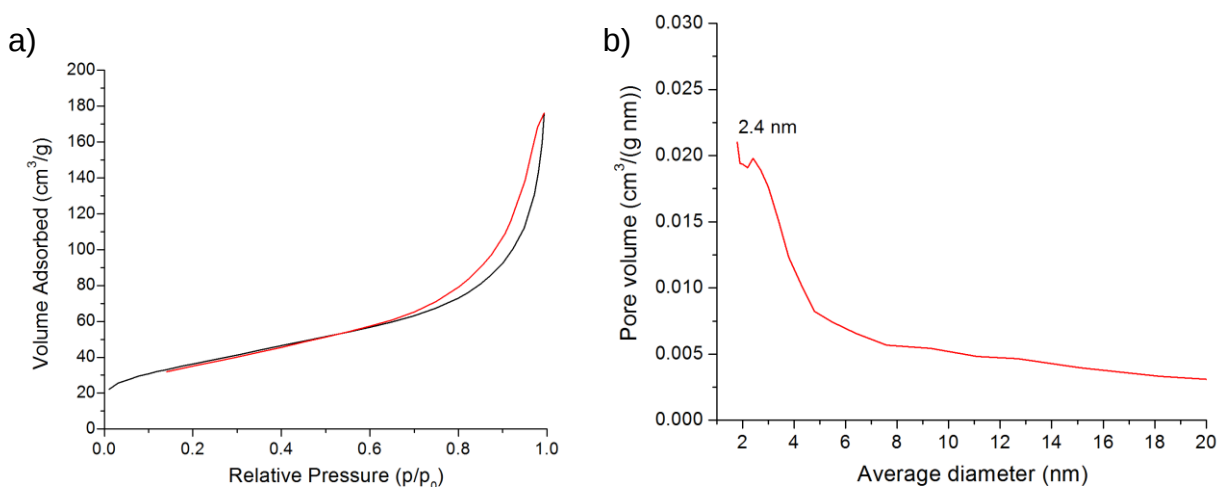


Figure 4-5. a) Nitrogen adsorption-desorption isotherms of PdO@m-CeO₂ nanoparticles prepared from Pd⁰@m-SiO₂ nanoparticles. The black and red curves show the adsorption and desorption isotherms, respectively. b) Pore size distribution of the nanoparticles as determined by BJH analysis.

The difference in the particle size and morphology does not explain the different colors exhibited by the samples, although the two PdO@m-CeO₂ samples differ in their chemical composition. Powder XRD patterns of both materials show predominantly cubic CeO₂ is present (Figure 4-6). Upon expansion of the XRD pattern, a small shoulder is observed for the sample prepared from PdO@m-SiO₂ nanoparticles, assigned to the (101) diffraction of tetragonal PdO (Figure 4-6b). Interestingly, this peak was not found in the XRD pattern of the sample prepared from the Pd⁰ core, suggesting a new compound of Pd was prepared in this case. No Pd was found in either samples since calcination was carried out under aerobic conditions.

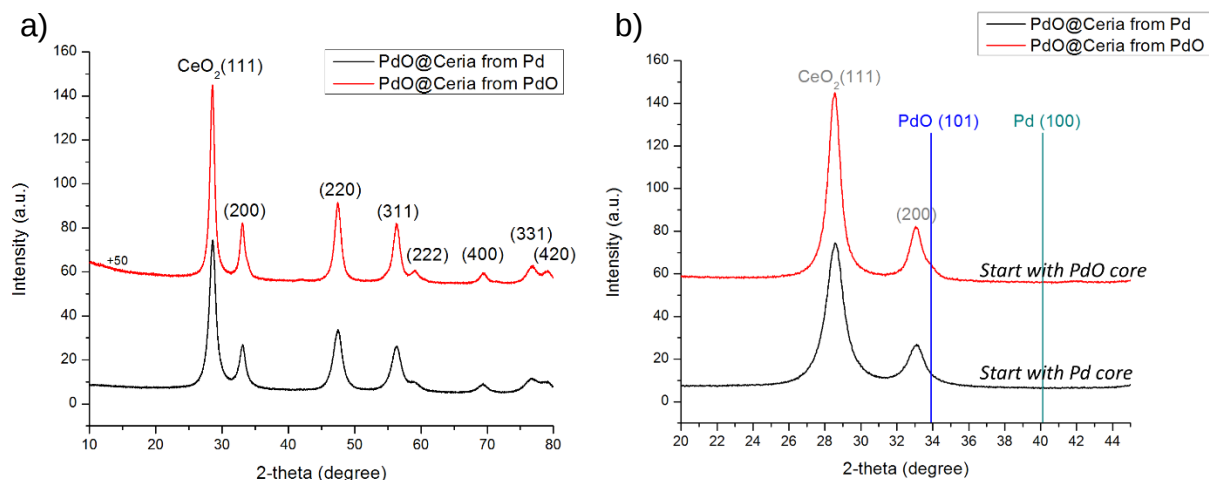


Figure 4-6. Powder XRD patterns of PdO@m-CeO₂ prepared from Pd⁰@m-SiO₂ and PdO@m-SiO₂ nanoparticles. a) Full angle plots. b) Expansion for identification of Pd-containing species.

XPS was used to analyze the different Pd compounds present in the samples. XPS spectra of both the nanoparticles show diagnostic doublets with intensities of 3:2 in the Pd 3d region, corresponding to Pd 3d_{5/2} and 3d_{3/2} (Figure 4-7). The XPS spectrum of the sample prepared using PdO@m-SiO₂ nanoparticles shows Pd peaks at lower binding energy. Fitting the XPS data suggests that PdO is predominantly present on the surface of the PdO@m-CeO₂, when starting with a PdO core. No other possible Pd species such as Pd²⁺ and Pd⁰ could be fit to the experimental data. When the CeO₂ sample was prepared from Pd⁰@m-SiO₂, peaks of higher binding energy were observed, and the experimental data was fit to species containing Pd²⁺. Detectable amounts of PdO were not present in this sample, suggesting oxidation of Pd⁰ to a different Pd²⁺-containing species. Furthermore, the presence of the Pd signals suggests that a substantial amount of the Pd core was near the surface, or possibly not completely encapsulated by the mesoporous CeO₂ shell, suggesting that the templating of CeO₂ from mesoporous silica may be imperfect.

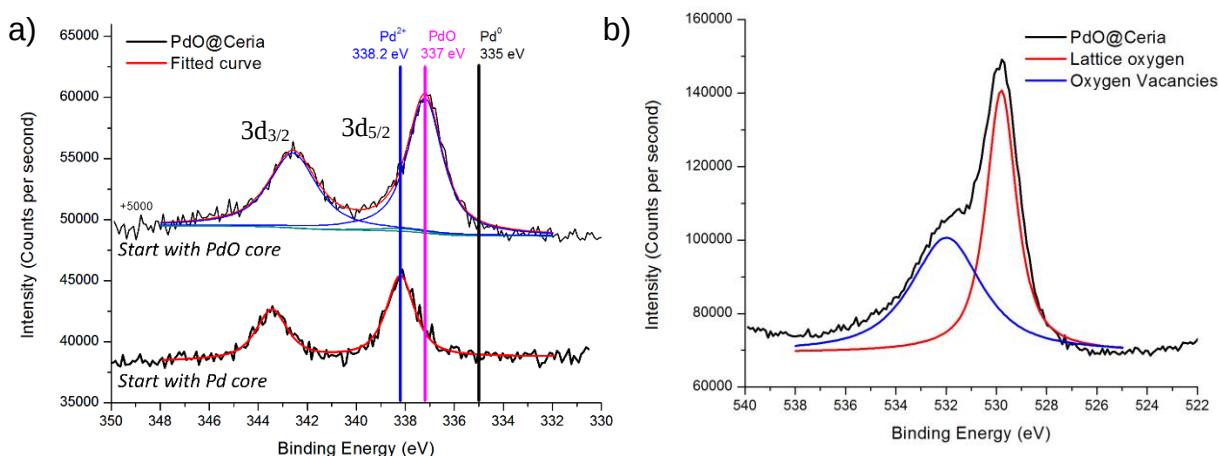


Figure 4-7. XPS of the PdO@m-CeO₂ nanoparticles: a) palladium 3d region; b) oxygen 1s region. The experimental data is shown as a solid black line, the fitted data as blue and red lines. All peaks are referenced to the carbon 1s peak at 285.0 eV.

The presence of Pd²⁺ ions in the sample is intriguing, as PdO would typically be preferably formed when Pd-containing samples are heated. One explanation for the presence of ionic Pd²⁺ is the possible formation of a solid solution with composition Ce_{1-x}Pd_xO_{2-δ}. This compound consists of Pd ions inserted in the crystal lattice of CeO₂, resulting in oxygen vacancies for charge balance (Figure 4-8). The presence of oxygen vacancies has been confirmed in XPS, where the peak corresponding to oxygen 1s was fitted to lattice oxygen and oxygen vacancies.¹⁶⁷ Interestingly, solid solutions of this type are typically prepared using a solution combustion method, typically requiring ignition of a fuel to generate enough heat for reaction to occur (~ 1500 °C).¹⁶⁸ As no fuel or temperatures above 1000 °C were used in the preparation of the PdO@m-CeO₂ nanoparticles here, the formation of Pd²⁺ ions may be due to confinement of the Pd core in the CeO₂, preventing oxidation of Pd into PdO. If Ce_{1-x}Pd_xO_{2-δ} is formed here, it may open new possibilities for a low temperature method for preparing solid solutions containing Pd and metal oxides, while

simultaneously nanoparticle morphology could be controlled. In any case, the possible formation of such solid solutions suggests that the replica method is not effective for preparing core-shell structures of metal oxides.

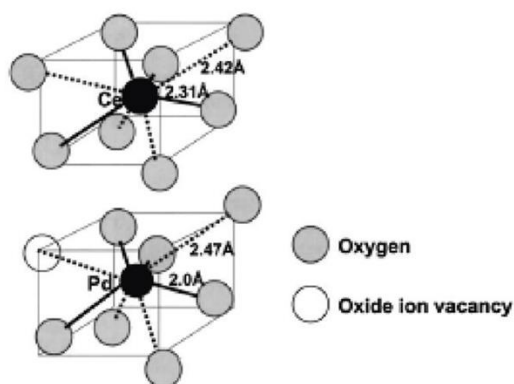


Figure 4-8. Crystal lattice showing similarities between CeO_2 and $\text{Ce}_{1-x}\text{Pd}_x\text{O}_{2-\delta}$. Reprinted from reference with permission.¹⁶⁸

4.2.2 Catalytic Activity of $\text{PdO}@m\text{-CeO}_2$ Nanoparticles

Pd nanoparticles supported on CeO_2 have been shown to be a promising catalyst for the oxidation of CH_4 to CO_2 .^{62, 63, 65} Since the $\text{PdO}@m\text{-CeO}_2$ nanoparticles prepared here are believed to contain dispersed Pd^{2+} ions in the CeO_2 crystal lattice with oxygen vacancies present, it is possible that these nanoparticles may exhibit high catalytic activities towards methane oxidation. In collaboration with Mr. Rahman Gholami from the UBC Department of Chemical Engineering, temperature programmed oxidation (TPO) measurements was used to probe the reactivity of the nanoparticles towards methane oxidation. Catalytic oxidation of methane was carried out using the custom built apparatus shown in Figure 4-9 by Mr. Gholami. The catalytic activity of the nanoparticles was measured by passing methane and oxygen over a bed of the nanoparticles. The

amount of products formed was monitored by a mass spectrometer at the column outlet. The TPO curve of the $\text{PdO}@m\text{-CeO}_2$ nanoparticles shows there is little catalytic oxidation of methane, with no conversion observed until elevated temperatures are reached (Figure 4-10). In contrast, the TPO curve of the $\text{Pd}^0@m\text{-SiO}_2$ nanoparticles showed better activities for the $\text{PdO}@m\text{-CeO}_2$ nanoparticles, with a light-off temperature ($T_{50\%}$) of 368 °C and complete combustion of CH_4 at 510 °C. $T_{50\%}$ is indicative of when 50% of the CH_4 is converted to CO_2 , and can be used to judge the effectiveness of the catalyst. However, compared to the state-of-the-art Pd catalyst, which has $T_{50\%}$ of < 300 °C and complete combustion around 400 °C, $\text{Pd}^0@m\text{-SiO}_2$ nanoparticles are not exceptional catalysts for methane oxidation.⁹⁴

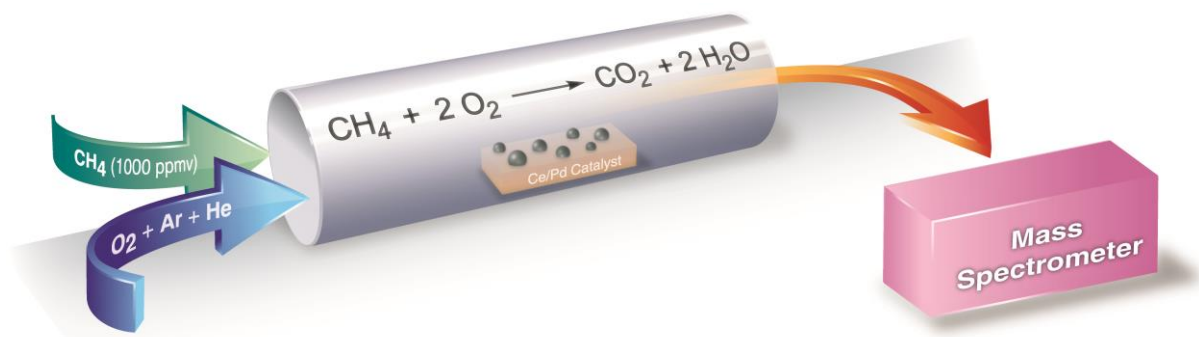


Figure 4-9. Schematic of the TPO reactor, where methane is oxidized over a bed of the catalyst to give carbon dioxide and water. The products are detected by a mass spectrometer.

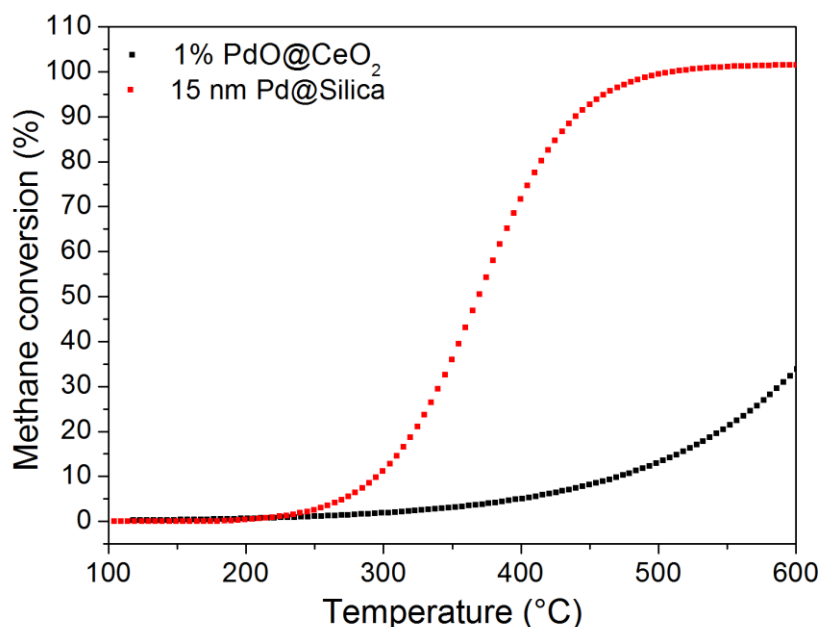


Figure 4-10. TPO of methane in the presence of Pd⁰@*m*-SiO₂ nanoparticles (red dots) and PdO@*m*-CeO₂ nanoparticles (black dots).

4.3 Size-Selective Catalysis using Pd⁰@*m*-SiO₂ Nanoparticles

In addition to templating, another interesting application of the modified nanoparticles is to utilize the unique morphology of the nanoparticles to limit access of certain substrates from undergoing reactions at the catalytic Pd⁰ core. Traditional heterogeneous Pd⁰ catalysts are prepared by anchoring Pd⁰ nanoparticles or Pd complexes to a high surface area support, where reactive Pd sites are exposed to the reaction mixture for catalytic processes. The Pd⁰@*m*-SiO₂ core-shell nanoparticles prepared in this study, however, have a flipped design, where Pd⁰ is only accessible by substrates that have passed through the silica channels. This opens up the possibility of utilizing the silica channels to selectively allow molecules to reach the reactive Pd center to undergo catalysis. The concept was first demonstrated by the Crooks group in 2001, who prepared

dendrimer-stabilized Pd⁰ nanoparticles that control access of substrates depending on the steric crowding around the catalytically active nanoparticles.¹⁶⁹ The concept was revisited by another report, where nanoparticles composed of Pd clusters surrounded by a porous silica shell prevented access by a cholesterol substrate to achieve size-selectivity of substrates.¹⁷⁰

The physical properties of the Pd⁰@*m*-SiO₂ nanoparticles were fully discussed in Chapter 3, where the silica shell was shown to be porous, consisting of mesoporous channels with an average diameter of 3 nm. Considering that most molecules are in the sub-nanometer (Angstroms) size range, these channels are too large to allow separation of most small molecules by size. One possibility is to examine hydrogenation of a larger molecule such as cholesterol. With the alkyl chain extended, cholesterol is 19 Å in length, slightly smaller than the average pore diameter of the core-shell nanoparticles (Figure 4-11). Hence, it is reasonable that cholesterol would experience more interaction with the silica walls in order to reach the Pd⁰ core, and the hydrogenation reaction would be slower. On the other hand, a smaller molecule would have less size restriction and could travel more easily through the silica channels.

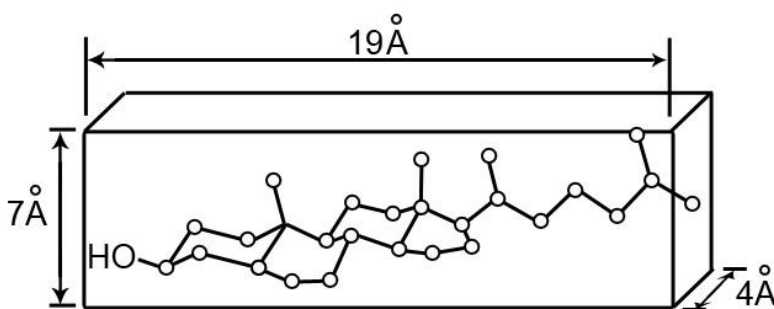
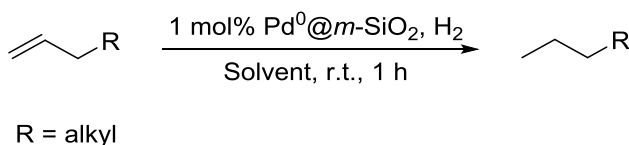


Figure 4-11. Dimensions of cholesterol. Reprinted from reference with permission.¹⁷¹

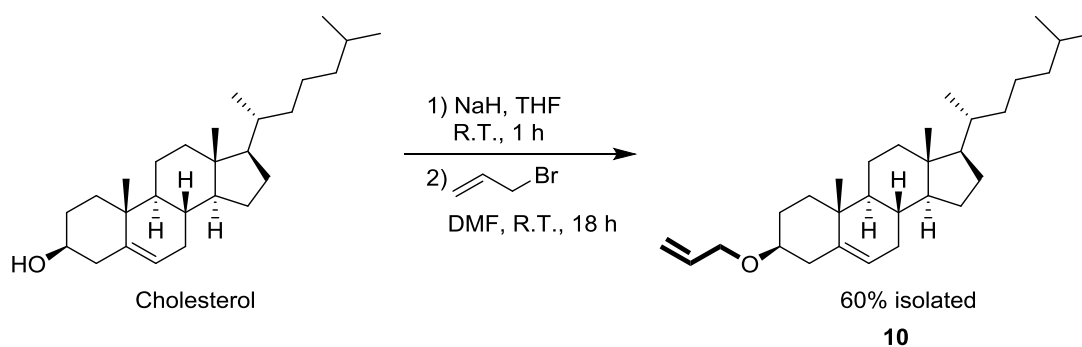
Pd⁰-catalyzed hydrogenation of alkenes was selected as a suitable test reaction (Scheme 4-1). Hydrogenation reactions involve the addition of an unsaturated substrate to a hydrogen gas-purged reaction vessel containing a suspension of the Pd-containing catalyst in a suitable solvent, often at room temperature.^{172, 173} A wide range of solvents such as EtOAc,^{174, 175} THF,¹⁷⁶ supercritical CO₂,¹⁷⁷ EtOH,¹⁷⁵ H₂O,¹⁷⁸ MeOH,^{179, 180} CH₂Cl₂,¹⁸¹ DMF-H₂O mixture,¹⁸² MeOH-H₂O mixture,¹⁶⁹ and ionic liquids¹⁸³ can be used for this catalytic transformation. With careful solvent choice, the consumption of the alkene can be monitored using ¹H NMR spectroscopy *via* integration of the alkene protons.



Scheme 4-1. General scheme of alkene hydrogenation using Pd⁰@*m*-SiO₂ nanoparticles as the catalyst.

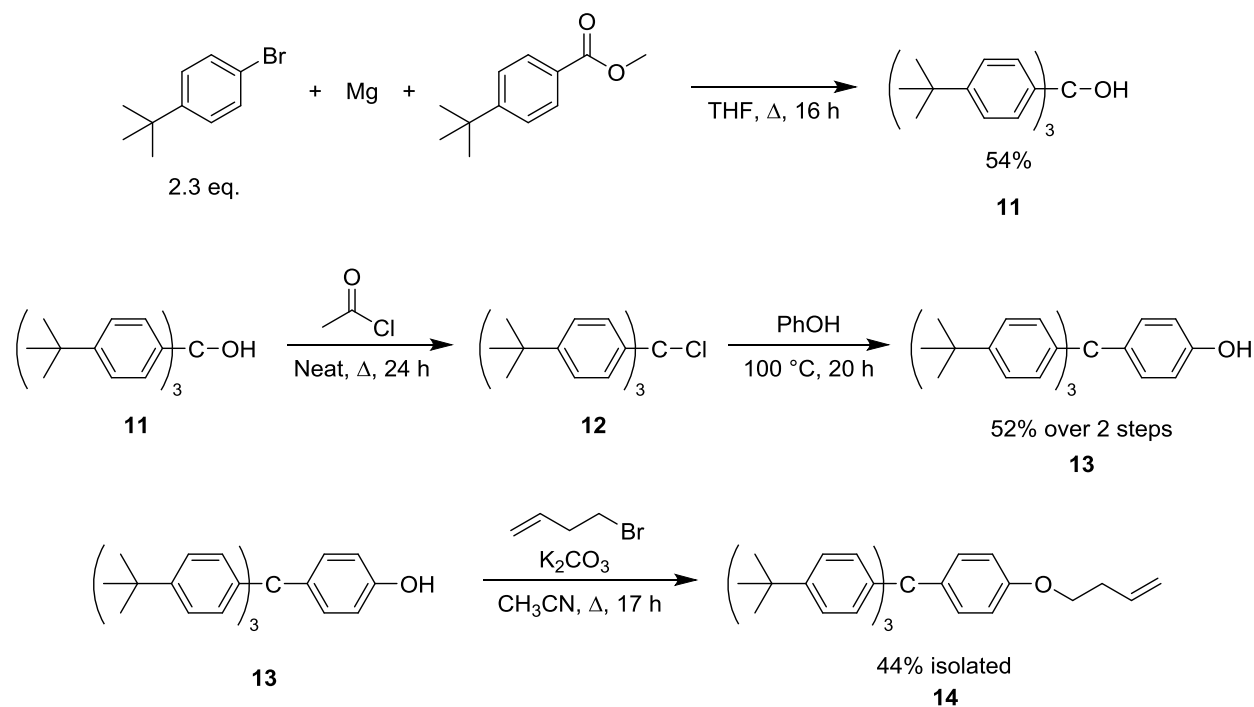
4.3.1 Synthesis of Substrates with Larger Dimensions

The internal alkene in cholesterol is relatively unreactive compared to terminal alkenes. For this reason, a terminal alkene must be installed to allow the hydrogenation reaction to readily occur. Following a procedure adapted from Jiménez-Núñez *et al.*,¹⁸⁴ an *O*-allyl derivative of cholesterol was prepared using the Williamson ether synthesis (Scheme 4-2). Deprotonation of the primary alcohol by sodium hydride (NaH) resulted in an alkoxide, which further reacted at room temperature with allyl bromide *via* an S_N2 reaction to give the *O*-allylated product **10**. Compound **10** was isolated as a white solid in 60% yield after column chromatography.



Scheme 4-2. Alkylation of cholesterol using the Williamson ether synthesis.

A second large substrate containing bulky *tert*-butyl substituted phenyl groups was also prepared using modified literature procedures (Scheme 4-3).¹⁸⁵⁻¹⁸⁷ Reaction of 4-*tert*-butylbromobenzene with magnesium resulted in the corresponding Grignard reagent, which was subsequently reacted with methyl 4-*tert*-butylbenzoate in THF heated to reflux to yield a tertiary alcohol **11**. Chlorination of the resulting tertiary alcohol with acetyl chloride and subsequent Friedel-Crafts alkylation afforded compound **12**, which was immediately reacted with phenol at 100 °C for 20 h without workup. Alkylation of the phenol by reacting **13** with 4-bromo-1-butene and K_2CO_3 resulted in the target compound **14**, which contains a terminal alkene. Compounds **10** and **14** were used as substrates in the hydrogenation reaction after purification.



Scheme 4-3. Synthesis of **14**. Procedure was adapted from literature.¹⁸⁵⁻¹⁸⁷

4.3.2 Size-Selective Hydrogenation Reactions Using Pd/C and Pd⁰@*m*-SiO₂ Nanoparticles

Using the large substrates **10** and **14** that contained terminal alkenes and smaller alkenes like 1-hexene, size-selective hydrogenation reactions were carried out using commercially available Pd/C catalyst and Pd⁰@*m*-SiO₂ nanoparticles in separate experiments for each substrate. The reactions were conducted in a closed system, with a round-bottom containing the Pd⁰@*m*-SiO₂ nanoparticles, internal standard, and a suitable solvent. The alkene was injected into the reaction mixture and the reaction was monitored by taking aliquots from the reaction mixture. In order to use ¹H NMR as the tool for monitoring the progress of the reaction, a solvent without a large

number of proton signals is ideal. Deuterated chloroform (CDCl_3) is a suitable choice, as only residual proton signals from the solvent contribute to the ^1H NMR spectra.

The progress of each reaction was monitored using ^1H NMR spectroscopy by comparing the integration of the terminal alkene protons to the internal standard. As the reaction proceeded, the peaks corresponding to the CH_2 and CH protons of the alkene decrease in intensity, and a broad peak grows between these two multiplets. This new signal is due to the product of Pd-catalyzed isomerization of the terminal alkene to an internal alkenes, indicating that the alkene functionality is accessible to the Pd^0 core.¹⁸⁸ Mesitylene (1,3,5-trimethylbenzene) was chosen as the internal standard for this study; this standard is soluble in all solvents used and the ^1H NMR signals of mesitylene at δ 2.3 and 6.8 ppm do not overlap with those of the alkenes, which are typically found

at δ 4.8 – 6.0 ppm. An example of the ^1H NMR spectra which are collected in CDCl_3 is shown in Figure 4-12. The experiment was conducted for each alkene separately unless indicated.

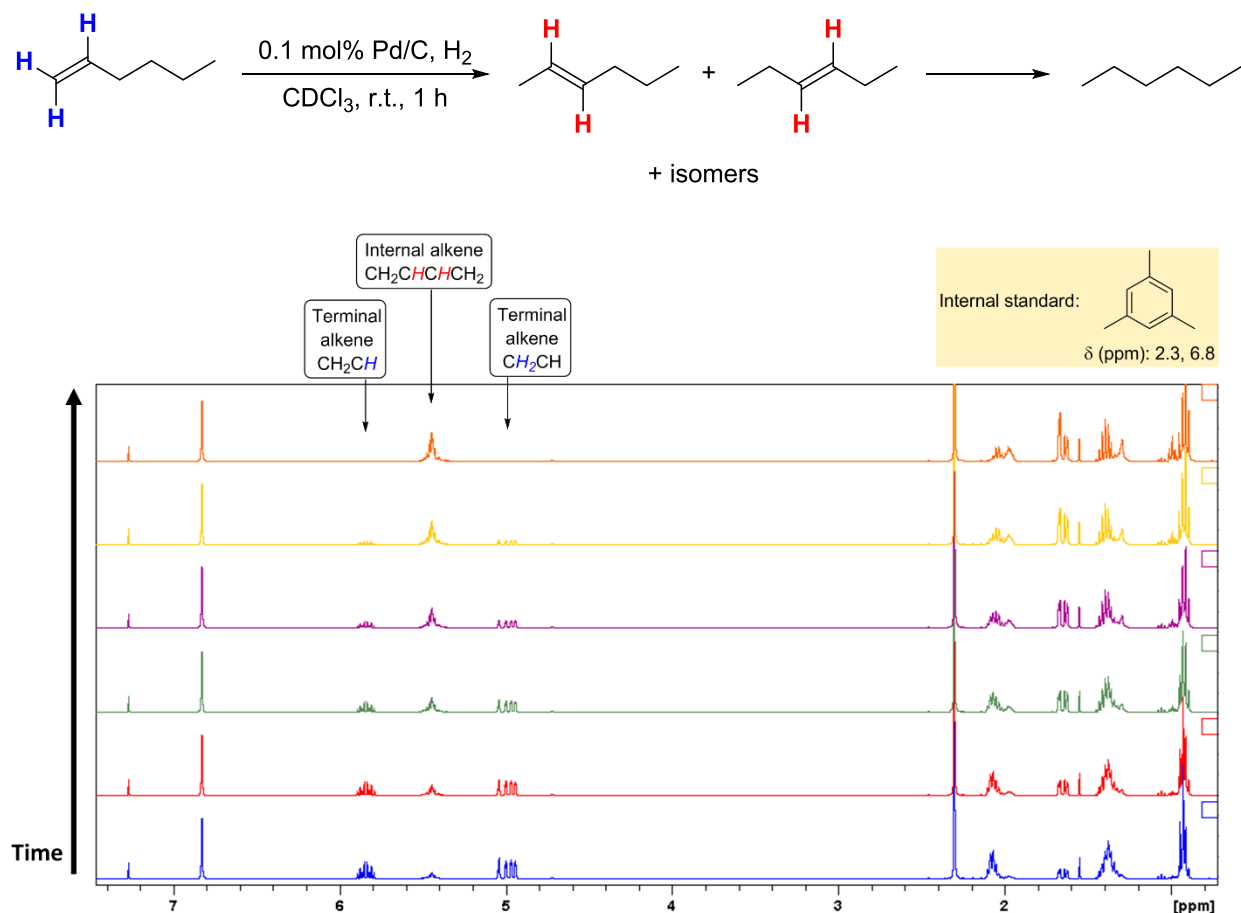


Figure 4-12. ^1H NMR spectra of the hydrogenation of 1-hexene by commercially available Pd/C in CDCl_3 .

Commercially available palladium on carbon (Pd/C) was chosen as the control for the size-selective hydrogenation reactions. The catalytically active Pd^0 centers are at the surface. The alkene signal was monitored using ^1H NMR spectroscopy as previously discussed, and the depletion of alkenes plotted against time (Figure 4-14). The smaller alkene, 1-hexene reacted quickly as expected, and was consumed completely within 30 min under these reaction conditions.

Hydrogenation of *O*-allyl cholesterol (**10**) proceeded slower but was nearly complete after 60 min. The slower reactivity of **10** in hydrogenation suggests differences inherent reactivity of the alkenes, which persists when other solvents such as THF are used.

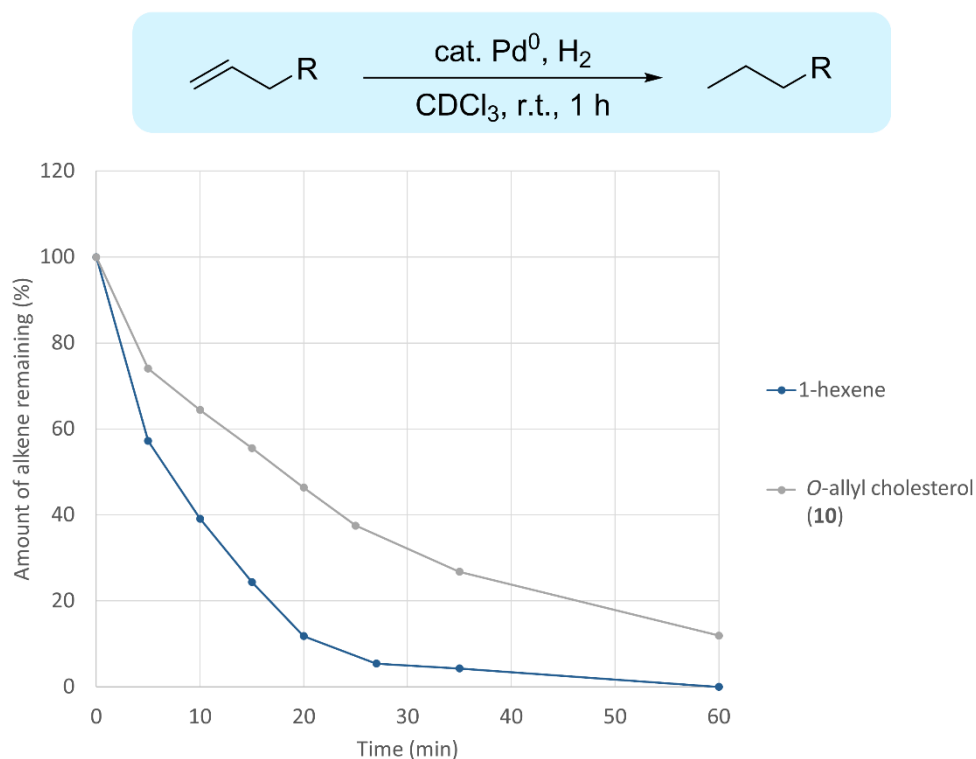


Figure 4-13. Consumption of 1-hexene and *O*-allyl cholesterol (**10**) in the hydrogenation reaction catalyzed by Pd/C (0.1 mol%). The amount of alkenes was determined by the integration of ^1H NMR spectrum collected at each time point. All ^1H NMR spectra were collected in CDCl_3 .

Using the acid-treated $\text{Pd}^0@m\text{-SiO}_2$ nanoparticles, size-selective hydrogenation reactions were attempted in CDCl_3 on a number of substrates of various sizes. Similar to reactions carried out using Pd/C as the catalyst, the smaller alkene, 1-hexene, reacted quickly, and was consumed completely within 30 min under these reaction conditions. Hydrogenation of *O*-allyl cholesterol

(**10**) was nearly complete after 1 h, suggesting that the pore diameter was large enough for **10** to enter and react at the Pd center.

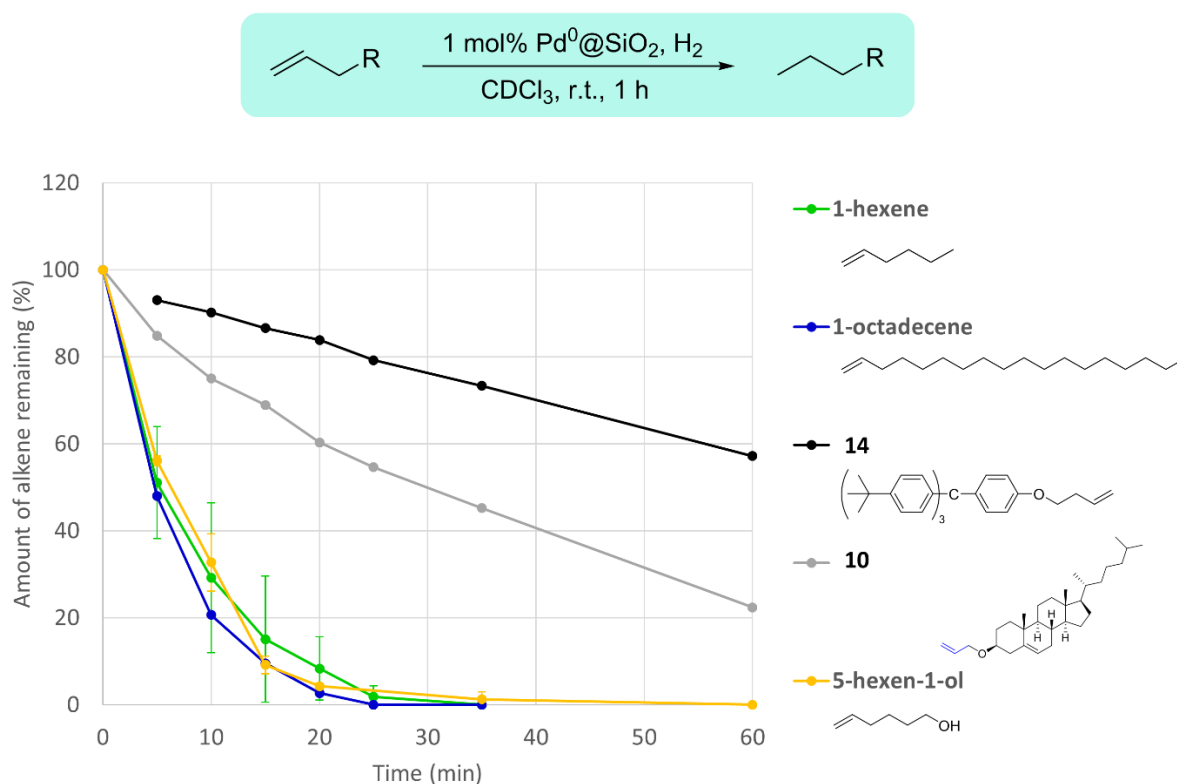


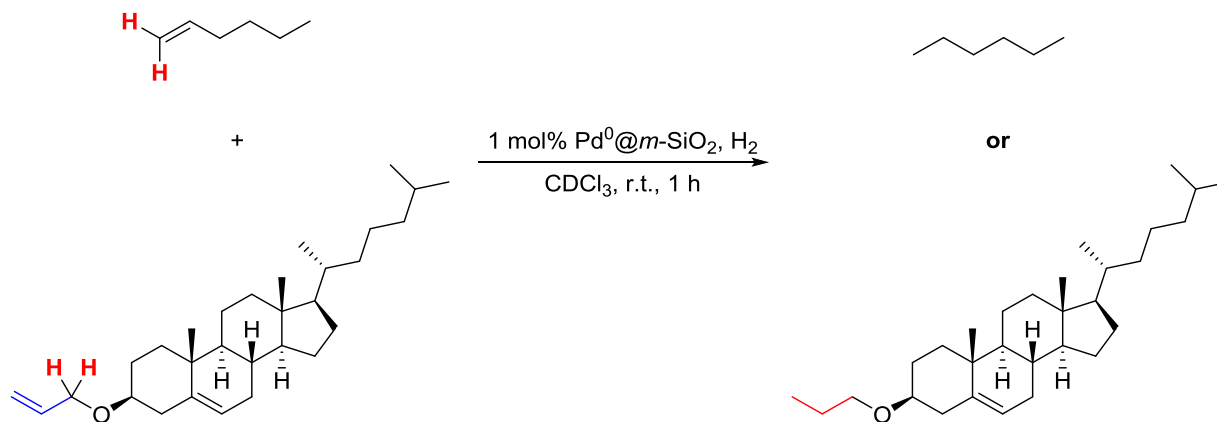
Figure 4-14. Overlay plots of the consumption of alkene vs. time in the hydrogenation of various alkenes using the acid-treated Pd⁰@*m*-SiO₂ nanoparticles. The amount of alkenes was determined by integration of ¹H NMR spectra collected at each time point. All ¹H NMR spectra were collected in CDCl₃.

Other substrates of various sizes were tested (Figure 4-14). Small molecule such as 5-hexen-1-ol have the same reaction profile as 1-hexene, where hydrogenation is complete after 30 min. The presence of –OH group in the substrate does not affect the reaction, suggesting a lack of interaction between the silica channels and the substrate. The long alkyl chain of 1-octadecene does not slow the reaction, and this species reacted as fast as the small molecules, possibly because

the alkyl group can coil, reducing the diameter. The larger compounds **10** and **14** react much more slowly than either 1-hexene or 1-octadecene.

4.3.2.1 Competition Hydrogenation of 1-Hexene and *O*-Allyl Cholesterol (**10**)

A competition experiment was performed, where a small and a large alkene were added to the reaction mixture at the same time (Scheme 4-4). If size is the determining factor, only the small alkene should be hydrogenated. From the ^1H NMR spectra, signals corresponding to the CH_2 protons of 1-hexene are observed at δ 5.9 ppm, while those of compound **10** are observed at δ 6.1 ppm (Figure 4-15). As the alkene protons of **10** overlap in the ^1H NMR spectra, the $-\text{OCH}_2-$ protons of **10** were used instead to monitor the reaction.



Scheme 4-4. Competition experiment of 1-hexene and *O*-allyl cholesterol (**10**) in CDCl_3 .

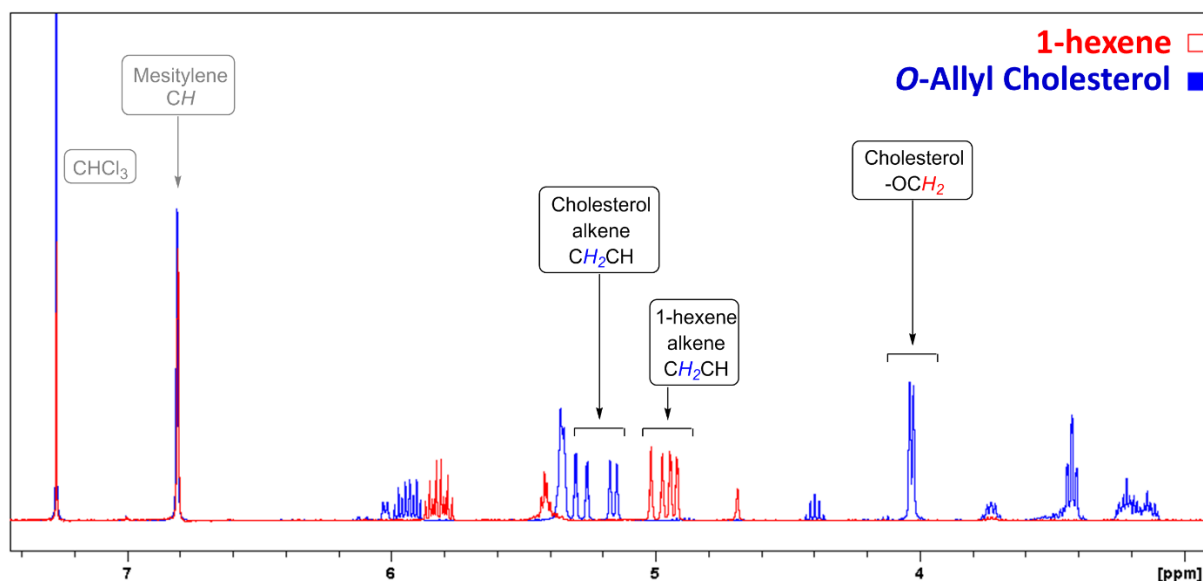


Figure 4-15. Overlaid partial ^1H NMR spectra showing the alkene protons of 1-hexene and *O*-allyl cholesterol collected in CDCl_3 .

The consumption of the two alkenes were plotted against time (Figure 4-16). The consumption of alkenes appeared to proceed similarly when both alkenes were added at the same time. However, monitoring the reaction using Pd/C (0.1 mol%) instead of acid-treated $\text{Pd}^0@m\text{-SiO}_2$ nanoparticles as catalyst resulted in similar trends. In both experiments, 1-hexene reacted rapidly with within 30 min. *O*-allyl cholesterol (**10**) reacted more slowly when $\text{Pd}^0@m\text{-SiO}_2$ nanoparticles were used as the catalyst, suggesting that the pores may slow down the larger substrate from reaching the catalytic Pd core. Using commercially available Pd/C as the catalyst gave similar trends, and was apparent because no differences in the ratios of 1-hexene and **10** were observed during the course of the reaction. This again suggests that the difference in reactivity is not determined by the size of the substrates or the porous silica channels, but the inherent reactivity

of the alkenes. However, with smaller pores, the difference in the reactivity may be more pronounced.

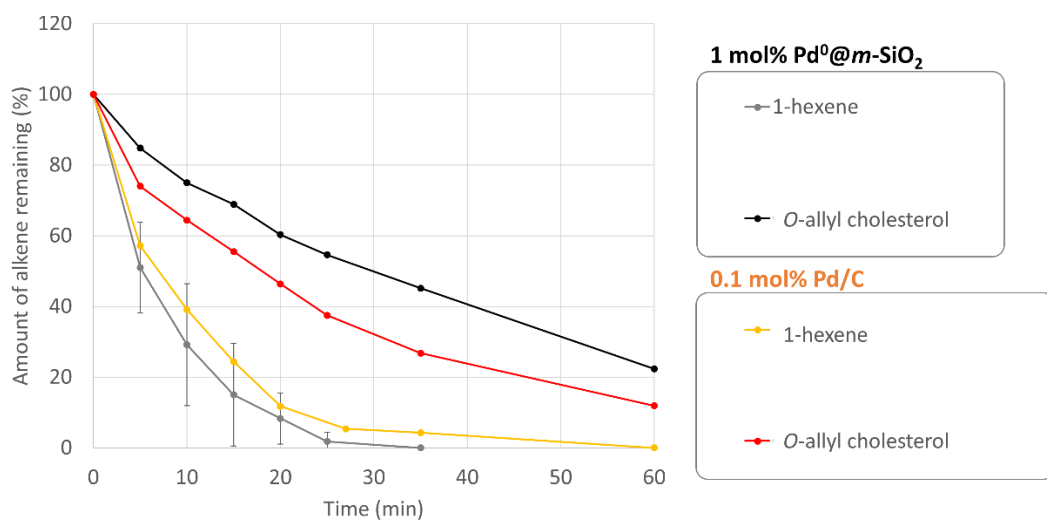


Figure 4-16. Consumption of 1-hexene and *O*-allyl cholesterol (**10**) in the competition hydrogenation reaction catalyzed by either acid-treated Pd⁰@*m*-SiO₂ nanoparticles (1 mol%) or Pd/C (0.1 mol%). The amount of alkenes was determined by integration of ¹H NMR spectra collected at each time point.

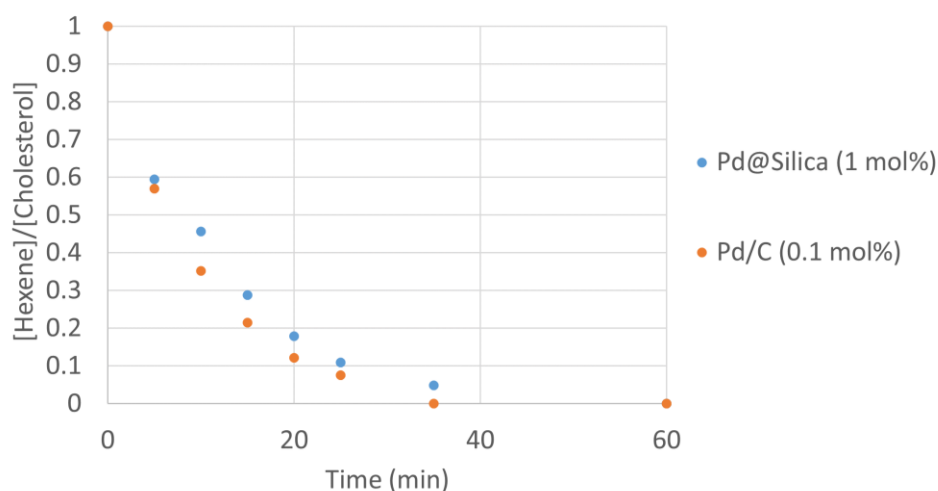
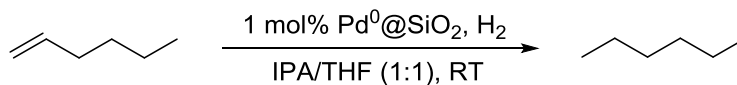


Figure 4-17. Overlay plots comparing the ratio of the consumption of 1-hexene and *O*-allyl cholesterol (**10**) vs. time, in the hydrogenation of various alkenes using the acid-treated Pd⁰@*m*-SiO₂ nanoparticles.

4.3.2.2 Size-Selective Hydrogenation Using Pore-Narrowed Pd⁰@*m*-SiO₂ Nanoparticles

As discussed in Chapter 3, the diameter of the silica channels of the Pd⁰@*m*-SiO₂ nanoparticles can be narrowed using a vacuum-assisted vapor deposition process. With these pore-narrowed samples, larger substrates should have more difficulty passing through the silica channel to reach the active Pd surface. Here, all of the hydrogenation reactions were conducted in a 1:1 mixture of THF and IPA using 1 mol% of pore-narrowed Pd⁰@*m*-SiO₂ nanoparticles as catalyst, using the previously discussed setup (Scheme 4-5). Using pore-narrowed Pd⁰@*m*-SiO₂ nanoparticles as the catalyst, hydrogenation of 1-hexene was monitored by ¹H NMR spectroscopy. The consumption of 1-hexene was plotted, and comparing to the rates of hydrogenation in CDCl₃ the hydrogenation reactions occurs much more slowly (Figure 4-18). As well, the hydrogenation of 1-hexene was much slower than that of the acid-treated Pd⁰@*m*-SiO₂ nanoparticles.



Scheme 4-5. Hydrogenation of 1-hexene using acid-treated or pore-narrowed Pd⁰@*m*-SiO₂ nanoparticles (1 mol%) as the catalyst.

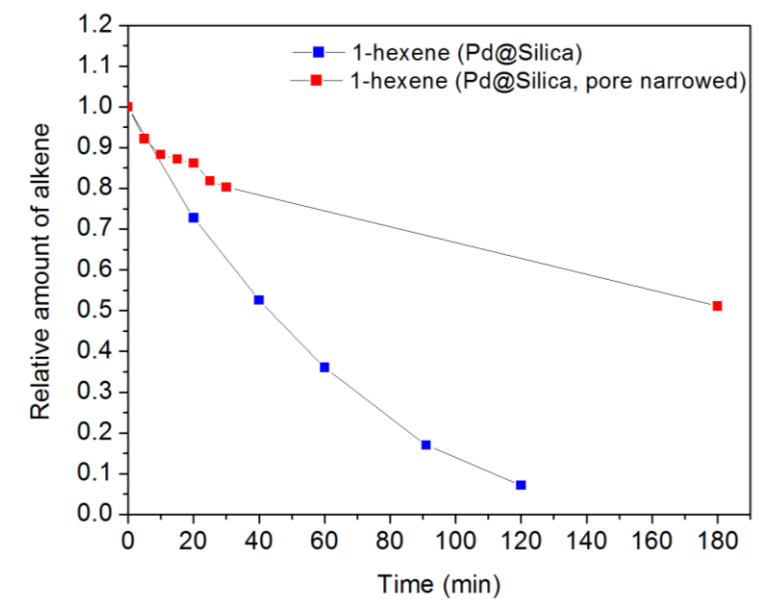
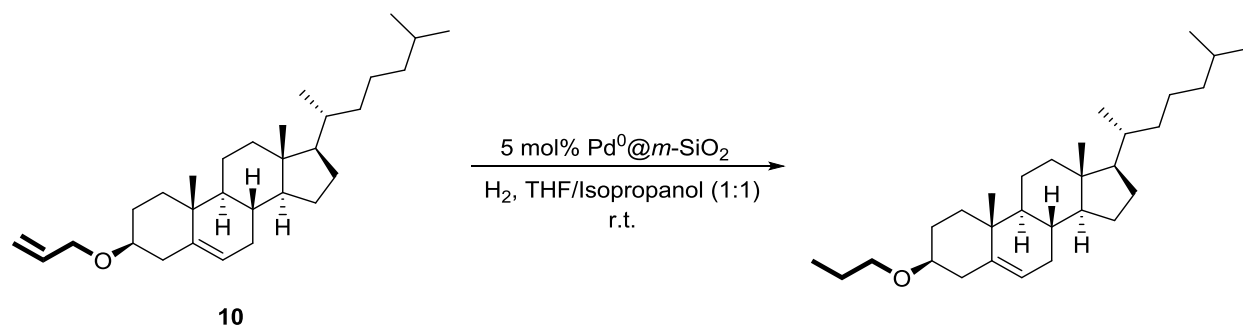


Figure 4-18. Overlay plots of the consumption of alkene vs. time in the hydrogenation of 1-hexene using the acid-treated (blue trace) and pore-narrowed (red trace) Pd⁰@*m*-SiO₂ nanoparticles.

The hydrogenation of 1-hexene was complete after 2 h, and as a consequence a higher loading of catalyst (5 mol%) was used to speed up the monitoring process (Scheme 4-6). When compound **10** was used as the substrate, no conversion to the corresponding alkane was observed, even after reaction for 6 h at room temperature. Pd⁰@*m*-SiO₂ nanoparticles without the pore-narrowing treatment resulted in reaction with **10**, which was complete after 2 h. This indicates that the size of the substrate has an impact on the hydrogenation reaction when using these core-shell nanoparticles.



Scheme 4-6. Hydrogenation of **10** using acid-treated or pore-narrowed Pd⁰@*m*-SiO₂ nanoparticles (5 mol%) as the catalyst.

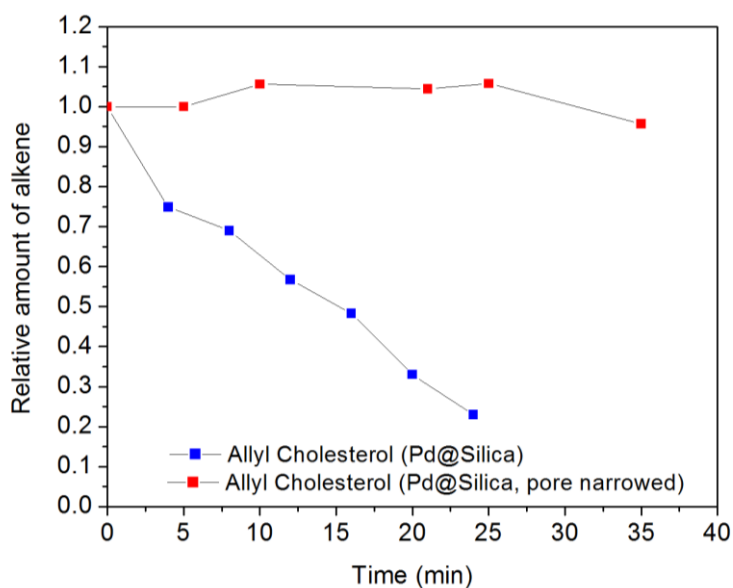


Figure 4-19. Overlay plots of the consumption of alkene vs. time in the hydrogenation of *O*-allyl cholesterol (**10**) using the acid-treated (blue trace) and pore-narrowed (red trace) Pd⁰@*m*-SiO₂ nanoparticles.

4.4 Conclusions

The utility of the Pd⁰@*m*-SiO₂ nanoparticles are demonstrated in this chapter. First, an attempt using the mesoporous silica structure as a template to generate new core-shell

nanoparticles was reported. PdO@m-CeO₂ nanoparticles were prepared by first infiltrating the silica channels with the appropriate precursor, calcined, then etched with 2 M NaOH to result in the new material. Both acid-treated and calcined Pd⁰@m-SiO₂ nanoparticles were used to prepare the PdO@m-CeO₂ nanoparticles, where materials of different compositions were obtained. CeO₂ core-shell particles prepared from calcined Pd⁰@m-SiO₂ nanoparticles (PdO@m-SiO₂) had varied morphologies nanoparticles and lower BET surface areas, attributed to the increased hydrophobicity of the silica shell through calcination. PdO was found on the surface and bulk of the nanoparticles, suggesting incomplete encapsulation of the PdO core.

When the Pd⁰@m-SiO₂ nanoparticles were used as the template in the preparation of PdO@m-CeO₂ nanoparticles, a yellow-colored material with high BET surface area was obtained. TEM images revealed the presence of an increased number of spherical nanoparticles. As well, Pd⁰ was not observed on the PXRD pattern. XPS indicated the presence of Pd²⁺, the presence of which was explained is consistent with the possible formation of a solid solution with composition Ce_{1-x}Pd_xO_{2-δ}. The formation of this substance is unusual as preparations of Ce_{1-x}Pd_xO_{2-δ} normally require extreme conditions. These nanoparticles were tested in the catalytic oxidation of methane, however low catalytic activity was found.

Size-selective hydrogenation was investigated as another application of the Pd⁰@m-SiO₂ nanoparticles. Using the porous silica shell as a selector, larger substrates were envisioned to have slower reactivity with the Pd core as the large size prevent the molecules from travelling rapidly through the channels. Hydrogenation of 1-hexene in CDCl₃ using acid-treated Pd⁰@m-SiO₂ nanoparticles occurs quickly, while the hydrogenation of a larger substrate, *O*-allyl cholesterol (**10**) proceeded slower. The same result was observed when the two alkenes were added together to the hydrogenation reaction. However, using commercially available Pd/C as a control yielded

similar results where compound **10** reacted more slowly than 1-hexene, suggesting that the difference in rates could be due, in part, to the inherent reactivity of the alkenes. As well, hydrogenation of **10** was attempted on the pore-narrowed Pd⁰@*m*-SiO₂ nanoparticles, and it was shown that no hydrogenation occurs for at least 6 h. This suggests that the pores are capable of slowing down larger molecules to react with the catalytic Pd center.

4.5 Experimental

4.5.1 General.

1-Hexene, 1-octadecene, mesitylene, 4-bromo-1-butene, and allyl bromide were purchased from Sigma-Aldrich. 5-hexene-1-ol was purchased from TCI America. Methyl 4-*tert*-butyl benzoate and 1-Bromo-4-*tert*-butylbenzene were purchased from Alfa Aesar. Cerium nitrate hexahydrate was purchased from Strem Chemicals. Cholesterol was provided by Dr. Christine Rogers from the undergraduate chemistry laboratory at UBC. All chemicals were used as received.

NMR spectra were recorded at room temperature on Bruker AV-300 and AV-400 spectrometers and referenced to residual solvent. All chemical shifts are reported in Hz. Low-resolution mass spectra (EI) were recorded by the staff of the UBC mass spectrometry facility using a Kratos MS-50 spectrometer. Elemental analyses were performed by Derek Smith from the UBC mass spectrometry/microanalysis lab on a Carlo Erba Elemental Analyzer EA 1108. Powder X-ray diffraction (PXRD) data were recorded on a 60 Bruker D8 Advance X-ray diffractometer in the Bragg-Brentano configuration, using copper K α radiation at 40 kV, 40 mA. Gas adsorption studies were performed using a Micromeritics ASAP 2000 system. X-ray photoelectron spectroscopy (XPS) analyses were carried out on a Leybold Max200 spectrometer using an aluminum K α X-ray source (Al K α = 1486.6 eV) operating at a base pressure of 1×10^{-9} Torr.

Initial survey scans were acquired with a pass energy of 192 eV, while higher resolution scans were acquired with a pass energy of 48 eV. Spectra were referenced to the C 1s peak at 285.0 eV. Samples were prepared for transmission electron microscopy (TEM) by drop-casting $\sim 3 \mu\text{L}$ of the dilute suspension in ethanol onto a carbon-coated 400-mesh copper TEM grid and drying in air under ambient conditions. Microscopy was carried out on a Hitachi H-7600 transmission electron microscope. An accelerating voltage of 100.0 kV was used.

4.5.2 Methods for Methane Oxidation Testing

A schematic of the setup used for methane oxidation testing is shown in Figure 4-9. The experimental setup for catalyst testing consists of a stainless steel fixed bed reactor (Length = 5 cm; I.D. = 0.9 cm) located inside an electric tube furnace with a PID temperature controller. Two thermocouples (K-type) inserted inside the reactor measure the temperature at the top and bottom of the catalyst bed. The reactor is connected to a feed gas system that includes electric mass flow controllers (Brooks 5850 TR) and a pump (Gilson 307), able to provide desired feed mixtures (CH_4 , O_2 , Ar, and He) at a total flow rate of $300 \text{ cm}^3 (\text{STP}) \text{ min}^{-1}$. There is a pre-heater in the gas flow line before the reactor to heat the reactants to 393 K. The gas flow lines connecting the pre-heater, the reactor and the quadrupole mass spectrometer are held at the same temperature as the pre-heater (393 K) using heating tape. After the reactant gas was fed to the reactor, the reactor temperature was increased linearly at $5 \text{ K} \cdot \text{min}^{-1}$ from 393 K to 873 K. Analysis of reactants and products was performed by a VG ProLab quadrupole mass spectrometer (MS) that continuously monitors the reactor exit gas line. The MS detects and records the intensity of mass peaks corresponding to CH_4 , O_2 , CO_2 , Ar, and He. A mixture of these gases was used to calibrate the MS and hence the concentrations of gases at the exit of the reactor were determined. Due to the

difficulty in quantifying the water content of the exit stream by MS, the water content was determined using the stoichiometry of the reactions.

4.5.3 Preparation of PdO@m-CeO₂ Nanoparticles by Pore-Filling of Pd⁰@m-SiO₂ Nanoparticles.

The procedure for the templating of PdO@m-CeO₂ nanoparticles from Pd⁰@m-SiO₂ nanoparticles was modified from that reported by Yen *et al.*⁷³ Acid-treated Pd⁰@m-SiO₂ nanoparticles (67.4 mg) were dried at 150 °C in *vacuo* for 2 h. Using an agate mortar and pestle, The dried nanoparticles and Ce(NO₃)₃·6H₂O (1.00 g, 2.30 mmol) were ground in the presence of small quantity of hexanes to result in a beige powder. The solids were transferred to a 100 mL round-bottom flask, and the mixture was heated to reflux in hexanes (20 mL) for 20 h. After cooling, the solid was collected by suction filtration and dried in a 60 °C oven. The resulting powder was placed in a vial and calcined at 600 °C for 4 h to obtain PdO@m-CeO₂ nanoparticles.

4.5.4 Preparation of PdO@m-CeO₂ Nanoparticles by Pore-Filling of PdO@m-SiO₂ Nanoparticles.

The procedure for the preparation of PdO@m-CeO₂ nanoparticles was analogous to the preparation of the nanoparticles from Pd⁰@m-SiO₂ nanoparticles (Section 4.5.3), except PdO@m-SiO₂ nanoparticles were used in the preparation. A brown powder was obtained after calcination.

4.5.5 Synthesis of O-allylated Cholesterol (10).

The procedure for the O-allylation of cholesterol was modified from that reported by Jiménez-Núñez *et al.*¹⁸⁴ Cholesterol (7.73 g, 1.50 mmol) was added to a suspension of NaH (60%

in mineral oil, 0.8 g,) in THF (100 mL) at room temperature. After 30 min, allyl bromide (2.59 mL, 1.75 mmol) was added while stirring. After stirring for 3 h, the reaction was stopped by the addition of water (100 mL). The aqueous phase was extracted with EtOAc (3 × 50 mL). The combined organic layers were dried over Na₂SO₄, and the volatiles were removed by rotary evaporation to result in a creamy yellow solid. The final product was then isolated by column chromatography (230 - 400 mesh silica gel, 9:1 hexanes/EtOAc as eluent, R_f = 0.52) as white powder (60%).

Characterization Data for 10: ¹H NMR (300 MHz, CDCl₃) δ 0.68 (s, 3H, alkyl CH₃), 0.85-2.41 (m, 48H, alkyl CH₂ and CH₃), 3.22 (tt, 1H, OCH), 4.03 (dt, 2H, OCH₂), 5.16 (d, 1H, C=CH), 5.31 (m, 2H, C=CH₂), 5.95 (m, 1H, H₂C=CH); MS (LREI, *m/z*, probe temperature 150 °C) 458 [M⁺]. Anal. Calcd for C₃₀H₅₀O: C, 84.44; H, 11.81; O, 3.49. Found: C, 84.35; H, 12.12.

4.5.6 Synthesis of Compound 14.

Compound **13** was prepared following the literature procedures.^{186, 187} The procedure for the allylation of **14** was modified from that reported by De Bo *et. al.*¹⁸⁷ A 25 mL round-bottom flask was charged with Compound **13** (2.13 g, 4.23 mmol), 4-bromo-1-butene (1.21 mL, 11.9 mmol), K₂CO₃ (5.04 g, 36.5 mmol), and acetonitrile (10 mL). The suspension was heated to reflux in a 110 °C oil bath for 16 h. After cooling, CH₂Cl₂ (10 mL) was added to the reaction mixture, and the residual white solid was removed by filtration and washed thoroughly with CH₂Cl₂. The filtrate was concentrated under reduced pressure to result in a white residue. The final product was then isolated by column chromatography (230 - 400 mesh silica gel, hexanes as eluent, R_f = 0.69) as white powder (44%).

Characterization Data for 14: ^1H NMR (300 MHz, CDCl_3) δ 1.32 (s, 27H, alkyl CH_3), 2.54 (m, 2H, OCH_2CH_2), 4.01 (t, 2H, OCH_2), 5.13 (m, 2H, $\text{C}=\text{CH}_2$), 5.91 (m, 1H, $\text{HC}=\text{CH}_2$), 6.80 (d, 2H, ArH), 7.11-7.23 (m, 14H, ArH); MS (LREI, m/z , probe temperature 150 $^\circ\text{C}$) 558 [M^+]. Anal. Calcd for $\text{C}_{41}\text{H}_{50}\text{O}$: C, 88.12; H, 9.02; N, 0.00; O, 2.86. Found: C, 87.77; H, 9.10; N, 0.12.

4.5.7 Procedure for the Size-Selection Hydrogenation Reactions Using $\text{Pd}^0@m\text{-SiO}_2$ Nanoparticles.

The procedure for the hydrogenation reaction was performed using the setup shown in Figure 4-20. $\text{Pd}^0@m\text{-SiO}_2$ nanoparticles (8.9 mg, 0.005 mmol Pd), mesitylene (23.3 μL , 0.167 mmol), and CDCl_3 (10 mL) were added to a 25 mL round-bottom flask. A hydrogen balloon is then attached to the reaction flask, the reaction mixture was purged with hydrogen gas for 15-20 min while vigorous stirring was maintained. After refilling the balloon with hydrogen, alkene (0.5 mmol) was added to the reaction using a syringe. Solid alkenes such as **10** were added by first dissolving in CDCl_3 . The overall volume of the reaction was maintained as 10 mL. Aliquots of the reaction mixture (0.5 mL) were removed every 10 min and were added to an NMR sample tube for analysis.

Similar procedure was used in competition experiments. The two alkenes were first dissolved in CDCl_3 and were added to the Pd nanoparticles suspension at once. The overall volume of the reaction was maintained at 10 mL.



Figure 4-20. Experimental setup for the hydrogenation reactions.

Chapter 5: Conclusion

5.1 General Conclusions

This thesis describes the synthesis of a range of nanomaterials containing Pd. Monodisperse, catalytically active Pd⁰ nanoparticles were prepared, and new insights into the mechanism of the formation of Pd⁰ nanoparticles were obtained. Core-shell nanoparticles consisting of Pd core and silica shell were also prepared, and some novel applications were demonstrated.

Chapter 2 describes the preparation of monodisperse, catalytically active Pd⁰ nanoparticles at low temperatures from Pd(acac)₂, 1-hexadecylamine, and TOPO. NMR and IR spectroscopic techniques showed that the nanoparticles are stabilized by 1-hexadecylamine. The monodispersity and shape of the nanoparticles were affected by changes in certain reaction conditions. As well, formation of Pd⁰ nanoparticles was explored using NMR spectroscopy, and a plausible mechanism for the formation of Pd⁰ nanoparticles was proposed by identification of intermediates present in the reaction mixture. Notable intermediates include a tetraaminopalladium salt (**1**), a Pd-amido complex, aldimine **4**, dialkylamine **5**, and ammonia. The presence of ammonia was confirmed by derivatization into *N,N*-dimethyl-*N'*-(phenylsulfonyl)formimidamide. The mechanism of formation of Pd⁰ nanoparticles was unknown prior to this study.

Additionally, Lewis bases such as TOPO and DMSO were found to greatly reduce the temperature at which highly monodisperse nanoparticles are formed. TOPO greatly enhances the nucleophilicity of amines through hydrogen-bonding, which leads to more rapid formation of compounds **2** and **3** through nucleophilic attack of 1-hexadecylamine. Faster formation of the ketimine **2** drives the equilibrium towards the Pd-amido complex, hence formation of the Pd⁰ nanoparticles occur at lower temperatures. A similar effect of TOPO was observed when another

precursor, $\text{Pd}(\text{OAc})_2$, was used to prepare Pd^0 nanoparticles in the presence of TOPO. These new insights provide new understanding to the mechanism of the formation of nanoparticles, the fate of organic compounds used, and the byproducts formed. Understanding the mechanism, especially the role of each reagent plays in the reaction, will help develop new methods of preparing nanoparticles at lower temperatures.

In Chapter 3 the preparation of spherical $\text{Pd}^0@m\text{-SiO}_2$ core-shell nanoparticles using a simple, scalable one-pot procedure is described. Calcination of the as-synthesized $\text{Pd}^0@m\text{-SiO}_2$ nanoparticles at 400 °C for 4 h in air resulted in calcined $\text{PdO}@m\text{-SiO}_2$ nanoparticles as a consequence of the oxidation of Pd^0 to PdO at elevated temperatures. Calcined $\text{Pd}^0@m\text{-SiO}_2$ nanoparticles was prepared using nitrogen gas during calcination; however, trace amounts of carbon were found on the sample by elemental analysis. Acid treatment of the $\text{Pd}^0@m\text{-SiO}_2$ nanoparticles was found to be the most suitable method in removal of CTAB, and the surface silanol groups on the nanoparticles were preserved, maintaining the hydrophilicity of the nanoparticles. The morphology, surface area, and pore diameter of the core-shell nanoparticles remained intact after removal of CTAB.

The reaction conditions were crucial in the preparation of the nanoparticles, where the temperature used to prepare the $\text{Pd}^0\text{-CTAB}$ nanoparticles greatly influenced the diameter of the $\text{Pd}^0\text{-CTAB}$ nanoparticles, and the amount of TEOS used in the subsequent reaction affected the quality of the $\text{Pd}^0@m\text{-SiO}_2$ core-shell nanoparticles produced. Furthermore, the pore diameter of the nanoparticles can be expanded by the introduction of DMHA to the reaction mixture prior to the formation of the silica shell around the $\text{Pd}^0\text{-CTAB}$ nanoparticles. However, expanding the pore diameter appears to destroy the morphology of the nanoparticles. On the other hand, narrowing of the pore diameter can be achieved using vacuum-assisted vapor

deposition of TMOS onto the surface of the nanoparticles. Subsequent calcination regenerates the surface silanols while oxidizing the Pd⁰ core to PdO, which was then reduced to Pd⁰ using NaBH₄. This one-pot preparation method for core-shell nanoparticles can be useful to prepare catalysts suitable for high temperatures in the industrial scale.

The utility of the Pd⁰@*m*-SiO₂ nanoparticles was demonstrated in Chapter 4. The mesoporous silica shell of the nanoparticles was used as a template to generate new core-shell nanoparticles. Acid-treated and calcined Pd⁰@*m*-SiO₂ nanoparticles were used to prepare the PdO@*m*-CeO₂ nanoparticles, yielding materials of different compositions. CeO₂ core-shell particles prepared from calcined Pd⁰@*m*-SiO₂ nanoparticles (PdO@*m*-SiO₂) had varying morphologies with CeO₂ nanoparticles showing incomplete encapsulation of the PdO core, and lower BET surface area. Attempts to use Pd⁰@*m*-SiO₂ nanoparticles as the template in the preparation of PdO@*m*-CeO₂ nanoparticles yielded a high BET surface area material containing spherical nanoparticles. The absence of Pd⁰ and presence of Pd²⁺ was explained by the possible formation of a solid solution composed of Ce_{1-x}Pd_xO_{2-δ}. These nanoparticles were tested for the catalytic oxidation of methane, however low catalytic activity was observed.

Size-selective hydrogenation was investigated using the porous silica shell of the Pd⁰@*m*-SiO₂ nanoparticles as a molecule size selector. Hydrogenation of a small molecule, 1-hexene, in CDCl₃ using acid-treated Pd⁰@*m*-SiO₂ nanoparticles occurs quickly, while the hydrogenation of a larger substrate, *O*-allyl cholesterol (**10**) proceeded slower. The same result was observed when the two alkenes were added together to the hydrogenation reaction. However, using commercially available Pd/C as a control yielded similar results where compound **10** reacted more slowly than 1-hexene, suggesting that the difference in rates could be due, in part, to the inherent reactivity of the alkenes. As well, hydrogenation of **10** was attempted on the pore-narrowed Pd⁰@*m*-SiO₂

nanoparticles. No hydrogenation of **10** occurs for at least 6 h, suggesting that the pores present in Pd⁰@*m*-SiO₂ nanoparticles are capable of slowing down larger molecules to react with the catalytic Pd center. The two applications show that these catalytically active core-shell nanoparticles could be used in interesting applications that other Pd-containing nanomaterials cannot be used for.

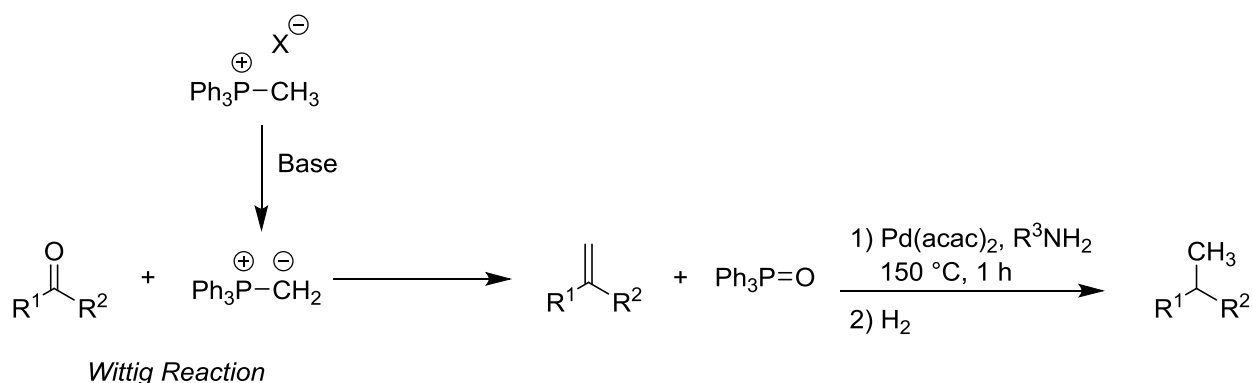
In conclusion, this thesis describes the novel preparative routes to new Pd-containing nanomaterials, from monodisperse Pd⁰ nanoparticles to Pd-containing core-shell nanoparticles. These nanomaterials can be used as industrially-relevant catalysts in a variety of Pd-catalyzed reactions, from cross-coupling reactions to oxidation of methane at elevated temperatures. These materials may open up new methods for the preparation of other noble-metal containing materials.

5.2 Future Work

Lewis bases such as TOPO and DMSO were demonstrated to facilitate the formation of Pd⁰ nanoparticles. It is likely that this process can be further enhanced using more Lewis basic species. Possible examples include compounds containing two phosphine oxide moieties, which may lower the amount of phosphine oxide required for the preparation of the nanoparticles. As differences in chemistry can be attributed to either steric or electronic effects, the use of phosphate compounds or sterically bulky phosphine oxides in place of TOPO may greatly affect the size and shape of the Pd⁰ nanoparticles formed.

As well, phosphine oxides are often viewed as useless byproducts to the Wittig reaction, where an aldehyde or ketone reacts with a triphenyl phosphonium ylide through a [2+2] cyclization to generate a new C=C bond and a phosphine oxide. An interesting proposal is a one-pot Tandem reaction, where a Pd⁰-catalyzed reaction proceeds after the Wittig reaction (Scheme 5-1). First, a

typical Wittig reaction is conducted to generate the alkene and the phosphine oxide. Heating of the phosphine oxide-containing mixture in the presence of Pd(acac)₂ and 1-hexadecylamine then result in the formation of Pd⁰ nanoparticles. The phosphine oxide is responsible for lowering the temperature required to form the Pd⁰ nanoparticles. Finally, hydrogenation of the alkene using H₂ results in an alkane as final product. Although this transformation may not be new, the idea of using the phosphine oxide byproduct in new methods may result in development of greener chemistry of Pd nanoparticles.



Scheme 5-1. Proposed scheme of the one-pot tandem Wittig reaction coupled with hydrogenation reaction highlighting the use of phosphine oxide to facilitate formation of Pd⁰ nanoparticles.

Finally, the exploration of size-selective catalysis using Pd⁰@m-SiO₂ nanoparticles should be continued. Aside from the size of molecules, the polarity of the substrates may be another idea to be considered. In Chapter 4, the silica channels of the core-shell nanoparticles was demonstrated to interact with molecules based on size of the molecules used. Hence, this idea could be extended to polarity changes, where increasing the hydrophobic of the silica pores may slow the speed with which hydrophilic molecules enter the pores. This can be achieved by reacting the surface silanol groups on the silica shell with organosilanes such as methoxytrimethylsilane (H₃COSi(CH₃)₃),

transforming the hydrophilic silanol groups to more hydrophobic methyl groups. Because the channel becomes more hydrophobic, hydrogenation of hydroxy-containing alkenes such as 5-hexene-1-ol should proceed slowly. These new ideas may open doors to new forms of catalytic reactions of Pd⁰ nanoparticles.

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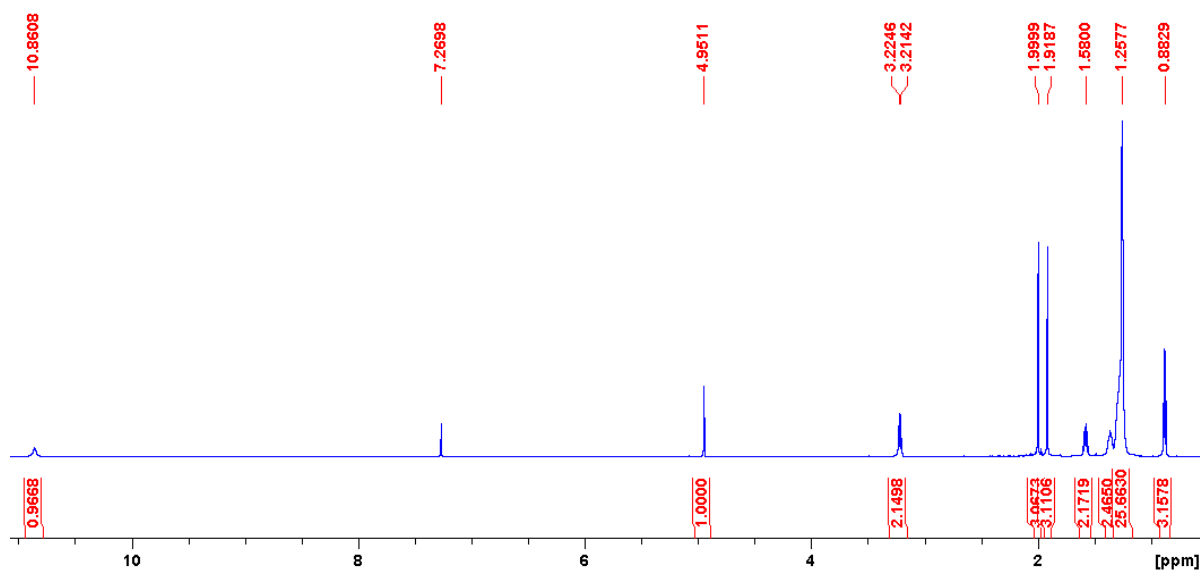
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Appendix

Appendix A

A.1 NMR Spectra

a)



b)

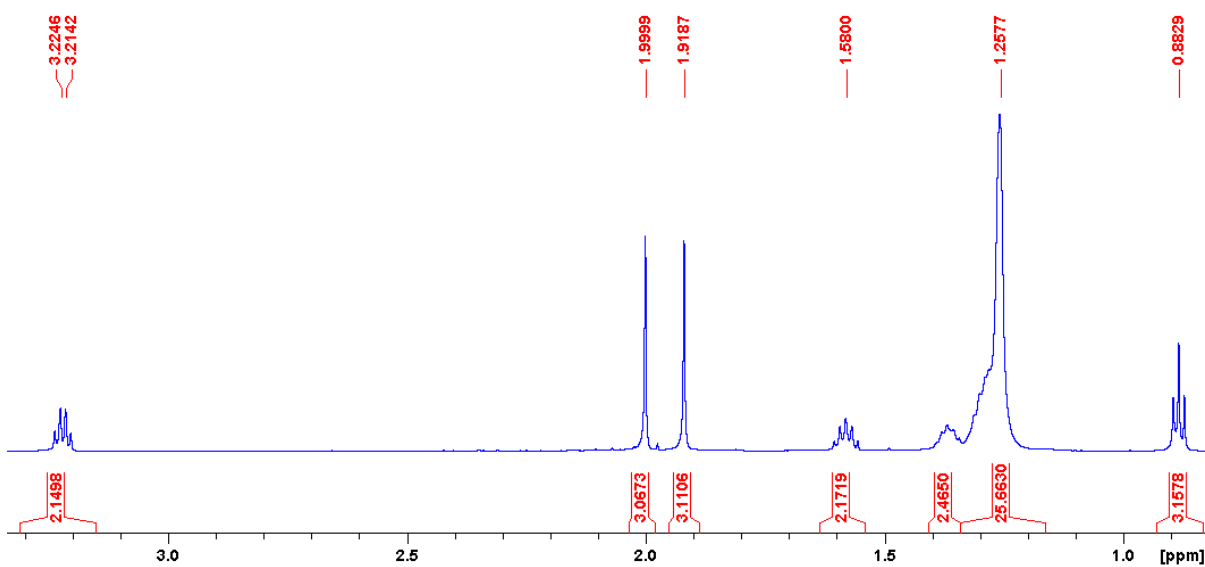


Figure A-1. ^1H NMR spectrum of complex 2 in CDCl_3 . a) Full spectrum. b) Zoomed-in spectrum.

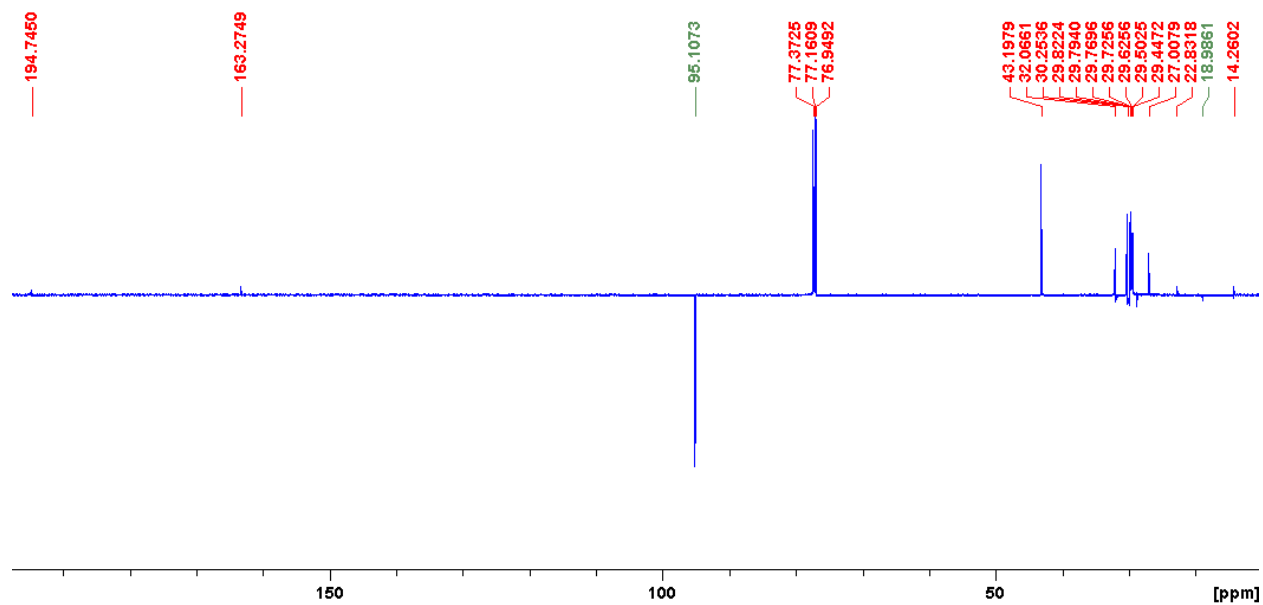


Figure A-2. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of complex 2 in CDCl_3 .

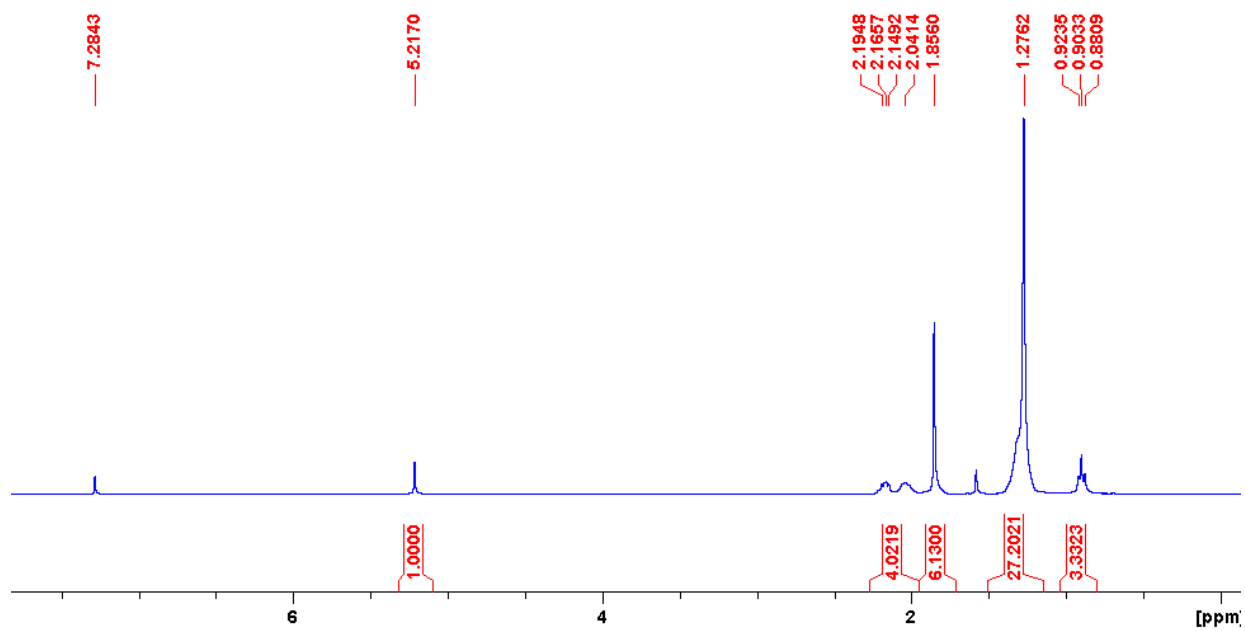


Figure A-3. ^1H NMR spectrum of complex 7 in CDCl_3 .

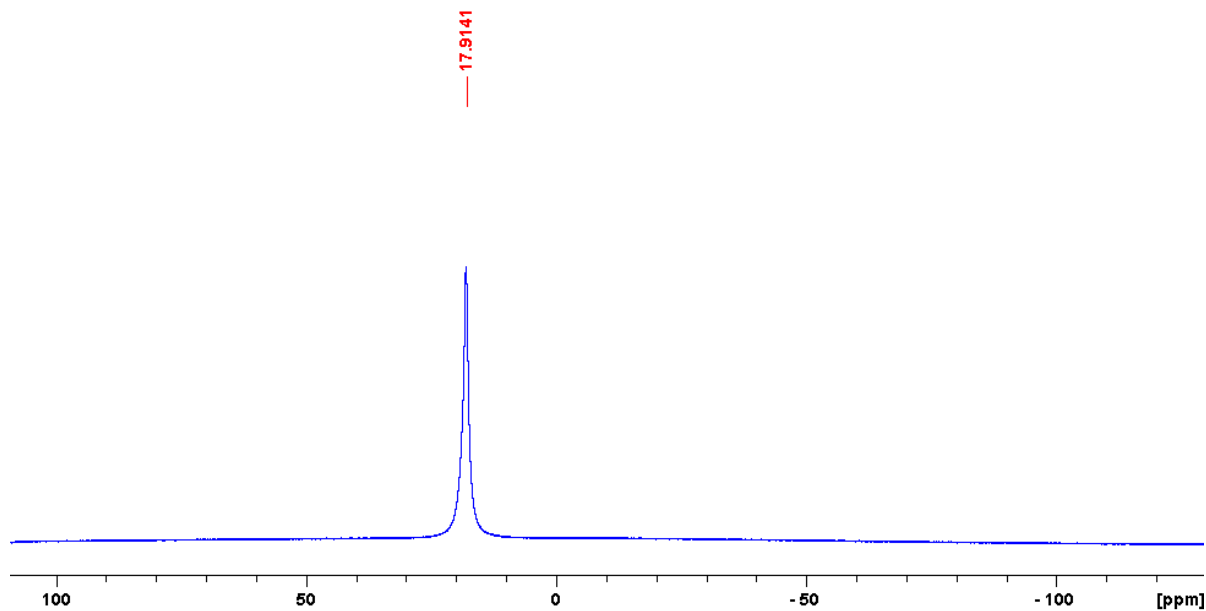


Figure A-4. ^{11}B NMR spectrum of the crude product generated from interacting the vapor of the reaction mixture with $\text{BH}_3\cdot\text{THF}$.

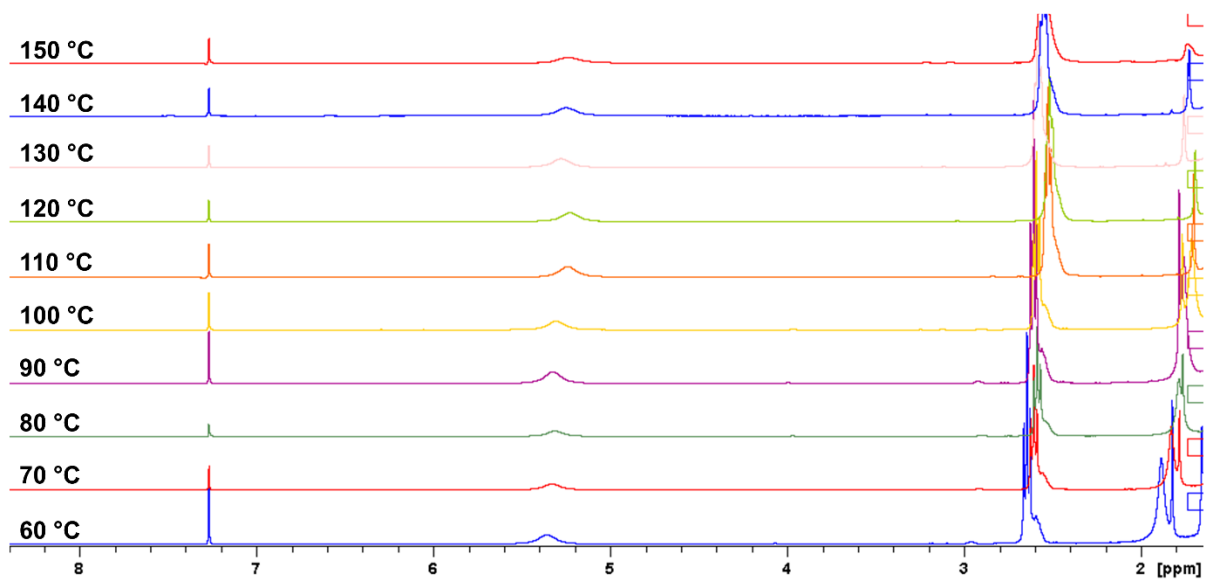


Figure A-5. Stacked room-temperature ^1H NMR spectra of the nanoparticle reaction mixture ($\text{Pd}(\text{OAc})_2 + 1\text{-hexadecylamine} + \text{TOPO}$) from 60 °C to 150 °C collected in CDCl_3 .

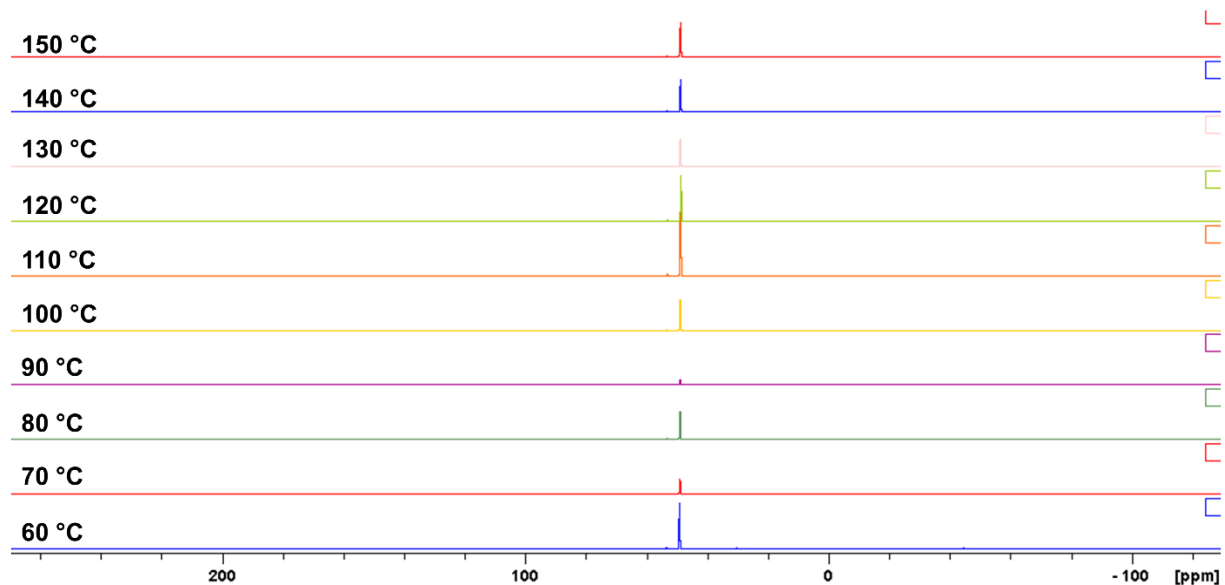


Figure A-6. Stacked room-temperature ^{31}P NMR spectra of the nanoparticle reaction mixture ($\text{Pd}(\text{OAc})_2$ + 1-hexadecylamine + TOPO) from 60 °C to 150 °C collected in CDCl_3 .

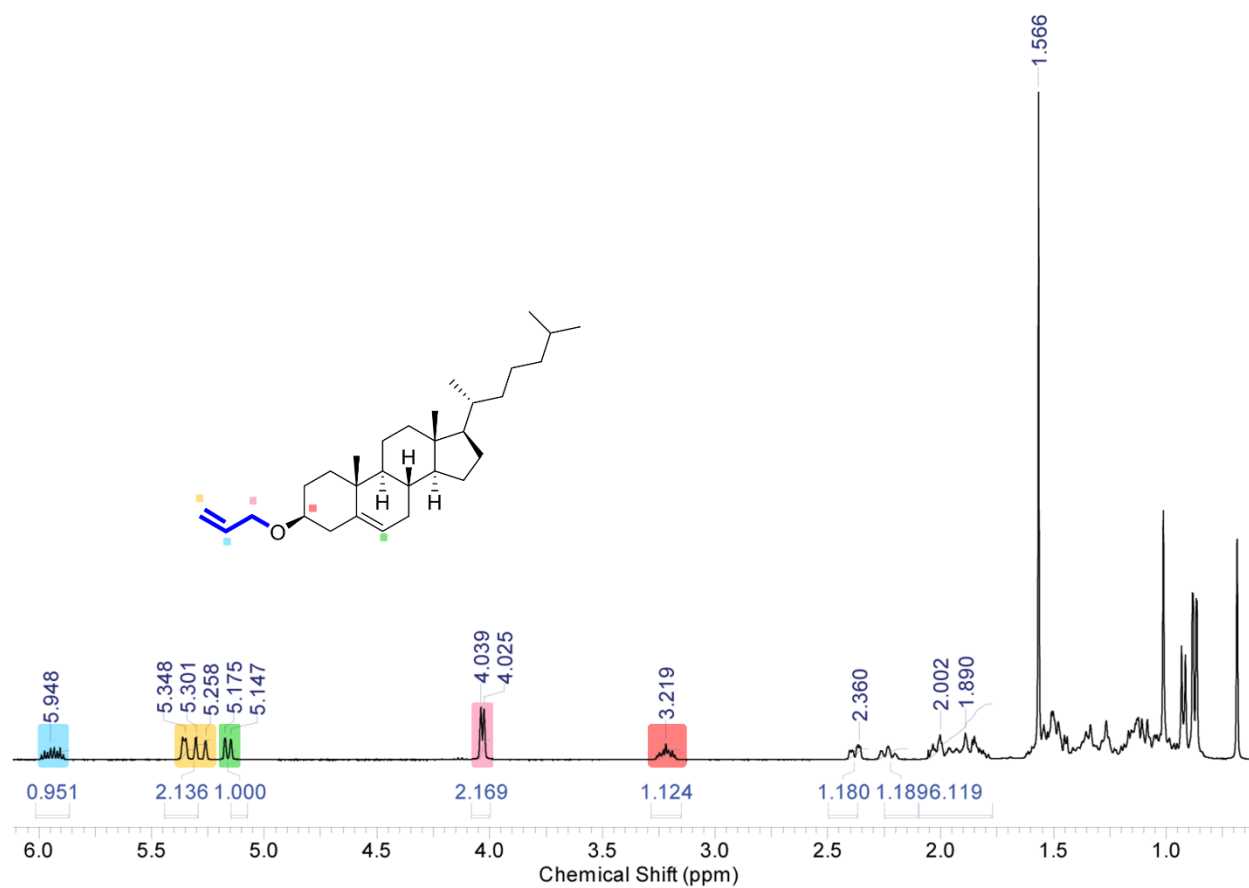


Figure A-7. ^1H NMR spectrum of **10** in CDCl_3 .

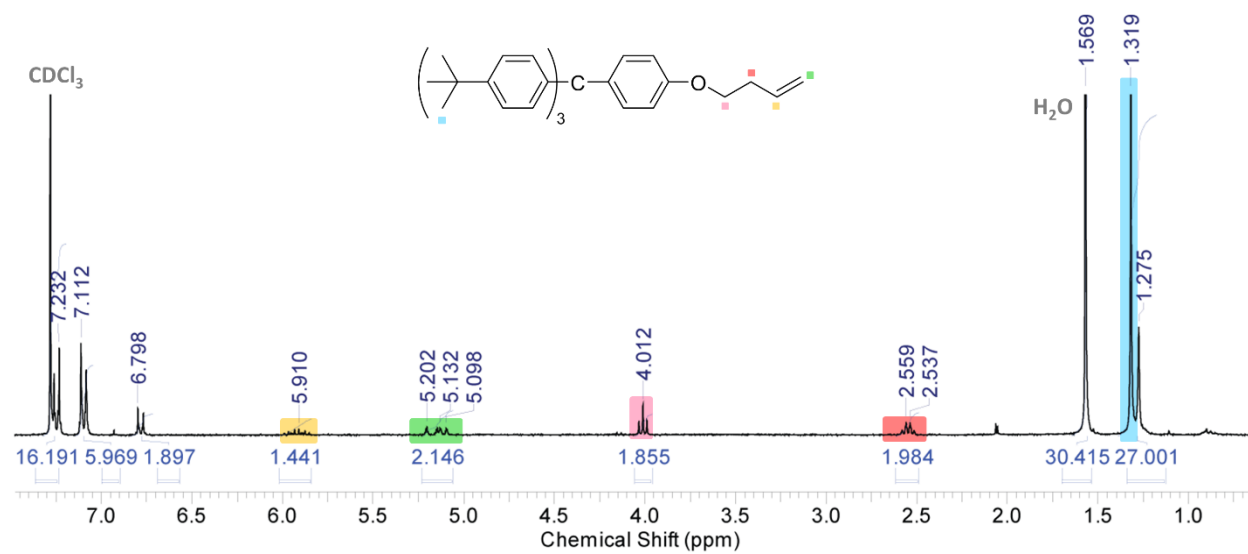


Figure A-8. ^1H NMR spectrum of 14 in CDCl_3 .