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**The Synthesis of Novel Metal and Metal Oxide Nanoparticles with Applications Towards
Catalysis**

by

Meredith Joanne McMurdo

A dissertation submitted in partial satisfaction of the

requirements for the degree of

Doctor of Philosophy

in

Chemistry

in the

Graduate Division

of the

University of California, Berkeley

Committee in charge:

Professor T. Don Tilley, Chair

Professor A. Paul Alivisatos

Professor Alexander Katz

Spring 2010

The Synthesis of Novel Metal and Metal Oxide Nanoparticles with Applications Towards
Catalysis

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Abstract

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Professor T. Don Tilley, Chair

This dissertation describes the synthesis of novel nanoparticles that are interesting for catalytic applications. The decomposition of $\text{RhCp}(\text{C}_2\text{H}_4)_2$ and $\text{Rh}(\text{hfacac})(\text{CO})_2$ were investigated, and the complex $\text{RhCp}(\text{C}_2\text{H}_4)_2$ was successfully shown to decompose to rhodium nanoparticles. Analysis of the decomposition chemistry was used to control nanoparticle seed formation and growth. New stabilizer ligands, both polymeric and molecular, were attempted for the synthesis of rhodium nanoparticles. Polymeric stabilizers were screened as replacements for the widely used polyvinylpyrrolidone (PVP) surfactant, however none afforded the high degree of control exhibited by PVP. However, molecular stabilizers were screened and small, monodisperse rhodium nanoparticles were synthesized with the stabilizer octadecylphosphonic acid, with a size and size dispersity of 1.92 ± 0.16 nm.

A concurrent hydrogenation catalytic process was also utilized for the synthesis of small rhodium seed particles. In this nanoparticle synthesis, a rhodium precursor and a stabilizer were combined in the presence of an olefin and hydrogen, which aids in decomposition of the rhodium precursor to nanoparticles, and also catalytically converts the olefin to a saturated compound. The rate of hydrogen uptake was monitored and fit to a two-step autocatalytic mechanism correlated to nanoparticle formation and growth. Two new rhodium complexes were synthesized that contained a stabilizer ligand, however the most successful attempt to produce small, monodisperse rhodium nanoparticles by this process was with the rhodium source $[(\text{COD})\text{Rh}(\text{NCCH}_3)_2]\text{BF}_4$, and the stabilizer $(\text{Bu}_4\text{N})_2\text{HPO}_4$ in the presence of an equivalent of Proton Sponge[™]. Rhodium nanoparticles synthesized by this process have a size and size distribution of 1.88 ± 0.27 nm. The presence of olefin and hydrogen pressure of 42 psi was found to be ideal for the stabilization of nanoparticles during their formation. Also, reactant concentrations and the rate of the cyclohexene consumption are crucial to yield nanoparticles with this excellent size dispersity. Growth reactions with these small rhodium nanoparticles have been successful the synthesis of larger nanoparticles under conditions involving alternate stabilizers.

The small nanoparticles were then tested and found to be useful as seed particles in the synthesis of larger rhodium nanoparticles. For each procedure, a mixture of 1-hexadecylamine, adamantane carboxylic acid, and 1,2-hexadecanediol was used to stabilize the nanoparticles. The use of synthesized seed particles allowed for the formation of tetrahedral (average edge length: 4.77 +/- 0.72 nm) or icosahedral shaped particles, depending on reaction temperature. Subsequent characterization revealed that approximately half of the tetrahedrally shaped nanoparticles are in fact triangular flat rafts, where one corner of the tetrahedron appears to be “cut off.” However, the use of in situ seeds resulted in the formation of multipod structures. The multipods are single crystals with 2-8 arms per multipod, that propagate both the (110) and (111) directions.

The synthesis and characterization of mixed-metal oxide spinel nanoparticles was then attempted for water oxidation catalysis. Nanoparticles of the compositions MnFe_2O_4 and CoFe_2O_4 (5.7 nm and 6.1 nm respectively) were synthesized according to a literature procedure with the stabilizers oleic acid and oleylamine, however they were characterized by ICP-OES to have low M:Fe (M = Mn, Co) ratios of 1:5 and 1:4 respectively. Nanoparticles of NiFe_2O_4 (8.0 nm) were also synthesized by a similar approach, and had the expected Ni:Fe ratio of 1:2 by ICP-OES. Cubic nanoparticles of Co_3O_4 were also synthesized, and through a subsequent cation exchange reaction with this material, $\text{Cu}_x\text{Co}_{3-x}\text{O}_4$ and $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ nanoparticles could be synthesized with varying degrees of copper or nickel incorporation. Linear scan voltammograms were conducted on anodes modified with these nanoparticle materials. For the mixed-metal ferrites, CoFe_2O_4 showed the lowest overpotentials in the water oxidation reaction in the range of 0-100 mA cm^{-2} . Copper modified Co_3O_4 nanoparticles had a lower onset potential than Co_3O_4 and performed with lower overpotentials at low current densities ($<20 \text{ mA cm}^{-2}$), however they suffered from higher overpotentials when compared to Co_3O_4 at higher current densities ($>20 \text{ mA cm}^{-2}$). The nickel modified Co_3O_4 nanoparticles were superior to the other $\text{M}_x\text{Co}_{3-x}\text{O}_4$ materials at all current densities measured (0-100 mA cm^{-2}).

To my family

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Meredith J. McMurdo

Chapter 1

New Strategies Toward the Synthesis of Rhodium Nanoparticles

Introduction

The widespread use of rhodium as an industrial catalyst, along with its high cost and rarity, has generated research aimed at the synthesis of rhodium metal catalysts that operate with maximum per-atom efficiency. Since heterogeneous catalysis is based on surface reactions, small nanoparticles offer an attractive approach for optimization of such catalysts, due to their high surface area to volume ratio. Recent developments in nanoparticle synthesis allow considerable control over the nanoparticle's size and shape.¹ Shape and size control in nanoparticle systems of various metals have been widely reported; however not until a recent publication from the Tilley and Somorjai groups had a system been demonstrated for nanoscale shape and size control been demonstrated with rhodium.² Since this initial publication, other research groups have reported related rhodium nanoparticle synthetic systems also affording shape and size control.³⁻⁵

Most reports on monodisperse rhodium nanoparticles share a few common features: the precursor is usually rhodium trichloride (anhydrous or as the hydrate), the precursor is decomposed by a polyol reduction method, and the surfactant used to stabilize the rhodium nanoparticle surface is polyvinylpyrrolidone (PVP).^{2,3,6} This is not unexpected, as rhodium trichloride is a readily available starting material, however strong reducing conditions are necessary for the decomposition to rhodium metal due to the complicated mechanism for reduction from the 3+ oxidation state. Also, PVP affords a high degree of control during various metallic nanoparticle syntheses. However, consideration of the commonly regarded mechanism for nanoparticle formation, including nucleation and growth⁷ suggests that there should be better approaches to the synthesis of metallic nanoparticles with precursors that decompose more readily, and with shape directing stabilizers that offer better particle size and shape dispersity.

Various reports describe nanoparticle formation kinetics.⁷⁻¹⁰ Briefly, nucleation occurs under conditions (including concentration of the monomer and temperature of the solution) that allow aggregation of monomer units to form a cluster. The role of the stabilizer is to allow expansion of the cluster while preventing the cluster from becoming too large as the system approaches the thermodynamic minima, corresponding to bulk metal. However, once a stable cluster (seed particle) is formed, growth can also occur, as additional monomer units are added to increase the size of the cluster. In general, fast precursor decomposition is regarded as the best way to produce nuclei with the highest degree of monodispersity; however, slow, controlled precursor decomposition allows the already present nuclei to grow uniformly. Potentially improving on these syntheses, rhodium trichloride (which requires harsh decomposition conditions) could be replaced with a precursor for which the decomposition is more controlled.

Chemical vapor deposition (CVD) precursors have been used for controlled decomposition by thermal methods. A thorough review of rhodium complexes studied as CVD complexes compares synthetic yields, deposition quality and other characteristics such as volatility.¹¹ This data was considered when choosing the CVD complexes to study in the present work. The complexes $\text{RhCp}(\text{C}_2\text{H}_4)_2$ and $\text{Rh}(\text{hfacac})(\text{CO})_2$ were chosen due to their ability to produce high quality films and their ease of synthesis.^{12,13} Thus, the first part of this chapter details the synthesis and characterization of such CVD rhodium precursors for the formation of rhodium nanoparticles.

Another potential improvement on nanoparticle synthesis is based on the nature of the nanoparticle stabilizer. PVP is a nanoparticle stabilizer that has yielded excellent results in terms of shape controlled nanoparticle synthesis, although it is unknown whether PVP is a shape-directing stabilizer or if thermodynamic factors dictate the resultant nanoparticle shape.^{2,3,6} However, a problem with PVP is that it strongly binds to the nanoparticle surface strongly. This poses potential problems for catalysis, because surface-bound ligands should be labile, to allow efficient diffusion of substrates to the rhodium surface. Also, the ability for surface modification due to the inherently labile nature of molecular stabilizers would be advantageous in order to adapt these nanoparticles to different solvent and stabilizer systems for various applications. This chapter describes attempts to prepare rhodium nanoparticles with new stabilizers, both polymeric and molecular in nature. Polymer stabilizers that have hydrolysable units (unlike PVP) could be advantageous in that they may be readily removed after the nanoparticles have been formed. The use of molecular stabilizers is also an attractive approach to nanoparticle synthesis; as such surface ligands may be more easily removed. Molecular stabilizers prevent aggregation of nanoparticles via electrostatic interactions or steric factors.¹⁴ Non-polymeric syntheses involving micelles have been widely reported for metal nanoparticles,^{15,16} however charge-neutral, molecular stabilizers that have been developed for semiconducting nanoparticles¹⁷ have been limited in scope for metal nanoparticles,¹⁸⁻²⁰ and are unexplored but for a few examples with rhodium nanoparticle systems.^{4,21} Various research groups have reported the replacement of surface species after nanoparticle formation with molecular stabilizer ligands, and a recent in-depth study describes details of such an exchange.²²

Results and Discussion

Decomposition of RhCp(C₂H₄)₂. The complex RhCp(C₂H₄)₂ was prepared according to the literature and was sublimed prior to use.¹² The complex was studied by differential scanning calorimetry (DSC) in order to observe an exotherm characteristic of precursor decomposition. This data is shown in Figure 1. Of note are the melting point (endotherm) at 73° C and the decomposition (endotherm) centered around 150° C, shown in the inset of Figure 1. Also, an exotherm begins slightly before 400° C, likely corresponding to a phase transition in the rhodium.

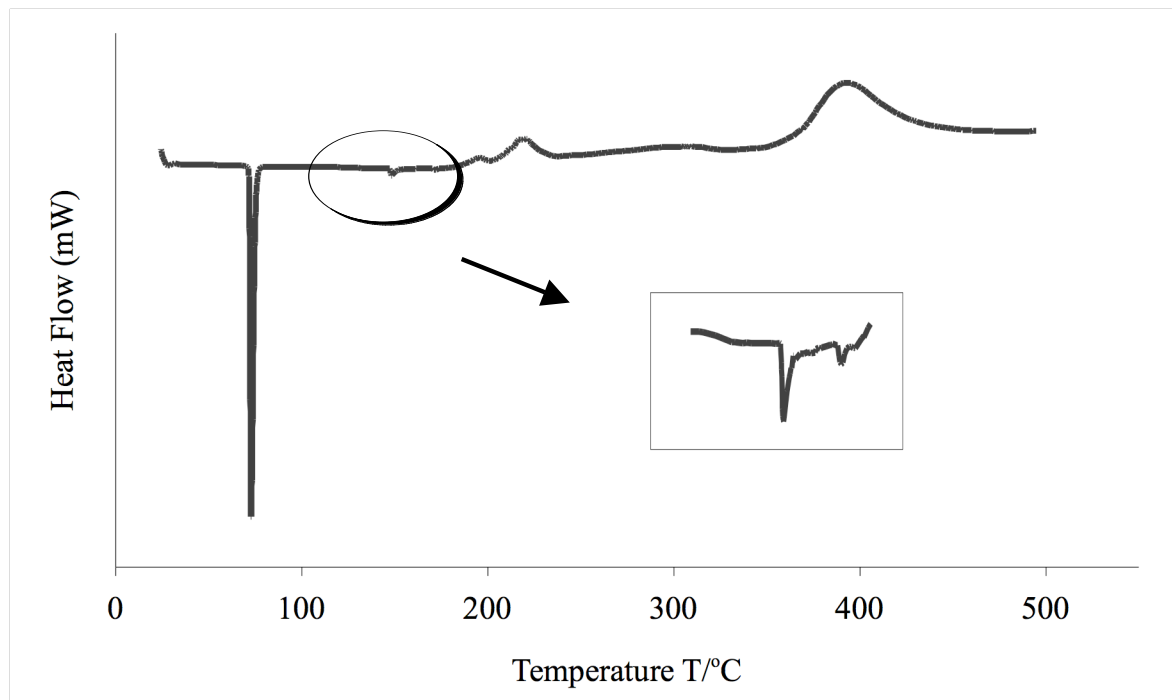


Figure 1. DSC trace for $\text{RhCp}(\text{C}_2\text{H}_4)_2$. Inset shows area centered around 150° C, indicating a probable decomposition endotherm.

Although DSC provides some insight into the decomposition behavior of $\text{RhCp}(\text{C}_2\text{H}_4)_2$, decomposition of the complex was also studied in solution since nanoparticle formation will occur in this phase. NMR spectroscopy was used to monitor the decomposition of the complex by observation of the change in integration of the ^1H peaks from the ligands attached to the metal. A sealed J-Young tube containing $\text{RhCp}(\text{C}_2\text{H}_4)_2$ dissolved in $\text{DMSO}-d_6$ was heated for 10 minutes at 10° intervals up to 120° C in the probe of the NMR spectrometer. However, this was the highest accessible temperature for the NMR instrument, and minimal loss of the cyclopentadienyl complex was observed (by NMR spectroscopy). Therefore, the sealed J-Young tube was heated with a temperature-controlled oil bath for 10 minutes at temperatures in 10° intervals beginning with 130° C and after each interval, an NMR spectrum recorded. Peak integration at each interval related to peak integration of the complex before heating was used to determine a percent decomposition of the complex. This data is illustrated in Figure 2. Thus it was concluded that slow decomposition occurs for this complex at 130° C; however, fast decomposition occurs at temperatures above 150° C.

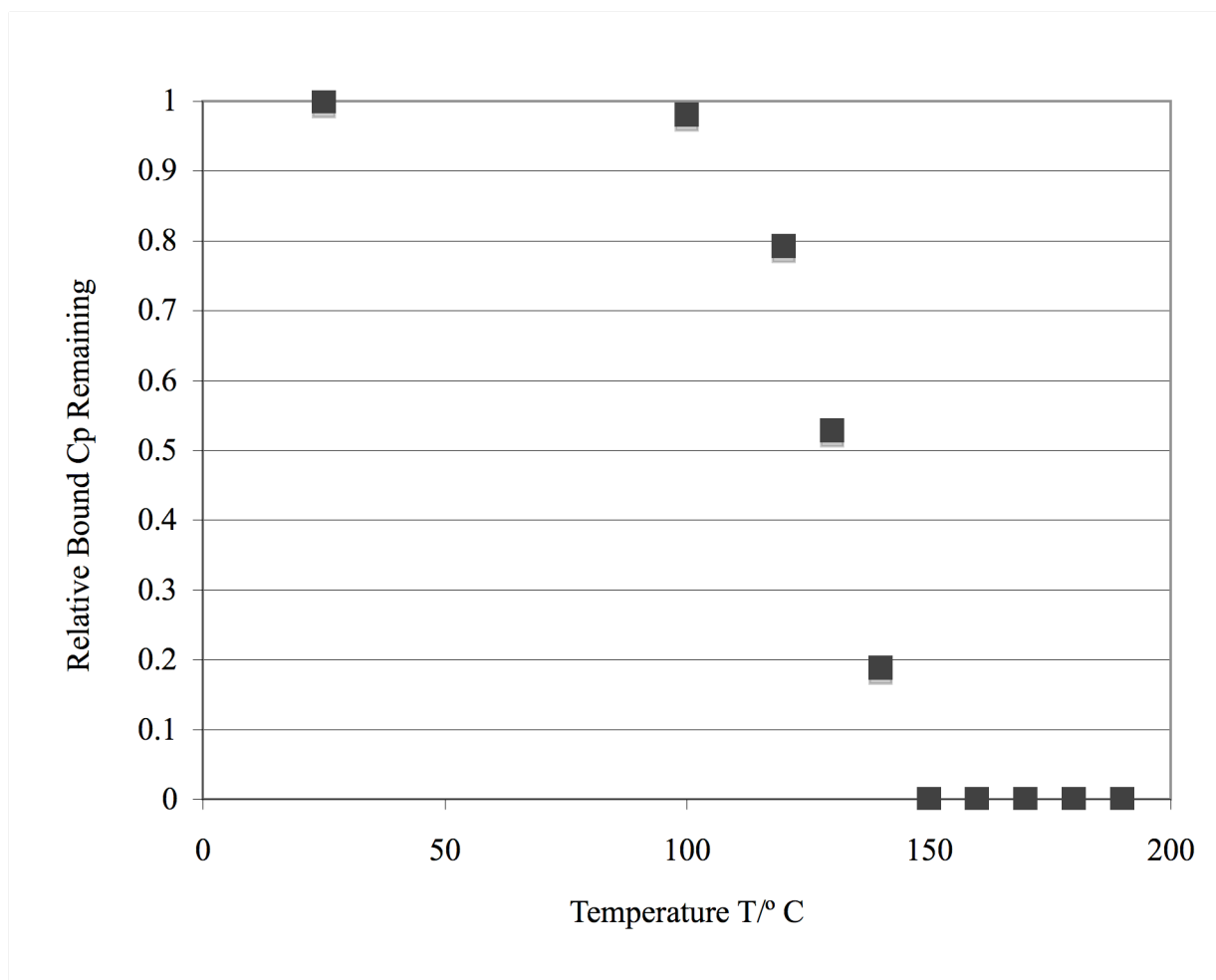


Figure 2. Relative amount of Cp remaining bound to rhodium based on the integration of the Cp peaks by ^1H NMR. After 10 minutes at 150° C, there was no peak integration of the bound Cp ligand.

Decomposition of $\text{Rh}(\text{hfacac})(\text{CO})_2$. The complex $\text{Rh}(\text{hfacac})(\text{CO})_2$ was prepared according to the literature and sublimed prior to use.¹³ The DSC trace was recorded and is shown in Figure 3. Two exotherms occur between 25 and 200° C, the first being the melting point at 77° C, and the second most likely the decomposition at 176° C. The decomposition exotherm for $\text{Rh}(\text{hfacac})(\text{CO})_2$ is sharper than that $\text{RhCp}(\text{C}_2\text{H}_4)_2$, which occurs at a higher temperature.

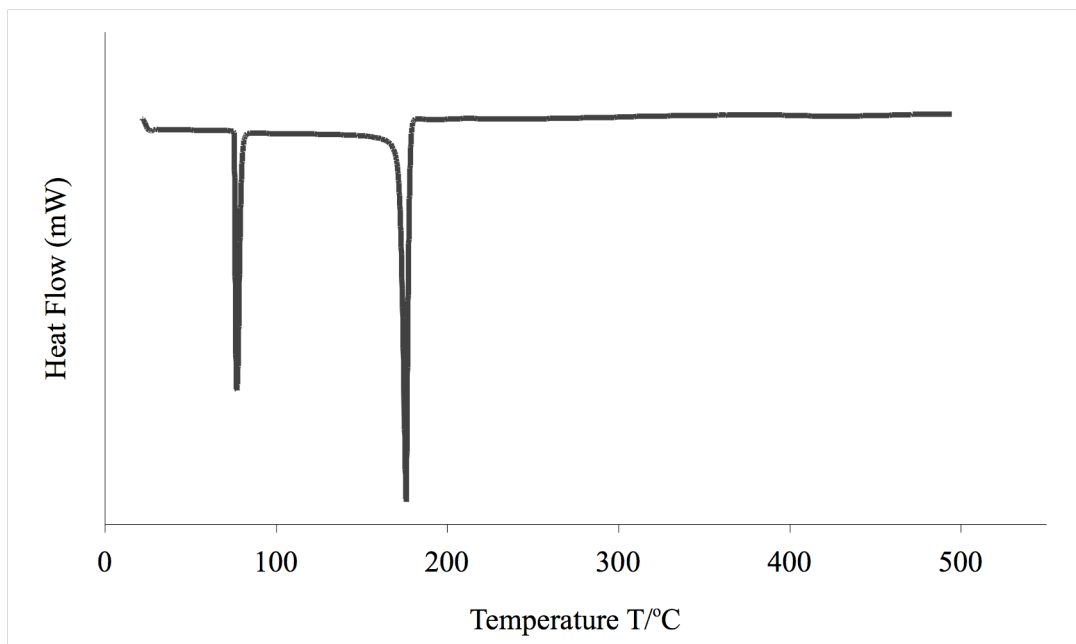


Figure 3. DSC trace for Rh(hfacac)(CO)₂ showing two distinct exotherms corresponding to the melting point and decomposition respectively.

The decomposition behavior of Rh(hfacac)(CO)₂ was also studied as a solution in DMSO-*d*₆ by NMR spectroscopy. As predicted by the DSC data, solution decomposition of this precursor began at higher temperatures than that for the RhCp(C₂H₄)₂ (Figure 4). However, even 10 minutes at 180° C was not sufficient to entirely decompose the rhodium complex. If this complex were to be used as a rhodium nanoparticle precursor, slow decomposition could be achieved at temperatures around 160° C, however fast (under 10 minute) decomposition would most likely require temperatures in excess of 200° C.

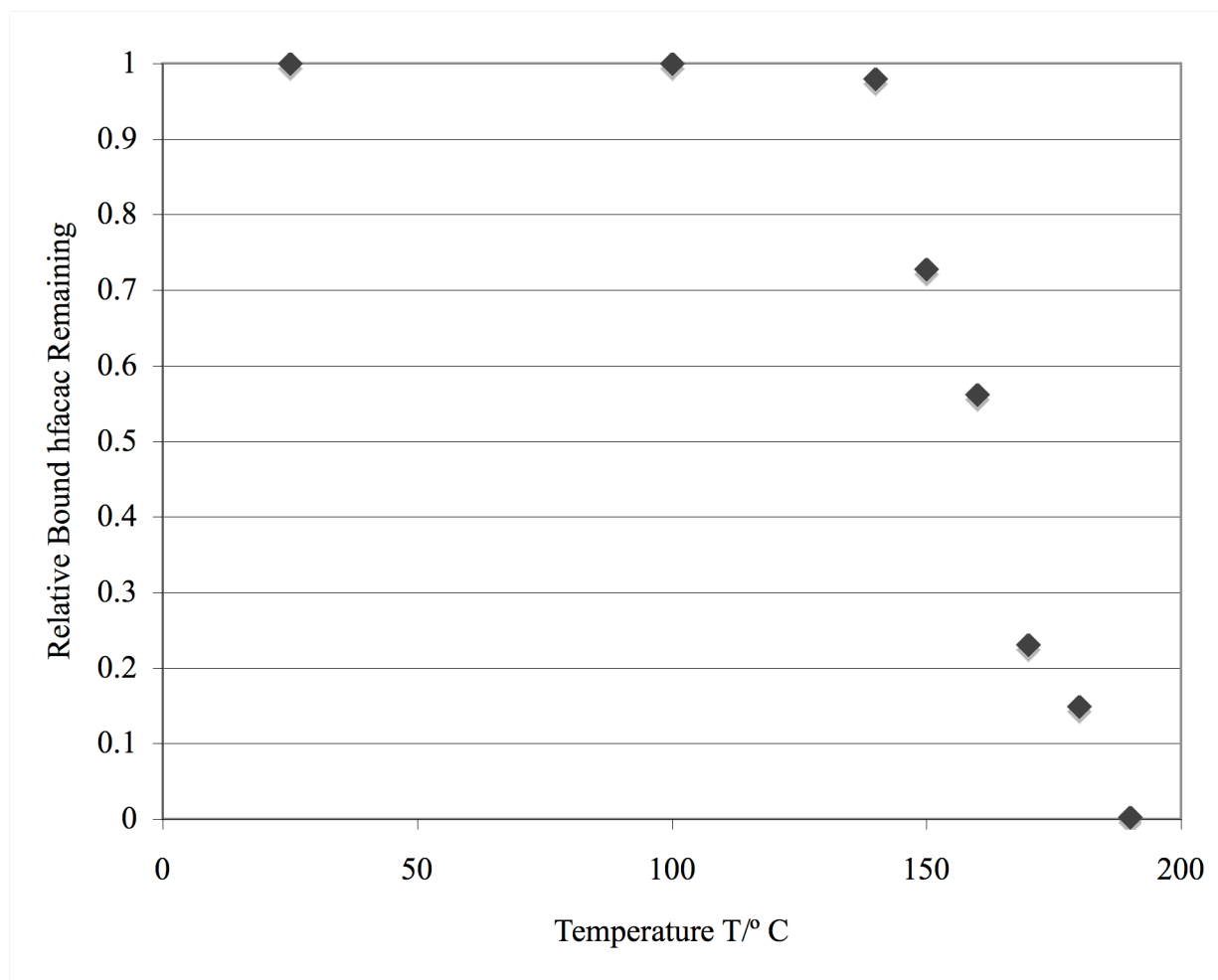


Figure 4. Relative amount of hfacac remaining bound to rhodium based on the integration of the hfacac peaks by ^1H NMR. After 10 minutes at 190° C, peak integration of the bound hfacac was zero.

Nanoparticle formation attempts with polymeric stabilizers. Poly(ethylene succinate), (PES, $(\text{OCH}_2\text{CH}_2\text{O}_2\text{CCH}_2\text{CH}_2\text{CO})_n$), was attempted as a nanoparticle stabilizer. The presence of a carbonyl group in this stabilizer could allow for coordination to the metallic rhodium surface, and oxygen in the backbone may allow for hydrolysis of the ligand after nanoparticle formation has occurred. Various syntheses were attempted with this polymeric ligand. The first attempt was patterned after related procedures known to produce rhodium particles, by decomposing $\text{RhCl}_3 \cdot x\text{H}_2\text{O}$ (40% Rh) in the presence of PES as a solution of ethylene glycol² (polyol reduction reagent²³). Whereas the product of the corresponding reaction with PVP is a brown solution of stabilized nanoparticles, the product of the reaction involving PES was a brown precipitate, indicating that rhodium nanoparticles were not stabilized by this system. Solubility tests indicated that PES was soluble in hot THF, thus THF (tetrahydrofuran) was attempted as the solvent. The rhodium precursor chosen was $[(\text{COD})\text{RhCl}]_2$ (COD = 1,5-cyclooctadiene) also due to its solubility in THF. Hydrazine and NaBH_4 were both screened as

reductants, however the rhodium precursor did not decompose with hydrazine (and hence no nanoparticles formed). A brown precipitate appeared when NaBH_4 was added to the solution, which precipitated out of solution upon cooling. The particles isolated were imaged by TEM and appeared polydisperse (Figure 5).

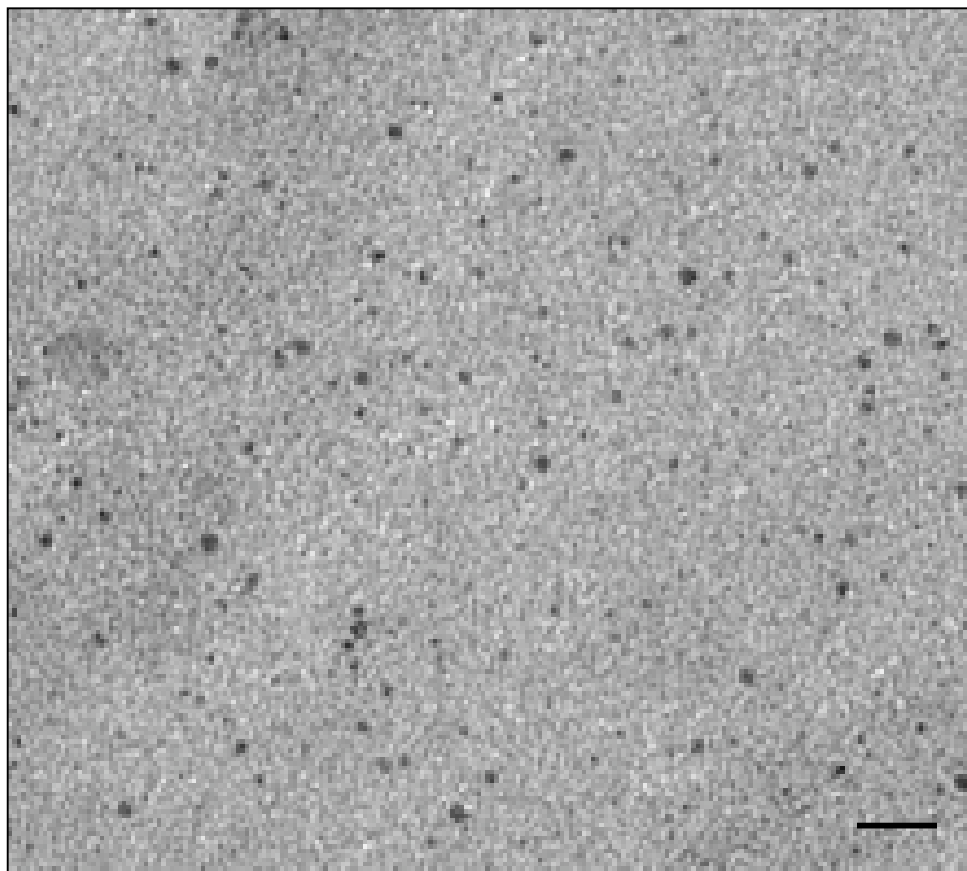


Figure 5. Representative TEM image of rhodium nanoparticles isolated in the reaction with polyethylene succinate stabilizer. Bar corresponds to 20 nm.

Polyethylenimine (PEI, $(\text{CH}_2\text{CH}_2\text{NH})_n$) was also attempted as a polymeric stabilizer, however with little success. This polymer has nitrogen in the polymer backbone, possibly suited for polymer decomposition after nanoparticle formation. Similar to the case with polyethylene succinate, hydrazine was insufficient to decompose the rhodium precursor, $[(\text{COD})\text{RhCl}]_2$. When NaBH_4 was utilized as a reductant, a black precipitate immediately formed, indicating that no nanoparticle stabilization had taken place, as the rhodium metal fell out of solution. Also, a reaction was attempted in ethylene glycol (solvent and reductant) with $\text{RhCl}_3 \cdot x\text{H}_2\text{O}$ (40% Rh) as the precursor, however no decomposition of rhodium (color change to brown) occurred even at 180°C .

The next polymeric stabilizer attempted in the synthesis of rhodium nanoparticles was poly(DL-lactide), another polymer with oxygen bridges in the polymer backbone and carbonyl groups. THF was the solvent choice due to the solubility of both the polymer and $[(\text{COD})\text{RhCl}]_2$. Poly(DL-lactide) was dissolved in 40° C THF and $[(\text{COD})\text{RhCl}]_2$ was added dropwise. After the addition of NaBH_4 , a brown color developed over 5 minutes. This indicated that rhodium nanoparticles had formed in solution. After cooling, the particles were centrifuged from the THF solution, however they remained well dispersed in THF after sonication. A TEM image is shown in Figure 6. The particles appear small (approximately 3 nm in diameter), however somewhat aggregated. Nevertheless, they have a monodisperse size distribution, and are well dispersed in THF.

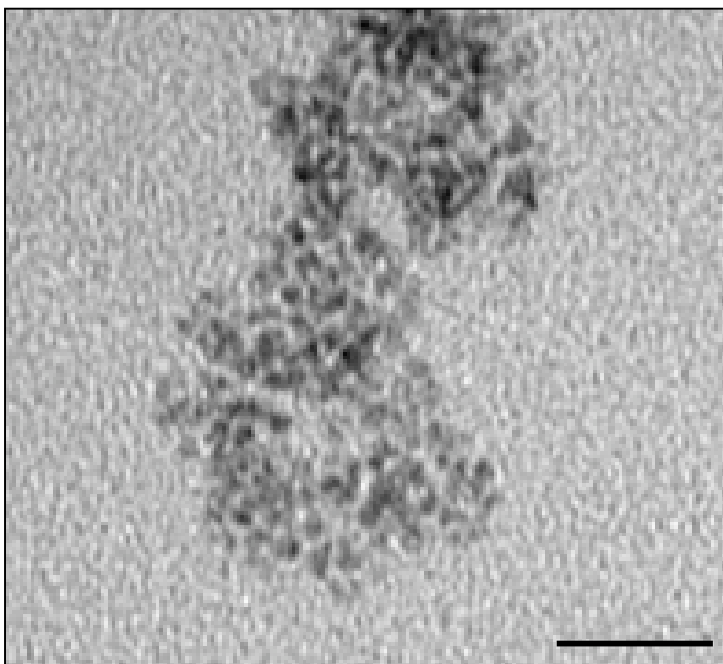


Figure 6. Representative TEM image of rhodium nanoparticles synthesized with poly(DL-lactide) stabilizer. Bar corresponds to 20 nm.

Nanoparticle formations with molecular stabilizers. Molecular stabilizers were explored as possible rhodium nanoparticle stabilizers. Since this class of stabilizers had been unexplored for rhodium, there were many possibilities to screen. (As far as we know, there is currently one report detailing oleylamine-stabilized rhodium particles)⁴ Although many stabilizers were tested, they all shared two characteristics: a donor atom or functional group with at least one lone-pair of electrons for coordination to the metallic rhodium surface, and a long alkyl chain for protection against particle agglomeration. This pursuit led to the testing of various functionalized stabilizers such as trioctylphosphine oxide, oleic acid, dodecylamine, octylphosphonic acid and octadecylphosphonic acid. The decomposition of the precursor $\text{RhCp}(\text{C}_2\text{H}_4)_2$ has been previously studied, and it is soluble in most nonpolar organic solvents. Thus, this precursor is well suited for systems containing high boiling point, non-coordinating

solvents and stabilizer molecules with long alkyl chains. This precursor was chosen for use as the rhodium source in the experiments with molecular stabilizers.

In a typical experiment, the stabilizer in octadecane or decane was heated to 160-180° C with constant stirring under a N₂ atmosphere. Then, RhCp(C₂H₄)₂ in a small amount of octadecane was quickly injected into the hot solution and the nanoparticles developed at this temperature over at least 1 h. The use of trioctylphosphine oxide (TOPO) has been shown in the past to stabilize various semiconductor nanoparticles¹⁷ and was employed for the stabilization of rhodium nanoparticles. The ratio of TOPO to rhodium attempted was 50 to 1, and the product upon isolation of the brown precipitate (only a small amount was isolated as a brown powder) was a mixture of larger (5-10 nm) and smaller (2-3 nm) nanoparticles (by TEM). These same conditions were employed with addition of 1,2-hexadecanediol as a mild reductant. Similar results were obtained, and it was difficult to isolate a solid product; and thus the use of this stabilizer was abandoned.

Oleic acid was also employed as a rhodium nanoparticle stabilizer, in the ratio of oleic acid to rhodium of 50 to 1. After the injection of RhCp(C₂H₄)₂ into a solution of oleic acid in octadecane, a brown color indicative of nanoparticle formation occurred after only 10 s. The reaction was continued for an hour, however isolation of any brown precipitate (rhodium nanoparticles) could not be accomplished by precipitation and centrifugation of the solution. This could be due to a small size of clusters or particles, which could be difficult to precipitate from solution. Another attempt to form rhodium nanoparticles utilized neat oleic acid at 180° C. After cooling the reaction flask, it could be seen that instead of the formation of a characteristic brown color, a bright purple-pink solution had resulted instead. The solution was determined by UV-Vis spectroscopy to have a maximum absorbance value of 524 nm. Although isolation of this rhodium species from the oleic acid was not accomplished, the synthesis bears resemblance to the formation of the complex Rh₂(OAc)₄, a blue-green complex. Further heating of this mixture to 300° C gave the precipitation of rhodium bulk metal instead of nanoparticle formation, and its use was therefore discontinued.

The use of dodecylamine was also attempted for rhodium nanoparticle stabilization. Decane was used as the solvent, the dodecylamine to rhodium ratio was 10 to 1, and the reaction was run at 180° C. Similar to the case with TOPO, a brown solution resulted at the end of a 1 h reaction time, however precipitation of any particles from solution could not be accomplished. The addition of 1,2-hexadecanediol to the reaction mixture was also attempted. In this case however, a brown precipitate was isolated and analyzed by TEM. Strangely, the observed structures formed had grown anisotropically as in the case of a rod, however they appeared crooked (Figure 7). It is unclear whether these structures are single crystals or aggregated particles.

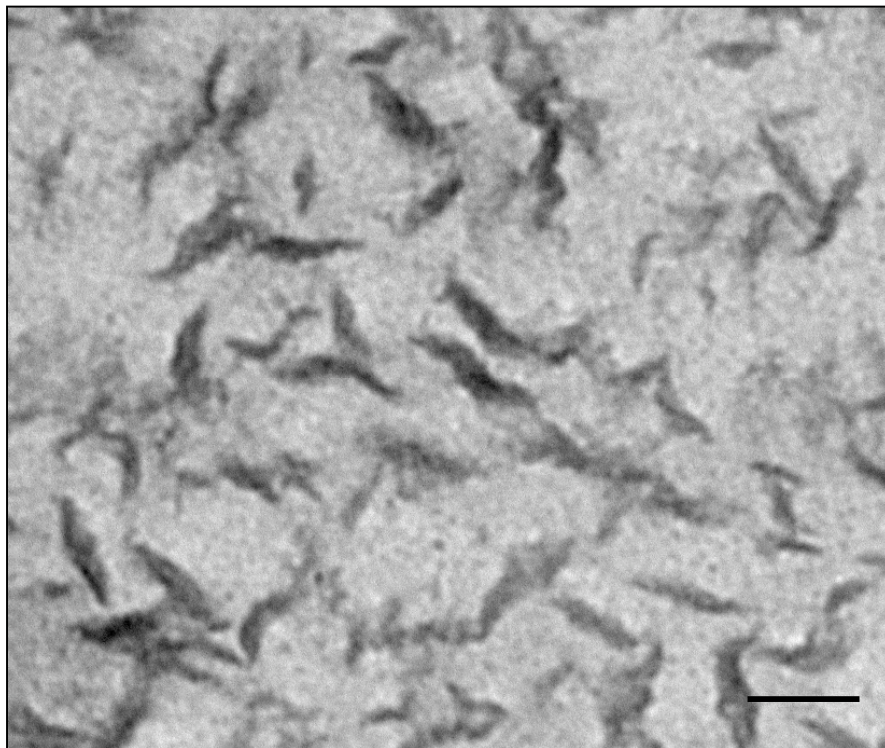


Figure 7. Representative TEM image of nanoparticle structures formed in the presence of the stabilizer dodecylamine. Bar corresponds to 100 nm.

Phosphonic acid stabilizers, previously used as structure-directing agents for semiconductor nanoparticles, were also examined in the synthesis of rhodium nanoparticles. Octylphosphonic acid and octadecylphosphonic acid were both employed as stabilizers with the solvent decane at 180° C, and with a stabilizer to rhodium ratio of 10 to 1. Although octylphosphonic acid did not stabilize any nanoparticles as indicated by the precipitation of bulk metal (during the synthesis), octadecylphosphonic acid-stabilized particles formed during the course of the 1 h reaction as indicated by the formation of a brown-colored solution ca. 10 min after rhodium injection during the synthesis. These nanoparticles were easily precipitated by the addition of hexanes and isopropanol to the final solution, and a powder was obtained that could be dispersed in acetone or methylene chloride. The uses of these small rhodium particles as seeds are further discussed in Chapter 3. A TEM image of the particles is shown in Figure 8 along with a corresponding histogram of their diameters. They are small, faceted and have a narrow size distribution (1.92 ± 0.16 nm). Due to this small size, no peaks are observed by powder XRD. They are air stable over months, and can be used subsequently in nanoparticle growth experiments, as explained further in chapter 3.

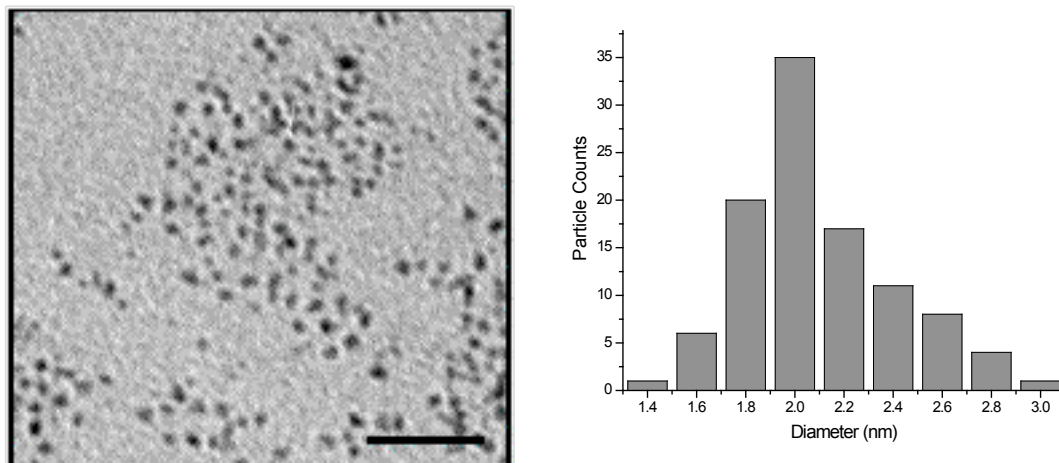


Figure 8. Representative TEM image of rhodium-ODPA seed particles and corresponding size distribution histogram obtained from particle counting. Bar corresponds to 20 nm in TEM image.

Conclusions

New synthetic approaches towards the synthesis of rhodium nanoparticles have been attempted. The decomposition of CVD rhodium precursors were studied by DSC and NMR and were shown to be suitable for rhodium nanoparticle formation. Also, new stabilizers were attempted for the synthesis of rhodium nanoparticles, both polymeric and molecular in nature, in order to replace the widely used PVP polymeric stabilizer. Although various polymeric stabilizers were able to effectively produce stable rhodium nanoparticles, none exhibited comparable control attained by PVP. However, various molecular stabilizers were also attempted for the synthesis of rhodium nanoparticles, and small, stable particles were synthesized with ODPA as a surface stabilizer. Further synthetic manipulations with these small particles in Chapter 3 will highlight the ability of these particles to act as seed particles in the synthesis of larger rhodium nanoparticles.

Experimental Procedures

General procedures. All experiments and manipulations were conducted in a nitrogen atmosphere either by standard Schlenk techniques or in a Vacuum Atmospheres dry box unless otherwise noted. Dry, oxygen free solvents were used throughout. $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ and $\text{RhCl}_3 \cdot x\text{H}_2\text{O}$ (40% Rh) were purchased from Aldrich and used as received. Polyvinylpyrrolidone, polyethylene succinate, polyethylenimine, and poly(DL-lactide) were also purchased from Aldrich. The following rhodium complexes were prepared according to literature-based preparations and sublimed prior to use: $\text{RhCp}(\text{C}_2\text{H}_4)_2$ ¹² and $\text{Rh}(\text{hfacac})(\text{CO})_2$ ¹³.

Characterization. DSC analysis was carried out on a TA Instruments DSC 2010 with a heating rate of $1^\circ \text{C min}^{-1}$ from room temperature to 500°C under a flow of nitrogen. Solution state ^1H NMR was recorded at 400 MHz using a Bruker AVB-400 spectrometer. Transmission

electron microscopy (TEM) was carried out on a Technai G2 S-twin operating at 200 keV. Samples were prepared by drop casting a solution of the nanoparticles on carbon-coated copper 400 mesh grids purchased from Ted Pella, Inc.

Synthesis of rhodium nanoparticles with polyethylene succinate. Reaction was completed in open air. Polyethylene succinate (64.2 mg, 0.45 mmol based on monomer unit) was added to 10 mL THF and heated to 50° C. A solution of [(COD)RhCl]₂ (10.6 mg, 0.044 mmol Rh) was prepared in 1 mL THF and added to the hot THF solution dropwise. The reducing agent, NaBH₄ (1.6 mg, 0.042 mmol) was added as a solution in 1 mL water, and the reaction continued at 50° C for 1 h before cooling to room temperature. A brown precipitate settled out of solution overnight and was isolated and dropped on a TEM grid for further analysis.

Synthesis of rhodium nanoparticles with poly(DL-lactide). Reaction was completed in open air. Poly(DL-lactide) (30.1 mg, 0.42 mmol) was dissolved in 10 mL THF and heated to 40° C. [(COD)RhCl]₂ (10.0 mg, 0.041 mmol) was dissolved in 1 mL THF and added dropwise to the solution of poly(DL-lactide). Next, NaBH₄ (1.7 mg, 0.45 mmol) in a small amount of water was added to the stirring solution of polymer and rhodium precursor. An opaque brown color immediately formed in the solution, indicating rhodium nanoparticles had formed. Reaction was stirred at 40° C for 30 minutes, and then particles were isolated by centrifugation. They were dispersed in THF and dropped on a TEM grid for analysis.

Synthesis of rhodium nanoparticles with RhCp(C₂H₄)₂ and various molecular stabilizers. In a typical experiment (unless otherwise noted), 5 mL of either decane or octadecane was heated to 180° C with 50 equivs of the indicated stabilizer (based on 10 mg RhCp(C₂H₄)₂). Then, RhCp(C₂H₄)₂ (0.010 g, 0.045 mmol) in 0.5 mL of decane or octadecane was injected quickly into the heated stirring solution and held at 180° C for 1 hour before slowly cooling to room temperature. Precipitation of the rhodium nanoparticles was attempted by the addition of isopropanol or ethanol to the reaction mixture and a centrifuge was used to isolate the particles from the supernatant. Occasionally, 1,2-hexadecanediol (0.012 g, 0.045 mmol) was incorporated into the hot stabilizer/solvent mixture before the injection of the rhodium complex to aid in decomposition (when noted).

Synthesis of rhodium nanoparticles with ODP. In a typical reaction, octadecylphosphonic acid (ODPA) (0.016 g, 0.048 mmol) was added to 15 mL of decane and the mixture was heated to 180° C. Cyclopentadienyldiethylene-rhodium(I) (0.010 g, 0.045 mmol) was dissolved in 1 mL of decane and this solution was then quickly injected via syringe into the stirred solution (1200 rpm) of octadecylphosphonic acid and decane at 180° C. The resulting solution was held at 180° C for 1 hour before it was cooled to room temperature at a rate of 60° C per hour. The particles were then precipitated by addition of hexanes (20 mL) and isopropanol (60 mL), followed by centrifugation of the mixture at 6000 rpm for 10 minutes. The supernatant was decanted away and the precipitate was subsequently dissolved in chloroform (15 mL), and then precipitated once more with 2-propanol (30 mL) before a second centrifugation step was used to facilitate isolation and further purification of the particles. This yielded a brown powder, which was vacuum dried before analysis. However, it is best to redissolve this powder immediately (without vacuum drying) for further use of the particles as a stock solution in chloroform. Elemental analysis was performed to roughly determine the percentage of stabilizer

(and consequently rhodium) in the stock solution. Anal. Found: C, 27.77; H, 4.05. The synthetic procedure was successfully scaled up by a factor of 10, to give samples with the same properties.

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Chapter 2

Small Rhodium Seed Particles Synthesized by a Concurrent Hydrogenation Method

Introduction

Rhodium metal is widely used in industrial applications, as it catalyzes a variety of reactions with high activity and selectivity. However, the increasing use and rising cost of this metal of low abundance has led researchers to establish routes to rhodium catalysts that make the most efficient use of this precious metal with the highest possible atom economy. Many of these catalysts are heterogeneous; being composed of rhodium particles dispersed onto an appropriate support, and therefore affords the advantage of being easily recycled. Research in nanoparticle chemistry has led to the discovery that increasing the surface area to volume ratio of the particle can be used to optimize chemical reactivity.^{1,2} The work described herein addresses the synthesis of small, monodisperse rhodium nanoparticles that are stable under a variety of reaction conditions and active in catalytic transformations.

The efficiencies of nanoparticle catalysts are thought to strongly depend on the surface properties of the catalytic particle, and clean, crystalline surfaces are considered ideal for catalysis.³ Bulky ligands or surfactants may crowd the active sites and prevent the diffusion of reaction species, thus limiting catalytic turnover. Conversely, lack of nanoparticle stabilization can cause sintering or aggregation during catalysis, thus affecting the lifetime of the catalyst and lowering the number of active surface sites in a sample. Another important consideration is the chemical precursors used to obtain the catalyst, and the yield of the resulting nanoparticle sample. Single source precursors, or precursors containing a ligand that can subsequently serve as an effective nanoparticle stabilizer, are promising starting points for direct, high yield routes to nanoparticles.

The Finke Group has considered many of these important factors in studying routes to iridium (and other transition metal) nanoparticles.⁴ This research has utilized single source, molecular precursors in the formation of nanoparticles, and the kinetics of this process has been monitored through concurrent hydrogenation studies (in most cases the hydrogenation of cyclohexene, but also other reactions⁵). In most of these nanoparticle formation reactions, it has been found that the kinetics of hydrogen uptake during nanoparticle formation directly correlate to the number of active surface sites available for hydrogenation catalysis.⁴ These active surface sites are formed in the course of the catalysis, and therefore hydrogen uptake is correlated to nanoparticle surface growth kinetics. This nanoparticle synthesis has been found to fit the Finke-Watzky two-step mechanism,⁶ which includes a nucleation step (eq 1) and an autocatalytic growth step (eq 2). In these equations, “A” represents the nanoparticle precursor and “B” represents the hydrogenation catalyst(s), most likely a nanoparticle species. Due to the nature of this two-step process, the alteration of k_1 and k_2 values through changing reaction conditions, allows control the nanoparticle size.⁷



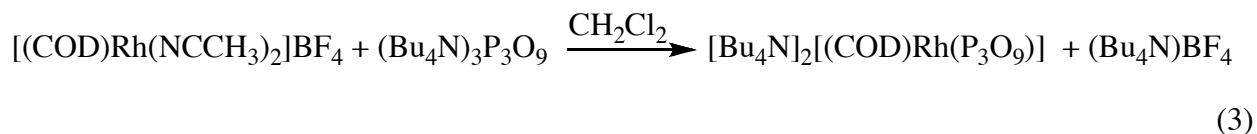
The approach outlined above for control of nanoparticle size via a concurrent hydrogenation reaction appeared to offer an attractive opportunity for the synthesis of rhodium nanoparticles of discrete size. In the synthesis of iridium nanoparticles described above, the

nanoparticle stabilizer is a combination of a polyoxoanion ($P_2W_{15}Nb_3O_{62}^{9-}$) with a Bu_4N^+ cation. The stabilization of rhodium nanoparticles with such polyoxoanions was also observed.^{8,9} Additionally, smaller anionic stabilizers, including HPO_4^{2-} , citrate³⁻, polyacrylateⁿ⁻, and Cl^- were also shown to stabilize iridium nanoparticles.^{10,11} Small iridium nanoparticles were obtained by use of single-source precursors, or by addition of a precursor and stabilizer in separate steps.⁹ Thus similar methods were investigated in this work for the synthesis of small rhodium nanoparticles.

The monohydrogen phosphate dianion seems to be a promising nanoparticle stabilizer for the synthesis of catalytic nanoparticles, since this species should be readily displaced by substrates for catalysis. Iridium nanoparticles with this stabilizer showed good air and water stability, and were easily prepared using a single source precursor, or by the combination of an Ir(I) precursor with $(Bu_4N)_2HPO_4$ prior to hydrogenation.¹⁰ Various tetrabutylammonium phosphate stabilizers, as well as a citrate stabilizer, were therefore explored in the synthesis of rhodium nanoparticles by the concurrent hydrogenation method. Also, synthetic parameters relating to the nanoparticle formation were optimized, and experiments pertaining to the mechanism of formation were attempted. This report also describes two newly synthesized single-source precursors that contain both rhodium and the HPO_4^{2-} stabilizer: $[Bu_4N]_2[(COD)Rh(P_3O_9)]$ (**1**) (COD = 1,5-cyclooctadiene) and $[Bu_4N]_2[(COD)_2Rh_2(P_2O_7)]$ (**2**). The rhodium complex $[(COD)RhH]_4$ was also studied as a potential precursor to nanoparticles.

Results and Discussion

Synthesis and characterization of 1 and 2. The complex $[Bu_4N]_2[(COD)Rh(P_3O_9)]$ (**1**) was prepared by the addition of $(Bu_4N)_3P_3O_9$ to $[(COD)Rh(NCCH_3)_2]BF_4$ in methylene chloride, and was isolated as a yellow powder by precipitation from hot acetone solution by the slow addition of diethyl ether (eq 3).



Peak integration of the room temperature 1H NMR spectrum was consistent with a 2 to 1 ratio of the $[Bu_4N]^+$ cation to the COD ligand. The 1H and ^{13}C NMR resonances for the COD ligand are analogous to those observed for the corresponding iridium complex.¹²

Attempts to synthesize the monophosphate rhodium complex were unsuccessful. The reaction of $[(COD)Rh(NCCH_3)_2]BF_4$ with $(Bu_4N)_2HPO_4$ produced a mixture of products by 1H NMR spectroscopy, and a single product could not be isolated. This is perhaps not surprising, since the corresponding reaction with the iridium analog produces a monophosphate polymer. However, crystals were grown in a solution of the reaction mixture in a mixture of ethyl acetate and ether at $-78^\circ C$, and yellow crystals of **2** were separated by the Pasteur method.

The molecular structures of **1** and **2** determined by single crystal X-ray crystallography are shown in Figures 1 and 2, respectively. The structure of **1** revealed an unexpected binding mode for the $P_3O_9^{3-}$ ligand. In the case of the iridium analog, three oxygen atoms interact with

metal center;¹² however, in the case of rhodium complex **2**, only two oxygen interactions are observed (Figure 1). The structure of **2** revealed that the isolated yellow crystals are $[\text{Bu}_4\text{N}]_2[(\text{COD})_2\text{Rh}_2(\text{P}_2\text{O}_7)]$ (Figure 2). This observation points to the ability of $(\text{Bu}_4\text{N})_2\text{HPO}_4$ to form the diphosphate, $(\text{Bu}_4\text{N})_4\text{HP}_2\text{O}_7$, under the given reaction conditions. The likely presence of the monophosphate and the diphosphate in this reaction mixture most likely led to the formation of several reaction products. Table 1 provides selected bond distances and bond angles for **1**, and various crystallographic parameters are included in Table 2.

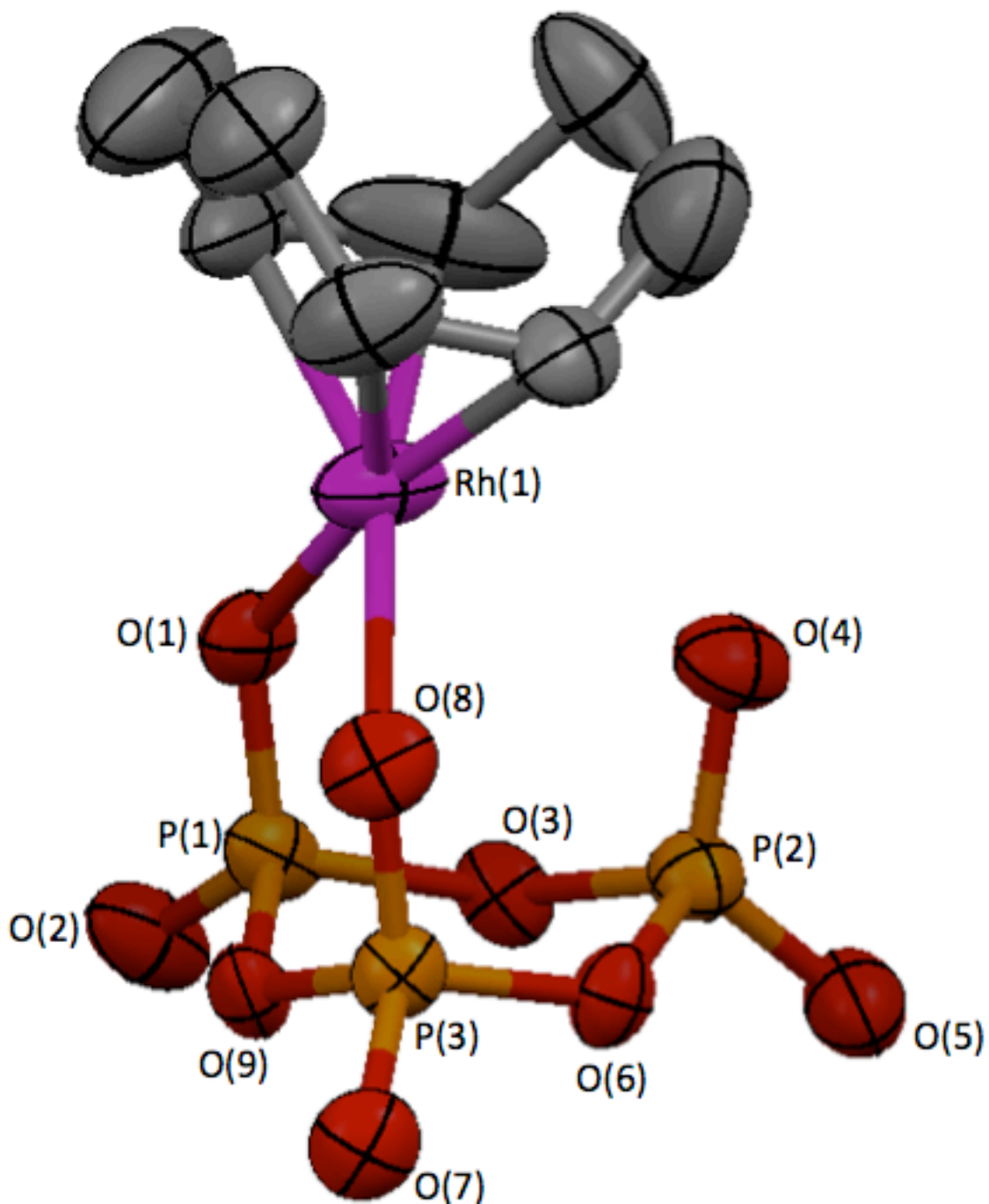


Figure 1. Molecular structure of **1** with thermal ellipsoids at 50% probability. Hydrogen atoms were omitted for clarity.

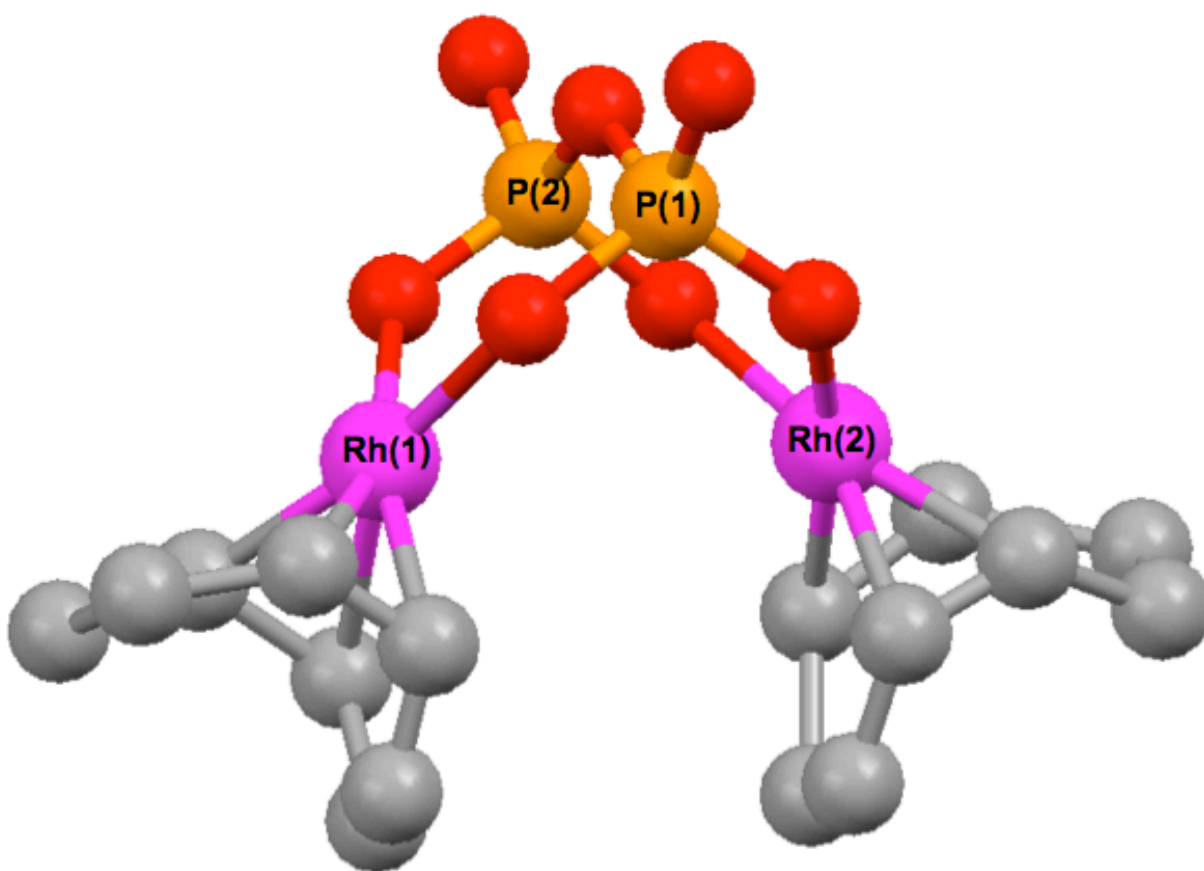


Figure 2. Molecular structure of **2**. Hydrogen atoms were omitted for clarity.

Table 1. Selected bond distances (Å) and angles (°) for molecular complex **1**.

[Bu ₄ N] ₂ [(COD)Rh(P ₃ O ₉)] (1)			
Distances (Å)		Angles (°)	
O(1)-Rh(1)	2.105(4)	O(1)-Rh(1)-O(8)	89.89(17)
O(8)-Rh(1)	2.192(5)	P(1)-O(1)-Rh(1)	127.7(2)
O(4)-Rh(1)	2.836	P(3)-O(8)-Rh(1)	126.1(3)
		P(1)-O(3)-P(2)	126.8(3)
		P(3)-O(6)-P(2)	128.0(3)
		P(1)-O(9)-P(3)	123.1(3)

Table 2. Crystallographic parameters for complex **1**.

[Bu ₄ N] ₂ [(COD)Rh(P ₃ O ₉)] (1)	
Empirical formula	C ₄₀ H ₈₄ N ₂ O ₉ P ₃ Rh
Formula weight (g mol ⁻¹)	932.91
Temperature (K)	143(2)
Wavelength	0.71073
Crystal system	Monoclinic
Space group	P2 ₁ /c
Unit cell dimensions	a = 11.2263(9) Å α = 90° b = 13.1475(11) Å β = 99.2990(10)° c = 33.573(3) Å γ = 90°
Volume (Å ³)	4890.2(7)
Z	4
D _{calc} (g cm ⁻³)	1.267
Absorption coefficient (mm ⁻¹)	0.496
F ₀₀₀	2000
Crystal size (mm)	0.20 x 0.15 x 0.15
Color, morphology	Yellow, block
Theta range for data collection	1.23 to 25.40°
Index ranges	-12 ≤ h ≤ 13, -10 ≤ k ≤ 15, -40 ≤ l ≤ 40
Reflections collected	22520
Independent reflections	7496 [R(int) = 0.0889]
Completeness to theta = 25.40°	83.1 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.8239 and 0.7749
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	7496 / 0 / 499
Goodness-of-fit on F ²	0.918
Final R indices [I > 2σ(I)]	R ₁ = 0.0781, wR ₂ = 0.1734
R indices (all data)	R ₁ = 0.1499, wR ₂ = 0.2049
Largest diff. peak and hole (e Å ⁻³)	1.537 and -1.164

Attempted nanoparticle formation with 1 and 2. Nanoparticle formation and concurrent hydrogenation of cyclohexene was attempted with complexes **1** and **2** as molecular rhodium precursors. The synthetic strategy used was analogous to those developed by Finke and coworkers⁴ and frequently used in subsequent studies.^{4,10,13-15} Briefly, 3.6 μmol of either **1** or **2** was combined with 2.5 mL of acetone with 3.6 μmol of Proton SpongeTM and 0.5 mL of cyclohexene in a Fisher-Porter bottle under N_2 . Proton SpongeTM was shown to speed up reactions in our system (believed to aid in the reduction of the rhodium precursor¹⁶), and thus was included as a reactant in most of the experiments described herein. The reaction vessel was pressurized to approximately 42 psi under H_2 and the H_2 uptake was monitored. Also, nanoparticle formation can be visually observed by a color change from yellow to brown.

With complex **1** as the molecular rhodium precursor and stabilizer, after 4 h the H_2 uptake had begun, indicating the hydrogenation of cyclohexene. However, instead of the characteristic formation of a brown colored solution, a metallic precipitate formed on the walls of the reaction vessel. Thus, it was concluded that complex **1** did not contain a suitable stabilizer for nanoparticle formation under these conditions.

In an attempted nanoparticle synthesis using complex **2**, no H_2 uptake was observed after 14 h. In this case, no metallic precipitate was observed, and the yellow color of the solution persisted. It should be noted that it was not possible to definitively say that all of the $(\text{Bu}_4\text{N})_2\text{HPO}_4$ had been removed from **2** due to the difficulty in isolating yellow crystals of **2** from the colorless crystals, which may in turn have caused a higher ratio of stabilizer to rhodium to be present in the system. Nonetheless, **2** did not decompose under the given reaction conditions.

Nanoparticle formation with $[(\text{COD})\text{Rh}(\text{NCCH}_3)_2]\text{BF}_4$ and $(\text{Bu}_4\text{N})_2\text{HPO}_4$. A nanoparticle synthesis was attempted with the rhodium precursor to **1** and **2**, $[(\text{COD})\text{Rh}(\text{NCCH}_3)_2]\text{BF}_4$, and 1 equiv of $(\text{Bu}_4\text{N})_2\text{HPO}_4$. The reaction solution contained 3.6 μmol of $[(\text{COD})\text{Rh}(\text{NCCH}_3)_2]\text{BF}_4$, $(\text{Bu}_4\text{N})_2\text{HPO}_4$, and Proton SpongeTM in 2.5 mL of acetone, along with 0.5 mL of cyclohexene in a Fisher-Porter bottle under N_2 (eq 4). (Note: This reaction can also be carried out in propylene carbonate with identical results.) The reaction vessel was sealed under 40 psi H_2 (static) and the pressure was monitored over time. After 2 hours, a deep brown color was observed and the pressure had dropped to a constant value of approximately 20 psi, indicating completion of the hydrogenation reaction. Pressure vs time data was converted to cyclohexene concentration vs time using standard calculations developed by Finke and coworkers.⁶ A graph illustrating cyclohexene consumption vs time is shown in Figure 3 and the corresponding fit to the 2-step autocatalytic mechanism is also shown. From this fit, the kinetic values for k_1 and k_2 were determined to be 0.107 (+/-0.011) h^{-1} and 7.461 (+/-0.189) $\text{h}^{-1} \text{M}^{-1}$, respectively (eqs 1 and 2). Gas chromatography analysis of the product mixture revealed the presence of cyclooctane, an indication that the precursor had decomposed along with hydrogenation of the 1,5-cyclooctadienyl ligand. TEM imaging of the isolated particles revealed small particles with a narrow size dispersity of 1.88 +/- 0.27 nm (Figure 4; 14% dispersity, particle counting using software ImageJ). HRTEM also illustrated the crystallinity of these rhodium particles (Figure 4, inset).

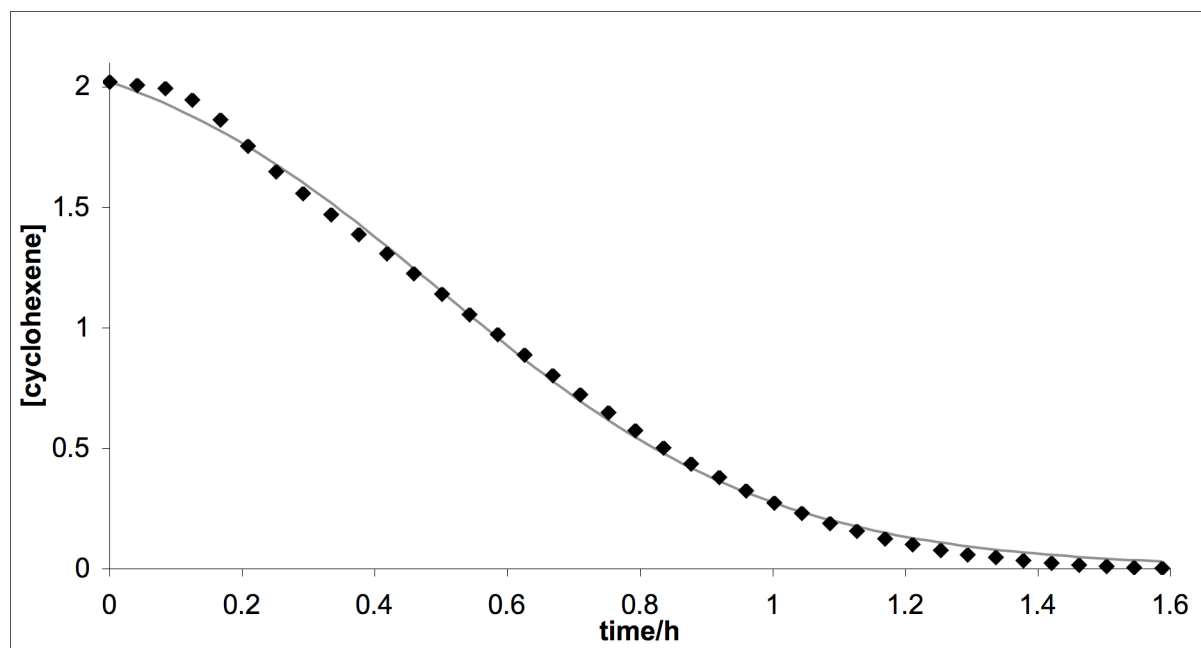
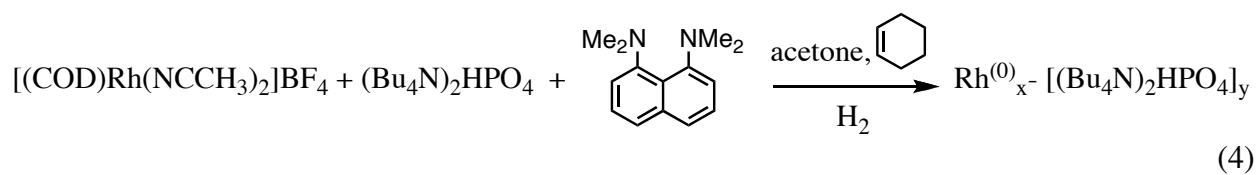


Figure 3. Cyclohexene concentration vs. time for the reaction shown in eq 2, calculated from measured pressure vs. time (♦). The drawn curve represents the best fit using the 2-step autocatalytic mechanism (eqs 1, 2).

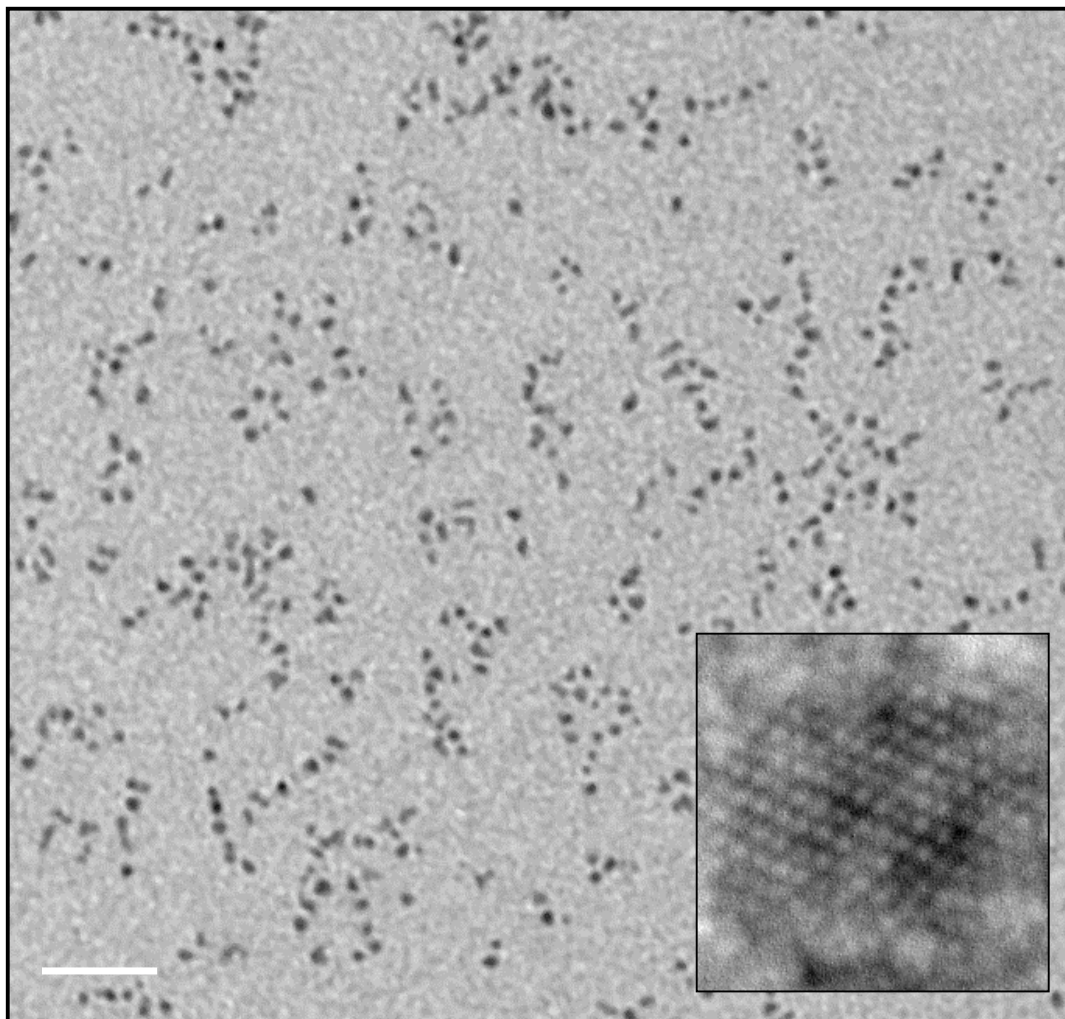


Figure 4. Representative TEM image of rhodium nanoparticles produced by the concurrent hydrogenation reaction in eq 4. Bar corresponds to 20 nm. Inset shows a HRTEM image of an individual nanoparticle.

Attempts were made to scale up the synthesis of the 1.88 ± 0.27 nm rhodium nanoparticles; however, these efforts failed to reproduce the monodispersity observed for the particles obtained on a small scale (by TEM). For example, a reaction volume of 60 mL (instead of 3 mL) in the Fisher-Porter bottle utilized concentrations of reactants and ratios of solvents (acetone 45 mL, 1-cyclohexane 15 mL) that were the same as in the initial reaction. The reaction vessel was pressurized to 42 psi H_2 , however due to the large quantity of cyclohexene, the reaction vessel was repressurized with H_2 multiple times during the course of the experiment. The rhodium nanoparticles isolated from this reaction exhibited an average size of 2.25 ± 0.56 nm (by TEM); which is slightly larger in size, but with a much higher standard deviation (25%).

Other attempts to scale up the reaction under varying reaction conditions (e.g., concentrations of reactants) are described below.

Attempted nanoparticle synthesis with [(COD)Rh(NCCH₃)₂]BF₄ and various stabilizers. Given the successful synthesis of small nanoparticles using [(COD)Rh(NCCH₃)₂]BF₄ as a rhodium precursor source and (Bu₄N)₂HPO₄ as a stabilizer, the previously synthesized phosphate stabilizer (Bu₄N)₃P₃O₉ was utilized as a potential nanoparticle stabilizer. A reaction was carried out as in eq 4, with replacement of (Bu₄N)₂HPO₄ with 1 equiv of (Bu₄N)₃P₃O₉. Over 4 h, a metal precipitate was observed (no nanoparticle formation) without any hydrogenation of cyclohexene. In a related reaction with 10 equivs of (Bu₄N)₃P₃O₉, no metal precipitate was observed, and after 6 h, there was no measurable H₂ uptake (indicative of cyclohexene hydrogenation).

The citrate (Bu₄N)₃C₆H₅O₇ was also investigated as a stabilizer. The citrate anion has been known to stabilize colloids and has been shown to be a good nanoparticle stabilizer in the case of iridium.¹¹ It is also reported that it can serve as a mild reductant, toward a metal precursor.¹⁷ The reaction of [(COD)Rh(NCCH₃)₂]BF₄, (Bu₄N)₃C₆H₅O₇, and Proton Sponge[™] in acetone (or propylene carbonate) and cyclohexene was attempted with the same conditions as in eq 4. However, no H₂ uptake or particle formation was observed over 3 h.

Mechanistic studies on the formation of 1.88 nm rhodium nanoparticles. Various synthetic parameters were varied in attempts to change the size of the rhodium nanoparticles. Since k_1 is related to nanoparticle nucleation and k_2 is related to nanoparticle growth,⁷ by changing the relative rate of the reactions of eqs 1 and 2, we hoped to control the size of the resultant nanoparticle. Thus, to investigate parameters that might allow size control, experimental conditions were varied from those used in the standard conditions outlined in eq 4. The influence of the cyclohexene concentration on the reaction is described by the results of Table 3. In all cases the reaction volume was held constant at 3 mL. The absence of cyclohexene, whether replaced by acetone (entry 2) or cyclohexane (entry 3, the result of the hydrogenation of cyclohexene), resulted in bulk metal formation in the flask. A lesser amount of cyclohexene, 0.25 mL, also resulted in bulk metal (entry 4). Doubling the amount of cyclohexene gave slightly larger nanoparticles with a broader distribution of sizes (entry 5), while 0.7 mL of cyclohexene (entry 6) gave results that were identical to those of the initial conditions (entry 1). Slightly less cyclohexene promoted the formation of both nanoparticles and bulk metal (entry 7). These results indicate that cyclohexene is necessary in the reaction mixture for the formation of rhodium nanoparticles. A volume of 0.5 to 0.7 mL seems to be ideal for formation of nanoparticles with a narrow distribution, whereas the inclusion of 1 mL of cyclohexene significantly widens the size distribution. This result implies that the olefin stabilizes the nanoparticle surface during the growth process. Olefins have been shown to bind to metal surfaces^{18,19} and they may therefore aid in the stabilization of the rhodium nanoparticles, prohibiting small clusters from transforming to bulk metal.

Table 3. Quantities of cyclohexene, cyclohexane, and acetone used in nanoparticle formation experiments with the corresponding result. ^aParticle size (by TEM) or reaction product.

Entry	Cyclohexene	Cyclohexane	Acetone	Result ^a
1	0.5 mL	0 mL	2.5 mL	1.88 +/-0.27 nm
2	0 mL	0 mL	3.0 mL	Bulk metal
3	0 mL	0.5 mL	2.5 mL	Bulk metal
4	0.25 mL	0 mL	2.75 mL	Bulk metal
5	1.0 mL	0 mL	2.0 mL	2.46 +/-0.60 nm
6	0.7 mL	0 mL	2.3 mL	1.85 +/-0.26 nm
7	0.4 mL	0.1 mL	2.5 mL	1.71 +/- 0.25 nm + bulk metal

Given the observed evidence for participation of cyclohexene in the formation of rhodium nanoparticles with a narrow size distribution, the effects of other olefins on nanoparticle formation was also examined. In all cases, 0.5 mL of cyclohexene was replaced by the olefin indicated in Table 4. The first entry corresponds to the standard conditions of eq 4. The more sterically hindered olefin, 1-methyl-cyclohexene led to formation of bulk metal (entry 2), while the reaction with 1-octene (entry 3) gave results similar to the standard conditions reaction (entry 1). These results further support the postulation that the olefin may help to stabilize the nanoparticle surface during the growth process, as the more hindered olefin (1-methylcyclohexene) did not support the formation of nanoparticles while the unhindered olefin (1-octene) reacted in a manner similar to cyclohexene. The addition of styrene resulted in no reaction, while the addition of benzene resulted in the formation of large nanoparticle bundles (hydrogenation of benzene did not occur under these conditions). These structures are shown in Figure 5.

Table 4. Unsaturated components used to replace cyclohexene in eq 4 and the corresponding result. ^aParticle size (by TEM) or reaction product.

Entry	Unsaturated Component	Result ^a
1	Cyclohexene	1.88 +/-0.27 nm
2	1-Methylcyclohexene	Bulk metal
3	1-Octene	1.93 +/-0.30 nm
4	Styrene	No reaction
5	Benzene	Insoluble nanoparticle bundles

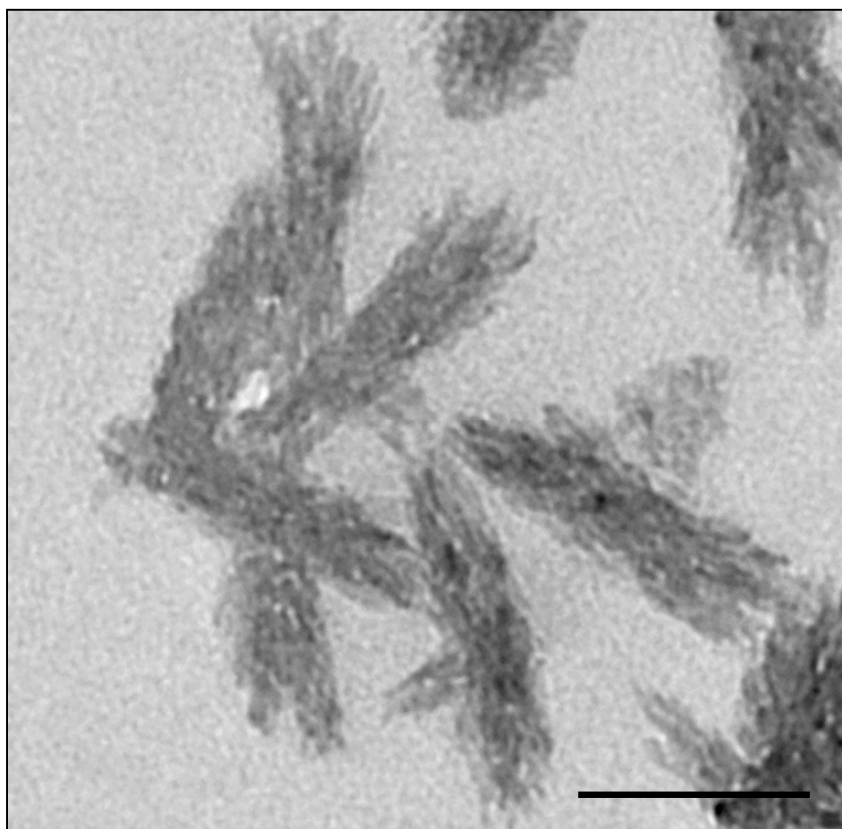


Figure 5. Representative TEM image of insoluble haystack structures produced in the nanoparticle formation reaction with benzene as the olefin as imaged by TEM. Bar corresponds to 100 nm.

Reactant concentrations were also varied in an attempt to gain insight into the mechanism of nanoparticle formation, as Finke and coworkers have successfully varied this parameter to control nanoparticle size.⁷ Modifications to the amount of Proton Sponge™ were also evaluated in these experiments. The various experimental conditions and the corresponding results are provided in Table 5. In all cases, the total solution volume remained 3 mL, and the concentrations of $[(\text{COD})\text{Rh}(\text{NCCH}_3)_2]\text{BF}_4$, $(\text{Bu}_4\text{N})_2\text{HPO}_4$, and Proton Sponge™ are given in Table 5. Entry 1 lists the conditions initially employed for the reaction in eq 4. Lower concentrations for all three reactants (by 50%, entry 2) and higher (by a factor of 2, entry 3) concentrations of all three reactants gave similar results to those of the initial conditions. At reactant concentrations ten times those of entry 1, nanoparticles of a similar average size were obtained; however the size distribution was wider (entry 4). Also worth mentioning were experiments in which either the $[(\text{COD})\text{Rh}(\text{NCCH}_3)_2]\text{BF}_4$ or the $(\text{Bu}_4\text{N})_2\text{HPO}_4$ concentration was doubled in the reaction mixture. In the case of the former (entry 5), bulk metal resulted from the reaction. This is apparently due to the fact that insufficient $(\text{Bu}_4\text{N})_2\text{HPO}_4$ is present to allow for nanoparticle stabilization. With excess $(\text{Bu}_4\text{N})_2\text{HPO}_4$ (entry 6), nanoparticle formation does not occur. In this case, the excess of stabilizer could prevent decomposition of the precursor to form nanoparticles, instead stabilizing the rhodium precursor. In entry 7, it was shown that Proton

Sponge™ is not necessary for nanoparticle formation (similar nanoparticles resulted with or without Proton Sponge™). However, it resulted in a much slower reaction (at least 12 hours instead of 1 or 2) and therefore it was typically used to speed up nanoparticle formation.

Table 5. Variations in concentrations of the reactants [(COD)Rh(NCCH₃)₂]BF₄, (Bu₄N)₂HPO₄, and Proton Sponge™ in the reaction of eq 4, with the corresponding results. ^aParticle size (by TEM) or reaction product.

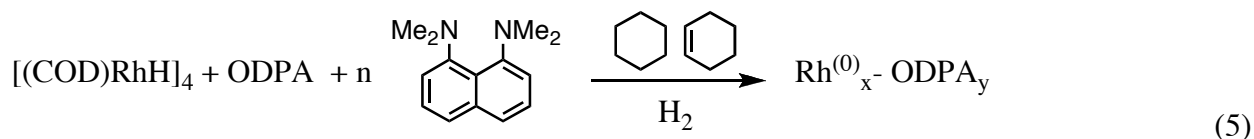
Entry	[(COD)Rh(NCCH ₃) ₂]BF ₄	(Bu ₄ N) ₂ HPO ₄	Proton Sponge™	Result ^a
1	1.2 mM	1.2 mM	1.2 mM	1.88 +/-0.27 nm
2	0.6 mM	0.6 mM	0.6 mM	2.13 +/-0.30 nm
3	2.4 mM	2.4 mM	2.4 mM	1.86 +/-0.32 nm
4	12 mM	12 mM	12 mM	2.11 +/-0.46 nm
5	1.2 mM	0.6 mM	0.6 mM	Bulk metal
6	0.6 mM	1.2 mM	0.6 mM	No reaction
7	1.2 mM	1.2 mM	0 mM	1.80 +/-0.32 nm

The role of hydrogen pressure was also investigated, and the results are summarized in Table 6. Entry 1 describes the conditions initially employed, and entries 2 and 3 provide results from varying the hydrogen pressure. The reaction of entry 4 involved replacement of cyclohexene with cyclohexane, to mimic conditions formed at the end of a hydrogenation/nanoparticle synthesis. It is interesting to note that at higher pressures, no reaction occurs, while at lower pressures, bulk metal is produced instead of stabilized nanoparticles. This result may suggest that a preferred rate of cyclohexene hydrogenation is necessary for the stabilization of rhodium nanoparticles during their formation.

Table 6. Pressure variation studies in the standard conditions reaction, and the corresponding result. ^aParticle size (by TEM) or reaction product.

Entry	Hydrogen Pressure	Cyclohexene	Cyclohexane	Result ^a
1	42 psi	0.5 mL	0 mL	1.88 +/-0.27 nm
2	65 psi	0.5 mL	0 mL	No reaction
3	20 psi	0.5 mL	0 mL	Bulk metal + yellow solution
4	20 psi	0 mL	0.5 mL	Bulk metal

Nanoparticle formation with the rhodium precursor [(COD)RhH]₄. The precursor [(COD)RhH]₄²⁰ was used as a potential precursor for the formation of rhodium nanoparticles (eq 5). This complex seems to be a potentially useful precursor to rhodium nanoparticles, due to its cluster core of four rhodium atoms separated only by bridging hydride ligands. This complex is insoluble in polar organic solvents such as acetone and propylene carbonate, so direct comparisons with the system described above using the precursor [(COD)Rh(NCCH₃)₂]₄BF₄ are not possible. Instead, concurrent hydrogenation and nanoparticle formation reactions were run in a cyclohexane/cyclohexene solution, with the stabilizer octadecylphosphonic acid (CH₃(CH₂)₁₇PO₃H₂, ODP A). This molecular stabilizer has been shown to facilitate shape-directed stabilization in other nanoparticle systems,²¹ and its use as a stabilizer in other rhodium nanoparticle synthetic systems is described in Chapter 1. Also of note, ODP A does not stabilize particles derived from the precursor [(COD)Rh(NCCH₃)₂]₄BF₄, most likely due to solubility issues during the synthesis. The variable “n” is the equiv of Proton Sponge™ added in the synthesis, where n = 1,2 or 3. It has been shown that 1 equiv of Proton Sponge™ aids in the decomposition of metal precursors during reductions with H₂.¹⁶ The reactions where n = 2 or 3 (1 or 2 excess equivs of Proton Sponge™ respectively) were attempted in order to aid in the removal of protons from the two hydroxyl groups on ODP A.



The hydrogenation results for n = 1,2 or 3 were the same within error for the rate of cyclohexene hydrogenation, however the hydrogenation reaction proceeded very quickly in all cases. For the case of n=1, k₁ = 7.93 (+/-0.27) h⁻¹ and k₂ = 23.96 (+/-0.70) h⁻¹M⁻¹. The precursor [(COD)RhH]₄ and rhodium nanoparticles are both dark brown in color, therefore no color change could be detected during nanoparticle formation. There are two possible explanations for the observed rapid hydrogenation. First, the precursor itself may be active for the hydrogenation of cyclohexene, therefore the extracted kinetic parameters could be independent of nanoparticle formation. The second hypothesis is that the mass transfer of cyclohexene and hydrogen in solution rather than the growth of nanoparticles limits the rapid hydrogenation of cyclohexene. The rates of cyclohexene hydrogenation observed in this system are similar to other systems limited by mass transfer observed by the Finke Group.⁸ Although kinetic parameters could not be used to indicate nanoparticle formation, the reaction was allowed to run for 2 hours (cyclohexene had been consumed 15 minutes into the reaction) and a sample was isolated for TEM analysis. The nanoparticles were somewhat aggregated, however they were small and approximately 2 nm in diameter (Figure 6).

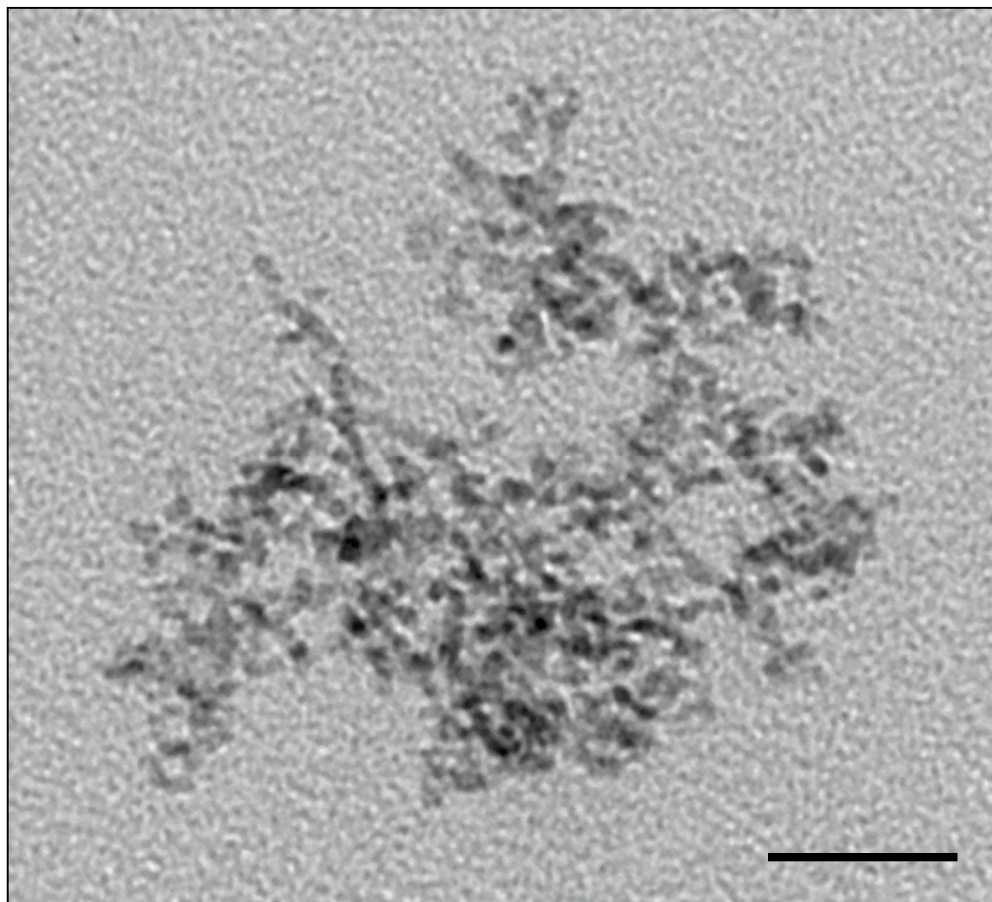


Figure 6. Representative TEM image of rhodium nanoparticles synthesized by equation 4, where $n = 1$. Bar corresponds to 20 nm.

Conclusions

This chapter highlights the synthesis of two new rhodium complexes with phosphate ligands. Although these complexes did not decompose to rhodium nanoparticles under concurrent cyclohexene hydrogenation conditions, a rhodium precursor with a tetrabutylammonium phosphate stabilizer produced small size, monodisperse rhodium nanoparticles. This reaction was optimized to produce 1.88 ± 0.27 nm nanoparticles, and experimental variations in reaction conditions gave insight into the mechanism of their formation. Surprisingly, the presence of olefin and high hydrogen pressure is necessary for the stabilization of nanoparticles during their formation. Also, reactant concentrations and the rate of the cyclohexene consumption seems crucial to yield nanoparticles with this excellent size dispersity. Although larger nanoparticles could not be synthesized by changing synthetic variables, the lack of bulky stabilizers on these nanoparticles will allow for easy surface exchange and the ability for tailoring to a variety of reaction conditions for further growth experiments.

Experimental Procedures

General procedures. All syntheses were performed under standard inert, air-free conditions. Acetone was dried over K_2CO_3 and distilled prior to use. Propylene carbonate was dried over Linde 5 Å type molecular sieves (dried 24 hr at 200° C under vacuum) for 12 hours and distilled prior to use. Cyclohexene was distilled over sodium. H_2 was purchased from Praxair and dried through a column of drierite prior to use. $[(COD)Rh(NCCH_3)_2]BF_4$ was prepared according to the literature procedure analogous for $[(COD)Ir(NCCH_3)_2]BF_4$ and its purity was verified by NMR. $(Bu_4N)_2HPO_4$ was prepared by the addition of aqueous Bu_4NOH to a solution of $(Bu_4N)H_2PO_4$ in acetonitrile, and the subsequent removal of water with molecular sieves. $(Bu_4N)_3P_3O_9$ was prepared through an ion exchange technique, by functionalizing Dowex beads (H^+ type) with Bu_4N^+ and then passing $Na_3P_3O_9$ through a column of the functionalized beads. $[(COD)RhH]_4$ was prepared according to the literature synthesis²⁰ and lyophilized from benzene to give a brown powder prior to use. Proton Sponge was obtained from Aldrich and used as received. Solutions of $[(COD)Rh(NCCH_3)_2]BF_4$, $(Bu_4N)_2HPO_4$, and Proton Sponge were prepared in either acetone or propylene carbonate and stored in Air-free flasks for use on a Schlenk line or in a glovebox. In order to facilitate high pressure reaction conditions, a Fisher-Porter bottle equipped with a home-built valve designed for attachment to a Schlenk line was utilized at UC Berkeley, or assembled in a glovebox and attached to a pressure monitoring device by Swagelok quick-connects for kinetic experiments conducted at Colorado State University.⁴ (See reference for a detailed description of the apparatus.)

Characterization. Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) were carried out on a Technai G2 S-twin operating at 200 keV. Samples were prepared by drop casting a solution of the nanoparticles on ultrathin carbon type-A, 400 mesh grids purchased from Ted Pella, Inc. The formvar layer on the TEM grids was removed prior to use according to the provided instructions.

Synthesis of $[Bu_4N]_2[(1,5-COD)Rh(P_3O_9)]$. $[(1,5-COD)Rh(NCCH_3)_2]BF_4$ (0.05 g, 0.13 mmol) and $(Bu_4N)_3P_3O_9$ (0.12 g, 0.13 mmol) were combined in 10 mL of methylene chloride and stirred overnight. The solvent was removed under vacuum to yield a yellow oil. Hot acetone (5 mL) was added to the oil and diethyl ether was slowly added (10 mL). The mixture was then placed in an ice bath and over a few hours, yellow cubic crystals formed and a crystal structure was obtained. 1H NMR (400 MHz, CD_2Cl_2) δ 3.78 (br, 4H), 3.24 (m, 16H), 2.41 (br, 4H), 1.63 (ov m, 20H), 1.56 (m, 4H), 1.44 (m, 8H), 1.00 (t, 8H). $^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2) δ 74.44, 58.58, 30.49, 23.93, 19.69, 13.50. ^{31}P NMR (161.9 MHz, CD_2Cl_2) δ -14.30.

Synthesis of $[Bu_4N]_2[(1,5-COD)_2Rh_2(P_2O_7)]$. This complex was not isolated but a few crystals were obtained for X-ray analysis and subsequent attempts at nanoparticle formation. $(Bu_4N)H_2PO_4$ (0.183 g, 0.54 mmol) was dissolved in 3 mL CH_3CN and 1M Bu_4NOH in H_2O (0.54 mL, 0.54 mmol) was added to the solution. This mixture was stirred for 3 h and then molecular sieves (5Å type) were added to remove the water and stirred overnight. This solution was added via cannula to $[(1,5-COD)Rh(NCCH_3)_2](BF_4)$ (0.05 g, 0.13 mmol) in 3 mL CH_3CN . This mixture was stirred for 3 h. Crystals of the complex were grown from dissolution in CH_3CN and the slow addition of Et_2O by vapor diffusion.

Synthesis of 1.8 nm rhodium nanoparticles through the concurrent hydrogenation of cyclohexene. 3.6 mmol each of [(1,5-COD)Rh(NCCH₃)₂](BF₄), (Bu₄N)₂HPO₄, and 1,8-(dimethylamino)naphthalene (Proton Sponge™) were added as a solution in acetone or propylene carbonate to a new, clean and dry test tube with a new stir bar inside a Fisher-Porter bottle as shown in equation 1. The apparatus and instrumentation for nanoparticle synthesis and characterization has been previously described.¹⁴ Pressure was monitored and recorded every 0.05 h and was converted to cyclohexene consumption. The total volume of solvent (either acetone or propylene carbonate) was 2.5 mL. Cyclohexene (0.5 mL) was then added to the solution. Hydrogen was then used to pressurize the Fisher-Porter bottle to 42 psi. The bottle was purged 10 times with hydrogen before the bottle was isolated at a static pressure of ~42 psi (2.90 bar). Over a few hours, the solution changes from yellow to brown and the pressure drops to around 25 psi (indicating the complete reaction of cyclohexene to cyclohexane). At this point, the reaction mixture was exposed to air. To remove excess proton sponge and (Bu₄N)₂HPO₄, hexanes (or acetone & hexanes if the solvent was propylene carbonate) was added until the solution begins to look cloudy, indicating particle precipitation. The suspension was then centrifuged at 7000 rpm for 5 minutes in order to precipitate the particles, and the supernatant was then discarded. The nanoparticles can later be dispersed in polar media (acetone, H₂O, ethylene glycol) with less than 1 minute of sonication. Nanoparticles prepared from acetone are oftentimes more difficult to redisperse, possibly due to a more thorough washing away of the (Bu₄N)₂HPO₄ during the centrifugation step.

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Chapter 3

Shape Controlled Synthesis of Rhodium Nanoparticles via a Seeded Growth Process

Introduction

Considerable effort has been devoted to investigations of metallic nanoparticles, and much of this research has focused on the development of general synthetic methods for control over the particle's size and shape.^{1,2} The ability to dictate size and shape at the nanoscale is an important goal because various applications, including (for example) catalysis and sensing, are dependent on these properties.³ Small nanoparticles with an inherently large surface area to volume ratio are generally thought to be preferred for high catalytic activity, but some effort has also been directed toward the shape-controlled synthesis of nanoparticles with specific surface structures. The sensitivity of various reactions to catalyst surface structure has been appreciated for many years,⁴ but such effects have been difficult to establish for nanoparticles since available synthetic methods tend to produce a range of sizes and shapes. A variety of synthetic tools have been employed to control nanoparticle size and shape through bottom-up approaches, and significant progress has been made in this area.⁵ However, a general solution-state synthetic method that allows a high degree of shape control for a variety of metals has yet to be discovered. A promising general approach is based on the seeded growth method, since it separates the energetically uphill nucleation process from the subsequent, spontaneous growth step. Thus, seeded growth has been used in selected cases to achieve good control over nanoparticle shape.⁶⁻⁸

The synthesis of discrete rhodium nanoparticles with specific dimensions has received relatively little attention, despite their potential use in selective catalytic transformations.⁹ Research in this area has yielded a few examples of rhodium particles of a certain shape and size, and in general this has required the use of nanoparticle surface-stabilizers that bind strongly to the metal surface. For example, the polymeric surfactant poly(vinylpyrrolidone) (PVP), which provides many interactions with the nanoparticle surface for each polymer chain, has proven useful in this regard.^{2,6,7,10,11} However, polymeric stabilizers that bind strongly to the nanoparticle surface may limit access for many molecules of interest (e.g., substrates for catalysis). Also, the poor solubility of PVP (and therefore PVP-stabilized nanoparticles) in organic solvents poses a problem for various solution-state catalytic reactions of organic substrates. Thus, it is important to develop alternative stabilizers that are labile, but effective in providing a high degree of structural control at the nanoparticle surface. For this reason, our attention has focused on molecular surfactants that make single interactions with the surface of the nanoparticle. Here, we report the growth on rhodium seed particles (synthesized with a phosphonic acid stabilizer and described herein Chapter 1) to enable the synthesis of larger rhodium nanoparticles with specific shapes by way of alkylamine and alkyl carboxylic acid stabilizers.

Results and Discussion

Seeded growth route to faceted rhodium nanoparticles. For the growth of rhodium nanoparticles from seeds, the precursor $\text{Rh}_2(\text{OAc})_4$ was chosen due to its high yielding synthesis and air stability. A large number of commonly used molecular stabilizers were examined for use in the growth step but the best results were obtained for the hexadecylamine/adamantane carboxylic acid mixture described below. Alkylamine/carboxylic acid mixtures have previously been observed to function as stabilizers for the synthesis of shape-controlled nanoparticles.¹² In addition, 1,2-hexadecanediol is known to serve as a mild reductant for metal precursors in high

temperature nanoparticle syntheses, and the mechanism of this type of polyol reduction has recently been investigated.¹³ The ratio of stabilizers utilized in this study was previously reported by Teng and Yang to be effective in the synthesis of platinum multipods.¹⁴

In a typical nanoparticle growth step, seed particles ($\bar{x} = 1.92$ nm, $\sigma = 0.16$, see Chapter 1, Figure 8) dissolved in the surfactant/solvent mixture of 1-hexadecylamine, 1,2-hexadecanediol, and adamantane carboxylic acid were suspended at 140° C to give a brown solution that darkened upon slow addition (over 1 h) of the growth precursor $\text{Rh}_2(\text{OAc})_4$. This resulted in an opaque brown solution, which solidified upon cooling to room temperature. This solid surfactant-nanoparticle mixture was dissolved in CHCl_3 with sonication, and then the particles were precipitated by the addition of ethanol to yield a brown precipitate and a colorless solution. Examination of this sample by TEM (Figure 1a) revealed the presence of nanoparticles that appear to have a triangular shape (as might be observed for tetrahedral particles¹⁵). At temperatures below 140° C, decomposition of the growth precursor was not observed. Higher temperature reactions were attempted at 150° C and 160° C; the resultant particles were the same size however they appeared more rounded (Figures 1b, 1c).

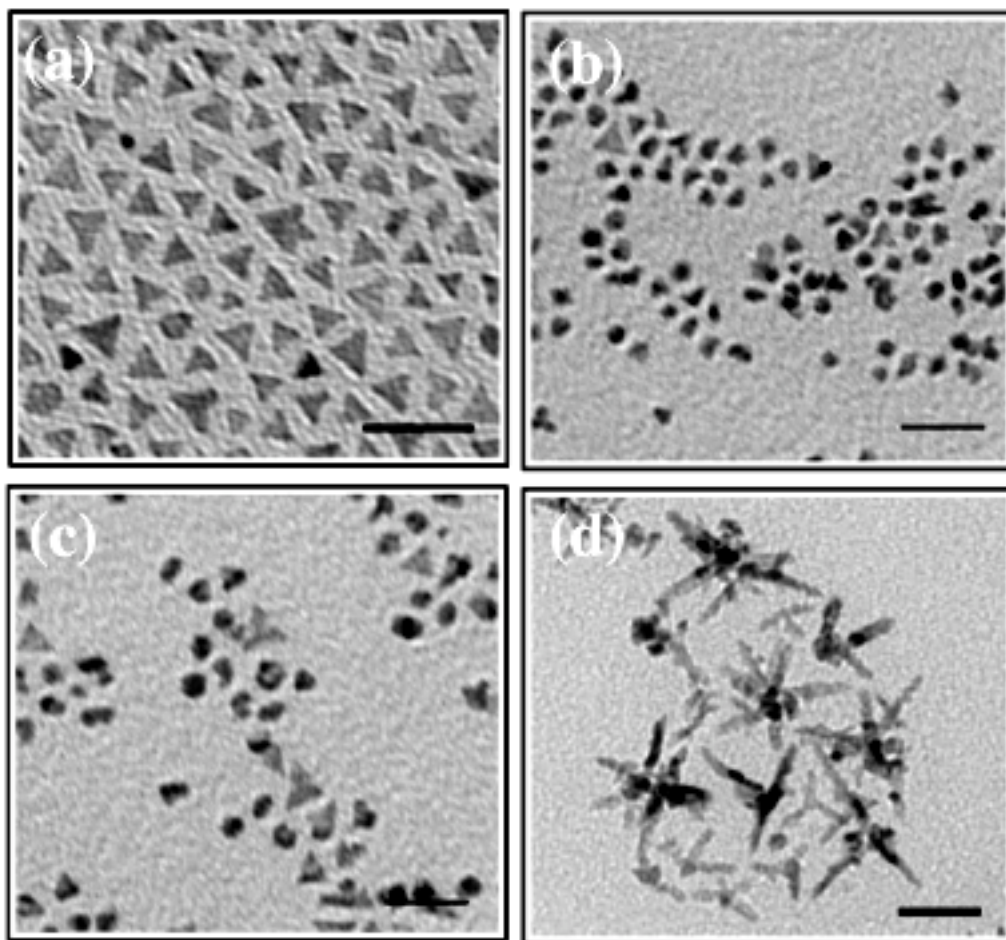


Figure 1. Representative TEM images of rhodium nanoparticles synthesized under standard conditions with growth on the preformed seeds at (a) 140° C, (b) 150° C, and (c) 160° C, and nanoparticles synthesized with in-situ prepared seeds before growth (d). Each bar corresponds to 20 nm.

The tetrahedrally shaped particles were further investigated using high angle annular dark field (HAADF) scanning transmission electron microscopy (STEM). The intensity of HAADF images is proportional to the n th power Z^n , $n=1.5-2$, of the average atomic number Z of the material being observed.¹⁶ "Z-contrast imaging" can thus be used to provide information on the 3D topography of the nanoparticles. This revealed that about 40% of the particles were tetrahedra (Figure 2), while about 40% may be described as triangular rafts, or tetrahedra with one severely truncated corner (Figure 3). These particles mostly arrange themselves with this "cut-off corner" facing upward on the TEM grid, as this provides the greatest interaction with the support. Figure 4 illustrates the distribution of shapes found in this sample. The remainder of the sample is composed of icosahedra (ca. 10%) and other related crystalline shapes (e.g., decahedra and cuboctahedra). Icosahedra are oftentimes present in fcc samples and have been hypothesized to result from a nucleation-induced effect (by computational studies).¹⁷⁻¹⁹ The powder XRD pattern exhibited the expected peaks for fcc rhodium metal, at 48.0° (111), 56.1° (200), and 83.4°

(220) (Figure 5). The particles appeared to be single crystals by HRTEM, and by use of the Debye-Scherrer formula, the crystalline domain size was determined to be 4.99 nm in the (111) direction and 4.74 nm in the (100) direction. These calculated values compare nicely to the particle size measurements determined by pixel counting of the side lengths on a recorded TEM image (4.77 $\pm$ 0.72 nm). This further supports the notion that these tetrahedra are mainly single crystalline particles.

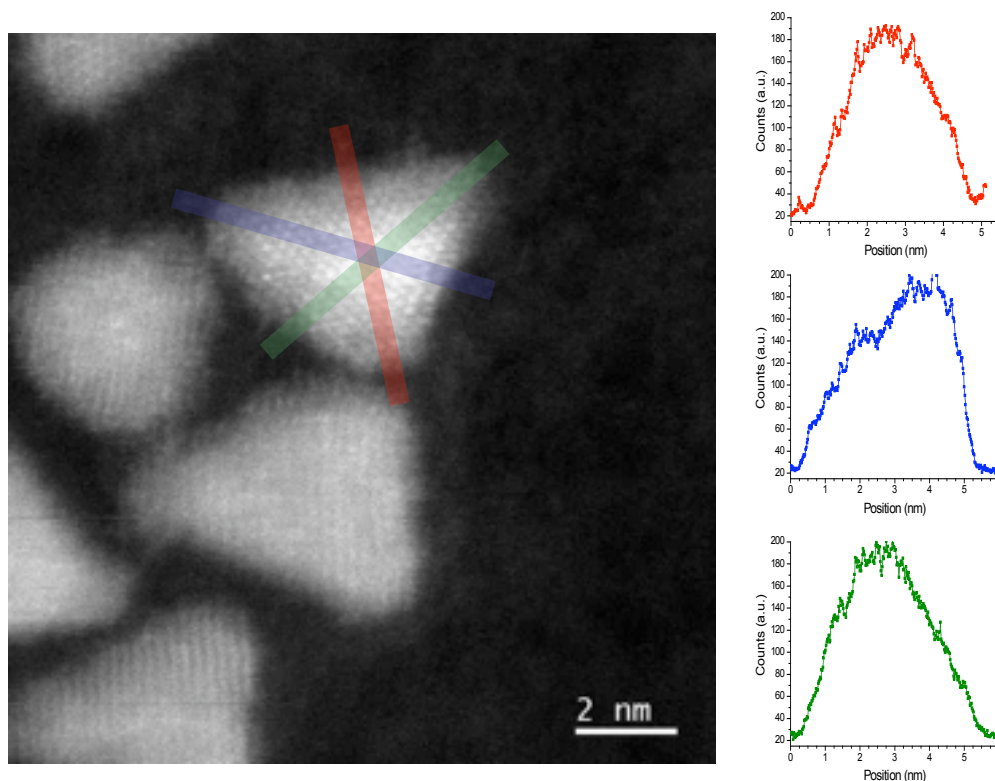


Figure 2. HAADF image of a rhodium nanoparticle and the corresponding line profiles across three different axes. As the intensity is proportional to the atomic number Z^n , $n=1.5-2$, this quasi 3-dimensional information verifies that this particle is a tetrahedron.

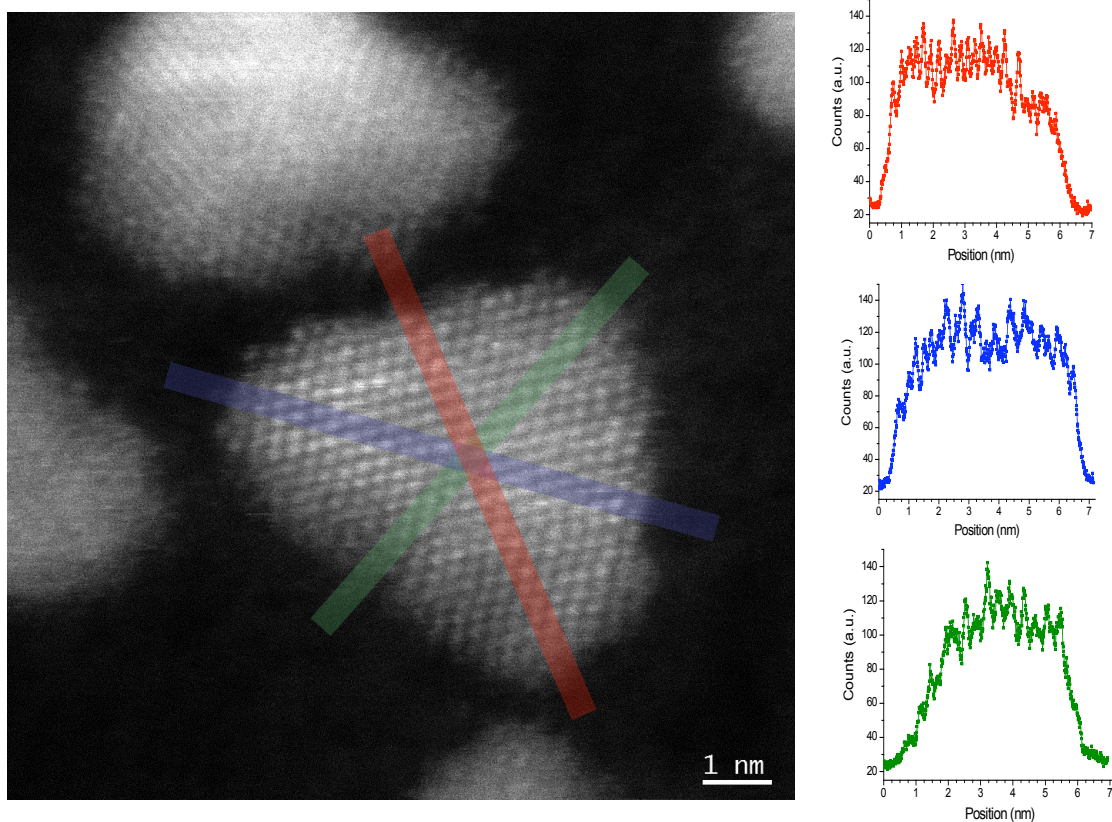


Figure 3. HAADF image of a rhodium nanoparticle and the corresponding line profiles across 3 different axes. Line profiles show that this particle is not a true tetrahedron, but a “flat-topped” triangle indicated by a plateau.

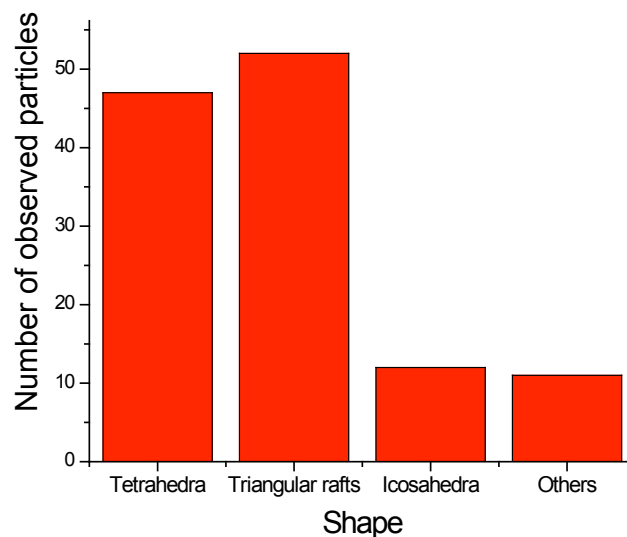


Figure 4. Statistical count of types of particle shapes in tetrahedra sample. By the method of particle counting by TEM, 82% of the particles appear tetrahedral. However, the line scans across Z-contrast STEM images revealed that over half of the tetrahedral shaped particles are in fact truncated flat-topped triangles.

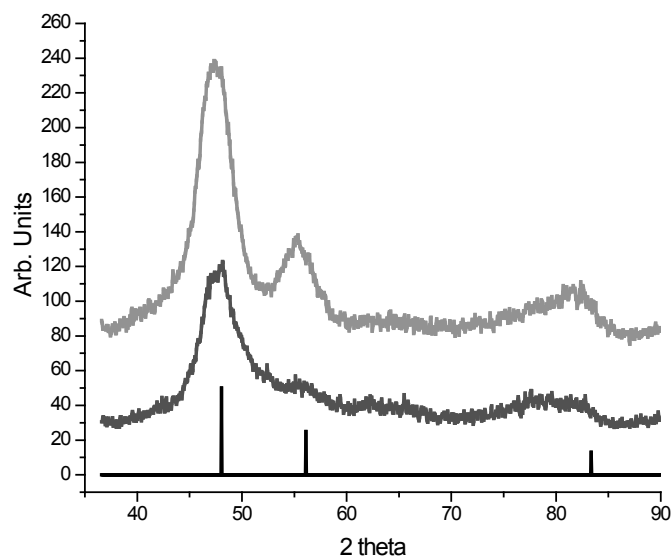


Figure 5. XRD pattern (offset) of rhodium long-arm multipods (lower) and rhodium tetrahedra (upper). The observed ratio are indexed to the pattern for bulk rhodium metal.

Calculations of average particle size from the concentration of seed particles and the amount of added growth precursor were in good agreement with measured particle diameters by TEM indicating a seeded growth mechanism. As a control, non-seeded growth was attempted under the same synthetic conditions as before but in the absence of seed particles. No nucleation of nanoparticles was observed at 140° C, supporting the seeded growth mechanism, as the energy threshold for particle nucleation requires a higher temperature.

In subsequent growth experiments, the seeded growth model was assumed and the ratio of the growth precursor to seed particles was varied to evaluate the method as a means of controlling particle size. When 0.5 times the normal amount of the precursor $\text{Rh}_2(\text{OAc})_4$ was added, the nanoparticles obtained were smaller and more rounded (Figure 6a). The largest particles formed under these conditions were tetrahedra, and were nearly the size of the tetrahedra obtained in the procedure described above. These results indicate that there may be a preferred size for rhodium tetrahedra of around 4.7 nm per edge, and if there is not enough growth precursor to form the tetrahedra, a somewhat spherical shape is preferentially adopted. Addition of more precursor, as reported above, appears to allow these smaller, spherically-shaped particles to “fill in” to the preferred tetrahedral shape. When additional growth precursor was added (1.5 times the normal amount of $\text{Rh}_2(\text{OAc})_4$ over 1.5 h), a polydisperse sample of nanoparticles with a variety of shapes, some exhibiting anisotropic growth, was observed (Figure 6b). These results are consistent with other observations that indicate a high tendency for rhodium nanoparticles to undergo anisotropic growth under a variety of conditions.^{6,7,20} Interestingly, in this particular system such anisotropic growth appears to dominate above a critical nanoparticle size of approximately 4.7 nm per edge (tetrahedra). This observation seems to be consistent with the only other report of rhodium tetrahedra prepared by a colloidal synthesis, where a mean size of 4.9 +/-0.4 nm was reported as the nanoparticle size.¹⁵

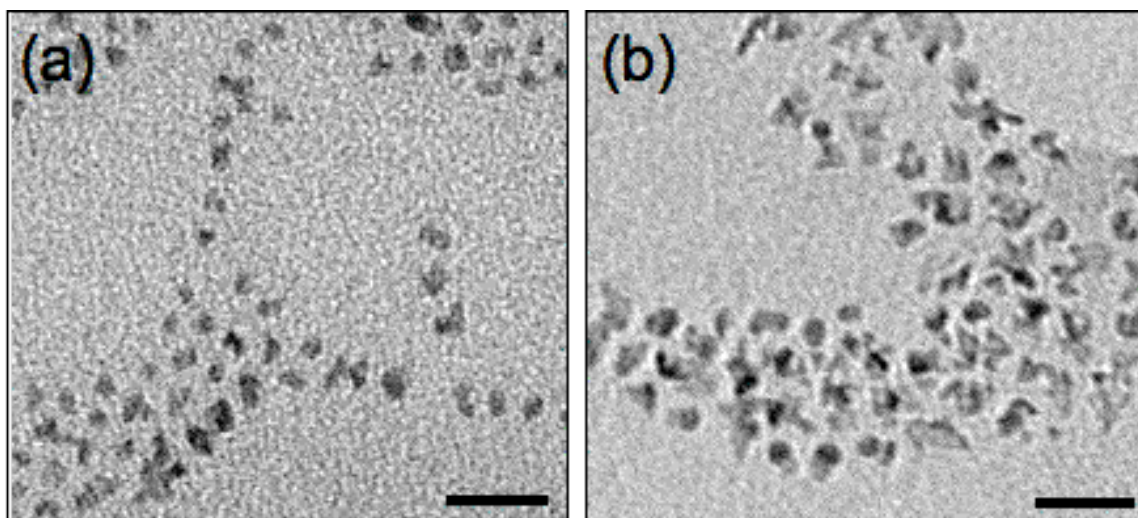


Figure 6. (a) TEM image of rhodium nanoparticles synthesized with 0.5 times the usual amount of growth precursor. (b) TEM image of rhodium nanoparticles synthesized with 1.5 times the usual amount of growth precursor. Each bar corresponds to 10 nm.

Synthesis and characterization of rhodium multipods. As a control experiment, and to better understand the role of the seed particles in the seeded growth synthesis of rhodium tetrahedra, attempts were made to isolate and characterize rhodium nanoparticles that form under the conditions described above, but in the absence of seeds. Thus, $\text{Rh}_2(\text{OAc})_4$ (0.008 g, 0.0359 mmol) in 1 mL of tetraglyme was added via syringe over 1 h to a mixture of 1-hexadecylamine, 1,2-hexadecanediol, and adamantane carboxylic acid heated to 140° C for a total of 2 h. Although these conditions lead to reduction of the $\text{Rh}_2(\text{OAc})_4$ precursor and nanocrystal growth in the presence of seeds, no conversion to rhodium nanoparticles was observed without the seeds, as indicated by the persistence of a colorless solution. Thus it appears that rhodium nanoparticle seeds are needed to initiate the reduction of $\text{Rh}_2(\text{OAc})_4$ at 140° C under these conditions. Further experiments showed that a temperature of 180° C is required for the decomposition of $\text{Rh}_2(\text{OAc})_4$ within a reasonable amount of time (ca. 10 min). Thus, the latter process was investigated as a potentially convenient method for the *in situ* generation of seed particles.

An initial (seed forming) amount of rhodium precursor solution (0.1 mL of a solution of 0.009 g $\text{Rh}_2(\text{OAc})_4$ in 1 mL of tetraglyme) was added to the heated (180° C) surfactant mixture (no preformed seeds present), and the resulting solution initially appeared colorless. The disappearance of the blue-green color of $\text{Rh}_2(\text{OAc})_4$, and the formation of a colorless solution indicated the rapid formation of an unknown molecular species before decomposition to rhodium nanoparticles. Over 10 minutes at 180° C, the solution changed to an opaque brown color, indicating the formation of rhodium nanoparticles. After maintaining this temperature for 1 h to further allow the seed particles to form, the growth step was accomplished by the constant addition of $\text{Rh}_2(\text{OAc})_4$ over 1 h, exactly as in the procedure that produced rhodium tetrahedra. This final solution was darker in color than that from the reaction that resulted in tetrahedrally-shaped particles. As shown by TEM (Figures 1d, 7), the product of this reaction was not rhodium tetrahedra as in the related procedure above, but rhodium nanocrystals with a drastically different, multipod shape. Attempts were also made to add more growth precursor (0.018 mg

$\text{Rh}_2(\text{OAc})_4$ in 2 mL tetraglyme) while keeping the seed-forming amount the same (0.1 mL). This resulted in snowflake-shaped nanoparticles, for which the arm length remained roughly the same as in the multipod case; however, the number of arms per particle increased significantly (Figure 8).

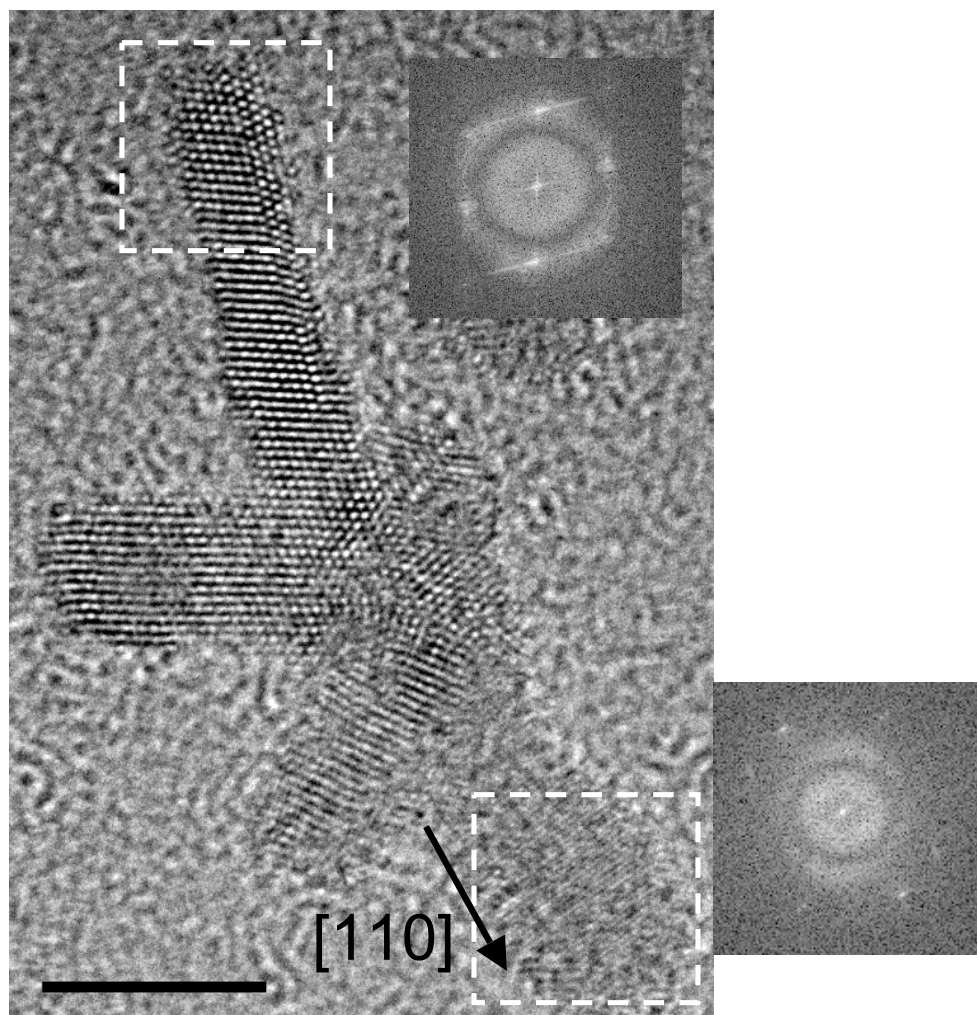


Figure 7. HRTEM image of a rhodium multipod, with FFT patterns displayed for the arm locations indicated on the image. The bottom right FFT image shows that the growth axis is in the $[110]$ direction, where d_{002} corresponds to a distance of 0.134 nm. Bar corresponds to 5 nm.

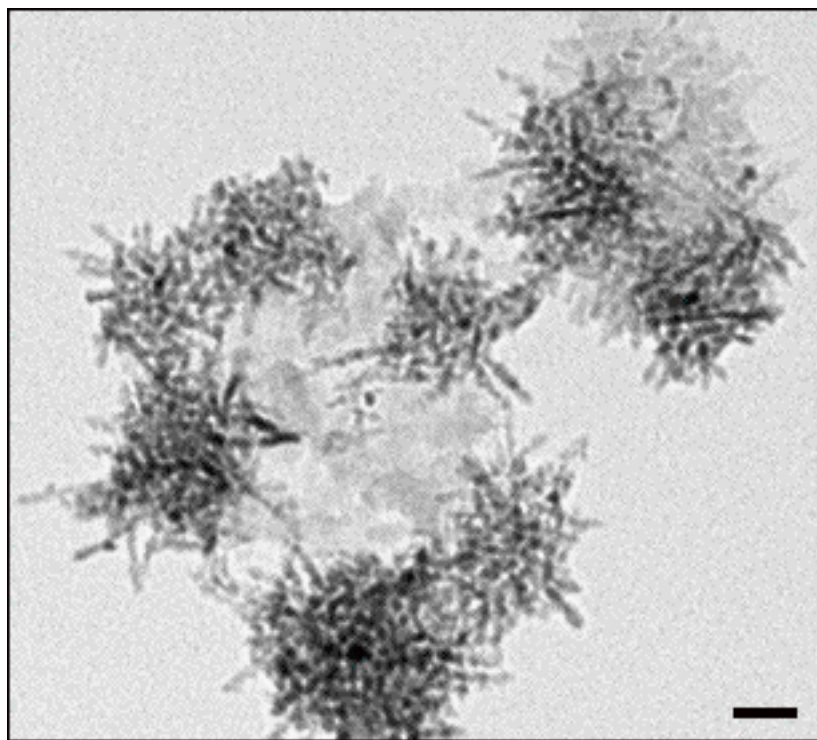


Figure 8. TEM image of snowflake rhodium nanoparticles synthesized by adding two times the amount of growth precursor compared to that used to produce the multipods of Figures 1d, 7. Bar corresponds to 20 nm.

Various research groups have reported the synthesis of rhodium multipod structures;^{6,7,20,21} however, the multipods observed here possess an unusually high aspect ratio. Previously reported rhodium multipods possess arms that are 2-3 nm wide and 9-11 nm long.^{6,7,20} The method reported here provides multipods with longer arms that are 15-20 nm in length, and consistently 3 nm in diameter. Also, there is evidence for the occasional growth of a second-generation branching point on some multipods as shown in Figure 1d. This feature has not been observed for previously reported rhodium multipods. The number of arms per multipod is as few as one; however, as many as eight are observed. All rhodium multipods reported so far have been obtained by a polyol reduction procedure that produces samples mostly containing tetrapods and tripods. The previously reported rhodium multipods were prepared with PVP as a stabilizing surfactant,^{6,7} however these results clearly show that this surfactant is not necessary for the formation of multipods.

Powder XRD studies revealed (111) and (220) Miller Index peaks, and a very broad peak corresponding to the (200) direction (Figure 5). The full-width at half maximum (FWHM) value could not be determined for the (200) peak, therefore the Debye-Scherrer formula was not applied in this case. However, for the (111) peak, the crystalline domain size was determined to be ca. 5 nm. HRTEM of the multipods revealed that some of the arms grew along the (220) direction (Figure 7), while others grew along the (111) direction. In general, data regarding the extent of (111) vs. (220) anisotropic growth is difficult to quantify by HRTEM; however, competitive growth in both of these directions has been previously reported for a platinum

system.¹⁴ This observation may help explain the non-uniformity in the number of arms per multipod, and in the shapes of some structures since anisotropy is induced for more than one direction.

It is interesting to note that dramatically different shapes (i.e., tetrahedra vs multipods) are accessible by change of the type of seed particles used. This result exemplifies the need for small, well-defined seeds in the synthesis of monodisperse nanoparticles of a given shape. Although it is possible that the morphology of seed particles changes upon cooling and isolation, particles isolated from the seed-forming reaction mixture that initiate the growth of multipods are larger than typical seed particles (3-5 nm, by TEM) and possess jagged edges and a broad distribution of shapes (Figure 9). Apparently, the larger and more polydisperse seed particles possess facets that are more differentiated in energy, and some of these faces act as efficient templates for directional growth of crystalline arms. The seed particles that lead to tetrahedra appear to possess facets that are more similar in energy and reactivity, resulting in isotropic growth. As observed in the TEM images, the multipod “cores” appear to be wider than the various arms that extend from them (ca. 5 nm, the size of many of the observed *in situ* seeds). This is consistent with a seeded (or two-step) growth mechanism. The large discrepancy in the size and shape of the seed particles used in this step may explain the variance of arms per multipod obtained in the growth step. As evidenced by the snowflake-shaped particles in Figure 8, the width and length of the multipod arms remains the same with additional added precursor. This observation suggests that a preferred arm size of 15 nm by 3 nm has been reached in this system.

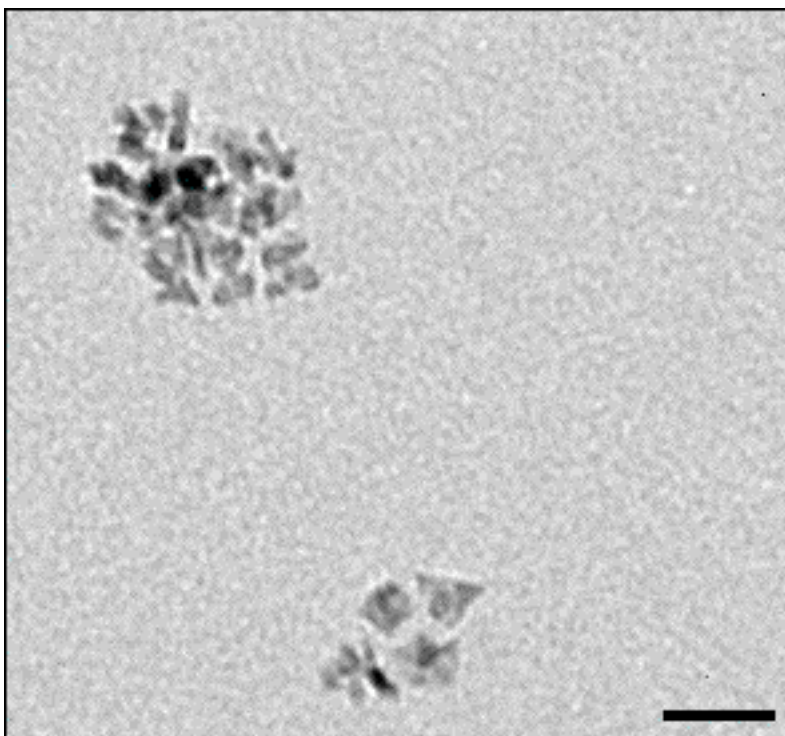


Figure 9. TEM image of isolated *in situ* seed particles prepared by injecting 0.1 mL of a solution of 0.009 g of $\text{Rh}_2(\text{OAc})_4$ in tetraglyme into the surfactant mixture at 180°C with a reaction time of 10 min. The sample was rapidly cooled and the particles were isolated to obtain the TEM image. Bar corresponds to 20 nm.

Conclusions

This research has demonstrated the utility of a seeded-growth process for obtaining two types of rhodium nanoparticles. Small, more monodisperse seed particles lead to tetrahedrally-shaped rhodium nanocrystals, about half of which are truncated at one corner. Use of less well-defined rhodium seed particles that are generated *in situ* provided anisotropic growth and the formation of multipod structures. These types of rhodium nanostructures have not previously been obtained with molecular stabilizers. The latter feature may enable the use of such particles in applications requiring access of molecular substrates or analytes to the nanoparticle surface. In addition, the observations described here may be of use in providing elements of structural control for other kinds of nanoparticles.

Experimental Procedures

General procedures. All reactions were performed under routine air-free conditions. Nanoparticle solutions were manipulated in the air after completion of the synthetic procedures. Cyclopentadienyldiethylene-rhodium(I) was prepared as reported in the literature and sublimed prior to use.²² $\text{Rh}_2(\text{OAc})_4$ was prepared according to standard procedures.²³ Decane was distilled

from sodium. Octadecylphosphonic acid was purchased from Polysciences, Inc. All other reagents were purchased from Aldrich and used as received.

Characterization of rhodium nanoparticles. Powder XRD patterns were collected on a Bruker D-8 GADDS Diffractometer with a CoK_α X-ray source ($\lambda = 1.79026 \text{ \AA}$). Most TEM images were recorded on a Tecnai G2 S-Twin operating at 200kV. The high angle annular dark field images (HAADF) of the rhodium tetrahedra were recorded using an aberration-corrected VG HB 501 equipped with a Gatan Enfina spectrometer and operating at a voltage of 100 kV. The HRTEM images of the multipods were recorded on a CM300 with a field emission gun and a Gatan Energy Filter. TEM samples were mostly prepared by drop-casting solutions of nanoparticles on ultrathin carbon type-A, 400 mesh copper grids purchased from Ted Pella, Inc. The formvar layer was removed according to the provided instructions prior to nanoparticle deposition. HRTEM samples were deposited on ultrathin carbon film on a holey carbon support film, 400 mesh copper grids also purchased from Ted Pella, Inc. Particle counting was performed by measuring a horizontal lines across at least 50 nanoparticles by using ImageJ software unless other wise noted.

Larger rhodium nanoparticles from seed particles. In a typical experiment, nanoparticle seeds (0.00271 mmol rhodium, see Chapter 1) suspended in chloroform were to a round bottom Schlenk flask and the chloroform was then removed under vacuum. 1-Hexadecylamine (2.0 g, 8.3 mmol), 1,2-hexadecanediol (0.4 g, 1.5 mmol) and adamantane carboxylic acid (0.09 g, 0.5 mmol) were added to the flask in a molar ratio of 16:3:1.¹⁴ The reaction vessel was then degassed by evacuated and refilled with N_2 multiple times before the reaction mixture was heated to 140°C under magnetic stirring at 1200 rpm. (Note: the brown color of the rhodium nanoparticle seeds was transferred to the solution, indicating dissolution and probable surfactant exchange.) $\text{Rh}_2(\text{OAc})_4$ (0.008 g, 0.0359 mmol, 13 equivs with respect to rhodium in the seeds) was dissolved in 1 mL of tetraglyme (aided by heating and sonication), and then added to the reaction mixture via a syringe pump over 1 h. The resulting solution was held at 140°C for 1 additional h before cooling to room temperature at a rate of $1^\circ \text{C}/\text{min}$ by the use of a programmable stir plate fitted with a thermocouple. To recover the nanoparticles from the solid surfactant mixture, 10 mL of chloroform was added to the flask and the solution was sonicated in order to solubilize all of the particles. Then, 35 mL of ethanol was added to precipitate the particles. They were recovered by centrifugation (7 krpm, 10 min) followed by decantation to remove the remaining, nearly colorless solution. One additional chloroform/ethanol precipitation was carried out for further purification. Note: The resultant black/brown nanoparticle sample should not be rigorously dried in vacuo, as doing so produces a powder that is difficult to redisperse in solvents.

In-situ seeded nucleation and growth of rhodium multipods. The following surfactants were added to a round bottom Schlenk flask: 1-hexadecylamine (2.0 g, 8.3 mmol), 0.40 g of 1,2-hexadecanediol (0.4 g, 1.5 mmol), and adamantane carboxylic acid (0.09 g, 0.50 mmol), in a molar ratio of 16:3:1 (same as in the procedure described above). The reaction flask containing the solvent-surfactant mixture was evacuated and refilled with N_2 multiple times before heating to 180°C with magnetic stirring at 1200 rpm. The rhodium precursor, $\text{Rh}_2(\text{OAc})_4$ (0.009 g), was dissolved in 1 mL of tetraglyme (aided by sonication and heating) and 0.1 mL of this solution was quickly injected into the Schlenk flask. The temperature and stirring rate were held constant for 1 h without further addition of the rhodium precursor. This procedure produces

a solution of rhodium particles referred to as “*in situ* seeds”. After the 1 h, the solution was cooled to 140° C and the remainder of the $\text{Rh}_2(\text{OAc})_4$ solution in tetraglyme was added over 1 h via syringe pump, with conditions and workup procedures identical to those described in the previous section, that produces larger rhodium nanoparticles from seed particles.

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Chapter 4

Synthesis of New Mixed-Metal Oxide Nanoparticles for Water Oxidation Catalysis

Introduction

The expansion of the world's energy consumption coupled with depletion of petroleum-based energy sources has led scientists to confront the challenge of finding alternative, abundant forms of energy. Carbon neutral sources of energy such as wind, hydroelectric, or solar are attractive solutions to this energy crisis because (unlike petroleum based sources), they are sustainable. Furthermore, carbon-neutral energy sources do not increase CO₂ levels in the atmosphere, and in this way do not contribute to the problem of global warming.¹

Although technologies are being developed to harness these sustainable energy sources, energy storage remains another issue that needs to be addressed in the development of alternative fuels.² An attractive solution to this problem involves the use of solar energy for production of storable, transportable, chemical fuels. For example, the synthesis and storage of hydrogen gas for use as a chemical fuel has been considered.³ The water splitting reaction ($2\text{H}_2\text{O} \longrightarrow 2\text{H}_2 + \text{O}_2$), an uphill reaction with a high activation energy barrier, produces hydrogen gas along with oxygen gas as a byproduct. Other reactions producing carbon neutral chemical fuels can also be envisioned, such carbon dioxide fixation ($\text{CO}_2 + 2\text{H}_2\text{O} \longrightarrow \text{CH}_4 + 2\text{O}_2$); however, in all cases, water oxidation is a necessary component as a half-reaction.^{2,4} The development of an efficient photovoltaic coupled with catalysts both for water oxidation and proton reduction allows the capability to tailor and optimize each component in this multi-step sunlight to fuel schematic.

Focusing on the water splitting reaction, the electrochemical half reactions at the anode and the cathode are described by eqs 1 and 2 respectively.



The reaction at the anode, (eq 1, the water oxidation reaction), is a thermodynamically demanding four electron reaction, with $E = -1.23 \text{ V} - 0.059 (\text{pH}) \text{ V}$ vs NHE. However, there is also a large overpotential associated with this reaction that motivates the development of catalysts to aid in the efficiency of the conversion of sunlight to chemical fuel. In nature, photosystem II makes use of the oxygen-evolving complex (OEC, CaMn_4O_4) in order to catalyze water oxidation with a low overpotential and high activity. Thus, various molecular complexes have been designed and used to catalyze this reaction,⁵⁻⁷ although they invariably suffer from low turnover frequencies (TOFs), high overpotentials, and low stability.

Recently, the interest in cheap, abundant, first row transition metal oxide materials has enjoyed a resurgence due to their ability to catalyze the water oxidation reaction when coupled with a photovoltaic material on a scale that could potentially meet the world's energy demands. A recent report details the use of an amorphous cobalt oxide film that electrochemically catalyzes the water oxidation reaction with a low overpotential at a neutral pH,⁸ and other reports have aimed to identify the active species.^{9,10} This catalyst differs from most other metal oxide electrocatalysts whose activities are usually reported in basic solutions. Other recent reports have examined cobalt and manganese oxide nanoscale materials for this reaction,^{11,12} and a recent publication describes the size dependence of Co_3O_4 nanoparticles for catalytic water electrolysis.¹³ The latter report demonstrates that Co_3O_4 nanoparticles are effective catalysts for

this reaction, and that smaller particles provide a lower overpotential for the water oxidation reaction.

Although various research groups are investigating the use of metal oxides (such as cobalt and manganese) for catalysis, less research has been focused on mixed-metal oxides, despite reports of improved efficiencies for catalytic oxidations.^{14,15} The spinel phase is a well-studied type of oxide structure with the formula $(M^{II})(M^{III})_2O_4$ which can feature the incorporation of two (or more) different metals.¹⁶ In normal spinel materials, $M(II)$ occupies tetrahedral holes and $M(III)$ occupies octahedral holes. However, inverse spinels also exist where $M(III)$ cations occupy the tetrahedral holes, and intermediate structures oftentimes form, where cation distributions lie between a normal and an inverse spinel. Crystal field theory is typically used to predict the cation distribution in these materials.¹⁷ Spinel materials have been used as anodes for electrochemical processes,¹⁸ and the induction of foreign cations into spinel materials has been shown to modify their properties.¹⁹ Recently, MCo_2O_4 ($M = Cu, Mn, Ni$) materials have been shown to be active as CO oxidation catalysts,²⁰ and various metal spinel oxide ferrites have been shown to be active as anodes for the water oxidation reaction.²¹ This report describes attempts to synthesize spinel mixed-metal oxide nanoparticles of similar (small) size, shape, and coordinating ligands, however with different chemical compositions for comparison in electrocatalysis. The materials $NiFe_2O_4$ and $CuCo_2O_4$ were initially targeted due to literature reports that demonstrate improved efficiencies in water oxidation reactions for such materials containing mixtures of these corresponding metals.^{14,15,21,22}

Results and Discussion

Synthesis and characterization of mixed-metal ferrite nanoparticles. Attempts were made to synthesize 6 nm $CoFe_2O_4$ and $MnFe_2O_4$ particles, as in a literature procedure, using metal acetylacetonate precursors, oleic acid, oleylamine, and 1,2-hexadecanediol, with benzylether as the solvent.²³ According to crystal field theory, $CoFe_2O_4$ is expected to be an inverse spinel, while $MnFe_2O_4$ a normal spinel.¹⁶ TEM images of nanoparticles prepared by this procedure are shown in Figure 1. As measured by particle counting of TEM images, the average size and size distribution was 6.1 ± 1.4 nm for the $CoFe_2O_4$ sample and 5.7 ± 1.2 nm for the $MnFe_2O_4$ sample. Powder X-ray diffractions of both samples displayed the expected peak broadening based on the nanoparticle size, and confirmed the spinel structure of the nanoparticles. However, p-XRD patterns were not able to differentiate the mixed metal oxide from Fe_3O_4 on the basis of peak locations. Therefore, the particles were subjected to ICP-OES analysis in order to verify the ratio of M to Fe. In the case of $CoFe_2O_4$, the ratio of Co to Fe was not the expected 1:2, but instead 1:4. In the case of $MnFe_2O_4$, the ratio of Mn to Fe was also lower than expected, 1:5. Parameter variations, such as removing 1,2-hexadecanediol from the reaction mixture and changing the initial precursor ratios (increasing the amount of Mn or Co relative to Fe) were explored in attempts to synthesize materials with the desired 1:2 (M:Fe) atomic ratios. However, the ratios obtained above by repeating the standard synthetic procedure were unfortunately not improved upon by these synthetic manipulations.

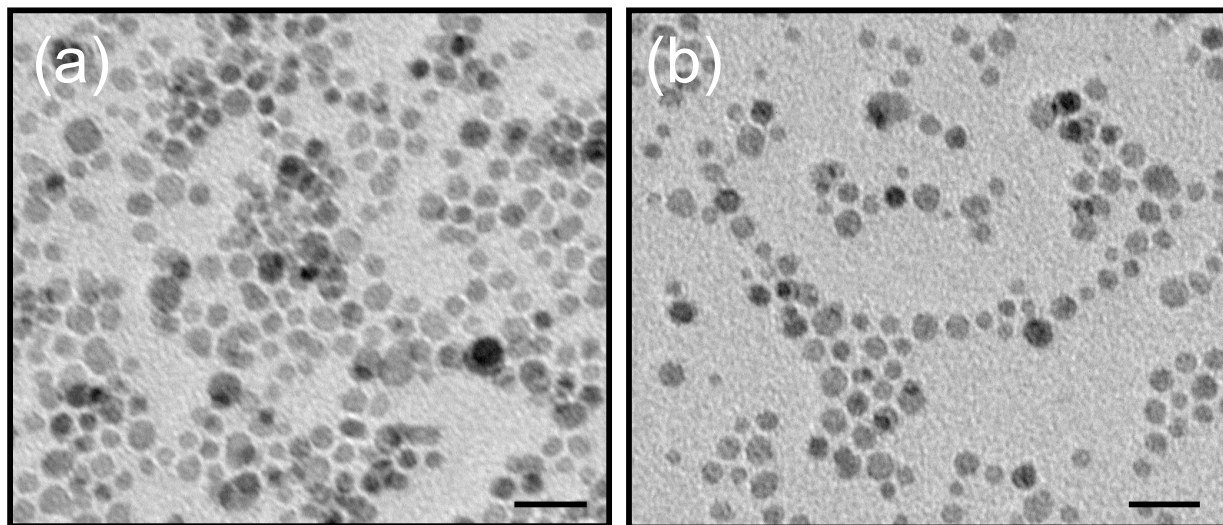


Figure 1. Representative TEM images of the as synthesized (a) CoFe_2O_4 nanoparticles and (b) MnFe_2O_4 nanoparticles. Each bar corresponds to 20 nm.

Additionally, attempts were made to synthesize NiFe_2O_4 (inverse spinel) by a synthetic route similar to that of the reported 6 nm MnFe_2O_4 and CoFe_2O_4 nanoparticles²³. Use of these conditions resulted in the formation of nickel metal, as detected by p-XRD peaks. Since 1,2-hexadecanediol has been shown to be a mild reductant (and may have been causing the decomposition of $\text{Ni}(\text{acac})_2$), it was omitted from the reaction mixture to yield a brown powder analyzed to be solely the desired spinel structure by p-XRD. TEM analysis of the sample indicated an average size and size distribution of 8.0 ± 1.9 nm (Figure 2a). The p-XRD pattern is also shown in Figure 2b and indicates a match to the pattern file (00-054-0964) for NiFe_2O_4 (Trevorite). Analysis by ICP-OES was in good agreement with the predicted ratio of Ni to Fe in a spinel structure (1:2).

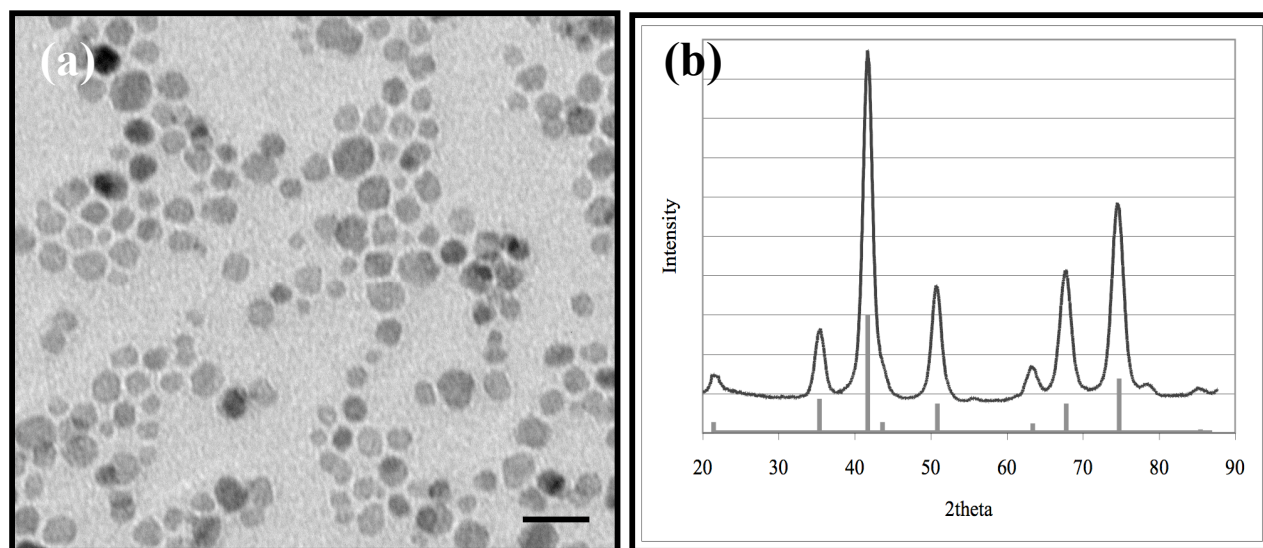


Figure 2. Representative (a) TEM image and (b) p-XRD pattern (indexed to the pattern for NiFe_2O_4 with the appropriate intensities) of synthesized NiFe_2O_4 nanoparticles. Bar in TEM image corresponds to 20 nm.

Synthesis and characterization of MCo_2O_4 ($\text{M} = \text{Co}, \text{Cu}, \text{Ni}$) nanoparticles. Many unsuccessful attempts were made to directly synthesize nanoparticles of the material CuCo_2O_4 via standard solution state decomposition methods. This material has been known to be difficult to prepare and has a low thermal stability.²⁴ The decomposition of Cu(II) complexes generally occurs at lower temperatures than those associated with decomposition of Co(III) precursors, as demonstrated by samples that usually contained copper metal and various phases of cobalt oxide according to p-XRD. Therefore, a new synthetic route to obtain CuCo_2O_4 was attempted: cation exchange reactions beginning with isolated Co_3O_4 nanoparticles.¹³ For such exchange reactions, Cu(II) sources were employed in attempts to replace Co(II) in the Co_3O_4 structure. Characterization of films of CuCo_2O_4 has shown that this material has a structure closer to inverse than normal, however can be classified as somewhat intermediate.²⁴ Cation exchange reactions have previously been observed and studied for systems involving sulfide and selenide materials.²⁵⁻²⁷

Cubic Co_3O_4 was prepared according to the literature procedure for small particles.^{13,28} Multiple autoclave reactors were employed simultaneously in order to scale-up the synthesis for cation exchange reactions with this material. The product obtained from this synthesis consists of mainly cube-shaped particles, with an average edge length (by TEM) of 5.2 ± 0.8 nm. Analysis of the particles by p-XRD indicated exclusively the CoCo_2O_4 spinel structure (matched to pattern file 01-080-1541) with line broadening corresponding to an average particle size of 12.3 nm as determined through Debye-Scherrer analysis of the (400) index. The larger crystalline domain size obtained through p-XRD measurements suggests the presence of larger nanocrystals that were not observed by TEM. The lack of a stabilizer in this synthesis may result in particle agglomeration and explain this inconsistency in the data. Figure 3 shows the TEM and XRD

obtained for this material. The final product was dried and isolated as a powder for further reaction.

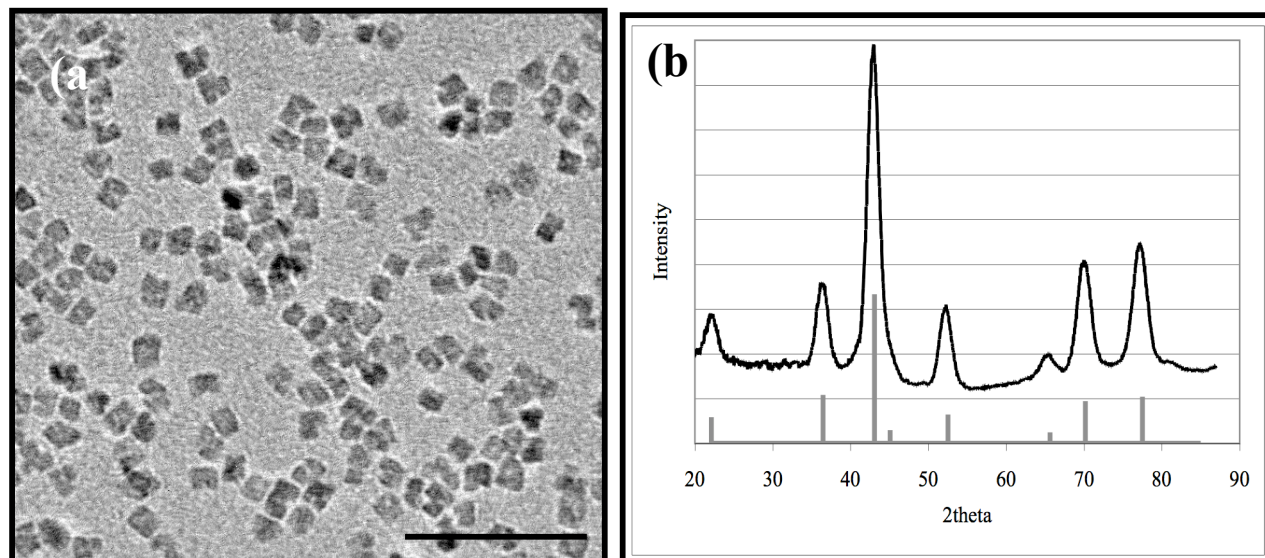


Figure 3. Representative (a) TEM image and (b) p-XRD pattern (indexed to the pattern for CoCo_2O_4 with the appropriate intensities) of the synthesized Co_3O_4 . Bar in TEM image corresponds to 50 nm.

The 5.2 ± 0.8 nm Co_3O_4 nanoparticles were subjected to a variety of conditions in the presence of Cu(II) sources in water. For the initial experiments, CuBr_2 was used as the copper precursor and it was always added in excess with respect to the Co(II) in the Co_3O_4 material. The use of $\text{Cu}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ as a precursor afforded similar results. After multiple washings with water and THF and isolation by centrifugation (to remove excess copper and cobalt salts), the particles were subjected to ICP-OES analysis in order to obtain the ratio of copper to cobalt. These results are summarized in Table 1. The results indicate that a small amount of copper is incorporated into the material (usually 1:12 Cu:Co), regardless of reaction conditions, except for the sample that was allowed to react for 40 days (1:6 Cu:Co). Analysis by p-XRD indicated that the spinel structure was retained after the exchange reaction, as indicated by the identical peak positions for Co_3O_4 and CuCo_2O_4 . Imaging of the particles by TEM showed that the particle size and shape was retained after copper incorporation. Also, an exchange reaction was attempted with somewhat larger Co_3O_4 nanoparticles (average diameter of 21 nm) discussed in a previous manuscript.¹³ This was attempted to determine whether the exchange was only occurring at surface sites. Since this larger nanoparticle sample has a lower surface area, a lower copper incorporation would have been observed by ICP-OES if selective surface substitution were responsible for copper incorporation. However, the exchange reaction with these nanoparticles (10 mg Co_3O_4 , 10 mg CuBr_2 , sonication for 1 h) resulted in a copper to cobalt ratio of 1:11 by ICP-OES; very similar to that observed with the smaller nanoparticles.

Table 1. Various amounts of CuBr₂ added to 10 mg Co₃O₄ in 10 mL H₂O with the reaction conditions listed and the resultant ratio of Cu to Co calculated from ICP-OES measurements.

Entry	CuBr ₂ (mg)	Reaction Conditions	Cu:Co ratio
1	10	Stir, 4 h	1:15
2	10	Stir, 12 h	1:12
3	30	Sonicate, 2 h	1:12
4	100	Sonicate, 2 h	1:12
5	10	Stir, 40 days	1:6

For one batch of Co₃O₄ nanoparticles, unusually large ratios (3:2) of copper to cobalt were observed (by ICP-OES) regardless of copper precursor or exchange reaction time. However, it was determined that the copper hydroxide phase, Cu₂(OH)₃Br, had formed (by p-XRD). This was most likely due to incomplete washing of the ammonium hydroxide used in the synthesis of Co₃O₄ nanoparticles. Thus, it is important for the solution not to be basic during the exchange reaction. A pH dependence study was also conducted, where well-washed Co₃O₄ nanoparticles (10 mg) were allowed to react with Cu(NO₃)₂·4H₂O (10 mg in 10 mL H₂O) at the measured pH of 5 (no pH adjustment) and a pH of 1 (adjusted with HCl). In the reaction with pH = 5, the resulting copper to cobalt ratio was 1:5 (by ICP-OES), whereas in the reaction with pH = 1, the copper to cobalt ratio was 1:47. In both cases, no hydroxide phase was detected by p-XRD. Thus, it appears important to maintain a neutral pH during the exchange reaction for higher loadings of copper to be incorporated however to prevent the formation of copper hydroxides.

Attempts were also made to incorporate nickel into the cobalt spinel material, targeting NiCo₂O₄ (inverse spinel). As with Cu(II), Ni(II) would be expected to incorporate into the M(II) sites of a spinel structure and replace Co(II) in the material.²⁰ Thus, Co₃O₄ (10 mg) was stirred with NiCl₂·6H₂O (20 mg) for 36 hours before the resulting particles were washed repeatedly with water and THF and isolated by centrifugation. Analysis by TEM indicated no change in the size and shape of the nanoparticles and p-XRD indicated the presence of a spinel phase similar to that of Co₃O₄. Analysis by ICP-OES indicated a nickel to cobalt ratio of 1:9.

Electrochemical water oxidation experiments with MFe₂O₄ (M = Co, Mn, Ni) nanoparticle modified anodes. Linear scan voltammograms were collected for nickel foam electrodes modified with the three ferrite nanoparticle samples discussed previously. The electrochemical data for these three samples is shown in Figure 4, and Table 2 illustrates potential differences at specific current densities amongst the three samples. The average nanoparticle size for the CoFe₂O₄ sample is slightly larger than that for MnFe₂O₄ (6.1 and 5.7 nm respectively by TEM); however the average nanoparticle size of the NiFe₂O₄ sample is considerably larger (8.0 nm), and thus inherently lower potentials might be expected due to size effects previously observed in these types of experiments.¹³ Although the CoFe₂O₄ and the MnFe₂O₄ samples exhibited similar electrocatalytic activities, the CoFe₂O₄ is superior to the

other two samples with respect to electrocatalytic activity for water oxidation, across all potentials measured in alkaline solution (pH = 14).

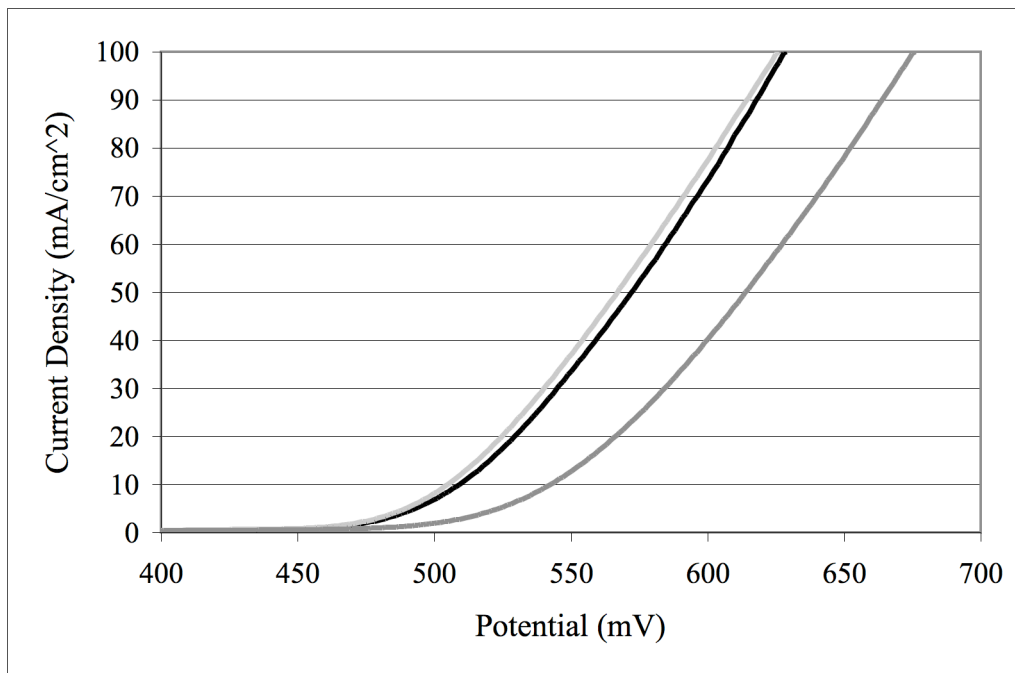


Figure 4. Polarization activities for three separate nickel foam working electrodes modified with 1 mg of the indicated metal ferrite nanoparticles swept from 200 to 1000 mV vs Ag/AgCl at 1 mV/s in 1.0 M KOH. NiFe₂O₄ (dark gray), MnFe₂O₄ (black), and CoFe₂O₄ (light gray).

Table 2. Electrochemical potentials for various samples of MFe₂O₄ at the specified current densities.

Sample	Potential at specified current density (mV)		
	10 mA cm ⁻²	50 mA cm ⁻²	100 mA cm ⁻²
NiFe ₂ O ₄	543	614	677
MnFe ₂ O ₄	510	573	630
CoFe ₂ O ₄	505	567	626

Electrochemical water oxidation experiments with M_xCo_{3-x}O₄ (M = Co, Cu, Ni) nanoparticle modified anodes. Linear scan voltammograms were collected on nickel foam electrodes modified with the 5.2 +/-0.8 nm Co₃O₄ nanoparticles (Figure 3) and samples of Co₃O₄ nanoparticles after copper exchange reactions at pH = 1 and 5. The sample prepared at pH = 1

(1:47 Cu:Co) exhibited a much lower degree of copper incorporation compared to the sample prepared at pH = 5 (1:5 Cu:Co). The electrochemical data for these three samples is shown in Figure 5. Table 3 illustrates potential differences at specific current densities amongst these three samples and also the nickel-exchanged $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ nanoparticles. It is interesting to note that the onset potential was lower for the copper-containing materials, while the Co_3O_4 nanoparticles exhibited higher electrocatalytic activity at higher potentials (>20 mA). The two copper-containing nanoparticle materials exhibited very similar electrochemical behavior. The $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ material exhibited the highest electrochemical activities across all measured potentials (Table 3).

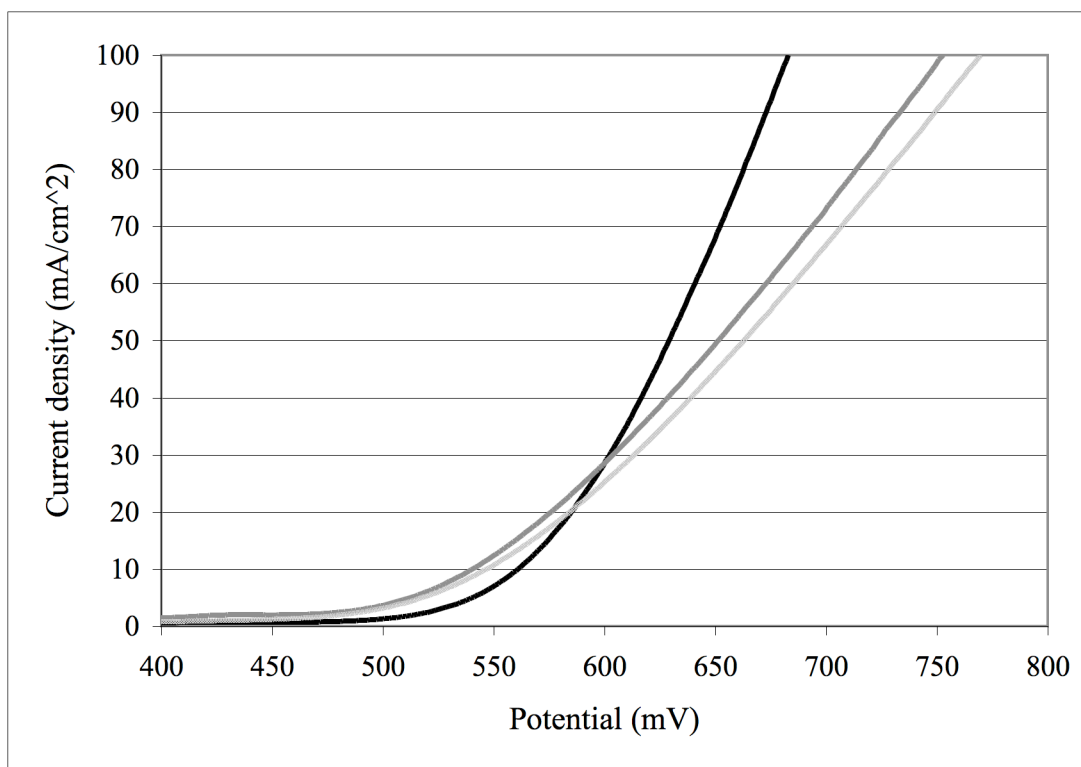


Figure 5. Polarization activities for three separate nickel foam working electrodes modified with 1 mg of the indicated $\text{M}_x\text{Co}_{3-x}\text{O}_4$ nanoparticles swept from 200 to 1000 mV vs Ag/AgCl at 1 mV/s in 1.0 M KOH. Co_3O_4 (black), $\text{Cu}_x\text{Co}_{3-x}\text{O}_4$ (Cu:Co 1:5, light gray), and $\text{Cu}_x\text{Co}_{3-x}\text{O}_4$ (Cu:Co 1:47, dark gray).

Table 3. Electrochemical potentials for various $M_x\text{Co}_{3-x}\text{O}_4$ samples at the specified current densities.

Sample	Potential at specified current density (mV)		
	10 mA cm ⁻²	50 mA cm ⁻²	100 mA cm ⁻²
Co ₃ O ₄	561	630	683
Cu _x Co _{3-x} O ₄ (Cu:Co 1:5)	547	663	770
Cu _x Co _{3-x} O ₄ (Cu:Co 1:47)	540	651	753
Ni _x Co _{3-x} O ₄	531	620	680

Comparative TOF Calculations per Surface Metal Atoms. It is difficult to say what the active surface area is during the electrocatalytic reaction. Nonetheless, calculations were performed with all metal surface atoms being considered active in the water oxidation electrocatalytic reaction to determine TOFs. Exposed (400) faces are assumed in each case, and for a spinel unit cell, 2 metal atoms are fully occupied and 4 are half occupied, giving 4 total surface atoms per unit cell (400) face. The calculated TOFs for the previously discussed $M_x\text{Co}_{3-x}\text{O}_4$ nanoparticles are all identical to Co₃O₄ due to the same size and shape of the particles before and after cation exchange, and the negligible change in density of the material. Table 4 compares the calculated TOFs for Co₃O₄ to the TOF for the synthesized NiFe₂O₄ nanoparticles at 10 and 50 mA cm⁻². Due to the discrepancy in nanoparticle sizes (present in both samples) in TEM vs. XRD, TOF calculations for both measured sizes are given (12.3 nm for Co₃O₄ and 13.8 nm for NiFe₂O₄). Surface areas (by XRD) were calculated assuming crystalline, cubic particles, where Debye-Scherrer analysis the (400) peak was used to determine the side length of a cube. The surface area (by TEM) of the Co₃O₄ particles was also conducted in this manner from the average measured particle edge lengths (5.2 nm) since the majority of the sample is cube-shaped. Since the NiFe₂O₄ nanoparticles appeared spherical (by TEM), the average diameter (8.0 nm) was used and a sphere was assumed in the surface area and volume calculations. Unit cell parameters and densities of the materials were compiled from their respective bulk values. A four-electron transfer was considered in the production of one molecule of O₂, and 100% Faradaic efficiency was also assumed. (For a sample calculation, see Supporting Information in reference 12)

Table 4. Calculated TOF data for Co₃O₄ nanoparticles and NiFe₂O₄ nanoparticles assuming all surface metal atoms are active catalytic sites.

Sample	SA _{TEM} (m ² g ⁻¹)	Metal surface atoms _{TEM}	TOF _{TEM} (s ⁻¹ M _{surf} ⁻¹)	SA _{XRD} (m ² g ⁻¹)	Metal surface atoms _{SXRD}	TOF _{XRD} (s ⁻¹ M _{surf} ⁻¹)
Co ₃ O ₄	189	1.15 x 10 ¹⁸	0.068 (50 mA) 0.014 (10 mA)	80.0	4.88 x 10 ¹⁷	0.16 (50 mA) 0.032 (10 mA)
NiFe ₂ O ₄	142	8.04 x 10 ¹⁷	0.097 (50 mA) 0.019 (10 mA)	82.0	4.66 x 10 ¹⁷	0.17 (50 mA) 0.033 (10 mA)

Conclusions

Well-defined mixed-metal oxide spinel nanoparticles, a previously unexplored class of materials for water oxidation electrocatalysis were synthesized and their behavior as electrocatalysts for water-oxidation was studied. A new synthesis for NiFe₂O₄ nanoparticles was devised, and a new method was developed for making nanoparticles of the composition M_xCo_{3-x}O₄ (M = Cu, Ni) by cation exchange reactions, starting from previously reported Co₃O₄ nanoparticles. Electrochemical water electrolysis was performed with anodes modified with the mixed-metal spinel nanoparticle materials, and by comparison, the Co_xFe_{3-x}O₄ material outperformed Mn_xFe_{3-x}O₄ and NiFe₂O₄ at all measured potentials. Also, Co₃O₄ nanoparticles were directly compared with samples of Cu_xCo_{3-x}O₄ and Ni_xCo_{3-x}O₄ as electrocatalysts. Although the copper modified nanoparticles showed lower onset potentials when compared to Co₃O₄ for water oxidation, they suffered from lower current densities at higher potentials. However, the nickel-modified nanoparticles exhibited higher electrochemical activities at all measured potentials. More experiments need to be conducted on these spinel nanoparticles pertaining to characterization and optimization with regards to degree of metal incorporation, however the initial electrocatalysis reactions indicate good potential, especially for the nickel-modified Co₃O₄ materials.

Experimental Procedures

General procedures. Reactions involving the synthesis of metal ferrite materials were performed under routine air-free conditions. Mn(acac)₂ and Fe(acac)₂ were prepared by reacting Mn(OAc)₂ or FeCl₃ respectively with acacH in slightly basic solution. The Mn(acac)₂ was dehydrated by heating to 100° C under vacuum for 4 hours while the Fe(acac)₃ was dried under vacuum at room temperature. Co(acac)₂·2H₂O was purchased from Aldrich and dehydrated by heating to 90° C under vacuum for 4 hours. Ni(acac)₂ (anhydrous) along with all other metal precursors discussed in this chapter were purchased from Aldrich and used as received. Nanoparticle solutions were manipulated in the air after completion of the synthetic procedures. The syntheses and the work-up procedures for MCo₂O₄ nanoparticles were manipulated in air.

Nanoparticle characterization. Powder XRD patterns were collected on a Bruker D-8 GADDS Diffractometer with a CoK_α X-ray source ($\lambda = 1.79026 \text{ \AA}$). TEM images were recorded on a Tecnai G2 S-Twin operating at 200kV. TEM samples by drop-casting solutions of nanoparticles on ultrathin carbon type-A, 400 mesh copper grids purchased from Ted Pella, Inc. The formvar layer was removed according to the provided instructions prior to nanoparticle deposition. Drawing and measuring horizontal lines across at least 50 nanoparticles was performed for particle counting purposes. (ImageJ software). ICP-OES was performed on an Optima 7000. Samples for ICP-OES were prepared by adding concentrated HNO_3 to dry nanoparticle samples and using a microwave digest for solubility purposes before diluting to 2% HNO_3 . Standard calibration curves were constructed by serial dilution of a standard 10 ppm solution with multiple metals purchased from Perkin-Elmer and in all cases, excellent line fitting to the calibration curves was achieved.

Nanoparticle-modified electrode preparation and electrochemical measurements. Electrodes modified with various metal oxide nanoparticles were prepared by well-dispersing (aided by sonication) 1.0 mg of the corresponding nanoparticle sample in approximately 2 mL of chloroform (MFe_2O_4) or water (MCo_2O_4). This solution was drop cast on 1 cm^2 of a 1 cm by 2 cm nickel foam electrode and the liquid evaporated (final loading of 1 mg/cm^2). Electrochemical measurements were performed on a Bioanalytical Systems model CW50 computer controlled potentiostat. Linear scan voltammetry and cyclic voltammetry measurements were performed using a two compartment H-cell with a standard 3-electrode configuration. Electrocatalysis was performed in 1 M KOH solution (measured to pH 14 using a pH meter) and referenced to a standard Ag/AgCl reference electrode. Platinum wire was used as the counter electrode. The working electrode (nanoparticle-modified nickel foam) was suspended with only the nanoparticle-modified side in the solution. Linear scan voltammetry was typically swept from 200 – 1000 mV with a scan rate of 1 mV/s. Current was measured to $\pm 100 \text{ nA}$.

Synthesis of MFe_2O_4 ($\text{M} = \text{Mn, Co, Ni}$) nanoparticles. The nanoparticle materials MnFe_2O_4 and CoFe_2O_4 were synthesized according to the literature procedure for 6 nm Fe_3O_4 with a precursor ratio of Mn or Co to Fe of 1:2.²³ For the synthesis of NiFe_2O_4 nanoparticles, $\text{Ni}(\text{acac})_2$ (0.123 g, 0.479 mmol) was combined with $\text{Fe}(\text{acac})_3$ (0.339 g, 0.960 mmol), and oleic acid (1.69 g), oleylamine (1.60 g) in benzylether (20 mL). The reaction mixture was heated to 200°C for 2 h, then 300°C (refluxing) for 1 h before cooling to room temperature. The particles were isolated by the addition of ethanol (30 mL) to precipitate followed by centrifugation (6000 rpm, 10 min). For a more thorough washing, the brown powder was dissolved in a small amount hexanes followed by the addition of ethanol to precipitate and isolate via centrifugation as described previously.

Synthesis of $\text{M}_x\text{Co}_{3-x}\text{O}_4$ ($\text{M} = \text{Co, Cu, Ni}$) nanoparticles. Cubic Co_3O_4 nanoparticles were prepared according to the literature procedures.^{13,28} Briefly, $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (200 mg, 0.803 mmol) was combined with NH_4OH (1 mL 25% solution in H_2O) in ethanol (10 mL). This mixture was stirred in open air for 5 minutes before sealing in a Teflon autoclave reactor and heating to 150°C for 3 h. Reactor was cooled overnight before centrifuging contents in autoclave (6000 rpm, 10 min) with a small additional amount of H_2O (used to rinse walls of autoclave) and a small amount of THF. Supernatant was discarded and brown precipitate was washed once more by dispersion in H_2O and precipitation with THF followed by centrifugation.

Cubic $\text{Cu}_x\text{Co}_{3-x}\text{O}_4$ nanoparticles were prepared by the reaction of Co_3O_4 nanoparticles with either CuBr_2 or $\text{Cu}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$. In a typical experiment, $\text{Cu}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (20 mg, 0.106 mmol) was added to a solution of Co_3O_4 nanoparticles (10 mg, 0.133 mmol Co, 0.044 mmol based on Co(II)) in 10 mL H_2O . The mixture was stirred or sonicated for 1 h before isolation via addition of THF, followed by centrifugation (6000 rpm, 10 min). One additional dissolution and centrifugation step was performed to insure the removal of excess Cu^{2+} . (Note: It is important for the solution pH to be neutral or slightly acidic to prevent the formation of copper hydroxide phases. Insufficient washing of NH_4OH from the Co_3O_4 nanoparticles can lead to basic reaction conditions.) Other reaction conditions for this system are discussed in the Results and Discussion section of this chapter.

Cubic $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ nanoparticles were prepared by the reaction of Co_3O_4 nanoparticles with $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$. Typically, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (20 mg, 0.084 mmol) was added to a solution of Co_3O_4 nanoparticles (10 mg, 0.133 mmol Co, 0.044 mmol based on Co(II)) in 10 mL H_2O . The mixture was stirred for 36 h before isolation of the particles via addition of THF, followed by centrifugation (6000 rpm, 10 min). One additional dissolution and centrifuge step was performed to ensure the removal of excess Ni^{2+} .

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