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Porous Core-Shell Nanostructures for Catalytic Applications

by

Trevor David Ewers

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 at BERKELEY

Committee in charge:

Professor A. Paul Alivisatos, Chair Professor Gabor Somorjai Professor Ronald Gronsky

Fall 2012

Porous Core-Shell Nanostructures for Catalytic Applications

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Abstract

Porous Core-Shell Nanostructures for Catalytic Applications

by

Trevor David Ewers Doctor of Philosophy in Chemistry University of California at Berkeley Professor A. Paul Alivisatos, Chair

Porous core-shell nanostructures have recently received much attention for their enhanced thermal stability. They show great potential in the field of catalysis, as reactant gases can diffuse in and out of the porous shell while the core particle is protected from sintering, a process in which particles coalesce to form larger particles. Sintering is a large problem in industry and is the primary cause of irreversible deactivation.

Despite the obvious advantages of high thermal stability, porous core-shell nanoparticles can be developed to have additional interactive properties from the combination of the core and shell together, rather than just the core particle alone. This dissertation focuses on developing new porous core-shell systems in which both the core and shell take part in catalysis.

Two types of systems are explored; (1) yolk-shell nanostructures with reducible oxide shells formed using the Kirkendall effect and (2) ceramic-based porous oxide shells formed using sol-gel chemistry. Of the Kirkendall-based systems, Au@Fe_xO_y and Cu@CoO were synthesized and studied for catalytic applications. Additionally, ZnO was explored as a potential shelling material. Sol-gel work focused on optimizing synthetic methods to allow for coating of small gold particles, which remains a challenge today. Mixed metal oxides were explored as a shelling material to make dual catalysts in which the product of a reaction on the core particle becomes a reactant within the shell. Dedicated to my loving parents, David and Leslie Ewers, brother, Richard Ewers, and my very supportive family. In memory of my grandfather, Richard Elliot Friedrichs, grandmother, Mary Dean Baird Ewers, and uncle, William (Bill) Ewers.

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Chapter 1 Introduction

Within the past few years, the number of publications on porous core-shell nanostructures for catalysis has drastically risen. The majority of these publications highlight the increased thermal stability porous oxide shells give to metal cores. With heterogeneous catalysts being a main component in most large scale industrial process, it is no wonder porous core-shell systems have received so much attention, as irreversible deactivation due to sintering and coarsening is the largest contributor to decreased catalyst lifetimes. However, despite the obvious advantage of thermal stability, the core-shell geometry may offer new possibilities in the field of catalysis.

This dissertation covers the guided synthesis of porous core-shell nanostructures for catalytic applications. The aim in these studies was to explore new possibilities for porous core-shell systems that take advantage of both thermal stability and added chemical specificity within the shell. A quick review of nanoparticle catalysis is given below as a motivator for utilizing porous core-shell geometries for catalytic studies.

1.1 Nanoparticles for Catalysis

The use of nanoparticles for heterogeneous catalysis is not a new concept. Historically, sub-micron sized dispersions of metal particles on porous supporting oxides have been routinely used in industry for various catalytic processes [13]. Smaller particle sizes allow for a higher surface area to volume ratio, minimizing the amount of costly metal catalysts required for a given reaction. More recently, alternative advantages of using nanoparticulate metal catalysts have been explored.

As with any heterogenous reaction on solid surfaces, reacting molecules must adsorb on a catalyst's surface before undergoing secondary reactions or dissociation. However, small nanoparticles exist within a size range in which their physical and chemical properties are intermediate to that of the elements making them up and their bulk counterparts [14]. Their surface structure and electronic properties can change greatly with size, influencing how molecules interact with their surfaces.

Gold, a metal known to be chemically inert in the bulk, is not a likely candidate for catalysis[15]; however, small gold nanoparticles have shown to be exceptional catalysts for a variety of reactions including low temperature CO oxidation [16], selective hydrogenation and selective oxidation reactions [17]. While gold's activity can be highly support dependent, correlations have been made to the size-dependent activity onset in gold clusters to the metal-to-insulator transition at like sizes [18].

Likewise, product selectivity can change with particle size and shape as the relative areas of differentially reactive faces change [19, 20]. Platinum nanoparticles between 1 and 7 nm have shown size-dependent selectivity for furan hydrogenation attributed to the changes in relative surface areas of $Pt\{111\}$ and $Pt\{100\}$ faces. The difference in the bonding orientation of furan on the two faces leads to alternative pathways during hydrogenation [21]. Similar face-specific selectivity was seen on shape-controlled platinum particles for the catalysis of methylcyclopentane ring opening [22].

While many reactions show size and shape dependence on nanoparticle catalysts, the particles themselves are not static [23]. Just as metal thin films have been seen to restructure under varying environmental conditions [24], so do nanoparticles. The restructuring of metal nanoparticles has been studied using various techniques including environmental transmission electron microscopy [25], x-ray absorption spectroscopy [26], and in situ x-ray diffraction [27]. Likewise, alloyed nanoparticle systems may reversibly undergo elemental surface sequestration under oxidizing and reducing conditions [28].

As mentioned earlier in reference to gold catalysis, nanoparticle catalysts often show support dependence [29]. The exact role of the support plays towards influencing catalytic processes is poorly understood. It is known that for many metal particles, the support induces a change in the metal's electronic properties [30]. However, other supportrelated factors such as spillover [31], particle wetting [32] and sacrificial donation of lattice species or surface adsorbates can facilitate in support promotion. For gold, it is thought that the active site for CO oxidation occurs at the interface between the gold particle and the reducible metal oxide support [33]. In layered nanoparticle systems of silica, platinum and ceria, particle interfaces can be used to do sequential chemistry in which the two interfaces act as reactive centers for tandem catalysis [34].

1.2 Geometry Optimizations for Particle Stability

1.2.1 Coarsening and Sintering

Particle coarsening and sintering are the dominating causes for irreversible deactivation in heterogeneous catalysts. Through these processes, particles are joined together and the total available surface area of active catalysts is decreased. Some catalysts, such as gold, show size-dependent activity per available surface site and will become catalytically inert with increasing size [18, 35]. Industry has long studied these these processes and have developed ways of minimizing them to extend the usable lifetime of catalysts before regeneration [36].

Sintering refers to the process in which touching particles densify through mass transport to eliminate voids and lower the excess free energy associated with surface area. The difference in particle surface curvatures at the particle junctions (negative curvature) and outer surfaces (positive curvature) cause mass migration to fill towards the contact region (see $\S2.1.2$). In crystalline particles, a grain boundary migration may also take place as mass transport proceeds [37].

Coarsening is the process in which small particles migrate on a surface and coalesce. There are two accepted mechanisms for particle diffusion that lead can catalyst coalescence: atomic migration (Ostwald ripening) and particle migration (coalescence). During Ostwald ripening, atoms detach from small particles and migrate randomly over a substrate until depositing on larger particles. During particle migration, the entire particle becomes mobile on the surface until coalescing with another particle [38, 39]. As particles grow, their mobility decreases with increasing particle size, causing the coalescence process to slow [40]. Of the two mechanisms, particle migration is the most commonly observed for catalytic systems.

Moreover, migration and coalescence of metal catalysts in porous oxide supports may block pores and restrict the flow of products and reactants [41]. Industry minimizes sintering by decreasing catalyst loading and increasing catalyst spatial dispersity within a support. In addition, catalytic conditions are optimized to lower the likelihood of particle sintering. This often means lowering the reaction temperature to reduce particle mobility at the expense of higher reaction turnovers associated with endothermic reactions [42].

Recent studies have focused on employing geometrical constraints to prohibit particle migration and coalescence. The use of two-dimensional mesoporous supports over linear porous networks has been shown to minimize sintering by trapping migrating particles at kinks in the pore structure [43]. Others have added particle surface anchors [44] or mesoporous silica overlayers [45, 46, 47] on supported particle catalysts to hinder particle migration. These methods work very well but rely on an initially well-dispersed supported catalyst such that multiple catalytic particles are not trapped together.

The full encapsulation of a catalytic particle within a thermally-stable porous shell completely eliminates sintering due to particle migration. Joo et al. found that encasing platinum particles in a mesoporous silica shell $(Pt@mSiO_2)^{1, 2}$ prohibited sintering and coalescence upwards of 750°C without a diffusional penalty for CO oxidation [48]. Since then, many other reports of using porous silica as a sintering-resistive coating have been

published [49, 50].

1.2.2 Pros and Cons of Particle Encapulation in Porous Shells

Single particle isolation using porous shells have shown to effectively protect against coalescence at higher temperatures [3, 48, 49, 50]. The majority of such utilize porous silica as a protective shell, which is highly thermally stable but does not contribute to catalytic activity. In many catalytic systems, the choice of supporting material have shown to drastically effect the overall catalytic activity of metal particles without themselves being catalytically active [51, 34]. These metal/support interactions are thought to influence the oxidation state of peripheral metal atoms through a charge-transfer process as well as provide additional sites for adsorption and spillover.

Likewise, the use of catalytically active shell material may allow for dual catalysis in which products from the core act as reactants within the shell. In this way product selectivity can be increased for tandem reactions [34]. This concept has already been demonstrated with micron sized particles. Bao et al. found that when pellets of a Fischer-Tropsh catalyst were coated with a porous isomerization catalyst, the selectivity for isoparaffins was much greater in the core-shell catalyst than a physical mixture of the two [52].

While such heterostructures have not been extensively studied in the literature, researchers have begun to look at other potential advantages porous shells have towards catalysis. Poison resistivity has been demonstrated when poisoning agents are larger than the pore diameters, allowing only small molecule reactants and products permeable to the shell [53]. In addition, narrow pores can act as a tunable switch to activate and deactivate a core catalyst as desired. For porous hygroscopic silica shells, water vapor can clog pores and block the diffusion of reactants into the shell due to strong adsorption of water within the pores. Upon flushing with dry gas, the water is removed, and the core particle is once again accessible to reactants [54]. Shell functionalization may present new opportunity to extend the switchable corking of shelled materials to other selective molecules and conditions.

Despite their potential advantage, core-shell systems suffer from intrinsic limitations towards catalysis. While narrow pores may block undesired molecules from reaching the core, it limits their catalytic applications to small molecules which can easily diffuse in and out of the pores. Current industrial catalysts use large, porous zeolitic materials as supports to minimize diffusional effects and reduce the effects of pore blockage from coking and sintering. The small pores in the core-shell geometry may reduce the flow of reactants and products through the shell and potentially block the pores if an interaction is strong enough.

 $^{{}^{1}\}mathrm{mSiO}_{2}$ is used to designate that the silica shell is mesoporous

 $^{^{2}}$ the *core*@*shell* nomenclature is commonly used to distinguish core-shell and yolk-shell systems from other nanoparticle heterostructures such as dimers

1.3 Dissertation Outline

The work presented in this dissertation highlights the directed synthesis of porous core-shell systems for catalytic applications in which the shell plays an active role in catalytic processes. Two synthetic methods were primarily used to form porous oxide shells on metal nanoparticles: diffusional-dependent oxidation of zero-valent metals (Kirkendall effect) and sol-gel processing. Chapter 2 gives a general background on nanoparticle synthesis as well as the two methods for producing porous oxide shells. In chapter 3, CO oxidation on Au@Fe_xO_y yolk-shell heterostructures was studied for its enhanced thermal stability and core/shell interaction dependent catalysis. In chapter 4, the synthesis of Cu@CoO was shown to be a unique system in which an oxidizable metal core, in contrast to the typical noble metal core, can be coated to form yolk-shell structures using the Kirkendall effect. In addition, its utility as a potential Fischer-Tropsch catalyst was addressed. Chapter 5 describes the oxidation process of small zinc particles and synthetic progression towards a volk-shell Cu@ZnO for methanol production. Chapter 6 highlights the difficulty in coating small gold particles in silica and methods towards overcoming these limitations. Finally, the modifications and improvement in mesoporous silica encapsulation are described in Chapter 6. The incorporation of titanium within these systems is address as well as their potential use for dual catalysis.

Chapter 2

Background

2.1 Formation and Shape Control of Metal Nanoparticles

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2.1.1 Basic Concepts in Colloidal Synthesis

General colloidal synthesis primarily consists of three components: reactive precursors for particle formation, surfactants to direct particle size and shape, and solvents to act as a reaction medium. The choice of precursors, surfactants, and solvents depend on the material and morphology desired. Typical reaction pathways include thermal decomposition, chemical reduction or oxidation, precipitation, sol-gel and galvanic exchange/replacement [55, 56, 57, 58]. For metal nanoparticles, thermal decomposition is often chosen because it can produce small, spherical particles that are monodispersed, having size distributions within 5% ($\sigma_r \leq 5\%$). Precursors consist of zero-valent organometallics that are rapidly injected into hot high-boiling solvents with stabilizing surfactants. These reactions are often conducted using standard air-free techniques, as many of the precursors typically used are toxic and/or pyrophoric. Thermal reactions are often conducted at temperatures between 120°C to 300°C. Figure 2.1 shows a typical reaction setup consisting of a stir bar, stir plate, heating mantle or oil bath, 3-neck round bottom flask fitted with a septum for injections, a thermocouple and a reflux condenser affixed to an inert gas line and bubbler.

When using ionic precursors, reducing agents may also be needed to produce zerovalent metals or alloys. This allows for the formation of nanoparticles at ambient temperatures or in aqueous solutions. For slow growth, mild reducing agents are used, such as carboxylic acids or thermally activated 1,2-alkanediols. Stronger reducing agents, such as sodium borohydride or superhydride, are required for fast nucleation processes or for metal complexes with very negative reduction potentials.



Figure 2.1: A typical reaction setup and concept for colloidal synthesis of nanoparticles.

Surfactants serve to direct particle growth, restrict particle size and stabilize colloidal suspensions to inhibit aggregation and precipitation. These surfactants, also termed ligands, bind onto particles through a surface-interacting functional group and contain a solvent-soluble chain that extends into solution for solubility. A wide variety of surfactants is used and range from organic molecules, polymers to ionic salts. The strength of the interacting functional group and concentration in solution dictates particle size and shape. Covalently interacting groups restrict size and enhance colloid stability, as they are not easily displaced. Weaker electrostatic interactions allow for dynamical adsorption and desorption of ligands within solution to provide greater variability during growth and post-synthetic processing; however, these ligands are more sensitive to environmental perturbation such as changes in ionic strength or dilution. Using multi-dentate ligands can increase the surface interaction for weakly bound functional groups, as is often the case when using polymers. Some common functional groups include carboxylic acids, amines, thiols, phosphines, phosphine oxides, and ammonium and carboxylate salts.

2.1.2 Formation Mechanism of Monodisperse Nanoparticles

The simplest and often most used model for particle nucleation and growth is the LaMer model, in which particle formation is separated into three stages: super-saturation, nucleation and growth [1]. Figure 2.2a shows monomer concentration versus reaction progression. In Stage I, monomers are either being formed or added to the solution, yet no particles nucleate despite passing the saturation point. Once the concentration of monomers reach the critical saturation point, particles spontaneously nucleate causing a decrease in monomer concentration (Stage II). When the concentration of monomers drops below the critical saturation (Stage III), nucleation of new particles ceases, and further monomer loss is obtained solely from particle growth.



Figure 2.2: (a) LeMer plot: Variation of the supersaturation as a function of time [1], (b) Growth model of Sugimoto: Change of the growth rate by the particle size [2].

Because growth will occur simultaneously during particle nucleation, it is important to have a rapid and short nucleation phase and slow growth kinetics to minimize size broadening [59]. Using very reactive precursors and rapidly injecting into a hot coordinating solvent often accomplishes this. The reactive precursors decompose quickly, making the nucleation phase short. Residual precursor complexes with the coordinating solvent, forming more stable complexes that will slowly deposit on nuclei for favorable slow growth kinetics.

Another method to produce monodisperse nanoparticles starts with all the desired precursors dissolved in solution at room temperature such that the critical monomer concentration is not reached. Upon heating, the precursors are more reactive, and the critical saturation point is lowered just below the monomer concentration causing spontaneous nucleation. This method produces fewer initial nuclei as only a small amount of monomers are used for nucleation resulting in larger average particle sizes. Because only a small amount of monomers is used, the nucleation time is short, and growth during this time is minimal [60, 2].

For a diffusion-controlled growth process, where the precipitation onto a growing particle is limited by the diffusion of monomers to the particles surface rather than the reaction of the monomers on the particles surface, two growth regimes exist: a size-focusing regime and a size-defocusing regime. These growth processes are governed by the Gibbs-Thompson effect in which the solubility of a particle in relation to its bulk solubility is a function of its size:

$$s_r = s_b exp(2\sigma V_m/rRT)$$

where s_r and s_b are the solubility of the particle and bulk solid, respectively; σ is the specific surface energy; V_m is the molar volume of the material; r is the radius of the particle; Ris the gas constant; and T is the temperature. When $2\sigma V_m/RT \ll 1$ and the diffusion thickness is considered infinite, the growth rate of particles as a function of size can be expressed as

$$dr/dt = K(1/r)(1/r^* - 1/r)$$

where K is a rate constant and r^* is the critical particle size for which the growth rate is zero at the current monomer concentration [61, 62].

Figure 2.2b shows growth rate as a function of particle size r versus the critical particle size r^* . When the average particle size is less than twice the critical particle size, defocusing occurs via an Ostwald ripening process in which smaller particles dissolve while larger particles grow more rapidly causing a broadening in the particle-size distribution. However, when the average particle size is greater than twice the critical particle size, smaller particles grow at a greater rate than larger particles, leading to a narrowing of the average particle size distribution [63]. At greater monomer concentrations, the critical particle size r^* is smaller. When the super-saturation of monomers is kept high and below the critical saturation point such that no nucleation occurs, size-focused growth predominates. For large monodispersed particles, small amounts of monomer are continuously added to maintain high monomer concentrations during long growth times. If the reaction proceeds long enough without further monomer addition, the solution will exit the size-focusing regime and Ostwald ripening will occur, causing a broadening in the size distribution.

2.2 Strategies for Controlling Size and Shape of Nanoparticles

Nanoparticles are synthesized under steric control of surfactants and/or kinetic regulation of nucleation and growth of metal monomers. Thus, one approach to obtain size-controlled nanoparticles is to adjust surfactant concentration [64, 65]. For example, a concentrated surfactant solution would result in small particle sizes, whereas larger particles would be obtained in a dilute surfactant solution. This steric control strategy has been previously employed to produce monodisperse gold nanoparticles ranging 1–4 nm in size [66, 67, 65, 68]. Another strategy for the size control of nanoparticles is to regulate relative rates of nucleation and growth. Rhodium nanoparticles ranging 5-13 nm in size have been synthesized by internally adjusting metal precursor concentration [69]. Likewise, the seeded growth strategy is often employed in a two-pot synthesis to increase particle size or deposit metal shells over pre-formed nanoparticle seeds by externally adding additional monomers for growth [70, 71, 72]. To avoid homogeneous nucleation of metal monomers, reaction temperature and metal precursor concentration are carefully controlled. The seeded growth technique has been utilized to produce ruthenium and rhodium particles up to 6 nm in size [73, 74].

Nanoparticle structure, shape and size are essential to catalysis and can be controlled though colloidal chemistry. The internal structure of a nanoparticle may vary for a given composition, as different crystallographic phases may be kinetically or thermodynamically isolated through colloidal-based synthesis. These structures not only determine the geometry of the facets, but may also influence the morphology of nanoparticles, as nanoparticle growth is highly influenced by the free-energies of terminal crystallographic faces. For densely packed atomic structures like face-centered cubic (fcc) crystals, {111} surface termination leads to 8-faced octahedra or 4-faced tetrahedra, whereas {100} surface termination leads to cubic shapes. Truncated octahedron shapes resulted from {100} truncation of octahedra, a special case of which is cuboctahedra consisting of 6-{100} tetragonal faces and 8-{111} hexagonal faces. Further truncation exposes higher index surfaces like {110} and gives rise to the complex surface structure of polyhedral nanoparticles.

For fcc crystals, {111} surfaces typically have the lowest surface free energies and thus are thermodynamically the most stable followed by {100} and then {110} surfaces. Since nucleation and growth of nanoparticles are kinetically-controlled by a number of factors—such as reaction time, temperature, precursor salts and surfactants—nanoparticles usually assume equilibrium shapes such as truncated cuboctahedra and polyhedra during colloidal chemical synthesis. To synthesize nanoparticles with cubic and tetrahedral (or octahedral) shapes, one approach is to employ surface directing agents along with surfactants. There are vast numbers of surface directing agents at disposal. Namely, alkali and organic salts of halides [75, 76], transition metal crystals, cations, and complexes (such as Ag^+ [77], Fe^{3+} [78], Co^+ [79], $W(CO)_6$ [80], etc.) reactive gas molecules (such as H_2 , O_2 , CO, NO, etc.) are noticeable examples of surface directing agents employed in colloidal synthesis of nanoparticles.

In the case of Pt group metal nanoparticles, bromide ions present in the reaction solution produce cubic shapes by stabilizing $\{100\}$ surfaces, whereas molecular hydrogen favors tetrahedral shapes with dominantly $\{111\}$ surfaces. As shown in Figure 2.3, NaBH₄ reduction of aqueous solution of H₂PtCl₆ in the presence of tetradecylammonium bromide (TTABr) salt produced ~15 nm Pt cubes, where TTABr acts as both a surfactant and a surface-directing agent. When dissolved H₂ was employed along with poly-vinylpyrrolidone (PVP) under similar reaction conditions, Pt tetrahedras are formed, which were controllable in the size range of 3–10 nm [81, 82]. Also shown in Figure 2.3, employing both dissolved H₂ and TTABr solution resulted in 15 nm Pt cuboctahedras, which is a structural intermediate between cubes and tetrahedras that possesses both {100} and {111} faces. Similarly, Ag⁺ ions are also known to favor cubic shapes when present in high concentrations. Exclusively cuboctahedral shapes are formed when trace amounts of Ag⁺ ions are present [77].

Recently, it has been shown that size tuning of shape-controlled nanoparticles is possible via colloidal chemical synthesis strategies. For instance, PVP-capped Pt nanocubes in the size range between 5 nm and 9 nm have been synthesized employing tetramethylammonium bromide (TMABr) as a surface directing agent with size control resulting from the percentage of Pt^{4+} in a Pt^{2+}/Pt^{4+} precursor mixture [83]. Pt^{4+} is thermodynamically more difficult to be reduced than Pt^{2+} , and thus fewer Pt nuclei would be initially generated for high Pt^{4+} fractions, leading to larger cubes as residual Pt precursor is reserved for particle growth. Likewise, small Pt cubes are generated with low Pt^{4+} fractions due to fast



Figure 2.3: Schematics illustrate a generic synthetic procedure for preparing Pt nanoparticles with cube, octahedron and cuboctahedron shapes.

nucleation of the Pt^{2+} precursor and lower residual Pt ions for further growth.

2.3 Porous Hollow Particle and Shell Formation Using the Kirkendall Effect

Hollow and yolk-shell¹ nanoparticles have been synthesized using the Kirkendall effect in which the differing diffusion rates of materials lead to a net directional growth in a forming alloy or oxide [3, 84, 85, 86, 87, 88, 89, 90, 91, 5]. In the case of solid-solid diffusion of copper and zinc to form brass, zinc diffuses faster than copper in the forming copper-zinc alloy, resulting in a net directional growth towards the copper-brass interface. To offset the diffusional gradient, vacancies migrate in the opposing direction and coalesce as voids at the zinc-brass interface (Figure 2.4a). In bulk systems, this effect is often unwanted and causes corrosion in electronic contacts of dissimilar materials [92]. In nanoparticle systems, however, hollow particles can be produced by alloying or oxidizing particles in which the initial particle is composed of a material with a faster diffusion rate into the forming alloy than the reactant precursor. Figure 2.4b-c shows the hollowing process for a CoSe hollow particle produced from a Co nanocrystal.

¹yolk-shell refers to a unique core-shell particle in which a void space is present between the core particle and the surrounding shell



Figure 2.4: (a) The Kirkendall effect at the boundary between two solids diffusing into each other at different rates, for example zinc and copper whose alloy (brass) grows in the direction of the faster-moving species (zinc). Unfilled voids are left behind and coalesce into large pores. (b) Diagram of the Kirkendall effect at the nanoscale to produce hollow particles. (c) Transmission electron microscope images tracking the evolution of CoSe hollow nanocrystals with time by injection of a suspension of selenium in o-dichlorobenzene into a cobalt nanocrystal solution at 455 K, from top-left to bottom-right: 0 s, 10 s, 20 s, 1 min, 2 min, and 30 min. The Co/Se molar ratio was 1:1 [3, 4].

The mechanism of growth has been heavily studied both theoretically and experimentally since the use of Kirkendall effect for nanoparticles. Two modes of growth have been been observed: (1) the formation of skeletal bridges that feed core material to the shell via surface diffusion [87] and, (2) the asymmetric erosion of core particles, minimizing the free surface area of the core particles during shelling [91]. The difference between the two depends on the rate of self-diffusion of the core material within itself relative to the rate of self-diffusion of the core material within the forming shell. When atomic diffusion within the core lattice is relatively slow compared to ionic diffusion within the shell, bridging forms, and surface diffusion across bridges facilitates the further erosion of core material. At high self-diffusion rates within the core, the core structure can maintain a thermodynamically favored shape to minimize the surface free energy. In this case, the uniform growth of the shell must be supported by the quick diffusion of cations and vacancies within the shell to allow for homogenous feeding of the core material.

The thickness of a shell and final size of a hollow particle can be controlled by tuning the flux of material within the forming shell. A net faster diffusion of core material outwards than shelling material inwards can lead to a hollow particle. The volume expansion caused from forming a new material must also be accounted for with the differential growth, such that

$$\frac{\Delta V}{V_A} = \frac{V_{AB} - V_A}{V_A} \le \frac{nD_A \Delta C_A}{mD_V \Delta C_B} = K$$

where ΔV is the change in volume between the initial core material, A and the final shell material, $A_n B_m$; V_{AB} and V_A are the volumes of the initial core particle and final shell material, respectively; D_A and D_B are the diffusion coefficients of either materials A or Bthrough the $A_n B_m$ phase; and ΔC_A and ΔC_B are the concentration drops of A or B across the $A_n B_m$ shell. When K is greater than $\Delta V/V_A$, a hollow particle may be formed [86]. The flux of the two materials within the forming shell is not only dependent on the self-diffusion of each constituent in the shell, but also influenced by the reaction probability at each interface (core/shell and shell/medium) and collision frequency of the shelling precursor on the particle. Changing the reaction temperature, concentration of the shelling precursor B, or the identity/reactivity of the shelling precursor B can all be used to influence difference in inwards and outwards growth of the forming shell [93].

To produce nested heterostructures, noble metal particles are first coated with a reactive metal shell. The outer metal shell is subsequently oxidized under controlled conditions to produce a porous shell, similar to their hollow analog. The noble metal core remains unreacted and resides in the void of the hollow metal shell.

For either case, the alloyed shells are polycrystalline despite the single crystalline nature of the initial particle. The grain boundaries between the crystallites that make up the shell contain pores that make the inner void accessible to small molecules. A previous study on platinum particles coated with a porous cobalt oxide shell confirmed their porosity [94]. In this study, carbon monoxide adsorption on the platinum core was monitored by IR spectroscopy. At temperatures above 200 K, platinum cores were accessible to carbon monoxide through the cobalt oxide shell by an activated surface diffusion mechanism within the pores. At lower temperatures, transport was prohibited, and no carbonyl stretching modes were observed.

The porosity of the shell can be influenced by controlling grain size. Larger grain sizes in the shell lead to greater irregularity in the morphology of the shell and should give a greater porosity at grains junctions. Smaller grains form more uniform shells, but have smaller pore diameters. The size of the grains can be influenced by changing the surfactants used during the coating process. For iron oxide shells, using an iron complexing agent such as oleic acid can minimize iron nucleation and promote the growth of larger grains on the the core particle's surface (Figure 2.5) [5]. Additionally, porosity can be changed post-synthesis through a secondary thermal treatment. Cheng et al. showed that for hollow magnetite particles the pore size could be increased as much as 2-4 nm (Figure 2.6) by resuspending particles in a high-boiling solvent and heating them at elevated temperatures in the presence of additional stabilizing ligands [6]. Similar to the as-synthesized method, the increase in porosity is attributed to a growth in grain size in the shell.



Figure 2.5: TEM phase contrast images of gold/iron oxide (core/hollow-shell) nanoparticles synthesized with a) 1:0 and b) 1:0.4 oleylamine/oleic acid molar ratios [5].



Figure 2.6: (a) TEM image of the 16 nm HNPs of Fe_3O_4 . (b) phase contrast image of a single HNP. (c) TEM image of the 16 nm PHNPs of Fe_3O_4 ,(d) phase contrast image of a single PHNP [6].

2.4 Sol-Gel Chemistry for Porous Oxides

Sol-gel chemistry has been around for quite some time. It began with the observation that a metal alkoxide, prepared from $SiCl_4$ and alcohol, gelled upon exposure to atmosphere back in 1846 [95]. Since then, it has expanded to become one of the most popular methods of producing a variety of technologically advanced ceramics and glasses produced industrially today. Despite the advancements, the basic chemistry and and methods still follow the same general protocal laid out in the mid 1900s [96, 97].

Sol-gel processing is a solution-based method that uses hydrolysis and polycondensation reactions to form colloid suspensions (sols) of extended network solids, which can condense into structural gels within solution by slow sedimentation or forced through centrifugation. A subsequent drying stage is often used to densify gels followed by thermal treatment to further condense the material through sintering of the particulates within the gel. One of the main advantages of this method is that it allows for the production of very thermally stable ceramic materials at relatively low annealing temperatures [98].

The properties of the materials produced through this method can be tuned by controlling the materials at various stages of the sol-gel process. Controlling the initial size of the colloidal sol influences the packing and sedimentation rate during the gelation process. Smaller colloids lead to more densely packed gels with smaller pores while larger particulates form more open networks for less dense materials. During the gel aging, further condensation can occur within solution to reinforce porous networks within the gel such that low density materials are less brittle. Likewise, other parameters within the drying and thermal treatment stages affect other properties of the final material in similar ways.

For ceramic coatings, gels can often be spun onto surfaces and annealed to make thin films with desired properties. In the case of colloidal coatings, gels can be formed directly on colloidal suspensions within solution. Stöber developed a method of producing uniform, micron-sized silica opals through base-catalyzed slow hydrolysis of alkyl silicates in alcoholic solutions [96]. His method has since been adapted to coat uniform silica shells on various nanoparticulate materials. The main criteria for silica coating by this method is a favorable interaction between the surfaces of the particles and the forming silica gel. In addition, strong repulsive interactions between the colloids must be maintained in order to prevent aggregation.

In the following discussion, a brief overview of ceramic sol chemistry is reviewed, as it directly applies to particle coating. The aging and gelation process were omitted, as it is not directly relevant to the thesis topic. However, numerous sources are available that cover all areas of sol-gel chemistry [99, 98, 11].

The general strategy for sol-gel synthesis is very similar to that described previously in section 2.1.1 for other generic colloidal syntheses; it involves a reactive precursor, reacting media, solvent, catalyst, and possibly a growth directing agent. The reactive precursor for the sol-gel process is typically a metal or metalloid alkoxide, but can also be various reactive salts. In place of the reducing agent that is typically used in metal particle formation, the reactive media for sol-gel synthesis is water, which facilitates hydrolysis of the chosen precursor. The addition of a solvent, typically alcohol, is often required as some alkoxide precursors are not miscible with water. In addition, sol-gel processing is typically catalyzed under acidic or basic conditions, the choice of which affects the growth kinetics, the morphology, and composition of the final oxide. The negative charge of the forming oxides restricts particles from aggregation through Coulombic repulsion, so no added surfactant is needed to regulate size. However, the addition of directing agents are sometimes used to influence pore size and structure during gelation. This is often done in autoclaves to produce oxides with highly ordered porous networks. By controlling the time, temperature, pH, and relative concentrations of the components mentioned above, an endless variety of mixed oxides can be produced with an array of different physical properties and geometries.

The kinetics of gelation are regulated by the hydrolysis and condensation of metal alkoxides under acidic or basic conditions. For silicon alkoxide under acidic conditions, hydrolysis requires the initial protonation of an alkoxide, withdrawing addition electron density from silicon and making it more susceptable to the nucleophilic attack by water. It then undergoes an S_N 2-like transition, liberating alcohol followed by deprotonation of the newly bound water to form a hydroxyl group (Figure 2.7a). Similarly, acid catalyzed condensation also requires the protonation of a hydroxy or alkoxy group prior to nucleophilic attack from the hydroxide of another silonol. Water or alcohol is liberated and the bound hydroxyl group is deprotonated to form a siloxane (Si–O–Si) bond (Figure2.7b). Condensation reactions occur most readily between neutral species and protonated silanols situated on monomers or at the end of chains because these species are relatively more basic and likely to be protonated [98]. This accounts for the typical chain-like growth seen during acid-catalyzed reactions. As seen in Figure 2.9, the condensation rate under acidic condition is slower than the hydrolysis rate, which accounts for the the production of much smaller sols (2-3 nm), as a greater number of nuclei are generated [7].



Figure 2.7: Acid-catalyzed (a) hydrolysis, (b) water condensation (R' = H), and alcohol condensation (R' = R) of silicon alkoxide.

HYDROLYSIS



Figure 2.8: Base-catalyzed (a) hydrolysis and (b) water condensation of silicon alkoxide.

Base-catalyzed hydrolysis of silicon alkoxides undergo a simple $S_N 2$ reaction in which a hydroxide acts as an electrophile and the alkoxide acts as the leaving group (Figure 2.8a). This reaction proceeds slower than the acid-catalyzed of equivalent concentration (Figure 2.9). The basic alkoxide oxygen tends to repel the nucleophile, -OH, and the bulky alkyl group adds additional steric crowding to the pentacoordinate transition state. For this reason, hydrolysis of fully coordinated tetraalkoxides occurs slowly, with each sequential hydroxylation proceeding more rapidly. Likewise, removal of an alkoxide from a polymeric silicon alkoxide is more difficult than from monomers [100]. The condensation reaction requires the initial deprotonation of a silonol prior to nucleophilic attack of a neutral silicic acid and loss of a hydroxyl or alkoxide leaving group (Figure 2.8b). Because terminal silanols of highly branched silica polymers are more acidic, they are most likely to deprotonate and act as electrophiles for neutral silicic acid monomers. This results in the cluster-like growth of base-catalysed sols with highly branched particles and where neutral monomers act as as feed stock for the growing clusters. In addition, small particles can undergo etching and act as further feed stock to nucleate on larger particles. This process is known as Ostwald ripening and is described in section 2.1.2. The final particle size is governed by the relative rates of particle etching and growth and can grow well into the micron regime depending on reaction conditions.

The choice of the precursor is important for regulating the rate of hydrolysis. Using bulky alkoxides provide steric hindrance from nucleophic attack. Additionally, longer alkyl groups are more electron donating and result in slower hydrolysis by reducing the electron affinity of the central metal atom (Table 2.1). The identity of the metal or metalloid used will greatly affect the rate of hydrolysis and condensation. For instance, titanium is more electropositive than silicon and will consequently have a faster rate of hydrolysis (Table 2.2). In addition, metals that have multiple oxidation states can proceed through more reaction pathways, increasing the rates of hydrolysis and condensation. Titanium has multiple stable, fully-hydroxylated species in both acidic ($[Ti(O)(H_2O)_5]^{2+}$ and $[Ti(OH)(H_2O)_5]^{3+}$) and basic ($[Ti(O)(OH)_4]^{2-}$ and $[Ti(OH)_5]^{-}$) conditions. Under acidic conditions each species can link together through oxolation or olation to form nuclei of octrahedron with shared



Figure 2.9: Ratios between the (1) hydrolysis and (2) polycondensation rates of TEOS at different pH values[7].

$Si(OR)_4$	Hydrolysis rate constant		
R=	$10^{-2} \text{ L mol}^{-1} \text{ s}^{-1} (\text{H}^+)^{-1}$		
C_2H_5 —	5.10		
C_4H_9 —	1.90		
$C_{6}H_{11}$ —	0.83		
$(\mathrm{CH}_3)_2\mathrm{CH}(\mathrm{CH}_2)_3\mathrm{CH}(\mathrm{CH}_3)\mathrm{CH}_2-$	0.30		

Table 2.1: Hydrolysis Dependence on Alkoxide Length [11]

equatorial or apical edges [8]. They then further grow to make various phases of titania, rutile being the most stable (Figure 2.10). With the existence of multiple reaction pathways, monomer coordination numbers, and geometries, controlling the phase and growth of forming oxides can be quite difficult. This becomes exceptionally more challenging when trying to form mixed oxides. Careful selection of precursors must be made to more closely match the hydrolysis and condensation rates of the different oxide precursors in order to co-condense the mixed oxide homogenously.

As previously stated, the use of alcohol as a co-solvent is important because many precursors are not soluble in water. It is important to choose the right alcohol because transesterification can occur, affecting the hydrolysis and condensation reaction rates. Typically, the alcohol and alkoxide are matched to eliminate the effects of transesterification.

Table 2.2: Metal dependence on hydrolysis [11]

	-	
ethoxide	$\operatorname{Ti}(\operatorname{OEt})_4$	$\mathrm{Si(OEt)}_4$
$\delta(M)$	+0.63	+0.32
Rate of hydrolysis pH=7	$10^{-3} \mathrm{M}^{-1} \mathrm{s}^{-1}$	$5 \times 10^{-9} \mathrm{M}^{-1} \mathrm{s}^{-1}$



Growth unit for brookite or anatase

Figure 2.10: Possible condensation pathway for titania nuclei of rutile, anatase, brookite starting from octahedral cations $[Ti(O)(H_2O)_5]^{2+}$ and $[Ti(OH)(H_2O)_5]^{3+}$ [8].

Changing the water to precursor ratio affects the rate of hydrolysis. For silica formation, the water to tetraethylorthosilicate (TEOS) ratio can range from less than 1 to over 50, depending on the desired polysilicate product. While four water molecules are necessary per TEOS monomer to fully hydrolyze, water is generated as a byproduct of the condensation reaction, making less necessary. At lower water concentrations, condensation and hydrolysis occur simultaneously. Alcohol condensation can also occur in absence of adequate silanol species. At high concentrations of water, full hydrolysis can be completed before condensation occurs. However, with the addition of more water and a constant alcohol/TEOS ratio, the hydrolysis and condensation rates decrease due to reactant dilution, resulting in longer gel times. This is evident in Figure 2.11 in which the gel time of an acid-catalyzed TEOS system was monitored for different water/TEOS ratios for three different ratios of ethanol and TEOS [9].



Figure 2.11: Time to gel vs water/TEOS ratio for 3 ratios of ethanol to TEOS [9].

The coating of nanoparticulate materials is typically done using a modified Stöber method. The main requirement is rendering the surface of the particles vitreophilic (glass loving). For some materials, such as iron oxide, this property is inherent and silica coating only requires the ligands on the material to be labile and easily displaced by forming silica clusters. Further growth of silica continues preferentially at the concave interfaces between surface-bound silica in accordance with the Kelvin equation (given in §2.1.2 under discussion of the Gibbs-Thompson effect). It relates the solubility of surfaces with the relative curvature of that surface. At the junction of two particles, an area of negative curvature (concave) is formed and becomes a site of preferential deposition and further particle adhesion due to the higher coordination environment. As the silica shell thickens, the initially roughened surface smooths to form a conformal coating around the particulate.

Organic soluble particles can also be coated by this method, but require either first performing a ligand exchange or coat particles using a reverse-micelle technique. In the reverse-micelle technique, a microemulsion is formed using an amphiphic polymer to stabilize a small aqueous phase (Stöber solution) within an organic media. The particles for coating exist in the organic phase, but get pulled into the aqueous phase after colliding with the aqueous micelles and exchaning their ligands for silica sols. Once within the micelles, further silica coating proceeds as normal [101, 102].

When a desired material to be coated is non-vitreophilic, such as gold, additional treatment must be done to increase the surface affinity for silica. One options include the use of charged ligands, such as alkylammonium halides, to render the surface positively charged [48]. Doing so provides favorable electrostatics for the deposition of negatively charged forming silica particles. Additionally, the use a silane coupling agent as a surface primer, such as 3-aminopropyltrimethoxysilane, has been shown to work very well on gold particles as small as 15 nm for forming a hydrated silica monolayer. This monolayer acts as a primer for further silica growth using activated silica in basic conditions. Once a base shell is form, particles are stable for further shell growth using the Stöber method [103].

Chapter 3

Au@Fe_xO_y as Heterogeneous Catalyst with Interactive Shell

3.1 Introduction

The goal of this study was to produce a yolk-shell system that exhibits both an interaction between the core and the porous shell as well as thermal stability. Gold encapsulated in a porous iron oxide shell (Au@Fe_xO_y) was chosen as a model catalyst for this endeavor. As previously mentioned in the introduction (see §1.1 and §1.2.1), small gold can be an exceptional catalyst for a variety of reactions but requires the strong interaction with a supporting oxide. In addition, the activity of gold is extremely size dependent and can completely deactivate for some reactions for diameters greater than 5 nm, making its protection against sintering greatly desired. CO oxidation is an ideal initial test reaction because it is a single product reaction in which both the reactants and product can diffuse through the narrow pores present in these heterostructures.

The thermal stability of Au@Fe_xO_y was investigated for the catalysis of CO oxidation. An interaction between the gold core and iron oxide shell is required for catalysis to occur in the absence of water vapor. Au@Fe_xO_y was found to be active and stable for temperatures up to 320°C. At higher temperatures, gold diffuses out of the shell and coalesces via an Ostwald ripening process. The iron oxide shell morphology remains stable until 400°C, where it undergoes an oxidative phase transition from a disordered iron oxyhydroxide to α -Fe₂O₃. Reversible deactivation occurs at temperatures below 80°C, most likely due to pore blockages from adsorbed intermediates.

The following discussion first reviews the synthetic methods developed for the Au@Fe_xO_y catalyst with core/shell dependent interaction. Second, the detailed investigation for CO oxidation on Au@Fe_xO_y is given. Included in the investigation is an outline of the interaction dependent activity, thermally-stable active range of the catalyst, and analysis of the deactivation regimes.
3.2 Synthesis

3.2.1 Chemicals

1-octadecene (ODE, 90%), diphenyl ether (DE, 99%), 1,2,3,4-tetrahydronapthalene (tetralin, 99%), oleylamine (OAm, 70%), oleic acid (OAc, 90%), t-butylamine-borane complex (TBAB, 97%), HAuCl₄·3H₂O, hexane, isopropanol, ethanol, and acetone were used as received from Sigma-Aldrich. Iron pentacarbonyl (Fe(CO)₅, 99.999%) was purchased from Sigma-Aldrich and purified by vacuum distillation prior to use. P-25 titania support was purchased from Degussa. Argon, helium, oxygen and 20% oxygen/argon mixture were purchased at Praxair and used without purification. Air-free techniques were used during synthesis unless noted otherwise.

3.2.2 Gold Cores

Multiple synthetic techniques can be employed to produce gold particles amenable to iron oxide coating [12, 104, 5]. Particles must be organic soluble and capping ligands using amines and thiols with long hydrophobic chains all work well [5]. The preferred method for producing small gold particles involves reduction with an amine-borane complex at controlled temperatures, as it allows for size-tunability while maintaining narrow size dispersion [12]. In a typical reaction, 10 mL tetralin and 10 mL oleylamine were mixed and heated to the desired temperature (Table 3.1) in an oil bath under argon flow. HAuCl₄·3H₂O (0.1 g, 0.25 mmol) was added and the temperature was allowed to stabilize for 10 min. TBAB (43.5 mg, 0.5 mmol) dissolved in 1 mL tetralin and 1 mL oleylamine was quickly added and allowed to react at constant temperature for one hour. The reaction was then cooled to room temperature and cleaned multiple times via centrifugation using hexane and acetone as a solvent/non-solvent combination. This reaction was scaled as much as five-fold for a single batch synthesis with no loss to particle dispersity nor size control.

Reaction temperature (°C)	Average Au diameter (nm)
2	9.5
10	8.1
15	7.3
20	6.4
25	5.3
35	3.3
40	2.4

Table 3.1: Average size of Au nanoparticles at different temperatures[12]

3.2.3 Au@Fe_xO_y Nanoparticles

Gold particles (20 mg) suspended in hexane were concentrated under vacuum and resusended in 20 mL phenyl ether. Oleylamine (0.15 mL) was added and the solution was degassed under vacuum at 60°C for 30 min. At 80°C under argon, $Fe(CO)_5$ (0.1 mL) was

slowly injected dropwise and allowed to react for 5 minutes before slowly raising the temperature to 180°C. Once the temperature was achieved, the reaction is allowed to continue another 30 min under argon. A 20% O_2/Ar gas mixture was then bubbled into the reaction solution at roughly 20 mL/min for 30 min at 180°C. The temperature was subsequently lowered to 100°C and oxidized for an additional 30 min before cooling to room temperature. The particles are cleaned via centrifugation using a hexane-isopropanol solvent/non-solvent combination.

Synthetic procedures for Au@Fe_xO_y were optimized from previous work [5] to allow for a high yield and coating of small particle. The previously published work on Au@Fe_xO_u coated 4.5 nm gold with iron oxide in 1-octadecene. They were able to modify the shell thickness and morphology by changing the ratio of oleic acid to oleylamine in solution. The higher temperatures were needed to account for the stabilizing effect of oleic acid towards iron within solution, prohibiting deposition. In the current work, oleic acid was omitted as a stabilizer as it complexes with iron and can act as an etchant, decreasing reactivity of $Fe(CO)_5$ on the gold surfaces. The solvent was also changed from 1-octadecene to phenyl ether as aromatic groups are believed to facilitate iron nucleation on gold through electron donation from the solvent to the gold [5, 105]. Likewise, the reduction of the $Fe(CO)_5$ injection temperature to 80° C from 180° C promotes the nucleation of iron on gold surfaces and minimizes self-nucleation of iron, as the decomposition temperature of $Fe(CO)_5$ is catalytically decreased to 135°C from 150°C by gold. In addition, the lower temperature protected gold from coalescence in solution prior to iron coating (a problem noted in the previous synthetic method, as they saw a broadening of the gold size distribution due to ripening). The slow rise in temperature allows for controlled decomposition of $Fe(CO)_5$ on gold. Around 120° C, small bubbles form due to the decomposition of Fe(CO)₅ on gold surfaces and the temperature is stepped slowly to minimized bubble formation and ensure no self-nucleation of iron. The subsequent oxidation at 180°C ensures vacancy-coalescent void formation to produce a yolk-shell geometry. Following these procedures, Au@Fe_xO_u can be scaled to gram quantities with no loss in particle quality. Figure 3.1 shows uniform coating of iron oxide for various sized gold particles.

If 1-octadecene was used as a solvent with a 1:0.4 oleylamine/oleic acid ratio for low temperature $Fe(CO)_5$ injection, a large amount of self-nucleated iron particles formed during temperature ramping (Figure 3.2(a)). In addition, only a fraction of gold showed the formation of thin iron oxide shells. In contrast, uniform coating of gold and fewer selfnucleated iron particles formed when phenyl ether was used as a solvent in the absence of oleic acid (Figure 3.2(b)). The larger core-shell particles with low contrast cores seen in Figure 3.2(a) are $Fe@Fe_xO_y$ in which full oxidation did not occur. These large particles most likely form from low-temperature self-nucleation of iron particles which grow with further heating and iron deposition. Large particles such as these were not seen when phenyl ether was used as a solvent, indicating all low-temperature nucleation of iron occurs on the gold surfaces.



Figure 3.1: Au@Fe_xO_y with various gold core diameters: (a) 4.6 \pm 1.1 nm, (b) 4.0 \pm 0.8 nm, (c) 2.8 \pm 0.4 nm and (d) 2.1 \pm 0.3 nm



(a) 1-octadecene

(b) phenyl ether

Figure 3.2: 4.0 nm Au coating with iron oxide using different solvents

Comparing the selected area electron diffraction (SAED) patterns between large particles coated using the previously published method[5] and the newly presented method for small particle coating reveals a decrease in shell crystallinity (Figure 3.3). While many rings fitting either the γ -Fe₂O₃ and Fe₃O₄ phases can be seen in the SAED of large cored heterostructures, only the gold rings can be readily distinguished for Au@Fe_xO_y with small gold.



Figure 3.3: Selected area electron diffraction of comparison of iron oxide shells

Fe EXAFS of as-made Au@Fe_xO_y reveal the phase of iron oxide to be a disordered iron oxide-hydroxide (Figure 3.4). The Au@Fe_xO_y nanoparticles are plotted against various iron oxide phases of increasing crystallinity. Peaks at 5.25 Å⁻¹ and 7.5 Å⁻¹ increase with crystallinity of iron oxide phase. The nanoparticles most closely resemble the biogenic phase, a disordered phase consisting of primarily of edge sharing Fe-O₆ octahedron and little to no corner sharing octahedron [106]. In addition, the shells show less crystallinity than the 2-line ferrihydrite phase, which is often used as a low temperature CO oxidation support for gold [107].

3.2.4 Au/Fe_xO_y Dimers

Gold/iron oxide dimers were produced to be used as a control to compare thermal stability against the Au@Fe_xO_y yolk-shell catalysts. Synthetic procedures are reproduced from Lee et al [108]. Gold particles (20 mg) suspended in hexane were concentrated under vacuum and added to 1-octadecene (20 mL) with oleylamine (1 mL) and oleic acid (1 mL). The solution is degassed under vacuum at 60°C for 30 min. At 120°C under argon, Fe(CO)₅ (0.1 mL) was slowly injected into the solution and allowed to react for 5 min before raising the temperature to 300°C. The reaction temperature was maintained for an additional 30 min before cooling to room temperature and exposing to air. Particles were cleaned via centrifugation using a hexane-isopropanol solvent/non-solvent mixture.



Figure 3.4: EXAFS of iron K-edge of as-made $Au@Fe_xO_y$ nanoparticles reveal iron oxide shell consists of a fairly amorphous iron oxide-hydroxide. Highlighted peaks show increasing crystallinity between $Au@Fe_xO_y$ and various references.

In this procedure, gold particles are first coated with an iron shell. At high temperatures, the iron dewets the golds surface to produce a dimer. Unfortunately, the high temperature treatment during the dimer synthesis caused the 2.8 nm gold to ripen in solution to 8 nm (Figure 3.5).



Figure 3.5: Au/Fe_xO_y dimers with 8 \pm 2 nm Au produced from 2.8 \pm 0.4 nm Au particles

3.2.5 Hollow Iron Oxide Particles

1-octadecene (10 mL) and oleylamine (0.11mL 0.34 mmol) was degassed under vacuum at 60°C for 30 min. Under an argon atmosphere, the temperature of the solution was raised to 200°C before $Fe(CO)_5$ (0.4 mL) was quickly injected. The solution temperature was maintained at 200°C for 20 min. The temperature was increased to 250°C and oxidized by bubbling a 20% O₂/Ar gas mixture at roughly 20 mL/min for 120 min before cooling to room temperature. Particles were cleaned via centrifugation using a hexane-isopropanol solvent/non-solvent mixture (Figure 3.6).



Figure 3.6: Hollow $Fe_x O_y$ nanoparticles

3.3 CO Oxidation

3.3.1 Characterization

Samples for transmission electron microscopy (TEM) are prepared by drop-casting nanoparticle solutions or wiping solid nanoparticle powders onto 400 mesh carbon-supported copper grids (Electron Microscopy Sciences). TEM images are taken using a Tecnai G^2 S-Twin electron microscope operating at 200kV using a LaB₆ filament.

Powder X-ray diffraction (XRD) was taken using a Bruker WAXS diffractometer using Co K α radiation (1.790 Å) and a general area detector. The instrument resolution was 0.5° in 2θ . Samples are prepared in air by depositing precipitant particles on a quartz substrate. Transmission EXAFS measurements of the Fe K edge (7110.75 eV) were performed at the Advanced Light Source at Lawrence Berkeley National Laboratory, beamline 10.3.2. Samples are prepared by spin-coating a suspension of Au@Fe_xO_y particles onto a Si chip with a silicon nitride window. Prior to EXAFS, the loaded chips were exposed to desired pretreatments and catalytic conditions. Over-adsorption was checked and confirmed to be under 2%. Data was prepared from transmission mode and glitches were removed before processing.

Simultaneous thermal analysis was conducted using a Setaram Sensys TG-DSC with aluminum pans. A blank run using two empty pans (one sample and one reference) was run under experimental conditions before loading the sample to ensure proper background subtraction. Au@Fe_xO_y (9.1 mg) was loaded into the sample pan and further dried within the instrument at 100°C for 36 min before analysis. A carrier gas of 20% O₂/Ar mixture was used with a flow rate of 20 mL/min. Initially, the sample was heated at a ramp rate of 1 K/min to 500°C. Subsequent runs were performed to 400°C under identical conditions with fresh particles to produce pre-transformation samples for characterization.

Samples were prepared for catalysis by drying Au@Fe_xO_y to approximate mass and resuspended in hexane to a known concentration. Particles were loaded in a MCF-17 support to roughly 2% by mass of gold by mixing MCF-17 and particle solutions under sonication until the solvent turned clear. Loaded MCF-17 was pretreated after drying at 250°C in air for 5 hours to remove residual organics. Catalytic testing was done in a laboratoryscale flow reactor at atmospheric pressure. The sample was loaded into quartz reactors at quantities such that less than 10% conversion is maintained for a desired temperature range and diluted with low surface area quartz sand. Gas flows were regulated with calibrated mass flow controllers at 8.6 mL/min O₂, 3.5 mL/min CO and balanced with 67.9 mL/min He. Temperature was controlled with a type-K thermocouple and a PID controller. Gas compositions were analyzed with a thermal conductivity detector (TCD) on a HP 5890 Series II gas chromatograph (GC).

Inductively coupled plasma atomic emission spectroscopy (ICP-AES) was used to determine percent loading of gold in loaded MCF-17 samples used for catalysis. Sample (5 - 10 mg) was dissolved in 4 mL aqua regia and diluted to 100 mL with water. A gold standard was prepared by serial dilution for a calibration curve. Both gold emission wavelengths at 242.785 nm and 208.209 nm were used for determining gold content.

Turnover frequencies (TOFs) were calculated by normalizing the CO conversion to the number of available gold surface sites. The number of surface sites was approximated using the determined gold content from ICP-AES, the average particle size determined from TEM analysis and the assumption of 10^{15} sites/cm². The total available surface area was approximated assuming the complete surface area from spherical gold particles was available for catalysis. Because the activity is know to occur at the interface between gold particles and the supporting oxide, the reported TOFs represent a lower limit normalized for particle

3.3.2 Shell interaction dependent catalysis

Gold is thought to interact strongly with ferrihydrite phases, a similarly disordered phase, of iron oxide and often forms mixed AuOOH·xH₂O species upon deposition. Post-calcination, Au(III) ions are thought to act as an adhesive layer between metal particle and support [109]. In our system, it is possible that the small gold stabilizes the amorphous phase upon oxidation due to differences in the surface properties of small gold nanocrystals in this size range.

CO oxidation was chosen as a probe reaction for $Au@Fe_xO_y$ support-enhanced catalysis because both the reactants and products are small, gaseous molecules that can diffuse readily through the porous shell under catalytic condition. In addition, this reaction yields a single product, which eliminates the effects of competitive multi-pathway that complicate analysis.

Au@Fe_xO_y samples were loaded on porous MCF-17 silica support for easy sample loading and facile gaseous transport through the flow reactor. Without an oxidative pretreatment at 250°C to remove ligands, particles remained inactive till temperatures greater than 220°C under catalytic conditions. Thermal gravimetric analysis confirms the loss of ligands at this temperatures (Figure 3.7). These ligands are most likely bound to the outside of the shell and hinder catalysis by blocking pores. During shell formation, iron nucleates on the gold surface, displacing ligands, making inner-shell ligands unlikely.

Catalytic activity of gold has been seen to be highly dependent on support material, particle deposition method, and size of gold deposits [33, 110]. It has been seen that more amorphous iron oxide phases show increased activity as a gold supports for CO oxidation [111, 107]. However, colloidal gold deposited or impregnated on reducible metal oxides typically show lower activities than analogs produced through precipitation methods due to greater particle/support interactions [112].

Support dependent activity was confirmed by testing the as-synthesized gold particles for CO oxidation on various supports. Small gold nanoparticles (2.8 nm) were loaded in MCF-17 with and without an iron oxide shell. Likewise, hollow iron oxide particles were loaded in MCF-17 without gold. As seen in table 3.2, only gold encapsulated in iron oxide showed appreciable activity, confirming the strong support interaction between gold and the iron oxide shell towards CO oxidation and little to no influence of the MCF-17 or the iron oxide shell alone. Loading the gold on a standard and more active P-25 titania support gave appreciable activity, futher supporting the necessity of the gold/support interaction for catalysis. In addition, the use of larger gold cores (4.6 nm) decreased the TOF relative to the small gold as expected (Table 3.2).

size.



Figure 3.7: (a) DSC/TGA of Au@Fe_xO_y: percent mass loss (red); heat flow (blue) with exothermic events in the positive direction. TEM image of particles (b) before analysis, (c) after heating to 400°C, and (d) after heating to 500°C. (e) Corresponding XRD patterns for samples at each temperature. The expected peak positions for Au (red) and α -Fe₂O₃ (black) are given as bars.

Sample	TOF (molec s^{-1} site ⁻¹ at 298.15 K)	Reference
$4.6 \text{ nm Au}@\text{Fe}_x\text{O}_y$	4×10^{-10}	this work
$2.8 \text{ nm Au}@\text{Fe}_x\text{O}_y$	0.001	this work
Au supported on Fe_2O_3	0.001 -0.01	[110]
$2.8~\mathrm{nm}$ Au supported on P-25	0.03	this work
$2.8~\mathrm{nm}$ Au on MCF-17	none	this work
Hollow $\operatorname{Fe}_x \operatorname{O}_y^*$	$< 1 \times 10^{-12}$	this work

Table 3.2: TOF for CO oxidation

*only slightly active above $225^{\circ}C$

3.3.3 Thermal Stability of $Au@Fe_xO_y$

3.3.3.1 Coalescence-protected active range of $Au@Fe_xO_y$

Au@Fe_xO_y was extremely stable against deactivation to temperatures upwards of 320°C. Below this temperature, gold particles were protected against coalescence by the oxide shell and remain catalytically active. Gold particles (2.8 nm and 4.0 nm) were loaded on P-25 titania support (4 and 2 wt% loading) for comparison against core-shell particles for thermal stability. Titania interacts strongly with gold and is thought to have mobilities similar to that of amorphous iron oxides as the interactions are correlated with defects. Likewise, Au-Fe₃O₄ dimers were synthesized using similar synthetic procedures as the yolk-shell particles for additional comparison. However, high temperature treatment during the dimer synthesis caused the 2.8 nm gold used in dimer preparation to ripen in solution to 8 nm. Figure 3.8 shows the sintering effects in each sample after heating under catalytic conditions at 250°C for up to 25 hours. While both the dimers and the titana supported gold show significant size growth from particle coalescence, no apparent change in the gold core nor iron oxide shell is observed for the yolk-shell particles. The clustering of the Au@Fe_xO_y in the post-catalysis image results from the loading of particles on the MCF-17 support. This support is also present for the dimers as well.

3.3.3.2 Support-Assisted Ostwald Ripening of Au above 320°C

At temperatures greater than 320°C, Au@Fe_xO_y undergoes a slow irreversible deactivation associated with gold migration and coalescence through the shell (Figure 3.9). Studies on size dependent melting of gold show the greatest melting point depression for particles less than 5 nm with 2.8 \pm 0.4 nm gold particles have a melting point of 745 \pm 42 °C [113, 114]. However, on strongly interacting reducible oxide supports, particle ripening may occur through atomic dissolution and migration at temperatures below the size-dependent melting point. This process is enhanced under reactive gases as strongly interacting gases can weaken the metal-metal bonds [115]. Within the yolk-shell geometry, strong particle/support interactions facilitate the dissolution of gold cores and the subsequent migration of gold atoms through the narrow pores at low temperatures. Similar behaviors are seen in other yolk-shell systems, such as Pt@mSiO₂, but occur at much higher



Figure 3.8: High Temperature sintering of 2.8 nmAu on various supports before catalysis (a, b, c) and after catalysis above 250°C for several hours (d, e, f): Au-Fe_xO_y dimers (a, d), Au on P25-TiO₂ support (b, e), and Au@Fe_xO_y (c, f). scale bars a and d are 50 nm and b, c, e, and f are 10 nm.

temperatures [48, 116].

3.3.3.3 Shell and pore stability to 400°C

The iron oxide shell remains stable under catalytic condition up to 400°C. Simultaneous DSC/TGA measurements in figure 3.7a show no change in particles after ligand loss till 400°C under oxidative conditions. Corresponding TEM images (Figure 3.7b-d) reveal further diffusional-dependent oxidation of shell not seen under catalytic conditions at temperatures below 400°C and massive sintering of both the shell and core afterward. An associated peak in the DSC trace is assigned to the oxidative phase transition of amorphous iron oxide to hematite. XRD of particles treated at 400°C and 500°C support this assignment (Figure 3.7e). XRD patterns of room temperature and 400°C treated Au@Fe_xO_y show no change in the amorphous iron oxide signal. The slight broadening in the gold peaks is attributed to the wetting and migration of gold within the iron oxide discussed earlier (see §3.3.3.2). At 500°C, the shell has undergone a full conversion to hematite phase and peaks of both iron oxide and gold sharpen resulting from particle sintering.

Grain size stability has been seen for maghemite, γ -Fe₂O₃, nanoparticles in which no grain growth occurs till after the phase transition to hematite, α -Fe₂O₃, above 400°C [117]. TEM images of Au@Fe_xO_y post-catalysis (Figure 3.8f) and temperature-dependent XRD (Figure 3.7e) support a similar morphology stability of the disordered iron oxide shell prior to the high temperature phase transition. Likewise, Ex situ EXAFS studies



Figure 3.9: Au@Fe_xO_y post-catalysis at 320°C reveals Ostwald ripening of gold through iron oxide shell at high temperatures: hollow iron oxide shell (blue), large sintered gold outside iron oxide shell (red), stable Au@Fe_xO_y that has yet to undergo gold diffusion through shell (green).

of Au@Fe_xO_y post catalytic treatment demonstrate the stability of the shell composition and morphology. Figure 3.10 shows Fe EXAFS of Au@Fe_xO_y for increasing time under catalytic conditions at 200°C. Fe EXAFS for disordered iron oxide phases is very sensitive to crystallinity (see §3.2.3); however, no significant change is seen for particles before and after pretreatment and after extended periods of catalytic treatment. Pores within shells exist between grain boundaries of the iron oxide crystallites making up the shell. With no apparent grain growth, increased crystallinity or compositional changes in the shell, the shell porosity can be assumed to remain stable against sintering at temperatures below the iron oxide phase transition.

3.3.3.4 Low temperature deactivation from pore blockage

Au on iron oxide is known to be active at low temperatures [109, 118, 119, 120, 107]; however, Au@Fe_xO_y was seen to reversibly deactivate at temperatures below 80°C. It was presumed that strong binding of CO oxidation intermediates within the pores of the shell blocked reactants and products from entering. Previous studies on Pt@CoO have shown binding of CO within CoO shells block the diffusion of gases within the shell at low temperatures. Gas diffusion through the narrow pores proceeded through a surface-assisted diffusion until a high enough temperature was reached such that gas-like diffusion occurs[94].

The desorption of gases from within the shell was tested by trapping gases within the shell at low temperatures, purge the reactor of excess gas-phase reactants and desorb trapped gases at higher temperatures (Figure 3.11). Initially, activity was confirmed at 250°C followed by a reduction in temperature to 25°C, which caused catalytic deactivation (Figure 3.11(a)). The flow reactor was then purged of reactant gases under flow of He. Once



Figure 3.10: Fe EXAFS spectra of 2.8 nm Au@Fe_xO_y under catalytic conditions at 200°C for various times. From bottom to top: particles as synthesized (blue), after pretreatment at 250°C for 5 hrs in air (green), under catalytic conditions for 6 hrs (red), 12 hrs (aqua), and 24 hrs (magenta).

no residual CO, O_2 , or CO₂ were detected, the reactor was changed to batch mode and the temperature was increased to 280°C to desorb any bound gas species (Figure 3.11(b)). Immediately, desorbed CO was detected in the gas phase, indicating the presence of adsorbed CO within the shell at room temperature. Over additional time, the CO was converted to CO_2 most likely using lattice oxygen as an oxidant.



Figure 3.11: CO oxidation intermediate adsorption study: (a) Deactivation of catalyst at room temperature (b) Desorption of CO as temperature is increased

This result does not conclusively show pore blockage by bound CO as the primary reversible deactivation mechanism, but encourages the further study towards the nature of gas diffusion within iron oxide shells.

3.3.4 Temperature Dependent Activity

The activity of $Au@Fe_xO_y$ particles for CO oxidation differ between batches. This is most likely the result of differences between the average porosity and and degree of disorder in the iron oxide shells. For this reason, the majority of measurements reported were done using the same batch of particles for a given size. An Arrhenius plot for $Au@Fe_xO_y$ is given in figure 3.12. The activation energy for $Au@Fe_xO_y$ was determined to be 46 kJ/mol. The apparent activation energies for gold on iron oxide can vary greatly depending on iron composition, reaction conditions and gold loading procedures; however, most vary between 12 and 70 kJ/mol. At 10% conversion, the reaction becomes diffusion limited and temperature dependence decreases. This occurs at various temperatures depending on the catalyst loading.



Figure 3.12: Arrhenius plot of 2.8 nm Au@Fe_xO_y

3.4 Conclusions and Future Opportunities

We have demonstrated a yolk@porous shell system in which the shell acts as an interactive support. CO oxidation on $Au@Fe_xO_y$ was found to only occur on the full nanoparticle heterostructure in which both the metal core and reducible metal oxide shell were in contact. Both gold particles and hollow iron oxide particles showed no activity for CO oxidation when loaded separately on an inert support.

Au@Fe_xO_y has been shown to be active and stable for CO oxidation between 80°C to 320°C. Reversible deactivation occurs at low temperatures most likely from pore blockage by adsorbed carbonate species. At intermediate temperatures, the iron oxide shell protects gold from sintering through particle coalescence while allowing reactive gases to flow through the shell. However, support-assisted Ostwald ripening of gold occurs at temperatures greater than 320°C in which gold monomers diffuse through pores in the shell and coalesce outside. The shell remains stable under catalytic condition till 400°C. At this

temperature, the disordered iron oxide phase transitions to hematite and undergoes massive sintering.

Previous studies of gold on reducible metal oxides have conflicting views on the coarsening mechanism of gold [115, 121]. Our study demonstrates a separation between particle coalescence and Ostwald ripening in these systems. In addition, active site inhomogeneities, such as metal particle size dispersity or sub-lattice metal ion inclusions, typically found in normal catalyst synthetic methods are minimized with solution-based yolk-shell synthesis. This makes the yolk-shell geometry with interacting oxide shells favorable for future mechanistic studies in similar catalytic systems.

Chapter 4

Cu@CoO as Fischer-Tropcsh Catalyst

4.1 Introduction

Until now, only stable, non-reactive core particles have been used to make nested structures through the Kirkendall method [122, 3, 5]. Copper nanoparticles oxidize easily and are known to undergo diffusional-dependent oxidation [90, 123]. Producing core-shell materials in which both the core and shell can undergo Kirkendall effect is academically interesting, as both may undergo a competative oxidative process. In addition, coating metals such as copper with porous oxide shells could prove useful for catalysis. Copper has been found to be industrially interesting for CO reduction chemistries [124]. Most methods for producing supported copper catalysts use a co-precipitation or deposition-precipitation method which both involve a thermal reduction of the metal salt with or onto a supporting material [125]. Using these methods, it is difficult to uniformly control particle size, morphology and distribution on the support. These discrepancies also make studying the mechanism for catalysis difficult as a multitude of variables can contribute to the reactions at the surface.

In the following discussion, the synthesis of Cu@CoO nanoparticles will be described in which the outer cobalt shell protects the copper core from oxidation. Additionally, preliminary work studying the effects of highly oxidizing and reducing environments on Cu@CoO using in situ high pressure x-ray photoelectron spectroscopy (HP-XPS) is reviewed. This may give insight into the potential use Cu@CoO has for Fischer-Tropsch catalysis.

4.2 Synthesis

4.2.1 Chemicals

1-dimethylamino-2-propanol, copper (II) methoxide, n-pentane, hexadecylamine (HDA), o-dichlorobenzene (DCB), oleic acid, trioctylphosphine (TOP), dicobalt octacarbonyl ($Co_2(CO)_8$), and isopropanol were purchased from Sigma-Aldrich and stored under air-free conditions. Chemicals that were not air-free were degassed prior to use. Argon, and 20% oxygen/argon mixture were purchased at Praxair and used without further purification.

4.2.2 Copper Precursor: bis(1-dimethylamino-2-propoxyl)copper

To make cobalt oxide encapsulated copper heterostructures, uniform copper particles were first synthesized by solvothermal decomposition of a chemical-vapor-deposition (CVD) precursor in hexadecylamine (HDA) [126]. The CVD copper precursor, bis(1dimethylamino-2-propoxyl)copper (Cu(OR)₂), was first synthesized by mixing copper (II) methoxide with two molar equivalents of 1-dimethylamino-2-propanol in n-pentane for six hours [127] under air-free conditions. The precursor was then purified through air-free sublimation at $60^{\circ}C/10^{-4}$ Torr to give purple crystals.

4.2.3 Copper Nanoparticles

Copper particles are very air sensitive and can be difficult to isolate. A variety of methods exist in the literature for making copper particles [128, 129]; however, most methods suffer from difficult cleaning procedures in which particles become sensitive to destabilization or oxidation. The method best suited to my purpose was found to be a modified procedure from Hambrock et al. They use HDA as a coordinating solvent and thermally decompose a CVD precursor at high temperatures. This method works very well, but the particles can be difficult to clean [126]. At room temperature, HDA will solidify and requires a large excess of solvent to re-dissolve such that particle isolation may be conducted. Slight modifications to this procedure use a co-solvent of squalane such that solidification does not occur upon cooling [130]. These particles are slightly smaller and more polydispersed but are much easier to handle. Both procedures have been used to make copper particles for CoO coating and are givin below.

The first procedure as duplicated from Hambrock et al. is as follows: HDA (3.5 g) was degassed at 100° C under vacuum for 30 minutes. The reaction solution was then heated to 300° C under argon. Cu(OR)₂ (160.7 mg) dissolved in octylamine (2 mL) heated to 60° C was then rapidly injected into the hot HDA solution and held at 300° C for an additional 30 minutes. The copper particle solution was then cooled, suspended in dry toluene, and cleaned by centrifugation under air-free conditions. A small amounts of methanol was used as a non-solvent to aid in precipitation of copper particles during cleaning. Figure 4.1 shows TEM images of as synthesized particles.



Figure 4.1: TEM of 15 ± 1 nm Cu particles.

The modified procedure is as follows: HDA (108.7 mg) was degassed at 100°C under vacuum for 30 min. Under argon atmosphere, squalane (5 mL) was added and pumped under vacuum at 80°C for 30 min. The solution was then heated to 200°C under argon. An air-free mixture of $Cu(OR)_2$ (121.5 mg) in mesitylene (1.25 mL) was quickly injected into the hot reaction solution. The temperature was maintained for 1 min before rapid cooling and cleaning. Air-free transfer techniques were used and vials for centrifugation were prepared in the glovebox with dry solvents. Isopropanol was used as a nonsolvent and hexane was used to resuspend particles. A small amount octylamine was also added during cleaning to stabilize against irreversible aggregation. Figure 4.2 shows TEM images of as synthesized particles.



Figure 4.2: TEM of 12 ± 2 nm Cu particles.

4.2.4 Cobalt Oxide Coating

Shelling of copper particles with cobalt oxide was done similarly to previous published reactions using the Kirkendall effect [3]. Copper particles were suspended in 40 mL o-dichlorobenzene (DCB) with oleic acid (0.1 mL) to stabilize. Half of the copper particle solution was transferred to a schlenk flask and heated to $140^{\circ}C$ under argon. An air-free solution of dicobalt octacarbonyl (100 mg), trioctylphosphine (0.02 mL) and DCB (7 mL) was then injected into the copper solution over the course of 10 minutes. The temperature of the reaction solution was then increased slowly to $180^{\circ}C$ over 20 minutes to promote slow nucleation of cobalt on copper particles. A stream of O_2/Ar mixture (120 mL/min) was then bubbled into the hot reaction solution for 3 hours. Once complete, the reaction solution was cooled and cleaned by centrifugation.

Figure 4.3 shows Cu@CoO at different stages of the coating process. After the initial cobalt coating, particles are significantly larger and are no longer spherical in shape. No obvious core-shelling could be inferred from TEM images by intensity due to the similar structure and contrast between the two materials; however, the changes in morphology and solution color suggest coating of Cu rather than aggregation or alloying. This has been seen in other Kirkendall systems, such as Ag@CoO, when the initial core particle is greater than 5 nm. Figure 4.4 shows an EDS line scan of Cu@Co core-shell particles prior to oxidation. It is clear from the line scan that copper is sequestered to the core of the particle and Co covers the entire width of the particle. Slight broadening due to beam size causes trailing of the elemental maps in the line scans. After oxidation, hollow and nested structures were obtained (Figure 4.3 c-d) that maintained the shape of their core-shell counterparts. Electron diffraction (Figure 4.3 d-inset) of oxidized particles show distinct peaks for both copper and copper oxide. In addition, energy dispersive spectroscopy (EDS) shows that for particles with a core material, copper is localized to the center when cobalt extends over the entire structure, which indicates a shelling mechanism rather than alloying during initial coating stages (Figure 4.5).

X-ray diffraction agrees with the above shelling geometry mechanism (Figure 4.6). The initial Cu particles have a pattern slightly shifted to higher 2θ values than the reference; however, the peak position is conserved through the coating and oxidation process, indicating that no alloying or significant oxidation of the copper core occurs. Additional peaks corresponding to a surface oxide is present on the copper particles due to extreme air sensitivity during sample preparation. Oxidation was minimized by loading copper particles onto a quartz substrate for powder XRD within the glovebox and coating with a thin grease protection layer. After coating with a cobalt shell, copper peak broadened to give a cobalt shoulder. If alloying occurred, the shoulder would not be present and the primary copper peak would shift to higher 2θ values to account for lattice contraction. The CuO peaks are no longer present because the cobalt shell protects the copper from room temperature oxidation. After high temperature oxidation, only the cobalt oxidizes to give CoO. Likewise, the cobalt shoulder of the copper peaks also decrease as it is converted to the oxide. It is important to note that despite the extreme sensitivity copper has to oxidation, it remains metallic copper post-oxidation. Longer oxidation times eventually cause the core to oxidize,



Figure 4.3: (a) TEM image of Cu particles pre-coating. (b) TEM image of Cu@Co particles before oxidation. (c) TEM image of Cu@CoO particles after oxidation.(d) HRTEM image of Cu@CoO particles (d - inset) electron diffraction of Cu@CoO particles, red lines outline copper diffraction, blue lines outline CoO diffraction.



Figure 4.4: (a) EDS line scan of three Cu@Co core-shell particles prior to oxidation. (b) the same line scan superimposed on the STEM image from which the particles were taken.



Figure 4.5: Energy dispersive spectroscopy (EDS) of Cu@CoO in STEM reveals localization of copper (yellow) within the core and cobalt (red) extended throughout the shell. The copper signal is weak due to relatively small size and concentration.

but this occurs much slower than for unprotected copper.

In bulk systems, the average self-diffusion distance of cobalt in copper at $180^{\circ}C$ after a day is 1×10^{-3} nm, making alloying unlikely (calculated from $\sqrt{D_{Co}t}$ with $D_{Co} =$ 4.06×10^{-8} nm² hr⁻¹ [131]). This supports the preferred coating over alloying of the two materials during pre-oxidative synthesis. However, it should be noted that alloying in nanomaterials would be expected to occur at lower temperatures than the bulk due to higher surface energies and atomic mobility within the particles. XRD cannot be used to elucidate the shelling/alloying of the pre-oxidative intermediate due to the large peak broadening in small particles. Copper, cobalt and brass have similar lattice structures with only small differences in d-spacing which are masked by line broadening.

Both cobalt and copper particles oxidize readily under normal exposure to oxygen. Table 4.2.4 shows the gibbs energy associated with copper oxide/cobalt metathesis reaction. The strongly negative values for the change in energy of these reactions indicates the preferred oxidation of cobalt. This may also explain the added stability and slower oxidation of the copper core in air over time.

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	Reaction	$\Delta \mathbf{G} \ (\mathbf{kJ})$		
	$Cu_2O + Co \rightarrow 2Cu + CoO$	-77.2		
	$\mathrm{CuO} + \mathrm{Co} \rightarrow \mathrm{Cu} + \mathrm{CoO}$	-88.5		
	*Calculated from reduction of oxides with			
	hydrogen at $400 K$ [132].			

Table 4.1: Selective Oxidation of Copper and Cobalt



Figure 4.6: XRD of Cu, Cu@Co before oxidation and Cu@CoO after oxidation. Reference patterns are given at the base for Cu (red), Co (blue), CuO (green), and CoO (black).

These results show that the shelling process using the Kirkendall effect is applicable to more complex systems in which both core and shelling materials may be reactive. In addition, the Cu@CoO heterostructures may prove interesting for various catalytic studies. The porous core-shell geometry may provide unique selectivity enhancing constraints on gas-phased catalysis. Both cobalt and copper are known to be good Fischer-Tropsch and methanolysis catalysts. By incorporating the two, it may be possible to increase selectivity towards mixed alcohols [133].

4.3 Ambient Pressure X-ray Photoelectron Spectroscopy of Cu@CoO

As previously mentioned, Cu@CoO has potential as a Fischer-Tropsch catalyst to convert syngas (a synthetically produced gas mixture of H_2 and CO that can also have CO_2 , H_2O and O_2 present in some concentration) to alkanes, alkenes and alcohols. Copper is known to be an alcohol promoting catalyst and will exclusively form methanol when loaded on a ZnO support. By having a alloyed or yolk-shell Cu/Co particle geometry, the formation of higher alcohols may be promoted.

In order to study the Fischer-Tropsch process on yolk-shell Cu@CoO, the particle stability in reducing and oxidizing environments was initially studied at various temperatures using high pressure X-ray photoelectron spectroscopy (HP-XPS). Below is a brief description of the instrument and how it works followed by the results of our in situ gas studies on Cu@CoO.

4.3.1 Instrumentation and Background

X-ray photoelectron spectroscopy (XPS) is one of the best techniques used to study the composition and electronic structure at surfaces. When a sample is irradiated with monochromatic x-ray radiation, photoelectrons are emitted from the atomic core and valance orbitals (Figure 4.7). Because the mean free path of the ejected electrons is small, only the photoelectrons closest to the surface can escape without being readsorbed. These electrons are collected and their kinetic energy is analyzed using an electron spectrometer. The binding energy (BE) of the electron can be calculated from the known incident x-ray energy $(h\nu)$ and the measured kinetic energy (KE) of the electron via

$$BE = h\nu - KE - \Phi$$

where Φ is the work function of the electron analyzer and accounts for additional kinetic energy loss to instrument.



Figure 4.7: Principles of x-ray photoelectron spectroscopy (XPS).

Because the binding energy is element specific, compositional information is obtained. In addition, the binding energy is sensitive to the electronic environment causing slight chemical shifts that give additional information about the local oxidation state. Furthermore, depth profiling can be done by tuning the x-ray energy. Higher incident x-ray energies result in ejected electrons with greater residual kinetic energy, allowing electrons deeper in the material to escape (i.e., increasing the mean free path).

Typically, XPS must be conducted in ultra-high vacuum because photoelectrons are strongly scattered by gas molecules. An electron with enough kinetic energy to have a mean free path of 1 nm in a solid material would have a mean free path of 1 mm in 1 Torr of gas. This distance is still shorter than the typical working distance between a sample and the entrance to the electrostatic lens system of an electron analyzer (which is a few centimeters). Recent advancements in high pressure XPS (HP-XPS) allow pressures up to 10 Torr. This is accomplished by taking advantage of differential pumps to create regions of quick pressure drop away from the sample through small apertures. Likewise, electrostatic lenses are used to focus electrons into the narrow apertures and increase the electron collection efficiency (Figure 4.8) [10].



Figure 4.8: (a) The principle of high-pressure x-ray photoelectron spectroscopy (HP-XPS). The sample is placed in a high-pressure chamber that is separated from the x-ray source by an x-ray-transparent window. Electrons and gas escape through a differentially pumped aperture. (b) A conventional HP-XPS setup. Several differential pumping stages are needed to keep the electron analyzer under vacuum when the pressure in the sample cell is close to 1 Torr or higher. There is a tradeoff between the pumping efficiency, given by aperture sizes and spacings, and the solid angle of transmission of electrons through the differential pumping stages. (c) The principle of HP-XPS using a differentially pumped electrostatic lens system. The electrons are forced onto the apertures using electrostatic lenses in the differential pumping stages, which increases the efficiency of the electron collection and allow for a reduction of the size of the apertures for improved differential pumping. (d) Differentially pumped electrostatic lens system and hemispherical analyzer (Phoibos 150, Specs GmbH, Berlin) of the HP-XPS instruments at ALS Beamline 11.0.2 and BESSY [10].

4.3.2 In situ HP-XPS of thermally treated Cu@CoO under oxidative and reductive environments

Oxidation and reduction studies were conducted at Beamline 11.0.2 of the Advanced Light Source. The HP-XPS uses 2 mm apertures between differential pumping stages and a front aperture of 0.3 mm. This allows pressures of 100 Torr or higher in the

sample cell without compromising the vacuum in the electron analyzer. However, the effective pressure limit is still 10 Torr due to electron scattering by gas molecules. The x-ray spot has a minimum size of 10 μ m \times 7 μ m.

In our studies, Cu@CoO was exposed to H₂, O₂ and CO gas at pressures up to 4 Torr at various temperatures. Initially, the untreated structure of Cu@CoO particles was confirmed to be metallic Cu with a CoO shell with XPS (Figure 4.9). The Co $2p_{3/2}$ and $2p_{3/2}$ binding energies (780.6 eV and 796.4 eV, respectively) match closely to CoO values found in the literature (780.5 eV and 796.6 eV, respectively) [134]. In addition, intense satellite peaks were found at lower binding energies of 785.7 eV and 802.0 eV. CoO is known to have very intense shake-up satellites because of the octahedrally coordinated Co^{2+} cations are high spin d^7 and charge-transfer occurs readily from the $2pe_a$ to the half-filled $3de_a$. This is not as prevalent in other oxides of cobalt, which only have weak satellites. The main oxygen 1s peak is found at 529.6 eV, which is also consistant with CoO. The secondary oxygen peak at 531.6 eV is assigned to either surface hydroxyls, under-coordinated lattice oxygens (O^{-}) or chemisorbed oxygen. The Cu 2p peak occurs at 933.1 eV and may be slightly oxidized as zero-valent copper occurs at 932.4 eV and Cu^2 + occurs at 933.5 eV [135]. Cu^+ cannot be distinguished from Cu^0 , as its binding energy is 932.2 eV. The weak Cu signal is attributed to the yolk-shell geometry and most likely can only be measured at defects in the shell or other thin regions.



Figure 4.9: XPS spectra for the (a) Co 2p region, (b) O 1s region, and (c) Cu 2p region for as prepared Cu@CoO nanoparticles prior to reduction.

Particles were then treated under sequential oxidative and reductive cycles in situ. Oxidative cycles consisted of ramping the temperature of Cu@CoO to 220°C over 7 minutes and holding at 220°C for 15 min before under 1 Torr of oxygen atmosphere before cooling to room temperature. Reductive cycles required ramping the temperature of Cu@CoO to 320°C over 11 minutes before holding at 320°C for 15 min under 3 Torr of hydrogen before cooling. Particles were also treated on TEM grids under identical conditions to produce a

visual comparison to XPS data. The x-ray energies for Co and Cu monitoring used were 980 eV and 1140 eV, respectively. This ensured the kinetic energies of the photoelectrons were roughly the same, giving an equal probing depth of roughly 0.6 nm for both Co and Cu.

Upon further oxidation, the CoO shell is converted to the more stable Co_3O_4 phase (Figure 4.10b). The satellite peaks diminish and the Co $2\text{p}_{3/2}$ and $2\text{p}_{1/2}$ binding energies shifts to 779.7 eV and 795.5 eV, respectively. These values are consistent with the literature values of 779.8 eV and 795.7 eV for Co_3O_4 [134]. Likewise, copper is seen to oxidize to Cu_2O . The Cu $2\text{p}_{3/2}$ and $2\text{p}_{1/2}$ binding energies shifted to 932.3 eV and 953.0 eV, respectively. These is close to the reported values of 932.9 eV and 252.7 eV [136]; however, other sources report Cu $2\text{p}_{3/2}$ values of 932.2 eV for Cu_2O [135], which compares more favorable.

Upon reduction, both the Co_3O_4 shell and Cu_2O core undergo full reduction to Co and Cu, respectively. The Co 2p3/2 sharpens and shifts to 778.4 eV, near the 778.1 eV reported in literature[137]. Copper 2p also sharpens and shifts to 232.5 eV. Likewise, the satellite peaks attributed with the oxide disappear.

The oxide and metal features of Co and Cu sharpen with each oxidative and reductive cycle, presumably because defects are being expelled with each cycle. Ex situ TEM of the corresponding redox cycles reveal the shape of the heterostructure is maintained between cycles (Figure 4.10c). When oxidized, a majority of the core copper particles hollow through diffusional-dependent oxidation. When reduced again, the number of particles that remain hollow diminish and the copper condenses into a solid particle on the inner wall of the shell. In addition, The shell size remains fairly constant between all redox cycles, but undergoes coarsening as the apparent grain size seems to grow. This may account for the observations of signal sharpening in XPS over the various cycles.

Analysis of the relative composition of Co and Cu in the shell shows the reversible surface sequestration of copper under oxidative conditions (Figure 4.10a). This is not readily apparent in the corresponding TEM images (Figure 4.10b) and Cu/Co mixing is unlikely as Cu has a low miscibility with Co [138, 139]. It is possible that during the redox cycles, the mean free path of the photoelectron is changed due to a change in material density. This would account for a difference in depth sampling and would give the appearance of a change in surface composition. Repeating the experiment with different probing x-ray energies would allow alternative depths to monitored and compared. Using a lower energy would narrow the analysis to just the outer layer of the shell. If the surface composition change is due to differences in the mean free path, using a lower probing energy would diminish the relative change in surface composition over the cycles. Additionally, if the change is actually due to surface sequestration, the composition change should increase at the narrower probing depth.



Figure 4.10: HP-XPS data showing (a) reversible surface composition change in Cu@CoO post oxidation and reduction cycling and (b) corresponding change in both Cu and Co to CuO and Co_3O_4 , respectively, during the redox cycle (from bottom to top). (c) Likewise, ex situ TEM under the same redox conditions show the reversible geometry change in the Cu@CoO.

4.4 Conclusions and Future Opportunities

This work has demonstrated the ability to coat oxidizable metal core particles using the kirkendall effect. Copper particles were protected by a cobalt shell and did not undergo oxidation until the cobalt shell had been fully oxidized. In situ HP-XPS studies reveal that the CoO shell will undergo further oxidation to Co_3O_4 upon oxidative thermal treatment. In addition, while both the core and the shell can be oxidized or reduced under thermal treatment, the geometry of the particles were maintained.

Further studies will be conducted to confirm whether copper can undergoes surface migration throught he shell. In addition, testing of Cu@CoO for Fischer-Tropsch synthesis will be conducted. Because the geometry is maintained under both oxidizing and reducing environments, the yolk-shell structure may remain stable under catalytic conditions, allowing geometry-influenced catalytic selectivity to be studied.

Chapter 5

Oxidative Growth of ZnO for Core-Shell Catalysis

5.1 Introduction

The formation of porous, nested heterostructures with a zinc oxide shell is very interesting for many catalytic processes. While ZnO has been used as a support for numerous hydrogenation, selective oxidation and isomerization catalysts, it is probably best known for its selective properties in methanolysis when joined with a copper catalyst. In the previous chapter, it was shown that reactive metal systems may be used to produce porous core-shell heterostructures using the Kirkendall effect under the right conditions. While copper and zinc are known to undergo alloying to form hollow structures, it may be possible to shell the materials at low temperatures with a reactive zinc decomposition precursor. In order to produce such materials, hollow zinc oxide particles must first be produced using the Kirkendall effect for solution-based oxidation.

Zinc has previously been shown to hollow during oxidation via the Kirkendall effect using non-solution based methods. Nakamura et al. studied the diffusional-dependent oxidation of zinc particles produced by the evaporation of zinc on TEM grids [140]. They found that the Kirkendall effect can be used to produce hollow ZnO particles at low temperatures for particles less than 20 nm in diameter. While zinc migration is unfavorable in the oxide lattice, electron tunneling in thin surface oxides can produce an electric field which pulls metal ions through the oxide film. However, this is highly thickness dependent and only occurs for thin films in the initial oxidation step. In addition, Qiu et al. found hollow ZnO rods could be synthesized using the Kirkendall effect on ultra-thin Zn rods produced by vapor deposition [141].

For solution based synthesis of ZnO using the Kirkendall effect, small stable Zn particles would have to be made using a zinc decomposition precursor in an organic solvent. Reports using diethylzinc as a decomposition precursor in organic solvents gave nonuniform rod-like aggregates, possibly from uncontrolled decomposition [142]. Slower nucleation and growth should lead to greater control resulting in more uniform particles, which may be

accomplished with a more stable zinc precursor. Dicyclohexylzinc has been used in many zinc related solution-based syntheses and may prove to be a better candidate for controlled particle growth [143, 144].

Eventually, the coating of zinc on copper particles will be desired to produce coreshell structures. For this reason, maintaining synthetic conditions of zinc particles similar to copper was desired. Previous attempts by Hambrock et al. to coat copper in solution with diethylzinc resulted in alloyed CuZnO particles [142]. The use of dicyclohexylzinc under similar conditions may result in a core-shell structure. It is interesting to note that similarly produced CuZnO alloyed particles by the same group as Hambrock showed catalytic activity for methanol synthesis [130]. This observation makes using porous core-shell geometry with clear separation of the two phases intriguing for studying possible mechanistic differences.

5.2 Grain Boundary Influence on Zn Diffusion

For the synthesis of Zn particles, dicyclohexylzinc was first synthesized by reacting zinc chloride with two equivalents of cyclohexylmagnesium chloride in dry ether for one hour under air-free conditions. Filtration of magnesium chloride biproduct and drying was subsequently done under air-free conditions to yield the air sensitive, white dicyclohexylzinc product [145]. During synthesis of Zn particles, dicyclohexylzinc dissolved in mesitylene was quickly injected into a solution containing squalane and hexadecylamine at $200^{\circ}C$ under air-free conditions. The temperature was maintained for an additional hour as particles were allowed to nucleate and grow before oxidation. Figure 5.1 shows the hexagonal plates produced by this method. A fairly wide distribution of plate sizes exist with a constant thickness of roughly 7 nm, as shown by Figure 5.1b. The non-uniformity of the side lengths of the hexagonal plates suggests larger plates form by the addition of smaller plates. Increasing or decreasing the reaction time increases or decreases the average size of the plates, respectively. Additionally, the {001} faces of the plates must be strongly passivated, as growth never occurs on these faces.

Oxidation of the zinc particles was done by bubbling a 20% oxygen in argon gas mixture into the reaction flask at 200°C post synthesis. Bubbling at elevated temperatures was maintained for over four hours to ensure maximum oxidation. Figure 5.2 shows images of Zn particles post oxidation. From Figure 5.2 a and d, it is clear that oxidation occurs predominately at the edges of the plates. The average oxide thickness at the edges was roughly 4 nm regardless of size of the initial zinc particle. If the {001} faces of the plate had similar oxidative rates to the {100} faces found at the edges, a full oxidation of the particles would be expected due to the relatively small thickness of the original plates. However, it is clear by both high resolution TEM and electron diffraction that the interior Zn particle was left intact. The electron diffraction pattern (Figure 5.2c) of a single Zn@ZnO particle shows the epitaxial growth of the ZnO layer. In addition, oxidation also occurs fastest at corners of the particles where two faces in the oxide layer meet to form a twin interface. This faster growth produces a spoked star geometry in the hexagonal particles (Figure 5.2 a and



Figure 5.1: (a) TEM of hexagonal Zn plates of varying sizes. (b) TEM side view of Zn plates of thickness 7 nm.

d) and allows growth of the oxide shell to be much greater than the 4 nm limit found on the edges. When the elongated edges get significantly large, they fracture to form smaller ZnO twinned particles as seen in Figure 5.2b. This is in good agreement with literature which proposes that Zn ion migration through the ZnO occurs by a vacancy mechanism which limits shell growth to small thicknesses [140]. The twin interfaces in our particles act as high vacancy channels that increase Zn ion mobility, resulting in greater oxide growth.

It is possible that these channels may be responsible for the hollowing seen in small particles in the literature [140]. The spokes of our particles extend much farther than the diffusion-limited growth of the edges. For very small particles the majority of the surface would exist near an edge of two faces. These would form twinning channels in which surface diffusion of Zn would be rapid and allow access to the entire core. The resulting oxide would be hollow and possibly have a shell thicker than would be allowed through conventional oxidation.

5.3 Attempts Towards Cu@ZnO for Methanol Production

CuZn alloys and dimers have previously been made for methanolysis [130, 142]. However, as of yet, no synthetic method for a core-shell particle has been reported. Attempts were made at growing ZnO shells on copper particles through the use of the Kirkendall effect. Hambrock and coworkers made alloys of Cu and Zn by co-injecting a copper precursor and diethylzinc into a hot squalane solution containing hexadecylamine (HDA) [142]. In attempts to form a core-shell structure, these procedures were repeated, except copper was first allowed to form and a more stable zinc precursor was used to allow for slower decomposition on the copper surface.

The reaction conditions are very similar to that described for producing copper particles previously (see §4.2.3). Hexadecylamine (108.7 mg, 0.45 mmol) was degassed at



Figure 5.2: (a) TEM of oxidized Zn@ZnO plates. (b) TEM of ZnO tips broken off from Zn@ZnO plates. (c) electron diffraction (ED) of single Zn@ZnO plate, shows epitaxial growth of ZnO. (d) High Resolution TEM of Zn@ZnO corner, inset - FFT of image.

100°C for 30 min under argon. Squalane (5 mL) was added and also degassed an additional 30 min. The solution was heated to 200°C under an argon atmosphere. A solution of bis(1-dimethylamino-2-propoxyl)copper (Cu(OR)₂, see §4.2.2, 121.5 mg) in mesitylene (1.25 mL) was made within the glovebox. The Cu(OR)₂ solution was quickly injected into the hot squalane/HDA solution and allowed to react under vigorous stirring for 5 minute. Subsequently, a solution of dicyclohexylzinc (35 mg $\text{Zn}(\text{C}_6\text{H}_{11})_2$ in 0.5 mL mesitylene) was injected and allowed to react for 6 minutes before exposing to air.

After primary injection of the copper precursor, the solution turned red within 2 minutes, indicating the formation of copper particles. Within 6 minutes of injecting the zinc precursor, the solution turned brown. The slow color change indicates that the decomposition of dicyclohexylzinc occurs slowly. TEM images of the particles at each stage are given in Figure 5.3. Oddly, the particles after Zn precursor injection (Figure 5.3b) have reduced in size and many smaller particles have formed in the background. X-ray diffraction of these particles most highly resembles pure copper or a copper/zinc alloy (Figure 5.4). The sharp intensity of the peaks makes it likely that the diffraction is primarily resulting from the large particles and not the smaller particles seen in the background. Upon oxidation, the solution turns a brownish green, indicating the formation of Cu_2O . This is also confirmed by XRD (Figure 5.4). In addition, the existence of ZnO is also present and likely to occur from de-alloying of the CuZn during oxidation. A residual CuZn alloy of some stoichiometry may be present, accounting for unidentified peaks and ones overlapping with the oxides. Figure 5.3 shows the presence of the yolk-shell geometry post-oxidation. This is not seen for Cu_2O particles produced from the direct oxidation of Cu particles (Figure 5.5). Cu_2O particles produced a mixture of hollow and not hollow particles, but the yolk-shell geometry was not observed.



Figure 5.3: TEM images of (a) Initial Cu particles, (b) CuZn particles before oxidation, and (c) Cu@ZnO particles.

This procedure requires much improvement to eliminate the nucleation of smaller particles. In addition, it is still uncertain the nature of the yolk-shell particles. Elemental mapping using energy dispersive spectroscopy (EDS) needs to be conducted to identify if Zn exists within the yolk-shell structures or if it only is present in the small background particles. However, this method shows promise for using the Kirkendall effect to produce



Figure 5.4: XRD of CuZn and CuZnO after oxidation. Reference spectra are given for Cu (red), CuZn (blue), ZnO (black), Cu₂O (green), and Cu_{0.7}Zn₂ (magenta).



Figure 5.5: (a) TEM image and (b) high resolution image of $\rm Cu_2O$ prepared from direct oxidation of copper particles.

porous yolk-shell structures of Cu@ZnO for catalytic studies.

5.4 Conclusions and Future Opportunities

Zinc diffusion through grain boundaries in forming zinc oxide shells were discovered to give elongated oxides relative to epitaxial oxide growth. The grain boundaries in the ZnO also formed at the edges of the initial Zn particles. By having a highly faceted Zn particle, one might generate many channels for accelerated Zn diffusion. In turn, a porous, hollow particle can be produced with a thick polycrystalline shell. Extending this concept to core-shell particles with Zn shells may produce yolk-shell particles with porous ZnO shells.

Initial studies to form yolk-shell particles with Cu@ZnO were inconclusive, but showed promise for making Zn coating for oxidation using the Kirkendall effect. Copper and zinc are known to easily alloy, making formation of a core-shell systems difficult without alloying. Using gold or another noble metal as a core could provide additional insight in the coating conditions for Zn metal. In addition, alloyed and pure metals may undergo different oxidation pathways, making noble metal cores interesting for comparative oxidation studies.

Chapter 6

Encapsulation of Small Gold in Silica for Catalytic Opportunities

6.1 Introduction

Encapsulation of gold particles in silica shells has been extensively studied over the past two decade because of its potential applications in non-linear optics, biolabeling and information storage. Gold colloids suffer from a strong dependence on solvation conditions for both its optical properties and stability. By coating gold in silica, the shell surface can be easily functionalized to make it suitable for various solution conditions without aggregation. In addition, thicker shells have been show to minimize optical shifts with changing dielectric environments.

One method for coating gold within a silica shell is by directly forming the silica on the gold surface. This is by far the most common method of coating; however, it suffers greatly from the poor interactions between the two materials. Unlike many metal oxide particles, gold particles possess no strong interactions with silica, making encapsulation difficult. Previous works have focused on derivatizing golds surfaces to render them vitreophilic [103]. However, despite the increased favorable interaction, only large gold particles, greater than 10 nm in diameter, can be coated by this method. Decreased particle sizes lead to larger surface curvatures that limit the growth of silica on the surfaces by hindering the condensation of monomers within solution and reducing the sticking probability of colliding silica clusters.

In order to include gold particles within silica, forming silica colloids must first adsorb onto the gold's surface. If multiple small silica colloids coat the gold, silanes will condense on the more concave surfaces at the silica interfaces and eventually lead to a uniform coating as growth continues. The reactivity of these surfaces to deposition follows the Kelvin equation, which relates solubility to the interfacial tension on curved surfaces. Regions of negative curvature (concave) have lower solubility and are sites for preferential deposition.
6.2 Ligand Influence on the Coating of Small Gold Particles

Small particles suffer from exceptionally large surface curvatures. As particle size decreases, the interparticle interfacial areas decrease. Consequently, lower densities of interacting functional groups at the interfacial surface reduce the sticking probability upon silica collision, making adsorption unlikely. In addition, small particles suffer from the same problems as larger particles. The negative charges on the gold particle surfaces make them repulsive to silica in basic conditions. In order to increase the likelihood of stickly, small gold particles were modified with various capping agents to reduce repulsive interactions. In addition, the concentration of gold particles in solution was drastically increased to increase the collision frequency of particles.

Small particles can be produced by various means to give contolled uniform sizes as well as surface functionality [12, 104]. To produce small particles for silica coating, dodecylamine (1.5 g) was dissolved in cyclohexane (25 mL). Aqueous formal dehyde (12 mL) was then added and stirred vigorously for 10 min to complex with the dode cylamine. The aqueous layer was then removed and the organic layer was washed twice with water to remove excess uncomplexed formal dehyde. A tetrachloroauric acid solution (89.3 mg HAuCl₄ in 25 mL water) was prepared. The cyclohexane solution was then vigorously stirred with 10 mL of the gold solution. After 40 min, the layers were separated and the organic layer was cleaned via centrifigation using ethanol as a non-solvent. Size selective precipitation was used to isolate the smallest partices for silica coating.

Ligand exchange was then performed on the particles to render them water soluble and give them the desired functionality. Roughly 2 mL of gold solution was shaken with desired ligand (11-mercaptoundececanoic acid (MUA) or 11-mercaptoundecanol) before washing and resuspending in isopropanol. Silica was then coated by adding a drop of ammonium hydroxide solution and 25 μ L of tetraethylorthosilicate and allowing the reaction to stir for an hour. The particles were then centrifugred and resuspend in water.

Additionally, small gold particles can be synthesized directly in the aqueous phase using trisodium citrate as a capping agent [146]. In this method, two reaction solutions are made: (1) a gold solution consisting of 1% tetrachloroauric acid (1 mL) and water (79 mL), and (2) a reaction solution of 1% trisodium citrate (4 mL), 1% tannic acid, (5 mL), a 28mM potasium carbonate solution (5 mL) and water (6 mL). Both solution are heated to 60°C before the quick addition of the gold solution to the reaction solution. The whole mixture is then boiled for one hour before cleaning via centrifugation. Silica coating is done as before with the ligand exchanged particles.

It was anticipated that small particles with negatively charged terminal acid groups like 11-mercaptoundecanoic acid and citrate would be have repusive charges and not stick to the silica. The 11-mercaptoundecanol capped particles have terminal functional groups that are neutral at the pH of silica coating and was expected to have higher collision frequencies due to a lack electrostatic repulsion. However, Figure 6.1 reveals that no silica coating occured on 11-mercaptoundecanol capped particles while acid capped gold had excellent coating.



Figure 6.1: TEM micrographs SiO_2 coated Au prepared by the Stöber method using gold particles capped with (a) 11-mercaptoundecanoic acid, (b) 11-mercaptoundecanol and (c) citrate.

The alcohol terminal gold had signs of silica coating despite the greater collision frequency. This is thought to occur because of the relatively strong binding of the ligand. While small silica particles may colloid with gold more frequently, they cannot displace the strongly bound thiol such that the sticking probability was diminished. Conversely, citrate capped gold collides with silica less frequently but has a weakly bound ligand that is easily displaced, giving a higher sticking probability. Multiple gold was encapsulated because of the higher concentrations used. The 11-mercaptoundecanoic acid capped gold showed the congregation of gold within the center of the formed silica. This can be explained by aggregation within solution. Even though the 11-mercaptoudecanoic acid capped gold should have the same problems the alcohol terminated gold due to the strongly bound thiol, the aggregated gold acts much like a large gold particle with plenty of surface area in which silica can interact.

Another concept is to further restrict reacting silicates withing microemulsions. In doing so, the reaction is restricted to confined regions such that the collision frequency is increased. Han et al. has demonstrated the use of microemulsions to encapsulate 12 nm gold particles within single uniform silica shells [101]. Organic soluble gold will have no repulsive charges and will undergo collisions with the micelles. When hydrolated TEOS species replace organic stabilizers, the gold particle is pulled within the aqueous micelle and further silica deposition can occur.

Two approaches were taken to incorporate smaller gold into silica using the reversemicelle method: (1) use as-made dodecylamine stabilized gold for organic transfer into the micelles, and (2) put aqueous citrate stabilized gold into the micelles initially and let the gold condense around it. It was believed that with a higher collision frequency, small gold would be coated within the micelles, as there is nowhere else for the gold to go.

The reverse-micelles synthesis was conducted as follows: Cyclohexane (5 mL) and the Igepal CO-520 (0.35 mL) are mixed. An ammonium hydroxide solution (0.5 mL) was added slowly under vigorous stirring. Finally, 20 μ L of tetraethylorthosilica was added and left to stir for 24 hours. For dodecylamine capped particles, gold particles were condensed and added to the cyclohexane phase prior to micelle preparation. For the citrate capped particles, gold was condensed and added to the ammonium hydroxide solution prior to micelle preparation.

Figure 6.2 shows the resulting silica coating of gold via the microemulsion method. Dodecylamine capped gold shows little to no particle incorporation. The smaller particle size decreases the sticking coefficient of the particles, making likelihood of gold inclusion into the micelles low before significant silica growth occurs. Conversely, citrate capped gold was already in the micelles. These gold particles were negatively charged and got pushed to the outskirts of the forming silica, resulting in gold-decorated silica beads.



Figure 6.2: TEM SiO_2 coated Au prepared by the microemulsion method using gold particles capped with (a) dedecylamine and (b) citrate.

6.3 New Routes Towards Gold Inclusion

While direct inclusion of small gold into silica is prohibitively difficult, vitreophilic materials can readily be incorporated into silica regardless of size. Caraliere-Jaricot et al. used vitreophilic CdSe-ZnS particles as a template for silica growth. They then etched out the semiconductor core with acid to produce a hollow silica shell. After soaking the hollow shells in a gold salt solution for multiple days, a sodium borohydride reducing agent was added to give Au@SiO₂ particles [147].

I attempted to recreate this using 3 nm CdSe dots (Figure 6.3a) and the reverse micelle synthesis. CdS particles were concentrated and diluted in dry chloroform $(1.728 \times 10^{-7} \text{ mol/L})$. Cyclohexane (10 mL), Igepal CO-520 polymer (1.3 mL), and CdSe solution (400 μ L) were thoroughly mixed. Tetraethylorthosilicate (80 μ L) was then added and stirred for 30 min. Ammonium hydroxide (150 μ L) solution was then added slowly and left stirring for 24 hours. Afterwards, the CdSe@SiO₂ (Figure 6.3b) were precipitated with isopropanol and washed several times. CdSe was acid etched by diluting the particles to 2 mL and adding enough nitric acid to reach a 1 M concentration. Once the core was etched, the hollow particles (Figure 6.3c) were cleaned multiple times via centrifugation. Soaking the particles in a 1% gold salt caused the solution to turn pink within hours. The particle solution was allowed to continue soaking for 1 day before being reducing further with sodium borohydride. Figure 6.3d show the final particles after attempted gold reduction.



Figure 6.3: (a) CdSe nanocrystals. (b) CdSe@SiO₂. (c) hollow SiO₂. (d) Au@SiO₂ post reduction.

The slow changing in color to pink during particle soaking most likely resulted in reduction of gold caused by insufficient cleaning after acid etching. However, this was not the cause of the failed reaction. Caraliere-Jaricot et al. used larger particles, resulting in a 8 nm void space [147]. My particles were much smaller and reactants were probably diffusion limited, resulting in a few loaded particles.

Despite the failure of the reaction, a greater observation came as a result. Secondary methods for gold loading in which gold is grown within the oxide shell can lead to greater polydispersity in particle size as well as the possible sub-lattice inclusion of salts within the oxide. For these reasons, many industrial catalysts are difficult to study and the use of direct encapsulation methods becomes favored for mechanistic studies. The use of molecular primers have allowed the encapsulation of larger non-vitreophilic particles, such as gold, in the past. The current study shows small vitreophilic particles can be easily coated despite their size. Additionally, these particles can often be etched under mild conditions without harming the oxide. It stands to reason that coating small non-vitreophilic particles in a vitreophilic shell could allow for facile silica coating much like a molecular primer. Additionally, these coating could be etched, leaving the gold and shell intact. Controlling the thickness of the sacrificial shell could allow for tuning of the void space. Control of this vacancy may prove useful in catalytic studies.

Currently, methods exist for producing silver and semiconductor shells on gold with high precision in thickness and uniformity [148, 149]. These methods can produce sacrificial shells to allow silica coating. Generally, a nonepitaxial shell of silver is grown on gold nanoparticles through a three-phase coating process. Direct silica coating can be done at this stage or further transformation of the silver shell to various semiconductors through sulfidation and cationic exchange processes. Small gold nanoparticles (Figure 6.4a) were made as described in section 3.2.2. Coating of gold in silver was done as described by Zhang and coworkers [148]. Gold nanoparticles (1 mg, 0.005 mmol) were condensed from solution by centrifugation and re-dispersed in oleic acid (0.4 mL) through sonication. Once the gold was fully dispersed, sodium oleate (0.3 g) was added and dissolved once again under sonication. Ethanol (4 mL) was then added dropwise to the sonicating solution followed by water (6 mL), again dropwise. Throughout the entire procedure, it is vital that the solution remains red and transparent to ensure a true emulsion is formed. Once the solution looked red and homogenously mixed, it was placed on a stir plate and silver nitrate (1 mL, 0.03 M aqueous solution) was added dropwise under vigorous stirring. Using a syringe pump, ascorbic acid (0.6 mL, 0.4 M aqueous solution) was added over a twelve hour period. The reaction was presumed complete 24 hours after the syringe pump was started. Toluene (10 mL) was added to the reaction to extract Au@Ag nanoparticles (Figure 6.4b). A small addition of dilute nitric acid facilitated the phase separation by protonating the large excess of sodium oleate phase-exchange agent.



Figure 6.4: TEM of (a) 2.8 nm Au particles, (b) Au@Ag particles, and (c) Au@Ag@SiO_2 particles.

Silica coating of Au@Ag nanoparticles was done using the reverse micelle-method just as in the coating of CdS described above. The use of a high concentration of Au@Ag caused multi-nuclei encapsulating within silica, as seen in figure 6.4c. For catalytic testing on Au@SiO2, silver can be removed by direct etching or by conversion to Ag_2S or further to CdS within the shell before acid etching.

Now that small gold can be coated in silica, a variety of techniques can be performed to transform the silica shell into an active supporting material such as aluminosilica [150] or porous titanium silicates [151]. In addition, this method is amenable to direct sol-gel coating of other materials or surface modification to incorporate active metal sites within the existing silica shell. The following chapter review work on silica modification to incorporate active titania for epoxidation chemistry. Small gold in titanium modified silica shells have direct application for these reaction, primarily propylene epoxidation.

Chapter 7

Pt@Pd@mTi_xSi_{1-x}O₂ Dual Catalyst for Selective Oxidation

7.1 Introduction

As previously discussed, numerous researchers have used porous silica shells to protect catalysts from high temperature deactivation. However, silica is a highly versitile and functional material. When used to produce mixed oxide systems, it can enhance or tune the acidity of supporting materials or provide local structure such that new properties can be derived. If the chemistry of a silica shell is changed making it a mixed metal oxide, additional versatility is gained to do dual catalysis.

Bao et al. realized the potential of the core-shell geometry for dual catalysis in 2008 [52]. However, he demonstrated its versatility with encapsulated micron sized beads of loaded catalysts rather than single particle encapsulation. Using a cobalt loaded alumina Fischer-Tropsch catalyst encapsulated in a zeolite membrane for isomerization chemistry, he showed that the porous core-shell geometry can give added selectivity for dual stream catalysis. His core shell geometry gave higher selective yields for isoparaffin formation over all carbon chain length than either the Fischer-Tropsch catalyst alone or a physical mixture of the Fischer-Tropsch and isomerization catalysts.

In a single particle porous core-shell geometry, additional benefits may be realized. The process of spillover, in which an adsorbed molecule migrates onto the support rather than desorbing, may further increase selectivity as it can put reactive molecules directly onto neighboring active sites of a secondary catalytic shell.

Propylene epoxidation is an interesting catalyst system to target. Titania or zeolitic titanium silicates can catalyze the direct epoxidation of propylene with hydrogen peroxide. However, hydrogen peroxide is expensive to make, so industry often prefers to generate the peroxide in situ. For this reason, loaded gold on titania or TS-1 is the preferred catalyst because gold is a weak catalyst and does not catalyze the hydrogen peroxide decomposition. Unfortunately, only small gold is active and sintering is a common problem industrially. The formation of a porous core-shell system with a small gold core and titania or titanium silicate shell would be ideal.

As seen in the previous chapter, coating small gold is very difficult with silica alone, much less a a binary material. In this chapter the formation of a palladium-based coreshell system will be synthesized. Palladium is also active for hydrogen peroxide formation, but also can catalyze its decomposition. The synthesis for forming the multi-component core-shell system, Pt@Pd@Ti_xSi_{1-x}O₂, will be described with an emphasis on methods for including titania within a porous silica shell. Finally, the use of this material for dual catalysis is discussed, using the selective oxidation of pyridine as a probe reaction.

7.2 Synthesis

7.2.1 Pt Nanoparticles

Tetredecyltrimethylammonium bromide (TTAB) capped platinum nanocubes were synthesized in accordance with literature [48]. In a 100 mL 3-neck round bottom flask, 5 mL of a 10 mM K_2PtCl_4 aqueous solution was mixed with 40 mL of a 120 mM TTAB aqueous solution. After allowing to mix for 10 min at room temperature, the reaction vessel was heated to 50°C and stirred an addition 10 min. Subsequently, 3 mL of a freshly made, ice-cold NaBH₄ solution was quickly injected, liberating hydrogen gas. The reaction temperature was maintained at 50°C for 20 hours under constant stirring. Throughout the reaction, the vessel remained sealed with the exception of a needle within a septum to prevent a build of pressure. This allowed for the accumulation of hydrogen gas in the headspace of the vessel to maintain a reducing environment.

Particle cleaning procedures proved very important towards proper silica coating (§7.2.4). Once cooled, the reaction solution was centrifuged at 3000 rpm for 30 min to remove large Pt particles. The precipitant was discarded and the supernatant was centrifuged twice more under the same conditions. Finally, the the particles were collected from the supernatant by centrifuging at 14000 rpm for 15 min. The precipitant was separated and re-dispersed in 5 mL of deionized water by sonication.

TEM analysis showed the particles to be composed of roughly 70% cubes and 30% cuboctahedrons with an average diagonal dimension of 14.6 ± 0.2 nm (Figure X). However, the particle morphology was found to be highly temperature sensitive. Deviations from 50 \pm 3°C over the 20 hour reaction time gave particles with larger variations in particle shape (Figure 7.1).

7.2.2 Pd Nanoparticles

Initially, palladium particles were synthesized using a procedures similar to Pt. In a 100 mL 3-neck round bottom flask, 5 mL of a 10 mM K_2PdCl_4 aqueous solution was mixed with 40 mL of a 120 mM TTAB aqueous solution. After allowing to mix for 10



Figure 7.1: TEM images of Pt with temperature sensitive morphologies: (a) irregular, (b) dendritic, (c) cubic, and (d) cubic and cuboctahedral.

min at room temperature, the reaction vessel was heated to 50° C and stirred an addition 10 min. Subsequently, 4 mL of a 250 mM ascorbic acid aqueous solution was injected. The reaction temperature was maintained at 50° C for 20 minutes under constant stirring. Cleaning procedures were done the same as Pt nanoparticles (see §7.2.1 for procedures).

Unlike TTAB coated Pt particles, Pd nanoparticles produced using this method show a high degree of morphological irregularity (Figure 7.2). Particles were found to be composed of cubes, cuboctahedraon, trigonal plates and rods with sizes around 50 nm in their greatest dimension.



Figure 7.2: TEM of Pd nanoparticles show large array of particle morphologies.

More recently, an alternative procedure for making cubic Pd nanoparticles with similar surface chemistry as the Pt system was developed. Literature on shape controlled Pd nanostructures use the addition of potassium halides to guide particle shape [152]. This procedure was modified such that TTAB is used as a surface binding agent to maintain similar surface functionality for the silica coating process.

In a 100 mL round bottom flask, 40 mL of 10 mM ascorbic acid and 25 μ L of a 1.0 M potassium bromide aqueous solution were added and stirred at room temperature. Over roughly 2.5 minutes, 5 mL of a 10 mM K₂PdCl₄ aqueous solution and 5 mL of a 20 mM TTAB solution were simultaneously added dropwise. The reaction was then left to

continue stirring for 2 hours at room temperature. Afterward, particles were isolated by centrifugation at 6000 rpm for 30 minutes. The supernatant was discarded and the pellet was kept for silica coating.

It is worth noting that the cleaning procedure for this reaction was much simpler as the sensitivity of the silica coating to core particle cleaning has been worked out. This greatly simplifies particle synthesis and makes these reactions amenable to quantity scaling. Details of the new silica coating procedures will be described in full in section 7.2.4.

Figure 7.3 shows primarily cubic Pd particles with a semi-porous nature (Figure 7.3a). This porosity can be beneficial as it will increase the surface area available for catalysis. However, mechanistic studies may be more difficult than on ordinary solid cubes because additional faces than just the $\{100\}$ are exposed.



Figure 7.3: TEM of Pd nanoparticles show primarily cubic shape and slight porosity

7.2.3 Pt@Pd Nanoparticles

Pt seeds can be used as a template for growing cubic Pd shells [153, 154]. To produce Pt seeds, the same Pt cube procedure from section 7.2.1 was followed; however, the reaction was only allowed to proceed for 6 hours rather than the full 20 hours. For Pd shelling, 3 mL of the Pt solution was added to a Pd solution consisting of 5 mL of 10 mM K₂PdCl₄ and 40 mL of a 120 mM TTAB aqueous solution. The solution was heated to 50° C and 4 mL of a 250 mM ascorbic acid aqueous solution was added. The reaction was maintained for 20 minutes before clean was done using the same cleaning procedures in section 7.2.1.

The as-synthesized Pt@Pd cubes showed exceptional morphology control and monodispersity (Figure 7.4). The diagonal dimension across the cube was measured to be 32.4 ± 0.6 nm. Comparing this procedure to that of the disordered Pd ($\S7.2.2$) reveals the importance of seed particles in guiding the shape of Pd nanocrystals. The only difference between the two procedures is the addition of the Pt seeds. This highlights how the initial particle nucleation can be the most important stage of a reaction and sets the course for the final morphology and size distribution.



Figure 7.4: TEM images of Pt@Pd nanoparticles.

Figure 7.5 gives the x-ray diffraction patterns of Pt nanoparticles, Pd nanoparticles and the Pt@Pd heterostructures. The lattices constants of the two materials match extraordinarily well and no compositional difference is seen between the samples. However, the core-shell geometry is clearly seen in Figure 7.4, so the formation of an alloy is unlikely.

7.2.4 Mesoporous Silica Coating

Silica coating procedures follow that reported in the literature [48]. In this synthesis, the positively charged ammonium groups on the TTAB ligand of the Pt attract the negatively charged forming silica, allowing for conformal coating. Additionally, silica condenses around the long chains of the ligand that stick out perpendicular to the nanoparticle's surface. Upon thermal removal of the ligand, ordered pores are left in place of the TTAB.

Pt nanoparticle solutions (5 mL) were diluted with 36 mL of deionized water in a 100 mL round bottom flask and stirred for 5 minutes. The addition of 1 mL of a 0.05 M NaOH aqueous solution was used to raise the pH of the solution between 10 and 11. After an additional 5 minutes of stirring, 500 μ L of a 10% vol. TEOS solution in methanol was added dropwise and the reaction was allowed to continue for 48 hours at room temperature. The resulting colloids were then centrifuged once at 3000 rpm for 5 minutes and the precipitate was discarded. The supernatant was then centrifuged again at 14000 rpm for 10 to



Figure 7.5: XRD images of Pt (green), Pd (blue), and Pt@Pd (orange) nanoparticles.

15 minutes and the precipitant was collected in 3 mL of deionized water and re-dispersed by sonication.

Figure 7.6 shows the resulting $\rm Pt@SiO_2$. The internal Pt particles maintain their cubic morphology and the silica shell grows in a rough conformal coating to give a final spherical morphology with a diameter of 36.0 \pm 0.4 nm. This results in an average shell thickness of 10.7 \pm 0.5 nm.



Figure 7.6: TEM images of $Pt@SiO_2$.

The coating procedure has been found to be very dependent on the particle cleaning procedures. If the particles are overcleaned, the labile TTAB ligand will dissociate from the particle surface to establish an equilibrium in solution solution. This causes particle aggregation and results in particle clumping during silica coating (Figure 7.7b). If particles are left dirty with a large excess of TTAB in solution, the excess positively charged TTAB helps stabilize forming silica such that separate silica particle form rather than coating on the surface of the particles of interest (Figure 7.7c). In order to establish favorable coating conditions, only a slight excess of TTAB is necessary to ensure particle aggregation does not occur and few self-nucleating silica form.



Figure 7.7: (a) Pt particles that are overcleaned loose stabilizing TTAB to solution during silica coating resulting in (b) aggregated Pt encapsulated in silica. If the particles are left dirty with a large excess of residual TTAB, (c) independently nucleated silica will form rather than coat Pt.

When coating Pd nanocubes, the ligand effect was taken into account such that stringent cleaning procedures that are typically done were not necessary. To coat Pd cubes in porous silica, the Pd pellet collected after centrifugation was suspended in 2.5 mL of a 3.25 mM TTAB solution and further diluted to 40 mL of deionized water. The actual concentration of TTAB solution used was unimportant as long as the final concentration of TTAB in solution was roughly 0.2 mM. If particles seemed to aggregate, a few extra drops of TTAB solution could be added to help disperse Pd cubes. The pH was then adjusted to be between 10 and 11 by the addition of 75 μ L of a 1.0 M NaOH aqueous solution. After the addition of 500 μ L of a 10% vol. TEOS solution in methanol, the reaction was stirred at room temperature for 24 hours. Cleaning is done by centrifugation at 9500 rpm for 10 min. The supernatant is discarded and the particles are cleaned once more in 40 mL isopropanol. Figure 7.8 shows uniform silica coating of cubic Pd nanopaticles through controlled TTAB concentration. In addition, the amount of self-nucleated silica particles was minimal. Calcination of these particles was done as described in section 7.2.5.1 for Pt@Pd core particles.



Figure 7.8: TEM images of cubic Pd@SiO₂.

The $Pt@SiO_2$ particles were calcinated to remove the TTAB pore directing agents still within the silica shell. The particles were placed in a tube furnace and dried at 80°C for 1 hour before raising the temperature to 350°C for 3 hours in air. Drying was performed to consolidate the silica network by forming bonds between terminal S–OH groups through condensation reactions. This strengthens the silica structure prior to high temperature calcination and thermal removal of ligands.

TEM images of the calcinated $Pt@mSiO_2$ (where the "m" refers to mesoporous) in Figure 7.9 reveal the porous nature of the particles. The average particle diameter shrinks to 32.5 ± 0.5 nm, giving a new shell thickness of 8.9 ± 0.3 nm. This shrinking process in known as syneresis and is caused by the expelling of water from the pores (much of which is liberated from further condensation). The spherical morphology of the shell was maintained despite the contraction.

Thermal gravimetric analysis (TGA) shows the mass change as particles are heated. Both Pt and Pt@SiO₂ particles were heated to 500°C in a synthetic air atmosphere. During sample heating, a carrier gas of argon was flowed at 20 mL/min with an auxiliary oxygen gas flowed simultaneously at 5 mL/min. The thermal profile is given in table 7.1 and consists of a solvent drying stage at 70°C, a calcination stage at 350°C, and a thermal stability test up to 500°C. Figure 7.10 shows the mass change for both Pt and Pt@SiO₂ over the given temperature profile. Pt shows stable weight until 200°C where it undergoes an 82% mass loss. Pt@SiO₂ looses roughly 4% of its initial mass prior to oxidative decomposition of the



Figure 7.9: TEM images of Pt@mSiO₂ after calcination

ligand at 200°C. This is attributed to the water desorption.

Zone	T start ($^{\circ}C$)	T end ($^{\circ}C$)	Scanning rate (K/min)	Duration (h:m:s)
1	20	70	10	00:05:00
2	70	70		03:00:00
3	70	350	5	00:56:00
4	350	350		02:30:00
5	350	500	5	00:30:00
6	500	500		02:00:00

Table 7.1: Temperature Profile for TGA of Pt@SiO₂

Thermal stability of the silica coated particles was confirmed up to 500° C. TEM images of Pt and Pt@SiO₂ after thermal analysis reveal massive sintering in the case of bare Pt and preserved morphology forPt@SiO₂ (Figure 7.11). This data gives further proof as to the benefits porous core-shell geometries have towards high temperature catalysis.

7.2.5 Titanium Incorporation within Silica Shell

7.2.5.1 Titanium Co-deposition

Co-deposition of titania with silica was made possible by the controlled hydrolysis of the titanium precursor to be at roughly the same rate as that of silica. Titanium hydrolysis is intrinsically fast, so a chelated titanium precursor was used to greatly reduce the rate of hydrolysis. In addition the pH and titanium precursor concentrations were adjusted to change the amount of titania incorporation within the forming oxide.



Figure 7.10: TGA analysis of Pt nanoparticles (blue) and pre-calcinated $\rm Pt@SiO_2$ particles (green).



Figure 7.11: TEM images of Pt after thermal treatment up to 500° C (a) with and (b) without silica coating.

The same synthetic strategies used to coat Pt and Pd in the previous section apply in the coating with titanium silicate. Generally, a 5 mL colloidal suspension (Pt, Pd or Pt@Pd) was diluted with 36 mL of deionized water in a 100 mL round bottom flask and stirred for 5 minutes. Different amounts of a 0.05 M NaOH aqueous solution were added to the mixture in order to adjust the pH within the desired range (typically, 10 or 12) and stirred for an additional 5 min. The high pH values were used to increase the hydrolysis rate of the titanium precursor [155]. A 10% vol. TEOS solution in methanol (Solution 1) and a 10% vol. Ti(iOPr)₂(acac)₂ solution in methanol (Solution 2) were prepared separately. Afterward, 500 μ L of Solution 1 and different amounts (10, 30, or 50 μ L) of Solution 2 were added simultaneously in the flask dropwise followed by a 48 hour reaction time at room temperature. The resulting colloid solution was isolated by first centrifuging at 3000 rpm for 5 min, discarding the precipitant to remove large aggregates. The supernatant was then centrifuged again at 14000 rpm for 10 to 15 minutes and the precipitant collected and redispersed in 3 mL of deionized water by sonication.

Figure 7.12 shows encapsulated metal catalysts within titania loaded silica. The majority of the images show shells produced at a pH between 12 and 13 because the higher pH gives favorable titanium precursor hydrolysis. Comparing Pt@SiO₂ (Figure 7.6b) with Pt@Ti_xSi_{1-x}O₂ (Figure 7.12a), it becomes apparent that the addition of titanium causes slight morphological issues. While all reaction conditions, including pH, were the same except the use of titania, titania loaded shells gave a rougher surface and slightly thinner shells (average diameter: 27.0 ± 0.3 nm with shell thickness of 6.2 ± 0.2 nm). This indicates that the less reactive titania precursor hinders the hydrolysis and condensation steps once incorporated in the lattice. Despite morphology, the composition of the shells shows no significant differences. The lack of density inhomogeneities within the shell suggests that titanium is homogeneously dispersed within the silica shell through the co-condensation process without isolated titania phases within the silica network. Titanium incorporation was confirmed with FTIR.

Figure 7.13 shows FTIR of both Pt@SiO₂ and Pt@Ti_xSi_{1-x}O₂. The intense stretching frequencies at 1097 and 797 cm⁻¹ are assigned to the symmetric ν_s (Si—O— S) and asymmetric ν_{as} (Si—O—Si) stretching vibrations, respectively [156]. In addition, the band at 465 cm⁻¹ corresponds to the the Si—O—Si bending modes. Ti^{IV} incorporation through Si^{IV} substitution is primarily associated with the band at 960 cm⁻¹ [157]. However, this band is not conclusive on the coordination environment of the Ti sites in the silica matrix. The additional decrease of the band at 465 cm⁻¹ with increasing titanium content suggests that the silica structure is partially altered by the formation of Si—O—Ti moieties. The weak band at 1630 cm⁻¹ is attributed to the bending vibration of water. This has been known to increase for increasing Ti content and is believed to occur because of the more favorable adsorption of water on terminal Ti sites. The Ti–O bond is less covalent than Si–O, resulting in greater Lewis acidity of coordinately unsaturated Ti sites as compared to silica, giving stronger water adsorption [158].



Figure 7.12: TEM images of (a) Pt@Ti_xSi_{1-x}O₂ at pH 10, (b) Pt@Ti_xSi_{1-x}O₂ at pH 12, (c-d) Pd@Ti_xSi_{1-x}O₂ at pH 12, and (e-f) Pt@Pd@Ti_xSi_{1-x}O₂ at pH 12



Figure 7.13: FTIR spectrum of Pt coated in SiO₂ (red) and $Ti_xSi_{1-x}O_2$ (black).

Figure 7.14 shows the increasing titanium incorporation with raising pH. This supports the assumption that higher alkalyne conditions facilitate the hydrolysis of the chelated Ti precursor. TEM images of Pt@Ti_xSi_{1-x}O₂ produced at pH 10 and 12 (Figure 7.12a-b) also support this claim. Shell thickness increases with increasing pH, with the shell thickness of 12.4 ± 0.2 nm (particle diameter: 39.5 ± 0.4) for pH 12.

Additionally, titanium incorporation was found to increase with increasing concentrations of titanium precursors at pH 12. Both adsorption bands at 960 cm⁻¹ and 1630 cm⁻¹ (Figure 7.15) were seen to increase with titanium loading.

While calcination of titanium loaded silica shells proceeds the same for the silica shell alone, the calcination temperature must be monitored in order to protect the core particle. Platinum, as seen in §7.2.4, is unaffected by high temperature calcination because it resistant to oxidation. Figure 7.16 shows the change in $Pd@Ti_xSi_{1-x}O_2$ upon calcination. Likewise, XRD further shows the partial oxidation of Pd to PdO at temperatures of 350°C.

A modified calcination procedure was performed for $Pt@Pd@Ti_xSi_{1-x}O_2$ to prevent oxidation of the inner Pd shell. $Pt@Pd@Ti_xSi_{1-x}O_2$ was placed in a tube furnace and dried at 80°C for 1 hour before raising the temperature to a maximum temperature of 275°C for 3 hours in air. By keeping the temperature below the oxidation temperature, Pd remained metallic. Figure 7.18 shows the temperature was sufficient to remove the TTAB from the shell's pores, but did not harm the morphology of the core. Additionally, XRD patterns of before and after catalysis shows no signs of particle oxidation (Figure 7.19).



Figure 7.14: FTIR spectrum 960 cm⁻¹ for Pt@Ti_xSi_{1-x}O₂ synthesized at different pH value. The nominal titanium concentration is given in parentheses.



Figure 7.15: FTIR spectrum of $Pt@Ti_xSi_{1-x}O_2$ synthesized with different Ti precursor concentrations at bands of (a) 960 cm₋₁ and 1630 cm₋₁.



Figure 7.16: TEM images of $Pd@mTi_xSi_{1-x}O_2$ nanoparticles post calcination



Figure 7.17: XRD pattern of Pd@mTi $_x$ Si $_{1-x}$ O₂ nanoparticles before (blue) and after (black) calcination.



Figure 7.18: TEM images of $Pt@Pd@mTi_xSi_{1-x}O_2$ nanoparticles after calcination



Figure 7.19: XRD pattern of Pt@Pd@mTi_xSi_{1-x}O₂ nanoparticles before (orange) and after (purple) calcination.

Differential scanning calorimetry (DSC) was used to probe the oxidative temperature of Pd in our multi-shell system. Samples were run both under oxidative conditions (20 mL/min Ar and 5 mL/min O_2) and in inert atmosphere (20 mL/min Ar). The temperature program is given in table 7.2. Below 300°C, samples in both oxygen and argon show similar exothermic decompositions and condensations resulting from shell shrinkage (Figure 7.20). Above 300C, the oxygen sample shows a distinct exothermic peak associated with Pd oxidation. Corresponding TEM and XRD were taken of sample after DSC treatment (Fig 7.21). XRD confirms that only the sample run in air oxidized. Additionally, the morphology of the oxidized sample underwent further distortion than the sample ran in argon.

T start ($^{\circ}C$) T end ($^{\circ}C$) Scanning rate (K/min) Duration (h:m:s) Zone 1 2080 1000:12:00280 80 01:00:003 80 500:34:002504 25004:00:002505525050000:50:006 01:00:00500500

Table 7.2: Temperature Profile for TGA of Pt@SiO₂



Figure 7.20: DSC of $Pt@Pd@Ti_xSi_{1-x}O_2$ nanoparticles in air (green) and argon (blue)



Figure 7.21: (a) XRD of Pt@Pd@Ti_xSi_{1-x}O₂ as prepared (orange) and after DSC in argon (purple) and air (blue). TEM of Pt@Pd@Ti_xSi_{1-x}O₂ after DSC in (b) argon and (c) air.

Additionally, FTIR was conducted on Pt@Pd@Ti_xSi_{1-x}O₂ before and after calcination at 275°C to ensure complete ligand removal (Figure 7.22). Stretching vibrations associated with asymmetric CH₂ stretching at 2925 cm₋₁ and symmetric stretching of both CH₂ and CH₃ at 2825 cm₋₁ was seen to vanish after calcination, indicating loss of TTAB and other carbonous species within the pores. In addition, the broad peak at roughly 3360 cm₋₁ associated with -OH stretching of water was seen to almost completely disappear, as the pores are evacuated and further surface condensation eliminates water byproduct.

7.2.5.2 Titanium Surface Loading

While titanium can be co-precipitated to make ordered titanium silicate structures, only titanium at the surface of particles are active to do catalysis. Surface coordination of titania can be made in anhydrous conditions such that condensation can occurs in solution between silanol groups existing on a silica surface and titanium precursors via alcohol condensation [159].

This technique was applied to silica and $Pd@SiO_2$ particles to create particle systems with only tetrahedrally coordinated surface titanium species for catalytic comparison against co-precipitation-based $Ti_xSi_{1-x}O_2$ particles. Particles to be surface treated were first dried under vacuum at 200°C for 24 hours to ensure particles were completely dry and only terminal hydroxyls of silica surfaces were present for condensation with titania. The dried particles were kept air free and transferred to the glove box where they were suspended in dry hexane. In addition, a teflon reaction flask was used for titania deposition to reduce the likelihood of titanium precursor condensing on the walls of the reaction flask. Assuming only 1-3 OH/nm² exists on silica, the amount of titanium isopropoxide was adjusted to give



Figure 7.22: IR spectrum of $Pt@Pd@Ti_xSi_{1-x}O_2$ nanoparticles before (red) and after (blue) calcination at 275°C for 3 hours. Spectra were vertically displaced for visual simplicity.

a sub-monolayer coverage. The titanium isopropoxide was added to the anhydrous solution and stirred for 24 hours at room temperature to allow to coordinate to the surface of the particles. The particles were collected via centrifugation and re-suspended in isopropanol for further washing and UV-Vis analysis.

The relative wt% of titanium incorporated into silica is insignificant to the bulk of the shell, making titanium incorporation determination via FTIR impossible. However, titanium undergoes coordination dependent adsorption in the far UV, allowing a simple method of detection as well as a probe of the coordination environment. Adsorption between 200 and 220 nm corresponds to tetrahedrally-coordinated Ti. Titania particles of the anatase phase have a characteristic adsorption band at 300 nm [159]. The absence of this band indicates that all the coordinated titanium is surface loaded and has not undergone self-nucleation of titania particles or clusters. Figure 7.23 exhibits a sharp absorption at 205 nm for the surface loaded tetrahedrally-coordinated titanium. No adsorption feature is present at 300 nm, indicating no formation of TiO₂.



Figure 7.23: Far UV-Vis adsorption of surface coordinated titanium on silica.

7.3 Pyridine Oxidation

The choice reaction for $Pd@Ti_xSi_{1-x}O_2$ is propylene epoxidation using propylene, hydrogen and oxygen. However, this reaction can be somewhat dangerous and is conducted at high pressures [160]. For this reason, a test reaction was choosen to be conducted under safe conditions.

Typically, the production of hydrogen peroxide from hydrogen and oxygen gas occurs on the metal surface. Generated hydrogen peroxide then diffuses to isolated titanium sites on the supporting material to form a titanium peroxo species that react with the alkene to form the epoxide [161]. The selective oxidation of pyridine to pyridine N-oxide was chosen as a probe reaction for expoxidation. Like propylene epoxidation, pyridine oxidation occurs over active titanium sites that have reacted with hydrogen peroxide to generate titanium peroxo species [162]. However, this reaction can be done in solution at reasonable temperatures [163]. Additionally, hydrogen peroxide can be generated in solution by bubbling hydrogen and oxygen gas in solution with a catalyst in which the concentration of gas is regulated by the solubility of gas in solution [164]. This allows for safer conditions in which to test the prepared catalyst.

7.3.1 Hydrogen Peroxide Generation

Hydrogen peroxide generation was tested by bubbling hydrogen and oxygen gas in an aqueous solution containing $Pd@SiO_2$ particles and a standard iodine/starch indicator used for iodometric titration. As hydrogen peroxide is generated on Pd, it reacts with potassium iodide and acid to form iodine. The iodine may then complex with a starch indicator to form a purple solution. Figure 7.24a shows the unreacted Pd@SiO₂ solution. After a few minutes of bubbling, the solution turned purple (Figure 7.24b), indicating the formation of hydrogen peroxide.



Figure 7.24: Pt@SiO2 solution with iodine/starch indicator (a) before and (b) after (diluted) bubbling with H_2 and O_2 gas.

Controls were done by taking $Pd@SiO_2$ solutions with the iodine/starch indicator and bubbling only hydrogen or oxygen gas. Neither gave a purple solution in a reasonable time period. Likewise, bubbling both hydrogen and oxygen gas into a iodine/starch solution without Pd@SiO₂ had no effect.

7.3.2 Titanium Influence on Pyridine Oxidation

Activity of the titanium sites in catalyst materials were tested by catalyzing the oxidation of pyridine to pyridine N-oxide. Typically, 45 mg of catalyst was suspended in a solution containing 2.5 mL of pyridine and 7.5 mL of either water, alcohol or a water/alcohol mixture. Alcohols have a higher solubility of hydrogen and oxygen, so the inclusion of this was suspected to promote peroxide formation. The reaction solutions were heated to 60°C and hydrogen and oxygen were bubbled at rates of 5 mL/min and 70 mL/min, respectively. After 24 hours, the conversion of pyridine to pyridine N-oxide was determined with by NMR.

It was found that no activity was present for Pd or Pt@Pd in Ti_xSi_{1-x}O₂. To ensure the lack of activity was not caused by poor formation of hydrogen peroxide by the core particle, oxidation of pyridine was done using hydrogen peroxide solution rather than the bubbling of hydrogen and oxygen gas. In addition, titania silicates were formed over silica particles using the co-deposition method as a control without a metal center. When pyridine and aqueous hydrogen peroxide was heated at 60°C for 24 hours in the presence of the catalyst, no conversion of pyridine to pyridine N-oxide was found. This suggests that the titanium in the silica titanium networks was either not at the surface of the particles or was present in the wrong coordination environment. It is generally understood that isolated, mononuclear, 4-coordinate Ti^{IV} sites tend to be the most active for selective oxidation [159].

Silica with surface-loaded Ti was tested under the same conditions reported above. In the absence of Pd, surface loaded silica gave a 10% conversion with a calculated turnover frequency of 0.01 with respect to estimated Ti loading when aqueous hydrogen peroxide was used as a oxidant. However, when Pd was present as a core material, no activity was measured for either the H_2/O_2 bubbling test or the aqueous H_2O_2 addition. It is suspected that the Pd core was too active for the dissociation of hydrogen peroxide. In addition the loading of Pd is extremely high relative to the shell material such that the few active Ti sites cannot compete with the Pd for hydrogen peroxide.

7.4 Conclusions and Future Opportunities

It has been shown that titanium can be incorporated into silica shells through direct co-precipitation methods and through surface modifications. These can be coated on both Pt and Pd cores to give very porous shells. Surface-loaded titanium was seen to be more active for selective oxidation as all the Ti sites are isolated and tetrahedrally coordinated. While the use of Pd cores proved not to be an active catalyst for the selective oxidation of pyridine using hydrogen and oxygen, these methods can be applied to gold core systems to produce highly active catalysts for epoxidation chemistry.

Chapter 8 Conclusion

Various core-shell materials in which a metal core is encapsulated in a porous oxide shell have been developed for potential catalytic applications. The utility of these structures for enhanced properties beyond thermal stability has been addressed. Two types of shell materials were made in which the resulting shells require different synthetic routes of formation. The first type of shell material was metal oxides formed using the Kirkendall effect, in which a metal particle is oxidized and the faster diffusion of metal than oxygen into the forming oxide results in a porous hollow particle. The second type of shell material was ceramic oxides produced using sol-gel chemistry that requires the hydrolysis and condensation of inorganic alkoxides.

Gold encapsulated in a porous iron oxide shell (Au@Fe_xO_y) was developed to test support-dependent catalysis in yolk-shell systems. This material was catalytically active for CO oxidation despite the inactivity of the gold or iron oxide alone. The activity derives from a support-dependent interaction between the gold and iron oxide and demonstrates the added functionality yolk-shell materials can have. In addition, the shell was found to provide a physical barrier against particle migration at temperatures under 320°C. This prevented particles from coalescing and, as a result, catalytically deactivate. At temperatures above 320°C, gold was found to diffuse out of shells through an Ostwald ripening process. The shell was thermally stable to a temperature of 400°C, at which point, it undergoes a phase transition and sinters.

Like Au@Fe_xO_y, copper inside of porous cobalt oxide (Cu@CoO) was also synthesized using the Kirkendall effect. This is one of the first examples in which two oxidizable metals were used to make a yolk-shell system where the "yolk" material does not also oxidize. The CoO shell was found to hinder the oxidation process of Cu during particle formation. However, extensive oxidation did eventually oxidize the copper core as well, producing a hollow Cu₂O particle inside a cobalt oxide shell. High pressure x-ray photoelectron spectroscopy was used to study particle behavior under oxidizing and reducing environments. These particles may have potential as a Fischer-Tropsch catalyst, which is currently being explored. The oxidation of Zn particles was studied to assess its potential as a porous shell using the Kirkendall effect. It was determined that grain boundaries play an important role in atomic transport during oxidation. When Zn nanoparticles were oxidized, ZnO shells formed spokes at locations of grain boundaries due to the faster diffusion of zinc through these channels. Additionally, formation of copper encapsulated in ZnO was explored by forming a zinc shell on small copper particles. These particles were desired for use as a methanol formation catalyst. However, difficulties preventing copper/zinc alloying lead to low yelds of yolk-shell particles.

Sol-gel chemistry was used to encapsulate small gold particles. The coating of small gold particles is extremely difficult because of their poor affinity for silica and large surface curvatures. A variety of methods were tested to render gold particle more vitreophilic including surface modification, confinement of gold within micelles of forming silica, reduction of gold in hollow silica shells, and shelling gold with a sacrificial inorganic shell. Of all the methods, it was found that coating gold with a thin silver shell made silica coating possible. The silver shell can then be removed to give single gold confinement within porous silica shells.

Lastly, methods were developed for producing mesoporous, mixed oxide shells of titanium silicate around platinum and palladium nanoparticles. The amount of titanium loading was tuned by controlling the pH and precursor concentration. In addition, titanium was surface loaded on porous silica shells through an anhydrous alcohol condensation of a titanium precursor. These nanoparticle heterostructures were produced to test for dual catalysis in which products from a reaction occurring on the core particle are used as reactants for catalysis within the shell. Pyridine oxidation was chosen as a test reaction in which hydrogen and oxygen were to be converted to hydrogen peroxide on the palladium core before reacting with pyridine on titanium sites within the shell. It was found that surface loaded titanium are active for the oxidation reaction, but the palladium cores decomposed hydrogen peroxide faster than the oxidation reaction could be completed.

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