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The Rational Synthesis of Bimetallic Catalysts on Oxide Supports

Andrew Phillip Wong
University of South Carolina

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THE RATIONAL SYNTHESIS OF BIMETALLIC CATALYSTS ON OXIDE SUPPORTS

by

Andrew Phillip Wong

Bachelor of Science
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Accepted by:

John R. Regalbuto, Major Professor
John R. Monnier, Committee Member
Todd J. Toops, Committee Member
A. Jochen Lauterbach, Committee Member
John W. Weidner, Committee Member
Cheryl L. Addy, Vice Provost and Dean of the Graduate School
DEDICATION

I dedicate this work to Nujhat for her constant company, support, encouragement, and unconditional love throughout my endeavors.

I also dedicate this work to my parents, Joseph and Sandra Wong, for your love and endless support. You have always encouraged and driven me to success. Lastly, I dedicate this work to my big sister, Jessica, who always knew what to tell me and whose smile touched so many people.
ACKNOWLEDGEMENTS

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ABSTRACT

Catalysts play an important role in many chemical reactions. However, simple impregnated monometallic catalysts are often limited in their function. One way to overcome this limitation is through the incorporation of a secondary metal to the catalysts. These bimetallic catalysts often have synergistic benefits not observed in the monometallic analogues.

Here, we focused on the synthesis of bimetallic catalysts using rational methods in order to improve catalyst function; specifically by tuning the particle size, morphology, and composition. The two methods of interests were Strong Electrostatic Adsorption (SEA) and Electroless Deposition (ED). An adaptation of SEA to bimetallic catalysts (co-SEA) was used to synthesize ultrasmall highly dispersed alloyed nanoparticles on high surface area oxide supports (alumina and silica). Bimetallic catalysts of Pt, Pd, Co, Cu, and Ni having ~1nm nanoparticles were synthesized over silica, and Pt-Pd bimetallics were synthesized over aluminosilicates. These co-SEA catalysts have improved bimetallic interactions due to the close proximity and well-mixing of atoms. The Pt-Pd catalysts were evaluated as diesel oxidation catalysts using a simulated diesel exhaust at ORNL. The co-SEA catalysts were more active and stable compared to conventional co-impregnated catalysts. Moreover, these highly alloyed co-SEA catalysts remained more alloyed after high temperature treatments (>700°C) when compared to typical co-impregnation catalysts.
Core-shell catalyst stabilization using surface free energy (SFE) principles was investigated through annealing treatments followed by catalyst characterization. The principle of anchoring low SFE metals on high SFE cores was demonstrated through the coupling of SEA for the nanoparticle cores and ED for the nanoparticle shells. The Ag-Ir core-shell materials resisted sintering with particle size growing only twofold for the bimetallic catalysts compared to over a tenfold size increase in the monometallic catalysts.

This work demonstrated the effectiveness of using rational synthesis methods for bimetallic catalysts over simple co-impregnations. Having precise control on particle morphology, whether core-shell or alloyed, and size are important in catalyst design where high metal utilization and intimate bimetallic interaction are desired to reduce the amount of expensive precious group metals. By utilizing ED and SEA, we demonstrated new possibilities in improved bimetallic catalyst design that were unachievable with current conventional methods.
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CHAPTER 1

INTRODUCTION

1.1 Overview

A catalyst is a material that enhances a chemical reaction without changing the equilibrium of the reaction. Catalytic processes account for 80 to 85% of chemical products around the world [1]. These products range from pharmaceutical, agricultural, petrochemical, and other commodity and specialty chemicals. Catalytic processes also have environmental applications; whether it is through cleaner power generation from fuel cells or through the abatement of automobile exhausts and power plant flue gases. Therefore there is great interest to understand the role of these catalysts and be able to systematically tune and synthesize effective catalysts.

Most catalysts can be divided into two different categories: homogenous and heterogeneous catalysts. A homogenous catalyst is in the same phase as the reactants. Homogenous catalysis is most often used in pharmaceutical applications or organic syntheses where both the reactants and catalyst are in a liquid phase. In heterogeneous catalysis, the catalyst is in a different phase than the reactants. Heterogeneous catalysis usually incorporates solid catalysts and either liquid or gas phase reactants. The focus of this work will be on heterogeneous catalysts especially the synthesis and application of supported bimetallic nanoparticles.

Investigations on bimetallic structures are often credited to Schwab and others when they investigated catalytic activities on different metals sites [2, 3]. The benefits of
bimetallic catalysts were further realized by the works of Sinfelt in the 1970’s. His investigations on bimetallic alloys demonstrated the synergistic effects of combining two metals [4-6]. Enhancements to catalytic functions can be divided into three categories: electronic, bifunctional, and ensemble effects. Electronic effects, caused by the redistribution of electrons, can change the properties of catalysts. The electron transfer between the two metals can change the oxidation properties and how strongly species bind to the active sites. Bifunctional catalysts usually require intimate bimetallic character where the two metals are in close proximity, essentially forming a site-pair. One metal can form a reaction intermediate that can closely react with the second metal atoms. Additionally, two separate reactions can take place on the individual metals which may enhance the reaction kinetics. Previous work using Ag-Ir catalysts showed the adsorption of O$_2$ onto Ag and CO onto Ir [7]. The close proximity of Ag-Ir atoms allowed the formation of CO$_2$ at higher reaction rates. Finally, an ensemble effect of two metals occurs when there is a geometric limitation which prevents certain molecules from interacting with the active sites. This can be caused by the second metal being preferentially located on corner/edge sites which alters product selectivity by changing the ensemble size of the active metal sites.

Efforts to improve catalyst functions through improved synthesis methods are highly desirable. Not only does metal utilization increase as the size of supported nanoparticles decrease, but fine control over particle morphology, especially in bimetallic nanoparticles, can alter catalyst selectively, reactivity, and stability. Two techniques, Strong Electrostatic Adsorption (SEA) and Electroless Deposition (ED) are highlighted in this study. The coupling of SEA and ED in this work has shown exceptional
reproducibility and control over catalyst particle size and morphology. Our group has shown that SEA can produce homogenous, highly-disperse nanoparticles (< 1.5 nm) over a multitude of supports [8-13]. These monometallic produced SEA nanoparticles can then be used as the starting core material for the ED process to create core-shell structures.

1.2 Catalyst Preparation

Catalyst syntheses aim to disperse nanoparticles across an anchoring support material. These high surface area, porous materials allow the nanoparticles to be disperse across the surface which allows for higher metal utilization, and thus higher number of active sites per mass of catalyst. However, challenges of metal agglomeration and sintering during catalyst syntheses (from high dispersion metal precursors to supported metallic nanoparticles) often make for less than ideal catalytic systems. The loss of dispersion is especially unwanted when expensive precious group metals are the active sites. Most techniques can be characterized into wet impregnation or dry impregnation depending if the solution volume is in excess or not, respectively. A series of various catalyst synthesis techniques are outlined below include two techniques used primarily in this work, Strong Electrostatic Adsorption and Electroless Deposition.

1.2.1 Impregnation

The most commonly used synthesis technique is incipient wetness impregnation (IWI), also known as dry impregnation (DI). A metal precursor is dissolved in water and impregnated into the support. The amount of water added is just enough to fill the pore volume of the support. Therefore, no metal is wasted. Advantages of IWI include being quick and simple as no filtration is necessary, and metal loading is known. However, as no measures are taken to maintain catalyst dispersion or in the case of bimetallic catalysts
to promote bimetallic interactions, these catalysts often end with larger particle sizes (>3nm) and weak bimetallic character [13, 14]. Limitations of IWI include the solubility of the precursor in the impregnation volume. These metal concentrations are often upwards of 15,000 ppm. In addition, the pores or ordered channels in supports, such as SBA-15 silica, prevent the complete wetting of the surface with the impregnating solution. Thus, the entire support is not fully utilized and agglomeration can occur in support channels [15].

1.2.2 Precipitation

A solution of a soluble metal salt can be carefully altered to favor the precipitation of the metal complexes into nanoparticles. The most common solution parameters to control include pH, precursor concentration, reduction/precipitation agent, complexing agent, and temperature [16, 17]. Through careful adjustments of these parameters, the kinetics of nanoparticle nucleation and growth can be controlled. Monodisperse nanoparticles can be created if the nucleation period is short, and “burst nucleation” is achieved [18]. Bimetallic nanoparticles can be created by the co-precipitation of two metals where full understanding of solubility kinetics is necessary to control particle morphology, size, and composition [19, 20]. These nanoparticles can be used in impregnation and colloid techniques, or they can be directly precipitated onto a support.

The co-precipitation of metals and support can also be used to incorporate the metals into the support lattice [21]. Two solutions of highly concentrated metal precursors and base (hydroxide or alkali carbonates) are contacted to form metal complexes that are less soluble. These less soluble complexes precipitate out followed by thermal treatments to achieve a metal catalyst.
Deposition-precipitation (DP) is an extension of precipitation methods where nanoparticles nucleate and grow on the support. Typically, an adsorption mechanism is used to ensure the precipitation of the metal only occurs on the support and not spontaneously in solution. The sequential or co-DP of bimetallic nanoparticles is possible; however, differences in deposition kinetics for each bimetallic combination requires extensive kinetic studies. Moreover, concentration/temperature gradients, well-mixing, and local fluctuations in nucleation and growth patterns need to be addressed. Therefore, even with moderate understanding of the deposition kinetics, co-precipitation/co-DP leads to inhomogeneous catalysts. Advantages of direct precipitation or deposition-precipitation include the ability to achieve very high wt. loading catalysts (>50% wt) [22].

1.2.3 Colloidal

Nanoparticles can be synthesized using a colloidal method beforehand and later added to a support through a wet synthesis technique. The synthesis of these nanoparticles can be controlled using various solvents and capping agents [23]. Therefore, there is some control over the particle size, uniformity, and composition in the case of bimetallic particles. However, the transition from nanoparticles in solution to supported nanoparticles is less controllable. A wet impregnation technique is usually employed where the support and the solution containing nanoparticles are continuously mixed. The solvent is evaporated off, and the nanoparticle remain on the support. The weight loading of these catalysts have to be confirmed after the wet impregnation, and the nanoparticles have to be thermally treated to remove any capping agents. Organic capping agents usually require a high temperature which can lead to nanoparticle sintering or segregation of bimetallic systems.
1.2.4 Atom Replacement Techniques

Ion-exchange (IE) and galvanic displacement (GD) can be used on select supports and bimetallic systems; however, they are relatively limited to special cases where suitable ions can be exchanged or redox reactions can be favored for GD. For IE to occur, there is typically a cation on the support that can be exchanged for a cationic precursor. This is common in zeolite catalysis, where defect sites between Al-Si groups allow proton exchange with metal cations. This can lead to highly-disperse atoms on these zeolite supports [24].

GD is a redox process where one metal is oxidized through a chemical reaction, and the other metal is reduced. This occurs when the secondary metal has a higher electrochemical potential that allows the redox reaction to proceed [25, 26]. While, bimetallic interactions are strong, this technique typically only leads to core-shell structures and is limited by finding the correct redox pairs of metals. Moreover, a limitation of both IE and GD is the amount of metal you can deposit onto the support. This is limited by the number of IE sites and the stoichiometry of the two metals for GD.

1.2.5 Thermochemical Treatments

Attention to the pre-treatment environments of the catalysts during drying and reduction to metallic nanoparticles can promote higher metal dispersion. Works by de Jong have focused on the decomposition kinetics of the metal precursors to supported metallic nanoparticles [27]. Through calcinations in air, inerts, or nitric oxide (NO), the precursor can form intermediates that interact strongly with the support and wet the surface. These mobile nitrate intermediates can then be removed, and highly-disperse metallic nanoparticle remain. A limitation to this method is that the pre-treatment environment for
each precursor varies and must be rigorously evaluated to have the optimum results. Therefore, this technique is specialized and difficult to extend to new systems. However, in practice this can be applicable to bimetallic systems as long as the pre-treatment environments are similar for both metals.

1.2.6 Strong Electrostatic Adsorption

Strong Electrostatic Adsorption (SEA) is a wet impregnation synthesis technique where metal precursors are adsorbed onto a charged surface. By carefully adjusting the pH of the solution, anionic or cationic metal precursors have a coulombic attraction to the support. Pioneering work by Brunell in the 1960’s showed the affinity of noble metal complexes to mixed-oxide surfaces [28]. More recent work has demonstrated noble and base metals alike can adsorb onto a variety of mixed-oxide and carbon supports [8, 9, 13, 29, 30]. Figure 1.1 shows the mechanism of how the support is charged [29].

Figure 1.1 Three regimes of the PTA/SiO₂ adsorption system.
The point of zero charge (PZC), or isoelectric point, of the support is the pH where the surface has no charge. As pH is adjusted away from the PZC, the functional groups of the surface are protonated or deprotonated depending if the pH is below or above the PZC, respectively. The adsorption of cationic platinum tetraammine can be observed over a deprotonated surface in a basic solution (Figure 1.1). These metal precursors adsorb as a monolayer retaining a number of hydration sheets. These hydration sheets provide high dispersion and separation of the precursors through steric hindrance, and the cumblic forces provide strong interactions between the precursor and support. These strong interactions prevent agglomeration and migration of the precursor during drying. Therefore, high metal dispersion is maintained after drying and reduction treatments for the genesis of nanoparticles.

To determine the PZC of a support, a high surface loading is used. Surface loading (SL) is a measure of how much support surface is in a solution volume.

\[
SL \left( \frac{m^2}{L} \right) = \frac{\text{grams of support (g) x surface area of support (} \frac{m^2}{g} \text{)}}{\text{solution volume (L)}}
\]

A support has a buffering effect that drives a solution’s pH towards the PZC [31]. By increasing the amount of support added to a solution and thus increasing the slurry thickness and SL, stronger buffering shifts the solution pH towards the PZC. Figure 1.2 shows the pH plateau representative of the PZC as SL is increased [31].
Figure 1.2 Buffering effect of oxides to the PZC for surface loadings of 0-180000 m²/L.

Common cationic and anionic precursors for low PZC and high PZC supports are shown in Table 1.1 [28]. Adsorption uptake surveys are used to determine metal precursor adsorption on supports.

Table 1.1 Common cationic and anionic precursors for electrostatic adsorption.

<table>
<thead>
<tr>
<th>Cationic Precursors</th>
<th>Anionic Precursors</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co(NH₃)₅²⁺, Ni(NH₃)₅²⁺, Cu(NH₃)₅²⁺, Ru(NH₃)₅Cl²⁺, Rh(NH₃)₅Cl²⁺, Pd(NH₃)₄²⁺, Ag(NH₃)₅²⁺, Ir(NH₃)₅Cl²⁺, Pt(NH₃)₄²⁺</td>
<td>MnO₄⁻, RhCl₆³⁻, PdCl₄²⁻, ReO₄⁻, OsCl₆²⁻, IrCl₆²⁻, PtCl₆²⁻, AuCl₄⁻</td>
</tr>
</tbody>
</table>
Figure 1.3 Adsorption surveys of Pt(NH$_3$)$_4^{2+}$ on silicas.

Figure 1.3 shows adsorption uptake surveys for Pt on different silicas [29]. No metal uptake occurs at the PZC (pH=4) when the support is neutrally charged. As the pH is increased, the surface becomes deprotonated, and Pt(NH$_3$)$_4^{2+}$ can electrostatically adsorb. Maximum adsorption density of a precursor depends on the steric hindrance caused by the number of hydration sheets retained. Most anionic complexes like PtCl$_6^{2-}$ retain one hydration sheet, whereas cationic species like Pt(NH$_3$)$_4^{2+}$ retain two hydration sheets [32]. At extreme pH’s, high ionic strength causes a retardation of metal uptake due to an electric double layer screening [33]. The optimum pH is used to synthesize the catalysts followed by filtration, drying, and reduction treatments in H$_2$.

The application of SEA to bimetallic systems can applied sequentially (seq-SEA) or simultaneously (co-SEA). Previous work in the Regalbuto group used sequential SEA
to selectively adsorb Pt/Pd and Pt/Co onto each other rather than onto the support [14, 34]. The succession of SEA followed by calcination/oxidation leaves metal oxide nanoparticles on the support. These metals oxides have their own PZC which varies from the PZC of the support. With careful selection of the metal precursor and adjustments of pH, targeted adsorption of the precursor can occur to form core-shell structures or isolated areas of separate nanoparticles. Figure 1.4C shows a schematic of using sequential SEA to form core-shell structures [14].

Figure 1.4 Schematic of co-SEA and seq-SEA.

Homogenously alloyed supported nanoparticles can be synthesized via SEA using a co-adsorption method (co-SEA). The simultaneous adsorption of two or more metals can
be applied by choosing similarly charged precursors. The precursors electrostatically adsorb as a mixed monolayer and exist as an alloy after reduction treatments. Figure 1.4B depicts the simultaneous adsorption of two precursors. The electrostatic interactions provide a method to retain high metal dispersion and to facilitate a homogenous surface after reduction treatments. The intimate mixing of atoms improves the bimetallic character of the catalysts unachievable by conventional methods.

Limitation of SEA to catalytic systems includes finding a suitable metal precursor with the correct charge. Moreover, due to the nature of the metal complex adsorbing in a monolayer, it is impossible to achieve more than a monolayer coverage of precursor. This works for low to medium weight loadings of metal on high surface area supports, but low surface area supports limit the total weigh loadings of metals. Increased weight loadings can be achieved by moving to a higher surface area support, as the adsorption density does not change, but the amount of available surface is vastly increased. The weight loading of a catalyst can also be increased by cycling SEA. After a completed cycle, the metal is reduced, and available surface is freed for the adsorption of the precursor.

1.2.7 Electroless Deposition

Electroless deposition (ED) is a reactive adsorption technique where a metal precursor is deposited as a shell material on an existing metal. This technique is similar to electroplating but uses a reducing agent (RA) instead of electrical power. Hence, the coining of the term “electroless plating” by Brenner and Riddell in 1947 [35]. ED is not only useful for catalysis, but the application of ED can be applied to metal plating and thin films.
The synthesis of bimetallic catalysts through ED using a reducible metal salt and a reducing agent (RA) proceeds as follows. First, a primary metal is dispersed onto a support. This deposited metal is now the active site for the application of the secondary metal by ED. The soluble RA interacts with the active sites, decomposes, and leaves adsorbates that can reduce the secondary metal salt precursor. This core@shell technique promotes excellent bimetallic interactions because the RA only decomposes on the active sites. Figure 1.5 depicts this process.

Figure 1.5 Schematic of electroless deposition where metal B is deposited on metal A.

ED can proceed two ways - catalytic or auto-catalytic. Initially, catalytic deposition is the only mechanism. In catalytic deposition, the secondary metal is reduced onto the primary metal with the goal to create an atom thick monolayer. However, a transition to auto-catalytic deposition occurs as the secondary metal can now act as active sites for ED. Therefore, it is rare to achieve a complete monolayer with an atom thickness. The conjunction of catalytic and auto-catalytic deposition leads to thicker shells and lower shell coverages. Control over whether catalytic vs auto-catalytic occurs depends mostly on the
choice of reducing agent, temperature, and extent of reaction; however, other ED conditions such as pH and stabilizing agent may also determine the deposition mechanism [7, 36, 37].

The success of ED largely depends on the optimization of the ED bath conditions. The soluble metal salt needs to be stable both thermally and chemically over a pH range. Common metal salts used in ED are shown in Table 1.2 [38]. The elevated temperatures aid in increasing the ED rate which follows an Arrhenius trend, and pH is controlled to avoid support-precursor interactions and to increase the electrochemical potential of the RA [36]. Thermal decomposition and precursor interactions with the support are unwanted as this would prevent ED on the primary metal.

**Table 1.2 Common precursors for Electroless Deposition.**

<table>
<thead>
<tr>
<th>Metal</th>
<th>Precursors</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>NiSO₄, NiCl₂, Ni(H₂PO₂)₂, Ni(CH₃COO)₂</td>
</tr>
<tr>
<td>Co</td>
<td>CoSO₄, CoCl₂</td>
</tr>
<tr>
<td>Au</td>
<td>KAu(CN)₂, KAuCl₄, Na₃Au(SO₃)₂</td>
</tr>
<tr>
<td>Ag</td>
<td>AgNO₃, NaAg(CN)₂</td>
</tr>
<tr>
<td>Pd</td>
<td>PdCl₂, Pd(NH₃)₄Cl₂</td>
</tr>
<tr>
<td>Pt</td>
<td>Na₂Pt(OH)₆, (NH₃)₂Pt(NO₂)₂, Na₂PtCl₆</td>
</tr>
<tr>
<td>Cu</td>
<td>CuSO₄, KCu(CN)₂</td>
</tr>
</tbody>
</table>

Previous work by Ohno et al. examined the oxidation potential of various reducing agents on noble and base metals [36]. The anodic oxidation potential of sodium hypophosphite, formaldehyde, sodium borohydride, dimethylamine borane, and hydrazine were correlated for the metals, and the trends are shown in Figure 1.6 [36].
The catalytic activity of the RA towards the metal determines the how the deposition will proceed. If the RA is more active on the secondary metal, auto-catalytic is favored. However, if the RA is more active on the primary metal, catalytic deposition is favored over auto-catalytic deposition. Core@shell structures are achieve when the secondary metal has a higher potential (less negative) than the primary metal. Thus, the RA must be carefully selected for different bimetallic systems. Moreover, the reduction potential of the RA has to be low enough to prevent the spontaneous reduction of the precursor in solution.

Recent work by the Monnier group at the University of South Carolina has demonstrated the ability to deposit a number of core@shell bimetallic pairs of Au, Ag, Co, Cu, Ir, Ni, Pd, Pt, Rh, Ru, etc. on a variety of supports [7, 37, 39-44]. By using ED, the surface composition can be precisely controlled, and catalytic performance can be optimized. Another benefit of using ED is that the secondary is applied in a reduced state.
Therefore, no high temperature treatments are needed to “clean” the metal which may sinter or alter the surface composition of the nanoparticle. Challenges of using ED include determining a successful ED bath and achieving complete catalytic deposition. An appropriate balance between the deposition rate, bath stability, temperature, RA and pH are all necessary parameters in the ED bath development.

1.3 Automotive Catalysis

The invention of the internal combustion (IC) engine has largely benefited society. However, the popular implementation of the IC engine in automobiles has raised concerns for emission control. Starting with the Clean Air Act of 1970s, catalytic converters have drastically reduced the amount of tail pipe emissions of IC powered automobiles [45, 46]. These emissions include carbon monoxide (CO), unburned hydrocarbons (HC), and nitrogen oxides (NOx). Through the last couple of decades, fuel formulations have changed, and engine combustion technologies have improved. As the engines become more efficient, less energy is wasted in the exhaust. The lower exhaust temperatures create a challenge for catalyst design and operations. Thus, continuous improvements and modifications in catalyst development are necessary in order to match the change in exhaust characteristics.

1.3.1 Gasoline Aftertreatment

For gasoline burn automobiles, the three-way catalyst (TWC) has been overall largely successful. The catalyst’s three functions include oxidizing CO and unburned HC’s into CO₂ and reducing NOx species into N₂. Optimized combustion conditions at a stoichiometric air/fuel ratio allow for simultaneous oxidation of CO and HC’s and the reduction of NO into N₂. Modern 3-way catalysts are in fact so good at their operating
temperature that over 60-80% of typical tail pipe emissions occur during the “cold start” period [45, 47]. The cold start period is the initial period of time after starting a car where the catalyst’s temperature is not high enough to promote activity. Figure 1.7 shows the high emission rate of pollutants in the first couple of minutes [47].

**Figure 1.7** Hydrocarbon emissions from a cold start.

### 1.3.2 Diesel Aftertreatment

In diesel automobiles, exhaust treatments are even more challenging. The operating conditions of diesel combustion leave a large excess volume of oxygen. This fuel lean condition causes the exhaust temperatures to be cooler than a gasoline IC exhaust. Moreover, excess oxygen in the exhaust drastically increases the levels of NOx emitted. Diesel IC engines also have poorer mixing of the air/fuel due to the fuel being injected during the compression stroke vs the intake stroke of gasoline engines. This inhomogeneous mixture of air/fuel causes more unburnt HC’s in the exhaust compared to gasoline IC engines.
Diesel exhaust systems overcome these challenges by incorporating three aftertreatment technologies. These three technologies are highlighted in Figure 1.8.

![Diagram of diesel exhaust system](image)

**Figure 1.8** Three components of modern diesel exhaust aftertreatment.

The diesel oxidation catalyst (DOC) is the first stage in the exhaust and experiences the highest temperatures. The role of the DOC is to oxidize CO and HC’s. Any conversion of NO to NO\textsubscript{2} can be helpful for downstream reactions, like soot oxidation; however, NOx cleanup is not the primary focus of the DOC. The DOC must be able to withstand elevated temperatures as it is closest to the engine and experiences large exotherms during regenerative cycles of the second stage of diesel aftertreatment, the diesel particulate filter (PF).

The PF’s role is to capture particulate matter that is emitted in the exhaust. The PF is structured as a honeycomb structure with channels that are alternatively blocked at the ends. The blockages at the end force the gases to permeate across the channel walls to the alternate channels that are unblocked at the exit. The particulates remain trapped on the PF as a layer of soot. The pressure drop across the PF increases as the soot accumulates. The soot can be removed through a regeneration process where extra fuel is added into the exhaust stream. The fuel combusts over the DOC and creates an exotherm on the DF. The extra heat oxidizes the carbonaceous soot into CO\textsubscript{2} [48].
The final stage in diesel exhaust aftertreatment is an ammonia selective catalytic reduction (SCR) catalyst. The NH$_3$ SCR catalyst reduces NOx species to N$_2$ [49, 50]. Most SCR systems incorporate a urea injection upstream of the SCR catalyst. The urea decomposes into ammonia, and reduces the NOx into N$_2$ and H$_2$O as shown in reactions 1-4 [51]. Common metals for the SCR catalyst include Cu, Fe, V, Mo, W, and Ag which aid in the following reactions [51, 52]:

**Standard SCR:**

\[ 4\text{NH}_3 + 4\text{NO} + \text{O}_2 \rightarrow 4\text{N}_2 + 6\text{H}_2\text{O} \quad (1) \]

**Fast SCR:**

\[ 2\text{NH}_3 + \text{NO} + \text{NO}_2 \rightarrow 2\text{N}_2 + 3\text{H}_2\text{O} \quad (2) \]

**NO$_2$ SCR:**

\[ 2\text{NH}_3 + 2\text{NO}_2 \rightarrow \text{N}_2 + 3\text{H}_2\text{O} + \text{N}_2\text{O} \quad (3) \]
\[ 4\text{NH}_3 + 3\text{NO}_2 \rightarrow 3\frac{1}{2}\text{N}_2 + 6\text{H}_2\text{O} \quad (4) \]

The SCR operates at a much lower temperature than the DOC; therefore, deactivation is caused more through poisoning rather than nanoparticle sintering [53].

Typical exhaust catalysts incorporate a high surface area, hydrothermally stable support for nanoparticle dispersion. The supports are then washcoated onto a ceramic monolith. For simplicity, this work will focus on catalytic materials existing as a powdered support. Different phases of alumina, especially gamma, are modified with promoters such as La, Ba, Si, Ce, etc [48]. These promoters aid the thermal stability of the support, alter the catalytic properties of the primary metals, and add support functionality such as oxygen storage capacity. Pt, Pd, and Rh are common precious metals used in automotive catalysis.
These expensive metals are necessary for low temperature activity; however, sintering of nanoparticles after elevated exhaust temperatures lead to the loss of metal dispersion. The metal dispersion of spent catalysts are often single digits percentages [54]. Therefore, it does not make economic sense to have >95% of the metal atoms inactive for catalysis. This work will highlight some attempts to improve nanoparticle stability and activity for diesel oxidation catalysts.

1.3.3 Diesel Oxidation Catalyst (DOC)

Alreadymentioned, the role of a DOC is to oxidize CO and unburnt HC’s. However, reaction intermediates and multiple reaction pathways complicate the chemistry. Reactions i-viii in Table 1.3 highlight some of the reactions occurring over the DOC taken from Johnson Matthey [51].

Reactions i-iii are the 3 main reactions occurring over the DOC. However, when modeling such catalysts, side reactions are implemented to achieve good predictions of catalyst performance that correlates with experimental findings. These side reactions are shown in Table 1.3 in reactions iv-ix. Thus, oxidation chemistry over the DOC is rather complex.

Platinum is the most common metal used in DOCs for a number of reasons [48]. The highly oxidizing environment of the diesel exhaust prevents complete three-way catalytic activity (CO, HC’s, NOx) and oxidizes metals that are less noble than Pt. Moreover, the lower temperature of diesel exhaust requires a more active metal than in the higher temperature gasoline automobile exhaust. The sulfur tolerance of Pt is also higher than many of the other precious group metals (PGM) and non-PGMs [48, 55]. These properties made Pt almost ubiquitous in DOCs. A limitation of using Pt includes the lack
of resistance to sintering at elevated temperatures in an oxidizing environment. The Pt is capable of forming a PtO$_2$ vapor species than can migrate across the support [56, 57]. This migration leads to very large Pt particles, upwards of 100 nm, where Pt dispersion is $< 1\%$ [58].

**Table 1.3** Reactions taking place over DOCs.

<table>
<thead>
<tr>
<th>Reaction Type</th>
<th>Reaction Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO oxidation</td>
<td>CO + $\frac{1}{2}$O$_2$ $\rightarrow$ CO$_2$</td>
</tr>
<tr>
<td>Oxidation of HC or oxygenate</td>
<td>C$_x$H$_y$O$_z$ + (x+y/4-2z/2)O$_2$ $\rightarrow$ xCO$_2$ + (y/2)H$_2$O</td>
</tr>
<tr>
<td>NO oxidation</td>
<td>NO + $\frac{1}{2}$O$_2$ $\rightarrow$ NO$_2$</td>
</tr>
<tr>
<td>HC SCR$^a$:</td>
<td>(1-S$_{NO_2}$/2)C$_x$H$<em>y$ + 9NO $\rightarrow$ 3(1-S$</em>{NO_2}$/2)CO$<em>2$ + 3(1-S$</em>{NO_2}$/2)H$<em>2$O + 4$/2$S$</em>{NO_2}$ N$<em>2$O + 4$/2$(1-S$</em>{NO_2}$)N$_2$</td>
</tr>
<tr>
<td>Steam reforming$^b$:</td>
<td>C$<em>x$H$<em>y$ + (x-$N</em>{WGS}$)H$<em>2$O + $N</em>{WGS}$CO$<em>2$ $\rightarrow$ (x+$N</em>{WGS}$)CO + (x+y/2-$N</em>{WGS}$)H$_2$</td>
</tr>
<tr>
<td>H$_2$ oxidation</td>
<td>H$_2$ + $\frac{1}{2}$O$_2$ $\rightarrow$ H$_2$O</td>
</tr>
<tr>
<td>NO$_2$ reduction by CO:</td>
<td>CO + NO$_2$ $\rightarrow$ CO$_2$ + NO</td>
</tr>
<tr>
<td>NO$_2$ reduction by HC:</td>
<td>C$_x$H$_y$ + (2x+y/2)NO$_2$ $\rightarrow$ xCO$_2$ + (y/2)H$_2$O + (2x+y/2)NO</td>
</tr>
<tr>
<td>Extra reaction to explain NO$_2$ conversion during vehicle test:</td>
<td>NO$_2$ $\rightarrow$ $\frac{1}{2}$N$_2$ + O$_2$</td>
</tr>
</tbody>
</table>

$^a$S$_{NO_2}$ is the selectivity to N$_2$O formation; $^b$N$_{WGS}$ is the number of molecules (apparently) reacting by the reverse water gas shift reaction.

Palladium was another metal that was adopted into DOCs with both benefits and limitations. Pd by itself is usually a poorer oxidation catalyst in these conditions. Pd likes to exist in a less active form as an oxidized metal. While Pd is an exceptional catalyst for high levels of CO (whereas Pt experiences CO poisoning), Pd, especially PdO, has
difficulty oxidizing HC’s. Considerations of using Pd have also changed in the last couple of decades. When the first DOC was introduced in 1989, the cost of Pt was cheaper than the cost of Pd [59]. By 2002, the cost of Pd was much cheaper than Pt, which created a large incentive to reduce the cost of the DOC by adding Pd as a cheaper secondary metal. However in most recent years, the price of Pt and Pd are similar.

Another limitation of using Pd instead of Pt includes the lower sulfur tolerance of Pd. Pd has much poor sulfur tolerance compared to Pt [55, 59]. Sulfur concentrations of diesel fuel in the early-2000’s were upwards of 500 ppm. This high concentration of sulfur was problematic for Pd catalysts because only a few ppm of sulfur can poison the catalyst over time. Regulations on sulfur content in diesel fuels became stricter, and ultra-low sulfur fuels became available by the end of the decade. The addition of a diesel PF in diesel aftertreatment has also helped Pd’s sulfur resistance. With the introduction of the PF, a PF regeneration cycle was also needed. This regeneration cycle temporarily elevates the temperature of both the DOC and the PF which would allow for desorption of sulfur species on the DOC along with PF regeneration. This decrease in fuel sulfur content, ability to desorb sulfur from the DOC, and lower price of Pd have promoted research towards Pd DOC formulations.

Efforts to stabilize the Pt by adding Pd has been widely implemented [48, 57-65]. This is by far the largest benefit of incorporating Pd into Pt-based diesel exhaust aftertreatment. There are multiple mechanism discussed by groups on how Pd improves the stability of the DOC. Pd is more stable than Pt in the oxidizing exhaust environment [48]. Morlang et al. attributed the added stability of the Pt-Pd bimetallics to the ability of Pd to interrupt PtO2 formation, and thus eliminating the vapor Pt species from forming and
rapidly sintering [57]. More recent work by Abayte et al. has rigorously studied Pt growth in sintering for DOC [56]. Using in situ microscopy, they determined Ostwald ripening occurred through the transport of vapor species and adatom diffusion across the support at higher and lower temperatures, respectively. Their recent research towards improved DOC materials has been to use an excess amount of Pd. This excess Pd would act as a “trap” for vaporized PtO$_2$ which would prevent Pt agglomeration [58, 66]. No matter the mechanism, there is a consensus that these Pt-Pd bimetallics have improve nanoparticle stability compared to Pt alone.

1.4 Dissertation layout

The majority of this worked focuses on improving bimetallic catalysts through the careful synthesis and characterization of the nanoparticles. These nanoparticles were used and studied for high-temperature applications such as the use for diesel oxidation catalysts. By understanding how to control the nanoparticle size and morphology, catalytic properties can be tailored rationally during nanoparticle synthesis. Improving nanoparticle stability for high-temperature applications is important because catalyst deactivation from nanoparticle sintering often makes a catalyst impractical.

Chapter 2 of this work focuses on synthesizing ultrasmall alloyed nanoparticles on silica. The extension of SEA to alloyed bimetallic systems (co-SEA) demonstrated excellent control over nanoparticle composition and degree of alloying. This relatively simple method can be generalizable as common noble (Pt and Pd) and base metals (Cu, Co, and Ni) were synthesized with the same results. The ultrasmall nanoparticles were ~1nm and were homogenous in size and composition across the silica surface. XRD,
electron microscopy, and temperature-programmed reduction were tools to demonstrate the effectiveness of co-SEA over common co-impregnation techniques.

Chapter 3 demonstrates the effectiveness of combining SEA and ED for high-temperature applications through the principle of nanoparticle stabilization from differences in surface free energies (SFE). A low SFE Ag shell was deposited on the high SFE Ir cores. Not only was Ag anchored to Ir, but the addition of Ag improved the stability of the Ir nanoparticles up to 800°C. Experimental and computational studies revealed the addition of active sites for the Ag-Ir bimetallic pair compared to the monometallic Ir and Ag analogues. This work lead to DOE funding for the application of H₂ production using stabilized Pt at reaction temperatures above 750°C.

Chapter 4 works to better understand Pt-Pd bimetallic catalysts and their application in diesel exhaust abatement. Core-shell and alloyed morphologies of various Pt-Pd ratios were examined. Catalytic trends of both Pt and Pd were determined from catalyst activity measures taken at Oak Ridge National Laboratory. It was determined that homogenously alloyed (co-SEA) bimetallic nanoparticles have increased stability at elevated temperatures. The core-shell materials had unique properties at lower temperatures, but any benefits were lost after hydrothermal ageing.

Chapter 5 is an extension of chapter 4. Learning from how the different nanoparticle morphologies aided diesel oxidation catalyst activity, we extended co-SEA Pt-Pd nanoparticle synthesis to a range of Pt-Pd ratios and supports. The commercial supports were modified aluminas, and the Pt-Pd ratios investigated were 1:0, 3:1, 1:1, 1:3, and 0:1. The Pt-Pd bimetallic catalysts were more stable at the harshest ageing condition;
however, the monometallic Pt catalysts continued to perform best at achieving 90% conversion of total hydrocarbons especially at milder hydrothermal treatments.
CHAPTER 2

SIMPLE, SCALABLE SYNTHESIS OF ULTRASMALL HOMOGENEOUSLY ALLOYED BIMETALLIC NANOPARTICLES

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2.1 Abstract

Supported nanoparticles containing more than one metal have a variety of applications in sensing, catalysis, and biomedicine. Common synthesis techniques for this type of material often result in large, unalloyed nanoparticles that lack the interactions between the two metals that give the particles their desired characteristics. We demonstrate a relatively simple, effective, generalizable method to produce highly-dispersed, well-alloyed bimetallic nanoparticles. Ten permutations of noble and base metals (Pt, Pd, Cu, Ni, and Co) were synthesized with average particle sizes from 0.9 to 1.4 nanometers, with tight size distributions. High-resolution imaging and x-ray analysis confirmed the homogeneity of alloying in these ultrasmall nanoparticles.

2.2 Introduction

Bimetallic nanoparticles (NPs) anchored on porous, high surface area carbon or oxide supports to prevent agglomeration, have many applications in chemical sensing, biomedicine, and especially catalysis [67, 68]. The most common method to prepare supported metal NPs is impregnation (IMP), in which just enough metal precursor solution is used to fill the pore volume of the support. Although this method is simple and quick, IMP generally yields NPs with large average size, broad size distributions, and in the case of multiple metals, inhomogeneous alloying. The highest possible metal utilization occurs when all atoms of a NP are accessible to the gas or liquid fluid phase, and this occurs when the particle size is about 1 nm, or clusters of several dozen of atoms [12, 69]. Optimal bifunctionality and synergy often occur when the atoms at the NP surface are well mixed [6, 70].
We demonstrate a simple method that can be applied to noble and base metals alike to synthesize ultrasmall (~ 1 nm) NPs with homogeneous alloying. The method is based on strong electrostatic adsorption (SEA) whereby charged metal precursors are strongly adsorbed onto oppositely charged oxide or carbon surfaces by controlling the pH relative to the surface point of zero charge (PZC) [28, 30, 71]. This interaction holds the precursors in place during drying, as opposed to IMP in which the metal precursors remain and aggregate in solution as drying occurs. The native hydroxyl (OH) groups on the surfaces are used to achieve the required surface charge; no explicit surface functionalization is needed. This method involves fewer steps than colloidal methods of NP synthesis and eliminates the problematic removal of the capping agents of those methods, because none is used.

Electrostatic adsorption has been demonstrated for a host of single metals on many different supports [11, 28, 30, 42, 71-77]. Over composite oxide surfaces, pH-controlled adsorption has been used to achieve selective metal adsorption onto one surface component or the other [78-80]. Most recently, preliminary attempts at simultaneous electrostatic adsorption of two metal precursors for the synthesis of bimetallic NPs has been applied to Pt and Pd [14] and Pt and Co [34]; this has been termed simultaneous or co-SEA. This method is schematized in Figure 2.1A, depicting an electrostatically adsorbed layer of a mixture of hydrated metal precursors, followed by a thermal reduction in H\textsubscript{2} needed to remove the metal ligands, reduce the metals to their zero-valent state, and nucleate the atoms into NPs.
2.3 Discussion

We now present a systematic application of this method using a common silica support with a variety of noble and base metal ammine precursor pairs (Pt, Pd, Co, Ni, and Cu ammines) as shown in Table 2.1. The silica support (Evonik Aerosil 300) has a PZC of 3.6, a value similar to other fumed silicas [11, 14, 72]. Adsorption of metal ammine precursors was measured as a function of pH for all pairs of metal complexes to determine their relative affinities for the support. Detailed methods and materials are found in the SI along with a complete set of uptake surveys for the remaining metal combinations. Uptake surveys for representative noble-noble (Pt-Pd), noble-base (Pd-Cu), and base-base (Ni-Co) metal pairs are shown in Figure 2.1B. For the Pt-Pd adsorption surveys, no adsorption of metals occurred near the PZC.

<table>
<thead>
<tr>
<th></th>
<th>Co</th>
<th>Ni</th>
<th>Cu</th>
<th>Pt</th>
<th>Pd</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co</td>
<td>0.86Co</td>
<td>0.94Ni/0.97Co</td>
<td>0.70Cu/0.66Co</td>
<td>3.2Pt/0.8Co</td>
<td>0.7Co/1.3Pd</td>
</tr>
<tr>
<td>Ni</td>
<td>1.84Ni</td>
<td></td>
<td>0.89Cu/0.63Ni</td>
<td>2.6Pt/0.79Ni</td>
<td>0.52Ni/1.2Pd</td>
</tr>
<tr>
<td>Cu</td>
<td></td>
<td>2.25Cu</td>
<td></td>
<td>2.2Pt/0.94Cu</td>
<td>1.0Cu/2.1Pd</td>
</tr>
<tr>
<td>Pt</td>
<td></td>
<td></td>
<td>0.95Pt</td>
<td></td>
<td>1.31Pt/0.7Pd</td>
</tr>
<tr>
<td>Pd</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.27Pd</td>
</tr>
</tbody>
</table>
Figure 2.1 The-SEA bimetallic adsorption schematic, adsorption density, and temperature programmed reduction profiles. (A) Metal precursors electrostatically adsorb as a mixed monolayer. Clusters of alloyed NPs form after H₂ reduction. (B) Adsorption surveys of noble and base metal pairs depict relative affinities of metals as a function of pH on the support. (C) TPR profiles (downwards peaks indicate H₂ consumption) of the monometallic SEA NPs are at a higher temperature, indicating a stronger support interaction compared to IMP nanoparticles. Bimetallic SEA NPs show improved reducibility from H₂ spillover over the monometallic analogs.

As the pH was increased, the OH groups of the silica became deprotonated, which allowed the cationic Pt/Pd ammine precursors to adsorb. Pd had a greater affinity than Pt to the support at lower pHs, and the opposite was true at higher pH values. Maximum adsorption of 1.3 μmol/m² occurred at an optimum pH (pH= ~11.5) followed by a decrease in uptake as more base was added. This decrease in uptake is attributed to the strong ionic strength in solution that creates double layer screening effect [30]; the metal complexes were prevented from experiencing the surface charge. A similar trend was observed in the
Pd-Cu adsorption survey, but the maximum adsorption occurred at a higher pH value. Adsorption uptake surveys of Ni and Cu containing solutions were kept above a pH of 11 to prevent precipitation. The base-base metal pair of Ni-Co, shown in Figure 2.1B, was consistent with the other uptake surveys.

In all cases, the maximum adsorption of complexes for complete monolayer coverage for the bimetallic systems was ~1.0-1.3 μmol/m². This result indicates that all of the metal complexes adsorbed with the same number of hydration sheaths and are similar sizes during adsorption [73]. The Co surveys with Pd, Ni, and Cu (Figure 2.1B and Figure B.1) revealed competitive adsorption, in that the Co ammine favored the silica surface. The high affinity of Co ammines for silica is known and ultimately results in the formation of a new phyllosilicate phase [81, 82]. Thus, the Co adsorption was independent of pH in these experiments. The relative concentration of Co was lessened to allow the adsorption of the other metal to achieve an atomic ratio of 1:1. All other metal pairs were adsorbed onto the support in a 1:1 atomic ratio at the monolayer capacity of the precursors, by controlling the metal precursor concentrations in solution. The metal concentrations employed are listed in Table B.1.

Temperature-programmed reduction (TPR) was performed to characterize the intimacy of alloying of the metals in the nascent NPs. Comparisons were made between monometallic and bimetallic NPs prepared by SEA and IMP. Detailed SEA and IMP synthesis parameters are provided in Appendix B, Tables B.1 and B.2. TPR profiles for the Pd-Cu series (Figure 2.1C) showed that the monometallic Pd in the IMP sample exhibited a low reduction temperature of ~100°C but that the monometallic Pd in the SEA sample required 150°C for reduction, indicating a much stronger interaction with the silica
support. The TPR for Cu IMP reduction peaks began with a shoulder ~190°C and had a sharp peak at 230°C. The broad shoulder of the IMP profile suggests a wide particle size distribution in which some of the larger particles were more easily reduced. The TPR for Cu SEA profile contains a sharp peak reduction peak at 220°C and a broader peak around 500°C.

When bimetallic NPs were compared, the Pd-Cu co-SEA NPs (Figure 2.1C center) showed two distinct peaks. The first peak at ~180°C was from the reduction of a Pd-Cu alloy, and the second peak at 400°C was the monometallic Cu peak at 500°C shifted to a lower temperature. We attributed the shift to lower temperature to hydrogen spillover from Pd to unreduced Cu complexes, indicating that there must be close proximity of Pd-Cu atoms in the co-SEA derived NPs. The bimetal Pd-Cu IMP NPs contained multiple reduction peaks between 80° and 250°C with distinct peaks that corresponded to the non-shifted monometallic Pd and Cu. Thus, unalloyed Pd or Cu existed in the IMP NPs.

Further evidence of hydrogen spillover in co-SEA bimetallic NPs observed in the Pd-Co TPR profiles (Figure 2.1C right). Although Co complexes are very difficult to reduce over silica and require temperatures of 700°C (20), by alloying Pd-Co, the spillover-assisted reduction of Co cations by Pd was observed at a temperature of 400°C. TPR profiles of additional metal combinations are shown in the Appendix B, Figures B.2 and B.3. The additional metal combinations exhibited similar results where the SEA NPs showed greater support interaction and commonly required a higher reduction temperature than the IMP NPs. The co-SEA NPs often had peaks shifted to lower temperatures compared to the monometallic SEA analogs, indicative of hydrogen spillover assisted reduction between the two metals. The IMP NPs contained broader peaks and more
reducible species, which agrees with having a larger particle size distribution and various NP compositions.

After a 400°C reduction in 10% H$_2$ balanced in He for 1 hour, x-ray diffraction (XRD) profiles were taken of each material. The XRD patterns of the co-SEA materials (Figure 2.2A) showed no distinct features between 30° and 45° 2θ, the range containing the most intense diffraction peaks. The very broad peaks observable in some patterns, with respect to the metal-free supports, were the result of highly-dispersed NPs. This interpretation was later confirmed by electron microscopy. XRD patterns of the co-IMP NPs, reduced at the same conditions (Figure 2.2B), showed strong XRD peaks for all of the IMP metal combinations. The intense XRD peaks between 30° and 45° 2θ were indicative of large NPs, i.e., x-ray diameters $d_{\text{XRD}} > 5\text{nm}$. Moreover, the non-Gaussian shape of the peaks, containing shoulders and sharp centers, suggests variable phase compositions and a wide particle size distribution, respectively.

Electron microscopy Z-contrast images of the co-SEA NPS (Figure 2.2C) show that they existed as ~1.0 to 1.3 nm clusters with narrow particle size distributions (standard deviations were about 20-30% of average particle size). This finding is consistent with the absence of peaks in the high sensitivity x-ray diffractometer, which has a size limit of ~ 1 nm [83]. In comparison, the microscopy images in Figure 2.2D showed the co-IMP NPs having broader particle size distributions and overall larger particle sizes (~5 to 25 nm). A NP-shape difference was also observed between the two synthesis methods. The co-SEA NPs produced more regular spherical particles, while more frequent irregular shapes and particle agglomeration were observed in the co-IMP NPs. A summary of the bimetallic NP sizes are shown in Table 2.2 with particle size distributions shown in Figure B.4. SEA
with single metals typically gives particles in the size range 1 to 2 nm (10); with co-SEA the NPs were about the same size or smaller.

![Figure 2.2](image)

**Figure 2.2** Bimetallic NP size characterization after 400°C reduction in 10%H+/helium. (A and C) XRD patterns and STEM images of co-SEA bimetallic NPs reveal extremely high dispersion. (B and D) XRD patterns and STEM images of co-IMP bimetallic samples show larger particles.

Although the 1 nm NPs were too small for individual NP elemental mapping, EDX/S was used in spot mode on multiple individual bimetallic NPs produced by co-SEA. These measurements help to determine composition consistency by comparing the nominal weight ratios to the actual weight ratios determined through x-ray analysis. The NPs were prepared near a 1:1 atomic ratio; thus, the weight percent and weight ratio of the two metals will vary depending on their molecular weights. Table B.3 shows the spot analysis of the
Pt-Pd NPs, which have an expected weight ratio of 0.65Pt:0.35Pd. The results showed the Pt-Pd NPs were consistent with the expected ratio. In all cases (Table B.4-B.12), the co-SEA NPs were bimetallic, with most individual NPs being near the predicated wt% for each metal.

Table 2.2 Average particle sizes of bimetallic NPs.

<table>
<thead>
<tr>
<th></th>
<th>co-SEA STEM** (nm)</th>
<th>IMP XRD** (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt-Pd</td>
<td>1.0 ± 0.2</td>
<td>9.4</td>
</tr>
<tr>
<td>Pt-Cu</td>
<td>1.2 ± 0.3</td>
<td>2.8*</td>
</tr>
<tr>
<td>Pt-Ni</td>
<td>1.1 ± 0.3</td>
<td>6.9</td>
</tr>
<tr>
<td>Pt-Co</td>
<td>0.94 ± 0.3</td>
<td>4.2</td>
</tr>
<tr>
<td>Cu-Co</td>
<td>1.3 ± 0.3</td>
<td>7.3</td>
</tr>
<tr>
<td>Cu-Ni</td>
<td>1.1 ± 0.3</td>
<td>14</td>
</tr>
<tr>
<td>Ni-Co</td>
<td>1.4 ± 0.3</td>
<td>15.0*</td>
</tr>
<tr>
<td>Pd-Ni</td>
<td>1.1 ± 0.2</td>
<td>6.4</td>
</tr>
<tr>
<td>Pd-Co</td>
<td>1.0 ± 0.2</td>
<td>7.3</td>
</tr>
<tr>
<td>Pd-Cu</td>
<td>1.1 ± 0.2</td>
<td>14.5</td>
</tr>
</tbody>
</table>

*2.8 nm is an average of three replicates (3.7, 2.5, and 2.3 nm); 15 is an average of 15.9, 15.2, and 13.9 nm.

** STEM size is number average diameter, XRD size is from the Scherrer equation.

EDXS mapping could be performed over the larger IMP NPs to determine the degree of alloying. These maps are found in Appendix B, Figures B.5 and B.6. Incomplete alloying occurred in most of the co-IMP bimetallic NPs, and the extent of alloying varied from particle to particle. The segregation of the metals was independent of the predicted structure obtained from phase diagrams, where most metal combinations do form alloys.
This incomplete alloying agrees with XRD data of the IMP NPs, which showed multiple phase compositions.

Finally, atomically resolved Z-contrast images were taken to individually characterize the co-SEA NPs (Figure 2.3). Careful examination of these images revealed a speckling effect, where higher atomic number elements are brighter and lower atomic number elements are dimmer. This phenomenon could be best observed in the samples in which the two metals have large differences in atomic number. Figures 2.3A and 2.3B show the clearest evidence of speckling of the Pt-Co and Pt-Cu NPs; this is direct visual evidence of a well-mixed alloy. Other combinations of Pd-Ni, Pd-Cu, and Pt-Pd (Figure 2.3C-D) with lower differences in Z also showed speckling, although less pronounced. The speckling effect has been reported most clearly in the case of solution-derived and somewhat larger Pt/Pd and other bimetallic NPs [84]. No speckling was observed in the Cu-Co NPs because of the very small Z difference and poor contrast; however, the Cu-Co NPs are most likely alloyed similar to the other co-SEA bimetallic combinations.

Simultaneous SEA can be extended to other surfaces such as alumina, titania, and carbon, as long as soluble metal precursors are available; in the current case cationic ammine complexes have been adsorbed over a low PZC silica surface. Over high PZC surfaces such as alumina and carbon, anions such as chloride complexes can be employed. The method is limited to the availability of suitably charged complexes. A potential drawback with the use of silica is the solubility of silica at the high pH at which the adsorption is performed. Silica dissolution during SEA was seen to be significant above pH 11 and with 24 hour contact times (28). Dissolution can be circumvented by working
at a pH of 10.5 or below, where dissolution is negligible (28), or can be minimized by using short contact times, as metal adsorption reaches equilibrium within minutes (4).

Figure 2.3 Atomically resolved Z-contrast images showing NP speckling of alloys (scale bar, 5 nm).

Another limitation is the amount of metal which can be applied in one co-SEA application. The normal uptake of about 1 μmol/m² of charged precursors (about 1 complex per nm²) corresponds to a steric maximum of close-packed complexes retaining one or two hydration sheaths (4). Metal loading thus depends on the specific surface area of the support; for a 200 m²/g support such as precipitated silica, typical metal loadings are limited to a few weight percent, while for high surface area materials such as mesoporous silica with 1000 m²/g, loadings of 10-15 percent are possible in a single SEA application.
Higher loadings can be achieved by repeated applications of SEA and reduction (this has been demonstrated for Pt on carbon (29)); the reduction transforms the hydrated, ligated precursors into metal nanoparticles and uncovers the support surface, onto which more precursor can be subsequently adsorbed.

Other methods for synthesizing highly dispersed, well alloyed bimetallic nanoparticles exist. It is suggested that bifunctional organics which chelate both a metal and a silica surface, demonstrated for single metals of ruthenium and iridium (30), can be applied to mixtures of metals (2). The method appears to be limited to silica, and due to the exotherm generated in removing the organic by oxidation, is also limited to low metal loadings (2). Alternatively, in limited instances supported nanoparticles may be derived from the decomposition of metastable bimetallic precursor species such as Keggin-type complexes continuing cobalt and molybdenum (31) or organometallic cluster complexes containing platinum and iron (32). Finally, well alloyed and size and composition-controlled bimetallic nanoparticles can be synthesized in the solution phase by colloidal methods (33) such as a recent study of 50 wt%, 4.5 – 6.5 nm PdPt nanoparticles on carbon (34). The higher achievable weight loading of this approach may offset the complexity of the synthesis and the difficulty in distributing the NPs into the support. If on the other hand ultrasmall, homogeneously alloyed bimetallic nanoparticles at moderate weight loadings are desired, simultaneous SEA provides a more generalizable and straightforward synthesis strategy.

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CHAPTER 3

STABILIZATION OF CATALYTIC SURFACES THROUGH CORE-SHELL STRUCTURES
3.1 Introduction

Catalytic stability is a focus for many industrial processes. Catalyst deactivation often limits catalyst time-on-stream through the loss of active sites, metal leeching, coke formation, etc [85-87]. Downtime of industrial processes can cause losses of millions of dollars each day; therefore, strong incentives exist to improve catalyst durability and activity. Although modifications to chemical processes can alter the rate of catalyst deactivation, in many cases harsh reaction conditions such as high-temperatures (automotive exhausts, dry reforming of methane, etc.) or hydrothermal aqueous phase reactions for biomass upgrading are unavoidable [46, 88, 89].

Several techniques to improve catalyst stability have been developed that focus on modifications to catalyst supports that increase the interaction of metal nanoparticles with the support. Support durability can be improved by use of promoters to improve both hydrothermal stability and interactions with supported nanoparticles, e.g., alumina doped with silica, La, Ba, etc [90, 91]. Methods to prevent metal sintering often involve selecting support materials that anchor the catalytic metal on the support surface or finding a way to incorporate the active metal sites into the lattice of the support like those found in homogenous precipitation methods [92, 93]. Another method to improve nanoparticle stability is by addition of a secondary metal. Bimetallic catalysts often have increased activity, selectivity, and even stability compared to their monometallic analogs [94-96]. The inclusion of secondary metals can increase nanoparticle stability by altering the physical properties in an alloyed, by changing oxidation states of one or both metals, or by providing a method of stronger interaction with the support [97].
This applies two synthesis methods, Strong Electrostatic Adsorption (SEA) and Electroless deposition (ED) to create bimetallic core-shell (core@shell) structures. SEA has been successful in creating highly-dispersed nanoparticles of various metals (Ag, Co, Ni, Pd, Pt, Ru, etc.) across multiple catalytic supports [8, 11, 13, 72]. SEA is achieved by controlling the pH of the solution during wet impregnation. The catalyst support’s Point of Zero Charge (PZC) governs the selection of the metal precursor and pH during synthesis. By working at pH values away from the PZC, the support surface will be charged, and oppositely charged metal ions can be electrostatically adsorbed to the support surface. Following reduction of the adsorbed metal precursors, nanoparticles of the metal are formed. These small nanoparticles are then used as cores for the deposition of shell metals by ED. The application of ED requires a reducing agent to be activated on the nanoparticle cores. Once the reducing agent (RA) is activated, the reduction of the second metal occurs as a shell layer. The deposition mechanism can be either catalytic or auto-catalytic depending on whether the RA is adsorbed/activated on the core or on the shell metal, respectively. Several core-shell bimetallic combinations of Au-Pd, Pt-Ti, Ag-Pt, Ag-Pd, Cu-Pd, Ag-Ir, etc have been synthesize using ED [7, 37, 41, 44, 76, 98].

This work focuses on enhancing the stability of catalytic surfaces by utilizing surface free energy (SFE) principles. Thermodynamics dictate a system will prefer to be in the lowest energy state possible. Therefore, low SFE metals will want to cover high SFE metals. By adding a lower SFE metal shell onto a higher SFE metal core, a bimetallic system is created which thermodynamically constrains the lower SFE metal to remain on the surface of the higher SFE metal core. Further, because the support almost always has the lowest SFE, there is yet another impediment for diffusion of the shell component onto
the support. Thus, it should be possible to design and synthesize numerous metal core-shell configurations to theoretically prevent sintering of the shell metal and stop the migration of the shell metal component onto the support surface. To test this hypothesis, a series of Ag coverages prepared by ED using an aqueous bath containing Ag(CN)$_2^-$ and hydrazine (N$_2$H$_4$) on Ir cores was synthesized and characterized following annealing at temperatures ranging from 200 – 800°C. Ir was chosen as the high SFE core and Ag as the low SFE shell because of their large differences in SFE’s, where the SFE of Ir is more than double that of Ag [99-102]. Literature values of the SFE’s of Ag and Ir are ~850 and 2400 ergs/cm$^2$, respectively [100, 103]. The stability of the cores to anchor the shell materials was determined by annealing treatments followed by chemisorption, XRD, and STEM.

### 3.2 Methods - Experimental

All catalytic support materials were calcined at 700°C for 4 hours before metal deposition. SEA was performed to deposit the iridium anionic precursor, potassium hexachloroiridiate (II) (K$_2$IrCl$_6$, Alfa Aesar 99.9%), over δ/θ-alumina (SASOL APA 0.2, BET SA- 37 m$^2$/g) and γ-alumina (UOP VGL-25, BET SA- 164 m$^2$/g) in low pH conditions. HCl and NaOH were used to adjust the pH. Potassium silver cyanide, KAg(CN)$_2$, and potassium gold cyanide, KAu(CN)$_2$, were used as the precursors for ED, and the RA were hydrazine and formaldehyde. Metal concentrations were analyzed by a Perkin-Elmer 2000DV ICP-OES and a Perkin-Elmer AA 400.

A Micromeritics ASAP 2920 was used to determine the number of catalytically active sites through H$_2$ pulse chemisorption. The catalyst was first reduce at 200°C in H$_2$ followed by hydrogen chemisorption at 40°C. Annealing treatments were performed under argon at 200, 400, 600, and 800°C for 4 hours each followed by hydrogen chemisorption
at 40°C. All catalyst pretreatments and evaluations were performed in situ. \( \text{H}_2 \) TPD measurements were also performed on the ASAP 2920 using the TCD. A Rigaku MiniFlex II equipped with a high sensitivity D/tex Ultra Si slit detector was used to obtain X-ray diffraction (XRD) patterns. Patterns were recorded from using a Cu-K\( \alpha \) radiation source (\( \lambda = 1.5406 \, \text{Å} \)) operated at 30 mA and 15 kV.

3.3 Methods - Computational

First principles theoretical studies were performed using the dispersion corrected relativistic density functional theory (DFT) within the generalized gradient approximation (GGA) proposed by Perdew, Burke and Ernzerhof (PBE) for the exchange and correlation functional [104]. The DFT-D3 method was used to include the Van der Waals corrections [105]. The computations are performed using the VASP code, and the Kohn–Sham orbitals were expanded using a plane wave basis set and the cutoff was set to 400 eV [106, 107]. The support was modelled by taking a periodic cell of 72 Al atoms and 108 O atoms in the structure of \( \alpha\)-\( \text{Al}_2\text{O}_3 \). The Gibbsite model of \( \alpha\)-\( \text{Al}_2\text{O}_3 \) included 63 Al atoms and 108 O atoms, and 27 H atoms. A dipole correction was incorporated along the z-axis of the slab. Due to the large size of the surface supercell only the \( \Gamma \) point was used for Brillouin zone integration. The structures were not considered optimized until the forces on the atoms were minimized to 0.01 eV/Å or less. The geometry optimization of the cluster supported on the surface was performed with the bottom two layers of the alumina support fixed, while the top three layers were free to relax.
3.4 Discussion

Strong Electrostatic Adsorption (SEA) was performed over the calcined supports. Adsorption density of the iridium precursors over δ/θ-Al₂O₃ and γ-Al₂O₃ is plotted against pH (Figure 3.1). In the acidic pH region, the anionic Iridium precursor, IrCl₆²⁻, adsorbed over the alumina supports (PZC~8.4). At a neutral pH near the PZC, only slight adsorption occurs. As the solution was acidified, the hydroxyl groups of alumina were protonated which allowed the negatively-charged anionic Ir complex to adsorb at greater densities. The decrease in uptake in strong acidic mediums can be attributed to the strong ionic strength; where the electrostatic charge between the protonated surface and Ir complex was weakened from other ions in solution. The maximum adsorption densities across these alumina supports were 0.75 and 1.1 umol/m² for the θ-δ and γ- aluminas, respectively. This maximum adsorption occurred around a pH final value of 4 for both alumina supports.

![Figure 3.1 Adsorption of Ir complexes.](image)

The pH₇对应的 maximum adsorptions were used for the Ir catalysts syntheses. One limitation of SEA is that the weight loading of the catalyst is limited by
the maximum adsorption density of the precursor and the surface area of the support. Therefore, only a limited amount of metal is adsorbed over these low surface area supports in a single SEA synthesis. Sequential cycles of SEA can be applied to increase the metal loading. Two cycles of SEA were required for Ir on δ/θ-Al₂O₃. Only one SEA cycle was necessary for the γ-Al₂O₃ as the surface area of the γ-Al₂O₃ was higher. The final wt. loadings of Ir on δ/θ-Al₂O₃ and γ-Al₂O₃ were 1.0 and 3.2 wt% Ir, respectively. All Ir catalysts were reduced at 400°C in 10 %H₂ for 1 hour. Initial particles sizes were below the limit of detection (<1.5 nm) through XRD analyses.

Electroless Deposition (ED) was applied to the SEA prepared Ir catalysts to form core-shell nanoparticles. The procedure was followed from previous work of bimetallic Ag-Ir core-shell structures by electroless deposition [7]. Similarly, potassium silver cyanide, KAg(CN)₂, was used as the silver precursor, and hydrazine was used as the RA. The ED bath was kept at pH 10, above the support PZC, to prevent any electrostatic interactions between the support and the anionic Ag ion. ED plots of Ag deposition on δ-θ Al₂O₃ and γ-Al₂O₃ are shown in Figure 3.2A and B, respectively. The deposition was fastest in the first 15 minutes when the RA and Ag concentrations were highest. The deposition slowed as the process continues, showing two things: 1) kinetics depends on the Ag concentration in solution and 2) the weak affinity for auto-catalytic deposition of Ag onto itself using hydrazine as a RA. The RA was replenished every 30 mins to facilitate hydrogen adsorption to the catalytic sites. Au was also deposited onto Ir via ED, and the ED behavior was similarly to Ag on Ir.
Incomplete deposition occurred at some of the higher Ag coverages within the duration of ED reaction. This can be observed in the 1.5 wt% Ag on γ-Al₂O₃ where Ag remained in the final solution. The reason being, Ir can easily activate hydrazine, and the deposition of Ag on Ir occurs. However, Ag is a poor activator of hydrazine; therefore, once the surface is a majority of Ag, it is difficult to deposit more Ag auto-catalytically. To achieve higher wt. loadings and coverages, the RA was changed to formaldehyde midway through the ED reaction, and the duration of the ED reaction was extended to promote further deposition. The temperature of the ED bath was also controlled to alter the ED reaction kinetics. Higher temperatures promoted faster ED kinetics as shown in Figure 3.2A for the targeted 2ML θ₂Ag runs. The lowest coverages of Ag were performed at 25°C; however, the temperature was increased, as necessary, up to 75°C to achieve the highest Ag coverages.

Figure 3.2 Electroless Deposition graphs of A) Ag on 1.0 wt% Ir δθ-Al₂O₃ B) Ag on 3.2 wt% Ir γ-Al₂O₃.
A summary of the bimetallic catalysts synthesized by ED are shown in Table 3.1. The core and shell metals, targeted coverages, theoretical monolayer coverages, and experimental coverages are listed. The shell wt% and experimental coverages were obtained through atomic absorption spectroscopy and H₂ chemisorption. Theoretical coverages assume a 1:1 shell atom to core metal active site and only catalytic deposition (single atom thick shell layer). Differences arise between the theoretical coverages and the experimental coverages obtained by chemisorption due to the auto-catalytic deposition of Ag which forms a multi-atom thick shell layer. These deviations between theoretical and experimental coverages are apparent in Figure 3.3, especially at higher loading of Ag where more auto-catalytic deposition occurred. This series of catalysts with different shell coverages was then annealed at increasing temperatures (200, 400, 600, and 800°C) to determine catalytic stability.
3.4.1 Chemisorption

The chemisorption results of the Ag-Ir bimetallic system supported on δ-Al₂O₃ are shown in Figure 3.4. The 1.0 wt% Ir catalyst was stable up to 400°C annealing temperatures shown by no change in the H₂ uptake from chemisorption between 200 and 400°C; not unexpectedly since the catalyst was originally reduced at 400°C. After a temperature of 600°C, the H₂ uptake decreased from 12.5 to 1.2 umol/g catalyst indicative of severe nanoparticle sintering. This decrease in H₂ uptake followed the predicted trend of losing active sites as annealing temperature increased. When 0.14 wt% of Ag was added by ED, the initial H₂ uptake of the catalyst was decreased from 12.5 to 10 umol/g catalyst. This decrease occurred because Ag is unable to chemisorb H₂ at these conditions. At 400°C, this same catalyst actually had a higher H₂ uptake than initial prepared, and at elevated temperatures of 600 and 800°C, the 0.14 wt% Ag bimetallic catalyst retained a
higher H\textsubscript{2} uptake compared to the Ir monometallic catalyst annealed at those same temperatures. The catalysts with higher Ag coverages (and wt. loadings) have reduced H\textsubscript{2} uptakes after 200°C. This direct correlation between increased Ag coverage and lower initial H\textsubscript{2} uptake further validates that the ED process creates a shell of Ag that is not capable of H\textsubscript{2} chemisorption at these conditions. The bimetallic catalysts with intermediate Ag loadings (0.21 and 0.35 wt %) showed a significant increase in H\textsubscript{2} uptake far beyond that of the Ir monometallic catalyst after annealing at 400°C.

Reasons for the large increase in H\textsubscript{2} capacity is discussed later, but it must be noted that the H\textsubscript{2} capacity of the bimetallic catalysts cannot surpass the monometallic catalyst unless the stoichiometry of H\textsubscript{2} to Ir site can be altered or the surface of Ag can now chemisorb H\textsubscript{2}. The H\textsubscript{2} uptake of the Ag-Ir bimetallic catalysts remained higher than the Ir monometallic catalysts after the elevated annealing temperatures of 600 and 800°C. The higher H\textsubscript{2} capacity for the bimetallic catalysts indicate the retention of active sites and improved catalyst stability.

The same annealing/chemisorption treatments were performed on a series of Ag-Ir bimetallic catalysts supported on γ-Al\textsubscript{2}O\textsubscript{3}, shown in Figure 3.5. The monometallic 3.2wt % Ir on γ-Al\textsubscript{2}O\textsubscript{3} exhibited similar chemisorption trends to the monometallic 1 wt % Ir on δθ-Al\textsubscript{2}O\textsubscript{3} after the various annealing pretreatments. The Ir on γ-Al\textsubscript{2}O\textsubscript{3} was stable up to 400°C, with only a slight deactivation compared to annealing at 200°C. After 600°C, there is a significant loss of active sites from 73 umol H\textsubscript{2}/g catalyst to 11 umol H\textsubscript{2}/g catalyst. A difference in the initial total amount of umol H\textsubscript{2}/g catalyst between the 1 wt% and 3.2 wt% monometallic Ir on Al\textsubscript{2}O\textsubscript{3} catalysts was expected. The weight loadings between the two monometallic Ir catalysts differ by a factor of 3. Moreover, H\textsubscript{2} pulse chemisorption
measurements indicate the metal dispersion increases from 49% dispersion for the 1 wt% Ir to 100% dispersion for the 3.2 wt% Ir. The doubling of metal dispersion and the tripling of weight loading increases the umol H₂/g catalyst by a factor of six. This six-fold increase represents the increase of initial hydrogen capacity from 13 to 82 umol H₂/g catalyst between the 1 wt% Ir and 3.2 wt% Ir, respectively.

**Figure 3.4** Chemisorption of H₂ on annealed Ag-Ir catalysts supported on δθ-Al₂O₃.

Reasons for the increase in Ir dispersion for the 3.2 wt% Ir on γ-Al₂O₃ may be reflected in the differences between support surface area of δθ and γ-Al₂O₃’s (37 vs 164 m²/g, respectively) and the number of SEA cycles required (2 vs 1, respectively). The use of one SEA cycle may aid in keeping lone Ir atoms separated, whereas multiple SEA cycles may place lone Ir atoms in close proximity which would promote particle agglomeration. The Ir atom density is lower on γ-Al₂O₃. Although no large differences were observed
between the two catalysts’ XRD particle sizes, H₂ to Ir stoichiometry is strongly dependent on Ir nanoparticle size [108, 109]. The H₂ stoichiometry to Ag and Ir is later investigated through computational studies.

**Figure 3.5** Chemisorption of H₂ on annealed Ag-Ir catalysts supported on γ-Al₂O₃.

When a Ag shell was added to the 3.2 wt% Ir on γ-Al₂O₃, the initial H₂ uptake for the bimetallic system was reduced by 80%, agreeing with higher Ag coverages yielding lower initial H₂ uptakes. After annealing at 400, 600, and 800°C, the Ag-Ir bimetallic catalysts exhibited increased capacity for H₂ from the initial state. The trends agree with the similar Ag-Ir system supported on δθ-Al₂O₃. However, at no point was the H₂ capacity for the γ-Al₂O₃ bimetallic systems higher than the maximum H₂ capacity of the monometallic Ir catalyst. This suggests the possibility of Ag sintering causing the exposure of the Ir surface. The migration of Ag into the bulk Ir is unlikely, since Ag and Ir are not expected to form a bulk alloy [110]. However, some suggest a surface alloy is feasible [111]. The final capacity of H₂ for the γ-Al₂O₃ bimetallic catalysts after treating at 800°C
was higher than the monometallic Ir which suggests the ability to stabilize the catalytic surface and improve the number of active sites for H\textsubscript{2} adsorption.

3.4.2 Particle size characterization

The particle sizes of these catalysts were determined through chemisorption, STEM images, and XRD patterns. The initial particle sizes of the monometallic Ir catalyst on $\delta\theta$-Al\textsubscript{2}O\textsubscript{3} were $d_{\text{chemi}} = 2.3$, $d_n = 1.4$, and $d_{\text{XRD}} = <2$ nm. After the annealing treatments of 200, 400, 600, and 800°C, the final particle sizes of the monometallic 1 wt% Ir/$\delta\theta$-Al\textsubscript{2}O\textsubscript{3} were $d_{\text{chemi}} = 21$, $d_n = 43$, and $d_{\text{XRD}} = 26$ nm. The two bulk particle size measurements obtained from chemisorption and XRD are in well agreement with each other. This significant increase in particle size was due to severe metal sintering after pretreatment in high temperatures. A clear suppression of nanoparticle sintering is observed for the Ag-Ir bimetallic particles. After the high temperature pretreatments, the XRD bimetallic particle sizes were between 19-22nm (shown in insert of Figure 3.6). Moreover, the Ir (111) metallic peaks in the bimetallic catalysts shown at 40.7° 2θ in Figure 3.6 are reduced in intensity compared to the monometallic Ir catalyst. This reduction of the Ir (111) peak suggests a bimodal distribution of the Ir, where many smaller Ir particles exist. No metallic Ag (111) peaks at 38.1° 2θ were observed by XRD for the $\delta\theta$-Al\textsubscript{2}O\textsubscript{3} bimetallic catalysts. A monometallic Ag catalyst was annealed under the same conditions at 800 °C to compare with the bimetallic catalysts. XRD results of the annealed monometallic Ag catalyst indicated particle sintering to 29 nm. Thus, the bimetallic nanoparticles had increase resistance to sintering with regard to both the monometallic Ag and Ir counterparts.
A similar XRD analysis was performed for the $\gamma$-$\text{Al}_2\text{O}_3$ annealed catalysts. The initial particle size of the Ir on $\gamma$-$\text{Al}_2\text{O}_3$ was $\sim$2nm by chemisorption and $<$2nm from XRD. After annealing treatments at 800°C, the Ir severely sintered as observed by a large Ir (111) peak in the XRD pattern in Figure 3.7. The final particle size for the 3.2 wt% Ir/$\gamma$-$\text{Al}_2\text{O}_3$ was $d_{\text{chemi}} = 17$, $d_0 = 56$, and $d_{\text{XRD}} = 23$ nm. Again chemisorption and XRD bulk particle sizes are in well agreement with each other. When 0.73 wt% Ag was added as a shell, Ir and Ag both were stabilized indicated by the lack of a Ag (111) peak and a less intense Ir (111) peak. Ag (111) and Ir (111) peaks exist in the higher bimetallic wt. loadings of Ag (1.5 and 2.8 wt%) annealed catalysts, but both peaks are less intense than either the Ag or Ir monometallic analogues. These low XRD intensities signify that a bimodal distribution
of Ir and Ag nanoparticles must coexist; where XRD detected some large clusters, and many small Ag-Ir clusters must remain below the limit of XRD detection.

**Figure 3.7** XRD diffraction patterns of monometallic and bimetallic γ-Al₂O₃ catalysts after annealing at 800°C.

To summarize the XRD data, the monometallic Ir and monometallic Ag catalysts sintered on both alumina supports. Anchoring the Ag as a shell by ED prevented the sintering of Ag compared with the monometallic Ag catalysts on the Al₂O₃ supports. This increased stability of the Ag agrees with SFE principles. Moreover, the addition of a Ag shell also increased the stability of Ir.

STEM was used to confirm the bimodal distribution and stabilization of the Ag-Ir nanoparticles. In Figure 3.8, STEM images and particle size distributions are shown after the different pretreatment temperatures. The monometallic 1.0 wt% Ir catalyst over δ₀-Al₂O₃ sintered from an initial dₙ = 1.4 nm to a dₙ = 43 nm (Figure 3.8A and B). All of the Ir existed as large particles. This severe sintering was prevented through the addition of
The bimetallic Ag-Ir catalyst (0.35Ag-1.0Ir wt.%) started with an initial $d_n =$ 1.5 nm and sintered to $d_n =$ 1.6 nm and $d_n =$ 6.7 nm after pretreatments of 400 and 800°C, respectively (figure 3.8C,D, and E). Many of these Ag-Ir nanoparticles remained small (<5nm) after 800°C. The images taken after 400°C annealing (Figure 3.8D) showed virtually no particle size difference from the initially prepared size. This validates Ir’s resistance to sintering up to 400°C which was observed from chemisorption in Figures 3.4 and 3.5. However, the unchanged particle size of the δ-Al₂O₃ bimetallic catalysts between the initial state at 200°C and after a pretreatment of 400°C cannot explain the abnormally high H₂ uptake of these Ag-Ir bimetallic catalysts after pretreatments at intermediate temperatures. If an Ag shell were to sinter and expose the Ir surface, the H₂ uptake would not surpass the maximum H₂ uptake of the monometallic Ir.

A STEM comparison was also made between an annealed monometallic Ir (3.2 Ir wt.%) and an annealed bimetallic Ag-Ir catalyst (2.8Ag-3.2Ir wt.%) supported on γ-Al₂O₃. Both γ-Al₂O₃ catalysts were initially small, but after annealing at 800°C, there were large difference in particle size (Figures 3.8F and G). The bimetallic Ag-Ir catalyst (Figure 3.8F) particle size was mostly unchanged at $d_n =$ 1.6 nm, and the monometallic catalyst severely sintered to $d_n =$ 56 nm (Figure 3.8G). The results of very little sintering for the bimetallic system over γ-Al₂O₃ agrees with the minute Ir (111) XRD peaks and high H₂ capacity after 800°C shown in Figures 3.5 and 3.7, respectively. The STEM images of both Al₂O₃ supports at various wt. loadings and Ag coverages suggest a clear indication that the bimetallic Ag-Ir catalysts are more sinter resistant.
Figure 3.8 STEM images of A-B) Ir/δθ-Al₂O₃, C-E) Ir/δθ-Al₂O₃, and F-G) Ag-Ir/γ-Al₂O₃ after various annealing temperatures.

3.4.3 Au-Ir

A bimetallic Au-Ir catalyst was also prepared and annealed to determine if the high H₂ uptake persisted for other bimetallic combinations. Similar to Ag, Au is not expected to form a bulk alloy or chemisorb H₂ at these conditions; however a Au-Ir surface alloy has shown slight H₂ adsorption capabilities due to the trapping of subsurface H [112-114]. The chemisorption results for the Au-Ir system are shown in Figure 3.9. As expected, the initial H₂ uptake following a 200°C annealing pretreatment was decreased due to Au covering the
Ir surface. This is in agreement with the Ag-Ir system where neither pure Au nor Ag was expected to chemisorb any H₂. Both the Ag and Au were deposited at the same wt. loadings. Since the molecular weight of Au is near double that of Ag, the number of Au atoms deposited are halved for the same wt. loading. Therefore the initial H₂ uptake of the Au-Ir catalyst will only be reduced by half the amount observed in the Ag-Ir system. These calculations are based off the assumption that the deposition mechanism proceeded in similar manners.

![Graph showing H₂ uptake vs. temperature for different catalysts](image)

**Figure 3.9** Comparison of H₂ chemisorption on annealed Ag-Ir and Au-Ir catalysts supported on δθ-Al₂O₃.

A large increase in H₂ capacity was observed for the Au-Ir catalysts pretreated at 400 and 600°C. The Au-Ir system retained a higher H₂ capacity after 600°C than the Ag-Ir system, but after 800°C, both bimetallic systems showed decreases in the H₂ capacity. The results indicate the same trends occurred on both Ag-Ir and Au-Ir systems.
3.4.4 H\textsubscript{2} Temperature-Programmed Desorption (H\textsubscript{2} TPD)

Hydrogen TPD was performed on the δθ-Al\textsubscript{2}O\textsubscript{3} catalysts to investigate the unusually high H\textsubscript{2} uptakes. The goal of H\textsubscript{2} TPD was to identify differences in H\textsubscript{2} adsorption behavior including the addition of new hydrogen species. The catalysts were first reduced in situ at 200°C in H\textsubscript{2} for 1 hour followed by annealing pretreatments in Ar at 400°C for 4 hours. The catalysts were then brought to 40°C and pretreated with H\textsubscript{2} flow. Ar was used to sweep away excess H\textsubscript{2}. The temperature was increased at a rate of 10°C/min, and H\textsubscript{2} desorption was measured by a TCD. The TPD profile of the 1 wt % Ir/δθ-Al\textsubscript{2}O\textsubscript{3} annealed at 400°C showed desorption of one H\textsubscript{2} peak at 270°C (Figure 3.10A).

The H\textsubscript{2} TPD profile of a bimetallic catalyst that was reduced and followed by annealing at the same conditions is shown in Figure 3.10B. The addition of 0.14 wt% Ag to the catalyst created two lower temperature H\textsubscript{2} desorption peaks at 100 and 160°C. This was attributed to an Ag-Ir interface since Ag by itself is incapable of adsorbing H\textsubscript{2} in this temperature range. H\textsubscript{2} adsorption on Ag occurs at temperatures below -90°C [115]. At higher wt. loadings/coverages of Ag, the two low temperature H\textsubscript{2} peak increased in size,
and the Ir H₂ desorption peak decreased in size (not shown). This confirms that the two low temperature peaks are influenced by the presence of Ag. After higher annealing temperatures at 800°C, the monometallic Ir catalyst exhibited very little H₂ desorption due to the reduction in the number of active sites (not shown). These weaker bound H₂ species might be attributed to one or more of the following: 1) Ir can alter the B.E. of H₂ to Ag so that now Ag is slightly capable of chemisorbing H₂ at these conditions. 2) Ag creates a surface alloy with Ir which contains an ensemble with different H to Ir stoichiometry 3) Ir can facilitate the dissociative adsorption of H₂ and transfer H atoms to Ag sites. These theories were investigated through computational analyses of H binding to Ag and Ir surfaces.

### 3.4.5 Computational Studies

Computational analyses were performed to obtain H binding energies on different Ag-Ir configurations on a model α-Al₂O₃ surface (Figure 3.11). The first principle DFT calculations were performed using Van der Waals corrections in VASP. The binding energy (B.E.) shows how strongly H atoms bind to the surface. A higher B.E. number (eV) indicates H binding is more energetically favorable.

H₂ binding to a Ag cluster and Ir@Ag were modeled in Figure 3.11A. The Ag and Ir atoms are drawn in silver and blue, respectively. Similar to the experimental and literature results, H₂ does not favor adsorption onto Ag. The B.E. of H to Ag was 0.19 eV which is very weak. Similarly, Ir@Ag has a low H binding energy (0.13 eV) and does not adsorb H₂. This agreed with experimental results where Ir@Ag systems exhibited decreased initial H₂ uptakes due to the burying of Ir by Ag.
Figure 3.11 Computational H binding energies of Ag-Ir systems on a model \(\alpha\)-Al\(_2\)O\(_3\) support. Ag is shown in grey. Ir is shown in blue.
Similar calculations was performed over Ir supported on a model α-Al₂O₃ surface (Figure 3.11B). H₂ has a strong affinity towards Ir clusters (2.99 eV) which is in agreement with experimental results. Another configuration investigated was a partial Ag shell. Here one Ir atom is exposed in the shell surface layer. H bind strength for this partial exposed Ir is also strong. Moreover, the stoichiometry of the H to Ir changes between the two configurations. In the larger bulk Ir clusters, H favors a 1:1 stoichiometry to Ir. However, when the Ir site gets smaller the stoichiometry changes to 2:1 H to Ir. This agrees with some literature results indicating H to Ir stoichiometry is above one for small nanoparticles of Ir [108, 109]. Interestingly, when an Ir atom is surrounded by 5 Ag atoms, it is energetically favorable for that Ir atom to adsorb 4 H atoms per Ir site. This is modeled in Figure 3.11C, where the H binding of the 1st pair and 2nd pair of H₂ molecules was 2.21 and 0.84 eV, respectively. These H atoms bind in a bridge type conformation between the Ag-Ir atoms.

The Ag-Ir system was modeled to determine if H₂ can dissociate on Ir and spillover to Ag (Figure 3.11D). This would give Ag some hydrogen capacity only when there is an Ir in close proximity for H₂ dissociation. The H binding energy for the spillover case is negligible at 0.01 eV. Therefore, H atoms cannot bind directly to Ag even if H₂ molecules are first dissociated into atoms.

Calculations were performed on the energetics of an Ir atom which is covered by a partial Ag shell (Figure 3.11E). Although the Ir is partial buried, it is energetically favorable for the Ag-Ir nanoparticle to undergo a reconstruction of atoms to expose the Ir for H₂ binding. The Ir can adsorb two H atoms with a B.E. of 0.98 eV. Upon removal of the H atoms, the Ir will reconstruct back into the partial Ag shell.
To summarize the computation studies, the H to Ir ratio can vary drastically depending on the morphology and arrange of Ag and Ir atoms. When Ir exists as a large cluster, the H to Ir ratio is 1 H per each Ir atom. As the Ir cluster becomes smaller and approaches single sites, the stoichiometry changes to 2 or 4 H atoms per Ir site. Although Ag does not strongly bind any H atoms, surface reconstruction of Ag-Ir systems may allow partial Ag shells to expose Ir atoms for hydrogen adsorption.

**3.5 Conclusion**

In conclusion, the combination of SEA and ED can form well-dispersed core-shell Ir@Ag nanoparticles on alumina supports. The Ag loading can be adjusted by changing reaction temperature, reducing agent, and reaction duration for the ED bath. Higher Ag coverages correlated to higher Ag wt. loadings and were determined through H$_2$ chemisorption. After high-temperature annealing treatments (400, 600, and 800°C), H$_2$ chemisorption behavior was found to be unexpectedly high for these Ag-Ir δθ-Al$_2$O$_3$ catalysts. H$_2$ TPD confirmed the addition of new bound species, and computational studies credit the additional H$_2$ capacity to changes in the adsorption stoichiometry of H to Ir (from 1:1 to 4:1 H to Ir atoms). The bimetallic core-shell catalysts exemplified improved catalyst stability over the monometallic counterparts through the retention (or addition) of active sites in H$_2$ chemisorption and the improved resistance to nanoparticle sintering through XRD and STEM nanoparticle analyses.
CHAPTER 4

THE CATALYTIC BEHAVIOR OF PRECISELY SYNTHESIZED PT-PD BIMETALLIC CATALYSTS FOR USE AS DIESEL OXIDATION CATALYSTS

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4.1 Abstract

The demands of stricter diesel engine emission regulations have created challenges for current exhaust systems. With advances in low-temperature internal combustion engines and their operations, advances must also be made in vehicle exhaust catalysts. Most current diesel oxidation catalysts use heavy amounts of precious group metals (PGMs) for hydrocarbon (HC), CO, and NO oxidation. These catalysts are expensive and are most often synthesized with poor bimetallic interaction and dispersion. The goal of this work was to study the effect of aging on diesel emission abatement of Pt-Pd bimetallic nanoparticles precisely prepared with different morphologies: well dispersed core-shell versus well dispersed homogeneously alloyed versus poorly dispersed, poorly alloyed particles. Alumina and silica supports were studied. Particle morphology and dispersion were analyzed before and after hydrothermal treatments by XRD, EDX, and STEM. Reactivity as a function of aging was measured in simulated diesel engine exhaust.

While carefully controlled bimetallic catalyst nanoparticle structure has a profound influence on initial or low temperature catalytic activity, the differences in behavior disappear with higher temperature aging as thermodynamic equilibrium is achieved. The metallic character of Pt-rich alumina-supported catalysts is such that behavior rather closely follows the Pt-Pd metal phase diagram. Nanoparticles disparately composed as well-dispersed core-shell (via seq-SEA), well-dispersed homogeneously alloyed (via co-SEA), and poorly dispersed, poorly alloyed (via co-DI) end up as well alloyed, large particles of almost the same size and activity. With Pd-rich systems, the oxidation of Pd also figures into the equilibrium, such that Pd-rich oxide phases appear in the high temperature forms along with alloyed metal cores. The small differences in activity after
high temperature aging can be attributed to the synthesis methods, sequential SEA and co-DI which give rise, after aging, to a bimetallic surface enriched in Pd.

4.2 Introduction

Diesel oxidation catalysts (DOCs) are a key part of a current diesel exhaust systems along with diesel particulate filters and selective catalytic reduction catalysts [46]. Current diesel oxidation catalysts for the treatment of hydrocarbons and NO are often heavy with precious group metals which makes them rather expensive. Pt is usually included in the DOC because NO oxidation is most active over Pt [27, 57, 116, 117]. Pt-only DOCs usually start with high initial activity for both HC and NO but are quickly deactivated after hydrothermal treatments. The primary cause for this loss of activity is due to Pt particle size growth and the loss of Pt dispersion due to high temperatures [57, 63, 86, 117-121]. However, other catalyst deactivation mechanisms also contribute to activity loss through support sintering, metal particle encapsulation, catalyst poisoning, and phase transformations [48, 85, 86, 122, 123].

Attempts to reduce the amount of Pt in current DOCs have been made by the addition of a second metal or modifying the support [48, 124-128]. Modifications include the addition of rare earth metals of BaO, La, or other oxygen storage compound in order to improve the activity and stability of the catalyst. Other metals studied for oxidation catalysts include combinations of Au, Co, Ni, and Pd on mixed oxide supports [129]. Bimetallic systems of Pt and Pd have been studied extensively and have been found to be promising DOCs for HC, CO, and NOx when compared to Pt-only catalysts [57, 63, 116-119, 125].
The Pt-Pd ratio has been found to be an important aspect of DOCs optimization for HCs and NO [63, 116, 117]. The dilution of Pt by a second metal not only reduces the cost of the DOC, but Pt-Pd bimetallic catalysts are often found to be more hydrothermally stable than Pt-only catalysts [57, 63, 116-118, 125]. These Pt-Pd bimetallic catalysts retain their dispersion and activity. However, the surface composition and particle morphology of these bimetallic catalysts often reconstruct after hydrothermal treatments. Many suggest that a surface enrichment of PdO occurs in an oxidative environment for Pd bimetallic catalysts [6, 57, 121, 129-132]. Most of these catalysts studied were synthesized by a simple co-impregnation method, which often lacks high metal dispersion and homogenous alloying.

The goal of this present study was to examine the behavior of bimetallic nanoparticles synthesized with precise compositions and morphologies, and their stability upon aging in a model diesel exhaust stream. We have reported the syntheses of these catalysts in a separate paper [26]: highly-dispersed core-shell and alloyed Pt-Pd bimetallic catalysts as well as single-metals supported on alumina and silica. The bimetallic core-shell structures were synthesized via sequential strong electrostatic adsorption (seq-SEA), and the bimetallic alloys were synthesized by simultaneous, or co-SEA. These are compared to traditional co-impregnated formulations. Catalyst performance was measured in a simulated diesel exhaust stream upon several aging conditions. Characterization by XRD, STEM, and EDX of fresh and aged samples provided insight to Pt-Pd particle morphology and size after a simulated catalyst lifetime.
4.3 Experimental

4.3.1 Catalyst Preparation

Detailed synthesis and characterization of the fresh catalysts can be found in [14]. Strong electrostatic adsorption (SEA) requires adjusting the initial pH of the solution to charge the support surface. Silica (Evonik Aerosil-300, BET area: 330 m²/g) and commercial γ-alumina (UOP VGL-25, BET area: 277 m²/g) catalysts were previously prepared by SEA [14]. Cationic precursors of tetraammine platinum(II) chloride (PTA) or tetraammine palladium(II) chloride (PdTA) were used over the low PZC SiO₂ for the noble metal cores. Anionic precursors of chloroplatinic acid (CPA) or sodium tetrachloropalladium (PdTC) were used as over Al₂O₃ for the noble metal cores. Sequential-SEA (seq-SEA) cycles on SiO₂ (CPA) and Al₂O₃ (PTA or PdTA) were used to form core-shell structures, and co-SEA syntheses were used to form homogenous alloys over SiO₂ (PTA and PdTA) and Al₂O₃ (CPA and PdTC). CPA and PdTC were used for the dry impregnation catalysts. HCl and NaOH were used to adjust the pH values for all solutions except for PdTC. PdTC was adjusted with HNO₃ and NH₄OH.

All fresh SEA catalysts were highly dispersed and in either core-shell or homogeneously alloyed morphologies. Dry Impregnation (DI) catalysts were synthesized using typical co-impregnation or incipient wetness. All catalysts were reduced (without calcination) in 10% H₂ balanced He prior to the initial evaluation, at conditions (150 – 210°C) identified by temperature programmed reduction [14]. The series of catalysts of different supports, Pt and/or Pd weight loadings and morphologies are shown in Table 4.1. Metal weight loadings of SEA-derived catalysts were typically set by the monolayer adsorption capacity of metal precursors on the respective supports. In some cases, repeated
cycles of SEA were employed to increase metal loadings so as to render metal loadings sufficiently high for characterization by STEM, X-ray maps, and XRD. While this meant that the atomic composition of metals could not be kept identical from case to case (Pt rich alumina, Pd rich alumina, and Pd rich silica catalysts), comparisons can be made directly between samples of a series, and cross comparisons can be made with due consideration of metal loading and particle size.

**4.3.2 Catalytic Activity**

Catalytic activity tests were performed at Oak Ridge National Lab at the Fuels, Engines and Emissions Research Center (FEERC). A model diesel exhaust feed consisting of 1500 ppm CO, 87 ppm C₃H₆, 87 ppm C₃H₈, 300 ppm NO, 10% O₂, 5% H₂O in Ar was used to evaluate the catalysts. A flow reactor with 35 mg of catalyst and a GHSV of 360,000 hr⁻¹ was heated to 500°C as a pretreatment, 750°C and held for 8 hours as a hydrothermal aging treatment, and heated again to 500°C for evaluation after hydrothermal aging. Figure 4.1 shows a temperature profile for the experiment. Gas concentrations were determined using a SRS RGA 100 mass spectrometer and Eco Physics CLD 822 NOx chemiluminescence.

![Temperature profile of the experimental setup. Ramp-up activities were measured at the indicated intervals.](image)

**Figure 4.1** Temperature profile of the experimental setup. Ramp-up activities were measured at the indicated intervals.
### Table 4.1 \(\text{Al}_2\text{O}_3\) and \(\text{SiO}_2\) catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Pt wt%</th>
<th>Pd wt%</th>
<th>Synth. Method</th>
<th>Initial Morphology</th>
<th>Initial Characterization [26] *this work</th>
<th>Pretr. @500°C</th>
<th>Aged@750°C</th>
<th>Morphology Transition</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Alumina support</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6.2Pt SEA</td>
<td>6.2</td>
<td>0</td>
<td>SEA</td>
<td>Pt-only</td>
<td>XRD (&lt; 1.5) nm *STEM 1.9 nm ± .6</td>
<td>5</td>
<td>15</td>
<td>11 ± 8 (\rightarrow) Pt</td>
</tr>
<tr>
<td>6.0Pt/1.28Pd seq-SEA</td>
<td>6</td>
<td>1.28</td>
<td>seq-SEA</td>
<td>Pt-core (Pt@Pd)</td>
<td>XRD 3.0 nm STEM 3.0 nm</td>
<td>9</td>
<td>20</td>
<td>26 ± 14 (\rightarrow) Pd-Pt</td>
</tr>
<tr>
<td>6.0Pt/1.28Pd co-DI</td>
<td>6</td>
<td>1.28</td>
<td>co-DI</td>
<td>Poorly Alloyed</td>
<td>Agglomerated</td>
<td>14</td>
<td>24</td>
<td>30 ± 16 (\rightarrow) Pd-Pt</td>
</tr>
<tr>
<td>5.3Pt/1.58Pd co-SEA</td>
<td>5.3</td>
<td>1.58</td>
<td>co-SEA</td>
<td>Homogenously Alloyed</td>
<td>XRD 2.0 nm STEM 1.7 nm</td>
<td>8</td>
<td>13</td>
<td>11 ± 7 (\rightarrow) Pd-Pt</td>
</tr>
<tr>
<td>2.0Pd SEA</td>
<td>0</td>
<td>2</td>
<td>SEA</td>
<td>Pd-only</td>
<td>XRD (&lt; 1.5) nm *STEM 0.8 nm ± .3</td>
<td>&lt; 2 nm</td>
<td>[12]</td>
<td>9.6 ± 20 (\rightarrow) Pd-Pt</td>
</tr>
<tr>
<td>2.0Pd/0.33Pt seq-SEA</td>
<td>0.33</td>
<td>2</td>
<td>seq-SEA</td>
<td>Pd-core (Pd@Pt)</td>
<td>XRD (&lt; 2) nm STEM 2.0 nm</td>
<td>[7]</td>
<td>11</td>
<td>[9] 7 ± 4 (\rightarrow) Pd-Pt</td>
</tr>
<tr>
<td>2.0Pd/0.33Pt co-DI</td>
<td>0.33</td>
<td>2</td>
<td>co-DI</td>
<td>Poorly Alloyed</td>
<td>Agglomerated</td>
<td>[13]</td>
<td>25</td>
<td>[17] 44 ± 23</td>
</tr>
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<td><strong>Silica support</strong></td>
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</tr>
<tr>
<td>4.0Pd SEA</td>
<td>0</td>
<td>4</td>
<td>SEA</td>
<td>Pd-only</td>
<td>XRD (&lt; 1.5) nm *STEM 1.6 nm ± .4</td>
<td>[4]</td>
<td>[6]</td>
<td>5 ± 2 (\rightarrow) Pd-Pt</td>
</tr>
<tr>
<td>4.0Pd/0.44Pt seq-SEA</td>
<td>0.44</td>
<td>4</td>
<td>seq-SEA</td>
<td>Pd-core (Pd@Pt)</td>
<td>XRD 2.0 nm</td>
<td>[9]</td>
<td>24</td>
<td>[8] 8 ± 7 (\rightarrow) Pd-Pt</td>
</tr>
<tr>
<td>3.2Pd/0.56Pt co-SEA</td>
<td>0.56</td>
<td>3.2</td>
<td>co-SEA</td>
<td>Homogenously Alloyed</td>
<td>XRD 1.3 nm STEM 1.1 nm</td>
<td>[8]</td>
<td>28</td>
<td>[8] 8 ± 6 (\rightarrow) Pd-Pt</td>
</tr>
<tr>
<td>4.0Pd/0.44Pt co-DI</td>
<td>0.44</td>
<td>4</td>
<td>co-DI</td>
<td>Poorly Alloyed</td>
<td>XRD 20 nm STEM 4.7 mn</td>
<td>19 [12]</td>
<td>34 [14]</td>
<td>21 ± 16 (\rightarrow) Pt-Pd</td>
</tr>
</tbody>
</table>

*Note: See text for detailed description of characterization methods and morphological transitions.*
4.3.3 Hydrothermal Aging

A separate hydrothermal aging procedure was performed in a benchtop flow reactor for catalyst characterization. These catalysts were treated at 500°C for 2 hours or 750°C for 8 hours in a feed of 1% CO, 10% H₂O, and 10% O₂ in N₂.

4.3.4 Post-Aging Characterization

Aged catalysts were characterized by x-ray diffraction (XRD) using a Rigaku MiniFlex II equipped with a high sensitivity D/tex Ultra Si slit detector with a nanoparticle size detection limit of about 1 nm [83]. Patterns were recorded from 10-80° 2θ using a Cu-Kα radiation source (λ=1.5406 Å) operated at 30 mA and 15 kV. The Scherrer equation was used to determine the bulk particle size, and peak location was used to determine oxide formation.

The electron microscopy images were taken at the University of Illinois at Chicago. A JEM-ARM200CF electron microscope capable of elemental mapping was used for determining particle morphology and size. This probe aberration corrected 200 kV microscope operated with a cold field emission source of 0.35 eV energy resolution. The microscope was equipped with a high steradian Oxford Instruments X-Max TLE 100mm² detector which permits elemental maps of nanoparticles even with insulating alumina and silica supports.

4.4 Results

4.4.1 Fresh Catalyst Characterization

Characterization of the fresh catalysts from [26] is summarized in the left hand side of Table 4.1. Additional STEM characterization of the fresh single metal Pt/alumina, Pd/alumina, and Pd/silica catalysts synthesized with SEA, shown in later Figures 4.4a,
4.5a, and 4.6a, respectively gave STEM-determined sizes of 1.9, 0.8, and 1.6 nm which agree with the prior XRD undetectability. The core-shell catalysts prepared by sequential SEA (Pd@Pt or Pt@Pd), confirmed to have that morphology in the previous work [26] were also small in size. The Pd shell on alumina supported Pt were 3.0 nm in diameter, the Pt shells on alumina supported Pd were 2 nm in diameter, and the Pt shells on silica supported Pd were 2 nm in diameter. Simultaneous SEA (or co-SEA) Pt/Pd nanoparticles were 1.7 nm on alumina, and 1.1 nm on silica. SEA gives the ability to make highly dispersed single metal, or bimetallic homogeneous alloyed or core-shell particles. The co-DI versions of each catalyst were initially poorly alloyed and agglomerated.

4.4.2 Initial and Aged Catalytic Activity

The activity of the fresh and aged catalysts was determined using light-off curves of the total reductants in the stream; CO₂ was the only carbon product. The light-off curves follow the characteristic shape of CO light-off, where CO inhibition prevents O₂ from reaching the catalytic surface until a certain temperature, followed by a steep rise in conversion aided by the exothermal oxidation of CO.

The light-off curves of the reductants for the Pt-rich alumina catalysts are shown in Figures 4.2a-d. Starting with the Pt-only, SEA-prepared catalyst designated as 6.2Pt SEA (Figure 4.2a), the initial activity was greatest with a T₅₀ of 190°C. A pretreatment at 500°C for 2 hours did not significantly affect the T₅₀; however, some of the low temperature activity was lost. After aging this catalyst at 750°C for 8 hours, a large decrease in activity was observed giving a T₅₀ of 264°C.

Light-off curves after adding a Pd-shell to the Pt catalyst (Pt@Pd) can be observed in Figure 4.2b for the 6.0Pt/1.28Pd seq-SEA catalyst. The initial activity was again greatest.
with a T$_{50}$ of 115°C; large decreases in activity followed pretreatment at 500°C and aging at 750°C. Notable low-temperature activity was observed for the fresh catalyst, indicated by the broad light-off curve of the initial ramp which began at just over 50°C, but this disappeared after pretreatment. The T$_{50}$ of the pretreated and aged catalyst rose to 155° and 200°C, respectively.

Results for the initially poorly dispersed, poorly alloyed Pt/Pd catalyst prepared by co-DI, (6.0Pt/1.28Pd DI) are shown in Figure 4.2c. For this sample, the pretreatment and aging actually improved the performance somewhat, such that the activity of the aged sample was as good as the aged core-shell sample of Figure 4.2b, with a T$_{50}$ of 200°C. Results of the initially well dispersed, homogeneous alloyed Pt/Pd catalyst via co-SEA (5.3Pt/1.58Pd co-SEA) are shown in Figure 4.2d. This sample displayed the most stable performance of all catalysts, with the T$_{50}$ decreasing about 10°C to 227°C after aging.

The palladium-rich, alumina-supported catalysts are shown in Figures 4.2e-g. The light-off curve for the well dispersed Pd-only catalyst (2.0Pd SEA) is shown in Figure 4.2e. Initial activity was lowest while the activity after pretreatment was highest. The T$_{50}$ of the aged sample slightly rose to 227°C.

The addition of a Pt shell to the Pd catalyst to form a Pd@Pt morphology (Figure 4.2f) greatly improved the initial activity of the catalyst, but the activity decreased upon pretreatment and then increased after aging by 5°C to a T$_{50}$ of 233°C, a few degrees higher than the Pd-only catalyst. Results of the analog DI catalyst on alumina (2.0Pd/0.33Pt DI) are shown in Figure 4.2g. Similar to the Pd-only catalyst (Figure 4.2e), initial activity was very low (T$_{50}$ about 325°C), and pretreating and aging the catalyst ultimately improved the T$_{50}$ to 242°C.
Finally, results of the palladium-rich series of catalysts on silica are given in Figure 4.3; the Pd-only catalyst is shown in Figure 4.3a. Unlike the Pd-only alumina catalyst which exhibited low initial activity ($T_{50} = 285^\circ$C), the initial activity was high ($T_{50} = 125^\circ$C) for the Pd-only silica catalyst. Activity decreased significantly with pretreatment and aging, such that the $T_{50}$ for the aged catalyst was 252$^\circ$C. Light-off curves from the addition of a Pt-shell to the Pd core (Pd@Pt, 4.0Pd/0.44Pt seq-SEA) are shown in Figure 4.3b. Adding Pt as a shell lowered the initial activity but reduced the deactivation from pretreatment and aging such that the aged $T_{50}$ was of 233$^\circ$C, about 20 degrees higher than the Pd-only catalyst in Figure 4.3a.

Results of the initially poorly alloyed, poorly dispersed co-DI catalyst (4.0Pd/0.44Pt DI) are shown in Figure 4.3c. Initial activity is once again the lowest and activity increases with additional pretreatment and aging, ending with a series-best $T_{50}$ of 218$^\circ$C. The initially well dispersed co-SEA catalyst (3.2Pd/0.56Pt co-SEA), shown in Figure 4.3d, yielded high initial activity but was much less stable than its alumina counterpart (Figure 4.2d), as the $T_{50}$ increased from pretreatment to aging and ended at 239$^\circ$C.

### 4.4.3 Aged Characterization

XRD was used to determine the sintering and oxidation which occurred during pretreatment and aging. STEM images and elemental maps provided a second estimate of particle size and revealed the structures of bimetallic nanoparticles.
Figure 4.2 Light-off temperatures for the total reductants to CO2 for the alumina catalysts: a) 6.2Pt SEA, b) 6.0Pt/1.28Pd seq-SEA Pt@Pd, c) 6.0Pt/1.28Pd DI, d) 5.3Pt/1.58Pd co-SEA, e) 2.0Pd SEA, f) 2.0Pd/0.33Pt seq-SEA Pd@Pt, g) 2.0Pd/0.33Pt DI.
The number average size is reported for STEM as the small number of particles imaged and wide particle size distribution gave artificially high volume averages. A comparison between the STEM and XRD particle sizes as well as cartoons of the aging process is included in right hand side of Table 4.1.

**Alumina Supported Catalysts**

Characterization of the series of Pt-rich alumina catalyst is given in Figure 4.4. The 6.2Pt SEA (Figure 4.4a) initially started with small (XRD transparent, sub-2 nm) particles which sintered to a XRD particle size of 5 and 15 nm after pretreating and aging, respectively, as calculated from the sharpened fcc Pt peaks at (111), (200), and (220) at 40°, 46°, and 68° 2θ. Size estimates of the aged and fresh Pt-only catalyst in Figure 4.4a are in reasonable agreement with the STEM size estimates. The Pt@Pd core-shell 6.0Pt/1.28Pd seq-SEA catalyst is characterized before and after aging in Figure 4.4b. The particles initially were 3 nm [14] and sintered to 9 and 20 nm, for the 500°C and 750°C aged samples. Formation of a small amount of PdO ((101) peak at 33.9° 2θ) was also observed after 500°C pretreatment, but the oxide disappeared after the high temperature aging step. (The rise in the peak at 32° 2θ is from the sintering of the alumina phase, seen in this and all other peaks of the aged alumina patterns in Figures 4.4 and 4.5.) Micrographs in Figure 4.4b for the aged sample suggest a slightly larger particle size at 26 nm. Elemental maps, of which a representative image is given in Figure 4.4b, revealed that the Pd initially in a shell [14] dissolved mostly into the Pt core, although a small percentage of images indicated the retention of some Pd surface enrichment.
Figure 4.3 Light-off temperatures for the total reductants to CO2 for the Pd-rich silica catalysts: a) 4.0Pd SEA, b) 4.0Pd/0.44Pt seq-SEA Pd@Pt, c) 4.0Pd/0.44Pt DI, d) 3.2Pd/0.56Pt co-SEA. (Initial morphologies are depicted in the insets.)
Characterization of the 6.0Pt/1.28Pd DI catalyst is given in Figure 4.4c. The initial particles were agglomerated and poorly alloyed [14]. After pretreating the DI catalyst at 500°C, a crystalline peak for PdO was observed similar to the co-SEA catalyst at 500°C, and the metallic particle size was around 14 nm. Aging at 750°C again decomposed the oxide and sintered the particles to 24 nm. Representative STEM images and elemental maps for the aged DI sample (Figure 4.4c) revealed that the large nanoparticles were virtually all homogeneously alloyed. The STEM size estimate at 30 nm, is in reasonable agreement with XRD.

The addition of Pd to the Pt catalyst via co-SEA produced alloyed particles <2 nm confirmed by XRD and STEM [14]. Metallic peaks are noticeable in Figure 4.4d for the pretreated 500°C and aged 750°C samples, with the higher temperature aged sample having sharper XRD peaks correlating to a particle size of 13 nm. Pd or Pd-rich oxide formation was observed in the 500°C aged sample at 33.9°, 41.9°, and 54.8° 2θ for the (101), (110), and (112)/(211) planes. No PdO peaks were observed for the sample aged at 750°C, suggesting that decomposition of PdO occurs at elevated temperatures. STEM images and elemental maps were taken after aging at 750°C (representative images shown in Figure 4.4d). The STEM particle size of 11 nm agrees reasonably with the XRD size of 13 nm. Elemental maps (typical map in Figure 4.4d) indicated homogeneous alloying of the high temperature sintered particles.
Figure 4.4 XRD patterns, STEM images, and elemental maps of Pt-rich alumina catalyst after hydrothermal aging. Elemental map colors are yellow for Pt and red for Pd. a) 6.2Pt SEA, b) 6.0Pt/1.28Pd seq-SEA Pt@Pd, c) 6.0Pt/1.28Pd DI, d) 5.3Pt/1.58Pd co-SEA.
<table>
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<tr>
<th>XRD</th>
<th>STEM (Aged)</th>
<th>STEM (Fresh)</th>
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<tr>
<td><strong>a) Pd-only</strong></td>
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<th>XRD</th>
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<td><strong>b) seq-SEA</strong></td>
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<td><strong>c) co-DI</strong></td>
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**Figure 4.5** XRD patterns, STEM images, and elemental maps of Pd-rich alumina catalyst after hydrothermal aging. Elemental map colors are yellow for Pt and red for Pd. a) 2.0Pd SEA, b) 2.0Pd/0.33Pt seq-SEA Pd@Pt, c) 2.0Pd/0.33Pt DI
Characterization of the Pd-rich alumina series is shown in Figure 4.5. Initially and after 500°C pretreatment of the 2.0Pd SEA Pd-only catalyst, the Pd particles were too small to be detected by XRD (Figure 4.5a). STEM images revealed a fresh particle size of 0.8 nm. After 750°C aging, only peaks from PdO were observed at 33.6°, 33.9°, 41.9°, 54.8°, and 71.6° 2θ. The peak breadths indicated an XRD particle size of 12 nm. This is in reasonable agreement with the STEM size estimate of 9.6 nm. Characterization for the Pt shell on Pd by seq-SEA is given in Figure 4.5b. Particle size was initially around 2 nm; aging the sample at 500°C gave oxide particles of about 7 nm in diameter. Further aging to 750°C increased the size of the oxide phase to 9 nm and created a metallic (111) peak around 11 nm in size. STEM images in Figure 4.5b indicated an average particle size of 7 nm, in rough agreement with the XRD particle size. Representative elemental maps of this catalyst (Figure 4.5b, right) revealed significant fractions of both alloyed and Pd surface-enriched particles.

Characterization of the 2.0Pd/0.33Pt DI catalyst is given in Figure 4.5c. Particles initially started on the small side due to the CEDI (charge enhanced dry impregnation) effect [14], but after aging at either 500 or 750°C, both sharp metallic and oxide XRD peaks existed. These peaks were the sharpest in the Pd-rich alumina catalyst series and corresponded to an aged at 750°C XRD particle size of 17 and 25 nm for the oxide and metallic peaks, respectively. STEM and elemental maps in Figure 4.5c show agglomerated particles and inhomogeneous morphology of the Pt-Pd. Significant phase separation occurred, with Pd being enriched on the surface. The large discrepancy of STEM and XRD can be explained by the presence of facets in the large agglomerates imaged in STEM.
Silica Supported Catalysts

Characterization of the Pd-rich silica-supported catalysts is shown in Figure 4.6. XRD patterns for the Pd-only 4.0Pd SEA catalyst is shown in Figure 4.6a. Initially too small to be detected, particles of PdO grew upon aging, to 4 nm after 500°C and to 6 nm after 750°C. XRD is in reasonable agreement with STEM, which showed a particle size of 1.6 nm for the fresh catalyst and 5 nm for the aged. Results of the seq-SEA-derived Pd@Pt sample are shown in Figure 4.6b. Initially metallic particles formed oxides when treated at 500°C. Further aging to 750°C created an addition set of sharp (111), (200), and (220) metallic peaks which indicated a particle size of 24 nm. The oxide particle size after 500 and 750°C were 9 and 8 nm, respectively. STEM images in Figure 4.6b show particles homogenously distributed across the silica surface. STEM particle size at 8 nm agrees with the oxide formation XRD size, but no evidence of the larger metallic particles were observed in the micrographs; this could be due to the small sampling area of STEM. Elemental maps in Figure 4.6b suggest the formation of alloyed particles, although some images indicate a few Pd@Pt core-shell remaining.

Results for the 4.0Pd/0.44Pt DI catalyst are shown in Figure 4.6c. The initial particle size of this sample had the sharpest XRD peaks, indicating the largest initial particle size. Crystalline peaks at 22° and 32.2° 2θ in the initial XRD pattern were due to salt (NaCl) left over from the DI preparation. These peaks disappeared at higher temperatures as Pt-Pd metallic and Pd oxide peaks form in both the 500 and 750°C aged samples. The XRD particle size for the oxide peaks for the 500 and 750°C aged samples are 12 and 14 nm, and the XRD particle size for the metallic peaks are 19 and 34 nm, respectively.
**Figure 4.6** XRD patterns, STEM images, and elemental maps of Pd-rich silica catalyst after hydrothermal aging. Elemental map colors are yellow for Pt and red for Pd. a) 4.0Pd SEA, b) 4.0Pd/0.44Pt seq-SEA Pd@Pt, c) 4.0Pd/0.56Pt DI, d) 3.2Pd/0.56Pt co-SEA
The micrographs in Figure 4.6c showed large particles that averaged 21 nm in size. Elemental maps for this catalyst showed an enrichment of PdO on the metal surface; this can also be seen in the Z-contrast images.

An initially homogeneously alloyed catalyst prepared by co-SEA (3.2Pd/0.56Pt co-SEA) is shown in Figure 4.6d. Similar trends as for the Pd@Pt catalyst were observed. Oxide particle size was 8 nm for both aging conditions, and sharp metallic peaks indicating 28 nm were observed in the sample aged at 750°C. The elemental maps and STEM in Figure 4.6d indicate large, alloyed particles but also smaller particles about 8 nm composed entirely of Pd (as PdO). (The single-pixel spots of color seen in the maps of Figure 4.6d are noise stemming from the difficulty of mapping small, individual nanoparticles; no individual atoms were observed in the Z-contrast images.)

4.5 Discussion

A number of factors might account for differences in reactivity brought on by high temperature aging of bimetallic catalysts:

1) Sintering/loss of metal sites

2) Change in degree of alloying; enhanced mixing vs. surface segregation vs. separation of metals

3) Change in the oxidation state of the metal

4) Elimination of residual salts from catalysts prepared by dry impregnation.

As will be discussed below, the first three considerations appear operative in correlating the reactivity data in Figures 4.2 and 4.3 with the characterization data in Figures 4.4-4.6.
4.5.1 Single Metal Catalysts

It is helpful to make an initial comparison of the reactivity of variously aged single metal catalysts, 6.2 wt% Pt/alumina, 2.0 wt% Pd/alumina, and 4.0 wt% Pd/silica. The respective activity of these catalysts is seen in Figures 4.2a, 4.2e, and 4.3a, while the characterization is seen in Figure 4.4a, 4.5a, and 4.6a.

The reduction in activity of the Pt-only, alumina-supported catalyst (Figure 4.2a) diminished with pretreatment and aging as would be expected as the particles grow from 1.9 (fresh) to 5 (pretreated) to 15 nm (aged). Sintering in-situ in the first temperature run-up is likely the cause of the irregularities in the initial light off curve. The large gap in $T_{50}$ from the pretreated to the aged sample, however, suggests more than sintering. Typical activation energies for this reaction are near 100 kJ/mol [48, 133, 134], for which rates double every 10°C. An increase in particle size from 5 to 15 nm would eliminate two thirds of surface sites, or about 15°C of activity, but the gap is about 60°C. A plausible explanation is that the reaction is structure sensitive, with smaller particles being more active. Work by the Ozawa group has found that increased Pt dispersion aids in HC and CO activity; however, they observed a significant support effect when comparing activities over different alumina supports [135, 136].

In the case of Pd, highly-dispersed Pd has been cited to be more active for CO oxidation than poorly dispersed Pd [55]. The Datye group observed the highest CO activity over atomically dispersed Pd supported on lanthanum modified alumina [137]. Others have claimed the dispersion of the metal has less effect on activity than does Pd oxide formation [138-140]. In the current results, the Pd-only catalysts display an interesting contrast in behavior which contains elements of both size and oxidation effects. The
alumina-supported catalyst (Figure 4.2e) is initially relatively inactive, requiring some sort of activation, while the silica supported catalyst (Figure 4.3a) is immediately active and deactivates substantially with aging. In the latter case, the large gaps in activity between fresh, pretreated, and aged light off curves is more than can be justified with only sintering. On silica the initial Pd particles size is less than 2 nm (Pd is XRD transparent) and sinters to 4 and 6 nm (Table 4.1) Pd oxide after pretreatment and aging. The reduction of active area by about half and then again by about 40% (from 4 to 6 nm) is again incommensurate with the large changes in T_{50} and again suggests a particle size effect with smaller PdO particles having higher inherent activity. Behavior over the different supports can be explained by PdO and not metallic Pd being the active Pd species for the oxidation reaction, which is often cited in the literature [126, 138, 139, 141-144], and that silica stabilizes Pd oxides when Pd exists as very small particles, while alumina does not. The spontaneous oxidation of small Pt particles on silica and alumina has been recently documented [76, 145]. Over alumina, Pd particles do not significantly sinter after the 500ºC pretreatment (Figure 4.5a; Pd phase is still unobservable) so the large increase in activity in Figure 4.2e can be attributed to the oxidation of metallic Pd nanoparticles. The effect of Pd oxidation state would then best be compared for the initial and pretreated Pd-only catalysts over alumina, which are about the same size (< 1.5 nm). The relatively small decrease in activity from the 500ºC pretreatment to the 750ºC aging of about 10 degrees is perhaps more commensurate with a loss of active area due to sintering.

Low initial reactivity and Pd activation occurs in three other cases – all the co-DI prepared samples (Figure 4.2c, 4.2g, and 4.3c). These DI-derived samples all contain Pd particles that are initially large and metallic (XRD patterns of Figures 4.5c, 4.6c, and 4.7c).
Ambient oxidation only happens in the smallest particles [76, 145] and so would not occur over the co-DI silica catalyst (Figures 4.3c and 4.6c). Also, the activation of the SEA-derived Pd-only catalyst over alumina is just as dramatic as those of the co-DI catalysts, and occurs to the same extent for the tetraammine coordination complex (Pd precursor over silica) as for a tetrachloride complex (Pd precursor over alumina). Thus, it can be suggested that the activation of the co-DI catalysts is mainly caused by the oxidation of Pd to PdO and not removal of residual salt.

Once oxidized, PdO has the highest intrinsic activity on alumina; 2 wt% catalysts with 12 nm size (Figure 4.5a and Table 4.1) show a $T_{50}$ of 227°C versus 4 wt% Pd on silica with 6 nm particles (Figure 4.6a) which has a $T_{50}$ after aging of 252°C; the silica supported PdO has twice the loading and twice the dispersion, so about 4 times more active sites but is 25°C (about 5 times) less active. Pd/alumina is also more active than Pt/alumina, as the 2.0 wt%Pd catalysts in Figure 2e with 12 nm size (Figure 4.6a and Table 4.1) have a $T_{50}$ (227°C, Figure 4.2e) lower than that ($T_{50} = 264°C$, Figure 4.2a) of 6.2 wt% Pt with 15 nm particles (Figure 4.4a, Table 4.1). The PdO has about 20% less active area but is 37°C more active.

4.5.2 Summary: Single Metal Catalysts:

PdO is the active Pd phase and the presence of metallic Pd in the fresh alumina catalyst causes low initial reactivity. Activity increases as it oxidizes, but decreases as the PdO phase sinters. Unlike over alumina, Pd on silica oxidizes spontaneously and exhibits high fresh activity. The drop off in reactivity over silica with sintering is incommensurate with increasing particle size (loss of active area) and suggests that smaller particles are
intrinsically more active. In the aged catalysts, PdO on alumina is more active per site than Pt on alumina, and Pd on alumina has higher intrinsic activity than Pd on silica.

### 4.5.3 Pt Rich, Alumina Supported Catalysts

Reactivity as a function of aging (Figure 4.2a-d) can now be compared for bimetallic catalysts in which Pd has been added to the Pt-only catalyst in three distinct ways; as a partial outer shell on well dispersed, SEA-derived Pt cores (the 6.2wt% Pt-only catalyst), as homogeneous, highly initially dispersed alloys via co-SEA, and as more poorly alloyed, larger, agglomerated particles via co-dry impregnation (Figure 4.4 and Table 4.1). The co-DI catalyst is seen in Figure 4.4c to have initial metal particles of about 10 nm in size; these are agglomerated and poorly alloyed [14]. The core-shell Pt@Pd catalyst prepared via seq-SEA [14] has initial size of about 3.0 nm (Figure 4.4b), while the fresh homogeneously alloyed [14] co-SEA particles are about 1.7 nm in average size (Figure 4.4d).

Adding a Pd shell to Pt produced the highest activity of fresh catalysts seen in this study; light off began at just over 50°C (Figure 4.2b). While this catalyst has a higher metal loading (an additional 1.28wt% Pd) than the Pt-only catalyst, the Pd has selectively adsorbed onto the Pt nanoparticles [26] such that no additional metal surface has been created, but only a bimetallic one. This must be a bimetallic effect as the partially covered surface is much more active than either the fresh activity of the well-dispersed Pt-only (Figure 4.2a) or PdO-only (Figure 4.3a) surfaces alone. Activity diminished considerably with pretreatment and aging as the average particle size grew from 3 to 9 and then 20 nm. These Pt-rich particles remain metallic in general (XRD patterns in Figure 4.4b) but small amounts of PdO form at the intermediate aging temperature. This is in accord with the Pt-
Pd solubility gap in the phase diagram [146]. As the Pd separates from the Pt phase it likely forms a relatively pure (unalloyed) PdO phase. The diagram also indicates that solubility commences at about 770ºC, and in fact the disappearance of the oxide peaks after the high temperature aging appears to bear this out. Unfortunately the lattice parameters of Pt and Pd are too close to identify the composition of the metal phase which reforms at high temperature.

The initially large and poorly alloyed co-DI particles show activation, as mentioned above, which is consistent with the initial presence of separate, large Pd metal particles. The sample also shows PdO at the intermediate temperature and then, only metal at the highest temperature treatment (Figure 4.4c), as occurred for the seq-SEA catalyst. STEM images (Figure 4.4c) reveal that the large particles are in fact well alloyed; thus, the alumina support has not been able to hinder high temperature equilibration to sintered, alloyed bimetallic particles. Another indication of metal-metal-support phase equilibrium is that the high-T aged activity of both catalysts is the same, T$_{50}$ = 200ºC, at about the same particle size (20 vs. 24 nm by XRD, 26 vs. 30 nm by STEM, Table 4.1).

The behavior of the alumina supported co-SEA catalyst is the most stable of all catalysts, with only a very small increase in T$_{50}$ (Figure 4.2d) as the nanoparticles grow from 1.7 to 8 to 13 nm (Figure 4.4d and Table 4.1). XRD characterization is similar to the seq-SEA catalyst with some oxide appearing at the intermediate temperature, which reverts to all metal at the highest temperature. STEM confirms homogeneous alloying at the highest temperature. The aged particles are somewhat smaller (13 nm) while the activity is substantially lower (T$_{50}$ = 227 vs. 200ºC) than the seq-SEA and co-DI samples. The relatively insensitivity of activity to particle sintering and the low relative reactivity both
suggest that the surface composition of the co-SEA catalyst is somewhat different from the other two (seq-SEA and co-DI) high T-aged catalysts. While the Pd/Pt ratio is a bit higher for the co-SEA sample, that it is more homogeneously alloyed would suggest that its Pd surface concentration is lower than the other two catalysts, leading to a lesser bimetallic surface effect.

4.5.4 Summary: Pt Rich, Alumina Supported Catalysts

Pd shells on Pt/alumina cores prepared by seq-SEA gave the highest initial activity of any catalyst in this study; this can be attributed to a bimetallic surface effect which is different from the fresh surface of homogeneous Pd/Pt alloys prepared by co-SEA. Aging sinters the co-SEA catalyst the least, but its activity is still below the sintered seq-SEA and co-DI catalysts, which may retain a more optimal surface composition higher in Pd. In the best cases, adding Pd to Pt improved the activity by lowering the T50 by 64°C.

4.5.5 Pd Rich, Alumina Supported Catalysts

Adding Pt as a shell onto Pd cores (Figures 4.2f) completely changes the nature of the active surface, as initial activity was not suppressed as in the Pd-only and co-DI catalysts (Figures 4.2e and g). The decrease in activity of the seq-SEA catalyst in Figure 4.2f appears to be proportional to the degree of sintering as the particles grow from 2 to 7 (oxide) and then 11/9 (metal/metal oxide) nm (Figure 4.5 and Table 4.1). Too small to be observed by XRD when fresh, the oxide phase (Pd or Pd-rich) appears again after intermediate aging but persists after the high temperature aging, likely due to the much higher Pd content. STEM images reveal alloyed particles, some of which appear to be surface enriched in Pd (Figure 4.5b, presumably PdO from XRD). Thus it appears the surface has undergone extensive reorganization if not a complete inversion in composition.
Surface enrichment of PdO is also suggested from the similar activity of the aged seq-SEA catalyst to the Pd-only catalyst.

The co-DI catalyst maps (Figure 4.5c) also did not appear to be as homogeneously alloyed as the seq-SEA catalyst or the Pt-rich alumina catalysts. High T-aged activity was poorer than the Pd-only catalyst, probably due to the large particle size (Figure 4.5c and Table 4.1).

It is informative to compare the Pd-only (PdO)/silica catalyst in Figure 4.2e with the Pt rich, Pt/Pd co-SEA catalyst of Figure 4.2d. Both have the same aged activity (T50 = 227°C) and both have about the same particle size. The weight loading of Pd is 2.0%, while the total metals in the Pt rich catalyst are 6.9%. The Pd-only catalyst has perhaps 50% less active sites but is as active on the whole. On the other hand, the Pt/Pd co-SEA catalyst in Figure 4.2d is not as active as the seq-SEA and co-DI Pt-rich catalysts in Figures 4.2b and c. Both of these comparisons are consistent with the discussion in the previous section that to be most active, Pd must be at the surface of the bimetallic particles.

4.5.6 Summary: Pd Rich, Alumina Supported Catalysts

Adding a Pt shell to Pd/alumina particles eliminated the need for the activation (oxidation) of the Pd particles and gave higher initial activity. However, in aged catalysts, the addition of Pt did not increase activity compared to the Pd-only catalyst.

4.5.7 Pd Rich, Silica Supported Catalysts

The final case is adding a Pt to silica supported Pd; activity trends are seen in Figure 4.3 and characterization is shown in Figure 4.6 and summarized in Table 4.1. Adding a Pt shell to a Pd-core catalyst greatly retarded the activity of the fresh catalyst (Figures 4.3a and b). This is opposite of the behavior over alumina, where addition of Pt to the alumina
supported Pd greatly increased activity (Figure 4.2f). But that was because the Pd/alumina, even at small size, appears to be metallic and must be oxidized to become active. On silica, the Pd-only catalyst is already oxidized and most active. Adding Pt to it keeps it in a reduced, metallic state after preparation (initial XRD pattern in Figure 4.6b) and therefore at low activity. With higher temperature treatments the metals can rearrange. A Pd oxide phase once again appears at the intermediate temperature, and like the Pd-rich alumina and the other silica catalysts, persists through high temperature aging. The reduction in activity is commensurate with particle growth from 2 (metal) to 9 (oxide) to 24/8 (metal/oxide) nm. The STEM images revealed virtually all alloyed particles (Figure 4.6b). As XRD confirms that Pd is wholly present as PdO, it must be that Pt is dissolved in the PdO lattice, at least at the intermediate aging temperature where no metal phase appears (500 aged in Figure 4.6b). More of a metal phase does appear after high temperature aging. Again, unfortunately, the lattice parameters of Pt and Pd are too close to identify the composition of the metal phase.

The co-DI catalyst behaves as the other two co-DI catalysts, with activity improving upon high temperature treatment (Figure 4.3c) as the particles become more alloyed (Figure 4.6c). The low initial activity is again associated with large particles of metallic Pd as seen in the initial XRD pattern of Figure 4.6c. Intermediate pretreatment generates mostly the oxide phase, which persists, with somewhat more metal, after high temperature aging. The Pd-rich surface layers seen in STEM (Figure 4.6c) should be oxide, per XRD (Figure 4.6c), and the alloying in this layer is indicated by this catalyst’s higher activity, $T_{50} = 218^\circ$C, with larger particles (34/14 nm metal/oxide), than the pure PdO catalyst ($T_{50} = 252^\circ$C, particle size 6 nm).
The silica-supported, Pd-rich co-SEA-derived nanoparticles show somewhat different behavior than alumina-supported, Pt-rich ones. In the latter case, the Pt-rich particles remained largely metallic and alloyed through treatment. Over silica, a significant fraction of Pd-only particles were evidenced in STEM maps, with another fraction of alloyed particles. The same affinity of the silica surface for Pd that causes small supported Pd particles to oxidize at ambient conditions may also stabilize pure PdO particles as they form, separately from Pt, at the intermediate aging step. The activity of the silica-supported co-SEA sample is not nearly as insensitive to aging as the alumina supported catalyst (Figure 4.2d), probably because of this separation of components during aging. Ultimately, the three Pt-containing aged catalysts have higher activity than the Pd-only catalyst, even though the bimetallic particles sizes are larger (Table 4.1). This is yet further evidence that a bimetallic surface enriched in Pd is the most active catalyst surface.

4.5.8 Summary: Pd Rich, Silica Supported Catalysts

Adding Pt shells to Pd cores on silica diminishes the initial activity due to the presence of Pt, retaining Pd in the metallic state. The addition of Pt to Pd/silica gives higher activity of aged catalysts, unlike over alumina, where the addition of Pt diminished aged activity.

4.6 Summary

While carefully controlled bimetallic catalyst nanoparticle structure has a profound influence on initial or low temperature catalytic activity, the differences in behavior mostly disappear at higher aging temperatures as thermodynamic equilibrium is achieved. The metallic character of Pt-rich alumina-supported catalysts is such that behavior rather closely follows the Pt-Pd metal phase diagram. Nanoparticles as disparately composed as
well-dispersed core-shell (via seq-SEA), well-dispersed homogeneously alloyed (via co-SEA), and poorly dispersed, poorly alloyed (via co-DI) end up as well alloyed, large particles of almost the same size and activity. With Pd-rich systems, the oxidation of Pd also figures into the equilibrium, such that Pd-rich oxide phases appear after the high temperature aging along with alloyed metal cores. The small differences in activity after aging can be attributed to the synthesis methods, sequential SEA and co-DI which give rise, after aging, to a bimetallic surface enriched in Pd.

From a practical standpoint, the preparation method for catalysts to be pretreated or aged at such high temperatures is relatively inconsequential over typical alumina and silica supports. Further improvements in performance, utilizing these two metals, might focus on support modifications which anchor the nanoparticles against sintering; over these sorts of supports the initial morphology will be more important.

Acknowledgements

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CHAPTER 5

HIGHLY DISPERSED PT-PD BIMETALLIC CATALYSTS FOR DIESEL EXHAUST TREATMENT
5.1 Introduction

Stricter vehicle emission regulations and recent advances in engine development have pushed the development of exhaust aftertreatment technologies. Advancements in engine technologies have improved automobile efficiency; however, as engines become more advanced, they waste less energy through heat in the exhaust. The lower heat dissipated results in engines with exhaust temperatures far cooler than before. Therefore, a strong need exists to improve the low-temperature activity of aftertreatment catalysts. Established by U.S. DRIVE in 2015, the target for diesel exhaust emissions is 90% conversion of all hydrocarbons by 150°C.

Diesel oxidation catalysts (DOC) have always used noble metals. Pt is the most commonly implemented noble metal in commercial DOCs [48]. The need for Pt arises from its excellent oxidation activity and high resistance to sulfur poisoning. Although expensive, these traits made the use of Pt in DOCs almost ubiquitous. Pd is another noble metal that has been given a lot of interest in aftertreatment systems [61, 63, 65, 116-118, 125]. The price of Pd compared to Pt has fluctuated in the last several decades. When DOCs were first incorporated, Pd was similarly priced to Pt. When the price of Pd dropped in 2002, there was a strong economic incentive to replace some Pt with Pd. However, recently the differences in price between Pt and Pd are negligible. Two other technologies added the transition from Pt-only catalyst to Pt-Pd. Firstly, the sulfur content in US diesel fuel has drastically reduced from over 2000 ppm before 1990 to less than 15 ppm by 2006 [147]. This prevents a large amount of sulfur poisoning over Pd. Secondly, the introduction of a diesel particular filter (DPF) and more importantly the regeneration cycle for DPFs now raised the DOC temperature and promoted sulfurization.
Many works found the combination of Pt-Pd in aftertreatment systems to be beneficial. Most credit improved stability of Pt-Pd nanoparticles compared to Pt alone as the reason for enhanced performance [50, 57, 63, 65, 125, 148]. The Datye group has studied the mechanisms of Pt sintering in oxidizing environments, and depending on the temperature, particle agglomeration through Ostwald ripening or ad atom vaporous PtO$_2$ agglomeration occurs [56]. The addition of Pd can capture the atoms of PtO$_2$ and form Pt-Pd alloys, and these Pt-Pd surface alloys also prevent the emission of PtO$_2$ [56, 58]. This retention of dispersion and active sites in bimetallic catalysts often leads to improved catalyst activity after simulated ageing procedures, whereas severe deactivation occurred on the monometallic counterparts.

Support modification can also have an effect on catalyst activity. These catalysts experience hydrothermal conditions which leads to support degradation and phase transformations. Alumina is the most commonly used commercial support due to its high surface area and stability. Modifications to alumina can further improve support and nanoparticle stability. When La or Si was added to Al$_2$O$_3$, the supports experienced increased stability [149, 150]. Moreover, lanthanum has been reported to stabilize atomic Pd on an Al$_2$O$_3$ support even after high temperatures [151].

While a number of bimetallic Pt-Pd papers exists for diesel exhaust abatement, many use common impregnation techniques to synthesis the catalysts [57, 62, 64, 148]. The common impregnation techniques do nothing to promote bimetallic interactions or control the nanoparticle sizes. Therefore the catalyst nanoparticles are often larger, inhomogeneous, and with wide particle size distributions which make comparisons between sets of catalysts difficult. This study focuses on the synthesis, characterization,
and evaluation of highly-dispersed alloyed Pt-Pd nanoparticles for DOCs on a number of modified alumina supports. The catalysts were synthesized using strong electrostatic adsorption which has shown to produce ultrasmall (~1-2nm) homogenously alloyed bimetallic nanoparticles on a variety of supports [13, 14]. Higher nanoparticle homogeneity allows improved comparison between Pt:Pd ratios across the various supports.

5.2 Methodology

5.2.1 Catalyst Preparation

The alumina supports were provided by Solvay Chemicals (#001-008), and the silica was Aerosil A300 from Evonik. These materials are listed in the SI in Table B1. The platinum and palladium cationic salts were tetraammine platinum (II) hydroxide and tetraammine palladium (II) chloride obtained from Sigma Aldrich.

Strong electrostatic adsorption (SEA) was used to synthesize the bimetallic alloys. The procedure of SEA extended to the co-adsorption of two metals (co-SEA) has been previously reported [13, 14]. By working in pH values above the point of zero charge (PZC) of the supports, the surface of the support is negatively charged. This allows the adsorption of the cationic precursors. HNO₃ and NaOH were used to adjust the pH of the solutions. Pt-Pd weight ratios of 1:0, 3:1, 1:1, 1:3, and 0:1 were made over the various supports. The total metal weight loading of the catalysts was 2 wt%. A drawback of using SEA comes from the limitation of how much metal can be adsorbed in one cycle. Synthesis of these catalysts took between 1-3 co-SEA cycles depending on the surface area of the support.
For comparison, incipient wetness (IWI) catalysts were synthesized at a 1:1 Pt-Pd ratio using typical co-impregnation of Pt and Pd precursors. All co-SEA and IWI catalysts were dried in an oven at 80°C overnight followed by reduction at 250°C in 10% H2 balanced He for 1 hour prior to the initial evaluation.

5.2.2 Catalytic Evaluation

Catalytic activity tests were performed at Oak Ridge National Lab at the Fuels, Engines and Emissions Research Center (FEERC). Evaluation followed the U.S. DRIVE 2015 protocol for the Low-Temperature Combustion of Diesel (LTC-D). A model diesel exhaust feed consisting of 2000 ppm CO, 835 ppm C2H4, 333 ppm C3H6, 111 ppm C3H8, 100 ppm NO, 400 ppm H2, 6% CO2, 12% O2, and 6% H2O balanced Ar was used to evaluate the catalysts. Total flowrate was 333 sccm. A flow reactor with 100 mg of catalyst and a GHSV of ~100,000 hr⁻¹ was heated to 700°C at a rate of 2°C/min. The activity of the catalyst was measured during the first ramp and referred to as a fresh catalyst. The temperature was held at 700°C for 4 hours as a degreening treatment. Degreening gas compositions were lean (10% O2, 5% CO2, 5% H2O, balanced Ar) and dictated by the LTC-D protocol. The reactor temperature was brought down from 700°C to 100°C at a rate of 2°C/min while measuring the degreened catalyst ramp-down activities. Finally, the catalyst was again heated at a rate of 2°C/min to measure ramp-up activity for the degreened catalyst.

Gas concentrations were determined using an Agilent 490 Micro GC, SRS RGA 100 mass spectrometer, and Eco Physics CLD 822 NOx chemiluminescence.
5.2.3 Hydrothermal Aging

A separate hydrothermal ageing procedure was performed in a benchtop flow reactor to age the samples at 800°C. These catalysts were treated at 800°C for 25 hours in hydrothermal conditions. The USDRIVE 2015 L-TCD ageing protocol was followed. These catalysts were identified as aged.

5.2.4 Characterization

Fresh, degreened, and aged catalysts were characterized by x-ray diffraction (XRD) using a Rigaku MiniFlex II equipped with a high sensitivity D/tex Ultra Si slit detector with a nanoparticle size detection limit of about 1 nm [83]. Patterns were recorded from 10-90° 2θ using a Cu-Kα radiation source (λ=1.5406 Å) operated at 30 mA and 15 kV. The Scherrer equation was used to determine the bulk particle size, and peak location was used to determine oxide formation.

STEM microscopy was taken at the University of South Carolina using a JEOL-2100F electron microscope capable of electron mapping. The aberration corrected microscope operated at 200 kV and was equipped with an Oxford Inca solid-state EDS detector for element mapping.

5.3 Discussion

Strong Electrostatic Adsorption surveys of platinum and palladium were performed over the supports (Figure 5.1A and B, respectively). The PZC of the alumina modified with silica Solvay supports (#’s 001-003, 005, and 006) are between pH 6 and 7 which is in line with mixtures of SiO₂ and Al₂O₃. The PZCs of pure SiO₂ and pure Al₂O₃ (#008) are around 3.5 and 8.2, respectively [31]. Working in pH values above the PZC deprotonates the support surface hydroxide groups and causes the surface to be negatively
charged. Cationic Pt and Pd precursors were then adsorbed. A maximum adsorption density is achieved at an optimum pH value. The maximum adsorption density of Pt is between 0.8 and 1.0 umol/m$^2$, and the maximum adsorption density of Pd is between 1.0-1.3 umol/m$^2$. Additional basification beyond the optimal pH causes the adsorption density to decreases due to high ionic strength in solution. The adsorption density surveys of pure SiO$_2$ and pure Al$_2$O$_3$ (#008) are shown for reference in Figure 5.1. The adsorption densities of both Pt and Pd for the modified Al$_2$O$_3$ supports fall between those obtained on the pure supports. Normally very little adsorption occurs around the PZC and in the basic pH regime on Al$_2$O$_3$ due to no charges on the support and Al$_2$O$_3$ having a high PZC, respectively. However, these modified Al$_2$O$_3$ supports show significant adsorption of both Pt and Pd between pH values of 6 and 7. Either ionic exchange is occurring on the supports or the bulk PZC does not reflect the localized PZC of areas containing Si. The modified Al$_2$O$_3$ supports are believed to be homogenous throughout with no isolated patches of SiO$_2$.

![Figure 5.1 Adsorption surveys of Pt (A) and Pd (B) over the various oxide supports.](image)

To synthesize alloyed bimetallic catalysts, SEA was extended to the co-adsorption of Pt and Pd. The conditions for the synthesis were the same as for the monometallic
catalysts, but both Pt and Pd precursors were simultaneously in solution. Figure 5.2 shows the co-adsorption of both Pt and Pd over support #003 in the basic pH regime. Equimolar concentrations were used for adsorption in Figure 5.2. Competitive adsorption was observed across the pH range with Pt favoring adsorption over Pd at higher pH values. To avoid limitations of competitive adsorption, the initial metal concentrations were adjusted accordingly to obtain the bimetallic wt. ratios of Pt:Pd (3:1, 1:1, 1:3).

![Figure 5.2 Simultaneous adsorption of Pt and Pd versus pH.](image)

X-ray diffraction (XRD) was performed on the synthesized catalysts to determine the bulk particle size. The equipped Rigaku D/tx Ultra Si slit detector is capable of nanoparticle detection of ~1.5 nm [83]. Figure 5.3 shows the XRD patterns for support #001 and the five Pt:Pd ratios synthesized. A common Pt-Pd IWI with a Pt:Pd wt. ratio of 1:1 was also synthesized for comparison. No metallic peaks of Pt or Pd are visible in the co-SEA samples for all the Pt:Pd ratios indicating the fresh catalysts exist as highly-dispersed nanoparticles below the detection limit (~1.5 nm). The XRD pattern of the co-IWI Pt-Pd catalyst shows a FCC (111) peak around 40°2θ which is attributed to metallic
Pt/Pd. This corresponds to an XRD nanoparticle sizes of ~5 nm obtained using the Scherrer equation.

![XRD patterns of fresh Pt-Pd catalysts before reaction.](image)

**Figure 5.3** XRD patterns of fresh Pt-Pd catalysts before reaction.

STEM images were used to corroborate the XRD particle sizes. STEM images (Figure 5.4) taken of support #003 with a 1:1 Pt:Pd ratio show excellent homogeneity of nanoparticles across the support. These small nanoparticles are typical of the SEA method and believed to be well-alloyed similarly to previous co-SEA syntheses [13, 14]. The STEM number particle size ($d_n$) was 1.3 ± 0.2 nm.

No noticeable particle size differences, determined by XRD and STEM, existed between the bimetallic nanoparticles or their monometallic counterparts. Moreover, the initial nanoparticle sizes across all modified Al$_2$O$_3$ supports were identical.
The catalytic activity of these catalysts were determined at ORNL using a simulated diesel exhaust stream. Detailed are described in the methodology. Light-off curves of the reactants were obtained to determine the activity of the catalysts before and after degreening pretreatments.

Series of Pt-Pd catalysts (wt. ratios 1:0, 3:1, 1:1, 1:3, and 0:1) over support #001 (70Al-30Si) and #002 (95Al-5Si) were used to determine the effect of Pt:Pd ratios on catalytic performance. The activities of the monometallic Pt and Pd catalysts on support #001 are shown in Figure 5.5 A and B, respectively. These Pt and Pd catalysts have been degreened at 700°C for 4 hours.

Oxidation over the degreened Pt catalyst (Figure 5.5A) had a signature light-off shape where no activity occurred up to 125°C followed by the complete oxidation of CO by ~150°C. Once the CO was oxidized, the free metal sites were able to oxidize both ethylene and propylene together by 160°C. Propane is more difficult to oxidize due to having fully saturated bonds, but significant activity towards propane occurred at
temperatures < 200°C. The overall total hydrocarbon (THC) activity of the Pt is good, as the targeted goal is a T₉₀ for THC by 150°C. C₂H₄, C₃H₆, and about 10% of C₃H₈ have to be oxidized to achieve 90% conversion of THCs. For ramp-down activities, there is little hysteresis towards propane; however, the Pt catalysts exhibited improved activities to CO, C₂H₄, and C₃H₆ by 10°C for the ramp down. This hysteresis and improved activity was most likely due to Pt active sites not being poisoned by CO when initially ramping up.

![Figure 5.5](image)

**Figure 5.5** Light-off curves of Pt (A) and Pd (B) monometallic catalysts (support #001) after degreening. Solid markers (●) are ramp-up activities. Open markers (○) are ramp-down activities.
The light-off activities of the degreened Pd catalyst are shown in Figure 5.5B. Light-off curves for Pd are less steep and are staggered. The staggered light-off curves indicate Pd’s ability to only oxidize one species at a time as opposed to the very steep light-off curves of Pt. After degreening the catalyst, Pd is most likely in an oxidized state. This PdO is highly active to CO with activity as low as 100°C. However, the Pd must not be able to remain fully oxidized as there is oscillatory CO activity until 180°C. At this point where CO is fully oxidized, C₃H₆ begins to light-off, followed by C₂H₄ and C₃H₈. The T₉₀ for the THCs was over 325°C for the Pd catalyst compared to only 180°C for the Pt catalyst. Hysteresis of the Pd catalyst light-off curves to higher temperatures during ramping down shows the oxidation state of Pd mostly likely changed. The degreening conditions are oxidizing, therefore Pd should exist as fully PdO when ramping down. PdO is less active towards HC oxidation [148]; therefore the increase in light-off temperatures by 10-40°C during ramping down agrees with literature findings. The CO activity for the Pd catalyst during ramping down was worse than that of ramping up. Thus, the most active state of Pd for CO oxidation is a mixture of Pd and PdO.

The T₅₀ and T₉₀’s for the gas species are plotted against the Pt:Pd weight ratios in Figure 5.6A-F. Figure 6A-E are for support #001, and Figure 5.6F is the THC activity for support #002.
Figure 5.6 $T_{50}$ and $T_{90}$ Light-off temperatures for CO, C$_2$H$_4$, C$_3$H$_6$, C$_3$H$_8$, and THC.
In all cases, the lowest achievable temperatures were the catalysts in the fresh state. A fresh catalyst was evaluated without any prior pretreatments or calcinations. All the fresh catalysts have similar particle sizes and were previously described and shown in Figure 5.3 and 5.4. The $T_{50}$ and $T_{90}$’s for the fresh catalysts followed similar trends across the different Pt:Pd ratios with the $T_{90}$ being at a higher temperature. Higher Pd content improved the CO activity (Figure 5.6A) for the fresh catalyst. This is observed in the reduction of $T_{50}$ and $T_{90}$ from ~140°C for pure Pt to ~120°C for pure Pd. For HC activity (Figure 5.6B-D), a decrease in catalytic performance was observed when adding more Pd to the system. Thus, Pt is more active to the hydrocarbons. This is especially true when considering that the number of atoms of Pd are twice that of Pt since they are at the same weight loadings and have similar nanoparticle sizes. Figure 5.6 E and F show clear superiority of Pt over Pd for THC activity for fresh catalysts over two different supports (#001 and #002). Catalytic performance trends (CO, C$_2$H$_4$, C$_3$H$_6$, and C$_3$H$_8$) comparing Pt:Pd ratio were similar over both supports #001 and #002; therefore, only THC’s for the various Pt-Pd ratios on support #002 are included.

The degreened catalyst (pretreatment at 700°C for 4 hours) $T_{50}$ and $T_{90}$’s are shifted to a higher temperature. This was due to catalyst deactivation from nanoparticle sintering. The CO oxidation trend for the various Pt:Pd ratios reversed, with Pt now being more active than Pd alone. Moreover, bimetallic combinations of Pt-Pd (3:1 and 1:1) showed the highest CO activity for the degreened catalysts. Reasons for this are investigated later. However, changes in oxidation states or nanoparticle size between fresh and degreened states could significantly alter the activity of these catalysts. Moreover, bimetallic catalysts can be more resistance to sintering which would increase the number of active sites.
compared the monometallic Pt or Pd [57, 63, 65, 125, 152]. The effect of Pt:Pd ratio on the individual HC activity is less clear. Bimetals of Pt-Pd often performed best at a specific weight ratio (between 1:1 and 1:3) rather than a linear trend. The $T_{50}$ and $T_{90}$ for $C_2H_4$ and $C_3H_6$ indicated Pt is the more suitable metal over Pd. Pd was better at achieving 90% combustion of $C_3H_8$; however, Pt achieved a lower $T_{50}$ for $C_3H_8$. Being able to initially combustion $C_3H_8$ is key, because it is the most difficult gas component to oxidize. Moreover, the target of 90% conversion of THC is achieved with only 10% of $C_3H_8$ conversion and complete oxidation of $C_2H_4$ and $C_3H_6$. Therefore the slippage of $C_3H_8$ through the exhaust is acceptable, if the other components light-off quickly. This is represented in the THC plots in Figure 5.6 E and F which clearly show the Pt monometallic catalysts were most effective at achieving 90% conversion of THCs in their fresh and degreened conditions. Additional monometallic Pt catalysts were evaluated on the other supports and exhibited similar performance ($T_{90}$’s $<200^\circ C$). The fresh and degreened THC light-off curves are found in Figure C.1.

Monometallic Pt catalysts and bimetallic catalysts with a 1:3 Pt:Pd ratio were chosen on support #005 and #006 to be aged and evaluated. These supports were selected for ageing because degreened monometallic Pt catalysts on both of these supports showed excellent activity. The ex-situ ageing procedure is described in the methodology and consisted of holding the catalysts at 800°C for 25 hours. Figure 5.7 A and B show the light-off curves of the aged 1:0 and 1:3 Pt-Pd catalysts on support #005. The light-off curves on support #006 are not shown due to having similar trends, but data can be found in Appendix C in Figure C.2.
The effects of ageing on the Pt catalyst can be observed in the C₃H₈ light-off curve. Degreased monometallic Pt catalysts had C₃H₈ trends similar to Figure 5.5A where complete C₃H₈ oxidation occurred by 400°C. However, the aged monometallic Pt catalysts were unable to convert 50% of the C₃H₈ by 500°C (Figure 5.7A). The light-off curves for the other gas species (CO, C₂H₄, and C₂H₆) are also shifted to higher temperatures by ~40°C indicating catalyst deactivation. Catalytic trends on the aged 1:3 Pt-Pd catalyst are shown in Figure 5.7B. The CO and C₃H₆ light-off temperatures improved compared to the
aged Pt catalyst. CO completely oxidized by 160°C for the bimetallic catalyst compared to after 200°C for the aged Pt catalyst. Moreover, complete C\textsubscript{3}H\textsubscript{8} conversion by 500°C was achieved for the bimetallic catalyst whereas less than 50% conversion of C\textsubscript{3}H\textsubscript{8} was achieved over the Pt monometallic. Hysteresis trends for the aged catalysts were similar to the degreened samples. In general, hysteresis effects over the monometallic Pt was less than the Pt-Pd. This was most likely due to having Pd oxidized into PdO which is less active for HC conversion.

The THC T\textsubscript{50} and T\textsubscript{90}’s for the aged catalysts are shown in Figure 5.8. The T\textsubscript{50} for the bimetallic catalysts on both supports (#005 and #006) was at a lower temperature than then monometallic Pt catalysts. However, the T\textsubscript{90} for the monometallic Pt catalysts was at a lower temperature than the bimetals. The reason the monometallic Pt catalysts achieved an improved THC T\textsubscript{90} was due to the steeper light-off curves for C\textsubscript{3}H\textsubscript{6}. The inability for the bimetallic catalysts to quickly reach full C\textsubscript{3}H\textsubscript{6} conversion resulted in the poor THC conversion (shown in purple in Figure 5.7B). Most literature results indicate bimetallic Pt-Pd being more active than either monometallic Pt or Pt. This holds true if looking only at T\textsubscript{50}’s. However, from these results T\textsubscript{50} performance cannot be correlated to T\textsubscript{90} performance. Moreover, differences between how quickly the Pt and the 1:3 Pt-Pd catalyst achieved T\textsubscript{50} and T\textsubscript{90}’s indicate tuning of the catalyst is possible depending on the feed condition and the amount of HC slip permissible.
Figure 5.8 $T_{50}$ and $T_{90}$ Light-off temperatures for THC on aged Pt and 1:3 Pt-Pd catalysts.

NO to NO$_2$ oxidation performance was collected simultaneously with the above HC data. The simulated exhaust feed gas contained 100 ppm NO. The reported NOx data for the degreened catalysts on support #001 are shown in Figure 5.9. The conversion of NO to NO$_2$ is an equilibrium reaction. The equilibrium curve of NO to NO$_2$ is shown in purple. The Pt only catalyst has the highest conversion of NO to NO$_2$. Pd by itself is poor at NO oxidation with no activity before 350°C; however, small amounts of Pt added to the Pd significantly lowers the onset temperature of NO oxidation. For the 1:1 and 1:3 Pt-Pd ratios, there are two peaks of NO oxidation. The low temperature peak is most likely due to NO oxidation from Pt sites, whereas the higher temperature peak is due to NO oxidation over Pd sites. Although the bimetallic catalysts were synthesized as an alloyed, either the degreening pre-treatment segregated some Pt and Pd atoms or the NO to NO$_2$ reaction is
sensitive to the individual Pt and Pd atoms in an alloyed surface. There is a direct correlation between the NO oxidation performance and the Pt-Pd ratio. As the Pt-Pd ratio shifts more towards Pd, the NOx performance significantly decreases.

![Graph showing NO oxidation performance with varying Pt-Pd ratios.](image)

**Figure 5.9** NO oxidation performance of the degreened catalysts.

Initial NOx performance over the fresh samples (not shown) exhibited oscillations in total NOx emitted at low temperatures. The oscillations were not from NO to NO₂ oxidation as NO₂ was undetected at these temperature intervals, but it is possible that any NO₂ that formed at these temperatures was an intermediate to another species. The products during these oscillations could be either N₂O or NH₃, although both were difficult to detect. Slight amounts of N₂O were detected by GC. Another possibility was that the catalysts exhibited HC SCR, where the HCs were the reductants and N₂ was emitted.
Regardless, these oscillations stopped after the catalysts were degreened. Thus, the ultrasmall nanoparticles of the fresh catalysts must be the cause of this phenomena.

The aged and degreened catalysts were characterized to correlate trends in catalyst performance. XRD was used to determine the bulk particle size and oxidation state of the metals. In Figure 5.10, the degreened catalysts on support #001 are shown.

![Figure 5.10 XRD of degreened catalysts on support #001.](image)

Differences between the bare support and evaluated catalysts are evident in peaks around 34 and 40° 2θ. The peak for PdO is 34.5° 2θ, and the peaks for metallic Pt and Pd are around 39.8 and 40.1° 2θ, respectively. After degreening treatments, the monometallic Pd catalyst existed solely as PdO. This phase transformation agrees with reaction data in Figures 5.5B and 5.7B showing a strong hysteresis of the Pd catalysts towards HC’s. The 1:3 Pt-Pd catalyst existed mostly as PdO, and a sharp metallic peak from Pt sintering
occurred. When Pt and Pd were added into equal weight ratios, both PdO and metallic Pt/Pd existed. The FCC (111) peak was less sharp in the 1:1 Pt-Pd catalyst which indicated some stabilization of the nanoparticles compared to the 1:3 Pt-Pd catalyst. Moreover, the PdO intensity for the 1:1 co-SEA catalyst was lower than the equivalent IWI catalyst. The lower PdO intensity for the co-SEA catalyst indicated that starting as highly-alloyed nanoparticles reduced the segregation of Pt and Pd to form PdO.

The Pt-rich catalysts (1:0 and 3:1 Pt-Pd) showed only metallic XRD peaks. This agreed with previous work that showed Pt-rich catalysts have a resistance to bulk oxide formation [12]. In addition, the degreened Pt catalysts show little hysteresis between ramping up and down for HC performance (Figure 5.5B and 5.7B) which agrees with the Pt surface remaining metallic. The metallic XRD (111) peak for the bimetallic Pt-Pd catalysts are shifted towards metallic Pd which occurs at a slightly higher 2θ than Pt. Thus, the nanoparticles in the bimetallic catalysts are alloyed in all cases.

The particle sizes of the degreened and aged catalysts were calculated from the XRD peak width using the Scherrer equation. The particle sizes of the fresh Pt-Pd catalysts all < 1.5 nm. After degreening treatments, the Pd catalyst existed as only PdO with a XRD nanoparticle size of 3.5 nm. The addition of some Pt in the 1:3 Pt-Pd catalyst showed a growth of PdO crystalline size to 5.1 nm and crystalline metallic nanoparticles of 14.8 nm. Going to equal weights of Pt-Pd further increased the PdO size to 6.2 nm, and the metallic nanoparticles had a slight reduction in XRD particle size to 10.2 nm. The Pt-rich catalysts (1:0 and 3:1) indicated no oxide formation, and the metallic nanoparticles sizes were 8.5 and 9 nm, respectively.
Summarizing the XRD characterization after degreening treatments, the Pt-rich catalysts exhibited no oxide formation due to Pt being more resistant to oxidation and remaining alloyed. This is consistent with other works that determined Pt-Pd existed as alloys when the composition was Pt-rich [148]. The metallic particle sizes for the 1:0, 3:1, and 1:1 catalyst slightly increased from 8.5 to 10.2 nm when increasing the Pd content. The 1:3 Pt-Pd catalyst had the largest metallic particles at 14.8 nm. No metallic nanoparticles were observed in the Pd-only catalyst as everything existed as PdO. The PdO particle size was smallest for the monometallic Pd catalyst at 3.5 nm and increased in size to 5.1 and 6.2 nm as Pt was added in the 1:3 and 1:1 Pt-Pd catalysts, respectively. PdO was most stable over these supports. Surprisingly, the monometallic Pt catalyst was as stable as the bimetallic catalysts after degreening conditions. It is important to note that the XRD particle size is a bulk measurement and may not accurately reflect particle size distributions between oxide and metallic phases of Pt and Pd. This is apparent in the 1:3 Pt-Pd XRD where the sharp metallic peak indicates large metallic particles; however, the area under this XRD peak is relatively small which indicates only a small fraction of particles must exist as such. Moreover, XRD tends to omit the smallest of nanoparticles and atoms.

XRD patterns were taken of the aged at 800°C samples. Performance data for these catalysts were shown in Figure 5.7 A and B. The monometallic Pt catalysts on support #005 and #006 sintered to 24 and 26 nm, respectively. The bimetallic aged 1:3 Pt-Pd catalysts on support #005 and #006 contain both metallic and oxide peaks. The metallic peaks were 13 and 16 nm, and the oxide peaks were 6.2 and 6.6 nm for support #005 and #006, respectively. A clear reduction in particle sizes existed for the bimetallic catalysts
compared to the monometallic Pt when treated at these ageing conditions. This differed from the trends of the degreened catalysts where the monometallic Pt and bimetallic Pt-Pd had similar metallic nanoparticle sizes. Therefore the sintering mechanism and duration of pretreatment between the degreening (700°C) and the ageing (800°C) catalysts most likely explains the differences in nanoparticle stability.

Figure 5.11 STEM and EDXS of degreened 3:1 Pt-Pd catalyst (A and B) and aged 1:3 Pt-Pd (C and D)

Microscopy imagery was used to corroborate the XRD particle sizes. Images were taken of a degreened 3:1 Pt-Pd catalyst and an aged 1:3 Pt-Pd catalyst. Representative STEM and EDX images of the degreened 3:1 Pt-Pd catalyst are shown in Figure 5.11 A and B. The nanoparticles in the images agree closely with the 9 nm XRD bulk particle size for the degreened catalyst. Mapping of these Pt-rich nanoparticles indicated an alloyed structure which is in agreement with no XRD oxide peaks. Therefore at this composition
and pretreatment, Pt and Pd are remain alloyed. Figure 5.11, C and D, shows images of the aged 1:3 Pt-Pd catalyst after the 800°C treatment. The nanoparticle size is in agreement with the XRD particle size of 16 and 6.6 nm for the metallic and oxide phases, respectively. The images indicated Pt-Pd segregation where partial alloying of the nanoparticle and enrichment of PdO coexisted.

There was no clear trend from XRD nanoparticle sizing between the catalyst performance and Al-Si ratio in the various supports. A possible reason can be that the Si in the bulk is not representative of the surface Si. Therefore, bulk and surface Al-Si ratios may differ drastically which makes any comparison between catalyst performance and bulk Al-Si ratio difficult. However, plotting light-off temperatures against surface area (SA) of the supports revealed that higher surface area supports have improved performed. This plot can be found in Appendix C in Figure C.3. The lowest surface area support had a THC $T_{50}$ and $T_{90}$ of 171 and 195°C compared to the highest surface area support with a THC $T_{50}$ and $T_{90}$ of 155 and 166°C, respectively. The simplest explanation for the improved activity can be credited to decreasing the density of atoms per area on the support. Although not confirmed by XRD, this would in theory slow the rate of nanoparticle sintering as nanoparticles and atoms have further to travel before agglomerating. It is important to note that the support which is lanthanum modified (SA- 171 m²/g) did not fit this SA correlation and was omitted when taking a trend lines. Although the lanthanum modified support was expected to be exceptionally hydrothermally stable, the lanthanum did little to the overall catalytic oxidation performance. In fact, apparent differences in catalyst support stabilities were not observed in the modified alumina supports treated at 700°C degreening treatments. BET analyses of the degreened catalysts showed all the alumina supports were
within 15% of the manufacturer’s original SA. Pure silica was also evaluated using the same degreening protocol and experienced near 60% SA loss.

5.4 Conclusion

In conclusion, we have demonstrated simple, effective way to produce highly disperse alloys of Pt and Pd. The co-SEA particle sizes are <1.5nm across all the supports and Pt-Pd ratios. These catalysts perform very well in their fresh state, but they deactivate in the harsh oxidizing hydrothermal conditions. However, the co-SEA nanoparticle have increased sinter resistance and phase segregation over equivalent Pt-Pd impregnation catalysts. The Pt was able to keep the Pd in a metallic state which aided HC performance. Among the degreened catalysts, the monometallic Pt catalysts were best at achieving 90% THC conversion. After ageing at 800°C, the monometallic Pt catalysts were still best at achieving 90% THC conversion; however, these Pt catalysts could only convert 50% of C\textsubscript{3}H\textsubscript{8} by 500°C. The 1:3 Pt-Pd catalysts were better at achieving 50% THC conversion at lower temperatures and were able to completely oxidize C\textsubscript{3}H\textsubscript{8} by 500°C. Therefore optimum catalyst composition highly depends on the permissible HC slip and exhaust composition.
CHAPTER 6

CONCLUSIONS
This study demonstrates the ability to synthesize improved bimetallic catalysts on oxide supports through the use of rational synthesis methods. Bimetallic alloys of Pt, Pd, Co, Cu, and Ni were synthesized on silica using co-SEA. The adaptation of SEA to bimetallic nanoparticles was a simple, generalizable way to produce ~1nm nanoparticles of various bimetallic combinations. These nanoparticles were homogenous in composition and uniform in size. TPR confirmed the intimate bimetallic characteristics of these nanoparticles that were unobservable in typical co-impregnation catalysts. Furthermore, XRD and STEM images indicated only highly disperse nanoparticles existed on the support. High Resolution Z-contrast images were taken of the co-SEA nanoparticles, and the speckling of atoms in the nanoparticles was a visual indication that the nanoparticles existed as a well-mixed alloy.

A series of Ag-Ir core-shell catalysts were synthesized by ED on alumina supports to demonstrate the principle of nanoparticle stabilization using surface free energy (SFE) principles. After high-temperature annealing treatments, the low SFE Ag shells were stable on the high SFE Ir cores. Interestingly, the stability of the Ir-cores was also improved by the addition of Ag, and the number of hydrogen adsorption sites, determined by chemisorption, increased for the bimetallic catalysts. Monometallic Ag and Ir catalysts were evaluated alongside the bimetallic Ag-Ir catalysts for comparison, and the annealed monometallic nanoparticles ended with particle sizes 5-25 times larger than the annealed bimetallic nanoparticles. Computational studies were performed to determine hydrogen binding energies on different Ag-Ir surfaces. The computational studies corroborated with the experimental studies in that Ag does not chemisorb hydrogen. However, depending on
the morphology of Ag-Ir, Ag can assist hydrogen adsorption to increase the H to Ir ratio from 1:1 on bulk Ir surfaces to 4:1 on isolated atoms of Ir surrounded by Ag.

Rationally synthesized Pt-Pd bimetallic catalysts were evaluated at the Fuels, Engines, and Emissions Research Center at Oak Ridge National Laboratory. Both core-shell and alloyed nanoparticles were evaluated using a simulated diesel exhaust. The core-shell materials had unique properties, but these properties were not sustainable after hydrothermal ageing treatments. The transformation of the core-shell structures to alloys and partially alloyed systems was unpreventable and dictated by thermodynamics and Pt-Pt phase solubility. Although activity was similar between a co-SEA and co-impregnation catalyst, the co-SEA alloyed Pt-Pd catalysts exhibited a 50% reduction in particle size growth. The similarity in activity was credited to isolated areas of Pd in the co-impregnation catalyst. Pd/PdO’s is excellent at oxidizing CO which is a primary component of vehicle exhaust.

Additional co-SEA bimetallic Pt-Pd catalysts were taken to ORNL to determine the effect of Pt-Pd ratio (1:0, 3:1, 1:1, 1:3, 0:1) on DOC performance. This studied focused on reducing the temperature of achieving 90% THC conversion. Although Pd catalysts are best at oxidizing CO, the Pt catalysts were best at oxidizing HC’s. Therefore overall THC performance was best over the Pt-rich catalysts. At the most severe ageing temperature, the addition of Pd to Pt reduced nanoparticle sintering compared to unprompted monometallic Pt. This increased stabilization was due to reducing the amount of Pt sintering through PtO2 volatilization.

The methods of ED and SEA used in this work allowed for precise control over particle size morphology. While improved nanoparticle stabilization was demonstrated
using core-shell (Ag-Ir) and homogenously alloyed (Pt-Pd) structures, there is still much room for improvement. Additional support modifications and bimetallic combinations should be investigated. Moreover, catalysts stability in various reaction environments (reducing, oxidizing, and inert) needs consideration when optimizing catalyst performance.
REFERENCES


APPENDIX A

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<tr>
<td>Licensed Content Author</td>
<td>A. Wong, Q. Liu, S. Griffin, A. Nicholls, J. R. Regalbuto</td>
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APPENDIX B

SUPPLEMENTATRY MATERIALS TO CHAPTER 2

Materials and Methods

Materials

Evonik Aerosil 300 (BET SA-282 m²/g) was used as the silica support. This is fumed silica with a PZC of 3.6. The cationic precursor salts used for SEA were hexaamminenickel (II) chloride (Sigma-Aldrich 99.999%), copper (II) nitrate hydrate (Sigma-Aldrich 99.999%), hexaamminecobalt (III) chloride (Sigma-Aldrich 99%), tetraammineplatinum (II) hydroxide hydrate (Sigma-Aldrich), and tetraamminepalladium (II) chloride monohydrate (Sigma-Aldrich 99.99%). Copper (II) nitrate was first dissolved in 5N NH₄OH followed by dilution in DI water in order to complex the copper into copper tetraammine as previously reported in the literature (7). Solutions containing either copper or nickel were made of 200 ml of 5N NH₄OH and 300 ML of DI water (18.2 MΩ•cm). DI water was used to dissolve the Pt, Pd, and Co precursors. Concentrations for all solutions were ~200 ppm for single metal adsorption surveys. The bimetal adsorption surveys were made of 100 ppm of each metal for a total concentration of 200 ppm. Adjustments to each of the metal’s concentration were performed if large amounts of competitive adsorption prevented simultaneous adsorption of the metals. Equal molar ratios of each metal were targeted on the support; thus weight loadings of each metal varied. The total weight loadings of the catalysts were governed by the adsorption densities of the precursors caused by steric hindrance in SEA.
The same metal precursors and silica support were used for the IMP catalysts. DI water was used to dissolve the precursors before impregnation into the support. IMP weight loadings were made to match the analogous bimetal SEA catalysts.

**Methods (Strong Electrostatic Adsorption, SEA)**

The pH of the room temperature precursor solutions was adjusted using HNO$_3$ or NH$_4$OH. The amount of support in the solution was controlled to give a surface loading (SL) of 1000 m$^2$/L. (SL is a measure of available surface in contact with solution.) A SL of 1000 m$^2$/g was achieved using 0.250 L of solution and 0.89 g of support with a SA of 282 m$^2$/g. The concentrations of metal ammine solutions used to achieve close to the desired 1:1 atomic ratio metals are summarized in Table B1. The pH adjusted solutions containing the support were placed on an orbital shaker for 1 hour. The supports were recovered using vacuum filtration and then were removed to air dry overnight. Samples were then placed in a muffle furnace for oven drying at 120°C for 4 hours followed by reduction treatments.

Aliquots of solution were taken before and after contacting with the support to determine metal adsorption. Metal concentrations were measured using an inductively-coupled plasma (ICP) equipped with an optical emission spectrometer (PerkinElmer Optima 2000 DV). Solutions containing high concentrations of NH$_4$OH were diluted to reduce the volatility of the solution before ICP analysis.
Methods (Impregnation, IMP)

IMP samples were prepared using the same precursors, support, and weight loadings as the SEA samples. The pore volume of the silica was determined to be 3.2 mL/g. Therefore for 0.5 g quantities of catalyst, the precursor was dissolved in 1.6 mL of DI water. The support was placed in a centrifuge tube, and the 1.6 mL precursor solution was added. The thick slurry was then shaken to ensure complete wetting of the support by the solution. The catalysts were left to air dry overnight before oven drying for 4 hours at 120°C. A summary of the preparation parameters is given in Table B2. Two IMP samples, for Pt-Cu and Ni-Co, which represented the smallest and largest IMP-derived particle sizes respectively, were synthesized in triplicate to assess reproducibility; these results are reported in the main paper in Table 2.2.

Reduction Treatments

Temperature programmed reduction was performed on the oven dried catalysts by using a Micromeritics 2920 equipped with a TCD. The temperature was set at a ramp rate of 5°C/min, and the reducing gas of 10% H₂ balanced Ar was set at a flowrate of 50 SCCM.

Oven dried catalysts were reduced in a horizontal furnace using 10% H₂ balanced He at 400°C with a soak time of 1 hour and ramp rate of 5°C/min. Total gas flowrate was 500 SCCM with a GHSV of 185 hr⁻¹.
XRD characterization

X-ray diffraction (XRD) patterns were obtained using a Rigaku MiniFlex II equipped with a high sensitivity D/ tex Ultra Si slit detector. Patterns were recorded from 10-80° 2θ using a step size of 0.02° and a Cu-Kα radiation source (λ=1.5406 Å) operated at 30 mA and 15 kV.

STEM characterization

STEM was performed on the pre-reduced catalyst samples with a JEOL JEM-ARM200CF STEM aberration corrected microscope with a cold field emission electron source. XEDS spectra and maps were acquired with a nominal 0.1nm probe and 140pA beam current using an Oxford X-Max 100TLE high solid angle windowless SDD detector and processed using Oxford AZtec software. To obtain average particle size and size distributions, at least 500 NPs were counted for each sample.
Figure B.1 Uptake surveys of bimetal pairs.
Figure B.2 TPR of bimetal nanoparticles (downwards peaks indicate H₂ consumption) (pt. 1).
Figure B.3 TPR of bimetal nanoparticles (downwards peaks indicate H2 consumption) (pt. 2)
Figure B.4 Size distribution of co-SEA nanoparticles.
Figure B.5 Elemental mapping of IMP nanoparticles (pt. 1).
Figure B.6 Elemental mapping of IMP nanoparticles (pt. 2).
Table B.1 Summary of SEA synthesis.

<table>
<thead>
<tr>
<th>BET SA of Aerosil 300</th>
<th>282 m²/g</th>
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<tbody>
<tr>
<td>Solution Volume</td>
<td>125 mL</td>
</tr>
<tr>
<td>Surface Loading</td>
<td>1000 m²/L</td>
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<tr>
<td>Mass of Support</td>
<td>.44 g</td>
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Prepare solutions for 1:1 atomic adsorption using metal concentrations (ppm):

<table>
<thead>
<tr>
<th>Ni</th>
<th>Co</th>
<th>Cu</th>
<th>Pt</th>
<th>Pd</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.94Ni/0.97Co</td>
<td>34</td>
<td>36</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.70Cu/0.66Co</td>
<td>27</td>
<td>30</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.89Cu/0.63Ni</td>
<td>31</td>
<td>31</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.2Pt/0.80Co</td>
<td>25</td>
<td>110</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.6Pt/0.79Ni</td>
<td>33</td>
<td>100</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.2Pt/0.94Cu</td>
<td>34</td>
<td>100</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.31Pt/0.70Pd</td>
<td></td>
<td>120</td>
<td>65</td>
<td></td>
</tr>
<tr>
<td>0.7Co/1.3Pd</td>
<td>27</td>
<td></td>
<td>75</td>
<td></td>
</tr>
<tr>
<td>0.52Ni/1.2Pd</td>
<td>50</td>
<td></td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>1.0Cu/2.1Pd</td>
<td></td>
<td>18</td>
<td>45</td>
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</tr>
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*Incomplete adsorption caused slight deviations from an atomic 1:1 ratio. Optimization of these concentrations may result in improved atomic 1:1 ratios.*
Table B.2 Summary of IMP synthesis.

<table>
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<th>Mass Used</th>
<th>Value</th>
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<tbody>
<tr>
<td>Evonik Aerosil 300 mass used</td>
<td>0.5 g</td>
</tr>
<tr>
<td>Pore volume of Aerosil 300</td>
<td>3.2 mL/g</td>
</tr>
<tr>
<td>IMP water volume to dissolve precursors</td>
<td>1.6 mL</td>
</tr>
</tbody>
</table>

Prepare 1.6 mL solutions by dissolving mass (g) of precursor:

<table>
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<th>Mass Composition</th>
<th>Mass of Precursor (g)</th>
<th>Mass of Precursor (g)</th>
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<tr>
<td>[Ni(NH$_3$)$_6$]Cl$_2$</td>
<td>0.0186</td>
<td>0.0220</td>
</tr>
<tr>
<td>[Co(NH$_3$)$_6$]Cl$_3$</td>
<td>0.0150</td>
<td>0.0207</td>
</tr>
<tr>
<td>Cu(NO$_3$)$_2$</td>
<td>0.0124</td>
<td>0.0186</td>
</tr>
<tr>
<td>Pt(NH$_3$)$_4$(OH)$_2$</td>
<td>0.0182</td>
<td>0.0244</td>
</tr>
<tr>
<td>Pd(NH$_3$)$_4$Cl$_2$</td>
<td>0.0156</td>
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</table>

0.94Ni/0.97Co 0.0186 0.0220 0.0150 0.0207 0.0124 0.0186
0.70Cu/0.66Co 0.0182 0.0244
0.89Cu/0.63Ni 0.0156
3.2Pt/0.80Co 0.0182 0.0244
2.6Pt/0.79Ni 0.0278 0.0168
2.2Pt/0.94Cu 0.0156
1.31Pt/0.70Pd 0.0158
0.7Co/1.3Pd 0.0102
0.52Ni/1.2Pd 0.0102
1.0Cu/2.1Pd 0.0147 0.0259
Table B.3 EDXS spot scanning of co-SEA 1.3Pt:0.7Pd.

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<tr>
<td>2</td>
<td>73.5</td>
<td>26.5</td>
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<tr>
<td>3</td>
<td>44.4</td>
<td>55.6</td>
</tr>
<tr>
<td>4</td>
<td>68.9</td>
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<td>5</td>
<td>70.2</td>
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<td>6</td>
<td>62.6</td>
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<td>7</td>
<td>44.7</td>
<td>55.3</td>
</tr>
<tr>
<td>avg</td>
<td>61</td>
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Table B.4 EDXS spot scanning of co-SEA 1.3Pd:0.7Co.

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<td>57.9</td>
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<td>7</td>
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<td>avg</td>
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Table B.5 EDXS spot scanning of co-SEA 1.2Pd:0.52Ni.

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<td>3</td>
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<td>4</td>
<td>56.4</td>
<td>43.6</td>
</tr>
<tr>
<td>5</td>
<td>88</td>
<td>12</td>
</tr>
<tr>
<td>6</td>
<td>84</td>
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<td>7</td>
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Table B.6 EDXS spot scanning of co-SEA 3.2Pt:0.8Co.

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<td>avg</td>
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Table B.7 EDXS spot scanning of co-SEA 2.6Pt:0.79Ni.

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<tr>
<td>avg</td>
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Table B.8 EDXS spot scanning of co-SEA 2.2Pt:0.94Cu.

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Table B.9 EDXS spot scanning of co-SEA 0.63Ni:0.89Cu.

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<tr>
<td>avg</td>
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Table B.10 EDXS spot scanning of co-SEA 0.94Ni:0.97Co.

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<th>Co wt%</th>
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</tr>
<tr>
<td>5</td>
<td>57.4</td>
<td>42.6</td>
</tr>
<tr>
<td>6</td>
<td>34</td>
<td>66</td>
</tr>
<tr>
<td>7</td>
<td>54.7</td>
<td>45.3</td>
</tr>
<tr>
<td>avg</td>
<td>55</td>
<td>45</td>
</tr>
</tbody>
</table>

Table B.11 EDXS spot scanning of co-SEA 0.66Co:0.70Cu.

<table>
<thead>
<tr>
<th></th>
<th>Co wt%</th>
<th>Cu wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nom.</td>
<td>49</td>
<td>51</td>
</tr>
<tr>
<td>1</td>
<td>17.2</td>
<td>82.8</td>
</tr>
<tr>
<td>2</td>
<td>35.9</td>
<td>64.1</td>
</tr>
<tr>
<td>3</td>
<td>5.5</td>
<td>94.5</td>
</tr>
<tr>
<td>4</td>
<td>63.9</td>
<td>36.1</td>
</tr>
<tr>
<td>5</td>
<td>17.7</td>
<td>82.2</td>
</tr>
<tr>
<td>6</td>
<td>29.8</td>
<td>70.2</td>
</tr>
<tr>
<td>7</td>
<td>45.1</td>
<td>54.9</td>
</tr>
<tr>
<td>avg</td>
<td>31</td>
<td>69</td>
</tr>
</tbody>
</table>
**Table B.12** EDXS spot scanning of co-SEA 2.1Pd:1.0Cu.

<table>
<thead>
<tr>
<th>#</th>
<th>Cu wt%</th>
<th>Pd wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nom.</td>
<td>32</td>
<td>68</td>
</tr>
<tr>
<td>1</td>
<td>20.7</td>
<td>79.3</td>
</tr>
<tr>
<td>2</td>
<td>14.9</td>
<td>85.1</td>
</tr>
<tr>
<td>3</td>
<td>31.6</td>
<td>68.4</td>
</tr>
<tr>
<td>4</td>
<td>31</td>
<td>69</td>
</tr>
<tr>
<td>5</td>
<td>31.4</td>
<td>68.6</td>
</tr>
<tr>
<td>6</td>
<td>19.8</td>
<td>80.2</td>
</tr>
<tr>
<td>7</td>
<td>33.4</td>
<td>66.6</td>
</tr>
<tr>
<td>avg</td>
<td>26</td>
<td>74</td>
</tr>
</tbody>
</table>
APPENDIX C

SUPPLEMENTARY MATERIALS TO CHAPTER 5

Table C.1 DOC Support Material.

<table>
<thead>
<tr>
<th>Support</th>
<th>Al (%)</th>
<th>Si (%)</th>
<th>Surface Area (m²/g)</th>
<th>PZC</th>
</tr>
</thead>
<tbody>
<tr>
<td>008</td>
<td>100</td>
<td>0</td>
<td>166</td>
<td>8.0</td>
</tr>
<tr>
<td>002</td>
<td>95</td>
<td>5</td>
<td>105</td>
<td>7.2</td>
</tr>
<tr>
<td>003</td>
<td>85</td>
<td>11 + 4% La</td>
<td>171</td>
<td>7.2</td>
</tr>
<tr>
<td>005</td>
<td>88</td>
<td>12</td>
<td>249</td>
<td>7.2</td>
</tr>
<tr>
<td>006</td>
<td>80</td>
<td>20</td>
<td>292</td>
<td>6.0</td>
</tr>
<tr>
<td>001</td>
<td>70</td>
<td>30</td>
<td>160</td>
<td>6.1</td>
</tr>
<tr>
<td>A-300 (SiO2)</td>
<td>0</td>
<td>100</td>
<td>282</td>
<td>3.5</td>
</tr>
</tbody>
</table>
Figure C.1 THC conversion of fresh and degreened monometallic Pt catalysts on supports 003, 005 and 006.
Figure C.2 Light-off curves for aged Pt (A) and aged 1:3 Pt-Pd bimetallic (B) catalysts on support #006. Solid markers (●) are ramp-up activities. Open markers (○) are ramp-down activities.
Figure C.3 Light-off temperatures versus surface area for the modified alumina supports. The open markers (○) are from the lanthanum containing support and were not used in the trend lines.