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Engineering Palladium-on-Gold Bimetallic Nanoparticles as Groundwater Remediation Catalysts

by

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ABSTRACT

Engineering Palladium-on-Gold Bimetallic Nanoparticles as Groundwater Remediation Catalysts

by

Michael O'Neal Nutt

Over the years, our groundwater sources have become contaminated with chlorinated organics, in particular trichloroethene (TCE) due to its exposure as a solvent to degrease metals and electronic parts in the automotive, metals, and electronic industries. Due to its prevalence and toxicity, TCE has been listed as one of the most hazardous organic compounds. Physical displacement methods (air stripping and carbon adsorption) are not as desirable as the catalytic breakdown of TCE into ethane using palladium-based materials. This thesis reports on the design, synthesis, characterization, and testing of Pd supported on gold nanoparticles (Au NPs) as a remediation catalyst for the hydrodechlorination (HDC) of TCE in water at ambient temperature and atmospheric pressure. The unique surface, structural, and electronic properties of 20 nm Pd/Au particles were found to contribute to the significantly enhanced HDC activity. Pd/Au NPs synthesized with smaller diameters (4 nm) reduced metals cost and increased effectiveness. Mass transfer effects during batch reactions were analyzed for the NP catalysts. Pd/Au NPs were immobilized on a support through electrostatic attractions, and demonstrated higher HDC activity compared to conventionally impregnated Pd and Pd-Au supported catalysts. Pd/Al₂O₃, Pd NPs, and Pd/Au
NP catalysts were found to be active for HDC of other chlorinated ethenes, with reaction mechanism studies supporting a sequential dechlorination pathway for TCE HDC. The reaction was found to be first-order in TCE and half-order in H₂ for our Pd/Au catalysts, but was different from the half-order TCE and first-order H₂ dependence of pure Pd catalysts. The Pd/Au nanostructure was more resistant to catalyst deactivation from chlorides and sulfides, relative to pure Pd catalysts.

As a different example of using NPs as a catalyst support, a sol-gelation method was developed for the synthesis of molybdenum oxide (MoO₃) supported on zirconia (ZrO₂) NPs. It was hypothesized that ZrO₂ NPs can support amorphous MoO₃ as a thermally stable, highly active oxidation catalyst. MoOₓ/ZrO₂ containing up to 23 wt% amorphous MoOₓ was successfully synthesized and the nanostructure was analyzed in the context of colloid chemistry. They were more active for methanol oxidation on a gram-catalyst basis than conventionally prepared MoOₓ/ZrO₂ catalysts, due to their higher MoOₓ content.
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To the future students who follow me: Houston is known for its food: have BBQ at the Rodeo and splurge one night at Fogo de Chao and Taste of Texas. Go see
NASA and pull for the Astros! During your years here, remember that this
graduate school experience is not complete until you have experienced South
Texas! Read *Harry Potter* (J.K. Rowling) and *Enders Game* (O.S. Card). Watch
*Alias* and *Lost* on DVDs. Listen to NPR, it is good to be knowledgeable of our
world. But during all of this… never forget what ever it is that you truly love.

To my wife (Kristal) and my late father (Bob F. Nutt), I dedicate this thesis.

Michael O'Neal Nutt

May 2006
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Chapter 1

Background and research motivation

1.1 Trichloroethene and the environment

Trichloroethene (TCE; C₂HCl₃) is a nonflammable, colorless halogenated organic compound that does not occur naturally in our environment.¹⁻³ TCE is synthesized via an oxychlorination process using ethylene dichloride and chlorine or hydrochloric acid.² In the 1970's and 80's, 80% of the nearly 300 million pounds of domestically produced TCE was used in metal degreasing applications.² In 1982, the EPA began regulating TCE and production dropped until the mid 1990's when it increased to 206 million pounds, due to TCE becoming a global feedstock for chlorofluorocarbon (CFC) replacements (accounting for 67% of TCE's current use⁴). TCE continues to be used as a solvent to degrease metals and electronic parts in the automotive, metals, and electronic industries, with smaller-scale use in textile cleaning and consumer products.²

TCE is one of the most common organic pollutants found in groundwater.¹⁻⁶ It contaminates ~60% of the waste sites on the Superfund National Priorities List, and is considered to be one of the most hazardous organic compounds at these sites because of its prevalence and toxicity.²⁻⁷ Due to its unique physical properties, TCE can easily vaporize into the air where 60% of its environmental exposure occurs. Air-born TCE will naturally breakdown after only a few weeks (half-life of 6.8 days); however, TCE found in soil and groundwater can remain much longer (half-life of 10.7 months).¹⁻⁸ Due to TCE's high density (1.46 g/mL)
and solubility in water (1100 mg/L), it can manifest itself in the bottom of a aquifer (Figure 1.1) as a dense non-aqueous phase liquid (DNAPL), continually saturating an aquifer.\textsuperscript{1} The U.S. Geological Survey (USGS) defines an aquifer as an underground layer of water containing permeable rock. Landfill disposal of hazardous waste containing chlorinated organics such as TCE was typical prior to the 1987 EPA regulation restricting it.\textsuperscript{2} For this reason, along with industrial spills and leaks, TCE has found its way into our soil and groundwater aquifers.\textsuperscript{1}

![Diagram of aquifers](image)

**Figure 1.1** Representation of unconfined and confined aquifers.

Because of its prevalence and toxicity, the EPA has set a stringent standard of 5 ppb TCE in drinking water. It has not been shown to build up in the cells of plants or animals; however, animal testing has shown an increase in liver and
kidney damage, nervous system changes, and the developments of liver, kidney, and lung tumors.\textsuperscript{2,3} Also, TCE naturally attenuates to vinyl chloride (VC; C\textsubscript{2}H\textsubscript{3}Cl), a known human carcinogen.\textsuperscript{8}

1.2 Current remediation technologies

Since the TCE groundwater problem has been identified, several different remediation technologies have been investigated. These include more traditional techniques such as gas-liquid and solid-liquid adsorption and bioremediation, as well as more novel technologies like chemical and catalytic reductions. Many of these technologies can be implemented as an \textit{in situ} or \textit{ex situ} operation. \textit{Ex situ} treatments involve the removal of contaminated groundwater from an aquifer to a treatment facility and the injection of the treated water to a clean aquifer. These techniques are termed “pump-and-treat” technologies due to the required well pumps for transport to treatment facilities. \textit{In situ} treatments involve the remediation of contaminated water and soil in place (\textit{i.e.}, underground). \textit{In situ} techniques are typically associated with lower costs and simpler technology than \textit{ex situ} treatments, but are prone to inefficiencies and less remediation control.\textsuperscript{9}

1.2.1 Gas-liquid adsorption

Gas-liquid adsorption is a mass-transfer process that involves the intimate contacting of a gas such as air with the contaminated groundwater. The driving force for gas-liquid adsorption is a concentration gradient between the two phases and process effectiveness depends on the contaminant having a low
Henry's Law constant \( H_{TCE} = 0.00892 \text{ atm-m}^3/\text{mol} @ 20 ^\circ \text{C} \).\(^1\) When implemented in an *ex situ* operation, the contaminated water is pumped from the aquifer to the surface where it enters the top of a tower, while gas enters the tower bottom through a distributor. As the water flows down the tower, it is broken up by ceramic packing into smaller (higher surface area) droplets, allowing contaminants to transport from the liquid to the gas (stripping).

*In situ* gas-liquid adsorption techniques, such as soil venting and in-well aeration, are based on the same premise. These methods involve the forcing of air down into the ground (*i.e.*, soil) or in an aquifer (*i.e.*, well) through spargers. Gas bubbles form and contact the contaminated water/soil, transferring TCE to the gas, and ultimately work their way to the surface.\(^1\) Since less equipment is needed, the cost of these *in situ* techniques is reduced. However, due to reduced intimate contacting obtained in the packed towers, their efficiency is also reduced.

Two major limitations exist with these methods: (1) as the concentration of TCE decreases in the liquid, larger volumes of air are needed to remove the lower concentrations of TCE and (2) with new clean air regulations, the now contaminated air must further be treated before it can be returned to the atmosphere.\(^1\) Of these limitations, the second is more detrimental. This requires that the air undergo thermal oxidation\(^1\) or that additional cleaning such as carbon adsorption be used to clean the TCE rich air (as described in the next section).
1.2.2 Solid-liquid adsorption

Solid-liquid adsorption involves the intimate contacting of an adsorbent material such as activated carbon with the contaminated groundwater. This remediation approach is typically carried out through *ex situ* pump-and-treat methods. The unit operation for solid-liquid adsorption is similar to that used in air stripping except the ceramic packing is replaced with granules of activated carbon. Activated carbon is carbon derived from coconut shells, wood, or charcoal that has undergone thermal, steam, or chemical activation creating a high surface area (500-1000 m²/g) microporous carbon. Three major limitations of solid-liquid adsorption also exist: (1) carbon’s large but finite surface area used to adsorb the chlorinated organic, which will require periodic replacement due to adsorption saturation, (2) the carbon is subjected to non-specific adsorption of many other groundwater species, such as dissolved organic compounds, which increases the frequency of replacement,¹ and (3) adsorbed TCE can leach from the activated carbon, preventing landfill disposal. The last limitation requires costly TCE incineration, which involves a rotary kiln operated at 1100 °C to insure that hazardous by-products such as phosgene (COCl₂) are not produced.¹,⁹

1.2.3 Bioremediation

Bioremediation is a promising *in situ* technique that may overcome limitations found in other methods due to its use of microorganisms to metabolically breakdown TCE under mild conditions. Bioremediation conditions that have
been investigated are anaerobic (in absence of oxygen) and aerobic (in presence of oxygen).\textsuperscript{1, 11-13}

The most promising degradation condition is anaerobic degradation where, TCE and other oxidized organics can be used as an electron acceptor.\textsuperscript{11, 14} This redox cycle requires a source of reducing agents that can donate electrons such as toluene, methanol, or hydrogen.\textsuperscript{1} Without an electron donor, TCE transformation is incomplete and leads to di-chloroethenes (DCE; \( \text{C}_2\text{H}_2\text{Cl}_2 \)) and vinyl chloride (VC; \( \text{C}_2\text{H}_3\text{Cl} \)), which are known human carcinogens.\textsuperscript{14} However, the addition of secondary chemicals to groundwater remains a significant drawback. Also, groundwater aquifer conditions are not steady, affecting the biochemical processes of bioremediation.

1.2.4 Zero-valent iron based reduction

Zero-valent iron, in the form of granular iron and nanoparticle (NP) suspensions, as a reducing agent is being used in the conversion of chlorinated organics into less hazardous compounds.\textsuperscript{15-18} Zero-valent iron oxidation can occur in the presence of an oxidizing agent (Equation 1; \( \text{pH} = 7 \)).\textsuperscript{19}

\[
\text{Fe}^0 \leftrightarrow \text{Fe}^{2+} + 2e^- \quad E_0 = +0.85 \text{ V} \quad (1)
\]

Oxygen dissolved in groundwater, as well as water in the absence of oxygen, can be used as an oxidant (Equations 2-4; \( \text{pH} = 7 \)).
\[ \text{O}_2 + 2\text{H}_2\text{O} + 4e^- \leftrightarrow 4\text{OH}^- \quad E_0 = +0.81 \text{ V} \quad (2) \]

\[ 2\text{H}_2\text{O} + 2e^- \leftrightarrow \text{H}_2 + 2\text{OH}^- \quad E_0 = -0.42 \text{ V} \quad (3) \]

\[ \text{H}_2 \leftrightarrow 2\text{H}^+ + 2e^- \quad E_0 = 0.41 \text{ V} \quad (4) \]

Note the standard electrode (Equation 4) is at pH 7, not pH 0. Chlorinated organics can undergo chemical reduction (Equation 5) with reduction potentials ranging from +0.5 to +1.2 V at pH 7, depending on the chlorinated species.\(^{20}\)

\[ \text{RX} + 2e^- + \text{H}^+ \leftrightarrow \text{RH} + \text{X}^- \quad (5) \]

The overall chemical transformation of chlorinated organics at pH 7 using zero-valent iron can involve oxygen (Equations 6) or not (Equation 7).

\[ 2\text{Fe}^0 + \text{RX} + 2\text{H}_2\text{O} + \text{O}_2 \leftrightarrow 2\text{Fe}^{2+} + \text{RH} + 4\text{OH}^- + \text{X}^- \quad (6) \]

\[ E_{0,\text{Net}} = +2.16 \text{ to } +2.68 \text{ V} \]

\[ \text{Fe}^0 + \text{RX} + \text{H}_2\text{O} \leftrightarrow \text{Fe}^{2+} + \text{RH} + \text{OH}^- + \text{X}^- \quad (7) \]

\[ E_{0,\text{Net}} = +0.93 \text{ to } +1.63 \text{ V} \]

Remediation of chlorinated aliphatics, polychlorinated biphenyls, and chlorinated benzenes has been demonstrated using various particle sizes of iron.\(^{15,16,18,21,22}\) Lien and Zhang have shown that the NP forms of iron metal provide advantages of higher reactivity per gram of iron, due to the higher surface to volume ratio of
NPs.\textsuperscript{23} Because of their small size, NPs also demonstrate greater transport effectiveness since they are subject more to Brownian forces than sedimentation forces\textsuperscript{23} and achieve deeper penetration into porous media. These two factors make iron NPs promising for \textit{in situ} treatment of chlorinated compounds.

Other metals, such as zinc, nickel, and tin have been used as zero-valent metal reagents for the dechlorination of chlorinated organics. With the introduction of 0.1 wt\% to 1.0 wt\% Pd to the surface of zero-valent iron, rates of dechlorination were found to increase by an order of magnitude.\textsuperscript{16,24} Also, fewer dechlorination by-products were found compared to zero-valent iron.\textsuperscript{23} In this case, Pd acts as a catalyst (\textit{i.e.}, accelerates reaction, without being consumed), unlike the iron particles, which get consumed. \textit{In situ} field studies using Pd/Fe bimetallic NPs demonstrated rapid dechlorination of TCE over a 4 week period.\textsuperscript{25} However, the fate of the Pd metal was not discussed. Presumably, the Pd metal remains underground once the iron metal is consumed.

\subsection*{1.3 Palladium catalysts}

Pd is one of the most used transition metals in catalysis. We were interested in its ability to catalyze hydrodehalogenation reactions at mild temperatures (20-30 °C) and ambient pressures (1 atm). It has already been mentioned that Pd can enhance the dehalogenation reaction rates over iron metal as a surface coating.\textsuperscript{23} It can also catalyze the reaction directly using hydrogen gas as the reducing agent.\textsuperscript{26-29} Lowry and Reinhard were the first ones to study the use of commercially available 1 wt\% Pd/(Al\textsubscript{2}O\textsubscript{3}) catalysts tested in both laboratory and
pilot-scale units while examining the effects of hydrogen concentration, pH, and poisoning/regeneration for hydrodechlorination (HDC) of TCE and other chlorinated organic compounds.\textsuperscript{27-29} As an advantage over other chemical transformation approaches (\textit{i.e.}, Fe remediation and bioremediation), Pd converts TCE into ethane with minimal formation of vinyl chloride and other chlorinated intermediates.\textsuperscript{27,29,30}

McNab \textit{et al.} successfully operated a down-well, pump-and-treat system using a commercial Pd/Al$_2$O$_3$ catalyst in field tests at the Lawrence Livermore National Laboratory (a Superfund site).\textsuperscript{31} Contaminated groundwater was pumped above ground, mixed with hydrogen gas, sent through catalyst beds, and released back underground. After 76 days of operation, the TCE concentration of the inflow groundwater (~3600 ppb) remained below 5 ppb at a flow rate of 4 L/min with periodic regenerations. A limitation to this becoming a more practical technology appears in the amount and cost of Pd used in the catalyst (Feb. 2006 spot price of $293/oz or $10.3/g). A solution to this problem would be to design and engineer a more active catalyst, thus requiring smaller amounts of palladium.

\subsection*{1.4 Pd-promoted gold catalysts}

The combination of Au and Pd to form a bimetallic catalyst has been studied for a number of reactions, including many oxidation and hydrogenation reactions (Table 1.1). It is clear that Au promotes Pd catalysis in the form of higher activity\textsuperscript{32-39} and more selective product distributions.\textsuperscript{32,40-43} Au is currently being used as an industrial promoter of Pd in British Petroleum's commercial
production of vinyl acetate from ethene, acetic acid, and oxygen, known as the Leap® process.\textsuperscript{44}

Different synthesis routes to Pd/Au bimetallics supported on a porous ceramic support have been studied, such as impregnation, equilibrium adsorption, co-precipitation, ultrasound irradiation, and sequential reduction.\textsuperscript{36,42,45-48} However, it is difficult to ensure that the catalyst preparation method leads to controlled contact of the metals and that there are no separate domains of Pd and Au co-existing with Pd-Au NP domains.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Reaction Conditions</th>
<th>Pd-Au Synthesis Conditions</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO oxidation</td>
<td>(G) / 450 K / 1 atm</td>
<td>Simultaneously reduced NPs (S)</td>
<td></td>
</tr>
<tr>
<td>CFC Hydrodehalogenation</td>
<td>(G) / 423 K / 1 atm</td>
<td>Impregnation-ion exchange (S)</td>
<td></td>
</tr>
<tr>
<td>Acetylene hydrogenation</td>
<td>(G) / 313 K / 1 atm</td>
<td>Impregnation-ion exchange (S)</td>
<td></td>
</tr>
<tr>
<td>1,3-cyclooctadiene hydrogenation</td>
<td>(L) / 303 K / 1 atm</td>
<td>Simultaneously reduced NPs</td>
<td></td>
</tr>
<tr>
<td>Thiophene desulfurization</td>
<td>(G) / 613 K / 1 atm</td>
<td>Simultaneously reduced NPs</td>
<td></td>
</tr>
<tr>
<td>Acetylene cyclization</td>
<td>(G) / 300 K / 1.5 atm</td>
<td>Sequentially reduced NPs</td>
<td></td>
</tr>
<tr>
<td>Alcohol oxidation</td>
<td>(L) / 433 K / 1 atm</td>
<td>Impregnation (S)</td>
<td></td>
</tr>
<tr>
<td>Vinyl acetate production*</td>
<td>(G) / 473K / 8 bar</td>
<td>Pd/Au impregnation</td>
<td></td>
</tr>
</tbody>
</table>

(G) = gas phase, (L) = liquid phase, (S) = supported, *Industrially used catalyst

The use of Pd/Au catalysts for the gas phase dehalogenation of CFCs has been studied.\textsuperscript{41,42,50} A patent has been filed claiming higher activity catalysts
depending on preparation conditions.\textsuperscript{50} Karpinski and coworkers demonstrated that well contacted Pd/Au provides a more selective catalyst as opposed to a more active one when compared to Pd alone.\textsuperscript{41,42} There have been no studies of Pd-Au bimetallic catalysts for aqueous-phase TCE HDC and, more generally, the treatment of halogenated compounds in water. In this thesis, I detail the synthesis and catalysis of Pd-on-Au NPs. In Chapter 2, I describe the synthesis and characterization of Pd/Au bimetallic NPs starting with 20 nm Au NPs. I show that these materials of variable Pd coverage can catalyze TCE HDC, and that they are more active than monometallic Pd NPs, pure Pd-based, and Pd/Au-based supported catalysts. In Chapter 3, I discuss the synthesis of Pd/Au NPs using 4 nm Au NPs, in order to reduce the Au amount and to study in greater detail the HDC activity dependence on nanostructure. I also describe work to immobilize these bimetallic particles on a variety of supports, moving a step closer to a field-ready catalyst. In Chapter 4, I describe work to understand the details of the TCE HDC reaction mechanism more deeply through reaction studies using other chlorinated ethenes.

An early research project during my thesis was to investigate the synthesis of molybdenum oxide (MoO\textsubscript{3}) supported on zirconia (ZrO\textsubscript{2}) NPs via a "sol-gelation" method. We were interested in employing a new synthesis route to thermally stable supported amorphous MoO\textsubscript{3} on ZrO\textsubscript{2}, which have been previously postulated to be highly active oxidation catalysts. In Chapter 5, I describe our synthesis, characterization, and preliminary methanol oxidation results.
1.5 References


Chapter 2

Designing Pd/Au bimetallic nanoparticle catalysts for trichloroethene remediation

2.1 Introduction

Trichloroethene (TCE) is one of the most common organic pollutants found in groundwater.\textsuperscript{1-3} It contaminates ~60\% of the waste sites on the Superfund National Priorities List, and is considered to be one of the most hazardous organic compounds at these sites because of its prevalence and toxicity.\textsuperscript{4,5}

A promising remediation technique involves the use of palladium metal as the basis of a chemical reduction remediation technology.\textsuperscript{6,7} As an advantage over other chemical transformation approaches, palladium converts TCE into ethane without the formation of vinyl chloride and other chlorinated intermediates\textsuperscript{8,9} that often occur with bioremediation\textsuperscript{10} and with iron metal.\textsuperscript{11} What may limit the applicability of this technology compared to other treatment methods is the amount and cost of catalyst (52 kg, at a pre-2000 cost of $270/kg\textsuperscript{12}). One solution to this problem would be to design and engineer more active catalysts.

In this work, we investigated the potential of enhanced catalytic performance of palladium catalysts through the use of gold metal. Gold is generally considered too noble a metal to participate in catalytic reactions, unless it is in the form of small NPs, in combination with other metals, or as cations.\textsuperscript{13-16} The combination of gold and palladium to form a bimetallic catalyst has been studied for a number of reactions.\textsuperscript{17-25} As far as we know, there have been no studies of these materials for the treatment of halogenated compounds in aqueous solution.
Different synthesis routes to Pd/Au bimetallics have been studied, such as co-precipitation, ultrasound irradiation, sequential reduction.\textsuperscript{18,21,23,26,27} For most of the Pd-Au bimetallic materials prepared on a porous ceramic support, it is difficult to ensure that the catalyst preparation method leads to controlled contact of the metals and that there are no separate domains of palladium and gold in addition to the Pd-Au domains. We sought to eliminate this issue by directing supporting palladium metal on the surfaces of freely suspended gold NPs. In this paper, we describe the synthesis and characterization of Pd/Au bimetallic NPs. We show that these materials of variable palladium coverage can catalyze TCE HDC, and that they are more active than monometallic palladium NPs and bulk Pd-based catalysts. Using the Pd/Au NP synthesis chemistry, we report on the preparation and catalysis of alumina-supported Pd/Au NPs.

2.2 Experimental methods

2.2.1 Synthesis

Monometallic Nanoparticles: Gold nanoparticles (Au NPs, diameter \~ 20 nm) were synthesized through the citrate reduction method.\textsuperscript{28} A gold salt solution was prepared by diluting 200 \(\mu\)L of a H\(\text{AuCl}_4\) solution (0.25 M; AuCl\(_3\) 99.99\%, Sigma-Aldrich) in 200 g of Nanopure water (>18 M\(\Omega\)-cm, Barnstead NANOpure Diamond). The solution was heated and stirred until boiling, after which 12 mL of a trisodium citrate solution (0.0345 M; 99.5+\%, Fisher) was added. Heating of the nearly colorless solution was continued, and after approximately 10 min of boiling, the solution was removed from the heat source. The resulting fluid was a dark wine red color, representative of colloidal gold NP suspension (or gold sol).
Palladium nanoparticles (Pd NPs) were synthesized through methanol reduction based on the method reported by Teranishi and Miyake.\textsuperscript{29} 14 mL of methanol (99.5%, Sigma-Aldrich) and 8 mg of poly(vinylpyrrolidone) (PVP; 29 kDa, Sigma-Aldrich) were added to 21 mL of Nanopure H$_2$O and refluxed for 10 min. 15 mL of a H$_2$PdCl$_4$ solution (2.39 mM; PdCl$_2$ 99.9+%, Aldrich) was added to the refluxing solution, and the resulting solution was refluxed for another three hours. The resulting palladium sol had a coffee-black color. TEM indicated a broad particle size distribution of 3-10 nm.

Bimetallic Nanoparticles: The synthesis of palladium-on-gold bimetallic nanoparticles (Pd/Au NPs) was carried by adding controlled amounts of palladium salt and a reducing agent to the gold sol. 2 mL of the gold sol was diluted with 4.5 mL H$_2$O such that the NP concentration was 3.6×10$^{11}$ NP/mL (= 1.46×10$^{-4}$ M). 0.5 mL of an ascorbic acid solution (0.1 M; 99+%, Sigma-Aldrich) was then added, for a final liquid volume of 7 mL. 8.6 µL aliquots of a H$_2$PdCl$_4$ solution (2.39 mM) added stepwise until the desired final solution volumes were reached; 8.6, 78.4, and 232 µL of total palladium solution corresponded to materials with a final palladium weight loading of 1.9%, 15.3%, and 35.1%, respectively. The suspension was stirred at room temperature for 0.5 hours, which ensured completion of the palladium deposition reaction. A control sample was prepared by adding the ascorbic acid solution without the palladium salt solution to the Au NPs.

A separate set of Pd/Au NPs were prepared with a wider range of palladium loading for X-ray photoelectron spectroscopy studies. 4.5 mL of water and 0.5 mL of 0.1 M ascorbic acid was added to 2 mL of the Au NP sol and mixed.
Aliquots of 8.7 µL of the palladium precursor (H₂PdCl₄) were added until the desired amount of palladium was reached. Total volumes of 8.7, 52.2, 130.5, and 261 µL of the palladium precursor were added to give 0.333, 2, 5, 10 calculated layers of palladium on the Au NPs. After 30 minutes, the sols were centrifuged overnight (~12 hr) at 4750 rpm. The settled NPs were transferred onto glass slides and allowed to dry at 70 °C for 2 h.

Alumina-supported Catalysts: As control samples, palladium supported on high surface area γ-alumina (Pd/Al₂O₃ with 1 wt% Pd) and palladium powder in the form of palladium-black (99.99% Pd) were obtained from Sigma-Aldrich (Table 2.1). Au/Al₂O₃ was prepared by incipient wetness impregnation of 8 g of γ-alumina (99.5%, Strem) with 5.6 mL of the HAuCl₄ solution (0.25 M). The resultant material was dried for 30 min at 120 °C and calcined in air (100 sccm) at 450 °C for 3 hours.³⁰

Two Pd/Au/Al₂O₃ materials were prepared by incipient wetness impregnation. For a 1 wt% palladium-containing sample, 2.23 g of the Au/Al₂O₃ material was impregnated using 1.55 mL of the H₂PdCl₄ solution (0.1 M), dried for 30 min at 120 °C, impregnated further using 1.55 mL of the H₂PdCl₄ solution (0.039 M), and dried for 30 min at 120 °C. For a 0.1 wt% palladium containing sample, 2.23 g of the Au/Al₂O₃ material was impregnated using 1.55 mL of H₂PdCl₄ solution (0.014 M) and dried for 30 min at 120 °C. Au/Pd/Al₂O₃ was prepared by incipient wetness impregnation of 1 g of Pd/Al₂O₃ with 0.9 mL of HAuCl₄ solution (0.56 mM) and dried for 30 min at 120 °C. All three materials were then calcined in air (100 sccm) at 450 °C for 3 hours, and reduced in a 50/50 (by volume) H₂/N₂ mixture (100 sccm) at 390 °C for 1 hour. Needed for the incipient wetness
method, the pore volumes of the different powders were determined through gas adsorption analysis and confirmed with a water uptake test.

**Table 2.1** Pd content and surface areas for monometallic NPs, bimetallic NPs, Pd-black, and alumina-supported materials studied for TCE HDC.

<table>
<thead>
<tr>
<th>Sample type</th>
<th>Pd amount (wt%)</th>
<th>Specific surface area (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd NP</td>
<td>100</td>
<td>86²</td>
</tr>
<tr>
<td>Pd black</td>
<td>~100</td>
<td>17</td>
</tr>
<tr>
<td>Pd/Al₂O₃</td>
<td>1</td>
<td>177</td>
</tr>
<tr>
<td>Au NP</td>
<td>0</td>
<td>15ᵇ</td>
</tr>
<tr>
<td>1.9-Pd/Au NP</td>
<td>1.9</td>
<td>15ᵇ</td>
</tr>
<tr>
<td>15.3-Pd/Au NP</td>
<td>15.3</td>
<td>15ᵇ</td>
</tr>
<tr>
<td>35.1-Pd/Au NP</td>
<td>35.1</td>
<td>15ᵇ</td>
</tr>
<tr>
<td>Au/Al₂O₃⁽ᶜ⁾</td>
<td>0</td>
<td>144</td>
</tr>
<tr>
<td>0.1-Pd/Au/Al₂O₃⁽ᶜ⁾</td>
<td>0.1</td>
<td>144</td>
</tr>
<tr>
<td>1-Pd/Au/Al₂O₃⁽ᶜ⁾</td>
<td>1</td>
<td>144</td>
</tr>
<tr>
<td>Au/Pd/Al₂O₃⁽ᶜ⁾</td>
<td>1</td>
<td>177</td>
</tr>
</tbody>
</table>

²Calculation based on spherical particles with a diameter of 6.1 nm

ᵇCalculation based on spherical particles with a diameter of 20 nm

⁽ᶜ⁾1 wt% Au loading

2.2.2 Characterization methods

UV-vis absorbance spectra of the monometallic and bimetallic NP suspensions were collected on a Shimadzu UV-2401 PC spectrophotometer using a quartz cuvette with a 1 cm path length. Hydrodynamic diameters (Dₘ) were measured using ZetaPALS dynamic light scattering (DLS) unit from Brookhaven Instruments Corporation utilizing a 656-nm wavelength laser with time intervals
of 15 minutes. X-ray diffraction (XRD) patterns of dried NPs and supported catalysts were collected on a Rigaku Ultima D/Max 2100 x-ray powder diffractometer utilizing Cu kα radiation (λ = 1.54056 Å). Grain size analysis was carried on the (111) peak of palladium and gold using Scherrer’s formula. BET (Brunauer-Emmett-Teller) surface areas and pore volumes of the supported catalyst powders were determined using a Micromeritics ASAP 2010 nitrogen gas adsorption analyzer. The NP materials were imaged using a JEOL 2010 transmission electron microscope (TEM) to derive information about particle size and morphology. Atomic compositions of the bimetallic NP surfaces were determined using a PHI Quantera SXM X-ray photoelectron spectrometer (XPS). The NPs were removed from the suspending fluid through centrifugation and deposited on a glass slide. The surface that is analyzed includes a sub-surface region of ~0.5-5 nm thickness.

2.2.3 Catalytic experiments

Batch reactor experiments were conducted in serum bottles (160 mL, VWR). Nanopure water (106 mL) and a magnetic stir bar were sealed in the reactor and sparged with hydrogen gas (99.999%, Matheson Trigas) for 12 min to displace oxygen dissolved in water and filling the headspace with a H₂ atmosphere (~1 bar). After the serum bottle was sealed with a rubber septum, ~3.5 μL of TCE (99.5%, Aldrich) was added, and 1 μL of pentane (99.7%, Burdick & Jackson) was added as an internal standard. The monometallic NP sols were diluted to 7 mL, and injected into the septum, and 7 mL of the bimetallic NP sols were injected after synthesis without further dilution such that a total of 2.5×10¹⁰ NPs
was added. Palladium-black and the powder alumina-supported palladium catalysts (2.9 and 16.4 mg, respectively) were suspended in 7 mL of H₂O before being injected into the reactor. The catalytic reactions were conducted at room temperature (22-25 °C) under constant magnetic stirring and monitored for ~80 min.

The reaction was monitored through headspace gas chromatography (GC), in which 100 μL of headspace gas in the septum bottle is withdrawn with a gas-tight syringe and injected into a HP5890 GC equipped with a flame ionization detector (FID) and a packed column (6' x 1/8" OD) containing 60/80 Carbopack B/1% SP-1000 (Supelco). Calibration curves were made for chlorinated ethenes, chlorinated ethanes, ethane, and methane. Headspace TCE gas composition was related back to the liquid-phase compositions using Henry's law (log Kᵢₜ=1.03 L atm mol⁻¹ @ 25 °C)³¹. The initial TCE concentration in the liquid was in the range of 57-92 ppm (1 ppm = 1 mg/L), below the saturation concentration of 1200 ppm at 25 °C³¹.

Reaction rate constants were determined from the first-order rate law of the TCE HDC reaction, as reported by Reinhard and coworkers⁹:

\[
\frac{-dC_{TCE}}{dt} = k_{app} C_{TCE} \quad (1),
\]

where \(k_{app} = k_{obs} \times C_{cat}\), where \(k_{obs}\) is the reaction rate (with units of L/gpd/min) and \(C_{cat}\) is the concentration of palladium metal charged to the reaction volume. Initial turnover frequencies (TOF's) were estimated using the initial TCE
concentration, the reaction rate, and total amount of palladium atoms charged to the reactor.

2.3 Results and discussion

2.3.1 Palladium particle size effect on catalysis

The nature of the palladium metal is clearly different in Pd NPs, palladium-black, and Pd/Al₂O₃. Palladium could be detected by XRD in the Pd NPs and palladium-black (Figure 2.1), with the broadened diffraction peaks indicating the presence of palladium nanocrystals (Table 2.2).

Whereas the Pd NPs are fully dispersed as a colloidal suspension, palladium-black is essentially bulk powder composed of aggregated NPs, which has a lower surface area compared to that calculated for the Pd NPs. The palladium metal dispersion (or the percentage of palladium atoms that are surface atoms) of palladium-black was calculated to be 3.8%, using the measured surface area value and assuming a palladium atom cross-sectional area of 0.0787 nm².

The Pd NPs were larger and more broadly sized than those reported by Teranishi and Miyake.²⁹ XRD analysis indicated a grain size of 6.1 nm, which we used as an estimate of the average particle size (Table 2.2). The metal dispersion of Pd NPs could be calculated by approximating the NPs as cuboctahedral structures formed as a closed-shell, close packing of palladium atoms.³² Pd NPs of dimension 6.1 nm would be equivalent to having 11 shells of palladium atoms surrounding a central atom to give a metal dispersion of 24% (1,212 surface atoms out of a total of 5,083 atoms).
Table 2.2 Grain sizes of palladium in various materials determined from XRD analysis.

<table>
<thead>
<tr>
<th>Sample type and name</th>
<th>Crystal Grain size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd NP</td>
<td>6.1</td>
</tr>
<tr>
<td>Pd black</td>
<td>8.2</td>
</tr>
<tr>
<td>Pd/Al₂O₃</td>
<td>—</td>
</tr>
</tbody>
</table>

Figure 2.1 XRD patterns of (a) Pd NPs, (b) Pd-black, and (c) Pd/Al₂O₃. XRD diffraction peaks at 2θ = 40.1° and 2θ = 46.7° are due to the (111) and (200) reflections of Pd, respectively.

The palladium in the NP form is more materials efficient than as an aggregated powder, exposing more surface atoms, which can participate in surface reactions. Pd/Al₂O₃ was estimated to have a metal dispersion of 21%, based on published value. No XRD peaks for palladium metal were detected, indicating
the 1 wt% palladium content had particle sizes below the XRD detection limit of
~4 nm (Figure 2.1c).

The effect of palladium particle size on TCE HDC was evaluated by comparing
Pd NPs, palladium-black, and Pd/Al₂O₃ (Table 2.3). The three materials were
active for the reaction, and their catalytic activities decreased as follows: Pd NP
> Pd/Al₂O₃ > palladium-black.

<table>
<thead>
<tr>
<th>Sample type and name</th>
<th>( k_{\text{obs}} ) (L/gpd/min)</th>
<th>Initial TOF ( \text{mol}<em>{\text{TCE}}/\text{mol}</em>{\text{Pd, surface}}/\text{min} )</th>
<th>Selectivity to ethane during reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Palladium-black</td>
<td>0.42</td>
<td>4.6</td>
<td>~98%</td>
</tr>
<tr>
<td>Pd/Al₂O₃</td>
<td>12.2</td>
<td>25.2</td>
<td>~98%</td>
</tr>
<tr>
<td>Pd NP</td>
<td>62.0</td>
<td>122.0</td>
<td>~98%</td>
</tr>
<tr>
<td>No Pd catalyst</td>
<td>0</td>
<td>0</td>
<td>—</td>
</tr>
</tbody>
</table>

The reaction rates appear to track with decreasing palladium dispersion (24%,
21%, and 3.8%, respectively), with Pd NP material as the most active per
surface palladium atom. Ethane was detected as the sole product, down to a
detection level of 0.3 ppm, and no other products were found. Reinhard and co-
workers reported on the TCE HDC activities of Pd/Al₂O₃ and palladium-black.⁹
Although the reaction testing conditions and catalyst samples were different,
their data indicated that Pd/Al₂O₃ was more active than palladium-black on a
palladium weight basis, consistent with our findings.
To assess the effect of metal dispersion on reaction rates, we calculated TOF values as molecules of TCE reacted per number of surface palladium atoms per minute (Table 2.3). The catalytic activities, based on TOF's, still followed the trend of Pd NP > Pd/Al₂O₃ > palladium black. While metal dispersion accounted for some of the difference in catalytic activity among the three materials, the TOF's indicate differences in the intrinsic surface reactivity of the palladium atom active sites for TCE HDC. This observation is similar to the findings of other research groups that surface palladium atoms of low coordination numbers found as surface defects (such as those located at the corners and edges of NPs) were the active sites for Suzuki and Heck carbon coupling organic reactions.³²-³⁵ For the Pd/Al₂O₃ material, it has been reported that the alumina support can promote palladium activity through electronic effects.³⁶

It is noted that the Pd NPs have an adsorbed layer of PVP that keeps the NPs in suspension through steric stabilization. The NPs remained in suspension during and after the reaction, indicating that these steric interactions were not disrupted by the surface reaction. The binding of the polymer to the surface may reduce the number of active sites accessible for reaction, leading to conservative TOF estimates. Control experiments showed that PVP and methanol present in the palladium sol did not affect the reaction rates (Table 2.3).

2.3.2 Nanostructure of Pd/Au bimetallic NPs and effect on catalysis

The gold sol was ruby red after synthesis and turned light pink after dilution with water and an ascorbic acid solution, exhibiting the characteristic plasmon resonance peak at ~520 nm (Figure 2.2a). Addition of 8.6 µL of the H₂PdCl₄
solution (2.39 mM) caused a change in the UV-vis spectra of the gold sol (Figure 2.2b), with a decrease in the intensity of the resonance peak and an increase in the absorption edge at wavelengths above 520 nm.

![UV-vis spectra of sols](image)

**Figure 2.2** UV-vis spectra of sols (2.3×10^{11} NP/mL) resulting from the addition of H_2PdCl_4 to a Au sol containing ascorbic acid: (a) Au NPs and Au NPs with (b) 1.9 wt% palladium, (c) 3.8 wt%, (d) 5.7 wt%, and (e) 11.4 wt%.

This change in optical properties follows a pattern theoretically predicted for Pd-coated Au NPs. Additional aliquots of palladium salt introduced to the above sol accentuated the differences in the UV-vis spectra, with a distinct change occurring between samples containing 3.8 wt% and 5.7 wt% palladium.

It is concluded that Pd^{2+} reduced and deposited onto the Au NP surface as a metal in the presence of ascorbic acid, a reducing agent commonly used to
prepare metal NPs.\textsuperscript{37,38} Without ascorbic acid, increasing amounts of palladium salt added to the gold sol led to negligible changes in the UV-vis spectra of the resultant sols (Figure 2.3).

![UV-vis spectra](image)

**Figure 2.3** UV-vis spectra of sols ($2.5\times10^{11}$ NP/mL) resulting from the addition of $\text{H}_2\text{PdCl}_4$ to the Au sol without the ascorbic acid. The arrow indicates the progression of UV-vis spectra with increasing amounts of Pd precursor.

Because the Au$^{3+}$/Au$^0$ pair ($E^\circ = +1.50$ V, vs. standard hydrogen electrode, pH = 0) has a more positive standard reduction potential than the PdCl$_4^{2-}$/Pd$^0$ pair ($E^\circ = +0.59$ V),\textsuperscript{39} Pd$^{2+}$ cannot be reduced by the surface Au$^0$ atoms of the Au NPs. More reactive metals, such as iron (Fe$^{2+}$/Fe$^0$, $E^\circ = -0.45$ V), can react with Pd$^{2+}$ to form palladium metal (Fe$^0$ + PdCl$_4^{2-}$ $\rightarrow$ Fe$^{2+}$ + Pd$^0$), as reported by Wang and Zhang in their preparation of palladium-coated Fe NPs.\textsuperscript{40} By a similar argument
(ascorbic acid + PdCl$_4^{2-}$ → dehydroascorbic acid + Pd$^0$), ascorbic acid can reduce Pd$^{2+}$ because the dehydroascorbic acid/ascorbic acid pair has a lower $E^\circ$ (calculated to be $+0.47$ V at pH 0) than that of the PdCl$_4^{2-}$/Pd$^0$ pair.$^{41}$

Calculations indicate that Pd/Au NPs containing 1.9, 3.8, 5.7, and 11.4 wt% palladium have $\frac{1}{3}$, $\frac{2}{3}$, 2, and 3 layers of palladium atoms, respectively. Samples with multiple layers of palladium exhibit significantly different UV-vis spectra compared to samples of sub-monolayer palladium coverages (Figure 2.2). The decrease in the 520-nm resonance peak and emergence of a $\sim$700 nm peak can be attributed to the formation of suspended aggregates, in which the gold cores electronically couple with one another.$^{42}$ Macroscopically, sols containing Pd/Au NPs with sub-monolayer coverage retained the pinkish hue of the diluted parent Au NPs, but those containing NPs with $>1$ monolayer coverage had a gray-violet tint.

Figure 2.4 illustrates the proposed scenario of how the Pd/Au NP structure evolves with increasing palladium loading, based on the UV-vis spectra (Figure 2.2). DLS experiments showed an increase in hydrodynamic diameter (from 20 nm to $\sim$150 nm) going from 3.8 wt% to 5.7 wt%, consistent with the onset of aggregation. TEM studies of these NP samples were carried out to corroborate the UV-vis data, but neither the state of aggregation nor the palladium shell thickness could be clearly ascertained (Figure 2.5). There was no evidence for the homogeneous nucleation and growth of Pd NPs during palladium coating of the Au NPs, as the UV-vis spectra of colloidal mixtures of Au and Pd NPs (Figure 2.6) did not resemble those of Pd/Au NP samples with equivalent palladium content.
Figure 2.4. Proposed evolution of Pd-on-Au NP structure with increasing palladium content.

Figure 2.5. TEM images of (a) Au NPs and (b) Pd/Au NPs (1.9 wt% palladium).

XPS experiments were performed to determine semi-quantitatively the surface composition of Pd/Au NPs. Based on the palladium $3d_{5/2}$ peak located at 335.3 eV and gold $4f_{7/2}$ peak located at 84.0 eV, the Pd/Au surface ratios were found to
increase with increasing total palladium loading (Table 2.4). For all but the lowest loadings, the Pd/Au surface ratio was higher than the Pd/Au in the bulk, providing experimental proof that the palladium was located on the Au NP surface.

![Absorbance spectra](image)

**Figure 2.6** UV-vis spectra of sols comprising of (a) Au NPs, (b) Pd NPs, and colloidal mixtures of the Au and Pd NPs representing equivalent amounts of palladium precursor added: (c) 6.3 wt%, (d) 13.1 wt%, and (e) 33.1 wt%.

For the material with the lowest palladium loading, the closeness and small values of the bulk and surface Pd/Au ratios suggest very high dispersion of the palladium. A small amount of unreduced palladium was also detected through XPS measurements, which we attribute to exposure to air during sample preparation (as noted by others\textsuperscript{18,43}).
Table 2.4. Calculated and experimental surface compositions of Pd/Au NPs.

<table>
<thead>
<tr>
<th>Palladium amount (wt%)</th>
<th>Calculated number of layers</th>
<th>Calculated Pd/Au bulk ratio</th>
<th>Pd/Au surface ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.9</td>
<td>$1/3$</td>
<td>0.022</td>
<td>0.018</td>
</tr>
<tr>
<td>7.3</td>
<td>2</td>
<td>0.131</td>
<td>0.229</td>
</tr>
<tr>
<td>16.5</td>
<td>5</td>
<td>0.328</td>
<td>0.499</td>
</tr>
<tr>
<td>28.2</td>
<td>10</td>
<td>0.655</td>
<td>2.40</td>
</tr>
</tbody>
</table>

The possibility of unreduced palladium participating in the TCE HDC reaction is remote, since the palladium would be expected to reduce to Pd$^0$ under the hydrogen atmosphere at room temperature.

Pd/Au NPs were highly active for the TCE HDC. Au NPs were inactive for the reaction, but a submonolayer of surface palladium on Au NPs (1.9 wt% palladium) led to a dramatic enhancement in activity (Figure 2.7). The most active of the Pd/Au NP materials, 1.9-Pd/Au NPs had rate constants 15, 77, and ~2200 times greater than those of pure Pd NPs, Pd/Al$_2$O$_3$, and palladium-black, respectively (Table 2.3). Increased palladium loadings in Pd/Au NPs led to NPs with decreased rate constants, suggesting that Pd/Au NPs with palladium coverages in excess of 1 calculated monolayer behave more like pure Pd NPs than submonolayer-covered Pd/Au NPs. We note that exposed palladium atoms do not account for the observed higher activities of the Pd/Au NPs, based on rough calculations of exposed palladium atoms.
The reaction products of Pd/Au NPs differ, depending on the palladium coverage. With >1 monolayer coverage, Pd/Au NPs produced mostly ethane (~92% selectivity), similar to the various forms of palladium catalysts (Table 2.3).

Figure 2.7 Experimentally determined TCE HDC rate constants (listed next to plotted points) of Pd/Au NPs with varying palladium content.

The formation of ethene was observed over 1.9-Pd/Au NPs at low TCE conversions, with ethene accounting for ~70% of the product with ethane as the balance. At higher TCE conversions, ethane became the dominant product, suggesting ethene hydrogenation occurred. The reaction mechanism of TCE HDC over Pd/Au NPs differs from that over palladium metal.

Under the aqueous and room-temperature reaction conditions used, H₂ and TCE likely adsorb dissociatively on the metal to form H atoms, Cl atoms, and
TCE fragments, as H$_2$ and chlorinated ethenes are known to do so over palladium surfaces under gas-phase and ultrahigh vacuum conditions.$^{44-47}$ We propose that the adsorbed TCE fragment dechlorinates and hydrogenates to form ethene, which further hydrogenates to form ethane. Lowery and Reinhard proposed a similar sequential reaction pathway over Pd/Al$_2$O$_3$, although they concluded that a lack of chlorinated byproducts suggested a direct conversion of TCE into ethane.$^9$

For the Pd/Au NPs, the observed catalytic behavior indicates the gold surface enhances the catalytic activity and can change the reaction products formed. How the gold promotes the catalytic activity of palladium for other reactions could be due to geometric effects, electronic effects, the participation of Au-Pd active sites, or the reduction of a palladium hydride phase.$^{48}$ For TCE HDC, an electronic inductive effect by the gold on the supported palladium metal may be responsible for the increased reaction rates, especially for the materials containing >1 monolayer of palladium.$^{44}$ For Pd/Au NPs with <1 monolayer of palladium, it is not clear yet how the exposed gold surface favors the formation of ethene over that of ethane. The selectivity data suggest that gold surface greatly enhances the conversion of TCE to ethene, but to a lesser extent, the conversion of ethene to ethane. The latter reaction then becomes the rate-limiting step in TCE HDC. We speculate there is a lower amount of available surface hydrogen atoms in Pd/Au NPs with submonolayer amounts of palladium since it is known that H$_2$ does not dissociate over gold surfaces,$^{49}$ allowing ethene to desorb more rapidly than it hydrogenates. Bonarowska et al. reported that gold lowered the amount of hydrogen that could be chemisorbed by
palladium in silica-supported Pd-Au alloy catalysts. Clearly, there is an observed synergy between the palladium metal and the gold surface for all Pd/Au NP materials for the HDC reaction.

2.3.3 Supported Pd and Pd/Au catalysts

With evidence that gold promotes the catalytic activity of palladium for TCE HDC in a bimetallic core/shell configuration, we sought to improve the performance of Pd/Al₂O₃ by using gold. XRD peaks for gold metal could be observed in the 1 wt% Au-impregnated γ-alumina, and after impregnation with 1 wt% palladium, reduction, and calcination, the grain size of the gold increased from 5.5 nm to 8.4 nm (Figure 2.8). A similar increase was found after impregnation with 0.1 wt% palladium. Palladium metal was highly dispersed on the support, as XRD peaks for palladium were not detected. Palladium metal appears to have a greater affinity for the Al₂O₃ support than the gold metal does, which suggests that selective metal deposition using ascorbic acid can lead to formation of Pd NPs directly on alumina in addition to palladium metal on the alumina-supported gold surface.

Pd/Au/Al₂O₃ samples of two different palladium loadings were analyzed for TCE HDC, and compared against Au/Al₂O₃ and Pd/Al₂O₃ (Figure 2.9). The supported gold material was inactive for the reaction, as in the case of the unsupported Au NPs (Figure 2.7), whereas both 0.1 wt% and 1 wt% palladium-containing materials were active.
Figure 2.8 XRD patterns of (a) the Al₂O₃ support, (b) Au/Al₂O₃ (1 wt% Au), and (c) 1-Pd/Au/Al₂O₃. XRD diffraction peaks at 2θ = 40.1° and 46.7° are due to the (111) and (200) reflections of palladium, respectively, and the XRD peaks at 2θ = 38.2° and 44.4° are due to the (111) and (200) reflections of gold, respectively.

Figure 2.9 Experimentally determined TCE HDC rate constants of Pd/Au/Al₂O₃ samples of varying palladium content: (a) Au/Al₂O₃, (b) 0.1-Pd/Au/Al₂O₃, (c) 1-Pd/Au/Al₂O₃, (d) Pd/Al₂O₃, and (e) Au/Pd/Al₂O₃.
The reaction rates were higher than that of Pd/Al₂O₃, providing indirect proof that there are Pd/Au NP domains that are supported on alumina. If the palladium did not coat the gold metal and formed only NPs on the support, then one would expect the materials to be no more active than Pd/Al₂O₃.

Impregnation of Pd/Al₂O₃ with the same amount of gold as in the other samples (1 wt%) should lead to the deposition of gold metal on the supported Pd NPs, the alumina surface, or both. The TCE HDC activity was not enhanced relative to the Pd/Al₂O₃, supporting the concept that the Pd-on-Au (and not the Au-on-Pd) configuration is responsible for the higher, observed catalytic activities.

2.4 Summary and conclusions

In summary, nanoscale effects are observed in a new type of catalyst for the destructive removal of chlorinated compounds. Stable suspensions of palladium-based NPs can effectively hydrodechlorinate TCE in water at room temperature under hydrogen atmosphere. Monometallic Pd NPs are more active than palladium-black and Pd/Al₂O₃ powders on a per-gram palladium basis. The higher activity could be due to the greater amount of coordinatively unsaturated palladium atoms located as surface defects on the Pd NPs. Bimetallic Pd/Au NPs exhibit a more significant increase in HDC activity than Pd NPs, with the greatest enhancement for Au NPs partially covered by palladium metal. Catalytically inactive for the reaction, Au NPs may be promoting the palladium activity through electronic or geometric effects, or through direct participation in the HDC reaction mechanism. The catalyst structure of palladium metal
supported on gold surfaces provides a new design criterion for ceramic-supported palladium catalysts and may be applicable to other bimetallic systems. The Pd/Au bimetallic materials are promising catalysts for dehalogenation of organic compounds and the reductive removal of hazardous inorganic salts that contaminate groundwater. Current efforts are focused on studying the long-term catalytic stability of the materials, optimizing the synthesis conditions for the alumina-supported Pd/Au catalysts, and understanding the source of the gold promotion effect.

2.5 References


Chapter 3

Elucidating the effects of Pd coverage on Au NPs for trichloroethene hydrodechlorination

3.1 Introduction

Trichloroethene (TCE) is considered one of the most common hazardous organic contaminants found in groundwater due to its prevalence and toxicity.\textsuperscript{1-5} The government has prioritized groundwater remediation by setting up Superfund National Priority Sites where treatment methods such as air-stripping, carbon adsorption, bioremediation, and \textit{in situ} thermal treatments are being investigated.\textsuperscript{3,6-8} There is also promise in the development of catalytic remediation technologies that utilize supported palladium metal as a catalysts for chemical reduction.\textsuperscript{9-13} As an advantage over other remediation approaches, palladium converts TCE into ethane with minimal formation of vinyl chloride and other chlorinated intermediates\textsuperscript{11,14} that often occur with anaerobic bioremediation\textsuperscript{7} and with iron metal.\textsuperscript{15}

In our previous work, we compared the TCE HDC catalytic activity of unsupported Pd NPs, palladium supported on alumina (Pd/Al\textsubscript{2}O\textsubscript{3}), and palladium-black, and found that the Pd NPs were more active due to more efficient use of the metal (\textit{i.e.}, higher palladium dispersion).\textsuperscript{16} Working towards the goal of increasing the dispersion and reducing the catalyst cost, we discovered that palladium catalytic activity was increased by as much as \textasciitilde70 times (943 L/g\textsubscript{Pd}/min) compared to Pd/Al\textsubscript{2}O\textsubscript{3} (12 L/g\textsubscript{Pd}/min), by supporting palladium metal on the surface of Au NPs. This report described the use of a Pd-on-Au (Pd/Au) bimetallic composition for the aqueous-phase remediation of
chlorinated compounds for the first time, complementing the work by others on the gas-phase hydrodehalogenation of halogenated compounds.\textsuperscript{17-19} The promotion effect of gold on palladium catalytic activity is a well-known phenomenon for a number of model reactions,\textsuperscript{20-23} including the commercial production of vinyl acetate.\textsuperscript{24-28} The general explanations for the synergistic combination of two metals are a geometric effect, an electronic effect, or a combination of both,\textsuperscript{29} depending on the metal composition and the reaction. The presence of mixed metal active sites and, unique to palladium-based catalysts, the suppression of a less active $\beta$-PdH phase have been hypothesized.\textsuperscript{30,31} It is not yet known how gold promotes palladium activity for aqueous-phase TCE HDC.

We were motivated by cost reduction considerations to synthesize Pd/Au NPs with smaller diameters than the $\sim 20$ nm particles used in our original study. Here, we report the successful synthesis and catalytic properties of Pd/Au NPs with gold particle diameters of 4 nm and with variable palladium loadings. We show that the colloidal NPs exhibit a clear volcano-shape activity dependence on palladium metal content. We identify three regions of catalytic activity and discuss the possible promotion effects of gold on palladium catalysis. Towards a practical catalyst for flow reactor studies and future spectroscopic studies, we present results for a NP immobilization strategy based on electrostatic interactions between the Pd/Au NPs and the porous support.

3.2 Experimental methods

3.2.1 Synthesis
Monometallic Nanoparticles: Gold nanoparticles (Au NPs) were synthesized by modifying the method reported by Slot and Geuze.\textsuperscript{32} A gold salt solution was prepared by diluting 100 \( \mu \)L of a H\textsubscript{2}AuCl\textsubscript{4} solution (0.296 M; AuCl\textsubscript{3} 99.99\%, Sigma-Aldrich) in 80 mL of Nanopure water (>18 M\( \Omega \)cm, Barnstead NANOpure Diamond). A second solution containing 0.04 g trisodium citrate (99.5+\%, Fisher), 0.05 g tannic acid (99.5+\%, Sigma-Aldrich), and 0.018 g potassium carbonate (99.5+\%, Sigma-Aldrich) dissolved in 20 mL of Nanopure water was prepared. Both solutions were stirred while being heated to 60 °C. Once this temperature was reached, the tannic acid solution was added to the gold chloride solution; an immediate color change (from pale yellow to reddish-brown) was observed. The solution was then heated and left to boil for 2 min, and then removed from the heat source. The final fluid had a dark brown-red color. 20-nm Au NPs (1.16\( \times \)10\textsuperscript{12} NP/mL) were prepared through the citrate reduction method, as previously described.\textsuperscript{16}

Palladium nanoparticles (Pd NPs) were synthesized using the above method by substituting the gold salt solution with an H\textsubscript{2}PdCl\textsubscript{4} solution (2.47 mM; PdCl\textsubscript{2} 99.9+\%, Aldrich). The procedure was carried in the same manner except that the reaction mixture was boiled for 25 minutes instead of 2 min. A portion of the water volume (72\%) evaporated during the boiling step. The resulting yellow fluid was aged overnight at room temperature, resulting in a coffee-black colored fluid. The NPs are \( \sim \)4 nm in diameter, according to transmission electron microscopy. 1 wt\% Pd/Al\textsubscript{2}O\textsubscript{3} (Sigma-Aldrich) was run as a reference sample.

Bimetallic Nanoparticles: The synthesis of bimetallic Pd/Au NPs was carried out by mixing specific volume (0-287 \( \mu \)L) of H\textsubscript{2}PdCl\textsubscript{4} solution (2.47 mM) to 2 mL
of the Au NP sol (1.26×10^{14} NP/mL) and stirring for at least 15 min. Hydrogen gas (99.99%; Matheson) was then bubbled through the synthesis fluid for 1 min. The resultant NP sol was left to sit at room temperature overnight. A control sample was prepared by bubbling H₂ gas through the Au NP sol without the palladium salt.

Oxide-supported Pd/Au bimetallic NPs: Three different oxide materials were used as supports for immobilizing the Pd/Au NPs: γ-alumina (Al₂O₃, 99.9%; Strem), magnesium oxide (MgO, 99.9%; Sigma-Aldrich), and silicon oxide (SiO₂, 99.9%; Cabosil-Cabot). For both Al₂O₃ and MgO, 0.47 g of powder were combined with 8 mL of a Pd/Au NP sol and stirred overnight at room temperature. For SiO₂, 0.20 g were suspended in 2.04 mL of ethanol for 10 min. 0.13 g of 3-aminopropyltriethoxysilane (APTES) was then added and stirred overnight. This slurry was washed three times with 3.8 mL of ethanol per wash to remove any unbound APTES. This amine-functionalized SiO₂ was combined with 8 mL of a Pd/Au NP sol and stirred overnight at room temperature. The NP-supported powders were concentrated into slurry form through centrifugation and decantation of the supernatant.

In immobilization stability tests, Au NPs were used instead of Pd/Au NPs. These Au NP-supported materials were underwent a washing procedure after the contacting the NPs. Nanopure water (6 mL) was added to the powders and stirred for 30 min. The suspensions were centrifuged, and the supernatant removed and analyzed for any Au NPs leached.

3.2.2 Characterization
UV-vis absorbance spectra of the monometallic and bimetallic NP suspensions were collected on a Shimadzu UV-2401 PC spectrophotometer using a quartz cuvette with a 1-cm path length. Au NP surface charge was characterized using Brookhaven Instruments Corporation ZetaPALS dynamic light scattering (DLS) apparatus utilizing a 660 nm wavelength laser and a dip-in (Uzgiris-type) electrode. X-ray diffraction (XRD) patterns of dried NPs and supported catalysts were collected on a Rigaku Ultima D/Max 2100 diffractometer utilizing Cu $\kappa_{\alpha}$ radiation ($\lambda = 1.5406$ Å). Dried NPs were prepared by concentrating 5 mL of the sol to $\sim$0.5 mL via evaporative drying at 70 °C, depositing the suspension on a glass slide, and drying at 70 °C. Grain size analysis was carried on the (111) reflection of bulk palladium and gold using Scherrer’s formula using Jade MDI software. BET (Brunauer-Emmett-Teller) surface areas and pore volumes of the supported catalyst powders were determined using a Micromeritics ASAP 2010 nitrogen gas adsorption analyzer. The NP materials were imaged using a JEOL 2010 transmission electron microscope (TEM), with particle size distribution measurements made using ImageJ program.\textsuperscript{33}

Electronic interactions between Pd and Au in our Pd/Au NPs were obtained from binding energy data determined using a PHI Quantera SXM X-ray photoelectron spectrometer (XPS). Poly-lysine coated slides were used to electrostatically bind Pd/Au-NPs of various loadings (10.9 wt% to 48.4 wt%). 50 $\mu$L of NP suspension was deposited on the glass slide and dried at 50 °C. Residual salts were removed by washing the immobilized NPs with nanopure water. This procedure was repeated 40 times to ensure a build-up of sample.
The surface that is analyzed includes a sub-surface region of \( \sim 0.5-5 \) nm thickness.

3.2.3 Catalytic experiments

TCE HDC batch reactor experiments were conducted in a manner similar to our previous study, except that larger reaction volumes were used here. Nanopure water (172 mL) and a magnetic stir bar were sealed in Boston Round screw-cap bottle (250 mL, Alltech) with Teflon tape wrapped threads and bubbled with hydrogen gas for 15 min to displace dissolved oxygen and to fill the headspace with a hydrogen atmosphere (1 atm). After the bottle was sealed with a teflon-rubber septum and bubbled, \( \sim 7 \) µL of TCE (99.5%, Aldrich) was added, and 0.2 µL of pentane (99.7%, Burdick & Jackson) was added as an internal standard. The Pd/Au NPs were injected through the septum, such that a total of \( 6.4 \times 10^{-8} \) moles of Pd were added. With the total Pd amount being constant, the Pd/Au NP concentrations ranged from \( 2.1 \times 10^{13} - 2.5 \times 10^{14} \) NP/mL. Sols of Au NPs (1 mL) and Pd NPs (1 mL) were injected into the reactor in control experiments, at particle concentrations of \( 1.26 \times 10^{14} \) NP/mL and \( 4.5 \times 10^{14} \) NP/mL, respectively. In testing the catalytic activity of supported Pd/Au NPs, the powders were suspended in 1.25 mL of water before being injected into the reactor. The catalyst weights and metal loadings (based on metal precursor amount) were as follows: 20 mg of MgO material (0.015 wt% palladium, 0.10 wt% gold), and 17.4 mg of SiO\(_2\) material (0.040 wt% palladium, 0.23 wt% gold). The catalytic reactions were conducted at room temperature under vigorous magnetic stirring.
The reaction was monitored through headspace gas chromatography (GC), in which 100 µL of headspace gas in the reactor is withdrawn with a gas-tight syringe and injected into an Agilent Technologies 6890 GC equipped with a flame ionization detector (FID) and a packed column (6-in × 1/8-in outer diameter) containing 60/80 Carbopack B/1% SP-1000 (Supelco). Calibration curves were prepared for chlorinated ethenes, chlorinated ethanes, and ethane. The initial TCE concentration in the liquid was approximately 60-70 ppm (1 ppm = 1 mg/L), far below the saturation concentration of 1200 ppm at 25 °C.\textsuperscript{34}

Reaction rate constants were determined by assuming a first-order rate dependence for the conversion of TCE during HDC:\textsuperscript{11}

\[ \frac{-dC_{TCE}}{dt} = k_{meas} C_{TCE} \]  

(1)

where the measured, apparent first-order rate constant $k_{meas} = k_{cat} \times C_{cat}$, where $k_{cat}$ is the palladium-normalized reaction rate constant (with units of L/gpd/\text{min}), $C_{cat}$ is the concentration of palladium charged to the reaction volume, and $C_{TCE}$ is the TCE concentration in the bulk fluid.

3.3 Results and discussion

3.3.1 Synthesis and characterization of 4-nm Pd/Au NPs

To generate smaller Au NPs than the ~20 nm NPs in our original study,\textsuperscript{16} we replaced the sodium citrate salt with a tannic acid/sodium citrate solution and reduced the heating time and temperature. This modified synthesis method led
to the consistent formation of uniformly sized 4 nm Au NPs (Figure 3.1a). The NPs had a Gaussian-like size distribution with a relative standard deviation of 21% (Figure 3.1b).

![Image](image.png)

**Figure 3.1** (a) TEM image and (b) particle size distribution of Au NPs measured from 850 particles in TEM images. Each bar in the histogram represents the total number of NPs counted with diameters ±0.25 nm of average bin size, e.g., 25 NPs with diameters in the 2.25-2.75 nm range were counted.

The XRD pattern of these Au NPs presented barely discernible metal diffraction peaks (Figure 3.2a and inset). Peak broadening analysis on the (111) peak of gold (2θ = 38.2°) indicated a grain size of 3.6 nm, indicating that at least a fraction of the NPs were single crystals of Au. The XRD pattern of Au NPs with a TEM particle size of 20 nm and a grain size of 17 nm is shown for comparison (Figure 3.2b).

The 4 nm Au NP sol exhibited a weak shoulder near 560 nm in its UV-vis absorbance spectrum (Figure 3.3a). For comparison, a suspension of 20 nm Au
NPs prepared through citrate reduction was ruby-red in color with the characteristic surface plasmon resonance peak at 520 nm (Figure 3.3c).

Figure 3.2 XRD patterns of dried (a) 4 nm Au NPs from tannic acid/citrate reduction method and (b) 20 nm Au NPs from citrate reduction method. The XRD peak (#) at 2θ = 40.5° comes from residual KCl from the K₂CO₃ and gold chloride precursors used. Inset: re-scaled XRD pattern of 4-nm Au NPs.

The 4 nm Au NP sol was brown-red in color, which was due to the presence of tannic acid at pH 6-7 (Figure 3.3b). We prepared a series of Pd/Au NP catalysts with varying palladium weight loadings up to 45 wt% palladium. Little difference in the UV-vis spectra could be observed with different palladium loadings due to absorbance interference from tannic acid.

To relate the palladium loading to a core/shell bimetallic structure, we modeled Pd/Au NPs as gold "magic clusters" with a palladium shell of variable coverage.
In the magic cluster model,\textsuperscript{35-37} a NP is treated as a central atom surrounded by closed shells of identical atoms, providing a helpful calculation method for estimating the Au NP concentration and the palladium surface coverage. Four-nanometer Au NPs were approximated as containing 7 shells of gold atoms (Table 3.1); based on the assumption of complete reduction of the gold precursor to form Au NPs, a concentration of $1.26 \times 10^{14}$ NP/mL was estimated.

![Graph](image)

**Figure 3.3** UV-vis spectra of (a) 4 nm Au NP sols synthesized from tannic acid/citrate reduction and (b) a solution resulting from the tannic acid/citrate reduction method in the absence of the gold precursor. Both liquids were diluted to \(~18\%\) of original concentration for UV-vis measurements. (c) UV-vis spectra of 20 nm Au NPs synthesized from citrate reduction method.

Palladium has an atomic radius of 1.40 Å, close in size to a gold atom (1.35 Å),\textsuperscript{38} and so the reductive deposition of palladium atoms onto the Au NP surface was
considered to be equivalent to the formation of an eighth shell of metal atoms (Figure 3.4).

Table 3.1. Magic cluster calculations of Au NPs

<table>
<thead>
<tr>
<th>Shell number (n)</th>
<th>Number of atoms in shell ( n_{atom}^{a} )</th>
<th>Total number of Au atoms in NP ( n_{tot}^{b} )</th>
<th>Calculated Au NP diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>1</td>
<td>0.27</td>
</tr>
<tr>
<td>2</td>
<td>12</td>
<td>13</td>
<td>0.80</td>
</tr>
<tr>
<td>3</td>
<td>42</td>
<td>55</td>
<td>1.34</td>
</tr>
<tr>
<td>4</td>
<td>92</td>
<td>147</td>
<td>1.88</td>
</tr>
<tr>
<td>5</td>
<td>162</td>
<td>309</td>
<td>2.41</td>
</tr>
<tr>
<td>6</td>
<td>252</td>
<td>561</td>
<td>2.95</td>
</tr>
<tr>
<td>7</td>
<td>362</td>
<td>923</td>
<td>3.48</td>
</tr>
<tr>
<td>8</td>
<td>492</td>
<td>1415</td>
<td>4.02</td>
</tr>
<tr>
<td>9</td>
<td>812</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

\( a \) Equation: \( n_{atom} = 10n^{2}+2 \)

\( b \) Equation: \( n_{tot} = (10n^{3}+15n^{2}+11n+3)/3 \)

Figure 3.4 Schematic of idealized Pd/Au NPs with 4 nm Au NPs and variable palladium surface coverage from 0 to 100% (with corresponding palladium content). The actual Pd/Au NPs will deviate from the model in terms of particle size distribution and spatial distribution of palladium atoms.

Thus, a 4 nm Au NP with a complete shell of palladium atoms, or 100% palladium coverage, is readily calculated to have a palladium content of 19.7
wt%. Surface coverages above 100% refer to the formation of additional shells on top of the complete eighth palladium shell (Table 3.2).

<table>
<thead>
<tr>
<th>Pd loading (wt%)</th>
<th>Pd surface coverage (%)</th>
<th>Rate constant $k_{cat}$ (L/g_Pd/min)</th>
<th>Mass-transfer-corrected rate constant $k_{corr}$ (L/g_Pd/min)</th>
<th>Initial turnover frequency TOF (mol-TCE/mol-Pd/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2.8</td>
<td>11.8</td>
<td>498</td>
<td>518</td>
<td>0.32</td>
</tr>
<tr>
<td>5.5</td>
<td>23.8</td>
<td>819</td>
<td>873</td>
<td>0.68</td>
</tr>
<tr>
<td>8</td>
<td>35.6</td>
<td>1345</td>
<td>1499</td>
<td>0.80</td>
</tr>
<tr>
<td>12.7</td>
<td>59.3</td>
<td>1956</td>
<td>2297</td>
<td>1.43</td>
</tr>
<tr>
<td>14.9</td>
<td>71.2</td>
<td>1903</td>
<td>2224</td>
<td>1.47</td>
</tr>
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<td>17.9</td>
<td>89.0</td>
<td>1839</td>
<td>2138</td>
<td>1.18</td>
</tr>
<tr>
<td>22</td>
<td>111.8</td>
<td>817</td>
<td>871</td>
<td>0.57 (0.64)$^b$</td>
</tr>
<tr>
<td>26</td>
<td>134.1</td>
<td>724</td>
<td>766</td>
<td>0.50 (0.66)$^b$</td>
</tr>
<tr>
<td>41.1</td>
<td>236.5</td>
<td>419</td>
<td>433</td>
<td>0.34 (0.71)$^b$</td>
</tr>
<tr>
<td>100$^a$</td>
<td>—</td>
<td>55</td>
<td>55</td>
<td>0.044 (0.13)$^b$</td>
</tr>
<tr>
<td>100$^c$</td>
<td>—</td>
<td>47</td>
<td>47</td>
<td>0.038</td>
</tr>
</tbody>
</table>

$^a$ Pure Pd NPs  
$^b$ Values in parentheses are based on calculated amount of exposed palladium atoms (mol-TCE/mol-surface-Pd/s)  
$^c$ Pd/Al$_2$O$_3$, with 1 wt% palladium on total catalyst weight basis and 100 wt% on total metals weight basis.

In order to observe any changes in the 520 nm Au NP UV-vis spectra, a solution of Au NPs was synthesized without K$_2$CO$_3$. Tannic acid absorbs significantly at wavelengths $>500$ nm at high solution pH. However, synthesis at lower pH values lowered particle monodispersity and increased the average particle size.$^{32}$ We prepared a series of Pd/Au NP catalysts with varying Pd weight loadings up to 36 wt% Pd (Figure 3.5a). As the Pd loading increased, the original Au NP peak fades into the background due to the interaction of Pd with the NP surfaces interfering with the Au surface plasmon.$^{39-41}$ The difference between the pure Au-NP absorbance at 520 nm and the absorbance at 520 nm
for each Pd/Au NP sample was quantified as a function of Pd loading (Figure 3.5b).

![Graph](image)

**Figure 3.5** UV-vis spectra of (a) 4-nm Au NP sols synthesized from tannic acid/citrate reduction with increasing loadings of Pd from 0 to 36 wt%. (b) Difference between Au NP absorbance at 520 nm from each Pd/Au NP absorbance at 520 nm as a function of Pd loading (calculated % coverages are labeled).

It could be seen that the absorbance changes were greatest at low Pd content and leveled off at higher Pd content. The absorbance change revealed a plateau near 20 wt%. These Pd/Au NPs were stable in suspension even at 100% coverage and above. In our previous work, we were using ascorbic acid to reduce the Pd and not pure hydrogen gas. This observation differed from our earlier work with ~20 nm Pd/Au NPs, in which >100% coverage Pd/Au NPs were partially aggregated; in suspension, these latter particles precipitated out of solution within 5 days. Our new synthesis method provides more colloidally
stable Pd/Au NPs due to the absence of ascorbic acid and its oxidized by-products.

3.3.2 Palladium coverage effect on TCE reaction rate

The TCE HDC reaction rate varied significantly with palladium content. Evidenced in the conversion-time profiles, the reaction rate increased significantly from 0 wt% palladium (pure Au NPs) to 12.7 wt%, and decreased with higher palladium content (Figure 3.6a,b). The reaction rate constant $k_{\text{cat}}$, derived from the observed first-order rate constant $k_{\text{meas}}$ by accounting for the palladium metal catalyst content, showed an unambiguous volcano-shape dependence on palladium content (Figure 3.6c).

For the most active catalyst (12.7 wt% palladium), the TCE conversion reached >99% in slightly over 1 hr, with the products being mostly ethane (88%) plus a small, identifiable amount of ethene (0.2%). Interestingly, C$_4$ compounds were detected in increasing amounts with reaction time (Figure 3.6d). Although the level of chlorination could not be determined, these butane/butane products were strong evidence of a coupling reaction progressing in parallel with the HDC reaction. These C$_4$ products were also found with pure Pd NPs, indicating that the coupling reaction was not unique to the Pd-Au combination. Lowry and Reinhard reported the presence of C$_4$ products during TCE HDC using Pd/Al$_2$O$_3$.\textsuperscript{12} Accounting for the coupling products, the carbon mass balance was in excess of 90%, which was typical for all catalyst compositions. The product distribution was also typical for the other catalyst compositions (Figure 3.6d). We
found that these NPs were also highly active for the HDC of dichloroethene isomers and perchloroethene.\textsuperscript{42}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure3_6}
\caption{TCE conversion-time profiles for Pd/Au NPs, with palladium loadings (a) 12.7 wt\% and below, and (b) 12.7 wt\% and above. (c) Reaction rate constants plotted against palladium loadings, with dotted line drawn to guide the eye. Repeatability of catalyst runs was checked for several Pd/Au compositions (as indicated by error bars). (d) TCE conversion and product distribution as functions of reaction time for Pd/Au NPs (12.7 wt\% palladium).}
\end{figure}

The most active materials (12.7-17.9 wt\% palladium) were found to have rate constants exceeding 1800 L/g\textsubscript{Pd}/min (Figure 3.6c, Table 3.2). These compositions were significantly more active than unsupported 4 nm
monometallic Pd NPs and Pd/Al₂O₃ (55 and 47 L/gₚd/min), which can be attributed to the much higher palladium dispersion of the Pd/Au NPs. These were roughly twice as active as the most active 20 nm Pd/Au NP catalyst (943 L/gₚd/min).¹⁶ This comparison is somewhat misleading, though, since the surface coverages are different (60-90% versus 33%, respectively). The 4 nm Pd/Au NPs with the closest surface coverage values (~24% and ~36%) have reaction rates of 819 and 1345 L/gₚd/min, respectively, which are comparable to that of 20 nm Pd/Au NPs.

3.3.3 Mass transfer analysis of NP catalyzed TCE HDC

Because of the large magnitudes of the reaction rate constants, it was possible that mass transfer limitations were present during catalysis, leading to measured rate constants that underestimated intrinsic surface reaction rates. Two possible sources of mass transfer limitations were identified (Figure 3.7): the diffusion through a boundary layer surrounding the catalytic NPs (mass transfer from bulk liquid to solid surface), and the transport across the headspace-water interface (mass transfer from bulk gas to bulk liquid).

The liquid-to-solid mass transfer step was considered first. At any given reaction time, the TCE molar flux to the NP catalyst surface is \( W_{\text{TCE}} = k_{\text{ls}}C_{\text{TCE,liq}} \), where the effective liquid-to-catalytic-surface mass transfer coefficient \( k_{\text{ls}} = k_{\text{g}}k_{\text{c}}/(k_{\text{r}}+k_{\text{c}}) \), \( k_{\text{c}} \) is the mass transfer coefficient, \( k_{\text{r}} \) is the surface reaction rate constant, and \( C_{\text{TCE,liq}} \) is the TCE concentration in the bulk fluid. The molar flux \( W_{\text{TCE}} \) can be calculated from the rate of change in TCE concentration (\( -\text{d}C_{\text{TCE}}/\text{d}t \)) divided by the total surface area of all the NPs in the reaction volume.
(termed volumetric surface area, or VSA). This leads to $k_{ls}C_{TCE} = (k_{meas}C_{TCE})/VSA$, or $k_{ls} = k_{meas}/VSA$. For the most active Pd/Au NP catalyst (12.7 wt% palladium), $k_{meas} = 1.43\times10^{-3}$ 1/s and $VSA = 2.09\times10^{-2}$ m²/L = $2.09\times10^{-1}$ 1/cm, leading to $k_{ls} = 6.6\times10^{-3}$ cm/s.

![Diagram](image)

**Figure 3.7** Illustration of the possible mass-transfer bottlenecks in the TCE HDC reaction studies using Pd/Au NP catalysts.

The mass transfer coefficient $k_c$ for TCE diffusing towards a spherical particle was calculated using the Frössling correlation, from which the Sherwood number $Sh$ equals 2 in the limit of pure diffusion. Since $Sh = k_cD_p/D_{TCE}$, where $D_p$ is particle diameter and $D_{TCE}$ is the diffusivity of TCE in water ($1.04\times10^{-5}$ cm²/s at 25 °C), $k_c$ was calculated to be 52 cm/s for a particle diameter of 4 nm. Calculated to be $1.14\times10^{-2}$ cm/s using the values of $k_{ls}$ and $k_c$, the surface reaction rate $k_r$ was found to be much smaller in magnitude than $k_c$. For the most active catalyst then, it was concluded that TCE diffusion to the NP surface had a negligible effect on measured reaction rates.
The gas-to-liquid mass transfer step was considered next. At any given reaction time, \( W_{\text{TCE}} \) also equals the TCE molar flux from the headspace to the water phase, or \( W_{\text{TCE}} = k_{\text{gl}}((K/RT) \times C_{\text{TCE,liq}} - C_{\text{TCE,\text{gas}}}) \), where \( k_{\text{gl}} \) is the gas-liquid mass transfer coefficient, \( K \) is Henry’s law constant (8.8\times10^{-3} \text{ atm} \cdot \text{m}^3/\text{mol} \) for TCE in water at 25 °C), \( R \) is the ideal gas constant, and \( T \) is temperature. Using published mass transfer data on TCE aqueous solutions, \(^{45} \) \( k_{\text{gl}} \) was estimated to be 3.42\times10^{-2} \text{ cm/s} \). This value was larger than \( k_{\text{eff}} \) but not overwhelmingly so, indicating that the effect of liquid-gas TCE mass transfer could not be neglected. The measured rate constants were thus corrected using the relation \( k_{\text{corr}} = k_{\text{r}} \times \text{VSA} \), where \( 1/k_{\text{r}} = \text{VSA}/k_{\text{meas}} - 1/k_{\text{gl}} \) (Table 3.2). The gas-liquid mass transfer effect roughly amounted to a 15% error in measured rates for the more active catalysts.

3.3.4 Correlation of catalysis to bimetallic structure

Initial turnover frequencies (TOF’s) for the Pd/Au NPs were calculated using \( k_{\text{cat,corr}} = k_{\text{corr}} / C_{\text{cat}} \) and initial TCE concentrations, and plotted against palladium content and palladium surface coverage (Table 3.2; Figure 3.8a). Except for pure gold, all NP samples had higher TOF’s than pure Pd NPs (0.044 1/s). The most active compositions were Au NPs with an incomplete shell of palladium atoms (i.e., decorated core bimetallic structure, as opposed to core/shell bimetallic structure). Three activity regions could be observed: (I) in the 0-70% surface coverage range, TOF values increased from zero to a maximum of 1.47 1/s; (II) in the 70-110% range, TOF values decreased to 0.57 1/s; and (III) above 110%, they decreased but to a lesser degree. The relationship between the measured
TOF values and the elementary steps that comprise the TCE HDC reaction pathway (i.e., TCE adsorption, \( \text{H}_2 \) dissociative adsorption, TCE dechlorination, double-bond hydrogenation, and ethane desorption) is not known.

![Graph showing Pd content and Initial TOF values normalized to total palladium content](image)

**Figure 3.8** (a) Initial TOF values normalized to total palladium content and plotted against palladium content and palladium surface coverage. (b) Initial TOF values for palladium surface coverages of >100%, normalized to exposed palladium atom content.

The rate-limiting step could be C-Cl bond breaking, drawing on Zhou et al.'s surface science study of palladium-catalyzed dechlorination of fluorochloroethanes in which they reported that “the rate constant for the dechlorination step is an important contributor to the overall rate law for catalytic hydrodechlorination.”\(^{46}\) It is known that chloroethenes adsorb to form surface-bound hydrocarbon fragments and Cl atoms on palladium\(^{47}\) and Pd-Cu alloy surfaces.\(^{48,49}\)
If isolated palladium atoms were the active sites, then TOF values should be constant with increasing palladium surface coverage in region I. The observed TOF increase indicates that individual palladium atoms are not the active sites, and suggests that two-dimensional ensembles or islands of palladium atoms are instead the active sites. Lambert and co-workers showed through scanning tunneling microscopy that palladium atoms formed 1-atom-thick, 3-nm-wide ensembles on gold surface defects at low palladium surface coverages (specifically 7%) after annealing at 300 K. Such nano-sized palladium ensembles may be present in the Pd/Au NPs, in which they form on the Au NP surface defects during the room-temperature palladium salt reduction step. These proposed palladium ensembles would adsorb and activate both TCE and H₂ for surface reaction.

The gold surface is not known to adsorb either TCE or H₂, but the Pd-Au interface could adsorb TCE. We suggest that the interface between palladium and gold atoms provides another set of active sites for TCE HDC, like the Pd-Cu sites proposed by Barbosa, Jugnet, and co-workers for TCE adsorption. Through surface science and density functional theory studies, they showed that TCE can adsorb at room temperature on two palladium and two copper atoms to form two Pd-C bonds and two Cu-Cl bonds. Since chloride atoms can bind to gold surfaces, it is reasonable that TCE adsorbs similarly on mixed Pd-Au metal sites.

We propose that the TOF decrease in region II is the formation of a second layer of palladium atoms before the completion of the first one, such that three-dimensional palladium ensembles are formed. This would lead to a decrease in
palladium dispersion, in that not all the palladium atoms are accessible for TCE HDC. Indeed, Lambert and co-workers showed that a gold film with 70% palladium coverage contained three-dimensional palladium ensembles.\textsuperscript{20} Gas-phase chemisorption measurements using H\textsubscript{2} or CO would be highly useful in quantifying palladium dispersion, but the colloidal state of the Pd/Au NPs presents challenges for this analytical technique. Another possible explanation is the reduction in the population of mixed Pd-Au metal sites with increasing palladium surface coverage.

In region III, the TOF decreases at a different rate with increasing palladium coverage. Above 100% palladium surface coverage, there are presumably no exposed gold atoms and therefore no mixed Pd-Au sites. Thus, the observed activity would be that of exposed palladium atoms only. We re-calculated the TOF values in this region by using surface palladium atoms instead of total palladium atoms (Table 3.2, Figure 3.6b). With the expectation that the TOF would be constant above 100% palladium coverage, we found the Pd/Au NPs to have comparable TOF values (in the range of ~0.6-0.7 1/s). These values are several times higher than that of pure Pd NPs (0.13 1/s), suggesting that the palladium catalytic activity is modified electronically by the underlying gold. The electronic effect in Pd-Au materials was recently observed by Hutchings and co-workers for alcohol selective oxidation.\textsuperscript{21}

Pd/Au bimetallic NP systems are commonly studied using XPS to identify any electronic perturbations between the two metals caused by each other.\textsuperscript{20,51-53} However, few observe shifts in binding energies associated with Pd. This could be due to synthesis methods where molar ratios of Pd to Au are high enough
that both metals can retain their bulk electronic characteristics or methods that undergo simultaneous reduction possibly forming alloys and mixed metal nanoparticles.\textsuperscript{52,53} In our system, the sequential reduction of Pd on Au NPs is strongly believed to form a core-shell nanostructure with low loadings of Pd. The Pd/Au NP samples were scanned for C, Pd, and Au. Carbon was used as an internal standard and the scans were shifted such that its 1s binding energy was 284.4 eV.\textsuperscript{54} Figure 3.9 illustrates the spectra obtained for Pd on Pd/Au NP and pure Pd NP samples. Due to the low loadings of Pd in the samples (compared to Pd NPs), the signal for the Pd metal is small but not insignificant. As shown in Figure 3.9a, the Pd metal peak assigned to 335.3 eV\textsuperscript{54} shifted to lower binding energies as the Pd loading decreased. The binding energy shift was quantified as a function of Pd loading (Figure 3.9b) and demonstrated a monotonically increasing binding energy shift as Pd loading decreased below 30 wt%.

\textbf{Figure 3.9} XPS spectra of (a) Pd/Au NP sols as a function of wt\% Pd loading (calculated % coverage) and pure Pd NPs. (b) Binding energy shifts as a function of Pd loading.
Goodman and coworkers show that binding energy shifts to lower values are indicative of a gain of electron populations, while shifts to higher values are a drop in electron populations.\textsuperscript{55,56} In our case, the shift of the 3d\textsubscript{5/2} binding energy to lower values represents an increase in Pd 3d electron populations as the Pd to Au ratio decreased. This data indicates electronic perturbation of Pd possibly induced by the underlying Au NP core, which may be contributing to the observed catalytic enhancement.\textsuperscript{21}

Gold is more expensive than palladium, but the Pd-Au combination is a more active catalyst than pure palladium. In terms of metals cost, we compared the most active NP composition (14.9 wt\%) with pure Pd NPs of 4 nm. Using the spot prices for gold and palladium at the end of 2005 ($513/oz and $258/oz, respectively) and taking into account the reaction rates, we calculated that the Pd/Au NPs were 2.7 times more cost-effective as a catalyst than the Pd NPs.

3.3.5 Immobilization of Pd/Au NPs on a support

Electrostatic adsorption was used to immobilize the Pd/Au NPs on a porous solid support. In this method, a metal oxide develops a surface charge based on the fluid pH and its isoelectric point (iep). The iep values for Al\textsubscript{2}O\textsubscript{3}, MgO, and SiO\textsubscript{2} are 5-6, 12, and 2, respectively.\textsuperscript{57} At pH values above the iep (at which the net surface charge is zero), the support surface is negatively charged; at pH values below the iep, the surface is positively charged. The Pd/Au NPs (and Au NPs) are negatively charged according to electrophoretic mobility measurements, and so positively charged supports would be needed.
To demonstrate that charge interactions can be used for immobilization, we contacted Au NP sols with Al₂O₃ (at two different pH values, 3 and 6), MgO (at pH 6), and SiO₂ (at pH 6), and measured the amount of initial uptake (Figure 3.10).

![Bar chart showing Au NP uptake for different supports and washes](image)

**Figure 3.10** Extent of Au NP adsorption (initial uptake) and release after several washes for the various supports.

At pH 6, Al₂O₃ and SiO₂ showed little adsorption for the NPs, since the pH was close to their IEP values. Reducing the pH to 3 using HCl, Al₂O₃ showed a significant increase in NP adsorption, consistent with the surface being more positively charged. The basic MgO support also showed significant NP adsorption at pH 6, as expected.

The stability of the immobilized NPs was tested for each support by rinsing the resultant powders with water (pH = 6) several times. The loss of NPs was most apparent for the Al₂O₃-supported NPs immobilized at pH = 3, in which the pH of the wash was insufficient to maintain the Al₂O₃ surface charge. On the other
hand, no NPs were removed from the MgO since the surface remained positively charged during the washes. Functionalizing the SiO$_2$ with amine surface groups significantly increased the adsorption and retention of NPs (Figure 3.10). The amine groups were protonated and positively charged at pH values below 10, thereby generating the desired positive surface charge.

Using functionalized SiO$_2$ and MgO, we immobilized Pd/Au NPs (12.7 wt% palladium) and tested the resultant supported catalysts for TCE HDC. Both materials were very active for the reaction, but less active than the unsupported Pd/Au NPs. Possible explanations for the reduced reaction rates are intraparticle mass transfer within the porous support and the loss of a portion of the Pd/Au NP surface due to contact with the oxide surface. In spite of these issues, the resulting supported Pd/Au NP catalysts were still significantly more active than the commercial source of Pd/Al$_2$O$_3$ (Table 3.3).

<table>
<thead>
<tr>
<th>Support</th>
<th>Pd loading of total catalyst (wt%)</th>
<th>Au loading of total catalyst supported (wt%)</th>
<th>$k_{cat}$ (L/g$_{pol}$/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unsupported$^a$</td>
<td>—</td>
<td>—</td>
<td>1956</td>
</tr>
<tr>
<td>MgO$^a$</td>
<td>0.014</td>
<td>0.10</td>
<td>1670</td>
</tr>
<tr>
<td>Amine-containing SiO$_2$$^a$</td>
<td>0.040</td>
<td>0.23</td>
<td>983</td>
</tr>
<tr>
<td>Control: Pd/Al$_2$O$_3$</td>
<td>1</td>
<td>0</td>
<td>47</td>
</tr>
</tbody>
</table>

$^a$ Palladium content of Pd/Au NPs = 12.7 wt%

### 3.4 Summary and conclusions
Pd/Au bimetallic NPs with a 4 nm gold core and controlled palladium loading were synthesized successfully, with all compositions more active for the aqueous-phase TCE HDC reaction than palladium-only catalysts. This material exhibited a well-defined volcano-shape activity dependence on palladium loading. Analysis of the batch reaction indicated that the liquid-to-particle surface mass transfer effect was negligible but the gas-to-liquid mass transfer effect was not. The TOF values (as moles of TCE converted per mole of palladium atoms per second) were corrected for the latter, and correlated to palladium surface coverage. Surface coverage was determined by modeling Pd/Au NPs as magic clusters with 7 shells of gold atoms and the palladium atoms in the 8th shell. The reaction data suggested palladium ensembles and Pd-Au mixed sites participate in the HDC reaction as adsorption and surface reaction sites. The very active compositions had a decorated core bimetallic nanostructure, exhibiting TOF's on the order of 1 1/s. Stable immobilization of the NPs was accomplished by electrostatically binding them to positively charged surfaces like MgO and amine-functionalized SiO₂. These supported Pd/Au NPs will serve as a model material for continuous-flow reaction studies and chemisorption studies.

3.5 References


Chapter 4

Reaction mechanism studies of aqueous-phase TCE HDC on Pd/Au NP catalysts

4.1 Introduction

Over the years, TCE has been used as a solvent to degrease metals and electronic parts in the automotive, metal fabrication, and electronic industries, with smaller-scale use in chemicals production, textile cleaning, and consumer products, which has led to its prevalence in our environment, in particular in groundwater.\(^1\)\(^-\)\(^6\) Because of its pervasiveness coupled with its toxicity to humans, TCE is considered one of the most hazardous organic contaminants found in groundwater.\(^1\)\(^-\)\(^4\),\(^6\) In recent years, there have been strong efforts to study Pd catalysts for aqueous-phase TCE.\(^7\)\(-\)\(^13\) Although this appears to be a promising treatment, low reaction rates require large reactor volumes of catalyst. In our previous work, we compared the TCE HDC catalytic activity of 1 wt % Pd/Al\(_2\)O\(_3\), unsupported Pd NPs, and Pd-on-Au NPs demonstrating a marked promotion effect of gold on palladium.\(^14\) A volcano-shape activity dependence was observed with a TCE TOF maximum of \(\sim 1.5\) 1/s occurring near 75% surface coverage.\(^15\)

There is no literature consensus in the driving force for promotional effects found in palladium/gold (Pd/Au) catalysts because promotion is reaction dependent. For example, ethene hydrogenation has been reported to be 4 times greater on PdAu catalysts.\(^16\) Au enhancement of Pd based dechlorination of various CFCs has been claimed,\(^17\),\(^18\) while Karpinski and coworkers found that there was more of a product selectivity enhancement rather than an increase in
CFC dechlorination rates.\textsuperscript{19-21} Goodman and coworkers have shown that the Au promotes Pd for vinyl acetate production through optimum spacing of Pd surface atoms due to alloying with Au.\textsuperscript{22} Hutchings and coworkers demonstrated increased TOFs (~25 times) for alcohol oxidation using Au-Pd catalyst nanocrystals over both monometallic supported Pd and Au catalysts at moderate temperatures (363-433 K) and pressures (1-2 bar).\textsuperscript{23}

To date, the reaction mechanism for aqueous phase HDC of TCE is not known for our Pd/Au catalysts. However, some effort has been made to understand this reaction on palladium surfaces. Reinhard and coworkers studied this reaction mechanism kinetically using a 1 wt % Pd/Al\textsubscript{2}O\textsubscript{3} catalyst in both batch and plug-flow reactors.\textsuperscript{11,13} Their analysis concluded that TCE was dechlorinated to ethane and could be modeled using a pseudo-first-order rate law.\textsuperscript{13} The reaction's hydrogen dependence was shown to obey a Langmuir-Hinshelwood formulation with a half reaction order.\textsuperscript{11} Furthermore, they concluded that the mechanism was a direct pathway opposed to a sequential pathway, due to the low amounts of intermediates measured.\textsuperscript{13}

In this chapter, we studied the aqueous-phase TCE HDC reaction mechanism through the use of other chlorinated ethenes as chemical probes. Combining our chemical probe data with results from surface science studies allows for the formulation of a proposed reaction mechanism for TCE HDC. The catalyst we studied was a 25% covered Pd/Au NP material. This was used as representative of Pd/Au NP catalysts. Also, the effects of hydrogen, chloride and sulfides were studied using both Pd/Au NP and Pd/Al\textsubscript{2}O\textsubscript{3} catalysts.
4.2 Experimental methods

4.2.1 Synthesis

Au NPs were synthesized using the tannic acid/sodium citrate reduction method by Slot and Geuze\textsuperscript{24} and detailed in Chapter 3. The final fluid had a dark brown-red color containing an estimated \(1.26\times10^{14}\) NP/mL and an average NP diameter of \(\sim 4\) nm, according to TEM.

Pd NPs were synthesized using the above method by substituting the gold salt solution with an \(\text{H}_2\text{PdCl}_4\) solution (2.47 mM; \(\text{PdCl}_2\) 99.9+%, Aldrich). The procedure was carried in the same manner except that the reaction mixture was boiled for 25 minutes instead of 2 min. A portion of the water volume (72%) evaporated during the boiling step. The resulting yellow fluid was aged overnight at room temperature, resulting in a coffee-black colored fluid. The NPs were \(\sim 4\) nm in diameter, according to TEM (Figure 4.1).

![TEM Image](a)

![Particle Size Distribution](b)

**Figure 4.1** (a) TEM image and (b) particle size distribution of Pd NPs measured from 450 particles in TEM images. Each bar in the histogram represents the total number of NPs counted with diameters \(\pm 0.25\) nm of average bin size, e.g., 45 NPs with diameters in the 2.75-3.25 nm range were counted.
The synthesis of bimetallic Pd/Au NPs with 25% coverage was carried out by mixing 27 μL of H₂PdCl₄ solution (2.47 mM) with 2 mL of the Au NP sol (1.26×10¹⁴ NP/mL) and stirring for at least 15 min. Hydrogen gas (99.99%; Matheson) was then bubbled through the synthesis fluid for 1 min. The resultant NP sol was left to sit at room temperature overnight. 25% Pd coverage was used to ensure that the catalysts were not so active as to cause TCE mass transfer to be a problem.¹⁵

4.2.2 Catalytic experiments

TCE HDC batch reactor experiments were conducted in a manner similar to our experimental set-up in Chapter 3. Nanopure water (172 mL) and a magnetic stir bar were sealed in Boston Round screw-cap bottle (250 mL, Alltech) with Teflon tape wrapped threads and bubbled with H₂ gas for 15 min to fill the headspace with a hydrogen atmosphere (1 atm). After the bottle was sealed with a teflon-rubber septum and bubbled, ~3 μL of chlorinated organics (TCE, 1,1 DCE, c-DCE, t-DCE (1,1-, cis-, trans-dichloroethene), PCE (perchloroethene), TCEa (1,1,2-trichloroethane)) (99.5%, Aldrich) were added, and 0.2 μL of pentane (99.7%, Burdick & Jackson) was added as an internal standard. Reaction experiments were conducted using our Pd/Au NPs, Pd NPs, and 1 wt% Pd/Al₂O₃ (Aldrich) catalysts. Pd/Au NPs and Pd NPs were injected through the septa as prepared above. In order to weigh a measurable quantity of catalyst, Pd/Al₂O₃ catalysts were diluted to 20 wt% with Al₂O₃ (Aldrich), ground together with a mortar and pestle and vortex mixed to create a homogeneous mixture of
powders. 15 mg of the mixture were added to water and injected through the septum as a slurry.

In addition to examining different chlorinated organics, the effect of hydrogen and chloride ion concentrations were examined. To control the hydrogen concentration, mixtures of H₂/He were bubbled in place of pure H₂, allowing for control over the hydrogen partial pressure. Chloride ion concentrations were controlled by the addition of sodium chloride. Sulfur poisoning studies were conducted by adding sodium sulfate to the catalyst solutions and sit overnight. The catalytic reactions were conducted at room temperature under vigorous magnetic stirring.

The reaction was monitored through headspace gas chromatography (GC), in which 100 μL of headspace gas in the reactor is withdrawn with a gas-tight syringe and injected into an Agilent Technologies 6890 GC equipped with a flame ionization detector (FID) and a packed column (6-in × 1/8-in outer diameter) containing 60/80 Carbopack B/1% SP-1000 (Supelco). Calibration curves were prepared for chlorinated ethenes, chlorinated ethanes, and ethane. Table 4.1 illustrates the initial concentrations of the reactants used in this study and their saturation values.

### Table 4.1 Reactant initial and saturated concentrations.

<table>
<thead>
<tr>
<th>Reactant</th>
<th>$C_{\text{initial}}$ [ppm]*</th>
<th>$C_{\text{saturated}}$ [ppm]$^{25}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>TCE</td>
<td>25</td>
<td>1472</td>
</tr>
<tr>
<td>1,1 DCE</td>
<td>22</td>
<td>2250</td>
</tr>
<tr>
<td>c-DCE</td>
<td>22</td>
<td>3500</td>
</tr>
<tr>
<td>t-DCE</td>
<td>22</td>
<td>6300</td>
</tr>
<tr>
<td>PCE</td>
<td>28</td>
<td>200</td>
</tr>
<tr>
<td>TCEa</td>
<td>25</td>
<td>4420</td>
</tr>
</tbody>
</table>

* (+/- 3 ppm) measured
4.3. Results and discussion

4.3.1 Development of a rate expression

The reaction mechanism for TCE HDC can be proposed to proceed through a series of elementary adsorption, surface reaction, and desorption steps (Figure 4.2). Referred to as the Langmuir-Hinshelwood model, it does not presume knowledge of exactly how the chemical species bind to the surface nor the nature of the active site.

![Diagram](image-url)

**Figure 4.2** Proposed reaction steps modeling the conversion of TCE to ethane. Left side illustrates chemical conversion steps. Right side illustrates adsorption/desorption steps. (* denotes an open active site).

The usefulness of this model comes in the form of a rate law, which can be validated experimentally via catalytic testing. Hydrogen is assumed to dissociatively adsorb on two generic active sites (denoted *) as hydrogen atoms.26,27 TCE is reversibly adsorbed to * where interactions with hydrogen
dechlorinate TCE to DCE to VC to ethene and ultimately hydrogenating to ethane. At each step, desorption of the intermediates to the bulk could occur and would develop into measurable intermediate concentrations. Also, with each dechlorination step, a surface bound Cl must desorb to regenerate an active site. This step is effectively an electron transfer between H and Cl to form their ionic species in solution. This simple model provides a starting point for analyzing the TCE HDC reaction mechanism.

If the rate-limiting step (rls) is assumed to be TCE* + H* \(\rightarrow\) DCE* + Cl* (the first HDC step), then the rate law is related to the reactant concentration in the following manner:

\[
\text{Rate} = k'C_{\text{TCE}} \cdot C_{H_2}^{1/2} \cdot C_{*}^2 \quad (1)
\]

where \(k' = k_{\text{rls}}K_{\text{TCE}}K_{\text{hydrogen}}^{0.5}\), \(C_*\) is the surface concentration of vacant sites and \(K_i\) is the adsorption/desorption equilibrium constant for species i. At this point, we do not differentiate the pathways to the different DCE isomers. Performing a site balance to remove \(C_*\) gives,

\[
C_{* \text{,total}} = C_* + K_{\text{TCE}}C_{\text{TCE}}C_* + (K_{H_2}C_{H_2})^{1/2}C_* + K_{\text{ethane}}C_{\text{ethane}}C_* + K_{\text{Cl}}C_{\text{Cl}}C_* + K_{\text{DCE}}C_{\text{DCE}}C_* + K_{\text{VC}}C_{\text{VC}}C_* + K_{\text{ethene}}C_{\text{ethene}}C_* \quad (2)
\]

where \(C_{* \text{,total}}\) is the total number of sites and is a constant as long as irreversible adsorption (poisoning) is not observed. Solving for \(C_*\) and substituting into Equation 1 gives
\[
\text{Rate} = \frac{k C_{TCE} C_{H_2}^{1/2}}{(1 + K_{TCE} C_{TCE} + K_{H_2} C_{H_2}^{1/2} + K_{\text{Ethane}} C_{\text{Ethane}} + K_{\text{Cl}} C_{\text{Cl}} + K_{\text{DCE}} C_{\text{DCE}} + K_{\text{VC}} C_{\text{VC}} + K_{\text{Ethene}} C_{\text{Ethene}})^2} \quad (3)
\]

where \( k = k' C_{\text{total}}^2 \). By assuming that the concentration of all surface intermediates is small, we simplify the rate expression, thus:

\[
\text{Rate} = k C_{TCE} C_{H_2}^{1/2} \quad (4)
\]

We hypothesize that the reaction is first-order in TCE concentration and half-order in \( H_2 \) concentration, assuming the surface is mainly full of vacant sites (i.e., the most abundant surface intermediate (MASI) is vacant sites), which results in the denominator of Equation 3 being equal to one.

4.3.2 Determination of kinetic dependence for Pd/Au and Pd NPs on TCE HDC

Our work has focused on developing new materials to increase the rate of TCE conversion to ethane compared to that of conventional catalysts. Earlier investigations in this area have demonstrated that aqueous phase TCE HDC obeys a pseudo-first-order rate law when a standard 1 wt% Pd/Al\(_2\)O\(_3\) powder catalyst is used.\(^{13}\) Our previous work on this material confirmed this first-order dependence on TCE. However, subsequent analysis of the Pd/Al\(_2\)O\(_3\) system led to different results.

We studied three different catalysts for TCE HDC over time: 1 wt% Pd/Al\(_2\)O\(_3\), Pd-NPs, and 25% coverage Pd/Au NPs (Figure 4.3). Data from each set was fit to both first and half-order rate laws. Both the Pd NPs and Pd/Al\(_2\)O\(_3\) catalysts
demonstrated better fits to the half-order rate law, while the 25% coverage Pd/Au NPs fit a first-order rate law best.

![Graphs](image.png)

**Figure 4.3** TCE conversion as a function of reaction time for (a) 25% coverage Pd/Au NPs, (b) Pd NPs, and (c) 1 wt% Pd/Al₂O₃. The solid lines represent a first-order fit while the dashed lines represent a half-order fit.

The difference between the two fits is subtle but important. A possible explanation of the non-first-order dependence comes from differences in adsorbed surface species. If the MASl for pure Pd catalysts is adsorbed TCE and vacant sites, then we lose the first-order TCE dependence in Equation 4 and get a non-linear dependence (Equation 5). Based on our data, the order can be approximated as half-order in TCE (Equation 5), which does not presume a particular surface reaction pathway.
Rate = \frac{kC_{TCE}C_{H_2}^{1/2}}{(1+K_{TCE}C_{TCE})^{1/2}} \rightarrow kC_{TCE}^{1/2}C_{H_2}^{1/2} \quad (5)

There exists the possibility that mass transfer limitations exist masking the half-order rate law as a first-order rate law. We compared the TCE conversion using Pd/Al₂O₃ with slow and fast stirring (Figure 4.4) and found that, indeed, the observed kinetics were affected by mass transfer.

![Graph showing TCE conversion over reaction time with fast and slow stirring](image)

**Figure 4.4** Experimentally induced mass transfer limitations on TCE HDC reaction using 1 wt\% Pd/Al₂O₃. ■ indicates no mass transfer limitation and a half-order fit. ◇ indicates mass transfer limitation and a first-order fit.

Fast stirring reveals the half-order dependence, but slow stirring masks the half-order with the first-order rate of mass transfer. We ensure rapid stirring for all our experiments. Being able to measure non-first-order dependencies indicates that our reactor test system is free of mass transfer limitations.
4.3.3 HDC of chlorinated ethenes

Our Pd/Au NP catalyst and the Pd/Al₂O₃ catalyst were used to hydrodechlorinate five different chlorinated ethenes: PCE, TCE, 1,1-DCE, cis-DCE, and trans-DCE; and their respective overall reaction rate constants are given in Table 4.2. In general, as the degree of chlorination increased (PCE > TCE > DCE), the rate constants decreased, while the location of the chloride in the DCE isomers appeared to influence the rate constants for both catalysts tested (trans-DCE > cis-DCE > 1,1-DCE).

<table>
<thead>
<tr>
<th>Reactant</th>
<th>First-order Rate Constant 25%-coverage Pd/Au NP [L/gpd/min]ᵃ</th>
<th>Half-order Rate Constant 1 wt% Pd/Al₂O₃ [(L mol)⁰.⁵/gpd/min]ᵇ</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCE</td>
<td>270</td>
<td>34</td>
</tr>
<tr>
<td>TCE</td>
<td>858</td>
<td>45</td>
</tr>
<tr>
<td>1,1-DCE</td>
<td>1519</td>
<td>55</td>
</tr>
<tr>
<td>cis-DCE</td>
<td>1813</td>
<td>104</td>
</tr>
<tr>
<td>trans-DCE</td>
<td>2303</td>
<td>107</td>
</tr>
</tbody>
</table>

\[
a : -\frac{dC_i}{dt} = k_{Pd/Au} C_{cat} C_i \quad b : -\frac{dC_i}{dt} = k_{Pd} C_{cat} C_i^{0.5}
\]

Figure 4.5 illustrates how the overall reaction rate constants for each chlorinated ethene are related to one another and to the proposed reaction mechanism. These five chlorinated compounds were considered into two groups to illustrate how (1) varying the number of Cl species to dechlorinate (PCE, TCE,
1,1-DCE) and (2) varying the location of Cl species (1,1-DCE, cis-DCE, trans-DCE) affects the overall reaction rate constant.

**Figure 4.5** Observed reaction rate constants for each reactant in relation to the sequential HDC surface reaction steps.

Figure 4.6 illustrates the first of these two concepts for both Pd/Au NP and Pd/Al₂O₃ catalysts where reactant conversion is plotted as a function of reaction time for PCE, TCE, and 1,1-DCE. Reactant conversion decreases with an increase in the number of Cl atoms per molecule for both catalysts (Figure 4.6a,b); however, the effect appears to be more significant for the Pd/Au NP catalyst, possibly due to its higher activity. Fitting the data to a first-order rate constant for Pd/Au NP catalyst and a half-order rate constant for Pd/Al₂O₃
catalyst and plotting it as a function of the number of Cl atoms per molecule give a linear relationship for both catalysts (Figure 4.6c).

![Graphs showing reaction data](image)

**Figure 4.6** PCE, TCE, 1,1-DCE HDC reaction data for (a) 25%-coverage Pd/Au NPs, (b) 1 wt% Pd/Al₂O₃, and (c) normalized rate constant data as a function of the number of chloride atoms in the chlorinated ethene. Solid lines represent numerical data fits.

This linear relationship indicates that each Cl on a chlorinated ethene is progressively easier to remove with less chlorinated ethenes, and that the relative reaction rate is proportional to the number of H atoms (k₁₁ > kₜ₇ > kₚ₇).

From the second grouping of chlorinated ethenes studied, we could investigate the effect of relative locations of Cl atoms in a chlorinated ethene. The difference among these molecules is relative chloride atom locations. The straight-line Cl−Cl distance in 1,1-DCE is the shortest (0.28 nm), followed by cis-DCE (0.33 nm), and lastly trans-DCE (0.45 nm). Figure 4.7 illustrates this effect.
on HDC activity for both Pd/Au NP and Pd/Al₂O₃ catalysts where reactant conversion is plotted as a function of time for cis-DCE, trans-DCE, and 1,1-DCE.

![Graphs](image)

**Figure 4.7** 1,1-DCE, t-DCE, c-DCE HDC reaction data for (a) 25% coverage Pd/Au NPs, (b) 1 wt% Pd/Al₂O₃, and (c) normalized rate constant data as a function of the Cl-Cl distance in the isomers of DCE. Solid lines represent numerical data fits.

When catalyzed with our Pd/Au NPs, a linear relationship developed and confirmed that not only is it the number of chlorides but the relative location that affects the rls. There is a strong correlation between Cl-Cl distance and reactivity of chlorinated ethene over Pd/Au NPs: the longer the Cl-Cl distance, the more reactive. For the Pd/Al₂O₃ catalyst, there was no clear trend with Cl-Cl distance, although the DCE with the shortest Cl-Cl distance was the least active over Pd/Al₂O₃. It is hypothesized that the increased activity is due to decreased
steric hindrance as the Cl-Cl distance increases, enhancing the susceptibility of the C-Cl bond to cleavage and replacement by adsorbed hydrogen.

![Chemical structures](image)

**Figure 4.8** (a) Illustration of the relationship between the Cl-Cl distance and the accessible region through which reaction can take place due to steric hindrance concerns. (b) Illustration of C-Cl bonds in TCE and most probable DCE products.

So, HDC of the first Cl in TCE should depend on the relative Cl-Cl distance within the TCE molecule (Figure 4.8b). The longest Cl-Cl distance (trans; Cl\(^1\)-Cl\(^3\)) should lead to either 1,1-DCE (removal of Cl\(^3\)) or cis-DCE (removal of Cl\(^1\)). However, due to the steric influence of the Cl\(^2\), it is more likely that Cl\(^3\) will be dechlorinated than Cl\(^1\). This suggests that TCE would preferentially hydrodechlorinate to 1,1-DCE > c-DCE > t-DCE.

4.3.4 Hydrogen concentration effects on TCE HDC
4.3.4.1 Hydrogen mass transfer analysis
For a rigorous analysis, mass transfer limitations must be evaluated to ensure the measured rates are representative of the reaction and not transport processes. For investigating H$_2$ transport, the major transport restriction to account for is the liquid-to-solid mass transfer step. This analysis parallels that for TCE in Chapter 3. At any given reaction time, the H$_2$ molar flux to the catalyst surface is $W_{TCE} = k_{ls}C_{\text{Hydrogen,liq}}$, where the effective liquid-to-catalytic-surface mass transfer coefficient $k_{ls} = k_c/k_r/(k_r+k_c)$, $k_c$ is the mass transfer coefficient, $k_r$ is the surface reaction rate constant, and $C_{\text{Hydrogen,liq}}$ is the H$_2$ concentration in the bulk fluid. The molar flux $W_{\text{Hydrogen}}$ can be calculated from the rate of change in H$_2$ concentration ($-dC_{\text{Hydrogen}}/dt$) divided by the total surface area of all the NPs in the reaction volume (termed volumetric surface area, or VSA). This leads to $k_{ls}C_{\text{Hydrogen}} = (k_{\text{meas}}*4*4C_{\text{TCE}})/\text{VSA}$. For the 25% coverage Pd/Au NP catalyst, $k_{\text{meas}} = 2.92\times10^{-4}$ 1/s and VSA = 3.66$\times10^{-1}$ 1/cm, leading to $k_{ls} = 7.8\times10^{-4}$ cm/s.

The mass transfer coefficient $k_c$ for H$_2$ diffusing towards a spherical particle was calculated using the Frössling correlation, from which the Sherwood number Sh equals 2 in the limit of pure diffusion$^{29}$. Since $Sh = k_cD_p/D_{\text{Hydrogen}}$, where $D_p$ is particle diameter and $D_{\text{Hydrogen}}$ is the diffusivity of H$_2$ in water (4.8$\times10^{-5}$ cm$^2$/s at 25 °C$^{30}$), $k_c$ was calculated to be 240 cm/s for a particle diameter of 4 nm. Calculated to be $7.7\times10^{-4}$ cm/s using the values of $k_{ls}$ and $k_c$, the surface reaction rate $k_r$ was found to be much smaller in magnitude than $k_c$. For the most active catalyst, it was concluded that H$_2$ diffusion to the NP surface had a negligible effect on measured reaction rates. A similar analysis was conducted on the Pd/Al$_2$O$_3$ catalyst resulting in $k_c = 1.9\times10^{-2}$ cm/s and $k_r = 8.78\times10^{-4}$ cm/s;
again, the transport rate of $\text{H}_2$ to the particle surface is not as small as for the Pd/Au NP case but still can be neglected.

The gas-to-liquid mass transfer step was considered next. At any given reaction time, $W_{\text{Hydrogen}}$ also equals the hydrogen molar flux from the headspace to the water phase, or $W_{\text{Hydrogen}} = k_{gl}((K/RT)\times C_{\text{Hydrogen, liq}}-C_{\text{Hydrogen, gas}})$, where $k_{gl}$ is the gas-liquid mass transfer coefficient, $K$ is Henry's law constant ($7.8\times10^{-4}$ mol/kg/bar for hydrogen in water at $25\,^\circ\text{C}$), $R$ is the ideal gas constant, and $T$ is temperature. Since values for $\text{H}_2$ were not available, published mass transfer data on oxygen aqueous solutions ($2.28\times10^{-2}$ cm/s)$^{31}$ was considered for the $k_{gl}$, thus approximated as $2\times10^{-2}$ cm/s. This value was much larger than $k_r$ ($7.7\times10^{-4}$ cm/s), indicating that the effect of liquid-gas hydrogen mass transfer on kinetics measured was negligible.

4.3.4.2 TCE HDC hydrogen concentration dependency

Analyzing the dependency of $\text{H}_2$ on TCE HDC involves controlling the partial pressure of $\text{H}_2$ in the headspace, which sets the aqueous-phase concentration. Each batch experiment at a different condition can be fit to a pseudo-rate constant times the TCE concentration ($k_{obs} \times f(C_{\text{TCE}})$). However, this rate constant ($k_{obs}$) is a function of $\text{H}_2$. A conversion versus time plot illustrates the dependence of various partial pressures of $\text{H}_2$ on both Pd/Au NP and Pd/Al$_2$O$_3$ catalysts (Figure 4.9). As the partial pressure of $\text{H}_2$ decreased and therefore, the liquid phase concentration, TCE conversion decreased for both catalysts. Plotting the fitted first- and half-order rate constants as a function of $\text{H}_2$ partial pressure (Figure 4.9c) demonstrated that for our 25% coverage Pd/Au NP
catalysts, the dependence of H$_2$ was half-order, as hypothesized in our rate expression (Equation 4). The Pd/Al$_2$O$_3$ catalyst appeared to have a first-order dependence on H$_2$ as predicted from our modifications of the rate law assuming that the MASl was TCE influencing the adsorption of H$_2$ (Equation 5).

![Graphs showing TCE conversion over time at different pressures](image)

**Figure 4.9** TCE HDC reaction data as a function of H$_2$ partial pressure. (a) 25% coverage Pd/Au NPs, (b) 1 wt% Pd/Al$_2$O$_3$, and (c) rate constant data as a function of the H$_2$ partial pressure. Solid lines represent numerical data fits.

The nature of H$_2$ interaction with Pd has deep roots in hydrogenation literature. It is well known that H$_2$ typically dissociatively adsorbs on open Pd surfaces as modeled in Figure 4.2.$^{26,27}$ However, there exist cases where hydrogen's dependence was first-order indicating molecular adsorption of hydrogen.$^{26,27}$ This...
was observed in olefin hydrogenation reactions where the MASI were olefins, decreasing the probability for adjacent vacant sites necessary for dissociated adsorption of $H_2$ to occur. As stated in Section 4.3.2, we suggested that the MASI of Pd/Al$_2$O$_3$ was TCE to explain the half-order dependence (Equation 5). If this is true, the adsorption mechanism for $H_2$ can change from dissociative ($H_2 + 2^* \rightarrow 2 \, H^*$) to non-dissociative ($H_2 + \ast \rightarrow H_2^\ast$) due to the decreased concentration of adjacent vacant sites. By deriving the rate law from this equation, we obtain the following expression for Pd/Al$_2$O$_3$ catalysts:

$$\text{Rate} = k C_{TCE}^{1/2} C_{H_2} \quad (6),$$

resulting in a first-order dependence on hydrogen. This suggests that crowding on the Pd surface leads to non-dissociative adsorption of $H_2$ on Pd/Al$_2$O$_3$ is not severe in the Pd/Au NP case, which further leads to the possibility that $H_2$ and TCE adsorb on slightly different active sites on Pd/Au surface.

4.3.5 Chloride concentration effects on TCE HDC

Chloride is a byproduct of the reaction due to the formation of HCl. Any chloride that is released during the reaction will combine with adsorbed hydrogen and desorb as ionic species ($Cl^\ast$ and $H^\ast$) in water. By adding sodium chloride to the reaction, we were able to control the chloride ion concentration and determine its effects on the rate expression. As the concentration of chloride increased for the Pd/Au NP catalyst, there appeared to be no effect on TCE
conversion (Figure 4.10a). However, the same was not true for Pd/Al₂O₃ catalyst. As chloride concentration increased, the conversion of TCE decreased.

![Graphs showing TCE conversion over time and rate constants as a function of chloride concentration.](image)

**Figure 4.10** TCE HDC reaction data in the presence of increasing amounts of chloride species (0 M to 0.02 M). (a) 25% coverage Pd/Au NPs, (b) 1 wt% Pd/Al₂O₃, (c) Rate constant data as a function of the chloride ion concentration.

Chloride has been hypothesized to poison active sites on monometallic Pd catalysts. However, one explanation is that at higher concentrations of chloride in solution, the surface is not best modeled as vacant sites but as both vacant sites and Cl⁺ sites (Equation 7).
Rate = \frac{kC_{\text{TCE}}^{1/2}C_{\text{H}_2}}{(1+K_{\text{Cl}}C_{\text{Cl}})^2} \quad (7)

At these elevated chloride concentrations (8 to 35 times what is produced in the reaction), the data suggests that $K_{\text{Cl}}C_{\text{Cl}}$ is no longer significantly smaller than 1 (Equation 7). One explanation is that the $\text{Al}_2\text{O}_3$ support can adsorb the excess Cl and increase the local surface concentration of Cl around Pd sites. Cl has no apparent deactivation effect on the reaction for our unsupported Pd/Au NP catalysts, in the same Cl concentration range.

4.3.6 Dissociative adsorption of TCE

Researchers have postulated that chloromethanes undergo dissociative adsorption involving the C-Cl bond under ultra-high vacuum (UHV) conditions at room temperature to explain its binding to a Pd surface and undergoing dechlorination.\textsuperscript{33} This mechanism has generally been extended to halogenated ethane and ethene adsorption at all reaction conditions.\textsuperscript{34,35} To test this effect under our reaction conditions, both TCE and 1,1,2-TCEa were used as reagents for dechlorination. The only molecular differences include the presence of a double bond in TCE and two extra hydrogen atoms in 1,1,2-TCEa. 1,1,2-TCEa was unreactive after 50 minutes on both catalysts tested, while TCE was successfully dechlorinated (Figure 4.11). These results suggest that when the reaction is performed under aqueous conditions, the presence of the C=C aids in the adsorption of TCE at room temperature.
Figure 4.11 TCE and 1,1,2-TCEa conversions on 25% coverage Pd/Au NP and 1 wt% Pd/Al₂O₃ catalysts.

UHV studies are used to examine the interaction of chlorinated organics on Pd surfaces. Under these conditions, the minimization of surface energy demands adsorption (both physisorption and chemisorption) to an unadsorbed-cleaned Pd surface, influencing the chlorinated organic-surface interaction. Under groundwater conditions, chlorinated organics will compete with other adsorbates, including water, where only chemisorbed species will ultimately dechlorinate. Chlorinated ethenes based on the dechlorination of chloroethanes are thought to dissociatively bind to the surface through the breaking of C-Cl bonds as shown by Park et al. with studies of PCE adsorption on Pd(100) under UHV. However, it was not shown how the PCE was bound to the palladium nor were dynamics on the dechlorination reported. Barbosa and coworkers using density functional theory demonstrated that TCE's most stable surface bound configurations involved binding using s-orbital and p-orbital electrons with Pd atoms in a PdCu alloyed surface at room temperature. Due to the inactivity of 1,1,2-TCEa on
both Pd/Au NPs and Pd/Al₂O₃ under aqueous phase reaction conditions, we conclude that the adsorption mechanism involves TCE’s binding to a Pd active site through the p-orbital electrons, which are not present in 1,1,2 TCEa.

4.3.7 Effect of sulfide poisoning on TCE HDC catalysts

Sulfur species are known to be a catalyst poison for hydrogenation reactions involving palladium, platinum, and rhodium.²⁶,³⁹ Evidence exists that sulfur adsorbs on low coordination sites including corner and edge atoms, defects, and grain boundaries.³⁹ When sulfur binds to a surface at low temperatures, its effect is the irreversible loss of active sites (i.e., a drop in active site concentration). Therefore, sulfur is typically considered “toxic” to catalytic metals. The degree of susceptibility of a metal to sulfur poisoning is determined by the number of accessible metal atoms deactivated through adsorption of sulfur molecules. This is called toxicity.³⁹ The initial toxicity is a linear region at low sulfur concentration where the number of active sites removed is due to sulfur poisoning.³⁹ This linear region can be extrapolated to zero activity intercepting the x-axis of sulfur atoms per exposed metal atom. After this linear region, the deactivation trails off until the activity approaches zero. In our sulfur poisoning analysis, Pd NPs instead of Pd/Al₂O₃ were compared to Pd/Au NPs, to remove any support effects from the Al₂O₃. Both decreased in TCE conversion as the S/Pd molar ratio increased, as expected using Na₂S as the sulfur source (Figure 4.12). Pd and Pd/Au catalysts were estimated to have an initial toxicity of ~0.3 S/Pd and ~0.6 S/Pd, respectively. The S/Pd ratios at which activity approached zero for the Pd NPs and Pd/Au NPs were 0.5 and 1 S/Pd, respectively. More sulfur was needed to
deactivate Pd/Au than Pd, and thus, Pd/Au materials were more resistant to sulfur poisoning than Pd NP catalysts.

![Graphs](image)

**Figure 4.12** TCE conversion as a function of time plots in the presence of increasing sodium sulfide for (a) 25% coverage Pd/Au NPs and (b) Pd NPs. (c) TCE dechlorination rate constant data on 25% coverage Pd/Au NPs and pure Pd NPs as a function of sulfur to exposed Pd molar ratio. Dotted lines used to determine the "initial toxicity" of sulfur on catalysts.

Studies of mixing noble metals, such as Pd-Pt and Pd-Au, have shown increased resistance to sulfur poisoning as well as enhanced hydrodesulfurization activity,\textsuperscript{40-42} which the studies attributed to reduced formation of Pd\textsubscript{4}S due to smaller Pd ensembles when alloyed with Au.\textsuperscript{40} Increased sulfur resistance could simply be due to exposed Au NP available for adsorption of sulfide species; it is
well known that sulfur has an affinity to bind to Au. This creates a type of sulfur guard for the Pd active sites allowing for extended life of the catalyst.

There are no published investigations on the effects of poisoning catalysts for aqueous HDC reactions. In fact, Pd-sulfur poisoning has mainly been studied for selective hydrogenation reactions of C₄ compounds.²⁷,³⁹ Table 4.3, is a list of hydrogenation reactions and metal catalysts used along with their initial toxicity data and if available zero activity data. As shown, most initial toxicity is between 0.3 S atom/metal atoms and as low as 0.1.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Hydrogenation Reaction</th>
<th>Initial Toxicity [S atom/Metal atom]</th>
<th>Zero Activity [S atom/Metal atom]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd</td>
<td>1-butene</td>
<td>0.2</td>
<td>0.5</td>
</tr>
<tr>
<td>Pd</td>
<td>1,3-butadiene</td>
<td>0.33</td>
<td>0.5</td>
</tr>
<tr>
<td>Pt</td>
<td>benzene</td>
<td>0.33</td>
<td>-</td>
</tr>
<tr>
<td>Pt</td>
<td>maleic acid</td>
<td>0.1</td>
<td>-</td>
</tr>
</tbody>
</table>

4.4 Summary and conclusions

Attempts to better understand the reaction pathway of TCE dechlorination in the presence of hydrogen were successful through the development of a proposed kinetic model. By probing the catalysts with reactants that varied in chemical species, we gained a deeper understanding of the TCE HDC reaction. A rate expression (rate = kC_{TCE}C_{H₂}^{0.5}) was developed for our Pd/Au NP catalysts supporting the 1ˢᵗ HDC step of TCE to form DCE isomers as the rate-limiting step. Chloride number was shown to influence the value of the reaction rate constant as demonstrated by increased HDC activity for decreasing chloride
number. Chloride location was demonstrated as a factor in the various isomers of DCE dechlorination (trans-DCE > cis-DCE > 1,1-DCE), which lead to the conclusion that not all chlorides in TCE are equally accessible. Adsorption through the C=C bond was suggested as the major reaction difference between TCE’s activity and TCEa’s inactivity. Excess chloride did not affect the Pd/Au NP dechlorination rates; however, the presence of sulfide did. Exposed Au in the Pd/Au NP catalysts was attributed to increased chloride and sulfide resistances.

Pd/Al₂O₃ were found to have a half-order TCE dependence and first-order H₂ dependence, which is different from Pd/Au NPs and from results of Reinhard. This change in order dependence could be due to high concentrations of adsorbed TCE, which could induce H₂ to adsorb non-dissociatively (half-order) instead of dissociatively (first-order). The first dechlorination step over Pd/Al₂O₃ was still the rate-limiting step. Experiments with Pd NPs verified the half-order dependence on TCE.

At higher chloride concentrations, Pd/Al₂O₃ demonstrated HDC deactivation possibly due to chloride adsorption to the Al₂O₃ support increasing its local surface concentration about Pd sites. Sulfur was shown to more deeply deactivate Pd NPs compared to our Pd/Au NP catalysts possibly due to the presence of exposed Au as a sulfide adsorption site.

4.5 References


Chapter 5
Colloidal processing of nanoparticle-supported MoO$_x$/ZrO$_2$

5.1 Introduction

With the advent of "bottom-up" synthesis techniques, interest in colloidal based materials as building blocks has developed. Systems of colloids have been controlled to form unique structures and compositions resulting in 2-D and 3-D assembled arrays,\(^1\)\(^-\)\(^4\) precipitated powders,\(^5\)\(^,\)\(^6\) or the formation of thin films.\(^7\)\(^,\)\(^8\)

Recently, colloidal zirconia (ZrO$_2$) has received a lot of attention.\(^9\)\(^-\)\(^{14}\) Materials synthesized from ZrO$_2$ NPs have been used in applications ranging from corrosion resistant materials\(^15\)\(^-\)\(^{20}\) and solid electrolytes\(^21\) to catalyst supports.\(^22\)\(^-\)\(^{27}\) The addition of secondary components to ZrO$_2$ NPs further improves chemical characteristics through improved control over the nanostructure. For example, components such as ceria\(^28\), sulphonate\(^29\), and phosphates\(^29\) are stabilized on the surface of ZrO$_2$ NPs producing enhanced proton conducting membranes. The addition of nickel ions\(^30\) to ZrO$_2$ NPs are investigated for their ability to thermally stabilize ions, enhancing optical properties. The addition of titania\(^31\) and silica\(^6\) promote higher surface area/thermally stable catalyst supports.

Recently, Wong et al. synthesized highly acidic catalysts from 5-nm ZrO$_2$ NPs through the addition of tungsten oxide precursor utilizing a NP/surfactant templating method ("nano-WO$_x$/ZrO$_2$").\(^5\) Nano-WO$_x$/ZrO$_2$ had high surface areas (130 m$^2$/g) and high thermal stability (873 K), as well as stabilizing unique surface structures not observed in conventionally impregnated materials.\(^5\) The ZrO$_2$ NP supports lead to extremely high tungsten oxide loadings (30 wt%), and the
tungsten oxide was in the form of an amorphous species. These amorphous species have been concluded to be active for acidic reactions such as isomerization, alkylation, and dehydration reactions.\textsuperscript{32-34} However, the method developed by Wong et al. to produce nano-WO\textsubscript{x}/ZrO\textsubscript{2} is limited to a single composition at which charge balancing between the (+) ZrO\textsubscript{2} NPs and the (-) tungsten oxide precursor precipitates from solution into a powder form.\textsuperscript{5} Controlling the aggregation process such that a gel is formed instead of a precipitated powder can provide control over the compositional range of amorphous metal oxide.

Amorphous metal oxides have also been shown to be active for oxidation reactions.\textsuperscript{25,26,35-37} Many studies of molybdenum oxide (MoO\textsubscript{3}) supported on preformed ZrO\textsubscript{2} supports demonstrated that optimum activity develops from this amorphous form.\textsuperscript{22,24-26,38} In this chapter, I discuss the synthesis and characterization of MoO\textsubscript{x}/ZrO\textsubscript{2} catalysts in which ZrO\textsubscript{2} NPs are used to support amorphous MoO\textsubscript{x}. The synthesis method is different from that for nano-WO\textsubscript{x}/ZrO\textsubscript{2}. I describe the nanostructure formation through this new synthesis method in terms of controlled colloid destabilization and gel formation. Lastly, I compare its catalytic activity against conventionally prepared MoO\textsubscript{x}/ZrO\textsubscript{2} for methanol oxidation.

5.2 Experimental methods

5.2.1 Synthesis
Amorphous molybdenum oxide supported on ZrO$_2$ NPs ("nano-MoO$_x$/ZrO$_2$") powders were synthesized by first dissolving ammonium heptamolybdate (AHM) (NH$_4$Mo$_7$O$_{24}$.4H$_2$O; 0 to 0.734 g; Strem) in nanopure water (>18 MΩcm; 16 g; Barnstead Nanopure Diamond). For MoO$_x$/ZrO$_2$ samples prepared with a porogen, 16 g of an ethylene oxide$_{20}$-propylene oxide$_{70}$-ethylene oxide$_{20}$ triblock copolymer solution (5.7 wt% in nanopure water, Pluronic P123, BASF) was used. The mixture was magnetically stirred in a 100 mL beaker until a transparent and colorless solution resulted (pH ~5-6). Then, while stirring, 10 g of a ZrO$_2$ NP sol (20 wt% ZrO$_2$; Zr-10/20; Nyacol) was quickly added. The solution immediately became milky-white before returning back to a transparent and colorless state. Depending on the AHM amount, the solution can form a gel. The time between adding the ZrO$_2$ sol and the disappearance of the vortex was denoted as “gel time$$_v$.”

To assist in gel formation at the lower amounts of AHM used, ammonium nitrate salt (NH$_4$NO$_3$, Fluka) was added or the synthesis temperature was increased to assist in gel formation. In the salt method, NH$_4$NO$_3$ was dissolved in the AHM/water solution prior to Zr-10/20 addition. In the temperature method, the AHM/water solution was heated in an isothermal water bath. Also, the Zr-10/20 sol was heated to the same temperature before its addition to the heated AHM/water solution. The resultant solution was kept at the same temperature until the gel formed.

The as-synthesized gel was left to age for 1 hr at 298 K, and dried overnight at 343 K in an oven, resulting in a material with a dry powder or glassy consistency.
The dried material was ground up with a mortar and pestle for ~10 min, and calcined in air at a heating rate of 3.2 K/min from 298 K to 773 K and for a soak time of 3 hr. The MoOₓ content was based on mass balance since all precursors were accounted for in the gel.

A conventional 6 wt% MoO₃/ZrO₂ catalyst was prepared via a incipient wetness impregnation method for comparison.²⁵ 0.105 g of AHM was dissolved in 0.370 g water. 1 g of ZrO₂ (Degussa; Vₚore = 0.14 cm³/g) was heated to 403 K for 1 hour to drive off moisture. 0.14 mL of the AHM solution was added to the ZrO₂ and mixed for 30 minutes. The powder was then heated to 773 K for 3 hours in air.

5.2.2 Characterization

Zeta potential and diffusion coefficient measurements of AHM-containing ZrO₂ NP sols were conducted using a ZetaPALS dynamic light scattering (DLS) unit from Brookhaven Instruments Corporation utilizing a 656 nm wavelength laser. The samples were synthesized according to the described procedure except that the precursor amounts were scaled down by 10 times; the solution was vortex mixed for 10 sec instead of magnetically stirred; and the synthesis mixture was diluted by 4 times using nanopure water to extend gel times from minutes to days and to raise the pH above 2 (the operational limit of the zeta potential probe). As an example, 0.05 g of AHM and 1.0 g of Zr-10/20 were combined with 6.5 g of nanopure water. These solutions were synthesized and allowed to equilibrate overnight prior to the measurement. “Gel times” denoted the time between NP
addition and when the sample solidified (i.e., the sample in the beaker did not flow when set upsidedown). Gel times was always greater than gel timev.

Powder x-ray diffraction (XRD) patterns were collected on a Rigaku Ultima D/Max 2100 X-ray powder diffractometer utilizing Cu Kα radiation (λ = 0.154056 nm) and calibrated with a silicon crystal standard. Typical scans ranged from 2θ = 20-70° using 40 kV and 40 mA at a step size of 0.5 °/min.

BET (Brunauer-Emmett-Teller) specific surface areas (SSA) and pore volumes (Vpore) of the final powders were determined using a Micromeritics ASAP 2010 nitrogen gas adsorption analyzer. SSA was determined using a 5-point adsorption analysis conducted at 77 K, while Vpore was determined using the cumulative nitrogen uptake at P/Po = 0.98.

Transmission electron microscopy (TEM) was used to obtain textural information about the final calcined powders using a JEOL 2010 transmission electron microscope (TEM).

Raman spectroscopy was used to detect nanocrystalline domains of MoO3. A Jobin Yvon LabRam-HR Raman spectrometer was used to obtain spectra from 100-1200 cm⁻¹ region. The visible laser excitation at 532 nm are generated by a Yag doubled diode pumped laser, 20 mW. The scattered photons were directed a single monochromater and focused on to a LN2 CCD detector. The Raman spectrometer was equipped with an in situ cell, where the catalyst was dehydrated at 450 °C for 1 h in flowing 10% O2/He, and the Raman spectra of the dehydrated samples were collected at room temperature.
Partial oxidation of methanol was conducted at 498 K by using a gas phase flow through reactor with a mixture of methanol, oxygen, and helium at a ratio of 6/12/82 (mol %). Approximately 10 mg of catalyst sample was used to obtain less than 10% conversion, to ensure differential conditions. Prior to reaction, the catalyst was heated to 623 K for 1 hour in oxygen. The reaction products were analyzed by an on-line gas chromatography (Agilent 6890) installed at the reactor outlet. Columns used for separation included 5 ft × 1/8 in Carboxen 1000 (45/60) connected to the thermoconductivity detector and a 60 m × 0.53 SPB-1 connected to the flame ionized detector.

5.3 Results and discussion

5.3.1 Gelation of ZrO$_2$ NP sol using AHM

Our goal was to synthesize high concentrations of thermally stable-amorphous MoO$_x$ species supported on ZrO$_2$ NPs. Wong et al. previously showed that ZrO$_2$ NPs can support up to 30% amorphous WO$_x$ as a thermally stable metal oxide framework$^5$. We attempted NP/surfactant templating, but were unsuccessful in producing “nano-MoO$_x$/ZrO$_2$.” One method of creating materials from NPs involves gelation. In gelation, the NPs in suspension interconnect to form a rigid network of NP chains that span the suspension volume.$^{39}$ Removal of the solvent without causing this NP network to collapse creates a porous nanostructure, which can be in the macroscopic form of a powder, film, or monolith. NP sols are stabilized against coagulation, and so controlled destabilization of the sol is necessary to induce gelation. ZrO$_2$ NPs are charge
stabilized at low pH (~1) in nitric acid. This pH is well below the isoelectric point for ZrO$_2$ (pH ~4-6), which results in highly positively charged NP surfaces. From our results, the zeta potential of these ZrO$_2$ NPs is $+42$ mV diluted to pH 2.

In this case, colloidal stability is described by the Derjaguin-Landau-Verwey-Overbeek (DLVO) theory, which states that the net potential ($\Phi_{\text{net}}$) between two NPs is a function of two potential energy terms: (1) the van der Waals long range attractive potential and (2) a like charged electrostatic repulsive potential \(^{41}\) (Equation 1).

\[
\Phi_{\text{net}} \propto \kappa^{-1} \Psi_o^2 \exp(-\kappa d) - A d^{-2} \quad (1)
\]

(repulsive) (attractive)

where $\kappa^{-1} = \text{Debye-Huckel length}$, $\Psi_o = \text{function of the particle's surface potential}$, $d = \text{separation distance between surfaces}$, and $A = \text{Hamaker constant (ZrO}_2\text{ at 298K = 7.23} \times 10^{-20} \text{ J).}^{42,43}$ Since there is little control over the attractive potential terms, the repulsive potential must be reduced to allow NPs to interconnect and form a gel. This can be done by adding an adsorbing salt that binds to the NP surface to reduce the surface charge potential ($\psi$) or by adjusting $\kappa^{-1}$ to reduce the repulsive potential through ionic strength (Equation 2).

\[
\kappa^2 = \frac{1000e^2 N_A}{\varepsilon_r \varepsilon_0 k_B T} \sum_i z_i^2 M_i \quad (2),
\]
where \( e \) is the charge of an electron, \( N_A \) is Avogadro’s number, \( \varepsilon_r \) and \( \varepsilon_0 \) are dielectric constants, \( k_B \) is Boltzmann constant, \( z_i \) is the formal charge of \( i \), and \( M_i \) is the molar concentration of \( i \). Changes to the surface charge potential can be observed by measuring changes in the NP sol’s zeta potential. Zeta potential (\( \zeta \)) is a measure of the charge potential of a particle at its boundary layer (i.e., the fluid layer surrounding the particle that moves with the particle). The magnitude of a particle’s zeta potential is a function of the surface charge potential evaluated at the fluid boundary layer (Equations 3 and 4),

\[
\psi = \frac{q}{4\pi \varepsilon_r \varepsilon_0} \frac{\exp(-\kappa (r - R_s))}{(1 + \kappa R_s)} \tag{3}
\]

\[
\zeta = \psi \bigg|_{r=R_{\text{boundary}}} \tag{4}
\]

where \( q \) = surface charge, \( r \) = distance of any point in the double layer from the center of the particle, \( R_s \) = radius of the spherical particle, and \( R_{\text{boundary}} \) = particle boundary layer radius.\textsuperscript{44,45}

To obtain the desired nanostructure through gelation in our system (Figure 5.1), we studied the effect of AHM on the colloidal stability of a ZrO\(_2\) NP sol. As ZrO\(_2\) was added to increased amounts of AHM and therefore, the AHM/ZrO\(_2\) molar ratio increased, the measured zeta potential decreased until it approached zero (Figure 5.2-left axis). The ZrO\(_2\) sol added to an aqueous solution of AHM developed a final solution pH of \( \sim \)1.5. Molybdate species at this pH develop from \( 3 (\text{Mo}_7\text{O}_{21}(\text{OH})_3^{3-}) \) to \( 4 (\text{Mo}_{19}\text{O}_{59}^{4-}) \) negative charges.\textsuperscript{46} These negatively charged
species adsorbed to the positively charged ZrO₂ NPs (Figure 5.1a), and decreased the NP’s zeta potential. However, only samples that had AHM/ZrO₂ molar ratios greater than 0.022 gelled (Figure 5.2-right axis). Researchers have shown that sols of TiO₂ and Al₂O₃ with zeta potentials below +14 mV can overcome their repulsive stabilizing potentials and coagulate.⁴⁴ This occurred for AHM/ZrO₂ molar ratios greater than 0.022. Once enough AHM has adsorbed to a ZrO₂ NP surface to reduce the zeta potential below +14 mV, the molybdate-ZrO₂ NPs began to interact (Figure 5.1b).

![Diagram](image)

**Figure 5.1** Gel formation mechanism between a ZrO₂ sol and a molybdenum oxide based salt to form a gel. Path 1: (a) (+)-ZrO₂ sol attracting (-)-AHM salt, (b) charge destabilized NPs interacting with each other to form a gel, and (c) final gel undergoes heat treatment to form nonporous nano-MoO₃/ZrO₂. Path 2: (d) (+)-ZrO₂ sol attracting a (-)-AHM salt in the presence of P123 porogen, (e) charge destabilized NPs interacting with each other to form a gel, and (f) final gel undergoes heat treatment to form porous nano-MoO₃/ZrO₂.
The modified NPs can bind through surface hydroxyl condensation reactions or through mutually adsorbed AHM molecules leading to gelation (Figure 5.2-right axis).

One could argue that the AHM does not adsorb to the NP surface and contributes to colloid destabilization by increasing solution ionic strength and reducing the repulsive potential. So, we tested this argument by replacing AHM with NH$_4$NO$_3$, a salt that has the same NH$_4^+$ cation as AHM and a nitrate anion, which does not adsorb onto ZrO$_2$ NP surfaces.$^{44}$

![Figure 5.2. Experimentally determined zeta potentials (left axis) and gel times (right axis) of the modified ZrO$_2$ sols with varying molybdate precursor content at room temperature. Samples at 0.027 and 0.035 had measured zeta potentials that were below the accuracy of the ZetaPALS instrument.](image)

The nitrate salt increased the solution ionic strength according to Equation 5 and reduced the Debye-Hückel length, therefore reducing the repulsive potential.
\[ I = \frac{1}{2} \sum_{i} M_i \cdot z_i^2 \quad (5) \]

At NH₄NO₃/ZrO₂ ratios with ionic strengths equivalent to those of AHM/ZrO₂ ratios studied earlier, the zeta potentials were significantly larger (Figure 5.3). The observed decrease obtained with AHM was not apparent with NH₄NO₃ (Figure 5.2) confirming that the destabilization of the ZrO₂ NP sol involved molybdate adsorption onto the NPs. While the increased ionic strengths (50-200 mmol/L) had a negligible effect on zeta potential, much higher ionic strengths did reduce the zeta potentials. This is consistent with DLVO theory, with zeta potential a function of ionic strength (Equation 6):⁴⁵

\[ \zeta = \frac{q}{4\pi \varepsilon \varepsilon_0 R_{\text{Boundary}}} \frac{\exp(-\kappa(R_{\text{Boundary}} - R_s))}{(1 + \kappa R_s)} \quad (6) \]

The trendline in Figure 5.3 is a fit of the form in Equation 6 demonstrating agreement with DLVO theory, where \( R_s = 5 \) nm, \( R_{\text{boundary}} = 5.7 \) nm, and \( q = 24 \) eV.

5.3.2 Factors affecting gelation rate

5.3.2.1 Gelation temperature effect

Temperature can be used to control gelation rates during sol-gel processing using metal alkoxide precursors.⁴⁷,⁴⁸ There are two major effects that temperature can have: 1) influence the NP's attractive/repulsive interactions
stabilizing the NPs (i.e., zeta potential) and 2) influence the probability of NP-NP interactions by increasing the number collisions (i.e., diffusion coefficient of NPs).\textsuperscript{48}

![Graph showing zeta potential vs. ionic strength](image)

**Figure 5.3** Experimentally determined zeta potentials of the ZrO\textsubscript{2} sols as a function of ionic strength by varying NH\textsubscript{4}NO\textsubscript{3} (▲) or AHM (○) concentration. The solid trendline is a fit of zeta potential on ionic strength as given in Equation 6.

The diffusion coefficient was experimentally determined from the measurements using DLS, which internally accounts for changes in solvent viscosity as a function of temperature. The ZrO\textsubscript{2} NP zeta potentials and diffusion coefficients were found to decrease and increase with increased temperature, respectively (Figure 5.4a). Thus, the observed decrease in gelation time with increasing temperature is consistent with reduced zeta potentials and higher NP collisions
Similar temperature effects have been observed with charged stabilized suspensions of Al₂O₃.⁴⁹

Figure 5.4. (a) Experimentally determined zeta potential (left axis) and diffusion coefficient (right axis) of ZrO₂ NP sols as a function of temperature. (b) Gel time as a function of temperature for a 0.025 AHM/ZrO₂ molar ratio.

5.3.2.2 Precursor concentration effects

It is known that precursor concentrations can have an impact on gel time due to the increased volume that the modified ZrO₂ NPs have to traverse to interact.⁴⁷ To test this, increasing amounts of water were added to the AHM solution prior to the addition of ZrO₂ NPs and the gel time was monitored (Figure 5.5). This log-linear plot of AHM precursor concentration versus gel time demonstrates that as the concentration increases by a factor of ~4, gel time decreases over 3 orders of magnitude, while maintaining a constant AHM/ZrO₂ ratio of 0.035.

5.3.2.3 NH₄NO₃ effect on stable AHM-containing ZrO₂ NP sols
We studied the addition of $\text{NH}_4\text{NO}_3$ to see if gelation time of AHM/ZrO$_2$ sols can be decreased. An AHM/ZrO$_2$ ratio of 0.0175 did not gel at room temperature (Figure 5.2).

**Figure 5.5** Experimentally determined gel times of the modified ZrO$_2$ NP sols as a function of AHM concentration at a constant AHM/ZrO$_2$ ratio of 0.035. Solid line used to guide eyes.

![Gel Times Graph](image)

**Figure 5.6** Experimentally determined gel times of the modified ZrO$_2$ NP sols as a function of $\text{NH}_4\text{NO}_3$/ZrO$_2$ at a constant AHM/ZrO$_2$ ratio of 0.0175 and synthesized at 313 K.
However, when the temperature was increased to 313 K, gelation occurred with a gel time, of 9 minutes (Figure 5.6). NH₄NO₃ was added to the AHM solution before the ZrO₂ NPs were added, and the gel time, was monitored (Figure 5.6). With the addition of NH₄NO₃, the gel time, was quickly reduced from 9 minutes to 1.5 minutes. The NH₄NO₃ salt increased the solution’s ionic strength, reducing the repulsive potential stabilizing the NPs, ultimately decreasing gel time. Further increases in NH₄NO₃ concentration had little additional effect on gel time,.

5.3.3 Effect of porogen on nano-MoOₓ/ZrO₂ structure

Once the gels formed, they were aged for 1 hour, dried overnight at 343 K, ground into a fine powder, and calcined in air at 773 K for 3 hours. The resulting materials were found to contain low surface areas (SSA = 8.5 m²/g) and pore volumes (Vₚore = 0.014 cm³/g). The final crystalline form consisted of only tetragonal ZrO₂, no crystalline MoO₃ was observed (Figure 5.1c, Figure 5.8). Applications in the areas of electrochromic⁵⁰ and electrical conducting⁵¹,⁵² materials might benefit from dense, low-SSA MoOₓ/ZrO₂ structure. However, for catalysis, high surface area porous MoOₓ/ZrO₂ structures are desired.

To increase the surface area, Pluronic P123 surfactant was introduced to the AHM-ZrO₂ process prior to gelation. P123 is an poly(ethylene oxide)-poly(propylene oxide) (EO₂₀PO₇₀EO₂₀) nonionic block copolymer (MW ~ 5750) that forms spherical micelles in water with a poly(propylene oxide) core surrounded by a poly(ethylene oxide) shell. P123 has been used as sacrificial
template to provide and control pore structures, pore sizes, and assist in nanostructured templating. Adding P123 minimally affected gelation times. We found that, of all the possible combinations of NPs, AHM, and P123, only two led to gel formation (Figure 5.7). P123 by itself did not induce gelation, nor did it prevent gelation of the AHM-ZrO$_2$ NP.

Processing and calcination of the three-component (AHM-P123-ZrO$_2$ NP) gel led to a material with a much higher SSA and $V_{pore}$ compared to AHM-ZrO$_2$ NP only (Figure 5.8).

![Venn diagram illustrating the binary and ternary combinations of ZrO$_2$ sol, molybdenum oxide precursor (AHM), and P123 porogen.](image)

The three-component's crystal structure was found to be x-ray amorphous, indicating that the ZrO$_2$ NPs were able to support and stabilize the MoO$_x$ from crystallizing at 773 K. This material is referred to as "nano-MoO$_x$/ZrO$_2"." The AHM-ZrO$_2$ NPs showed the formation of crystalline ZrO$_2$ domains, indicating that a portion of the ZrO$_2$ NPs were able to make contact during calcination; however,
no crystalline MoO\textsubscript{3} was observed. It is hypothesized that the ZrO\textsubscript{2} NP support, in the absence of P123, increased nearest neighbor ZrO\textsubscript{2} contacts allowing for larger crystalline domains to develop (Figure 5.1c). For nano-MoO\textsubscript{x}/ZrO\textsubscript{2}, this ZrO\textsubscript{2}-ZrO\textsubscript{2} interaction was minimized until the P123 decomposed (~650 K), by which time the MoO\textsubscript{x} and ZrO\textsubscript{2} have started forming the stable amorphous structure (Figure 5.1f). The two remaining binary combinations (AHM-P123 and P123-ZrO\textsubscript{2} NP) did not form gels; however, they were processed identically to gelled samples and used as control experiments. Neither material could produce a binary metal oxide since both materials use one precursor with P123 only. AHM-P123 led to the formation of highly crystalline MoO\textsubscript{3} with low SSA and V\textsubscript{pore}, while P123-ZrO\textsubscript{2} NPs led to crystalline ZrO\textsubscript{2} with very low SSA and V\textsubscript{pore} (Figure 5.8).

<table>
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</tbody>
</table>

**Figure 5.8** XRD pattern, SSA, and pore volume of the materials synthesized from (a) AHM-ZrO\textsubscript{2} NPs, (b) AHM-P123-ZrO\textsubscript{2} NPs, (c) P123-ZrO\textsubscript{2} NPs, and (d) AHM-P123. (■) - orthorhombic MoO\textsubscript{3}, (▲) - tetragonal ZrO\textsubscript{2}. 
P123 was clearly necessary to generate a porous structure due to the observed increased SSA and $V_{\text{pore}}$. TEM analysis of the calcined nano-MoO$_x$/ZrO$_2$ material synthesized demonstrates no ordered$^{53}$ or even worm-like$^5$ porous structure existing, all of which have been produced using P123 (Figure 5.9). Since the P123 is not necessary for gelation of the AHM-ZrO$_2$ NPs, it is hypothesized that P123 merely occupied space during the sol-gelation process, and once calcined, left behind a randomly porous structure.

![TEM image of nano-MoO$_x$/ZrO$_2$ formed using P123.](image)

**Figure 5.9** TEM images of nano-MoO$_x$/ZrO$_2$ formed using P123.

5.3.4 Calcination temperature effect on nano-MoO$_x$/ZrO$_2$ structure

We studied the thermal stability of nano-MoO$_x$/ZrO$_2$ gels by testing the effect of calcination temperature. As the calcination temperature was increased from 773 K to 873 K, a mixed phase of mainly tetragonal ZrO$_2$ crystallized with small domains of crystalline hexagonal zirconium molybdates [Zr(MoO$_4$)$_2$] forming (Figure 5.10).
Figure 5.10 XRD pattern, SSA, and pore volume of nano-MoO$_x$/ZrO$_2$ calcined to (a) 973 K, (b) 873 K, and (c) 773 K. (■) - hexagonal Zr(MoO$_4$)$_2$, (▲) - tetragonal ZrO$_2$.

As the temperature further increased to 973 K, the XRD intensity for Zr(MoO$_4$)$_2$ crystallites increased. At high temperatures (>873 K), high concentrations of MoO$_x$ (5 Mo-atoms/nm$^2$) in contact with ZrO$_2$ have been shown to form Zr(MoO$_4$)$_2$ crystallites.$^{24,27}$ Even though crystallization occurred at 873 K and higher, the final material did not completely collapse, as was shown for the AHM-ZrO$_2$ NP material at 773 K.

5.3.5 Gelation temperature effect on nano-MoO$_x$/ZrO$_2$ structure

We studied the effect of gelation temperature on calcined nano-MoO$_x$/ZrO$_2$ to see if enhanced gelation led to any differences in nanostructure. For an AHM/ZrO$_2$ ratio of 0.025, it took ~8 minutes to form a gel (gel time,$_t$) at room
temperature and the resulting material was found to contain a small amount of crystalline ZrO$_2$ (Figure 5.11).

![XRD pattern](image)

**Figure 5.11** XRD pattern, SSA, and pore volume of nano-MoO$_3$/ZrO$_2$ synthesized at (a) 323 K, (b) 313 K, (c) 306 K, and (d) 298 K. (■) – tetragonal ZrO$_2$.

As gelation temperature increased, SSA and $V_{\text{pore}}$ decreased while the intensity of ZrO$_2$ XRD peaks increased. These results were interpreted as, increasing the gelation temperature allowed for more ZrO$_2$ NP-NP contacts with less AHM in between them (Figure 5.12). Since gelation time is reduced as gelation temperature is increased (Figure 5.4b), there is less time for AHM to coat the ZrO$_2$ NPs and uniformly spread, ultimately leaving ZrO$_2$ exposed to crystallize (Figure 5.12). However, no crystalline MoO$_3$ was observed even for samples with high tetragonal ZrO$_2$ content.
5.3.6 NH$_4$NO$_3$ concentration effect on nano-MoO$_x$/ZrO$_2$ structure

AHM/ZrO$_2$ gels with ratios less than 0.025 are difficult to prepare due to long gelation times or no gel formation at all. Thus, we studied the use of NH$_4$NO$_3$ to assist in these limitations and to determine its effect on the resultant nanostructure. A lower ratio of AHM/ZrO$_2$ (0.0175) was used and synthesized at 313 K to show its effects on materials that would typically not gel. As the NH$_4$NO$_3$/ZrO$_2$ ratio increased, its impact was increasing the ZrO$_2$ support's XRD intensity (Figure 5.13). These results were consistent with the concept that increased ZrO$_2$ NP contact leads to formation of ZrO$_2$ crystalline domains.

5.3.7 Controlling MoO$_x$ content of nano-MoO$_x$/ZrO$_2$

With the effects of several synthesis parameters known, we synthesized a wide range of MoO$_x$ compositions with nano-MoO$_x$/ZrO$_2$. The conditions used to create AHM/ZrO$_2$ materials ranging from 0.011 to 0.035 are shown in Table 5.1.
Figure 5.13 XRD pattern, SSA, and pore volume of nano-MoO₃/ZrO₂ synthesized at 313 K with (a) 0 NH₄NO₃/ZrO₂, (b) 0.5 NH₄NO₃/ZrO₂, (c) 2.7 NH₄NO₃/ZrO₂, and (d) 4.3 NH₄NO₃/ZrO₂. (■) - tetragonal ZrO₂.

Table 5.1 Synthesis conditions for variable AHM loaded samples used in Figure 5.14.

<table>
<thead>
<tr>
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<tbody>
<tr>
<td>8.6</td>
<td>0.011</td>
<td>0.293</td>
<td>313</td>
<td>14.5</td>
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<td>11.4</td>
<td>0.016</td>
<td>0.258</td>
<td>313</td>
<td>3.5</td>
</tr>
<tr>
<td>14.2</td>
<td>0.020</td>
<td>0.196</td>
<td>313</td>
<td>2.0</td>
</tr>
<tr>
<td>16.9</td>
<td>0.025</td>
<td>0.142</td>
<td>298</td>
<td>8.0</td>
</tr>
<tr>
<td>20.6</td>
<td>0.031</td>
<td>0.072</td>
<td>298</td>
<td>3.5</td>
</tr>
<tr>
<td>23.0</td>
<td>0.035</td>
<td>0.000</td>
<td>298</td>
<td>1.0</td>
</tr>
</tbody>
</table>
As the composition of AHM is decreased, gel time increased until no gel formation occurred. A 15-minute maximum gel time was set to obtain consistent synthesis times. Initially, as AHM concentration decreased, increasing amounts of NH₄NO₃ were added. Next, gelation temperature was increased from 298 K to 313 K in addition to increased NH₄NO₃ loadings until the AHM/ZrO₂ ratio was so low (0.011) that even with excess NH₄NO₃ and a gelation temperature of 313 K, gel time was just below 15 minutes. The loadings of nano-MoOₓ/ZrO₂ ranged from 8.6 wt% to 23 wt%. Based on our previous studies, as the AHM concentration decreased and the NH₄NO₃ and gelation temperatures increased, support ZrO₂ crystallinity increased; however, the supported MoOₓ did not crystallize. Indeed, the final calcined nano-MoOₓ/ZrO₂ materials followed these trends (Figure 5.14).

![Figure 5.14](image)

**Figure 5.14** XRD pattern, MoOₓ content (wt%), SSA, and pore volume of nano-MoOₓ/ZrO₂ synthesized at AHM/ZrO₂ molar ratios of (a) 0.011, (b) 0.016, (c) 0.020, (d) 0.025, (e) 0.031, and (f) 0.035. ■ - tetragonal ZrO₂.
The highest loaded sample (23.3 wt%) was submitted for Raman analysis to further examine for the presence of MoO\textsubscript{3} nanocrystalline domains. Compared to a reference 8.8 wt% MoO\textsubscript{3}/ZrO\textsubscript{2} sample containing MoO\textsubscript{3} crystallites, the observed surface structures were different (Figure 5.15). The characteristic crystalline peak was not observed in our 23.3 wt% nano-MoO\textsubscript{x}/ZrO\textsubscript{2} material; however, a broad strong peak assigned to O-Mo-O was present, characteristic of the amorphous MoO\textsubscript{x} species.

Metal oxides, such as molybdenum oxide, are believed to spread along another metal oxide surface (i.e., Al\textsubscript{2}O\textsubscript{3}, ZrO\textsubscript{2}, TiO\textsubscript{2}) until it is completely covered.\textsuperscript{24} On pre-made supports, any additional metal oxide will begin to form crystalline domains.

![Raman Spectra](image_url)

**Figure 5.15** Dehydrated Raman spectra for (a) 23.3% nano-MoO\textsubscript{x}/ZrO\textsubscript{2} and (b) 8 wt% MoO\textsubscript{3}/ZrO\textsubscript{2}.

Since we are forming our material (both support and surface metal oxide) simultaneously by coating ZrO\textsubscript{2} NPs with AHM, surface area of the final material
is a function of the AHM loading. Plotting the SSA against the weight loading MoO$_x$ results in a linear relationship suggesting a self-regulating mechanism of MoO$_x$ spreading across the ZrO$_2$ NPs (Figure 5.16). Consistent with Figure 5.12, as the AHM loading increased, less ZrO$_2$ NP-NP interactions occur, which ultimately reduce crystallization of the support, allowing for SSA of the final nano-MoO$_x$/ZrO$_2$ to increase.

![Graph](image)

**Figure 5.16** Plot of SSA as a function of MoO$_x$ loading (wt%). Solid line used to guide eyes.

5.3.8 Catalytic experiments

Partial oxidation of methanol conducted at 503 K was used as a probe reaction to test the catalytic activity of our nano-MoO$_x$/ZrO$_2$ materials. Product distributions arising from methanol oxidation provide additional information on the nature of the surface (Figure 5.17).$^{54}$ Acidic (dimethyl ether; DME), basic (CO, CO$_2$), and
redox (formaldehyde, HCHO; dimethoxymethane, DMM; methyl formate, MF). Note that MF is the most basic redox product and HCHO the most acidic redox product. For comparison to our nano-MoO$_x$/ZrO$_2$, a 6 wt% MoO$_3$/ZrO$_2$ was synthesized via incipient wetness impregnation because its been shown to be the highest loading of MoO$_x$ (4.3 Mo atoms/nm$^2$) without the formation of MoO$_3$ crystallites.\textsuperscript{25,55} Since our materials stabilize higher loadings of MoO$_x$, above surface densities of 4.3 Mo atoms/nm$^2$, the proper comparison of reactivity would be in the absence of crystalline MoO$_3$.

\textbf{Figure 5.17} Relationship between a catalytic surface and possible methanol oxidation product distributions. Moving from left to right the product evolution moves from acidic (DME) to redox (HCHO, DMM, MF) to basic (CO, CO$_2$) in nature.\textsuperscript{54,56}

Table 5.2 illustrates the results of six different materials tested for partial oxidation of methanol. This set of materials were all run at similar reactor conditions including C$_{\text{MeOH}}$/C$_{\text{Oxygen}}$/C$_{\text{Helium}}$ = 6%/12%/82%, $T_{\text{rxn}}$ = 503K, and the average space velocity = 0.69 g cat-h/mol MeOH. On a per gram catalyst basis,
our 23.3 wt% loaded MoO₅/ZrO₂ was 4 times more active than the 6 wt% conventional sample. The higher activity came from the higher MoOₓ content, as the activities of all materials on a per gram MoO₃ basis were similar.

Another important comparison comes from the product selectivity data. Five of the six samples tested were under differential conditions (conversion < 10%) except for the 23.3 wt% nano-MoO₅/ZrO₂ calcined at 973 K, whose conversion was 30%.

**Table 5.2** Catalytic results on the partial oxidation of methanol at 503 K and SV = 0.69 g cat-h/mol MeOH.

<table>
<thead>
<tr>
<th>Sample [wt %]</th>
<th>Surface Density [Mo/nm²]</th>
<th>Rate* [mol/g cat/h]</th>
<th>Rate* [mol/g MoO₃/h]</th>
<th>Methanol Conversion [%]</th>
<th>Product Selectivity HCHO DME DMM MF</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.6</td>
<td>6.2</td>
<td>0.02</td>
<td>0.17</td>
<td>1.2</td>
<td>76.9    4.4   17.7   1.0</td>
</tr>
<tr>
<td>14.2</td>
<td>6.9</td>
<td>0.12</td>
<td>0.84</td>
<td>7.7</td>
<td>71.8    9.7    14.5   4.0</td>
</tr>
<tr>
<td>16.9</td>
<td>7.2</td>
<td>0.10</td>
<td>0.61</td>
<td>7.8</td>
<td>67.8    14.8   15.0   2.4</td>
</tr>
<tr>
<td>23.3 (T=773K)</td>
<td>8.0</td>
<td>0.17</td>
<td>0.73</td>
<td>9.6</td>
<td>69.0    16.7   12.4   2.0</td>
</tr>
<tr>
<td>23.3 (T=973K)</td>
<td>18.9</td>
<td>1.78</td>
<td>7.74</td>
<td>30.0</td>
<td>56.0    37.6   2.0    2.8</td>
</tr>
<tr>
<td>Conventional</td>
<td>6.0</td>
<td>0.04</td>
<td>0.66</td>
<td>3.2</td>
<td>66.7    3.7    27.8  1.8</td>
</tr>
</tbody>
</table>

* \( \text{rate}_{\text{cat}} = \frac{F_{\text{MeOH}} \cdot X_{\text{MeOH}}}{g_{\text{cat}}} \) \( \times \text{rate}_{\text{MoO}_3} = \frac{100 \cdot \text{rate}_{\text{cat}}}{(\text{MoO}_3 \, \text{wt} \%) } \)
Therefore, product selectivities of the nano-MoO\textsubscript{x}/ZrO\textsubscript{2} and the 6 wt% conventional MoO\textsubscript{x}/ZrO\textsubscript{2} catalysts can be directly compared. As shown in Table 5.2, the selectivity to MF for all catalysts were comparable at \~2%. The major differences arise in the acidic (DME) and redox (HCHO, DMM) product selectivities. While the conventional material and 8.6 wt% sample were highly selective toward redox products (95% HCHO and DMM), DME selectivity increased as the MoO\textsubscript{x} content of nano-MoO\textsubscript{x}/ZrO\textsubscript{2} materials increased from 4.4% to 16.7%. The combined DMM and HCHO selectivities correspondingly decreased from 94.6% to 81.4%. These two combined observations suggested that as the MoO\textsubscript{x} loading was increased for the nano-MoO\textsubscript{x}/ZrO\textsubscript{2} materials, the surface acidity strength increased. This could be in part due to the nature of the ZrO\textsubscript{2} support influencing the surface MoO\textsubscript{x} layer as a “ligand effect”. At low loadings of MoO\textsubscript{x} in nano-MoO\textsubscript{x}/ZrO\textsubscript{2}, the ZrO\textsubscript{2} support was crystalline, (Figure 5.14) and as the loading increased, the support became more amorphous. Hino and Arata discovered that WO\textsubscript{3}-ZrO\textsubscript{2} became superacidic when x-ray amorphous form of ZrO\textsubscript{2} was used during synthesis of supported metal oxide catalysts\textsuperscript{57} which suggested the influence of the amorphous ZrO\textsubscript{2} NP based support.

Lastly, the 23.3 wt% nano-MoO\textsubscript{x}/ZrO\textsubscript{2} catalyst calcined to 973 K was also characterized using methanol oxidation. This material contained crystalline Zr(MoO\textsubscript{4})\textsubscript{2} species in addition to crystalline ZrO\textsubscript{2}. As shown in Table 5.2, this material was very active for methanol conversion. At similar reactor conditions to those of the other experiments, the conversion of methanol was 30% as compared to 8-10%. This corresponded to rates an order of magnitude greater
than the other nano-MoO$_x$/ZrO$_2$ materials, with high selectivity to acidic products (38%) at the expense of redox products (58% HCHO and DMM). Iglesia and coworkers reported that for the conversion of DME to HCHO, Zr(MoO$_4$)$_2$/ZrO$_2$ catalysts were more active than MoO$_x$/ZrO$_2$ catalysts; however, product distributions appeared to be more redox (75% HCHO and 15% MF) in composition.$^{26}$

5.4 Summary and conclusions

We developed a new synthesis route to MoO$_x$/ZrO$_2$ material with thermally stable amorphous MoO$_x$ content (up to 23 wt%). This “sol-gelation” method involves the charge destabilization of ZrO$_2$ NPs using AHM as an adsorbing salt to form a gel. This gel can be made porous by including a block copolymer surfactant (Pluronic P123) in the synthesis procedure without modifying the solution chemistry. Using colloid chemistry approaches, the mechanism of gel formation could be understood in terms of adsorbing AHM salts reducing the repulsive stabilizing potentials. Increased gelation temperature and increased AHM and NH$_4$NO$_3$ concentrations were shown to decrease gelation times and to induce the crystallization of the ZrO$_2$ support upon calcination to 773 K. Finally, 8.6 to 23.3 wt% amorphous MoO$_x$ were synthesized and tested for methanol oxidation activity. It was shown that the nano-MoO$_x$/ZrO$_2$ materials were more active on a per gram catalyst basis than conventionally impregnated 6 wt% MoO$_x$/ZrO$_2$ due to higher loadings of the thermally stable amorphous MoO$_x$. The
presence of amorphous ZrO$_2$ is believed to influence the product distribution by making the nano-MoO$_x$/ZrO$_2$ more acidic.

5.5 References


Chapter 6
Recommendations for future work

In this thesis, the use of nanoparticles as building blocks to obtain unique catalytic surface structures was investigated. Nanoparticles of gold were used to support and promote palladium domains for the hydrodechlorination of trichloroethene. A massive effort was undertaken to understand the synthesis and catalytic action through detailed characterization and testing; however, not all aspects of the material are fully understood. Currently, surface enhanced Raman spectroscopy (SERS) is being investigated as a probe for in situ Pd/Au reaction data due to the difficulties encountered with infrared spectroscopy (IR) in the presence of water. SERS would allow us to better understand what is occurring on our bimetallic NP surface. Information on adsorbed species and how the reaction mechanism proceeds will assist us in further modifying our design of our NP based catalytic materials.

A major limitation of our system is that we work with extremely small nanoparticles (4-nm in diameter) and many structural characterization techniques such as XRD are ineffective. However, EXAFS (extended x-ray absorption fine structure) spectroscopy is a technique that can provide local metal structure information for nanoparticles in solution. The information obtained includes nearest neighbor distance, number, and compositional data. This group is collaborating with Dr. Jeff Miller of BP, an expert in EXAFS with a beamline at Argonne National Labs. In addition, surface structure and compositional information can be obtained allowing us to probe the surface of our Pd/Au NPs
and help us identify the surface structure both \textit{ex situ} and \textit{in situ}. The major hurdle to overcome for this technique is to create a highly concentrated Pd/Au NP sols while maintaining the synthesis constraints of maintaining small Au NPs, ensuring that the same nanostructure is retained, and dealing with the build up of synthesis precursors in concentrated solutions.

Additional methods to obtain surface composition and structural information are to use chemical probes to interact with the surface and being able to the probe the surface to measure its effect. Typically, supported catalysts are tested using the chemisorption of gas molecules on their surfaces. This can be coupled with IR to obtain vibrational frequency data that is correlated to a molecular bond stretch. However, obtaining a highly loaded supported Pd/Au NP sample with enough metal to measure adsorption is a ways off. However, research conducted for this thesis included the study of sulfur poisoning on our Pd/Au NP and monometallic Pd NP catalysts. Similarly, by using chemicals that irreversibly bind to particular elements (\textit{i.e.}, Pd or Au), the TCE reaction could be used as a titration method for the number of active sites available for reaction.

Further application studies for TCE remidation need to be undertaken to test the viability of the supported Pd/Au NPs as a full-scale catalyst. This includes laboratory flow through reactor development testing longevity and deactivation studies coupled with catalyst regeneration tests. Once the material has been shown to be consistently active, to display a resistance to deactivation with typical groundwater impurities, and to regain original activity after regeneration, scale up studies for mass production should be investigated.
The advantages of our method of interacting palladium with gold coupled with its promotional effect could possibly extend to other desired reactions. The core-shell nanostructure of our Pd/Au materials could be eliminated through high temperature treatments forming Pd/Au alloys. Low temperature applications such as in hydrogenation reactions and more recently investigated alcohol oxidation reactions could benefit from our controlled nanostructure. From here, the extension to trimetallic materials allows us to not only further influence the catalytic activity, but to integrate additional non-catalytic demands on our system. Examples exists, such as utilizing an inexpensive metal as a NP core (iron) and more effectively utilizing our precious metals shells (gold and palladium) reducing costs. Integrating attributes unique to the third component, such as magnetism, could ultimately allow for unique reactor designs that can stagnantly suspend NPs in a flowing stream under the influence of a external magnetic field. This would allow for the direct implementation of catalytic colloidal sols into a reactor design without having to introduce a support for immobilization of the NPs, which could adversely affect the catalyst's activity and introduce mass transfer limitations. Also, a simple design like this allows for ease of unloading the catalytic nanoparticles just by turning off the external magnetic field and diverting the flow to a tank for collection, then reloading by introducing a new batch of particles upstream with the magnetic field re-energized. This work is being explored in the group.