RICE UNIVERSITY

Developing Gold-based Nanostructures to Study Catalytic Reactions in Water

by

Kimberly N. Heck

A THESIS SUBMITTED
IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE

Doctor of Philosophy

Approved, Thesis Committee:

[Signatures]

Michael S. Wong, Associate Professor
Chemical and Biomolecular Engineering, Chemistry

Clarence A. Miller, Louis Calder Professor
Chemical and Biomolecular Engineering

Pedro Alvarez, Department Chair, George R.
Brown Professor of Engineering, Civil and
Environmental Engineering

Naomi J. Halas, Stanley C. Moore Professor
Electrical and Computer Engineering, Chemistry,
Bioengineering

Houston, Texas

MAY 2009
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ABSTRACT

Developing Gold-based Nanostructures to Study Catalytic Reactions in Water

By

Kimberly Nadia Heck

Gold-based catalysts are effective for reactions that occur in water. They are not well understood though, with regard to the nature of active sites and surface reaction mechanisms. Water presents interesting challenges in performing catalytic studies, as it interferes with infrared spectroscopy commonly used to detect surface intermediates under reaction conditions. Insights leading to improved catalysts can be gained if gold-based nanostructures could be designed, engineered, and tested for a given chemical reaction. Two gold-based water-phase catalytic reactions were considered for this thesis: glycerol oxidation and hydrodechlorination of chlorinated ethenes.

Glycerol is a by-product of biofuel production, and is considered a possible non-petroleum feedstock for chemicals if efficient conversion processes exist. It can be oxidized using Au catalysts in alkaline solution, but the surface reaction mechanism is not known and the role of basic pH is not fully understood. Gold nanoshells (Au NSs) were used for the first time to study glycerol oxidation through surface-enhanced Raman spectroscopy (SERS). Raman bands for surface-adsorbed glyceric acid, the major reaction product, were detected. High oxygen content and high pH values led to carbon monoxide surface species, indicating carbon-carbon cleavage. When the glycerolate:O₂ ratio was constant, higher pH led to advance decomposition, due to the activation of O₂ by adsorbed hydroxide ions.

The catalytic HDC of chlorinated ethenes can potentially remove these contaminants from groundwater. This reaction occurs at room temperature and uses palladium-coated gold nanoparticles (Pd/Au NPs), which are more efficient than pure Pd. The Au NSs were coated
with Pd and used to study the surface intermediates of 1,1-dichloroethene HDC through SERS. Pathways were ascertained through careful Raman band assignments to probable chemical species and analysis of bulk reaction products, leading to the formulation of a reaction mechanism.

Gold enhances Pd catalysis for HDC, presumably through the generation of palladium-based active sites, though the true active site is unknown. The effects of chloride and sulfide on the activity of Pd/Au NPs for trichloroethene HDC were studied to provide information about active sites and deactivation properties. The activity of Pd/Au NPs was unaffected by NaCl, while that of the pure Pd catalysts decreased. Pd/Au NPs were resistant to sulfide poisoning compared to pure Pd catalysts. This increased resistance is attributed to the formation of small Pd islands on the Au NPs.
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Chapter 1

Introduction

1.1. Surface Spectroscopies

Characterization of the binding and/or reaction of reactants at catalyst surfaces in situ is of great importance to the understanding and improvement of heterogeneous catalytic reactions. Electron energy loss spectroscopy (EELS), for example, has been satisfactory in detecting molecules bound to model surfaces, but suffers from the need for expensive equipment and ultra-high vacuum environments, and hence cannot be used to replicate actual in situ behavior of catalytic reactions, which typically occur at or above atmospheric pressure and in the presence of solvent. Fourier-transform infrared spectroscopy (FTIR) (often coupled with the use of attenuated total reflectance (ATR) techniques) and normal Raman spectroscopy have also been used to characterize adsorption processes, but the technique is not surface selective and signal-to-noise ratios often suffer from solvent effects. Moreover, with the growing trend toward greener aqueous-based reactions, the technique is particularly challenged due to the strong adsorption of water O-H stretches. Additionally, contemporary techniques often require integration times much longer than actual reaction times. Clearly there is still a need for a surface selective, easy to implement method to provide time-dependent highly resolved spectra for analysis of catalytic reactions in situ, since this knowledge is not only interesting from a scientific perspective, but could also help lead to tailoring of catalysts to avoid certain byproducts, or even to on-line reactor sensors, which could be integrated into control systems to ensure selectivities to desired products.

The use of surface enhanced Raman spectroscopy (SERS) as a probe for adsorption and reaction of chemicals at catalytic surfaces has been attempted previously, with many groups attempting to overcome the inherent SERS limitation to
coinage metals, and extend to typical catalytic materials, such as Pd, Rh, Pt and Ir\textsuperscript{1,5}. Previous studies have focused primarily on the study of electrochemical reactions, where the substrates typically are roughened Au electrodes coated with 1-2 nm of catalytic metal or covered with platinum-group metal nanoparticles. More recently, structured substrates consisting of solely of the catalytic material have been introduced\textsuperscript{6,7}. Overall, the techniques have enjoyed only moderate success, offering typical enhancements of $10^4$-$10^6$. Perhaps due to this relatively weak enhancement, most of these studies focused on the mere adsorption of molecules to surfaces in aqueous and gas phases. The few studies of dynamic reactions show both poor temporal and spectral resolution, and were conducted in the gas phase.

A goal of this thesis is to combine a more enhanced SERS substrate to in-situ aqueous catalyzed reaction systems. Using Au nanoshells (NSs), for example, will enhance the Raman signal by up to $10^{12}$, allowing for greater spectral and temporal resolution, and may make the aqueous phase detection of molecular transformations on catalytic surfaces realizable. In one instance we studied Au NSs as a catalyst on its own, studying glycerol oxidation in alkaline solution. In the other, we studied Au NSs coated with a small amount of Pd to mimic a Pd-on-Au NP catalyst for aqueous phase hydrodechlorination (HDC) of dichloroethylene.

### 1.2. Gold-Catalyzed Glycerol Oxidation

Glycerol is a major byproduct of biodiesel production, and is formed from the base-catalyzed desaponification of triglycerides derived from waste fats. Because of the interest in the production of biodiesel production, the price has expected to fallen from $0.80 in 2007 to $0.38 by 2009. Moreover, according to the Department of Energy, a 2% replacement of diesel fuels by biodiesel from 2004-2012, 800 million lbs. of new glycerol would be produced\textsuperscript{8}. The current annual market for glycerol in 600 million
lbs./yr\textsuperscript{9}, thus green conversion into more valuable chemicals is desired. Fortunately, glycerol has been shown to be converted to finer chemicals, such as glyceric acid, a chemical intermediate predicted to be useful in the polymer industry\textsuperscript{8}. The relatively mild reaction conditions (in alkaline solution, relatively low O\textsubscript{2} pressure \(\leq10\) bar, with Au catalyst) and great selectivity to specific products (hence requiring less process steps for separation) make the reaction very environmentally attractive as well as economically feasible.

While the reaction shows promise to help solve the glycerol problem, the actual mechanism is poorly understood. While a number of studies have proposed reaction mechanisms, these are based on the detection of byproducts detected in trace amounts or not at all. In general, however, most studies agree that the first step in the oxidation reaction is the abstraction of a H atom from one of the glycerol alcohol groups by a hydroxyl anion, forming glycerolate\textsuperscript{10-13}. Indeed, studies which have varied the pH of their solutions have been able to correlate a first order rate constant to the concentration of glycerolate, rather than the concentration of glycerol (pK\textsubscript{a}=14.15)\textsuperscript{10-13}. However, some authors have speculated that that OH\textsuperscript{-} may have a larger role in the reaction by interacting with the Au catalyst surface, for example, by chemisorbing to the Au and supporting coadsorbed O\textsubscript{2} via hydrogen binding\textsuperscript{11}. This finding is not completely surprising, as there have been theoretical studies which suggest chemisorbed H\textsubscript{2}O could stabilize coadsorbed O\textsubscript{2} via this mechanism\textsuperscript{14}.

Understanding of the reaction is further complicated by the fact that Au supported on an inert support is active for the reaction, and that particles of up to 42 nm are also active\textsuperscript{10}. The nature of the active site on Au, once considered the noblest of all metals, is somewhat controversial. Traditionally, Au was thought to only be catalytically active if the Au particles were sufficiently small, loaded onto a metal oxide support, and/or
actually cationic Au\textsuperscript{15}. In light of recent studies, however, the first two points, at least, have proved unnecessary, though more desirable.

There have been no spectroscopic studies into the glycerol oxidation reaction. This is primarily due to the need for an aqueous environment, as gas-phase analogues to glycerolate and other ions in the system would be difficult to study in water-free systems (such as a UHV or FTIR chamber). Chapter 3 details our in-situ SERS investigations into this reaction system, which is currently being written as a manuscript.

1.3. Pd-on-Au (Pd/Au) Catalyzed Hydrodechlorination of Chlorinated Ethylenes in Groundwater

Chlorinated ethylenes (CE), such as tetrachloroethylene (PCE), dichloroethylene (DCE), and especially trichloroethylene (TCE) are ubiquitous contaminants of groundwater. All of these compounds and their isomers are suspected carcinogens, have been linked to liver damage, nervous system damage, lung damage, and, with extreme exposure, can cause death in humans\textsuperscript{16}. Commercially TCE is most often used as a metal degreaser, however, it is also used as a solvent for paints and varnishes. PCE is primarily used in drycleaning, is also a solvent for degreasing, and is a chemical intermediate in the production of fluorochemicals for refrigeration purposes. Finally, DCE is most often used as a solvent for extractions, and as a cleaning agent for circuit boards\textsuperscript{16}. TCE is the most prevalent contaminant of groundwater, occurring at 852 of 1,430 of the EPA’s National Priorities List sites, however, PCE and DCE are also quite common, being found at 771 and 616 of these sites respectively.

Research into catalytic methods for remediation of chlorinated compounds from groundwater dates back to 1992, when Kovenklogu et al. demonstrated the HDC trichloroethane in groundwater by Pd catalysts and hydrogen gas. In 1995 Reinhard and coworkers demonstrated that aqueous phase TCE and other chlorinated ethylenes
could similarly be reduced to ethane in the presence of hydrogen at room temperature over commercially available Pd on Al₂O₃ (Pd/Al₂O₃) and Pd on C (Pd/C) catalysts. The group then demonstrated the feasibility of a flow through reactor to be used in conjunction with a pump-and-treat system to remediate the contaminants.

Reinhard and coworkers studied the effect of the aqueous concentrations of H₂ and O₂, the presence of ions normally found in groundwater, and studied the catalyst’s performance with an expanded set of chlorinated compounds, including saturated chlorinated compounds which were found to be unreactive.

Because chlorinated intermediates such as DCE and VC were detected in trace amounts in the reactor effluent and in batch reactions, the group proposed a reaction pathway of TCE → DCE → VC → ethylene → ethane. Each of the dechlorination steps represent the addition of one H to a carbon and the elimination of HCl, and the final step (k₆) represents the addition of an H₂ atom to saturate the double bond. This pathway is in part confirmed by Wong and coworkers, who observed similar intermediates in the HDC of TCE over Pd/Au catalysts.

The pathway of a chemical reaction is important to understand, as it gives one an insight into what possible byproducts may be formed. In the context of environmental remediation, the desired products from the reaction are the nontoxic ethylene and ethane, while the partially dechlorinated byproducts are still toxic and should be avoided. By knowing the reaction steps one can attempt to minimize the formation of the unwanted byproducts by changing reaction conditions or modifying the catalyst.

In 2005, Nutt et al. prepared a series of Pd catalysts supported on 4 nm diameter Au NPs. Prepared by the successive reduction of Pd salt onto Au NPs, the catalysts ranged from 2.4 to 40 wt% Pd, corresponding to a calculated surface coverage of 10% of a monolayer to approximately 2.5 shells of atoms around the NP. The maximum rate of these catalysts was found to be 1900 L/min/g Pd, ~200x the rate of the commercially
available Pd/Al₂O₃. The Pd atoms on the Au NP are proposed to be the active site for the reaction, since Au alone is found to be inactive.

Supported metals often show different rates than unsupported metals due to promotional or inhibitory interactions with the supporting material, blocking of the active sites of the metal particles partially embedded in the support, and diffusional effects caused by the porosity of the material²³, ²⁴. To rule out these effects Nutt et al. ²² synthesized an analogous set of Pd NPs. While reactions run with these showed an enhancement over the Pd/Al₂O₃ catalyst used by Reinhard and coworkers¹⁷, ²¹, the rate constant, normalized to surface atom of Pd, still did not show the degree of enhancement shown by the Pd/Au NP catalyst. I co-authored a review article on this subject matter, which was published recently Journal of Chemical and Biochemical Technology.²⁵

We explored the reaction of DCE, as an analogue to TCE, at the Pd/Au surface, by detecting proposed intermediate products and identifying the reactant’s mode(s) of binding to the Pd/Au surface. By identifying the ways in which the reactants bind and transform on the catalytic active site, it can be tailored to improve activity and/or selectivity to desired reaction products. This work is the subject of Chapter 4, and its contents led to a publication in the Journal of the American Chemical Society.²⁶

1.4. Effect of Chloride and Sulfide on Pd/Au Catalysts

Towards the application of Pd/Au catalysts to real groundwater systems, the long-term durability of the Pd/Au NP catalysts needs to be addressed with regard to catalyst deactivation. Groundwater typically contains a multitude of substances which could impact Pd/Au NP catalytic performance ¹⁸, ²⁷, ²⁸. Perhaps the most pertinent to address are chloride (Cl⁻) and hydrosulfide (SH⁻, "sulfide" for short) ions, where the former can be found at concentrations ranging from 1.0-1000 mg/L and latter can be
produced naturally from native anaerobic bacteria. Both chemical species are known to adsorb onto Pd surfaces \(^\text{29-32}\) and to reduce Pd activity \(^\text{17, 20, 33-42}\). In this work, we studied the effects of sulfide and chloride ions on TCE HDC reaction rates of Pd/Au NPs, observing that chloride had no effect and sulfide had a markedly less effect compared to Pd NPs and PdAl\(_2\)O\(_3\). We performed catalytic titration experiments using sulfide as the poison to gain insights into the nature of the active sites for TCE HDC sites. Chapter 5 details my analysis of the effect of sulfide and chloride on the Pd/Au catalysts, and is the subject of a manuscript in preparation.

1.5. References


Chapter 2

Introduction to Raman and Surface-Enhanced Raman Spectroscopies (SERS) and SERS Substrates

2.1. Raman Spectroscopy

The theory of Raman spectroscopy was introduced in 1982\(^1\). Raman is complementary to IR spectroscopy, in that it can be used to identify vibrational modes of a given chemical species. The vibrational spectrum obtained from a sample compound through Raman is often a unique fingerprint of the compound, and hence can be used for its identification\(^2\).

Raman spectroscopy measures changes in the energy of monochromatic light scattered off of a chemical sample. In a typical experiment, a sample is irradiated with a monochromatic light source (such as a laser). When illuminated with the light, the sample scatters the light in three ways; with no change in energy (Rayleigh, or elastic scattering), with a decrease in energy (Stokes scattering, due to the absorption of energy in the form of photons), or with an increase in energy (anti-Stokes scattering, due to the emittance of energy as photons from the molecules in excited states). The process can be represented by a transition to and from a virtual state, as shown in Figure 2-1\(^2\).
Figure 2-1 – Adsorption of incident photons and transition to and from a virtual state for Stokes, Rayleigh, and Anti-Stokes scattering. \( E_0 \) is the ground state energy level, \( E_1 \) and \( E_2 \) are excited states, \( h\nu_i \) is the incident (laser) energy, \( h\nu_s \) is the energy of the scattered light.

The vast majority of radiation undergoes Rayleigh scattering. Stokes scattering is the second most likely mechanism for room temperature experiments, while relatively less of the radiation undergoes anti-Stokes scattering. Because of its relative prevalence over anti-Stokes scattering, the shifts in energy due to Stokes scattering is collected. This is commonly called the Raman shift (from the incident radiation), and is expressed in terms of the wavelength or wavenumber (cm\(^{-1}\)) of the scattered light. As can be seen from Figure 2-1, the magnitude of this shift is indicative of the energy required for the molecule to reach one of its excited states, and is given by

\[
\Delta \nu = h\nu_i - h\nu_s.
\]

Equation 2-1

The experiment involves monochromatic light focused through a microscope objective on the sample. The backscattered radiation is collected through a photomultiplier or CCD camera, and the wavelengths are separated through the use of a spectrophotometric grating. The signal from the separated wavelengths is then sent to a
computer to generate a Raman spectrum, which shows the intensity of the scattered light versus the Raman shift.

As previously mentioned, the signal gained from the Raman experiment is complementary to that obtained in infrared absorption spectroscopy, in that it originates from vibrational modes of molecules. The selection rules for allowed Raman transitions are found from changes in the polarizability tensor of the molecule, while allowed IR modes are found from the change in the dipole moment of the molecule. Because of this, one will not always see the same modes for each technique\(^2\). For example, H\(_2\)O is known to have a large broad band in IR spectroscopy due to the hydrogen-bonding effect on the O-H stretches. The band is often so strong that the analysis of aqueous samples via IR spectroscopy cannot be accomplished, as subtraction of the H\(_2\)O background only yields noise. In Raman however, the O-H stretch is a weak feature (as it does not significantly change the polarizability), and aqueous samples can easily be analyzed\(^3\).\(^4\).

### 2.2. Surface Enhanced Raman Spectroscopy

In 1974 Fleischmann and coworkers observed a great enhancement in Raman scattering when a sample was taken off a roughened silver electrode\(^4\). Thus began the interest in surface-enhanced spectroscopy. It was soon found that the greatest enhancement of the Raman signal occurred exclusively on noble metal electrodes, such as Cu, Ag, and Au\(^3\). Furthermore, only electrodes where the surface was roughened (e.g., by cycling the metal through subsequent oxidation and reduction cycles) showed an enhancement. The focus was also extended to the use of metal nanoparticles, which were deposited on substrates, used in solution, or partially aggregated in solution, all of which also were able to show enhancement of the Raman signal\(^3\).
During the early years of SERS, the mechanism of enhancement was completely unknown, and aspects of it still remain under debate today. It is generally agreed that the mechanism is due to a combination to two factors; enhancement of the local electromagnetic field around the nanoscale metal particle due to the excitation of surface plasmons (the electromagnetic effect), and enhancement of particular modes due to the chemical species’ interaction with the surface through processes such as charge transfer (the chemical effect)\(^3\).

2.2.1. Electromagnetic Effect

When noble metal nanoparticles imbedded in dielectric materials (such as water, air, or silica) are illuminated with visible light at a particle wavelength, their conduction electrons (also known as surface plasmons) undergo collective oscillations, which can be viewed as oscillating multipoles, such as dipoles or quadrapoles, depending on the incident wavelength. These collective oscillations create an electromagnetic (EM) field near the particle’s surface, the resonance at which these oscillations occur is termed the plasmon resonance.

The isolated metal sphere model is commonly used to describe the enhanced field at the surface of the particle\(^5\). In this model, electrostatics are used to describe the EM properties of a sphere of radius \(R\) (where \(2R<<\)incident wavelength) and complex, wavelength dependent dielectric constant \(\varepsilon_m = \varepsilon_{\text{real}} + i\varepsilon_{\text{imag}}\) in an electromagnetic field \(\mathbf{E}_0\). The external field created by the internal polarization of the particle scales with its volume, and is represented by the field of a point dipole \(\mathbf{p}\) at the center of the sphere where

\[
\mathbf{p} = 4\pi\varepsilon_0\varepsilon_\text{a}(\varepsilon_m - \varepsilon_\text{a})(\varepsilon_m + 2\varepsilon_\text{a})^{-1}R^3 \mathbf{E}_0
\]

Equation 2-2
where $\varepsilon_0$ is the permittivity of vacuum and $\varepsilon_s$ is the dielectric constant of the solvent medium. Near the surface of the particle (in the direction of $\mathbf{E}_0$) the local EM field ($\mathbf{E}_{\text{surf}}$) is at a maximum, and can be expressed by

$$\mathbf{E}_{\text{surf}} = 3\mathbf{E}_0 \varepsilon_m (\varepsilon_m + 2\varepsilon_s)^{-1}$$

Equation 2-3

Hence, when $\varepsilon_{\text{real}}$ approaches $-2\varepsilon_s$, the field at the surface reaches a maximum. This wavelength at which this occurs is known as the dipolar plasmon resonance wavelength, equivalent to the SPR band, and the absolute magnitude of the EM field will then be dependent on $\varepsilon_{\text{imag}}$. This expression for the EM field at the surface is valid as long as the particle is much smaller than the incident wavelength. As the diameter of the particle increases, however, destructive interference from retardation cause the surface enhancement to diminish and shift to longer wavelengths$^5$.

For a given wavelength ($\lambda$), $p$ also determines the sphere’s absorption ($\sigma_a$) and Rayleigh scattering ($\sigma_s$) cross sections, which are given by

$$\sigma_a = 8\pi^2 R^2 \varepsilon_s^{-0.5} \lambda^{-1} \left| \text{Im}\left[\frac{(\varepsilon_m-\varepsilon_s)}{(\varepsilon_m + 2\varepsilon_s)}\right]\right| = 2\pi \lambda^{-1} \varepsilon^{-1} \varepsilon_s^{-0.5} \left| \text{Im}(p/E_0) \right|$$

Equation 2-4

$$\sigma_s = (128/3)\pi^5 R^6 \varepsilon_s^2 \lambda^{-4} \left| \frac{(\varepsilon_m-\varepsilon_s)}{(\varepsilon_m + 2\varepsilon_s)} \right|^2 = (8/3)\pi^3 \lambda^{-1} \varepsilon_s^{-2} \left( p/E_0 \right)^2$$

Equation 2-5

Hence, for small particles absorption, proportional to the volume of the particle, is dominant. As the particle size increases, however, scattering becomes the dominant process$^5$. 

15
Because it relies on $\varepsilon_m$, $\varepsilon_s$, and R, it is easy to determine that the SPR of a metal sol depends on the type of metal, size, and surrounding dielectric environment\textsuperscript{8-8}. Additionally, however, the SPR is also dependent on the particle shape. By varying any of these parameters, the SPR of the band can be shifted, and the relative contributions to the absorption and scattering can be tuned to nearly any wavelength. This is significant, since one can tune the SPR of a particle to commonly available laser frequencies (i.e. 514 nm, 630 nm, or 780 nm), hence maximizing the local EM field of the particle. The EM field felt by a molecule ($E_m$) adsorbed or near the particle is then given by the sum of the incident field and the localized field\textsuperscript{7}

$$E_m = E_0 + E_{surf}$$

Equation 2-6

The total Raman response of the system at a given Stokes shifted frequency ($\omega$) is a function of the frequency, and distance from the center of the particle ($r$)\textsuperscript{7}.

$$E_{Raman}(r, \omega) = E_{dipole}(r, \omega) + E_{particle}(r, \omega)$$

Equation 2-7

where $E_{particle}$ and $E_{dipole}$ is the Raman response of the particle and the molecule's dipole respectively.

While this simple model can be used to describe the behavior of molecules near particles in solution, greater Raman enhancements have been observed on arrays of nanoparticles\textsuperscript{9-11} and aggregated nanoparticles\textsuperscript{3, 5, 11} than those theoretically predicted by EM calculations for single nanoparticles\textsuperscript{5, 12, 13}. This effect is due to the coupling of the EM fields between the particles, which creates a greatly increased local field at the
junction of the particles termed "hot spots." Thus, spectra from molecules located in these junctions will show an even greater enhancement than if located near a single particle alone\textsuperscript{3, 5}.

2.2.1.1. Tailored SERS Substrates

With the development of the theory of EM enhancement in SERS, there has been an effort over the last decade to improve on the traditional gratings and roughened electrodes commonly used for SERS, and engineer SERS substrates whose SPR is tuned to the incident laser wavelength, thus maximizing the local EM field. Many shapes have been considered for intensification of the Raman signal, including spheres\textsuperscript{3, 5, 10-12}, bowties\textsuperscript{14}, rings\textsuperscript{15}, and hollow spherical shell shapes\textsuperscript{16}.

Spherical gold nanoparticles are perhaps the most easily synthesized of the substrates, and hence have been studied in the greatest detail. Single gold nanoparticles have been predicted both theoretically\textsuperscript{12} and shown experimentally\textsuperscript{11} to offer enhancements of $\approx 10^5$. However, Liu \textit{et al.} showed that EM coupling of Au NPs placed less than 2x the particle diameter away from each other could offer enhancements of up to $10^4$\textsuperscript{11}. Additionally, for closely packed arrays of Au NPs SERS enhancements of up to $10^7$ have been observed\textsuperscript{10}.

To improve on the SERS enhancement, in 1998 Halas and coworkers developed the Au nanoshell (NS)\textsuperscript{16}. NSs consist of a dielectric silica core coated with a continuous shell of Au. The group has shown that the SPR of NSs can be predicted by "plasmon hybridization" that is, the NS resonance can be predicted by the hybridization of the SPRs of a Au NP the size of the complete shell and a cavity the size of the silica core\textsuperscript{6}. Because the scattering and absorption cross sections also depend on the size of the core and the shell, the relative contributions from each can also be tuned. This model has allowed the group to theoretically predict and subsequently synthesize NSs whose
SPR is tuned to particular wavelengths\textsuperscript{6-8}. While this model assumes perfectly smooth surfaces, the group has shown that greater enhancements are obtained with roughened NS surfaces, which, as long as the shell is continuous, create localized hot spots on the shell surface. Using roughened NS tuned to the incident wavelength (780 nm) the group has shown an enhancement in the SERS response of $\sim10^{10}$ for a single NS\textsuperscript{7}. This is in contrast to Au NPs, which must be closely packed to exhibit significant enhancement.

Even more exotic nanoshapes have been synthesized to maximize the EM response of the particle. Moerner and coworkers have studied the EM enhancement of gold triangles separated by a small gap, called bowties\textsuperscript{14}. The triangles are approximately equilateral and 100 nm in size. By changing the size of the gaps between the particles (and hence, the degree of EM coupling), the group was not only able to tune the SPR of the system, but also to find the configuration of maximum EM enhancement. This system exhibiting the maximum EM at the pump laser wavelength (830 nm) contains a 16 nm gap, and the maximum EM field enhancement is predicted to be at the two facing tips of the particles. Using p-mercaptoanilide as a probe molecule, an enhancement of $\sim10^7$ was achieved\textsuperscript{14}. Since only an enhancement of $10^4$ is predicted from theoretical work\textsuperscript{14}, it is believed that there may be a significant chemical effect due to planar (rather than) linear orientation of some molecules to the surface.

Another system recently developed for SERS is Au nanorings with inner diameter of 100 nm and wall thicknesses of approximately 10-20 nm. Aizpurua \textit{et al.} recently synthesized Au nanorings via colloidal electron beam lithography\textsuperscript{15}. The nanorings can be tuned to absorb in the visible light to near IR range, and tend to blue shift with increasing ring thickness.

Fabrication of the more exotic shapes, such as bow ties and rings, is generally complicated as they involve the use of electron lithography\textsuperscript{14,15}, which limits their use as they must be used on their assembled substrate. However, other shapes, such as
spheres and shells, can be easily synthesized using wet chemistry methods\textsuperscript{3, 5, 10, 11, 15}, and can more easily be used for Raman spectroscopy, either in solution, or when deposited on a substrate.

2.2.2. Chemical Effect

While, with a properly designed SERS substrate, the EM should give the major contribution to the Raman signal, there is sometimes an increase in the Raman signal due to interactions between the adsorbate and the metal, called the chemical effect. This effect originates from a specific interaction of a chemisorbed molecule with the metal surface, in which there is charge transfer either from the molecule to empty energy levels of the metal surface or from occupied surface levels of the metal to the molecule. In either case, the electron transfer can be viewed as an electron excitation of the chemisorbed molecule-surface atom, and will result in the appearance of a new electronic (vibrational) band\textsuperscript{3}.

In addition to the new bands, when the chemical effect is significant, one will often see fluctuations in the relative intensities of vibrational bands\textsuperscript{15}. This effect is thought to be due to the fact that only a small amount of molecules are undergoing this process, and the fluctuations in the bands are caused by changes in the molecules' orientation with the surface.

Currently, the exact magnitude of the contribution of the chemical effect to the SERS signal remains under debate. Researchers have claimed the magnitude of the enhancement due to charge transfer to be anywhere from $10^6$ to $10^{15}$\textsuperscript{3, 15} though it is recognized that these numbers are clearly molecule-surface atom specific.
2.2.3. SERS of Chemical Reactions

Because the strong SERS signal originates primarily from molecules adsorbed to or near the surface of the SERS material, this spectroscopy has been used to examine both electrochemical and catalytic reactions at the interface of SERS active materials, such as Au$^{17-19}$ and Ag$^{20}$ electrodes, or roughened Au electrodes thinly coated with Pd$^{21-23}$, Pt$^{18,21,22}$, or Rh$^{22,23}$.

While IR spectroscopy is the method used primarily to detect binding modes and molecular transitions at the surfaces, SERS offers many advantages besides the large enhancement. While much knowledge has been gained from IR by analyzing catalytic surfaces for gas phase reactions under ultra high vacuum conditions (UHV), signals from solvent molecules tend to mask the IR spectrum when the concentration of the solvent (i.e. reactor pressure) increases, and the data obtained from UHV studies must be artificially extrapolated to high pressure conditions. Methods like attenuated total reflectance (ATR) have been developed to minimize solvent effects in IR spectroscopy, with a particular emphasis on H$_2$O, which has broad strong peaks across the entire spectrum. ATR works by bouncing the IR beam along a crystal, and molecules within ~1 μm of the interface with the crystal are detected. While this method has been used to successfully image CO adsorbed from water onto a Pt surface$^{24}$, the influence of H$_2$O solvent molecules on the obtained spectra was not eliminated, and the CO peaks were somewhat small. In SERS, however, the analysis of aqueous samples is easily achieved, as the Raman modes of water are weakly active$^3$. Finally, collection times in SERS (as low as <1 s) are much faster than in IR spectroscopy, making the real time analysis of chemical transitions more realizable.

Notably, Weaver and others have carried out extensive SERS investigations of catalytic metals, focusing primarily on aqueous-phase electrocatalytic interfaces in which the substrates were roughened noble metal electrodes or nanoparticles coated with 1-2
nm of catalytic metal. Some of the reports detailed the adsorption characteristics of catalytically relevant molecules, such as ethylene, methanol, and carbon monoxide, as a function of electrode potential; evidence of possibly catalyzed molecular transformations was seen (for reviews, see references\textsuperscript{25, 26, 29}). More recently, structured substrates consisting solely of the catalytic material have been introduced.\textsuperscript{30, 31} These materials approaches offer enhancements of $10^4$-$10^6$, though spectral and temporal resolution remains limited. Engineered substrates have not been developed for studying or monitoring catalytic reactions.

2.3. References


Chapter 3

Understanding OH⁻ Promoted Glycerol Oxidation over Au

3.1. Introduction

First discovered by Hutchings's group in 2002¹, the selective oxidation of glycerol in alkaline solution by Au catalysts has been repeated by a variety of groups, who have proposed a variety of mechanisms. Hutchings and coworkers were the first to suggest that glycerol deprotonation to glycerolate (pKₐ = 14.15) (Figure 3-1) by hydroxyl anions in solution is a key factor in the oxidation reaction²⁻³. They suggest that glycerolate is subsequently oxidized to form glyceraldehyde or dihydroxyacetone, even though glyceraldehydes was only detected in trace amounts, and dihydroxyacetone was not detected at all. These intermediates are expected to further oxidize, and while the reaction was up to 100% selective to glyceric acid, the group also detected further oxidized species, such as tartronic acid. Another finding was the formation of oxalic acid, a two carbon species, evidence of carbon-carbon cleavage during the reaction.

\[
\text{HO-CH(OH)CH(OH)OH + HO}^- \rightarrow \text{HO-CH(OH)CO(OH)O}^- + \text{H}_2\text{O}
\]

Figure 3-1. pH dependent conversion of glycerol to glycerolate.

Demirel et al. also studied the reaction, and in general, agreed with the deprotonation and initial oxidation step, but initially suggested a complicated reaction network composed of nine possible products and intermediates, even though only four were detected⁴. In a subsequent study, the group produced a model of a much simpler
reaction network in which glycerolate is initially converted to glyceraldehyde or dihydroxyketone\textsuperscript{4}. It was recognized that these two intermediates could interconvert in solution via OH\textsuperscript{-} catalysis. The glyceraldehyde goes on to form glyceric acid, which can be further oxidized to tartronic acid, which can undergo C-C cleavage to either form glycolic or oxalic acid. Using Langmuir Hinshelwood kinetics, the group was able to successfully model their experimental data, and concluded the adsorption of glycerolate, glyceric acid and tartronic acid were the most relevant steps in the reaction. However, the model contradicts their earlier mechanism, and there in situ experimental data to support this conclusion.

Davis and coworkers also studied the reaction, and while agreeing with the need for the formation glycerolate in the reaction, once again proposed a new reaction pathway\textsuperscript{5, 6}. After being oxidized to the initial aldehyde or ketone, their mechanism suggests the existence of other pathways, including one which leads to the formation of lactic acid, which was detected in trace amounts. The group, however, performed an additional experiment, in which they performed a set of CO oxidation experiments in water over Au/C catalysts. Because there should not be an interaction between the CO and OH\textsuperscript{-}, and because the reaction rate decreased in neutral and acidic conditions, another role of the hydroxyl anions has been proposed, that by coadsorbing to the Au catalyst surface it serves to stabilize chemisorbed O\textsubscript{2} via hydrogen bonding\textsuperscript{6}. However, despite the formulation of these complicated mechanisms and proposed roles of OH\textsuperscript{-} anions, there has been limited work into actually understanding the interaction of the Au catalyst with the reactants. This is not particularly surprising, since the detection of molecules on catalytic surfaces is generally done via various spectroscopic methods, such as electron energy loss spectroscopy, and infrared spectroscopies (often coupled with attenuated total reflectance cells). The former requires ultra-high vacuum, and the latter cannot be implemented due to the strong interference of water in the regions of
interest, making an in-situ study unrealizable by these techniques. Moreover, because
the suspected reactant, glycerolate, is an ionized species, there are no suitable
molecular analogues which could be used in an inert gas or vacuum environment to
even perform an ex-situ study. Hence, by using pure Au nanoshells as a glycerol
oxidation catalyst, we suspect that similar results may be gained for this reaction
mechanism.

3.2. Experimental

3.2.1. Preparation/Immobilization of Au NSs

Au NSs were synthesized as described previously\textsuperscript{7}. Briefly, 1 mL of 120 nm
diameter silica colloid (Precision colloid P120) was added to 26 mM
aminopropyltrimethoxysilane in ethanol and aged overnight. The solution (500 \mu L) was
then added to 40 mL of a sol of 1-2 nm Au NPs, previously prepared via the Duff method
and aged for at least 2 weeks. The sample was aged overnight to allow the electrostatic
self-assembly of the negatively charged Au NPs to the positively charged amine groups
on the modified silica colloid. The sample was then centrifuged and redispersed in
deionized water three times to ensure the removal of excess Au NPs, leaving a final
volume of \textasciitilde1 mL. The sample (15 \mu L) was added to 3 mL of an aqueous solution of 370
\mu M HAuCl\textsubscript{4} and 18 mM K\textsubscript{2}CO\textsubscript{3} and was stirred. The gold salt was then reduced onto the
silica cores by adding 30 \mu L of 30 wt \% formaldehyde and shaking vigorously for 5 min.
The sample was then centrifuged and redispersed in deionized water to ensure the
removal of excess gold salt. The final volume of the solution was 3 mL.

To immobilize the NSs for SERS experiments, a silicon wafer was first prepared
by plasma-cleaning for 5 minutes to remove surface impurities. Afterwards, the wafer
was placed in a 5 wt\% solution of poly(diallyl dimethylammonium) chloride, and left for
11 minutes for self-assembly of the polymer to the silicon surface. Then, 20 \mu L of
concentrated solution of Au NSs was placed on the wafer, and allowed to self-assemble for 30 minutes. After thoroughly rinsing with deionized water, the wafer was adhered to an 18 mm round microscope coverslip NS side up for use in the SERS analysis chamber.

3.2.2. SERS of Glycerol

Similar to our study on the SERS of dichloroethylene, to remove any possible surface impurities, the sample was then plasma cleaned under vacuum (Harrick Plasma Cleaner/Sterilizer, PDC-32G) for ~1 minute before placing it in the sealed analysis chamber. The analysis chamber (Warner Instruments RC-43, volume of 213 µL without Au NS sample, complete with inlet and outlet ports) was then mounted inside the Raman spectrometer. To ensure there were no surface oxygen chemisorbed to the Au NSs, prior to any experiment, 10 mL deionized water saturated with H₂ was flowed over the sample which was left to sit for 10 minutes. Then, to ensure no chemisorbed H₂ was present, 10 mL of N₂ (inert) saturated deionized water was flowed over the sample, and spectra taken to determine surface cleanliness.

We analyzed the interaction of glycerol with the catalyst surface both in the presence and absence of O₂ and at different pHs. Because the surface SiOₓ layer of the silicon substrate dissolves at ~pH 12 (causing the detachment of the self-assembled NSs), we chose pH 11 as an upper limit for our analyses. Solvents used to pretreat the Au NSs were prepared by adding 180 mL of deionized water each to Boston Round screw top bottles (Alltech, 250 mL). The threads were wrapped with Teflon tape and sealed with a Teflon rubber septum. Three bottles (for catalyst rereduction, rinsing with inert, and reactive removal of chemisorbed reaction products) were bubbled with UHP H₂, N₂, and O₂ respectively, for 1 h. For the chemisorption and reaction experiments, similar bottles were filled with 179 mL deionized water and 1.8 mL of a solution of 1 M
NaOH for the pH 11 experiments, or 180 mL deionized water and 180 μL of 1 M NaOH for the pH 10 experiments. Because of the viscous nature of glycerol which makes accurate measurement and addition difficult, a stock solution was made using 50 g/L of glycerol in deionized water, and 480 μL of this solution was added to the bottles. Finally, the bottles were bubbled for 1 h with N₂ or with O₂:N₂ gas mixtures (100:0 and 20:80). The O₂ concentrations present in the aqueous phase were estimated to be 1.32 and 0.27 mM, respectively, using a Henry’s law constant of 756.7 atm/M.

To perform each experiment, 3 mL of one of the glycerol solutions was flowed over the NS substrate and spectra was acquired using a Renishaw inVia micro-Raman spectrometer with a 785 nm excitation laser and a 40X long working distance objective. Spectra were obtained over time using 0.05 mW laser power and 10 s integration times. Given that the self-assembly process involved randomly distributes the NSs across the substrate, in order to compare the spectra of one solution to another, several precautions were undertaken. First, the microscope spot was kept constant for both solutions. Second, between the two experiments, the substrate was cleaned in-situ by flowing 3 mL of the O₂ saturated deionized water to react off any species remaining at the end of the experiment, then 3 mL of N₂ saturated deionized water was used to replicate the initial conditions. To ensure there was no hysteresis effect, all experiments were repeated with the reversed order of solution injection (i.e. a pH 10 before 11 experiment was repeated as a pH 11 before 10 experiment).

3.2.3. Bulk Reaction Experiments

To further understand glycerol oxidation, bulk reactions were performed over Au/C catalysts in alkaline solution while keeping the presumed active species, glycerolate constant while changing pH. A 0.1% Au/C catalyst was prepared first by forming a solution of Au nanoparticles. Briefly, 1 mL of a gold salt solution (1 wt% = 25
mM; prepared by adding 1 g HAuCl₄·3H₂O (99.99%, Sigma-Aldrich) to 99 g deionized H₂O) was added to 79 mL of deionized H₂O. A second solution of 0.04 g tannic acid, 0.05 g trisodium citrate, and 0.0173 g of K₂CO₃ in 20 mL deionized water was also prepared. Both solutions were heated to 60 °C, and then the tannic acid solution was rapidly added to the gold salt solution under vigorous stirring. The solution immediately turned reddish brown, indicating the formation of Au nanoparticles (NPs). The temperature of the solution was increased until boiling, and allowed to boil for 25 minutes. Finally, the solution (calculated particle concentration of 2.9×10¹⁵ NP/L) was removed from the heat source and stored in a separate container.

The as prepared sol was then added to a suspension of 1 g of activated carbon in 20 mL H₂O which had been sonicated for 1.5 hours, and stirred for 2 hours before filtering. The catalyst was washed with 100 mL deionized water, at which point the wash water was clear. The wash solution was brown in color from the organic species formed in the reduction, but there was no trace of red indicating the activated carbon retained all of the Au NPs.

Glycerol oxidation experiments were performed in batch reactors prepared by adding either 18.5 mL H₂O, 500 μL of a 50 g/L glycerol stock solution and 25 μL 1 M NaOH or 14 mL H₂O 5 mL of the 50 g/L glycerol stock solution, and 2.5 μL 1 M NaOH and a stir bar to a 250-mL, Teflon-sealed glass bottle. The bottles were sealed with a cap outfitted with a rubber septum, and sparged with O₂ gas for 15 minutes to saturate the H₂O and fill the headspace. To start the reaction, 0.2 g of the prepared catalyst dispersed in 2 mL H₂O was injected into the reactor. 0.5 mL of the solution was withdrawn after 30 minutes and analyzed via high performance liquid chromatography.

Glycerol oxidation is a relatively slow reaction, especially at atmospheric pressure. Even though we chose conditions (atmospheric pressure, lower pH) which lower the reaction rate, to further minimize the effect of the formed carboxylate species
on the pH, sampling was done after 30 minutes. These samples yielded resolvable results on the HPLC, even though the conversion was negligible (~1%) in both cases. pHs of the two experiments were taken at the end of the reaction to ensure both were approximately at their starting conditions.

3.2.4. SERS of Carbon Monoxide

To further understand the role of hydroxyl in the oxidation reaction, we investigated the adsorption of CO to the surface as a function of pH. The pretreatment of the samples was similar to that given in section 3.2. Five different pH solutions were tested, at pH 11, 10, 9, 8 and 7. The solutions were prepared by adding 180 mL of deionized water to the aforementioned bottles, then the appropriate amount of 1 M NaOH or 0.1 M NaOH to each. The bottles were then sealed as before, and sparged with UHP CO gas in a fume hood. To perform the experiments, the solutions were added to the NS substrate as before, and 8 spectra (at a given spot) for each sample were recorded and averaged. Between the introduction of the CO saturated solutions, 3 mL of N₂ saturated deionized water (neutral pH) was used to clean the surface. Spectra were obtained to ensure the surface was once again clean. To make sure the effect was not due to changes in ionic strength, the results were repeated using samples treated with NaCl to ensure constant ionic strength (0.001 M) between the samples. Table 3-1 summarizes the amounts of NaOH, NaCl, and the ionic strength of each sample.
### Table 3-1. Experimental conditions of CO SERS experiment

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<th>NaCl (M)</th>
<th>Ionic strength</th>
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<tr>
<td>Constant Ionic Strength</td>
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### 3.3. Results and Discussion

#### 3.3.1. Addition of Glycerolate Under Inert Conditions

We first investigated the interaction of glycerolate with the Au NS surface, by preparing an aqueous solution at pH 11 (upper limit of our studies, since the surface oxide layer of the silicon substrate dissolves ~pH 12, thus releasing any self-assembled polymer or nanoshells) and containing 1.3 mM glycerol ($pK_a = 14.15$), then sparging with N$_2$ (inert) to remove any dissolved O$_2$. Using a similar protocol described elsewhere, we exposed the solution to immobilized Au NSs anchored inside of a sealed analysis chamber. As shown in Figure 3-2a, no changes occur in the spectra after injection of the solution. The results from a similar experiment where the pH was lowered to 10 also did not exhibit significant peaks (Figure 3-2b). Representative scans from each plot are shown in Figures 3-2c and 3-2d. Figure 3-2c exhibits two weak peaks, at ~1000 cm$^{-1}$ and 1550 cm$^{-1}$, which correspond to the Si-O stretch of the surface oxide layer and
residual carbonaceous residue not removed by plasma cleaning. Figure 3-2 d shows similar small peaks also ascribed to the carbonaceous residue. While it is possible that surface selection rules could render the molecule Raman inactive, we can definitively say that we see no evidence of glycerolate chemisorption to the Au surface.

![Graphs](image)

**Figure 3-2:** Time resolved SER spectra of (a) 1.3 mM glycerol, pH 11, N₂ sat. water, and (b) 1.3 mM glycerol, pH 10, N₂ sat. water (c) representative scan from plot (a), (d) representative scan from plot (b).

### 3.3.2 Addition of Glycerolate in the Presence of O₂

Figure 3-3a shows the effect of an otherwise identical solution containing only 26 μM dissolved O₂ resulted in the almost immediate appearance of strong spectral features, particularly at 1566 and 1189 cm⁻¹, and does not match the neat spectrum.
(Figure 3-3d) In an attempt to identify these features, we studied the SERS of several model compounds, looking for possible chemisorbed forms of glycerol derivatives. SERS analysis of glyceraldehyde (1.3 mM, pH 11, sparged with N₂) indicated no chemisorption of this possible first-step aldehyde intermediate. In addition, no peaks could be ascribed to dihydroxyketone, which could theoretically form in solution by the aqueous base-catalyzed interconversion of glyceraldehyde. An analysis of glyceric acid under identical conditions, however, led to similar spectral features, at 1590 and 1172 cm⁻¹ (Figure 3-3b, neat spectrum in Figure 3-3e). Because no modes were found which could be assigned to carbonyl groups (~1700 cm⁻¹), we assign the 1590 cm⁻¹ and 1172 cm⁻¹ to the asymmetric stretch (νₐₐ) and symmetric stretch (νₛ) of carboxylate groups at the surface, where the large spectral separation of the modes implies unidentate binding of the molecule to the surface. The presence of carboxylates rather than carboxylic acids is expected under the high pH conditions.
Figure 3-3- (a) SER spectrum of 1.3 mM glycerol, pH 11, in 2% O₂ sat. water, (b) SER spectrum of glyceric acid @ pH 11 in N₂ sat. water, (c) SER spectrum of 1.3 mM ethylene glycol, pH 11, in 2% O₂ sat. water, (d) neat glycerol, (e) neat glyceric acid and (f) neat ethylene glycol. * corresponds to νₐs(COO) for a, b, and c; νₐs(COOH) for e. † corresponds to ν(C-OH).

Because of our inability to isolate an aldehyde or ketone intermediate on the surface, we propose that the reaction proceeds without the glycerol/glycerolate or
intermediate aldehyde or ketone directly adsorbing to the Au surface. Instead, oxygen is the surface species through which chemisorption and reaction occurs. Our proposed mechanism is shown in Figure 3-4. First, a hydrogen on the deprotonated CO' group is abstracted by surface oxygen, resulting in the transfer of electrons on the O' to the C-O bond, forming a C=O group. The surface O₂ undergoes O-O cleavage to form OH'. In the second step, surface O or O₂ attacks the carbonyl moiety, eliminating a H⁺, and resulting in a surface bound carboxylate species.

![Chemical structures](image)

Figure 3-4- Proposed mechanism of surface oxidation. (a) The H atom of the carboxylate group is abstracted by chemisorbed O₂, forming glyceraldehyde and hydroxyl species. (b) Glyceraldehyde is attacked by chemisorbed O, eliminating a H ion, resulting in (c) a surface bound glyceric acid.

This mechanism appears to be a general one for the oxidation of alcohols. While mono-alcohol species would be ideal (e.g. methanol, ethanol, propanol, etc.), the pKₐs of these species range about ~16. As an analogous molecule to glycerol, ethylene glycol was chosen, due to its similar pKₐ to glycerol. A similar experiment was conducted at pH 11 using 26 μM O₂, and 1.3 mM ethylene glycol (OHCH₂CH₂OH, pKₐ = 14.2) in place of glycerol. Similar to the glycerol experiment, the result shown in Figure 3-3 c once again show no evidence of ketone or aldehyde species, but instead a large modes at ~1200 and ~1500 cm⁻¹ which can only reasonably be assigned to the presence of carboxylate species.
To further understand the reaction and mechanism, we looked at the effect of O$_2$ concentration on the spectra. As can be seen in Figures 3-5a and 3-5b, increasing the dissolved O$_2$ concentration from 260 µM to 1.3 mM led to the characteristic SERS peaks appearing at earlier times. These results suggested that the higher O$_2$ content causes more rapid formation of the surface carboxylate species. While there is some shifting in the spectra over time, because most of the possible products are structurally similar (containing carboxylate groups), the expected products cannot be easily differentiated from one another. No bands appeared in the ~1700 cm$^{-1}$ region, which would have indicated the presence of chemisorbed aldehydes or ketones at the catalyst surface.
Figure 3-5- Time resolved SER spectra of (a) 1.3 mM glycerol, 20% O₂ @ pH 11 and (b) 1.3 mM glycerol, 100% O₂ @ pH 11. (c) and (d), magnification of the high wavenumber regime of (a) and (b) respectively. As can be seen, the higher O₂ sample appears to carboxylize more rapidly, as shown by the appearance of sharp intense peaks earlier than the lower O₂ sample. Additional oxidation is apparent in the high O₂ sample, as shown by the formation of CO fragments in the high wavenumber regime. The low O₂ (c) sample shows little evidence of CO.

Closer inspection of the time-resolved spectra, particularly in the high wavenumber regions, revealed a new spectral feature. As shown in Figures 3-5c and d, the higher O₂ sample leads to the formation of a relatively strong peak ~2075 cm⁻¹. We ascribed this peak to the stretching of the C-O bond of chemisorbed CO¹¹ on the gold surface, which is supported by running the experiment with CO dissolved in water at pH 11 under N₂. Carbon-carbon cleavage in the glycerol oxidation reaction has been
reported by everyone who has studied this reaction, and one and two carbon intermediates including glycolic acid, oxalic acid, formaldehyde, and CO₂ have been detected.⁶,¹²-¹⁴. CO₂ likely came from the oxidation of CO, a reaction well-known to be gold catalyzed [ref]. These results suggest that high O₂/glycerol ratios favor C-C cleavage and further oxidation.

3.3.3. Effect of pH

Hutchings and co-workers reported a strong pH effect in glycerol oxidation, in which low pH’s did not catalyze reaction etc.. This pH effect motivated us to study two different pH’s on the reaction spectroscopically. Figure 3-6 shows the high wavenumber region of a glycerol sample containing 260 µM dissolved O₂ at pH 10. At this lower pH, a SERS peak at ~2100 cm⁻¹ was observed and assigned to atop-bound CO, which was not observed at the higher pH of 11. The presence of chemisorbed CO indicated C-C cleavage and further oxidation, even though the O₂/glycerol ratio of 0.2 did not change. The lower pH presumably reduced the glycerolate concentration by 10-fold, suggesting that a higher O₂/glycerolate ratio, not a higher O₂/glycerol ratio, correlated to increased oxidation.
Figure 3-6- (a) Time resolved SER spectra of 1.3 mM glycerol, 20% O₂ @ pH 10, (b) high wavenumber region. The high wavenumber region shows evidence of CO formation, as compared to the higher pH sample (Figure 3-5c).

To determine if the only role OH⁻ serves is to deprotonate glycerol to glycerolate, we decided to run another experiment, in which we kept the glycerolate (and O₂/glycerolate ratio) constant while changing pH. Figures 3-7 a and b shows the results of a sample containing 1.3 mM dissolved O₂, 1.3 mM glycerol at pH 10 and a sample containing 1.3 mM dissolved O₂ and 0.13 mM glycerol at pH 11, both calculated to have a glycerolate concentration of 90 nM. The spectra differed dramatically, both temporally and in intensity. At higher pH, glycerol appeared to react much faster than at lower pH, as shown by the almost immediate appearance of the strong peaks characteristic of carboxylate species at ~1550 cm⁻¹. Additionally, the ~2100 cm⁻¹ peak of absorbed CO was much more intense at the higher pH, indicating a higher degree of oxidation even though the glycerolate/O₂ ratio was the same at the lower pH. The higher OH⁻
concentration appeared to have some additional effect on glycerol oxidation, besides glycerol deprotonation.

Figure 3-7- Time resolved SER spectra of (a) 1.3 mM glycerol, 100% O₂ @ pH 10 and (b) 0.13 mM glycerol, 100% O₂ @ pH 11.

3.3.4. Bulk Reaction Analysis

To support the data gathered in section 3.2.3, bulk experiments were performed, keeping the glycerolate/O₂ ratio constant. Figure 3-8 shows the results of these experiments. While conversion was negligible (~1% in both cases), selectivity clearly differs between the samples. Notably, the higher pH sample is more than 7x more selective to oxalic acid (a two carbon product), and approximately half as selective to glyceric acid (a three carbon product) than the pH 10 sample. The implications of these results also imply that there is an additional role OH⁻ plays in the reaction, as the pH 11 sample showed evidence of advanced oxidation, suggesting that O₂ is more activated.
3.3.5. CO Chemisorption to Probe Au Charge

To resolve this phenomenon, we revisited the spectra taken in Figure 3-7. Indeed, closer inspection of the spectra revealed subtle differences. The ~2100 cm\(^{-1}\) peak in the pH 10 sample was slightly blueshifted from that in the pH 11 sample, from 2077 to 2075. Inspired by the work of Mihaylov et al.\(^{11}\), who recently found that the v(CO) frequency redshifts as the Au surface becomes more negatively charged, a more systematic analysis of the effect of pH on the Au was conducted by preparing samples at pH 7-11 and saturating them with CO gas. The results are shown in Figure 3-9. The frequency red-shifted by 16 cm\(^{-1}\) as the pH was increased from 7 to 11. Indeed, a plot of the peak wavenumber versus OH\(^{-}\) concentration initially decreased rapidly before tapering off, suggesting that there is a saturation of OH\(^{-}\) on the surface at some point. According to Mihaylov these findings suggest that the Au surface becomes more negative when exposed to higher pHs, which may arise from the donation of electrons from the OH\(^{-}\) to the Au surface.
Figure 3-9 (a) SER spectra of chemisorbed CO at (i) pH 7, (ii) pH 8, (iii) pH 9, (iv) pH 10, and (v) pH 11 (offset for clarity). (b) CO peak location as a function of [OH\(^-\)] (log scale). The CO peak shifts redshifts by 16 cm\(^{-1}\) from pH 7 to pH 11, implying the Au surface is becoming more negative with increased OH\(^-\).

This finding is supported by the results of Kita and coworkers \(^{15}\), who found that the infrared absorption spectrum of CO on Au electrodes also shifted from 2048 cm\(^{-1}\) in 1 M H\(_2\)SO\(_4\) to 1981 cm\(^{-1}\) in 0.2 M NaOH indicating the CO bond was becoming weaker. Although they did not rule out other possibilities, they concluded that the origin of the behavior was due to the Stark effect, the phenomenon that describes the shifting of spectral modes when exposed to electric fields, or this case, the electric double layer (DL) at the Au electrode surface. While Kita and coworkers could change the DL thickness by changing the charge of the electrode surface, we can similarly modify the DL surrounding the Au NSs by changing ionic strength of our solutions.

To confirm our hypothesis on the donation of electrons to the surface, we repeated the CO experiments using solutions containing both NaOH and NaCl to maintain a constant ionic strength of 0.001 M. Thus, the samples should have the same DL thickness (equal to the inverse of the Debye-Hückel parameter = 9.62 nm). Indeed,
our hypothesis is validated as the results of these experiments (Figure 3-10) are nearly identical to that shown in Figure 3-9. The red-shifting of the C-O stretching mode with increasing pH at constant ionic strength clearly indicates the weakening of the C-O bond, possibly due to the increased interaction of oxygen to the Au surface. This suggests that electron density could be donated to chemisorbed $O_2$ during glycerol oxidation, thereby weakening the O-O bond, and increasing glycerol oxidation.

![Graph](image)

Figure 3-10- (a) SER spectra of chemisorbed CO at (i) pH 7, (ii) pH 8, (iii) pH 9, (iv) pH 10, and (v) pH 11, all ionic strength of 0.001 M (offset for clarity). (b) CO peak location as a function of $[OH^-]$ (log scale). The CO peak shifts redshifts by 16 cm$^{-1}$ from pH 7 to pH 11, implying the Au surface is becoming more negative with increased OH$^-$.  

This possible charging effect may be part of the origin of the catalytic activity of Au in alkaline solution, which is a significant finding from our results. For years, the active species of Au has been under debate. There has been considerable debate into the nature of the active sites of Au catalysts for oxidation catalysis, with many citing that the metal size be sufficiently small ($<4$ nm), Au must interact with a metal-oxide support, and/or that cationic Au is the true active species$^{16}$. The first two reasons, however, have
not proved universal, as it is found that particle sizes of up to 42 nm are catalytically active in the context of aqueous phase glycerol and CO oxidation\textsuperscript{12}, and Au nanotubes with length scales on the order of nanometers have been found active for gas phase CO oxidation\textsuperscript{17}. In fact, Haruta suggested in a recent commentary that Au particle size may not be critical to activity in general, but rather the interaction of Au with metal-hydroxyl species or H\textsubscript{2}O\textsuperscript{18}. While the former reactions were performed on a carbon support (presumed to be inactive) and the latter were wholly unsupported, it should be noted that both of the reaction systems did have some interaction with hydroxyl. The Au/C experiments were clearly in contact with liquid water with a clear presence of hydroxyl anions, which could bind to the Au surfaces, hence promoting the reaction\textsuperscript{12}. For the nanotube experiments, it should be noted that the addition of water vapor for the gas phase experiments or the addition of hydroxyl for the aqueous phase experiments amplified the reaction rate by 70 times\textsuperscript{17}. The presence of water or hydroxyl could be the key to promoting the reaction. It has been theorized that the presence of hydroxyl groups (from water or a metal-hydroxyl support) helps to stabilize chemisorbed O\textsubscript{2} in these oxidation reactions, hence accelerating the reaction\textsuperscript{19}. In contrast, the findings from the CO experiments suggest that the electronic effect of OH\textsuperscript{-} on Au may also have a role in activating adsorbed O\textsubscript{2}.

3.4. Summary and Conclusions

This study explores in-situ the oxidation of glycerol on Au NS catalysts. There is no evidence that glycerol or glycerolate chemisorbs onto Au in inert conditions. However, upon the addition of O\textsubscript{2}, strong peaks assigned to carboxylate species appear in the spectra. The absence of any peaks corresponding to ketones or aldehydes suggests a mechanism in which the glycerolate molecule is oxidized to a ketone or aldehyde without binding to the surface, and then subsequently transformed into the
observed surface bound carboxylate. Additionally, we show that by increasing the $O_2$/glycerolate ratio increases the amount of C-C bond cleavage, as evidenced by the observed peaks ascribed to CO. However, the hydroxyl anion appears to have more of a role in the reaction than simply deprotonating glycerol; when the $O_2$/glycerolate ratio is constant, there appears to be a higher degree of oxidation with increasing pH. The consequence of these findings is significant for gold catalysis as a whole. While we cannot confirm or deny the importance of chemisorbed OH$^-$ stabilizing $O_2$, the electronic effect suggests a new promotional mechanism by the OH$^-$. In our mechanism, OH$^-$ adsorbs to the Au surface, donating electron density to the Au. As a consequence, this excess electron density is back donated to coadsorbed $O_2$, which serves to weaken the O-O bond. This bond weakening increases the reactivity of the $O_2$, which increases the oxidative behavior we observed in the higher vs. lower pH experiments.

3.5. References


Chapter 4

Exploring the Surface Reaction of 1,1-Dichloroethene over Pd/Au Nanoshell Catalysts

4.1. Introduction

Reinhard and coworkers demonstrated that aqueous phase TCE and other chlorinated compounds could be reduced to ethane in the presence of hydrogen at room temperature over commercially available Pd on Al₂O₃ (Pd/Al₂O₃) and Pd on C (Pd/C) catalysts. The group then demonstrated the feasibility of a flow through reactor to be used in conjunction with a pump-and-treat system to remediate the contaminants. Because chlorinated intermediates such as DCE and VC were detected in trace amounts in the reactor effluent and in batch reactions, the group proposed a reaction pathway of TCE → DCE → VC → ethylene → ethane.

Each of the dechlorination steps represent the addition of one H to a carbon and the elimination of HCl, and the final step represents the addition of an H₂ atom to saturate the double bond. This pathway is in part confirmed by Wong and coworkers, who observed similar intermediates in the HDC of TCE over Pd/Au catalysts.

The pathway of a chemical reaction is important to understand, as it gives one an insight into what possible byproducts may be formed. In the context of environmental remediation, the desired products from the reaction are the nontoxic ethylene and ethane, while the partially dechlorinated byproducts are still toxic and should be avoided. By knowing the reaction steps one can attempt to minimize the formation of the unwanted byproducts by changing reaction conditions or modifying the catalyst.

In 2005, Nutt et al. prepared a series of Pd catalysts supported on 4 nm diameter Au NPs. Prepared by the successive reduction of Pd salt onto Au NPs, the catalysts ranged from 2.4 to 40 wt% Pd, corresponding to a calculated surface coverage of 10%
of a monolayer to approximately 2.5 shells of atoms around the NP. The maximum rate of these catalysts was found to be 1900 L/min/g Pd, ~200x the rate of the commercially available Pd/Al₂O₃. The Pd atoms on the Au NP are proposed to be the active site for the reaction, since Au alone is found to be inactive.

Supported metals often show different rates than unsupported metals due to promotional or inhibitory interactions with the supporting material, blocking of the active sites of the metal particles partially embedded in the support, and diffusional effects caused by the porosity of the material⁴–⁵. To rule out these effects Nutt et al. ³ synthesized an analogous set of Pd NPs. While reactions run with these showed an enhancement over the Pd/Al₂O₃ catalyst used by Reinhard and coworkers¹–⁶, the rate constant, normalized to surface atom of Pd, still did not show the degree of enhancement shown by the Pd/Au NP catalyst.

We seek to explore the reaction of DCE, as an analogue to TCE, at the Pd/Au surface, by detecting proposed intermediate products and identifying the reactant’s mode(s) of binding to the Pd/Au surface, as described in Chapter 3. By identifying the ways in which the reactants bind and transform on the catalytic active site, it can be tailored to improve activity and/or selectivity to desired reaction products. Additionally, the facile identification of DCE at the surface may be able to help the detection of such pollutants in the field. Through the use of SERS, it may be easier to identify potential environmental threats in groundwater.

4.2. Experimental

4.2.1. Preparation of Pd/Au NS

The multi-step preparation is detailed as follows (Figure 4-1a). Au nanoshells (NSs) were prepared as described previously⁷. Briefly, 1 mL of 120-nm diameter silica colloid (Precision colloid P120) was added to 26 mM aminopropyltrimethoxysilane in
ethanol, and aged overnight. The solution (500 μL) was then added to 40 mL of a sol of 1-2 nm Au NPs, previously prepared via the Duff method⁹ and aged for at least 2 weeks. The sample was aged overnight to allow the electrostatic self-assembly of the negatively charged Au NPs to the positively charged amine groups on the modified silica colloid. The sample was then centrifuged and redispersed in deionized water three times to ensure the removal of excess Au NPs, leaving a final volume of ~1 mL. The sample (15 μL) was added to 3 mL an aqueous solution of 370 μM HAuCl₄ and 18 mM K₂CO₃ and stirred. The gold salt was then reduced onto the silica cores by adding 30 μL of 30 wt% formaldehyde and shaking vigorously for 5 minutes. The sample was then centrifuged and redispersed in deionized water to ensure the removal of excess gold salt. Final volume of the solution was 3 mL.

Figure 4-1: (a) Synthesis schematic for catalytic Pd/Au NSs; (b) and preparation schematic for NS SERS substrate; (c) SEM of 0.1 ML Pd/Au NSs (scale bar: 500 nm), (d) EDS of 0.1 ML Pd/Au NS.

The UV-visible spectrum of the Au NSs was fit using Mie scattering theory to determine the size and concentration of particles. Quantitative agreement between
experimental and theoretical NS spectra was obtained for 60-nm radius SiO₂ core and 22-nm Au shell thickness (Figure 4-2a and b), with the overall radius of 82 nm confirmed by analyzing 200 particles with SEM (Figure 4-2c). The concentration of NSs was determined to be $1.18 \times 10^9$ particles/mL.

![Image](image.png)

Figure 4-2- (a) UV-vis spectra of Au NS and Pd/Au NSs; (b) Mie scattering calculations for Au NS and Pd/Au NSs; (c) SEM of Au NSs

Au NSs coated with a sub-monolayer of Pd metal (Pd/Au NSs) were synthesized analogously to the previously reported synthesis of Pd/Au NPs. H₂PdCl₄ (7.2, 21.6, 57.6, 72, or 216 μL of 2.4 mM solution) was added to 18 mL of the as-synthesized Au NSs and stirred. The Pd salt was reduced by bubbling the solution with UHP H₂ gas for 5 minutes.

Scanning electron microscope (SEM) images and electron dispersive x-ray (EDX) spectra of the Pd/Au NSs were obtained using a FEI Quanta 400. For particle size analysis, 30 μL of either Au NSs or Pd/Au NSs was drop-dried onto an SEM stub. For EDX analysis, the Pd/Au NSs prepared with 7.2 μL H₂PdCl₄ solution were repeatedly drop-dried onto a stub until a visibly thick layer was formed. The spectrum was obtained using an EDX detector attached to the SEM.
In order to characterize any changes in plasmonic behavior upon the addition of Pd, UV-vis absorbance spectra of the NSs were collected on a Shimadzu UV-2401 PC spectrophotometer using a polystyrene cuvette with a 1-cm path length.

4.2.2. Preparation of samples for SERS analysis

To immobilize the NSs, 5-mm×5-mm×0.5-mm polished Si wafers were cleaned in 3:7 solution of 30 wt% H₂O₂ and 30 wt% H₂SO₄ for 1 h. The wafers were then rinsed in deionized water and dried, before adding to a solution of 0.1 wt% poly(vinylpyridine) (MW ~40,000) in ethanol. After aging overnight, the wafers were rinsed in ethanol and dried. 50 µL of a concentrated solution of the NSs (volume reduced from 18 mL to 128 µL by centrifugation and removal of supernatant) was then pipetted onto a wafer and allowed to assemble overnight, schematically shown in Figure 1b. After rinsing with deionized water to remove unattached NSs, the wafer was adhered to the center of an 18 mm round microscope coverslip using slide adhesive. Samples used in the reaction and chemisorption experiments were then plasma-cleaned under vacuum (Harrick Plasma Cleaner/Sterilizer, PDC-32G) to remove surface impurities for 2 min just prior to Raman analysis.

4.2.3. Characterization of SERS effectiveness

To determine the SERS effectiveness of Pd/Au NSs relative to the Au NSs, 10 µL of 440 µM para-mercaptoaniline (pMA) in ethanol was added to samples prepared as in the previous section. pMA is a highly Raman active species, and has been used in a number of experiments to determine SERS efficiency. The samples were aged overnight to ensure the formation of a complete monolayer on the nanoshell surfaces in parafilm-sealed Petri dishes, and then rinsed with ethanol prior to analysis.
SERS spectra were obtained using a Renishaw inVia micro-Raman spectrometer with a 785-nm excitation laser and a 40× working distance objective. Spectra were obtained using 0.05 mW power and 10 second integration times. For each sample, eight spectra were acquired at different spots and averaged. Standard deviation between spectra for each sample was less than 5%.

4.2.4. SERS monitoring of adsorption & reaction of 1,1-DCE

To perform the adsorption and reaction experiments, the plasma-cleaned sample was mounted in a sealed analysis chamber with inlet and outlet ports (Warner Instruments RC-43, 213 μL volume without Pd/Au NS sample), and mounted inside the Raman spectrometer. Prior to the acquisition of spectra from the substrate, the reduction of Pd was ensured by flowing 10 mL of H₂ saturated deionized H₂O and allowing to sit for 10 minutes.

We chose to study 1,1-DCE (1,1-dichloroethene), a less chlorinated form of TCE that lends itself to simpler spectral interpretations and that is hypothesized to be a reaction intermediate for TCE HDC. Solvents used to perform the chemisorption and reaction experiments were prepared by adding 180 mL of deionized water each to Boston Round screw top bottles (Alltech, 250 mL). The threads were wrapped with Teflon tape and sealed with a teflon-rubber septum. Two bottles (one used for catalyst re-reduction and the other, for rinsing) were bubbled with UHP H₂ and N₂, respectively, for 1 hr. Additional bottles were bubbled for 1 hr with N₂ or with H₂:N₂ gas mixtures (volume ratios of 20:80 and 100:0) for use in the chemisorption and/or reaction experiments. The H₂ concentrations present in the aqueous phase were estimated to be 16.3 and 81.9 mM, respectively, using a Henry’s law constant of 1228 atm/M. After the bubbling step, 1 or 5 μL of 1,1-DCE was added, such that the H₂:1,1-DCE molar ratio was the same; the amount of 1,1-DCE dissolved in the liquid phase was estimated to be
50.9 or 254.5 μM, respectively, using a Henry’s law constant of 26.1 atm/M and a
density of 1.21 g/L. The liquid-phase H₂ amount was set approximately 6% in excess to
what is needed for complete conversion of 1,1-DCE to ethane (CH₂=CCl₂ + 3H₂ →
CH₃CH₃ + 2 HCl). The bottles were placed on a rocking platform to allow dissolution and
equilibration of 1,1-DCE between the gas and liquid phases.

Spectra ranging from 100-1700 cm⁻¹ Raman shifts were obtained using 0.76 mW
of laser power and 10 second integration times, a total acquisition time of one minute per
spectrum. Ten spectra were obtained at a single spot prior to the changing of solvents
to establish a baseline and ensure the cleanliness of the substrate.

For the chemisorption experiments, the analysis chamber was first flushed with
N₂-saturated H₂O to remove excess H₂ from the cell, and to remove possible
chemisorbed H₂. The chamber was then flushed with 3 mL of the N₂-saturated 1,1-DCE
solution (50.9 or 254.5 μM) and spectra were collected over time. Similar experiments
were performed using Au NSs (without Pd metal).

Experiments involving a chemisorption-reaction sequence were performed
similarly. After flushing with N₂-saturated H₂O, 3 mL of the 254.5 μM sample was added.
Spectra were obtained repeatedly for 30 minutes, after which 1 mL of either 0:100,
25:75, or 30:70 H₂:N₂ was quickly flushed through the cell, and spectra were taken
continuously until no other changes occurred.

For the reaction experiments, 3 mL of low-concentration (1,1-DCE, 50.9 μM; H₂,
16.3 mM) or high-concentration (1,1-DCE, 254.5 μM; H₂, 81.9 mM) solutions were
added, and spectra were collected over time until no noticeable changes in the spectra
were observed.

Baseline corrections in the spectra were performed by normalizing to the silicon
520 cm⁻¹ mode, to account for any minor drifts in focus over the experimental time frame.
The baseline was corrected by subtracting an average of the initial ten spectra taken to
determine surface cleanliness.

4.2.5. Analysis of bulk reaction products

To analyze the products using the SERS analysis chamber, the same protocol
was used as in the SERS reaction experiments, except that aliquots of fluid were
removed (~200 μL) at 0, 12, 30, 41, or 100 minutes with a 1-mL needled syringe and
injected into a 2-mL septum-capped vial. After allowing the gas and liquid phases of the
sample to equilibrate for 30 min, 250 μl of headspace gas was 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, ethane, and butane. The zero time point
samples were verified to match the initial 1,1-DCE concentrations of 50.9 and 254.5 μM
for the low and high concentration experiments, respectively.

Upon analysis of the products, it became apparent that, at later time points, the
carbon balance did not always close, possibly due to evaporation from the gas-tight
syringe before injection into the GC. To correct for this, we assumed evaporation of all
components was equal and re-scaled the measured concentrations with the same
correction factor, such that the total carbon balance was met for all time points.

The superficial first-order rate constant was determined by linear fitting of
ln(C/C₀) versus time profiles, where C is 1,1-DCE concentration and C₀ is the initial 1,1-
DCE concentration. Selectivities were calculated by dividing the concentration of each
product by the amount of 1,1-DCE reacted.
4.3. Results and Discussion

4.3.1. Characterization of SERS Efficiency

The average Pd/Au NS diameter was found to be 164 nm, according to SEM analysis (Fig. 4-1c), indicating no detectible size increase after the addition of Pd metal. Electron dispersive x-ray (EDX) spectroscopy of the lowest loaded sample (7.2 µL H₂PdCl₄ solution) confirmed the presence of Pd (Fig. 3-1d). We estimated that the different Au NS surfaces had coverages of 0.1, 0.3, 0.8, 1 and 3 monolayers of Pd atoms, from the addition of 7.2, 21.6, 57.6, 72, or 216 µL of 2.4 mM H₂PdCl₄ solution, respectively.

The plasmon resonance spectrum of the Au NSs decreased in intensity and red-shifts with the addition of the Pd metal, similar to what had been observed with Pd-coated Au NPs. The relatively large imaginary part of the Pd dielectric constant in the visible light regime damps the plasmon resonance, as seen in the Mie theoretical modeling of Au nanoshells with 100% Pd coverage (Fig. 4-2b).

The intensity of the SERS spectrum obtained from pMA-functionalized Au and Pd/Au NSs decreased with the presence of Pd on the NS surface due to damping of the Au NS plasmon resonance (Fig. 4-3). An interesting feature of this SERS spectrum is the shift in the intense, low-frequency peak near 390 cm⁻¹. This vibrational mode was assigned to coupling between the metal-sulfur bond stretch and a pMA ring deformation. This peak shifted to 406 cm⁻¹ with the addition of only 0.1 ML Pd, indicating an increase in the surface-pMA bond strength and the possible binding of pMA to Pd surface atoms. The trend continues with added Pd, reaching a maximum shift to 421 cm⁻¹ for the highest Pd loaded sample (3 ML), indicating a larger interaction with Pd for the higher loaded samples.
4.3.2. Adsorption of 1,1-DCE

As shown in Figures 4-2a and 4-3, the plasmon resonance and hence the SERS intensity is significantly damped for large coverages of Pd. For this reason, we chose to perform our DCE experiments on the sample with the lowest loading of Pd, 0.1 ML. Figure 4-4a-c shows the results of contacting the 0.1 ML Pd/Au NSs with an aqueous solution of 1,1-DCE at 50.9 μM. After an induction period, there appeared to be two different time-dependent adsorption states: the initial state (0-20 minutes; Fig. 3b), with Raman spectra featuring bands at 214, 954, ~1060, ~1160, ~1250, 1430, and 1550 cm⁻¹, and the final state (37-52 minutes; Fig. 3c), with bands found at ~225, ~390, ~1165, ~1455, and ~1500 cm⁻¹. The peaks can be assigned to wavenumber regions that represent particular Raman-active vibrational modes of surface-bound 1,1-DCE, based on reported assignments for chemisorbed ethylene¹³, TCE¹⁴, free 1,1-DCE¹⁵, and corroborated with ab initio density functional theory calculations. Peaks in the 1500-1600 cm⁻¹, 1220-1290 cm⁻¹, and 1000-1100 cm⁻¹ range were assigned to CC stretching, CH₂ scissoring, and CH₂ wagging modes of π-bound 1,1-DCE, respectively. The sharp peaks at 954, ~1160, and 1430 cm⁻¹ were further assigned to the CC stretching, CH₂
wagging, and CH$_2$ scissoring modes of di-σ-bound 1,1-DCE. The other closely located peaks suggest different metal adsorption sites, sites of different binding strengths, or binding states intermediate to those of the π- and di-σ-bound 1,1-DCE species. The low-frequency features below 400 cm$^{-1}$ may be due to C-M (M = metal) or C-Cl bonds. These results provide direct evidence of 1,1-DCE undergoing chemisorption from water.

1,1-DCE adsorption is dynamic, as the initial state changes substantially into a new stable state (Fig 4-4a). Signals for π-bound 1,1-DCE were lost, with residual di-σ-bound 1,1-DCE showing the weak peaks at ~1165 and ~1455 cm$^{-1}$. A sharp and intense peak at ~1500 cm$^{-1}$ may be due to the CC stretch of vinylidene (=C=CH$_2$) species; this value is slightly blue-shifted from the theoretical value of 1490 cm$^{-1}$ for vinylidene on Pd(111)$^{16}$ and red-shifted from that for vinylidene on Si surfaces$^{17}$, and in the range predicted by our ab initio calculations. The bands at 230 cm$^{-1}$ and ~390 cm$^{-1}$ can be attributed to Cl-M and C-M bond stretchings, respectively, consistent with the removal of chlorine from 1,1-DCE to form vinylidene. This process is summarized in Figure 4-5.
Figure 4-4: (a) Waterfall plot of time-resolved spectra gathered from the chemisorption of 50.9 μM 1,1-DCE on Pd/Au NSs and (b,c) individual scans at 20 and 49 minutes after injection of 1,1-DCE solution. (d) Waterfall plot of time-resolved spectra gathered from the chemisorption of 254 μM 1,1-DCE and (e,f) individual scans at 10 and 28 minutes after injection of 1,1-DCE solution.
Figure 4-5- Proposed surface intermediates of 1,1-DCE after adsorption on Pd/Au NS SERS substrate based on spectroscopic results. The arrows are drawn to indicate the probable sequence of identifiable species.

Figure 4-6d-f shows the results of contacting the Pd/Au NSs with an aqueous solution of 1,1-DCE at a higher concentration of 254.5 μM. Unlike the 50.9 μM case, Raman peaks appeared almost immediately after injection of the DCE solution. The peaks at ~220 and ~400 cm⁻¹ (Cl-M and C-M bond stretchings) indicated DCE dechlorination. Bands centered at ~1500 cm⁻¹ and ~1200 cm⁻¹ were quite broad, spanning at least 100 cm⁻¹, suggesting vinylidene and other adsorbed species. The band positions did not change much with time, but their intensities increased continuously until ~20 minutes, after which the spectra stabilized. It is likely that the broad band at ~1500 cm⁻¹ represents unsaturated oligomeric species on the metal surface, as they have previously been assigned to conjugated olefins.¹⁸,¹⁹ This is not unexpected, as previous kinetic studies with TCE using Pd-based²⁰,²¹ and Pd/Au-based⁹ catalysts have reported trace amounts of carbon-coupling products at low H₂/TCE concentration ratios. These olefinic species were observed due to the higher DCE surface concentration, leading to increased interactions between chemisorbed DCE species (i.e., surface crowding effect). These species could be removed from the NS surface by contacting with H₂-containing water (Figure 4-6a) but not with N₂-containing water (Figure 4-6b).
Figure 4-6- (a) Waterfall plot of time-resolved spectra gathered from the chemisorption of 254 μM 1,1-DCE on Pd/Au NSs and with the addition of (a) H₂ sat. H₂O after 30 min or (b) N₂ sat. H₂O after 30 minutes.

Control experiments using Au-only NSs and the 254.5 μM DCE (Figure 4-7) solution showed no Raman peaks at all. These results indicated that solvated 1,1-DCE could not be detected at these concentrations and was observable only in the presence of Pd metal, suggesting Pd ensembles or Pd-Au mixed sites as active sites for chemisorption. While the surface structure of Pd on the Au NSs is not known precisely, the metal mostly likely are present as two-dimensional atomic ensembles or islands.
4.3.3. Reaction of 1,1-DCE

For the experiment using the 50.9 μM DCE and 16.3 mM H$_2$ solution, the resulting spectra differ dramatically from the non-H$_2$ case, with Raman peaks (additional to those associated with π-bound and di-σ-bound DCE) appearing and changing rapidly with time (Figure 4-8a-e). We hypothesized that H$_2$ dissociatively adsorbed to form atomic H species, which would accelerate the dechlorination of adsorbed DCE. The vinylidene species may have been present (~1480 cm$^{-1}$) with dechlorination occurring as early as 5 minutes after H$_2$ introduction, inferred from the appearance of broad bands below 400 cm$^{-1}$ (Cl-M and C-M bonds). In contrast, dechlorination was not observed until 20 minutes when there was no H$_2$ (Figure 4-4b). Vinyl surface species (-HC=CH$_2$) may have been present also, with small features at ~1230, ~1360, and ~1580 cm$^{-1}$ that represent CC-CH bending, CH$_2$ scissoring, and CC stretching, respectively$^{24}$, which would have formed from vinylidene hydrogenation (Figure 4-8b). Ethylidyne (≡C-CH$_3$, with a CC stretch at 1118 cm$^{-1}$ and CH$_3$ umbrella mode at 1326 cm$^{-1}$ $^{25}$) is a different
vinylidene hydrogenation product but was not detected. Further hydrogenation led to π- and di-σ-bound ethene, which could have contributed to the peaks close to those of π- and di-σ-bound DCE. Intriguingly, the distinct peak at 1193 cm⁻¹ may be assigned to an ethyl surface species (-CH₂CH₃, CH₂ wagging mode), resulting from hydrogenation of adsorbed ethene. Peaks were detected in the 600-900 cm⁻¹ range (C-Cl stretches from the population of chlorinated surface species), but were not detected in the absence of H₂ (Fig. 3-4b), suggestive of partially dechlorinated 1,1-DCE surface species.
Figure 4-8- (a) Waterfall plot of time-resolved spectra gathered from the reaction of 50.9 μM 1,1-DCE and 16.3 mM H₂ on Pd/Au NSs, and individual scans at 12, 30, 41 and 100 minutes (b, c, d, and e respectively) after injection of 1,1-DCE/H₂ solution. (f) Waterfall plot of time-resolved spectra gathered from the reaction of 254 μM 1,1-DCE and 81.9 mM H₂ on Pd/Au NSs, and individual scans at 12, 30, 41 and 100 minutes (g, h, i, and j, respectively) after injection of 1,1-DCE/H₂ solution.
While more specific peak assignments could not be obtained, general trends in the SERS spectra were observed with increasing time (Figure 4-8a). The ~250 cm\(^{-1}\) peak (M-Cl) increased and then slightly decreased after 30 min, suggesting that surface Cl eventually hydrogenated to form HCl, which then desorbed into the water phase. The peaks in the 600-900 cm\(^{-1}\) range (C-Cl) disappeared by 41 min, indicating complete dechlorination of surface species. The 1100-1600 cm\(^{-1}\) range became more intense, with broad peaks centered ~1200 cm\(^{-1}\) and ~1500 cm\(^{-1}\) similar to those observed in the absence of H\(_2\) at a higher 1,1-DCE concentration (Figure 4-4f). The peak at ~1530 cm\(^{-1}\) could be the CC stretch of a well-defined longer-chain olefinic surface species. Changes in the SERS spectra seemingly terminated at 41 min, likely due to blockage of catalytic sites by olefinic species and adsorbed Cl. This observation did not signify that the catalytic reaction terminated at 41 min, as reaction products still formed at 100 min (as shown in next Section). Rather, it indicated that the signals for the oligomeric species dominated those of surface intermediates directly involved in catalytic reaction pathway.

Similar trends were observed in the SERS spectra when DCE and H\(_2\) concentrations were increased by five-fold (Figure 4-8f-j). The resulting higher concentrations of surface species led to increased reaction rates, as shown by the more intense ~240 and 400 cm\(^{-1}\) peaks (Cl-M and C-M stretches). New peaks at ~1115 and ~1330 cm\(^{-1}\) were found at early reaction times\(^{25}\), indicative of ethylidyne species which were absent at lower reactant concentrations.

4.3.4. Analysis of 1,1-DCE HDC bulk reaction products

To confirm that the HDC reaction was occurring during SERS analysis, we removed and analyzed the aqueous-phase content of the SERS chamber at 0, 12, 30, 41, and 100 min. For both low and high concentration conditions, 1,1-DCE concentrations decreased with 100% selectivity towards ethane production; 1,1-DCE
conversion reached 9% by 30 min (Figure 4-9). Beyond 30 min for the low-concentration experiment, 1,1-DCE reacted more slowly (vide infra) and ethane selectivity dropped to 95% as ethene began to form, attributed to reduced H₂ reactant concentration. The product concentrations did not change much from 41 min to 100 min. Combining with the SERS observations in the same time range (Figure 4-8a), vinylidene and longer-chain olefinic as well as chloride surface species may be blocking enough active sites to slow down 1,1-DCE consumption. Deactivation due to surface site blockage likely is responsible for observed slower reaction kinetics beyond 30 minutes (above 9% conversion of 1,1-DCE).
Figure 4-9- (a) Concentration-time profiles and (b) product selectivities from the HDC reaction of 50.9 μM 1,1-DCE and 16.3 mM H₂, and (c) concentration-time profiles and (d) product selectivities from the HDC reaction of 254 μM 1,1-DCE and 81.9 mM H₂ using Pd/Au NS SERS substrate. The dashed traces show the expected 1,1-DCE concentrations using 0.003 min⁻¹ as the first-order reaction rate constant.

Beyond 30 min for the high-concentration experiment, 1,1-DCE also reacted more slowly and ethane selectivity dropped to 95% as ethene and C₄ molecules (butanes and butanes, which we did not further differentiate due to experimental limitations) began to form. Vinyl chloride (from incomplete dechlorination of 1,1-DCE) and 1,1-dichloroethane (from hydrogenation of 1,1-DCE) are theoretical by-products; they were not detected though, consistent with that observed with Pd/Au NPs.³ ⁹ ²³ Carbon-coupling reactions led to the olefinic surface species observed via SERS at low
and high reactant concentrations (Figure 4-8), and to C₄ reaction products only in the latter case (Figures 4-9 c,d). The C₄'s appeared in parallel with ethene, indicating that both originated from the same surface species.

We considered the decrease in 1,1-DCE concentration to follow an exponential trend through 30 min. The implication that the HDC reaction was first-order in 1,1-DCE and zero-order in H₂ was reasonable, given the low extent of reaction (<9% conversion). For both low and high reactant concentration conditions, an approximate rate constant of 0.003 min⁻¹ was calculated, giving a lower-bound estimate of initial reaction rate constant of 0.872 L/gPd/min (assuming no NSs were lost during preparation and experimentation). The initial turnover frequencies (= 1,1-DCE molecules initially reacted per Pd atom per min) for the low and high reactant concentrations were 0.0047 and 0.023 min⁻¹, respectively.

The turnover numbers (TON = total number of 1,1-DCE molecules reacted per Pd atom) at the low and high reactant concentration cases at 100 min were calculated to be 0.17 (= 1.17 nmoles DCE reacted ÷ 6.89 nmoles Pd) and 1.21 (= 8.3 nmoles DCE reacted ÷ 6.89 nmoles Pd), respectively. That TON exceeded one proved that the nanoshells are catalytically active for HDC. We note that TON can be calculated to be less than one for catalyzed reactions when rates are slow or at short reaction times. These cases occurred in our study involving low and high reactant concentrations, respectively.

To note, Pd/Au NPs (25% Pd coverage) have a rate constant of 1519 L/gPd/min for 1,1-DCE HDC, allowing us to estimate through that Pd/Au NPs (10% Pd coverage) have a rate constant of ~600 L/gPd/min, much higher than the 0.872 L/gPd/min for Pd/Au NSs (10% Pd coverage). However, this is an incompatible comparison because the reaction conditions were very different. The Pd/Au NSs were immobilized on a surface during catalysis, and the H₂ reactant amount was 6% in excess of the
stoichiometric amount needed for complete reaction of 1,1-DCE. In contrast, Pd/Au NPs were stably dispersed in water during batch reactor kinetic studies, and 1,1-DCE and \( \text{H}_2 \) concentrations were 77\% and 2416\% respectively higher; the \( \text{H}_2 \) amount was \~1400\% in excess of the stoichiometric amount needed.\textsuperscript{23}

Summarizing the spectroscopic and bulk reaction data together, we propose a simple model of the 1,1-DCE HDC reaction on Pd/Au NSs as a series of surface reactions (Figure 4-10). 1,1-DCE chemisorbs in two different binding states, eventually dechlorinating to form vinylidene species. Vinylidene then hydrogenates to form ethylidyne (at high precursor concentration) and vinyl intermediates. Surface oligomers form detectibly as spectator species from the carbon coupling of, perhaps, vinylidene groups. Ethylidyne can hydrogenate to form ethane but at a rate much slower than is observed spectroscopically, and so it may be a spectator species here also.\textsuperscript{26, 27} In contrast, the vinyl group hydrogenates to form surface-bound ethene. Its hydrogenation then occurs to form the ethane product (detectible through gas chromatography but not through SERS) via the classical Polanyi-Horiuti pathway, i.e., surface ethene \( \rightarrow \) surface ethyl \( \rightarrow \) surface ethane \( \rightarrow \) desorbed ethane.\textsuperscript{28, 29} The consumption of 1,1-DCE leads to the quantitative formation of ethane, until surface site blockage by oligomeric or chloride species slows hydrogenation kinetics sufficiently for surface-bound ethene to desorb into the water phase as a product. High 1,1-DCE reactant concentrations lead to high surface species concentrations, with surface site blockage leading to side-product formation of \( \text{C}_4 \)’s in addition to ethene.
Figure 4-10- Proposed surface intermediates of 1,1-DCE and H₂ under reactive conditions on Pd/Au NS SERS substrate based on spectroscopic results. The aqueous-phase 1,1-DCE, ethane, C₂'s, and ethane species were identified and quantified via gas chromatography. The arrows are drawn to indicate the probable sequence of identifiable species. The H surface atoms come from the dissociative adsorption of dissolved H₂.

4.4. Summary and Conclusions

This study shows the successful synthesis and application of Pd-supported Au NSs for the detection of water-phase adsorbates. The Pd metal provided direct binding sites on the Au surface (either as Pd ensembles or Pd-Au mixed sites), effectively lowering the concentration detection limit for SERS. Significantly, chemical reactions of adsorbate species can be observed as they proceed on the catalyst surface with time, providing a newfound ability to detect and identify reaction intermediates in water under ambient conditions in situ. Presented here is the first spectroscopic evidence of water-phase hydrodechlorination as a sequence of dechlorination and hydrogenation steps, leading to the implication that 1,1-DCE, TCE, PCE, and other related contaminants degrade in a similar fashion using Pd-supported Au NP catalysts. Additionally, the Pd/Au NSs may also be useful for the detection of contaminants in groundwater.
4.5. References


Chapter 5

Effect of Chloride and Sulfide on Pd/Au catalysts

5.1. Introduction

Chlorinated ethenes constitute a class of volatile organic compounds considered to be some of the most harmful groundwater contaminants. These compounds and their isomers are probable human carcinogens, have been linked to liver damage, nervous system damage, lung damage, and, with extreme exposure, can cause death in humans. One of the most prevalent of these compounds is trichloroethene (TCE), which has also been found at 832 of 1,430 National Priority List Superfund sites at concentrations far above the US EPA maximum containment level of 5 ppb. Still used as a metal degreaser and in textile manufacture, TCE ranks 16th on the Comprehensive Environmental Response and Compensation Liability Act of 2005 (CERCLA) priority list of hazardous compounds. It also shows up in groundwater as a result of biotic degradation of perchloroethene. TCE is particularly threatening if left untreated, as it will degrade through natural attenuation to vinyl chloride, the 4th most hazardous substance on the CERCLA list.

We recently reported on the highly efficiency of palladium-decorated gold nanoparticles (Pd/Au NPs) for the catalytic room-temperature, water-phase hydrodechlorination (HDC) of TCE into ethane. The Pd/Au NP catalytic activity was directly controlled by the Pd metal surface coverage of the 4-nm Au NPs. A maximum rate (~1800 L/g\textsubscript{Pd}/min) was found near 70% surface coverage, nominally 100× higher than Pd/Al\textsubscript{2}O\textsubscript{3} (~12 L/g\textsubscript{Pd}/min). Observed for some other catalytic reactions, Au promotes Pd metal for TCE HDC catalytic activity possibly by creating an Pd-Au interface as population of active sites, by inducing the formation of Pd surface
ensembles as the active sites, or by modifying the electronic structure of the Pd metal. Recent extended x-ray absorption spectroscopy results prove that the Pd/Au NPs have a surface that is enriched in Pd atoms, i.e., the NPs have a Au core with Pd on the surface.

Towards their application to real groundwater systems, the long-term durability of the Pd/Au NP catalysts needs to be addressed with regard to catalyst deactivation. Groundwater typically contains a multitude of substances which could impact Pd/Au NP catalytic performance. Perhaps the most pertinent to address are chloride (Cl\(^-\)) and hydrosulfide (SH\(^-\), “sulfide” for short) ions, where the former can be found at concentrations ranging from 1.0-1000 mg/L and latter can be produced naturally from native anaerobic bacteria. Both chemical species are known to adsorb onto Pd surfaces and to reduce Pd activity. The rapid poisoning of Pd-based catalysts during aqueous-phase hydrodechlorination by sulfide ions is a well-known problem. In this work, we studied the effects of sulfide and chloride ions on TCE HCl reaction rates of Pd/Au NPs, observing that chloride had no effect and sulfide had a markedly less effect compared to Pd NPs and Pd/Al\(_2\)O\(_3\). We performed catalytic titration experiments using sulfide as the poison to gain insights into the nature of the active sites for TCE HCl sites.

5.2. Experimental

5.2.1. Preparation of Pd/Au NPs and Pd NPs

The Pd/Au NPs were prepared as previously reported. Briefly, 1 mL of a gold salt solution (1 wt% = 25 mM; prepared by adding 1 g HAuCl\(_4\)-3H\(_2\)O (99.99%, Sigma-Aldrich) to 99 g deionized H\(_2\)O) was added to 79 mL of deionized H\(_2\)O. A second solution of 0.04 g tannic acid, 0.05 g trisodium citrate, and 0.0173 g of K\(_2\)CO\(_3\) in 20 mL deionized water was also prepared. Both solutions were heated to 60 °C, and then the heating...
tannic acid solution was rapidly added to the gold salt solution under vigorous stirring. The solution immediately turned reddish brown, indicating the formation of Au NPs. The temperature of the solution was increased until boiling, and allowed to boil for 25 minutes. Finally, the solution (calculated particle concentration of $2.9 \times 10^{15}$ NP/L) was removed from the heat source and stored in a separate container.

For the Pd coatings, a specified amount (15-60 µL) of a 2.4-mM $\text{H}_2\text{PdCl}_4$ solution (prepared from 0.0426 g of $\text{PdCl}_2$ (99.99%, Sigma-Aldrich) dissolved in 100 mL deionized water and 480 µL 1 M HCl solution) was mixed with 2 mL of the as-synthesized Au NP sol. The resulting solution was then bubbled with hydrogen gas (99.999%, Matheson) for two min. After bubbling, the solution was aged in a sealed vial overnight at room temperature prior to use. Assuming complete reduction of Au and Pd ions into metal, 15, 30, and 60 µL of Pd salt solution yielded Pd/Au NPs containing 3.5, 6.8, and 12.8 wt% Pd, respectively. They respectively correspond to 4-nm Au NPs with 15%, 30%, and 60% of monolayer (ML) coverage by Pd metal atoms (Table 5.1).

<table>
<thead>
<tr>
<th>Catalyst nanomaterials tested</th>
<th>Pd weight loading (wt% Pd)</th>
<th>Estimated Pd dispersion (%Pd surface atoms)</th>
<th>Calculated amount of surface Pd atoms, charged to reactor (nmol)</th>
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<tr>
<td>15% ML</td>
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<td>21$^a$</td>
<td>493</td>
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</table>

$^a$Taken from Reference $^5$. 

75
The Pd NPs were prepared using the same procedure for Au NP synthesis, except the Au salt solution was replaced by 10.4 mL of a H₂PdCl₄ solution (2.4 mM) combined with 69.6 mL of H₂O. A dark coffee-brown sol containing 4-nm Pd NPs (calculated particle concentration of 2.9x10¹⁵ NP/L) was the result. A Pd/Al₂O₃ (1 wt% Pd) catalyst was purchased from Sigma Aldrich, and used as is.

5.2.2. Catalyst Testing

5.2.2.1. Reactor Set-up

The catalytic testing of the NPs was conducted similar to our previous studies. Batch reactors were prepared by adding 168.6-172.5 mL of H₂O (so as to keep the volume constant at 173 mL after addition of the catalyst sol/suspension) and a stir bar to a 250-mL, Teflon-sealed glass bottle. The bottles were sealed with a cap outfitted with a rubber septum, and sparged with H₂ gas for 15 minutes to saturate the H₂O and fill the headspace. TCE was then added (3 μL, 99.5%, Aldrich), resulting in a liquid concentration of approximately 43 ppm (43 mg/L, 325 μM), far below the saturation concentration of 1200 ppm at 25 °C. Pentane (0.2 μl, 99.7%, Burdick & Jackson) was added as an internal standard for gas-chromatography (GC) headspace analysis. The reactors were stirred rapidly for at least 3 hr or until the measured concentrations showed no change over time, indicating total dissolution of the TCE and pentane and the establishment of vapor-liquid equilibrium.

5.2.2.2. Reaction Analysis

The catalyst was introduced into the reactor via syringe injection of an aliquot of sol (containing Pd/Au or Pd NPs) or suspension (containing Pd/Al₂O₃). For GC headspace analysis, 100-μl aliquot samples of the headspace gas in the batch reactor
were 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 pH of the reaction medium was monitored using pH paper (Whatman Panpeha pH indicator strips, Sigma-Aldrich) before injection of the catalyst and at the end of the reaction. At complete conversion of TCE, the pH should drop to a value of 3.1 theoretically, due to HCl formation. For all catalyst samples tested, i.e., Pd/Au NPs, Pd NPs, and Pd/Al$_2$O$_3$, for both chloride and sulfide testing studies, the initial reactor pH was ~6.0 and the final pH was ~5.5. This slight pH decrease, as observed by others$^{18,32}$, indicates the reaction system has some buffering capacity that limits pH change. The Pd and Pd/Au NP reaction systems contain small amounts of citrate, carbonate, and tannic acid, which are buffering ions. In the Pd/Al$_2$O$_3$ case, the alumina support could buffer the solution around its point-of-zero charge (generally between pH 6.4 and 9.5)$^{33}$.

5.2.2.3. Testing of Chloride Effect

Prior to charging with H$_2$, TCE, pentane, and catalyst, solutions of 1 M NaCl (prepared from 5.84 g 99.99% NaCl (Fisher) and 100 mL deionized water) were added to the reactor such that the total reaction volume (accounting for the eventual added catalyst sol/suspension) was 173 mL, giving final concentrations ranging from 0-0.02 M chloride. The following catalyst aliquots were injected: 2 mL of the 30%-Pd/Au NP sol; 1 mL of the Pd NP sol combined with 1 mL of H$_2$O; and 25 mg of Pd/Al$_2$O$_3$ suspended in 2 mL of H$_2$O.
5.2.2.4. Testing of Sulfide Effect

Hereafter, the term "sulfide" refers to the hydrosulfide ion, the dissociated form of hydrogen sulfide ($H_2S \leftrightarrow H^+ + SH^-$, $pK_a = 7.05$ at 20 °C $^{34}$). A sulfide solution (0.01 M) was prepared by dissolving 0.0211 g Na$_2$S·9H$_2$O (98%, Sigma-Aldrich) in 8.78 mL deionized water ($Na_2S + H_2O \leftrightarrow 2Na^+ + SH^- + OH^-$), and combined with catalyst sol/suspensions before injection.

For Pd/Au NP sols, 4 mL of 15%-Pd/Au NPs, 2 mL of 30%-Pd/Au NPs, or 0.5 mL of 60%-Pd/Au NPs (Table 5-1) were treated with 0 to 13 μL of the sulfide solution, to vary the sulfide:surface Pd atom (S:Pd$_{surf}$) ratio from 0 to 1.8. One mL of Pd NP sol was diluted with 1 mL of H$_2$O (so as to keep the final liquid volume in the reactor constant at 173 mL), and treated with 0-9.0 μL of sulfide solution to vary the sulfide:surface Pd atom (S:Pd$_{surf}$) ratio from 0 to 1. Similarly, a Pd/Al$_2$O$_3$ suspension (25 mg powder in 2 mL of H$_2$O) was treated with 0-49 μL of sulfide solution. All suspensions were stirred briefly then left unstirred at room temperature for at least 3 hr prior to injection. The total reaction volume was 173 mL.

The concentrations of surface Pd atoms in the reactor after catalyst injection were 0.42 μM, 0.51 μM, and 2.85 μM for the Pd/Au NPs, Pd NPs, and Pd/Al$_2$O$_3$ catalysts, respectively. For Pd and Pd/Au NPs $^7$, the magic cluster structural model was used and the complete reduction of the gold and palladium precursor salts was assumed. We estimate that each of the nanoparticle sols contains $2.91 \times 10^{15}$ NPs/L. For the Pd NPs, we assume that the surface atoms are contained only in the 7th shell, and hence the concentration of surface Pd in the sol is 88 μM. In the case of the bimetallic Pd-Au NPs, if the added Pd is assumed to constitute a partial 8th shell around the Au NP, we estimate that it covers approximately 15-60% of the Au NP surface, resulting in a surface Pd concentration of 18-72 μM. The amount of surface Pd on the
Pd/Al₂O₃ sample was estimated using the literature reported metal dispersion of 21% ³², which indicates a surface concentration of 210 µg of surface Pd per gram of Pd/Al₂O₃.

5.2.2.5. Testing the Effect of adding Au NPs to Pd/Au NPs

To study the effects of adding Au NPs on sulfide deactivation of Pd/Au NPs, 1 to 3 mL of the Au NP sol were mixed with 2 mL of the Pd/Au NPs prepared with 30 µL of H₂PdCl₄ (to get 30%-Pd/Au NPs) before adding 2.4 µL of the sulfide solution.

5.3. Results and Discussion

5.3.1. Determination of Reaction Rate Constant

Reaction rate constants for the conversion of TCE by Pd-based catalysts have generally been assumed to be pseudo first-order in TCE concentration, and zero-order in H₂ concentration (from very high H₂ concentrations) ⁶, ⁷, ³²:

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

Equation 5-1

where the fitted first-order rate constant \(k_{\text{meas}} = k_{\text{obs}} \times C_{\text{cat}}\), where \(k_{\text{obs}}\) (units of L/gPd/min) is the rate constant normalized by the amount of catalyst present, and \(C_{\text{cat}}\) and \(C_{\text{TCE}}\) are the concentrations of the catalyst and TCE, respectively. Accounting for exposed Pd atoms, initial turnover frequency values can be calculated as TOF = \(k_{\text{obs}} \times C_{\text{TCE,0}} \times \text{Pd atomic weight} \times \text{Pd dispersion/60}\). It is noted that \(k_{\text{obs}}\) is equivalent to \(-\frac{(dC_{\text{TCE}}/dt)_{0}}{C_{\text{cat}}/C_{\text{TCE,0}}}\), where \(C_{\text{TCE,0}}\) is the initial TCE concentration.

As previously reported, Pd/Au NPs catalyze TCE HDC with a first-order dependence on TCE concentration ⁶, ⁷. Figure 5-1a shows Pd/Au NPs with 30% Pd
coverage exhibiting this first-order dependence, in the absence and presence of additional chloride. The first-order rate constants are listed in Table 5-2. However, the monometallic Pd NPs and Pd/Al₂O₃ catalysts did not show this behavior (Figures 5-1b and 5-1c). TCE conversions were linear with time, indicating zero-order dependence on TCE concentration; conversions leveled off above a conversion of ~80%.
Figure 5-1. Fractional conversion of TCE vs. time for (a) Pd/Au NPs (30% ML), (b) Pd NPs, and (c) Pd/Al₂O₃ at various chloride concentrations. Points are experimental results. Solid lines in panel (a) are first-order best fits, and dashed lines in panels (b) and (c) show initial slopes used to determine initial TCE HDC activity. (d) Initial turnover frequencies at different chloride concentrations, with dashed lines drawn to guide the eye.
Table 5-2. Parameters and results from chloride poisoning studies for 30%-Pd/Au NPs, Pd NPs, and Pd/Al₂O₃. Reaction conditions: C_{TCE,0} = 221 μM, room temperature.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Reactor chloride concentration (mmol/L)</th>
<th>Constant k_{obs} (L/gpd/min)</th>
<th>Initial rate (\cdot r_{TCE} \times 10^{-3}) (mol-TCE/gpd/min)</th>
<th>Initial turnover frequency TOF (mol-TCE/mol-Pd_{surf}/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd/Au NPs</td>
<td>0</td>
<td>900</td>
<td>292.5</td>
<td>0.52</td>
</tr>
<tr>
<td>(30% ML)</td>
<td>1</td>
<td>809</td>
<td>262.9</td>
<td>0.47</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>885</td>
<td>287.6</td>
<td>0.51</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>907</td>
<td>294.7</td>
<td>0.52</td>
</tr>
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<tr>
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<td>42.7</td>
<td>0.076</td>
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<tr>
<td></td>
<td>1</td>
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<td>30.0</td>
<td>0.052</td>
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<td></td>
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<td></td>
<td>20</td>
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</table>

According to studies by Kopinke et al.\textsuperscript{12} Reinhard and co-workers\textsuperscript{32}, and us\textsuperscript{5}, Pd/Al₂O₃ catalysts were reported to be first-order in TCE. By running the reaction for a longer period of time in this work, however, we observed clearly and reproducibly the non-first-order dependence on TCE. We found that the reaction rates for Pd NPs and Pd/Al₂O₃ catalysts were first-order at low TCE concentrations (<1 ppm, close to the 1 ppm used by Kopinke et al.\textsuperscript{12} Reinhard and co-workers\textsuperscript{32}) and non-first-order at high TCE concentrations (29 ppm, as used in this study)\textsuperscript{35}(Y.L. Fang, K. N. Heck, et al., in preparation). An interesting implication is that the higher TCE concentrations lead to
competitive chemisorption of TCE on the active sites of Pd NPs and Pd/Al₂O₃ catalysts, which does not happen with Pd/Au NPs.

Since rate constants for catalysts exhibiting different rate laws cannot be compared, we chose to compare initial reaction rates and initial TOF values instead (Table 5-2). Whereas the TOF’s for Pd/Au NPs was derived from initial reaction rates via the first-order rate constants, the TOF’s for the pure Pd-based catalysts were derived in a different manner. The initial reaction rate of the monometallic Pd catalysts was characterized as

\[-\left(\frac{dC_{\text{TCE}}}{dt}\right)_0/C_{\text{cat}} = -r'_{\text{TCE}}\]

Equation 5-2

where \(-r'_{\text{TCE}}\) (units of mol-TCE/gpds/min) is the initial slope of the first 3-4 data points of a TCE concentration-time profile divided by Pd catalyst reactor charge amount. Accounting for exposed Pd atoms, initial turnover frequency values were then calculated as TOF = \(-r'_{\text{TCE}}\times\text{Pd atomic weight}\times\text{Pd dispersion}/60\), which was equivalent to the TOF definition given earlier for Pd/Au NPs.

5.3.2. Effect of Chloride on the Rate of HDC Reaction

As shown in Figure 5-1 and Table 5-2, the activity of the Pd/Al₂O₃ and Pd NPs fell drastically with increasing chloride concentration, decreasing as much as 30% of its original activity at the highest chloride concentration used. This chloride effect is seen in other catalytic systems, such as both gas-phase oxidation and gas- and liquid-phase HDC reactions. In gas-phase HDC, HCl formed as a byproduct of the reaction and
inhibited the activity by reversibly competing with the chlorinated reactant for active sites \cite{28,32}. In water-phase HDC, this species may play a similar inhibitory role \cite{27}.

In contrast to our observations with Pd/Al$_2$O$_3$ and Pd NPs, Lowry and Reinhard reported that a chloride concentration of 0.028 M had no effect on activity on the aqueous-phase HDC of TCE over a Pd/Al$_2$O$_3$ catalyst \cite{18}. This difference could be attributed to the higher pH of 9.6 used by Lowry and Reinhard compared to the lower pH used in our reaction system (i.e., initial pH of 6, lowering to 5.5 by the end of the reaction). The higher pH values led to increased Pd/Al$_2$O$_3$-catalyzed TCE HDC rates, which could have masked the chloride inhibitory effect we observed \cite{18}.

A reasonable explanation for the deactivation of the pure Pd catalysts (Pd NPs and Pd/Al$_2$O$_3$) is the chemisorption of chloride to the Pd surface. In an electrochemical study of halide adsorption at Pd electrodes, Soriaga and coworkers showed that chloride can oxidatively adsorb to Pd(111) crystals under acidic conditions via the reaction \cite{36}

\[
H^+(aq) + Cl^-(aq) + Pd(111) \rightarrow Pd(111)-Cl + \frac{1}{2}H_2
\]

Equation 5-3

The amount of Cl added to the reactors was far in excess of the amount of surface Pd atoms, and so by way of the law of mass action, the amount of chlorine surface species would also increase if there was sufficient amount of hydronium ions H$^+$(aq). Acid and neutral pH conditions would favor chlorine surface species formation (leading to greater susceptibility to catalyst deactivation and lower HDC rates) and basic pH would disfavor chlorine surface species formation (leading to catalyst deactivation resistance and higher HDC rates). From \textit{in situ} surface-enhanced Raman spectroscopic investigations, we recently found that surface-bound chlorine can form on Pd-Au catalytic surfaces in the closely related reaction of 1,1-dichloroethylene HDC \cite{37}.
Whereas Pd-only catalysts deactivated significantly, the activity of the Pd/Au NPs unexpectedly remained constant and unaffected by Cl concentration at the same condition of near-neutral pH (Figure 5-1a,d), suggesting that the extent of chlorine surface species formation on the Pd metal was lowered in the presence of Au. This reduced binding affinity to chlorine atoms may be correlated to the increased d-band electron density of Pd caused by the Au, as previously observed through x-ray photoelectron spectroscopy.7

5.3.3. Effect of Sulfide on the Rate of HDC Reaction

Figure 5-2 shows the results for the sulfide poisoning experiments on monometallic Pd and Pd/Au NP (30% ML) catalyst, in which sulfide-to-surface Pd atom ratios were considered. In the absence of sulfide, the activity measured for the control catalysts had initial TOF values of 0.076 and 0.050 moles_{TCE}/mole_{Pd}/min for the Pd/Al₂O₃ and Pd NP catalysts, respectively. The Pd/Au NP catalyst had an initial TOF 0.52 moles_{TCE}/mole_{Pd}/min, in agreement with our previous work, considering the different amounts of TCE initially present in the reactors (3 µL in this study vs. 7 µL)7.
Figure 5-2. Fractional conversion of TCE vs. time for (a) Pd/Au NPs (30% ML), (b) Pd NPs, and (c) Pd/Al₂O₃ at various S:Pd$_{surf}$ ratios. Points are experimental results. Solid lines in panel (a) are first-order best fits, and dashed lines in panels (b) and (c) show initial slopes used to determine initial TCE HDC activity. (d) Initial turnover frequencies with S:Pd$_{surf}$ ratio, with dashed lines drawn to guide the eye.
Table 5-3. Parameters and results from sulfide poisoning experiments for 30%-Pd/Au NPs, Pd NPs, and Pd/Al₂O₃. Reaction conditions: C_{TCE,0} = 221 μM, room temperature.

<table>
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<tr>
<th>Catalyst</th>
<th>Sulfide added (μg)</th>
<th>S:Psurf molar ratio</th>
<th>First-order rate constant k_{obs} (L/g_Pd/min)</th>
<th>Initial rate (-r_{TCE}) (mol-TCE/g_Pd/min)</th>
<th>Initial turnover frequency TOF (mol-TCE/mol-Pd_{surf}/s)</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>S:Psurf molar ratio</td>
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<td></td>
<td></td>
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TCE HDC activity of the Pd/Au NP and Pd NP catalysts monotonically decreased with added sulfide, while added sulfide had little effect on the Pd/Al₂O₃ catalyst until S:Psurf ratio of 1. The latter observation could be due to the Al₂O₃ support material.
Al₂O₃ has been studied for its use as a gas-phase adsorbent of sulfide and other sulfur containing compounds, where the adsorption is theorized to occur either to strong Lewis acid sites of the Al₂O₃ or to surface hydroxyl groups via hydrogen bonding.\textsuperscript{38-41} While there is no data available for the aqueous phase adsorption of sulfide, it is feasible that all of the sulfide could have been adsorbed to the Al₂O₃. If each sulfide atom (the ionic radius of sulfide is 1.84 Å → cross sectional area of 10.63 Å\textsuperscript{2}) populates an amount of area on the support (BET surface area of Pd/Al₂O₃ = 155 m\textsuperscript{2}/g\textsuperscript{32}) equal to its cross sectional area, then 25 mg of catalyst would have a monolayer adsorption sulfide capacity of 2.19 mmol. In our batch studies, the maximum amount of sulfide added to the Pd/Al₂O₃ catalyst was 0.49 μL (4.9 nmol), which is six orders of magnitude less.

The deactivation of Pd NPs by sulfide could be analyzed more quantitatively. Complete deactivation observed at a S:Pd\textsubscript{surf} ratio of 0.5, suggesting that 2 Pd atoms are involved in the HDC reaction. This ratio is close to those found from STM and EXAFS studies of H₂S on Pd surfaces, in which surface saturation corresponded to a S:Pd\textsubscript{surf} ratio of 0.43 (= 3 S atoms chemisorbed on 7 Pd atoms\textsuperscript{14-18}) for Pd(111) and to a S:Pd\textsubscript{surf} ratio of 0.5 for Pd(001)\textsuperscript{13}. The rapid decrease in TCE HDC reaction rate with sulfide content indicated preferentially adsorption on Pd atoms of highest activity, which are often correlated to atoms with the lowest coordination number\textsuperscript{13,42}.

Interestingly, the Pd/Au NP catalyst deactivated more slowly than the Pd NPs and Pd/Al₂O₃. This material did not fully deactivate until a S:Pd\textsubscript{surf} ratio one of ~1 was reached (Figure 5-2d). The Au apparently enhances the sulfide poisoning resistance of Pd for TCE HDC. This beneficial presence of Au was seen in gas-phase hydrodesulfurization thiophene by alloyed Pd-Au/Al₂O₃ catalysts by Venezia et al.\textsuperscript{43,44} For this reaction, it was concluded that Au prevented the bulk formation of catalytically inactive Pd₅S crystallites.

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5.3.4. Effect of Adding Au NPs to Pd/Au NPs for TCE HDC

Lambert and coworkers showed that Pd atoms form two- and three-dimensional islands on Au(111) at low (7%) and high (70%) Pd coverages, respectively, at room temperature\textsuperscript{45, 46}, leaving the underlying Au exposed. Perhaps another explanation for the enhanced deactivation resistance is the adsorption of sulfide onto the exposed Au surface of Pd/Au NPs, as sulfide compounds are well-known to bind to Au surfaces\textsuperscript{43, 44, 47, 48}. Adsorption onto Au would reduce the sulfide amount available to bind to the presumed Pd active sites. To test this idea, we combined varying amounts of Au NPs (containing no Pd) to the Pd/Au NPs (30\% ML) prior to the sulfide treatment step, and determined the reaction rate constants of the resulting NP mixtures.

From Figure 5-3, it can be seen that the rate constants did not change when Au NPs were added, indicating that the sulfide ions did not adsorb onto the Au NP surfaces. Otherwise, the rate constants should have increased with increasing amounts of Au NPs as the Au NPs removed the sulfide from solution. Wierse et al. showed that surface saturation coverages of 0.5-0.6 S: Au_{surf} could be reached when sulfide ions adsorbed onto Au surfaces in water, but the sulfide was thought to be weakly physisorbed onto the Au surface\textsuperscript{48}. According to Zhang et al., the Pd-S bond of thiol capped Pd NPs is shorter than (and hence stronger than) the Au-S bond in thiol capped Au NPs\textsuperscript{49}. These results suggest that sulfides preferentially bind to Pd-based sites (i.e., Pd atoms or Pd-Au mixed sites) over pure Au sites of the Pd/Au NPs.
Figure 5-3. Measured $k$ of 30% Pd/Au NPs as a function of added Au NPs. Line drawn to guide the eye. The $S: \text{Pd}_{\text{surf}}$ ratio for all samples was 0.6.

5.3.5. Effect of Pd/Au NP Composition

Sulfide deactivation experiments were carried out on Pd/Au NP catalysts with varying Pd surface coverages (Figure 5-4a). Besides 30% ML coverage, 15% and 60% ML coverages were studied. All materials exhibited lowered reaction rates with added sulfide, but the deactivation characteristics differed. Complete deactivation occurred at $S: \text{Pd}_{\text{surf}}$ ratios of 1.8, 1.0, and 0.8 for 15%, 30%, and 60% ML coverages, respectively. In essence the 15% ML samples are only completely poisoned with 2x the amount of added S per Pd$_{\text{surf}}$, while there is only a small difference in the amount of S per Pd$_{\text{surf}}$ for the 30% and 60% ML samples.
Figure 5-4. a) TOF values and b) rate of TOF change (calculated using 3-point numerical differentiation) of (□) 60%, (▲) 30%, and (◆) 15% Pd/Au NPs as a function of S:Pd ratio. Lines are drawn to guide the eye.

The 15% and 30% deactivated with a linear dependence on S:Pd_{surf} ratio. However, the highly active 60%-ML Pd/Au NPs deactivated very rapidly at low S:Pd_{surf} ratios and slowly at higher ratios. Analyzing the rate of deactivation change with S:Pd_{surf} ratio provided additional insights into the sulfide poisoning effect (Figure 5-4b). For the 30% ML case, the rate of TOF change was constant with increasing sulfide content (at -0.57 s^{-1}), which can be interpreted as the NP catalysts containing active sites that have equivalent catalytic activity. For the 15% ML case, the rate of TOF change was also constant but at a lower value (at -0.15 ds^{-1}). This suggested that active sites also had equivalent catalytic activity at this lower Pd surface coverage. These sites were less active than those at 30% ML coverage, but they deactivated to a lesser extent with increasing S:Pd_{surf} ratios. The 15%-ML sites became more active above a S:Pd_{surf} ratio of 0.6, and did not completely deactivate until a S:Pd_{surf} ratio of nearly 2.

Finally, for the 60% ML case, the calculations suggest 2 different rates of TOF change, -3.0 ds^{-1} and -0.51 ds^{-1} at low and high S:Pd_{surf} ratios, respectively, with a transition range between these values. This behavior likely indicates the presence of two different populations of active sites on the catalyst surface, in which the highly active
sites deactivate first in the presence of sulfides and the less active sites deactivate more slowly. These less active sites of the 60% ML Pd/Au NPs may be equivalent to the active sites of the 30% ML Pd/Au NPs, based on the similar rate of TOF change. Sautet and coworkers conducted both theoretical and experimental studies on the dechlorination reaction of TCE over a model (110) PdCu catalyst, consisting of alternating rows of Pd and Cu at the surface\textsuperscript{60, 51}. The group found that the carbon-carbon double bond preferentially adsorbed on two adjacent Pd sites, while the carbon-chloride bond cleavage was assisted by the Cu atoms, where chloride fragments preferentially remained. These studies underlined the importance of the proximity of Pd and Cu during the reaction, the so called geometric effect.

Such geometric effects may also be affecting our Pd/Au NPs. The fact that the 15% ML poison at approximately \(\sim 2x\) the rate of the 30% and 60% ML samples maybe due to isolation of Pd atoms on the lowest loaded sample. Baddeley et al. observed the formation of 3-D islands of Pd on (111) Au at coverages of at least 70% ML Pd\textsuperscript{45, 46}, while at 7% ML coverage isolated atoms occur. The isolation of the Pd atoms from each other likely increase the number of active sites per Pd atom, which may be able to adsorb more S. In addition, previous XPS data shows that the lower the Pd loading, the more the electronic effect on the Pd\textsuperscript{52}. Because we have shown evidence that, under these conditions, Au is more resistant to S adsorption to Pd, the electronic effect may also make the Pd more resistant.

The same effects are also at play with the 30% sample. Compared to the 15% ML sample, the greater amount of Pd increases the likelihood of forming larger, planar 2-D islands. In addition to the fact the formation of these islands imply that the Pd atoms will have less available sites for reaction, in comparison to the 15% ML sample, because these sites have more Pd-Pd interactions, there is less of an electronic effect from the Au substrate, and hence a lower resistance to S compared to the 15% sample. Finally,
for the 60% Pd/Au sample, a similar geometric/electronic effect may be present. Since 3-D islands form when 70% ML Pd is deposited on Au, this should decrease available sites, since they are buried within the islands. In addition, the rate of change of the fall in the poisoning suggests at least two distinct active sites. The most active (from which results the extremely high activity of the catalyst compared to other samples) sites are likely the result of the formation of 3-dimensional islands of Pd, which are the first to poison. Their atomic separation from the Au surface likely reduces the electronic effect, though the activity is promoted. The rest of the sites, which poison slower, are likely similar to the large islands proposed for the 30% ML sample, as they have a comparable rate of activity. While all samples exhibited activities greater than monometallic Pd on a per surface Pd basis, this analysis implies that there is an optimum amount of electron transfer from Au to Pd to observe the greatest activity. The 15% sample likely is affected by the Au to the highest degree, which improves its resistance at the cost of activity. On the other hand, the 60% sample, consisting of sites more removed from the Au surface, is less affected by the Au, increasing its activity at the cost of deactivation resistance.

5.4. Summary and Conclusions

This study focused on the performance characteristics of Pd/Al₂O₃, Pd NP, and Pd/Au NP catalysts for the aqueous hydrodechlorination of TCE after exposure to aqueous sulfide or in chloride solutions. The addition of chloride had no effect on the activity of Pd/Au NPs, in contrast to Pd NPs and Pd/Al₂O₃, which deactivate in the presence of chloride. In the case of the monometallic Pd, the deactivation is likely due to chloride adsorbed to Pd active sites. The chloride resistance of the Pd/Au NPs may possibly be due to the presence of surface Au atoms, which may repel chloride adsorption, or the altered electronic state of the submonolayer Pd relative to
monometallic Pd. At the sulfide concentration range examined, the Pd/Al₂O₃ catalyst showed little deactivation behavior, which could possibly be due to interactions of the sulfide ions with the Al₂O₃ support. The activity of the Pd NP catalyst decreased rapidly with added S, and became completely inactive at a S to Pd_{surface} ratio equal to 0.5, which is similar to the reported surface saturation values of S on Pd. In comparison, the Pd/Au catalysts showed much better resistance to S poisoning than the Pd catalyst. The possibility of partial partitioning of S to inactive Au atoms was eliminated, as the addition of pure Au NPs to the catalysts prior to deactivation had no effect. The S resistance was found to be compositionally dependent, increasing as the ML coverage of Pd decreased, with the best resistance occurring at S:Pd_{surface} of ~1.8 for the 0.15 ML sample. The S poisoning results may be due to a partial decrease in the S-Pd interaction due to the possible modification in the electronic structure of Pd, or the inhibition of the formation of a mixed Pd-S overlayer observed in various analyses of monometallic Pd. These results show promise for the use of Pd/Au NP catalysts for the treatment of groundwater, which can contain large amounts of sulfide or chloride.

5.5. References

3. (United States Environmental Protection Agency, 1995).


42. Somorjai, G. Introduction to Surface Chemistry and Catalysis (Wiley Interscience, New York, 1994).


Chapter 6

Future Work

This thesis has advanced the study of mono and bimetal catalyzed reactions in water. In particular, we have examined the oxidation of glycerol over Au NS catalysts, the hydrodechlorination of DCE over Pd/Au NSs, and finally studied the effect of common groundwater poisons on the activity of Pd/Au NPs. However, continued research could lead to further advancements.

In particular, the use of Pd/Au NPs for HDC of chlorinated ethenes in the field has yet to be demonstrated. To do so, either the immobilization of the Pd/Au NPs must be improved, or the synthesis of the catalyst must be changed, since the relatively expensive catalyst will be lost if left in suspended NP form. Instead of trying to support colloids onto a suitable support, a more traditional synthesis route may be more appropriate for large-scale manufacture. For example, one can imagine the sequential impregnation and calcination of Au and Pd on a typical catalyst support to try to recreate the Au core-Pd shell characteristics of the colloidal system. With additional research into fabrication of the catalyst, a less complicated, scalable, immobilized, and effective catalyst can be manufactured to treat contaminated areas.

Additionally, different types of groundwater pollutants, where HDC over Pd has shown some effectiveness should be screened, for example, chlorobenzene and chloroform. Such screening could be beneficial to the remediation of multiple contaminants at a single site, and may lead to less expensive all-in-one treatments. Additionally, this could lead to remediation of additional contaminated areas, where chlorinated ethylenes are not the primary component.

The SERS work can also be extended to other water based reactions, for example, the oxidation of glucose over Au, which is also performed under basic
conditions. One may even be able to perform reactions in organic solvents, given that the nanoshell is properly tuned to the solvent’s dielectric and the solvent is weakly Raman active in the region of interest, for example, saturated hydrocarbons such as hexane.

Finally, additional improvements can be made to the analysis chamber used in this study, which can be used for approaching the conditions used in operando spectroscopy (spectroscopic measurements under actual steady-state reaction conditions). Construction of a custom cell with materials which have greater solvent resistance (such as stainless steel) would be beneficial to study of reactions in different media. Additional improvements include the ability to go to higher pressures and temperatures, so as to be able to conduct reactions in harsher conditions. Finally, a flow system should be incorporated, so as to examine surface intermediates under steady-state conditions.