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Improving Palladium Catalysis with Self-Assembled Monolayers

Stephen Todd Marshall
marshast@colorado.edu

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IMPROVING PALLADIUM CATALYSIS WITH SELF-ASSEMBLED MONOLAYERS

by

STEPHEN T. MARSHALL

B.S., Carnegie Mellon University, 2005

A thesis submitted to the
Faculty of the Graduate School of the
University of Colorado in partial fulfillment
of the requirement for the degree of
Doctor of Philosophy
Department of Chemical and Biological Engineering

2010
This thesis entitled:
Improving Palladium Catalysis with Self-Assembled Monolayers
written by Stephen T. Marshall
has been approved for the Department of Chemical and Biological Engineering

______________________________
J. William Medlin

______________________________
John L. Falconer

Date________________________

The final copy of this thesis has been examined by the signatories, and we Find that both the content and the form meet acceptable presentation standards Of scholarly work in the above mentioned discipline.
ABSTRACT

Marshall, Stephen T. (Ph.D., Chemical and Biological Engineering)
Improving Palladium Catalysis with Self-Assembled Monolayers
Thesis directed by Associate Professor J. William Medlin

Improving selectivity in catalytic systems is of primary interest to a number of fields. One means of achieving selectivity is through the use of promoters, or deposited materials that improve catalytic properties. Here, we present the modification of palladium surfaces with self-assembled monolayers (SAMs) formed from thiols.

SAM coatings are employed in two systems: metal-insulator-semiconductor (MIS) sensors and supported palladium catalysts. On MIS sensors, modification with alkanethiol SAMs results in enhanced sensitivity to acetylene. Excellent selectivity for acetylene over ethylene is also observed. The functionalized sensors would serve as excellent acetylene detectors in a variety of applications including the detection of fault gases in transformers and detecting trace acetylene in ethylene production plants. Supported palladium catalysts were modified with SAM coatings for the selective reduction of 1-epoxy-3-butene (EpB) to 1-epoxybutane. Aside from having significant relevance for the production of value added chemicals, this reaction serves as an excellent probe for the conversion of unsaturated oxygenates derived from biomass and it is difficult to achieve high selectivity over conventional catalysts.

Experiments probing the mechanism for the enhancement observed in sensors and catalysts showed increasing order of the SAM coating results in increasing sensor response or catalyst activity. By varying the chemical composition of the thiols used to create SAMs and by
comparing these coatings to surface sulfur, we uncovered that surface sulfur is largely responsible for the enhancement of these devices. However, the hydrocarbon tails of thiols play an important role in controlling surface order.

The reaction of EpB on coated and uncoated palladium surfaces was studied in more detail using temperature programmed desorption and high resolution electron energy loss spectroscopy on model systems in ultra-high vacuum. These experiments showed that on clean palladium, EpB ring opens to form an aldehyde-like intermediate; however, on surfaces coated with SAMs no ring opening is observed. Comparing the desorption energy of EpB to similar molecules suggests it binds through its olefin functionality, and comparing the desorption spectra at different surface coverages on coated surfaces suggests less well-ordered self-assembled monolayers decrease activity by preventing adsorption in active sites.
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Although the title page of this thesis lists me as the sole author, the work presented here was performed with help and advice from a large number of graduate students, undergraduates, and one high school student. All of the members of the Medlin research group have been very helpful and have aided in large amount of this work. April Corpuz performed the DRIFTS experiments and Hans Funke performed the CO chemisorption experiments described in chapter 3. Marykate O’Brien and Brittany Oetter spent long hours working on the catalysis experiments in chapter 3 and debugging an apparatus that I’m sure will be a workhorse for the Medlin group in years to come. Wenyu Zhang is one of the few undergraduates I’ve worked with who showed great proficiency and independence working with UHV systems and helped with a number of the experiments in chapter 4.

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CHAPTER 1

Introduction

“I hence will name it the catalytic force of the substances, and I will name decomposition by this force catalysis. The catalytic force is reflected in the capacity that some substances have, by their mere presence and not by their own reactivity, to awaken activities that are slumbering in molecules at a given temperature.”

- J.J. Berzelius, 1836

In 1962, Julia Child exclaimed to television audiences, “How about dinner in half a minute?” With a few seemingly simple shakes of pan, she produced a voluptuous omelette that salivated beautifully upon being pierced by a fork. Enamored with the prospect of such a decadent meal, I began making omelettes daily shortly after witnessing Child’s masterpiece. Despite the simple ingredients: 2 eggs, a little water, butter, salt, and pepper; making an omelette as appetizing as Child’s took nearly a month of daily practice.

Making a supported metal catalyst is another seemingly simple endeavor: mix metal salts with the rough equivalent of sand or dirt and sufficient amount of water. Add heat and remove the unwanted components of the salt with air or hydrogen, and, voila, a substance is created whose “mere presence” can perform the equivalent of modern alchemy. However, just like Child’s omelette, reality often trumps the simplicity implied by theory. The mystical authority which J.J. Berzelius assigned to catalysts in 1836 provides an excellent framework for appreciating the daunting complexity of heterogeneous catalysts. Indeed, novel catalysts for industrial applications are often convoluted systems with a large number of components, such as Mo$_{12}$BiFe$_2$NiCo$_7$MgSb$_{0.9}$Ti$_{0.1}$Te$_{0.02}$Cs$_{0.4}$O$_x$, an oxidation catalyst. Surface scientists have
quantified with great success the importance of metal attributes such as structure and crystallinity\textsuperscript{4-6}, the combination of metals in bimetallic surfaces\textsuperscript{7-8}, and metal-support interactions\textsuperscript{9-10}; but what occurs above the metal surface between a myriad assortment of adsorbates can have a profound impact on catalyst behavior and is of increasing interest for the understanding of practical systems.

The importance of these adsorbate-adsorbate interactions is widely recognized in non-catalytic systems. A striking example is the formation of self assembled monolayers (SAMs) on metals such as Au, Ag, Cu, and Pd; an area of specific interest for this thesis that will be reviewed in more detail later in this chapter. One type of SAM is composed of alkanethiols, which contain a sulfur “head” group and an alkyl “tail.” As these monolayers are deposited on the metal surface, they form multiple phases characterized by increasing interaction of adsorbates\textsuperscript{11}, as shown in Figure 1-1. The final phase of monolayer formation results in a well-defined crystalline structure\textsuperscript{12-13}. The full monolayer’s geometry is dependent on the interactions of neighboring thiols, and changes to the structure of thiols results in changes to monolayer properties\textsuperscript{12}. Whereas low thiol coverages or disordered monolayers may readily break down on metal surfaces, the fully formed monolayer is more thermally stable and serves as an excellent etch resist\textsuperscript{14-15}. 
Interactions between adsorbates may also result in more subtle changes to surface structure. Relaxations in a metal lattice resulting from nearby metal ad-atoms can affect the adsorptive and diffusive properties of additional ad-atoms\textsuperscript{16}. These effects are elegantly illustrated by the STM imagery of Eigler and coworkers, which demonstrates the effect of

\textbf{Figure 1-1.} Phases observed during the formation of alkanethiol SAMs on fcc(111) surfaces including disordered thiols (top), a striped phase (middle), and a full monolayer (bottom) (hydrogen not shown).
ordered structures of adsorbates on the nearby electronic density through iconic shapes such as the quantum corral and quantum mirage\textsuperscript{17-18}.

To place the goal of studying such effects for catalysis in context, consider the specific interactions that govern the behavior of biological and homogeneous catalysts. To the surface scientist, the mechanisms governing these catalysts represent a lofty goal: specific, tunable interactions between adsorbates (substrates) and moieties near the active site of catalysts that improve selectivity and activity, often in very diverse environments. Such interactions are ubiquitous in enzymes\textsuperscript{19} and have been successfully engineered into homogeneous catalysts through, for example, the modification of porphyrin with aromatic ligands\textsuperscript{20-21}. Recently, manipulation of these interactions has garnered significant interest for the development of “biomimetic” heterogeneous catalysts for a variety of reactions\textsuperscript{22-25}.

This dissertation will present a new type of surface modification that can improve the performance of catalytic sensors and heterogeneous catalysts. Before discussing this modification, the basic concepts and methods underlying this thesis will be discussed and a few areas of specific concern will be reviewed.

1.1 Concepts in heterogeneous catalysis

Although Berzelius’ definition of a catalyst provides a meaningful historical context, it serves as a poor scientific definition of the effect as studied today. A superior definition was given by Ostwald in 1894. He stated a catalyst changes the rate of a reaction without changing the position of the chemical equilibrium\textsuperscript{26}. The rate at which the catalyst enhances reaction is referred to as activity or reactivity. Thus, a catalyst with high activity has a fast rate.
Although catalysts don’t change the position of the chemical equilibrium, many reactions are so slow that a catalyst that enhances only a select subset of possible reactions can produce a pseudo-steady state with only desired products. A catalyst that performs such a function is said to be selective and the ratio of the amount of desired product formed over the total amount of product formed is called selectivity. A catalyst with high selectivity is a prized asset, because such a catalyst can reduce costs associated with buying feedstocks, waste disposal, and separation\textsuperscript{27}. Indeed, some researchers call the development of highly selective catalysts the predominant challenge of catalysis research today, even if such advances cause reduced activity\textsuperscript{28}.

Selectivity can be further characterized by the nature of the reaction. For example, chemoselectivity refers to the preferential reaction of one functional group over another on the same molecule, regioselectivity refers to preferential reaction of one functional group over the same functional group at different locations on the same molecule, and enantioselectivity refers to producing a product with specific chirality\textsuperscript{29}.

Another common definition for catalysts is that they are substances that increase the rate of a chemical reaction without being consumed. Although theoretically sound, this definition ignores a process known as deactivation. All catalysts suffer from reduced activity over time due to a variety of processes including changes in catalyst shape from aggregation of catalyst particles (sintering), the leaching of catalytic material into the reactor effluent, or the adsorption of poisons, which are materials that bind tightly to the catalyst and change its state so that it is no longer active. Poisons are commonly impurities within the reactant feed stream, although similar effects may result from tightly bound species formed from reactants, such as the formation of carbonaceous deposits or coke on alkyne or olefin hydrogenation catalysts\textsuperscript{30}. 
Catalysts are primarily characterized by the phase in which they reside with respect to the reactant phase. When in the same phase as the reactants they are called homogeneous, and in a different phase they are called heterogeneous. The work in this thesis is performed solely with heterogeneous catalysts; however, it is useful here to review a few fundamental concepts of homogeneous catalysts as they illustrate effects that are more obtuse on their heterogeneous counterparts.

The homogeneous catalysts most similar to those used in this work are organometallic transition metal complexes. These complexes consist of a central metal atom or atoms attached to a set of ligands through atoms such as phosphorus or carbon$^{27}$. An example of a transition metal complex is shown in Figure 1-2. This catalyst shows high chemoselectivity for the reduction of unsaturated epoxides$^{31}$. 
Changing the composition and structure of ligands affects the electronic properties of the active metal center and can also sterically hinder the adsorption of undesirable reactants. Different ligands can produce remarkable changes in selectivity. For example, changing the ligands on nickel organometallic complexes results in the formation of a variety of polymerization and cyclic products from butadiene showing different regioselectivity$^{29}$. Unlike their homogeneous counterparts, heterogeneous catalysts exist in a different phase than the reactants. The heterogeneous catalysts used in this work are supported metal catalysts, which consist of small particles of catalytic metal distributed within the pores of a high surface area.

**Figure 1-2.** Example of a homogeneous catalyst consisting of a bi-nuclear palladium complex with phosphine ligands (hydrogen not shown).
area material such as alumina, silica, or carbon. Reactants diffuse through the pores of the support and adsorb on the surface of the metal where reaction takes place.

The presence of the support’s mass transfer barrier and the buried nature of the catalytic material confer significant disadvantages compared to homogeneous catalysts. The well known and precisely engineered structure of homogeneous catalysts produces higher activity (per gram catalyst) and selectivity. The mechanisms by which these catalysts operate are also far better understood\textsuperscript{27,29}. Nevertheless, a majority of industrial processes utilize heterogeneous catalysts over homogeneous catalysts due to their greater stability and ease of recovery\textsuperscript{32}.

Utilizing a support material for heterogeneous catalysts may at first appear detrimental, as it can induce mass transfer barriers. However, placing the catalytic metal in a supporting material rather than using the pure metal offers a few advantages. In the pure metal a large fraction of metal atoms are buried under the catalyst surface and unavailable for reaction. The fraction available on the surface for reaction is commonly referred to as the catalyst dispersion\textsuperscript{32}. The metal loading on supported catalysts is typically less than 10 wt %, and in some cases may be 0.5 wt % or lower\textsuperscript{30}. The low weight loadings of these catalysts present a higher dispersion than pure metal catalysts. A controllable dispersion also enables the user to select catalysts that exhibit crystal planes that show higher activity or selectivity\textsuperscript{33}. Many catalytic metals are expensive and using a support reduces costs associated with procuring these materials. Finally, support materials can interact with the catalytic metal to alter its geometric and electronic structure in favorable ways\textsuperscript{34-36}.

The parameters available to tune catalyst behavior aren’t limited to choice of material and support. Industrial catalysts are commonly employed with a variety of additional species that
modify the surface environment, called promoters\textsuperscript{3,37}. Promoters can be classified into four categories (from reference 32):

- **Structural promoters.** These species modify the metal surface in order to present a desirable crystallinity. Examples include the addition of alumina to iron oxide catalysts for ammonia synthesis or the addition of lead and boron to molybdenum catalysts for hydrotreating and hydrodesulfurization catalysts.

- **Electronic promoters.** These species modify the electronic environment of the metal surface to improve catalyst activity or selectivity. Examples include the addition of potassium oxide to iron oxide catalysts for the synthesis of ammonia and the addition of alkali metals to silver catalysts for epoxidation reactions.

- **Textural promoters.** These species prevent changes to the catalyst structure that can result in deactivation, such as sintering. Examples include the addition of zinc oxide to copper catalysts or rhenium to platinum catalysts for reforming reactions.

- **Poison resistance promoters.** These species reduce the buildup of tightly bound adsorbates that poison the desired reaction. Examples include the addition of potassium oxide to alumina catalysts or the addition of potassium to nickel catalysts for steam reforming.

The structural and electronic effects that result from coadsorbates are of prime interest for this work. The physical origins of the adsorbate-adsorbate interactions created from promoters and other adsorbates can be loosely described by one or more out of six categories: through-surface effects, ensemble effects, surface restructuring, dipole-dipole interactions, non-specific interactions, and molecular recognition:
• **Through-surface effects.** Through-surface effects occur due to a modification of the electronic structure of the metal surface by a coadsorbate. These effects primarily occur by two mechanisms: electron donation or withdrawal from the surface by an adsorbate, particularly an adsorbate that is significantly more electropositive or electronegative than the surface atoms; and redistribution of the density of states of the metal atom\(^{38}\). The latter mechanism results in a change in the \(d\)-band center of the surface metal atoms, which affects the strength of bonds formed between the metal atoms and the adsorbate\(^{39}\). The influence of through-surface effects is similar to the electronic effect of ligands on homogeneous catalysts, so these effects are commonly called “ligand effects.” Unlike some of the effects discussed below, ligand or through-surface effects do not result in direct interactions between adsorbates. One example of these effects is the electron-withdrawing role of Cl in its use as a promoter in ethylene epoxidation reactions\(^{40}\).

• **Ensemble effects.** These effects are also not generally a result of direct interactions between adsorbates, but rather are characterized by an adsorbate changing the size of available clusters of metal atoms so that only certain size clusters are available. Since competing reactions may require different numbers of adjacent metal atoms, these effects can change both catalyst activity and selectivity\(^{41}\). For example, the addition of controlled amounts of gold on a palladium surface has been proposed to create distinct ensembles that improve the rate of formation and the selectivity for vinyl acetate synthesized from acetic acid, ethylene, and oxygen\(^{7,42}\).

• **Surface restructuring.** An adsorbate can produce dramatic changes in the geometric structure of a surface that modifies the reactivity of other adsorbates. Again, direct
interactions between the two adsorbates may not be present and these effects could be considered long range or indirect. Surface restructuring is elegantly illustrated by poisons such as sulfur. When deposited on a palladium surface and heated, sulfur absorbs into the palladium bulk and changes both the geometric and electronic structure of the surface, making it incapable of dissociating hydrogen. These effects result in a change in crystallinity observable using low energy electron diffraction (LEED)\textsuperscript{43}. Similarly, tightly bound oxygen atoms on ruthenium surfaces change the surface structure to more closely resemble an oxide, rendering it active for CO oxidation, whereas more weakly bound oxygen does not\textsuperscript{44}.

- **Dipole-dipole interactions.** Adsorbates can produce charges or electrostatic forces on surfaces that alter the way nearby adsorbates bind. Unlike through-surface effects, these effects are confined to the area near the charge inducing adsorbate. For example, adsorbed cesium promotes the epoxidation of ethylene on silver catalysts by an electrostatic effect that reduces the barrier for epoxidation relative to the competing combustion reaction\textsuperscript{45}. Such effects are also present for processes involving electrochemical reactions, such as at the anode of a proton exchange membrane (PEM) fuel cell. In these systems, the direction of the electric field and the resulting orientation of water molecules can have a stabilizing or destabilizing effect on adsorbed oxygen\textsuperscript{46-47}.

- **Non-specific interactions.** These interactions are characterized by weak, non-covalent interactions between adsorbates that can modify binding energy. Such effects commonly occur at high coverages for adsorbates that would otherwise bind tightly. These interactions are observed in the reactivity of Pt-group metals for several reactions in aqueous solutions including oxygen reduction. In this chemistry, hydrogen bonding
interactions between near-surface water and adsorbed intermediates clearly affect the structure and reactivity of adsorbed intermediates such as molecular oxygen\textsuperscript{47-48}. These effects are also observed for the adsorption of acetate anions on Pd surfaces. Nearby water atoms can stabilize the acetate anion by 57 kJ/mol\textsuperscript{49}. Another excellent example is the hydrogenation of olefins, where ensemble effects coupled with high coverages can cause preferential binding in a more active weakly bound state\textsuperscript{50}. For olefin hydrogenation reactions, this effect may result in rate acceleration as catalysts become more covered with carbonaceous deposits as the reaction proceeds\textsuperscript{41,51}.

- **Molecular recognition.** Adsorbates can contain functional groups that interact with other adsorbates in specific ways that govern binding. These adsorbates provide a chemical “key-hole” which additional adsorbates must fit into. These interactions are non-covalent like van der Waals’ interactions; however, they are grouped differently due to their high degree of specificity. Molecular recognition is most easily recognized in the active site of enzymes in which amino acids near the active site interact with substrate molecules to confer high selectivity\textsuperscript{19}. Similarly, chiral cinchona alkaloids adsorbed on Pt modify the surface environment to create a binding pocket that promotes the asymmetric hydrogenation of α-ketoesters\textsuperscript{25}.

Despite the complex nature of heterogeneous catalysts, catalysis research can provide a wealth of mechanistic information. Aside from quantifying activity and selectivity, one useful tool is the determination of apparent activation energy, which is the enthalpic barrier to reaction. To illustrate how this value is computed, consider a simple reaction A $\rightarrow$ B. First, a mass balance is constructed for the reactor, where $F_{\text{out}}$ is the molar flow of reactant out of the reactor,
$F_{in}$ is the molar flow of reactant into the reactor, $r$ is the rate of production of reactant, and $W$ is the mass of catalyst:

$$F_{out} - F_{in} = \int r dW \quad (1.1.1)$$

The rate of production of reactant is assumed to follow a simple power law, where $k$ is an Arrhenius type prefactor, $[A]$ refers to the concentration of species A (the reactant), and $n$ is the reaction order. The prefactor, $k$, can be expanded into its typical Arrhenius form, where $E_a$ is the apparent activation energy, $R$ is the gas constant, $T$ is the temperature, and $C$ is a constant:

$$r = k[A]^n = C \cdot \exp\left(\frac{-E_a}{RT}\right)[A]^n \quad (1.1.2)$$

If the amount of A reacted is kept small (i.e., a low conversion) and there are no temperature gradients, the rate will constant throughout the reactor, enabling the simplification:

$$F_{out} - F_{in} = r\int dW = rW \quad (1.1.3)$$

$$\frac{F_{out} - F_{in}}{W} = r \quad (1.1.4)$$

Equation (1.1.4) enables the calculation of rate data from experimental measurements. Next, taking the logarithm of equation (1.1.2) gives:

$$\ln(r) = \frac{-E_a}{RT} + \ln(C) + n \cdot \ln([A]) \quad (1.1.5)$$

A plot of $\ln(r)$ versus $-\frac{RT}{1}$ will produce a straight line with a slope equal to the apparent activation barrier. This plot is commonly called an Arrhenius plot and provides
mechanistic information about the surface reaction. The value of apparent activation energy can also reveal mass transfer limitations, as such processes typically have a different temperature dependence than reactions.\(^{52}\)

Developing atomistic detail from catalysis experiments is often difficult, as a large fraction of reactions occur on poorly defined surfaces buried within the pore structure of support. For this reason, model systems consisting of metal single crystals in ultra-high vacuum (UHV) are commonly employed. These systems offer a few key advantages:

- **Uniformity.** Heterogeneous catalysts consist of particles with a variety of crystalline planes. Studying reactions on single crystals enables correlations between activity and underlying metal structure. Single crystals also have a well defined and uniform composition, whereas heterogeneous catalysts may possess modifiers, such as Cl, that are remnants of the preparation process that the user may not be aware of.\(^{33}\)

- **Cleanliness.** Single crystal surfaces can be cleaned and kept clean under ultra-high vacuum conditions (\(\sim 10^{-10}\) torr), which enables the researcher to prepare well-defined structures free of the myriad adsorbates that cover heterogeneous catalysts under operating conditions.\(^{53}\)

- **Accessibility of surface probes.** Although some techniques enable the acquisition of spectroscopic information on heterogeneous catalysts, the accessibility of the metal surface on single crystals generally enables the use of probes with superior resolution. Many powerful electron based techniques, like low energy electron diffraction (LEED) or high resolution electron energy loss spectroscopy (HREELS), will only operate using a flat geometry.\(^{54}\)
Atomistic understanding of processes on single crystal surfaces requires a system for describing the structure of adsorbed molecules. The most commonly used system defines the geometry of adsorbates based on two unit vectors for the surface plane. For the fcc(111) surface shown in Figure 1-3, these vectors are defined as A1 and A2. To describe the overlayer structure on the right side of the figure, two more vectors, B1 and B2, are defined and characterized as a transformation of A1 and A2. B1 and B2 are both \( \sqrt{3} \) times larger than A1 and A2, and they rotated with respect to A1 and A2 by 30°. Thus, this overlayer structure is referred to as \((\sqrt{3}\times\sqrt{3})R30\). A detailed overview of overlayer structure and other examples can be found in reference 55.

**Figure 1-3.** A diagram of vectors used to characterize overlayer structures on single crystal surfaces. The structure shown here is a \((\sqrt{3}\times\sqrt{3})R30\) structure on a fcc(111) surface.
Both ordered and disordered overlayer structures can be characterized by surface coverage. For the (√3x√3)R30 overlayer shown in Figure 1-3, there is one adsorbate atom for every three metal atoms, so the coverage of this structure is 1/3 monolayer or 33%. This nomenclature, although common and useful, is deceptive in that it suggests 100% coverage indicates a completely filled surface. Metal surfaces offer a variety of sites including above surface atoms (atop sites), in between two surface atoms (bridge sites), or in between three surface atoms (hollow sites); so the total number of sites exceeds the number of surface metal atoms. For some adsorbates, such as ethylene on Pt(110), chemisorbed states can be observed above surface coverages of 100% or 1 monolayer.$^{56}$

### 1.2 Metal-insulator-semiconductor sensors

The use of metals to perform useful chemistry extends beyond the fields of heterogeneous and homogeneous catalysis. One area of interest is gas sensing. The ability to selectively detect gases using inexpensive tools is a highly sought after venture. Transformer head spaces, hydrogen fuel cells, and hydrogen plasmas are just a few environments where the detection of hydrogen and hydrogen containing compounds by a robust sensor would be very valuable. Metal-insulator-semiconductor (MIS) sensors represent a potential means to cheaply allow for the real-time detection of these gases. These devices were first discovered in the 1970s and have been the topic of ongoing research today.

MIS sensors consist of a layer of n or p doped silicon and a layer of a catalytic gate metal, such as Pd, Pt, or Ir, separated by a thin (<100nm) layer of silicon dioxide. The sensor gate metal can dissociate hydrogen and hydrogen atoms adsorbed on the surface can diffuse to the
metal-SiO$_2$ interface and cause a shift in the capacitance-voltage (CV) curve for the device. Figures showing this sensing mechanism and the CV curve shift are shown in Figures 1-4 and 1-5. Responses are commonly characterized by measuring the change in voltage required to maintain a constant capacitance at the inflection point of the capacitance voltage curve$^{57}$. Previous work has shown that the change in the CV curve is related to the hydrogen partial pressure for many decades of hydrogen pressure$^{58}$. Due to the high sensitivity of these devices, large surface areas are not required, which makes the use of MIS sensors amenable to gas sensing within small spaces in machinery such as transformers and reactors.

**Figure 1-4.** The commonly accepted sensing mechanism for MIS devices. Hydrogen dissociatively adsorbs on the metal surface and diffuses to the metal-insulator interface where it forms charges. These charges change the capacitance characteristics of the device.
Despite the sensitivity of these devices for hydrogen, numerous drawbacks have prevented their widespread use. First, due to the inaccessibility of the metal-insulator interface, it is difficult to characterize the cause of the CV curve shift. This difficulty has led to the development of vague mechanisms and an inability to apply fundamental knowledge and first principles to improve product design. Numerous theories have been presented, attributing shifts to hydrogen induced dipoles on the insulator$^{59,61}$, hydrogen induced dipoles on the metal$^3$, and even changes in the insulator-semiconductor interface$^{62}$. Nevertheless, the nature of hydrogen

**Figure 1-5.** Capacitance-voltage curve shift observed upon addition of hydrogen to MIS devices. Typically, the voltage at the inflection point of the curve is tracked to produce data in a voltage versus time format.
adsorption states at this interface has never been directly measured. Knowledge of these states would significantly aide in the design of better sensors.

A second drawback is the promiscuousness of the catalytic gate metal. Metals such as Pd and Pt excel at dissociating hydrogen; however, they also excel at catalyzing other reactions. Species such as oxygen, CO, and unsaturated hydrocarbons can react with hydrogen or directly react with the surface to change the response, as shown in Figure 1-6. This action allows for detection of gases other than hydrogen; however, it adds complexity to interpreting sensor response and can mask the presence of hydrogen. In this way, MIS sensors are similar to heterogeneous catalysts and the same notions of activity and selectivity can be applied to sensor response. Many solutions to the problem selectivity have been proposed including the use of thin oxide\textsuperscript{63} and polymer\textsuperscript{64} membranes to filter out the effect of contaminant gases.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1-6}
\caption{Mechanisms by which unsaturated hydrocarbons may affect MIS sensor response. These mechanisms may decrease hydrogen response (remove hydrogen from the metal-insulator interface), or increase hydrogen response (add hydrogen to the metal-insulator interface)}
\end{figure}
1.3 Coverage and the chemistry of olefins and alkynes on platinum group metals

Central to this thesis is the chemistry of hydrogenating carbon-carbon double or triple bonds on the surface of metals such as palladium. The addition of hydrogen to a carbon-carbon bond is a seemingly simple reaction, yet paradigms for understanding the hydrogenation of even the simplest olefins continue to change despite considerable attention\textsuperscript{33}. Why, after nearly 80 years of study\textsuperscript{65}, is a definitive molecular scale mechanism for this reaction still elusive? As discussed below, the answer partly lies in the role of adsorbate-adsorbate interactions in controlling the surface chemistry.

![Proposed mechanisms for the hydrogenation of ethylene on platinum group metals.](image)

**Figure 1-7.** Proposed mechanisms for the hydrogenation of ethylene on platinum group metals. (a) the classic Horiuti-Polanyi mechanism with di-σ bound ethylene, (b) a modified Horiuti-Polanyi mechanism with π-bound ethylene, (c) hydrogen transfer through carbonaceous deposits.

Conventional wisdom long held that ethylene hydrogenation to ethane occurred through the so-called Horiuti-Polayni mechanism\textsuperscript{65} where hydrogen was added stepwise to a di-σ bound intermediate formed from the creation of two metal-carbon bonds. Indeed, on clean Pd(111) and Pt(111) ethylene preferentially adsorbs in this state and forms other more tightly bound spectator species at temperatures above 50 K\textsuperscript{50,66}. Nevertheless, under reaction conditions the catalyst surface is covered with a wide range of species that have a profound impact on ethylene hydrogenation. Numerous previous reports have reviewed the effects of such carbonaceous deposits on the behavior of heterogeneous catalysts\textsuperscript{30,41}, so herein we will focus our discussion.
on surface science techniques used to identify and elucidate properties of adsorbates affected by carbonaceous deposits.

Ethylene hydrogenation reactions exhibit a variety of unusual behaviors that defy explanation by the classical Horiuti-Polanyi mechanism. These behaviors include structure insensitivity, common activation barriers across groups of similar metals, and rate acceleration upon aging. Such behaviors led some researchers to hypothesize that carbonaceous deposits play a critical role the reaction mechanism\textsuperscript{51}. Indeed, microcalorimetry experiments performed for ethylene adsorption on Pt(110) (2x1) by King and coworkers show that such deposits change the binding state of ethylene\textsuperscript{56}. In contrast to more traditional thermal desorption spectroscopies, this method permits the quantification of heats of adsorption of strongly bound species (such as ethylidyne) that will not desorb intact. King and coworkers found as coverage increases, ethylene formed more weakly bound species that required fewer sites. At high coverage (>1 monolayer), ethylene exclusively adsorbed through a π-bound state. Similarly, infrared absorption studies noted the presence of weakly adsorbed π-bound ethylene on Pt(111) at 112 K in a background pressure of $10^3$ Pa. The species was observed even when the crystal was precovered with more tightly bound species such as ethylidyne and di-σ bound ethylene\textsuperscript{67}. These works demonstrated the ability of carbonaceous deposits to affect the ethylene binding state; however, further work was required to determine if the modified state was preferable for hydrogenation reactions.

Making such a determination is difficult, as it requires a surface sensitive analytical technique that can operate under reaction conditions. Luckily, sum frequency generation (SFG), pioneered by Somorjai and coworkers, can satisfy such demands. Unlike previously employed methods, SFG allows for the determination of the vibrational structure of surface adsorbates at
atmospheric pressures without gas phase interference through the combination of two light sources at the metal surface. Under these conditions reaction products can be simultaneously quantified using traditional techniques such as gas chromatography (GC) and compared to observed surface adsorbates. Somorjai and coworkers noted that on a surface precovered with ethylidyne the quantity of di-σ bound ethylene decreased whereas the quantity of π-bound ethylene remained constant. Despite this change the rate of hydrogenation on the surface remained constant. These results strongly suggest that the π-bound species was more active for hydrogenation. In addition, experiments performed dosing ethylene at conditions to produce only the di-σ bound species showed this species is capable of hydrogenating to ethane, but at a slower rate than its pi-bound counterpart.

This work was subsequently confirmed by Neurock and coworkers using density functional theory (DFT) to identify coverage dependent binding states and activation barriers for ethylene on the Pd(111) surface. At low coverage ethylene preferentially adsorbs in a di-σ arrangement and has a high, 88 kJ/mol, activation barrier for hydrogenation to ethane. However, at a high, (√3x√3)R30°, coverage, ethylene is preferentially adsorbed in the more weakly bound π-bound state and has an activation barrier for hydrogenation of 36 kJ/mol, which agrees closely with observed activation barriers on heterogeneous catalysts.

When adsorbate-adsorbate interactions play a dominant role in producing the active state, studying model systems under UHV conditions can be difficult due to the so-called “pressure gap.” The low pressures and exposures commonly used in UHV cannot reproduce the state of the metal surface under realistic operating conditions. UHV studies do have the advantage of being able to isolate adsorbates at low temperatures; however, isolating the π-bound species on platinum group single crystals by dosing only ethylene requires temperatures below 50 K.
which are difficult to achieve. Nevertheless, researchers have discovered the coadsorption of hydrogen or deuterium with olefins preferentially produces the pi-bound state\textsuperscript{66,72-74}. Incidentally, hydrogenation reactions are commonly performed under a large stoichiometric excess of hydrogen\textsuperscript{33}, so this system serves as an excellent model of heterogeneous catalysts. In addition, high pressure studies of ethylene reaction on Pd(111) in excess hydrogen produce similar products and kinetic parameters as supported palladium catalysts\textsuperscript{75}.

The difference in vibrational modes between the di-σ and π-bound species has enabled the differentiation and isolation of these two species in surface science studies. Whereas di-σ bound ethylene on Pd(111) primarily exhibits an intense mode at 1100 cm\textsuperscript{-1}, π-bound ethylene exhibits an intense mode at 935 cm\textsuperscript{-1}, closer to the gas phase value of the CH\textsubscript{2} wagging mode\textsuperscript{72}. When hydrogen is pre-adsorbed on the surface in doses up to 30 L, the ethylene binding state shifts from predominantly di-σ bound to π-bound at sub-ambient temperatures. These changes are also observed using temperature programmed desorption, as the ethylene desorption temperature decreases by approximately 80 K when the surface is pre-covered with hydrogen\textsuperscript{66}.

Similar results are observed for ethyl iodide on Pd(111). This species decomposes on the metal surface to form an ethyl (C\textsubscript{2}H\textsubscript{5}) intermediate which can hydrogenate to form ethane or decompose to ethylene. TPD experiments show on deuterium pre-covered Pd(111), ethyl iodide adsorbed at low temperature rapidly forms ethane by 160 K; however, on the clean surface at low coverage, ethyl iodide preferentially forms ethylene which desorbs at temperatures around 250 K\textsuperscript{74}.

Recent results suggest the mobility of co-adsorbates may play an important role in the hydrogenation of ethylene on surfaces covered with carbonaceous deposits. High pressure STM studies of Pt and Rh surfaces at room temperature reveal a lack of order on ethylene covered
surfaces at room temperature, indicating that carbonaceous adsorbates are highly mobile. When a small amount of carbon monoxide is introduced into these systems, ordered structures appear, indicating the carbonaceous adsorbates are no longer mobile. This change is also accompanied by a reduction in the rate of ethane formation and an increase in the activation energy from 9.6 kcal/mol to 20.2 kcal/mol, the energy required to remove carbon monoxide from a clean Pt(111) surface and restore surface mobility. A similar effect is observed on supported platinum particles. It has been hypothesized that CO poisons ethane production by preventing coadsorbates from moving to make space for incoming reactant molecules. These results explain the enigmatic observation that a surface that is seemingly completely covered with carbonaceous deposits can still be as active for ethylene hydrogenation as a clean surface.

Carbonaceous deposits play similar roles in other chemistries. For example, in the hydrogenation of acetylene to ethylene carbonaceous deposits alter catalyst behavior in ways that may be either favorable or unfavorable. Similar to any catalyst performing hydrocarbon chemistry, acetylene hydrogenation catalysts operate with a large number of carbonaceous deposits on the metal surface. Although the stronger binding of acetylene over ethylene is largely responsible for the observed selectivity in ethylene-rich feed streams, it has been suggested that acetylene binds too tightly to the clean metal surface to be active and a carbonaceous overlayer is necessary for good activity. This assertion is supported by DFT studies which show the presence of carbonaceous deposits can destabilize adsorption by up to 150 kJ/mol.

The role of carbonaceous deposits in altering selectivity is not clear. It is widely accepted that the formation of large amounts of carbon on acetylene hydrogenation catalysts is a deactivation mechanism; however, smaller amounts may improve selectivity. Ponec and
colleagues noted that the formation of carbonaceous deposits on a Pd/SiO$_2$ catalyst simultaneously decreased activity while improving ethylene selectivity. However, when this experiment was performed using a catalyst with a greater number of impurities, ethylene selectivity decreased$^{79}$. Similarly, Monte Carlo modeling of acetylene hydrogenation catalysts in industrial conditions suggests acetylene hydrogenation activity may be either promoted or poisoned by varying the concentration of polymeric carbonaceous deposits$^{81}$. These results suggest adsorbate-adsorbate interactions in this system may be even more complicated than for the hydrogenation of olefins.

1.4 The chemistry of epoxides on transition metal surfaces

Work with heterogeneous catalysts in this dissertation focuses on the conversion of unsaturated epoxides. Although significant conversion of epoxide rings is not observed (nor desired) on the functionalized surfaces presented in this work, it is useful to briefly review this chemistry.

Epoxides can ring open on platinum group metals through the cleavage of a C-O bond. For the unsaturated epoxide, 1-epoxy-3-butene, on Pd and Pt catalysts, primarily the more sterically hindered C-O bond on the 2$^{nd}$ carbon is broken to form aldehydes or primary alcohols$^{82}$. Although never observed spectroscopically, many researchers postulate that this ring opening on Pd and Pt occurs through an oxametallacycle intermediate$^{83-86}$. This intermediate consists of a ring structure formed between one or more metal atoms and the opened epoxide ring. DFT modeling of oxametallacycles suggests these structures are unstable on platinum group metals compared to aldehydes, which are the common products of epoxide ring decomposition$^{87}$. 
Nevertheless, understanding of oxametallacycle chemistry can be gleaned from Ag surfaces, on which these structures are more stable. Silver catalysts are commonly employed in epoxidation reactions of olefins\(^{88,89}\), which has led to a large number of fundamental studies on oxametallacycle intermediates on Ag single crystals. On Ag(110), this ring opening reaction has an activation barrier of 35 kJ/mol\(^{90}\), which is similar to barrier for olefin hydrogenation on platinum group metals\(^{33,51}\). The oxametallacycle intermediate observed in ring opening reactions requires an ensemble of between two and three surface atoms\(^{88}\), which is larger than the ensemble required olefin hydrogenation reactions\(^{50}\). DFT models predict similar ensemble size requirements on metals such as Pt\(^{91}\). While the chemistry of ring opening reactions and oxametallacycle formation on platinum group metals is not well understood, it is clear that epoxide ring opening reactions occur readily and protecting epoxide rings from reaction is a considerable challenge.

### 1.5 The chemistry of self-assembled monolayers

In the work described in the following chapters, self-assembled monolayers are used to functionalize palladium surfaces. Here, we elaborate on the information provided in the beginning of this chapter to briefly explore the history, formation, structure, and characterization of SAMs on metal surfaces.

Although the conceptual framework was developed earlier, pioneering work in the self-assembly of alkanethiols, disulfides, and other molecules was first conducted by Nuzzo and Allara in the 1980s on Au substrates\(^{92-93}\). Gold was chosen due to its ease of preparation and relative inability to decompose the adsorbates; however, subsequent experiments would
demonstrate the ability to form SAMs on a wide variety of surfaces including Ag $^{13,94}$, Cu $^{13}$, Pd $^{12,15}$, and oxides $^{95}$.

SAMs are commonly deposited on surfaces from dilute solutions; however, similar films may be deposited from the vapor phase in UHV systems $^{11,93}$. Typically, the metal substrate is immersed in a dilute, 1-10 mM, solution of thiols and a full SAM will form within 24 h $^{96}$. The simplicity of the deposition process belies a far more complex assembly process at the molecular scale. There is significant disagreement within the literature regarding the details of this process, but for certain aspects a general consensus has been reached. Up to 90% of the initial thiol coverage of a SAM forms within the first few minutes of immersion in solution and the remaining thiols adsorb far more slowly over a period of up to 72 h. Exact time frames for deposition vary between studies and no clear trends with thiol tail functionality have been observed $^{97}$.

The study of film formation from the vapor phase using STM in UHV has provided a wealth of information regarding structures that form during the assembly process. Thiols initially adsorb on the Au(111) surface in disordered structures, then can form the “striped phase” shown in Figure 1-1. More disordered structures may form after the striped phase, after which full, SAM-like structures will form in expanding islands $^{11,98}$. The full SAM structure shows a regular (\sqrt{3}x\sqrt{3})R30 structure on the Au(111) surface.

A majority of studies of SAMs are performed on the (111) crystal plane of fcc metals; however, studies of other planes suggest significant structure sensitivity. SAMs on Au(100) form a c(2x2) structure, which has a higher coverage than its (111) counterpart $^{99}$. Similarly, studies of SAMs gold nanoparticles show thiol coverages greater than 60% $^{14}$, likely due to higher coverage on corner and edge sites, as model studies show sulfur binds more tightly at
these locations. SAM formation can also result in changes to the geometric structure leading to vacancies or reconstructions, and defect sites in the metal lattice can affect the nearby packing structure.

Vibrational spectroscopy has been used extensively to determine the degree of molecular organization with SAMs deposited on Pd, Ag, Cu, and Au. In particular, SAMs exhibit a greater number of gauche defects with increasing disorder, causing the methylene \( \delta^- \) stretching mode to shift from \( \sim 2920 \text{ cm}^{-1} \), a value consistent with crystalline alkanes, to 2928 \text{ cm}^{-1} \), a value consistent with liquid or solution phase alkanes. For alkanethiol SAMs on Pd, longer alkyl tails tend to exhibit greater order. Disordered SAMs may still have the same thiol coverage as their ordered counterparts; however, the orientation of the tails will be different.

1.6 Sulfur as the universal poison… or highly effective promoter

If one were to choose the most famous and feared catalyst poison, the result would undoubtedly be sulfur. In one of the first studies of catalytic phenomena, Michael Faraday identified sulfur’s ability to completely prevent water formation on macroscopic platinum. Subsequent work continued to enhance sulfur’s rotten reputation, and considerable efforts have been made to remove sulfurous species from petroleum feedstocks due to its ability to poison reforming catalysts. Considering this history, coating a catalytic surface with the high concentrations of sulfur present in SAMs seems foolhardy; however, in a few cases, including some bearing resemblance to the chemistry studied in this thesis, sulfur has proved to be a highly effective surface modifier for improved chemoselectivity.
In the mid 1990’s Hutchings and coworkers made a curious discovery: the addition of 1 µL thiophene per 0.1 g of 5 wt% Cu/Al₂O₃ catalyst greatly improves selectivity for the formation of unsaturated alcohols from α-β unsaturated aldehydes such as acrolein and crotonaldehyde. This reaction is of considerable interest due to the difficulty of achieving high selectivity and its value as a probe for other chemistries. Unsaturated aldehydes typically form saturated aldehydes on transition metals, shown in reaction pathway in Figure 1-8. The improvement Hutchings reported varied significantly with the source of sulfur, with thiophene modified catalysts showing the greatest improvement and other sulfur sources, such as SO₂, showing much milder effects. However, reproducing these effects was difficult, as evidenced by the lower selectivities and activities reported by other laboratories.

![Figure 1-8](image)

**Figure 1-8.** Reaction pathways of σ-β unsaturated aldehydes on platinum group metals. Transition metals tend to form saturated aldehydes with greater selectivity than unsaturated alcohols. For crotonaldehyde, R = methyl; for acrolein, R = H.

To understand this unusual behavior, researchers have turned to molecular scale studies of unsaturated aldehyde adsorption on sulfur coated Cu. DFT studies show sulfur produces geometric and electronic effects that vary significantly with coverage. At low coverages,
sulfur causes a distortion in the geometry of the Cu(111) lattice resulting in expansion near the adsorbed S and compression in the neighboring atoms. This effect is coupled with changes in the surface work function and charge that does not vary directly with coverage. These results showed that at low coverage, the Cu(111) surface retains some of its metallic character whereas at higher coverages the character was closer to a non-metal. Similarly, spectroscopic evidence suggests sulfur promotes binding through the formation of Cu$^+$ cations, but can also block hydrocarbon adsorption on more oxidized copper atoms$^{112}$. These results may explain some variation in catalysis results, as sulfur preferentially forms a $(\sqrt{7} \times \sqrt{7})$ R19.1° on the Cu(111) surface which has a high (0.43 ML) coverage resulting from introduction of sulfur into the subsurface$^{113-114}$, whereas at low coverage surface sulfur forms more mobile species$^{115}$.

Sulfur’s promotional effect results in changes in adsorption geometry that increase selectivity. DFT studies of acrolein and crotonaldehyde binding on Cu(111) surfaces show the addition of sulfur increases binding strength of both the aldehyde and olefin functionality of these molecules, and acrolein and crotonaldehyde adsorb close to surface sulfur, where direct interactions are possible$^{116}$. Similarly, sulfur can improve binding of molecules with only olefin functionalities; however, the strength of such binding is highly coverage dependent$^{117}$. Combined spectroscopic and DFT investigations indicate that addition of sulfur also results in tilting the olefin functionality of crotonaldehyde and acrolein away from the surface with respect to the aldehyde functionality, which is more pronounced at lower coverages$^{118-119}$.

The effects observed on copper catalysts are applicable to other systems and chemistries. The use of thiophene to promote chemoselective hydrogenation of unsaturated aldehydes has been reported on Ru$^{120}$ and Au$^{121}$ catalysts. Similarly, the modification of Pd-nanoparticles with thiols can promote the selective hydrogenation of unsaturated oxygenates$^{122}$ and amines$^{123}$.
1.7 Thesis goals

Developing novel catalytic systems for high selectivity applications is in many respects the focus of modern catalysis research. Functionalization with self-assembled monolayers offers an excellent opportunity for catalyst development due to the ease of application of these films, their regular structure, and diverse chemical composition.

The first goal of this thesis is to identify two systems, metal-insulator-semiconductor sensors and supported palladium catalysts, where the use of SAMs can improve performance beyond the capabilities of the bare metal catalyst.

The second goal of this thesis is to uncover details of the fundamental mechanisms by which SAMs improve the performance of catalytic materials. The majority of experiments conducted for this thesis focus on this goal. Although the SAM coated systems tested in this thesis are not optimized, and may show superior performance with further experiments refining sensing or reaction conditions, it is the belief of the author that developing mechanistic understanding of the function of SAMs will provide insight on the future capabilities of these surface modifications outside the limited scope of this thesis and serve as a basis for further research.

1.8 Thesis organization

Below is a brief description of the contents of the remaining chapters of this thesis.
Chapter 2. Selective Acetylene Detection through Surface Modification of Metal-Insulator-Semiconductor Sensors with Alkanethiolate Monolayers

The enhancement of MIS sensors with alkanethiol SAMs for the detection of acetylene over ethylene is described and mechanisms for the observed enhancement are postulated based on experiments performed using a variety of alkanethiols, thiols functionalized with polyethylene-glycol groups, and sensors sulfided with hydrogen sulfide.

Chapter 3. Making Palladium Catalysts Selective using Self-Assembled Monolayers

Supported palladium catalysts are functionalized with both alkanethiol and alcohol-thiol SAMs for the chemoselective conversion of 1-epoxy-3-butene to 1-epoxybutane and 2-butenal to butanal. The SAM coated catalysts are characterized and experiments similar to those performed in chapter 2 are conducted to develop hypotheses for the enhancement.

Chapter 4. Common decomposition pathways of 1-epoxy-3-butene and 2-butenal on Pd(111)

Surface science experiments are presented to understand the interaction of 1-epoxy-3-butene and 2-butenal with the uncoated Pd(111) surface. Results serve as a foundation for understanding the chemistry of these reactants on the SAM coated surface.

Chapter 5. Mechanistic insights into the chemoselective hydrogenation of unsaturated oxygenates on palladium functionalized with self-assembled monolayers

Surface science experiments are presented on a Pd(111) surface functionalized with alkanethiol SAMs to glean fundamental knowledge of the interaction of 1-epoxy-3-butene and 2-
butenal with the SAM coated surface. Hypotheses proposed in chapter 3 are revisited and revised.

Chapter 6. Conclusions and future directions

The work in the previous chapters is summarized and the main results are reviewed. Ideas for expanding this work into other fields of catalysis are proposed and means of overcoming the limitations of SAM coated catalysts identified are addressed.

1.9 References


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CHAPTER 2
Selective Acetylene Detection through Surface Modification of Metal-Insulator-
Semiconductor Sensors with Alkanethiolate Monolayers

Abstract

Palladium based metal-insulator-semiconductor sensors were functionalized with self-assembled monolayer coatings derived from alkanethiols with 6, 12, and 18 carbons. The functionalized sensor showed enhanced response to acetylene in a hydrogen background while showing negligible response to a similar gas, ethylene. The presence of sulfur alone on the surface resulted in a small acetylene response, suggesting that palladium-sulfur bond formation plays a role in the response. However, the response of alkanethiol self-assembled monolayer coated sensors was five times greater, indicating that the alkyl chain also affects acetylene detection.

2.1 Introduction

Functionalization of metal-insulator-semiconductor (MIS) sensors enables the selective detection of many analytes despite the sole ability of hydrogen atoms to directly produce a response in these devices. A common approach for enhancing the selectivity of these sensors, and other metal-oxide-semiconductor capacitor or transistor-like devices, is the application of surface coatings to improve the detection of analytes of interest. Monolayer and thin coatings
that bind through analyte-specific interactions have been exploited in the detection of amines\textsuperscript{1-2} and complex biomolecules such as penicillin and DNA\textsuperscript{3}; however, their utility in modifying the performance of small gas sensors has not been widely studied, likely because of an expected lack of specific interactions. Instead, membrane coatings such as polymers\textsuperscript{4} and metal oxides\textsuperscript{5} have been applied for the specific detection of hydrogen and light gases.

MIS sensors consist of a layer of doped silicon and a layer of a catalytic gate metal separated by a thin (<100 nm) layer of a dielectric. The sensor gate is composed of a metal that can dissociate hydrogen, such as Pd, Pt, or Ir. Hydrogen atoms adsorbed on the surface can diffuse to the metal-insulator interface and cause a shift in the capacitance-voltage (CV) curve of the device which produces a measurable response\textsuperscript{4}. Gas response is determined by measuring the change in voltage (bias) required to maintain a constant capacitance at the inflection point of the CV curve\textsuperscript{4,6}. Previous work has shown that the response scales with the hydrogen partial pressure from the ultra high vacuum range (<10\textsuperscript{-8} torr) to near atmospheric pressures\textsuperscript{6}. Due to the high sensitivity of these devices, large surface areas are not required, which makes the use of MIS sensors applicable to gas detection within small spaces in machinery such as transformers and reactors.

Here, we focus on the selective detection of acetylene in a hydrogen background. The detection of acetylene in hydrogen containing environments is important in many applications including the detection of fault gases in transformers\textsuperscript{4} and in ethylene streams for polyethylene production\textsuperscript{7}. In this chapter, we report the enhancement of acetylene selectivity on MIS devices coated with a self-assembled monolayer (SAM) film derived from alkanethiols and discuss possible mechanisms for this enhanced response.
2.2 Experimental methods

Sensor Fabrication. Devices used in this study were fabricated at the Compound Semiconductor Research Laboratory at Sandia National Laboratories in New Mexico. The devices consisted of an n-Si base (1-100 ohm-cm), 50 nm of thermally grown SiO$_2$, and 50 nm of Pd deposited through electron beam evaporation. Chromium-gold ohmic contacts were adhered to both sides of the sensors to improve signal quality. This fabrication technique yielded a device structure similar to previous work$^4$.

SAM Deposition. The SAM deposition protocol was based on a method reported in a previous study of alkanethiol SAMs on Pd$^8$. The sensors were first cleaned in alternating baths of water and detergent (Electron Microscope Sciences Micro 90, 2% in water) followed by rinsing in isopropanol (Fischer Scientific, 99.9%) and alternating baths of acetone (Fischer Scientific, 99.5%) and toluene (Fischer Scientific, 99.9%). Next, the sensors were placed in a UV-ozone cleaner (Boekel model 135500) for 20 min. The clean sensors were then placed in a 10 mM solution of hexanethiol (C$_6$SH), dodecanethiol (C$_{12}$SH), or octadecanethiol (C$_{18}$SH) (all thiols from Fluka, >95%) in ethanol (Sigma Aldrich, 200 proof) and the solution was purged with nitrogen (Airgas, ultra-high purity). Polyethylene glycol (PEG)-containing SAMs were deposited by placing the sensor in a solution of 10 mM HS(C$_2$H$_4$O)$_{113}$CH$_3$ (synthesized in house) in 95% ethanol (5% water) (Sigma Aldrich) and purging with nitrogen (Airgas, ultra-high purity). The sensors were allowed to remain in the thiol solutions for 24 h before being rinsed with ethanol (Sigma Aldrich, 200 proof) and tested.

To verify the quality of the SAM coatings, advancing water contact angles were measured before testing with analyte gases. Although deposition procedures for alkanethiol SAMs are well-established, it is nevertheless well-known that subtle differences in conditions
can result in significant variability of SAM formation kinetics or even final SAM quality. For this reason, as described in more detail below, multiple samples were prepared and evaluated for each alkanethiol studied in this work, and advancing water contact angle was employed as a measure of relative coverage. Evaluation of absolute alkanethiolate coverage is in practice difficult, though previous studies of similar monolayers on Pd surfaces have estimated that formation of a full monolayer corresponds to a coverage near 0.33 monolayers. The maximum contact angle observed in the present studies was 102°, which is ca. 10° below values measured in previous studies of model surfaces, but still indicates a highly hydrophobic surface. The average receding water contact angle was ca. 14° smaller than the advancing angle, consistent with a significant degree of roughness in the monolayer surface, likely associated with grain boundaries and defects on the Pd surface.

Since SAM coatings on Pd are known to oxidize over a period of days at room temperature, care was taken to minimize exposure to air by acquiring water contact angles and placing the coated sensor in the testing apparatus immediately upon removal from the thiol solution. Typical exposure times for sensors to air did not exceed 20 min.

Surfaces coated with atomic sulfur were fabricated by exposing the sensor to 100 ppm H₂S in nitrogen (Airgas) until equilibration of the sensor response (~2 hrs). Since H₂S dissociates on the palladium surface, leaving surface hydrogen and sulfur, the change in sensor response is a measure of the extent of sulfur dosing.

**Flow Cell Testing.** Sensors were fixed in a system described elsewhere and connected to a capacitance meter (Boonton). Changes in the CV curve of the sensor were measured by recording the voltage required to maintain the capacitance at the inflection point of the CV curve. The system was heated through a combination of a conductive button heater (Heatwave Labs
Inc.) located underneath the sensor and heating tape (Omega Engineering) wrapped around the system. The temperature of the sensor was measured by a thermocouple fixed to the sample holder. The sensor was first exposed to 500 ppm H$_2$ in N$_2$ at a flow rate of 400 sccm. After reaching equilibrium, the system was exposed to varying doses of dilute acetylene or ethylene in nitrogen. For testing of SAM coated sensors with varying tail lengths and functionalities, devices coated with each SAM tail functionality were exposed to 20, 100, and 400 ppm acetylene in the hydrogen / nitrogen background at 50°C. Each experiment was repeated three times using separate devices. For acetylene / ethylene selectivity studies, devices were exposed to three repeated doses of 100 ppm acetylene followed by three repeated doses of 100 ppm ethylene in the hydrogen / nitrogen background at 25, 50, 75, and 100°C. Response in every case was evaluated by taking the difference between the steady state bias after acetylene or ethylene exposure and before acetylene or ethylene exposure. Error was computed by taking a standard deviation of computed values. In all cases, the acetylene or ethylene was removed after exposure to demonstrate a return to the original hydrogen response. This final step is important to distinguish real response from a well known drift problem where the CV curve can shift up to 10 mV/hr$^{12}$. The total flow rate was kept constant to prevent background hydrogen from having an effect on the response. All gases were ultra high purity and obtained from Airgas.

2.3 Results and discussion

Figure 2-1 shows representative responses of C$_{18}$ SAM coated and uncoated sensors to doses of 100, 400, and 20 ppm acetylene in a background of 500 ppm hydrogen in nitrogen at 50°C. This concentration range (including the hydrogen concentration) is important for detection
of acetylene in fault gas analysis of electrical transformers, and the selected sequence shows the effect of both increasing and decreasing concentration. These results demonstrate an increase in acetylene response from no statistically significant response in the uncoated sensor to a significant response that varies with acetylene concentration in the C$_{18}$ SAM coated sensor. The SAM coated sensor also shows a reduced apparent response to hydrogen, which we attribute to the well known poisoning effect of sulfur on surface reactions and the reduced number density of vacant adsorption sites due to the monolayer coating.
The response of an MIS sensor is directly attributable to the steady-state hydrogen concentration in the device; hence the apparent response to acetylene represents an indirect effect due to a change in the atomic hydrogen concentration at the metal surface and metal-insulator interface. The response to acetylene in the opposite direction of the hydrogen response suggests that acetylene consumes hydrogen through a surface hydrogenation reaction, which lowers the steady state concentration of interfacial hydrogen. A decrease in hydrogen response according to this mechanism is well-known for reactive gases such as $O_2$, and Pd is known to be an active catalyst for acetylene hydrogenation. It is important to note that while Pd is capable of catalyzing the hydrogenation of acetylene, our results suggest that acetylene hydrogenation does not occur at a sufficiently rapid rate on the uncoated devices to alter hydrogen absorption into sensing sites.

The increase in acetylene response on SAM coated sensors indicates the relative enhancement of one or more processes in the acetylene hydrogenation mechanism with respect to hydrogen uptake. One possibility for the increased response is that the adsorption of acetylene is enhanced with respect to that of hydrogen on the monolayer-coated sensor, so that the rate of acetylene hydrogenation relative to the rate of hydrogen absorption into the device increases. Another possibility for the enhanced response is that the presence of the sulfur based species, while likely poisoning both acetylene and hydrogen reactions on the Pd surface, has a larger negative effect on hydrogen uptake than acetylene hydrogenation, enhancing the relative rate of acetylene hydrogenation with respect hydrogen absorption and promoting response. We are
unaware of any previous studies in the literature which are consistent with such an effect; however, studies of catalytic reactions on surfaces highly covered by SAMs are rare.

Previous investigators have noted that alkanethiol monolayers on Pd are oxidized during room-temperature exposure to air over a period of several days, altering the surface functionality through formation of surface sulfates and sulfites\textsuperscript{8}. To test the effect of surface oxidation, the C\textsubscript{18} SAM coated sensor was also exposed to simulated air (20\% O\textsubscript{2} in a N\textsubscript{2} background, Airgas, not shown above) at 50\(^\circ\)C. Following equilibration under this mixture, the oxygen was removed and the sensor was allowed to re-equilibrate before being retested as above. Sensor response to 100 ppm acetylene after exposure to oxygen decreased by 75 percent. Sensor response was not further tested in oxygen containing environments, since significant quantities of oxygen are not present in the desired transforming fault gas application and because of the greatly reduced response\textsuperscript{4}. However, the results do suggest that air exposure should be minimized in any application of these sensors.

Also tested was the effect of varying hydrogen concentration on the coated sensor response to 100 ppm acetylene (not shown). No response was observed without hydrogen present; however, responses were statistically invariant for hydrogen concentrations ranging from 50 to 500 ppm. The insensitivity of the response to hydrogen partial pressure in this range makes the device amenable to use in environments such as transformers\textsuperscript{4}, where background hydrogen may vary between environments although not significantly over time. In applications where hydrogen pressures are more variable, an acetylene-insensitive (uncoated) sensor could potentially be employed together with a SAM-coated sensor in an array.

One question of fundamental interest is whether the increase in acetylene response is due to the interactions of acetylene with the hydrocarbon tail of the SAM, or to changes in sensor
surface chemistry. It is relatively straightforward and a common practice, for example, to decrease the length of the hydrocarbon tail to probe the effect of monolayer thickness. We compared response trends of alkanethiol-coated sensors of variable tail length (C₆, C₁₂, and C₁₈). These three lengths are a representative subset of alkanethiol SAMs previously reported on Pd⁸. Furthermore, in an attempt to approximate a “zero” tail length, response was also characterized for sensors exposed to H₂S. H₂S dissociates on the sensor surface, leaving only sulfur, which, although known to adsorb through a different process than alkanethiol SAMs on other surfaces¹⁵, provides some indication of the effect of surface sulfur itself on the process. Previous work has shown sulfur deposited through H₂S can form a maximum coverage of 0.33 monolayers on Pd(111)¹¹, which is similar to coverages reported for alkanethiol SAMs on polycrystalline substrates⁸. All sensors were tested in the same manner as the initial C₁₈ alkanethiol SAM tests.

![Figure 2-2](image.png)

**Figure 2-2.** Representative response data for C₁₈, C₁₂, C₆, and PEG thiol SAMs to acetylene. a: added 100 ppm acetylene; b: increased acetylene concentration to 400 ppm; c: decreased acetylene concentration to 20 ppm; d: removed acetylene. Data collected at 50°C in a background of 500 ppm H₂.
Figures 2-2 and 2-3 show response-time data and average responses to acetylene, respectively, for the H$_2$S and thiol coated sensors grouped by tail length. Note that the time zero point in Figure 2-2 is for a sensor that has already been equilibrated in hydrogen. Also shown are results for a sensor coated with a thiol containing 113 polyethylene glycol (PEG) units. The PEG-SAM created a highly hydrophilic surface (advancing water contact angle of 11°) with the same palladium-sulfur linkage as in the hydrophobic alkanethiol SAMs. The results in Figure 2-3 are for average responses of three devices for each sensor type having different advancing water contact angles (sulfur coverages). The total coverage is highly sensitive to small variations in preparation conditions, and cannot be assumed to be constant$^{16}$. However, for the data shown in Figure 2-3, the average advancing contact angle is indistinguishable among the three alkanethiol tail lengths (96±2° for C$_6$ thiols, 95±5° for C$_{12}$ thiols, and 95±1° for C$_{18}$ thiols). As shown by the figure, the different alkanethiol tail lengths result in indistinguishable response levels. The response of the PEG-SAM coated sensor was significant—possibly indicating that hydrophobicity itself is not paramount in achieving enhanced response to acetylene—but approximately a factor of two smaller than that of the alkanethiol coated sensors. Response on the PEG-SAM coated sensor was also sluggish and thus difficult to measure reproducibly, likely because of the slow diffusion of acetylene across the relatively thick film$^4$. The response noted in the H$_2$S coated case indicated that palladium-sulfur bonds do result in a small sensitivity to acetylene, reduced by a factor of 5–10 relative to the alkanethiol-coated sensors.
Since the advancing water contact angle did not vary with alkanethiol tail length and tail length had negligible impact on response, the responses for the alkanethiol SAMs can be plotted as a function of contact angle to show the effect of coverage. Figure 2-4 shows these data for responses to 20, 100, and 400 ppm acetylene. This result demonstrates that increasing thiol coverage (as measured by increasing hydrophobicity) leads to greater response.

**Figure 2-3.** Effect of tail length on acetylene response for SAM coated sensors in a background of 500 ppm H₂. (white: 20 ppm, light gray: 100 ppm, dark gray: 400 ppm)
Due to the difficulty of measuring acetylene adsorption on a SAM coated surface, reasons for the large apparent differences between alkanethiol and PEG-thiol SAM coated sensors and atomic S-coated surfaces remain unclear. One explanation for these results is that the presence of alkyl or PEG pendant groups changes the surface sulfur coverage relative to H$_2$S treated surfaces, because the attractive van der Waals forces between tail groups offset repulsive interactions between sulfur atoms, or enables the formation of structures such as disulfides$^{16}$. In this mechanism, differences in interactions between alkanethiol and PEG tails would lead to the noted differences in response between these two sensor types. Another possibility, however, is that the presence of tail groups in the near surface region create an environment within which the adsorption of acetylene in enhanced. The reduction in response after oxidizing adsorbed

Figure 2-4. Effect of advancing water contact angle on response of alkanethiol SAM coated sensors exposed to 20 ppm (triangles), 100 ppm (circles), and 400 ppm (squares) acetylene in a hydrogen background (symbols are larger than error bars). Note that the data in the figure are reported for nine total tests of separately prepared devices, consisting of three separate device preparations (and subsequent tests) using C$_6$, C$_{12}$, and C$_{18}$ thiols. (See methods section for details.)
alkanethiols, and thus removing tail groups, supports this possible mechanism. In this mechanism, differences in acetylene interaction with the hydrophilic PEG groups and the hydrophobic alkane groups would lead to the noted differences in response between these two sensor types. Nevertheless, further experimentation, likely on model surfaces, will be required to more clearly elucidate the mechanism for enhanced response. Studies in which the analytes, surface composition, and SAM functionality are varied may also help in developing an improved understanding of the effect of SAMs observed in this work.

One area of interest for any sensor technology is selectivity for an analyte over other analytes with similar properties. For an acetylene detector, selective detection for acetylene over ethylene is often desired for catalytic acetylene hydrogenation\(^7\) or in the fault gases of transformers\(^4\). Representative data for acetylene and ethylene testing in a hydrogen background are shown in Figure 2-5 for a C\(_{18}\) alkanethiol SAM coated sensor at 50\(^\circ\)C. The average sensor responses for this sensor type to three repeated exposures of 100 ppm acetylene or ethylene in a hydrogen background at different temperatures are shown in Figure 2-6. These data indicate that the SAM coated sensor achieves excellent selectivity for acetylene over ethylene in a hydrogen background at 50\(^\circ\)C. No response to 100 ppm acetylene or ethylene was noted in the absence of hydrogen.
The acetylene selectivity is not unexpected, as palladium catalysts have long been known to show excellent selectivity for acetylene hydrogenation over ethylene hydrogenation in industrial processes\textsuperscript{14}. Interestingly, the activity and selectivity for acetylene hydrogenation on supported Pd catalysts has been found to be partly determined by the coverage of a carbonaceous layer that accumulates under operating conditions on the surface. It has been suggested that this carbonaceous layer functions by modifying the active site environment at the Pd surface to (in some cases) favor reaction of acetylene\textsuperscript{17-18}. Although the present study is focused on hydrocarbon functionalities bound to the surface through a sulfur atom, a similar phenomenon—the modification of active sites by a layer that in other contexts could be considered a catalyst poison—may be responsible for the observed sensing behavior.
The acetylene response appears to go through a maximum between 50 and 75°C. Reasons for this maximum are not clear, although it may result from changes in either SAM chemistry or surface reaction chemistry. It has long been known that SAMs of alkanethiols formed on gold will restructure below 100°C through a chain melting effect\(^{19}\). Reflectance absorbance infrared spectroscopy studies of alkanethiol SAMs on Au(111) have revealed a low-temperature process (below 75°C) where the alkyl tails take on a more vertical alignment: the angle that the tails form with respect to the surface normal is reduced by \(\sim 10^\circ\)\(^{20}\). This effect may change the impact of the alkyl tail on acetylene binding and thus potentially alter reactivity. In addition, above 75°C significant disorder is noted in the alkyl tail\(^{20}\) which could further alter...

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**Figure 2-6.** Average responses of a C\(_{18}\) alkanethiol SAM coated Sensor to 100 ppm acetylene (gray) and 100 ppm ethylene (white) in a background of 500 ppm hydrogen at 25, 50, 75, and 100°C.
sensitivity. Finally, adsorption, reaction, and diffusion steps within the hydrogen sensing and acetylene reaction mechanisms are temperature-dependent. Since the activation barriers associated with each of these mechanisms are not equal\textsuperscript{13,21-22}, altering temperature will alter the relative rates of these processes and thus the sensitivity to acetylene. It is difficult to predict the direction of temperature effects on relative rates because of the unknown barriers for the surface reactions on SAM coated surfaces. However, similar effects of temperature on sensor response have been demonstrated in micro-kinetic models of the impact of oxygen on hydrogen response\textsuperscript{22}.

### 2.4 Conclusions

Acetylene response in a hydrogen background has been introduced into metal-insulator-semiconductor gas sensors by the incorporation of a self assembled monolayer (SAM) coating. Whereas an uncoated sensor shows virtually no response to acetylene, the SAM coated sensor shows a response that increases with increasing gas phase acetylene concentration and SAM coverage. Unlike previous coating strategies for light gases which relied on membrane-like coatings, this SAM coating functions by altering the sensor surface in a way favorable for acetylene detection. In addition, the sensor shows excellent selectivity for acetylene over ethylene at 50°C. Thus, this work suggests SAM coatings may enable the creation of a highly selective acetylene detector in hydrogen containing environments.

### 2.5 References


22 Fogelberg, J., Eriksson, M., Dannetun, H. & Petersson, L. G. Kinetic modeling of hydrogen adsorption/absorption in thin-films on hydrogen-sensitive field-effect devices -
CHAPTER 3

Making palladium catalysts selective using self-assembled monolayers

3.1 Abstract

The selective reaction of one part of a bifunctional molecule is a fundamental challenge in heterogeneous catalysis and a critically important task for many processes including the conversion of biomass-derived intermediates. Selective hydrogenation of unsaturated epoxides to saturated epoxides is particularly difficult given the reactivity of the strained epoxide ring, and traditional platinum group catalysts show low selectivity for these reactions. We describe a new approach for the preparation of highly selective Pd catalysts involving the deposition of n-alkanethiol self-assembled monolayer (SAM) coatings. These coatings improve the selectivity of 1-epoxybutane formation from 1-epoxy-3-butene on palladium catalysts from 11% to as high as 94% at equivalent reaction conditions and conversions. Although sulfur species are generally considered to be indiscriminant catalyst poisons, we find that the reaction rate to the desired product on a catalyst coated with a thiol containing an 18 carbon aliphatic tail was 40% of the rate on an uncoated catalyst. Interestingly the activity decreased for catalysts coated with less ordered SAMs having shorter chains. The behavior of SAM-coated catalysts was compared to catalysts where surface sites were modified by carbon monoxide, hydrocarbons, or sulfur atoms. The results suggest that the SAMs restrict sulfur coverage to enhance selectivity without significantly poisoning the activity of the desired reaction.
3.2 Introduction

Heterogeneous catalysts are widely used in industrial processes due to their stability and ease of catalyst recovery compared to their homogeneous counterparts. However, the promiscuity of these catalysts commonly leads to low selectivity, which increases costs of product purification and waste. In contrast to their heterogeneous counterparts, biological and synthetic homogeneous catalysts commonly achieve high selectivity through specific non-covalent or steric interactions between functional groups on the catalyst and reactant. For example, enzymes are able to achieve excellent selectivity through selective interactions between a reactant and amino acid residues near the active site. Similarly, synthetic homogeneous catalysts engineered through the modification of porphyrin with aromatic ligands are highly selective for chiral epoxidation and reactions of proteins and aromatics. Although heterogeneous catalysts modified with chiral organic ligands are employed to enable selective asymmetric hydrogenation, analogous modifiers for chemoselective reactivity have not been identified.

The hydrogenation of unsaturated epoxides is one class of reactions where identifying such modifiers would prove valuable. These molecules are useful model compounds for a growing feedstock of unsaturated oxygenates that are derived from biomass. In addition, a model unsaturated epoxide reactant, 1-epoxy-3-butene (EpB), can be cheaply and selectively produced from butadiene on supported silver catalysts. EpB contains two functional groups, a C-O-C epoxide ring and a C=C double bond. Selective hydrogenation of the double bond produces epoxybutane, a valuable commodity chemical used in the manufacture of polyethers, surfactants, glycols, polyesters, epoxy resins, and fuel additives. However, EpB forms many products with hydrogen, as demonstrated in Figure 3-1, and selective hydrogenation of the
double bond is difficult. Surface science studies show that EpB forms strongly bound intermediates on Pd(111) through facile epoxide ring opening to form an aldehyde intermediate\textsuperscript{11}. Unlike other metals such as Ag\textsuperscript{12}, Pd causes irreversible ring opening. Reacting EpB with hydrogen on supported Pd and Pt catalysts yields epoxybutane with a selectivity of less than 20\% at temperatures above ambient and conversions greater than 5\%\textsuperscript{13}.

Here, we modified conventional Pd/Al\textsubscript{2}O\textsubscript{3} catalysts with alkanethiol coatings. When deposited on a metal surface from a dilute solution, these thiols spontaneously arrange to form a self-assembled monolayer (SAM)\textsuperscript{14}. The thiol species typically form a commensurate epitaxial layer like the (√3x√3)R30 structure of n-alkanethiol SAMs (in this case propanethiol) on Pd(111) surfaces shown in Figure 2. Thiol monolayers consist of a sulfur atom “head” with a hydrocarbon “tail”, which can comprise a number of functionalities such as alkanes, alkenes,

**Figure 3-1.** Reaction pathways of 1-epoxy-3-butene on platinum metal catalysts. Achieving selectivity to epoxybutane is a considerable challenge.
alcohols, acids, amines, and aromatics. Herein, we show that surface modification with alkanethiols can be used to produce a well-defined near-surface environment that alters reactivity for multifunctional compounds.

### Figure 3-2. Models of a propanethiol SAM on Pd(111). The left model shows the surface arrangement of sulfur atoms (small spheres) in a (√3x√3)R30 structure on palladium surface (large spheres). Hydrocarbon tails (cylinders) are tilted away from the surface normal. The right model shows a top down view using space filling rendering, which shows the viewer the free sites between thiol adsorbates available for reaction.

### 3.3 Experimental methods

**Materials.** 5 wt% Pd/Al₂O₃, 1-Propanethiol, 1-hexanethiol, 1-dodecanethiol, 1-octadecanethiol, 1-dodecene, 1-hexene, crotonaldehyde (2-buten-1-al, 97%), and 200 proof HPLC grade ethanol were obtained from Sigma Aldrich. All thiol and alkene purities were greater than 97%. 1-Epoxy-3-butene (EpB, >98%) was obtained from Alfa Aesar and all gasses were ultra high purity and were obtained from Airgas.

**Preparation and Characterization of Catalysts.** Prior to thiol deposition and/or testing, 7.0 mg (uncoated case) or 50.0 mg (coated cases) of 5% Pd/Al₂O₃ catalyst diluted to 300mg with Al₂O₃ was packed into a glass reactor tube and cleaned by oxidation at 573 K in 20% oxygen for 2 hrs. The catalyst was then reduced at 473 K in 20% hydrogen for greater than 2 h and cooled to room temperature in an inert flow of He. Thiol coatings were deposited by immersing the packed catalyst bed at room temperature in 10 mM ethanolic solutions of
propanethiol, hexanethiol, or dodecanethiol or 1 mM ethanolic solutions of octadecanethiol for 24 hrs, except where specified otherwise. The coated catalyst was dried in an inert flow of nitrogen or helium for at least 12 h before being tested. Sulfur coated catalysts were prepared by exposing 50.0 mg of 5% Pd/Al₂Ο₃ catalyst packed in a glass reactor tube to 1000 ppm H₂S in N₂ at a flow rate of 200 sccm for varying amounts of time and then purging with N₂. The catalysts aged in alkenes were prepared by exposing 50.0 mg of 5% Pd/Al₂Ο₃ catalyst to a flow of helium with 1% propylene or 1-hexene or 0.1% 1-dodecene for 4 h at 373 K.

Coated and uncoated catalysts were characterized using diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) to collect spectra in the C-H stretching region (2800 cm⁻¹ to 3000 cm⁻¹) using a Thermo Nicolet 6700 FTIR. DRIFT spectra were corrected by subtracting a background spectrum of oxidized and reduced 5% Pd/Al₂Ο₃ catalyst and adjusting for baseline drift. A resolution of 4 cm⁻¹ was used.

Carbon monoxide chemisorption (Quantachrome Autosorb-1) was also utilized to characterize the surface area of exposed Pd on the coated and uncoated catalyst. We measured a metal surface area using carbon monoxide (CO) chemisorption of 4 m²/g on the uncoated catalyst that dropped to 0.2 m²/g after coating with hexanethiol, indicating 94% of the metal surface was modified by the adsorbed thiol. The palladium metal dispersion was 20 % and the average metal particle diameter (assuming a spherical shape) was 7 nm.

**Catalytic Tests.** Reaction products were quantified using a gas chromatograph (HP5890) equipped with a flame ionization detector, a Poraplot-Q capillary column (Varian), and peak simple software (SRI). The packed catalysts were exposed to a feed stream with a 10:1 H₂ to EpB ratio, produced by entraining EpB in a He flow at 298 K with a bubbler. A constant feed flow rate of 25 sccm for thiol and sulfur coated catalysts was chosen to produce 5 ± 2% conversion of EpB unless otherwise noted. Reactions were conducted at 313, 323, and 333 K by
heating the glass reactor tubes in a temperature-controlled clamshell style furnace. Selectivities were calculated by dividing the conversion to one product by the total EpB conversion. Turnover frequencies were calculated based on the number surface area of the uncoated catalyst. This method does not account for reductions in the number of active sites resulting from the thiol coating or carbonaceous deposits and may underestimate the true turnover frequency.

Experiments testing crotonaldehyde hydrogenation were conducted similarly using a 25:1 H₂ to crotonaldehyde feed ratio and 1 gram of uncoated or hexanethiol coated 5% Pd/Al₂O₃ catalyst at 313 K.

**Temperature Programmed Desorption (TPD) Experiments.** TPD experiments were conducted in an ultra high vacuum chamber with a base pressure of ~10⁻¹⁰ torr (10⁻⁸ Pa). This system is described in detail elsewhere. The system was equipped with a Smart-IQ+ quadrupole mass spectrometer (VG Scienza) and a model NGI3000-SE sputter gun for cleaning (LK Technologies). EpB and epoxybutane were dosed in equivalent quantities to the hexanethiol SAM coated Pd(111) sample at 100 K using a direct dosing line facing the sample. Similar doses produced a coverage on clean Pd(111) of approximately 0.1 monolayer in previous work. Cooling below ambient temperature was accomplished through a liquid nitrogen reservoir located in thermal contact with the sample. Experiments were conducted by heating the sample at a constant rate of 1 K/s until the sample reached 323 K.

The Pd(111) crystal (Princeton Scientific) was cleaned primarily through cycles of cooling and heating in 5x10⁻⁸ torr O₂ (7x10⁻⁶ Pa) between 400 K and 1000 K prior to hexanethiol SAM deposition. When this cleaning method was insufficient, mild sputtering with Ar⁺ ions (1-3 keV) and annealing was utilized. Temperature was measured using a thermocouple welded next to the crystal on a copper sample stage. The hexanethiol SAM was deposited by removing the clean Pd(111) crystal from vacuum and placing it in a 10 mM solution of hexanethiol in
ethanol for 12 hrs. The crystal was then removed from the solution and rinsed with ethanol. Before being reinserted into the vacuum chamber, the quality of the coating was evaluated by measure the advancing contact angle of water using goniometry. Previous work shows surface hydrophobicity correlates well with SAM quality\(^\text{16}\). For the hexanethiol SAM coated Pd(111) surface used in these studies, an advancing contact angle of 120° was acquired, indicating a high-quality SAM similar to those observed on polycrystalline palladium\(^\text{14}\).

### 3.4 Results and discussion

Figure 3-3 summarizes the effectiveness of alkanethiol SAMs on conventional Pd/Al\(_2\)O\(_3\) catalysts in enhancing selective EpB reduction to epoxybutane. Alkanethiol coatings with varying tail lengths were evaluated and characterized including propanethiol (C3), hexanethiol (C6), dodecanethiol (C12), and octadecanethiol (C18). On uncoated palladium catalysts, selectivity for epoxybutane at 313 K was 11% at 5% EpB conversion, consistent with previous studies\(^\text{13}\). After applying the alkanethiol coatings, the selectivity for epoxybutane increased to 80–94% at the same conversion depending on thiol tail length and terminal group, as shown in Figure 3-3. On the coated catalysts, crotonaldehyde was the major byproduct (3-15%), with butyraldehyde and alcohols as minor products (< 2% each). The uncoated catalyst primarily produced crotonaldehyde (36%), alcohols (44%), and butyraldehyde (7%) along with small amounts of deoxygenation and decarbonylation products in addition to epoxybutane.
Experiments were also conducted varying the amount of catalyst (up to 200 mg) and the total feed flow rate to evaluate selectivity as a function of EpB conversion for the uncoated and octadecanethiol coated catalysts at 313 K. Whereas selectivity on the uncoated catalyst exhibited a maximum of 31 ± 3% at less than 1% EpB conversion and decreased to 8 ± 2% at between 99 and 100% EpB conversion, selectivity on the C18 coated catalyst was greater than 99% at less than 1% conversion, and 53 ± 2% at between 99 and 100% conversion.

As shown in Figure 3-3, the activity of the SAM-coated catalysts (displayed as apparent turnover frequency) decreased relative to the uncoated catalyst, and increased significantly with

**Figure 3-3.** Selectivity and turnover frequency for epoxybutane formation on uncoated 5% Pd/Al₂O₃ and 5% Pd/Al₂O₃ coated with SAMs of alkanethiols. A decrease in activity was observed upon coating; however, selectivity to epoxybutane increased dramatically. (C18: 1-octadecanethiol, C12: 1-dodecanethiol, C6: 1-hexanethiol, C3: 1-propanethiol, C6OH: 1-mercapto-6-hexanol, C3OH: 1-mercapto-3-propanol, TG: thioglycerol)
increasing thiol tail length despite the increasing thickness of the monolayer film above the active surface. The most active SAM-coated catalyst, C18, exhibited epoxybutane formation rates that were approximately 40% of the rate for the uncoated catalyst. Each experiment was conducted over a period of up to 12 hrs, during which no deactivation was observed. Experiments conducted at 323 and 333 K showed similar trends as the results in Figure 3-3.

Taken together, the data in Figure 3-3 suggest that while the identity of the moiety attached to the thiol group (i.e., the so-called tail group) is a major determinant of the activity of the modified catalyst, the selectivity is essentially independent of the tail group identity, and is therefore likely to be due to the arrangement of the sulfur atoms. This conjecture is supported by additional experiments we performed in which the catalyst was coated with SAMs comprised of hydroxy-terminated C3 and C6 alkanethiols (C3OH, C6OH) and thioglycerol (TG). Although the activity associated with monolayers produced from the hydroxylated thiolates varied significantly, as shown in Figure 3-3, the selectivity was again high. These results are examined in more detail below.

Vibrational spectroscopy has been used extensively to determine the degree of molecular organization with SAMs deposited on Pd\textsuperscript{14}, Ag\textsuperscript{17}, Cu\textsuperscript{17}, and Au\textsuperscript{17,18,19,20}. In particular, SAMs exhibit a greater number of gauche defects with increasing disorder, causing the methylene $d^-$ stretching mode to shift from $\sim$2920 cm\textsuperscript{-1}, a value consistent with crystalline alkanes, to 2928 cm\textsuperscript{-1}, a value consistent with liquid or solution phase alkanes\textsuperscript{18}. Diffuse reflectance infrared Fourier transform (DRIFT) spectra of the alkanethiol coated catalysts deposited from 10 mM ethanolic solutions are shown in Figure 3-4, and peak assignments are shown in Table 3-1. For the C3 coated catalyst, the methylene $d^-$ stretching mode was observed at 2929 cm\textsuperscript{-1}, indicating the thiol tails were highly disordered and in a liquid-like state. On the C6 and C12 coated catalysts this mode was observed at 2925 and 2923 cm\textsuperscript{-1} respectively, indicating more ordered monolayers.
The C18 coated catalyst exhibited this mode at 2921 cm$^{-1}$, consistent with an ordered SAM on polycrystalline palladium$^{14}$. The correlation between alkyl chain order and catalytic activity is striking, and suggests that within the homologous series of alkanethiols, coatings with greater molecular order have higher activity compared to less well-ordered coatings.

**Figure 3-4.** DRIFT Spectra for alkanethiol SAMs on 5% Pd/Al$_2$O$_3$. The position of methylene d$^\prime$ stretch is annotated for each coating and the position of this stretch in a well-ordered SAM is indicated by the dashed line. (C18: 1-octadecanethiol, C12: 1-dodecanethiol, C6: 1-hexanethiol, C3: 1-propanethiol)
Table 3-1. Peak positions for observed vibrational modes of thiol coatings on 5% Pd/Al₂O₃ and modes observed previously on polycrystalline substrates. (C18 SAM: previously observed 1-octadecanethiol SAM on polycrystalline Pd, C3: 1-propanethiol, C6: 1-hexanethiol, C12: 1-dodecanethiol, C18: 1-octadecanethiol)

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<tr>
<th>Mode</th>
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<th>C6</th>
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Quantifying reaction rates at different temperatures enables the determination of apparent activation energies. Apparent activation energies for olefin hydrogenation reactions are generally found to be 33–42 kJ/mol on a variety of metals with different electronic and geometric structures[1,21]. Values outside this range indicate a change in the reaction mechanism for hydrogenation or a change in the rate determining step, such as the desorption of tightly bound CO to make space for the reactant[22] or mass transfer limitations[1,23]. Experimental values for activation energy were 41 ± 3, 42 ± 3, 41 ± 4, and 39 ± 2 kJ/mol for the C3, C6, C12, and C18 coated catalysts respectively. These values indicate thiol coated catalysts appear to behave similarly to their traditional metal counterparts and likely share a similar olefin hydrogenation mechanism. In addition, these results suggest that the presence of the SAM does not induce a significant mass transfer barrier for the diffusion of EpB through the SAM coating to the metal surface.

The contrast between the uniformly high epoxybutane selectivity for all the alkanethiol coatings and the activity varying with tail length suggests differing mechanisms for the effect of
the SAMs on selectivity and activity. One possible mechanism by which SAMs may enhance selectivity is through site blocking to control ensemble sizes. Surface modification to control metal ensemble size is a common and effective practice to improve selectivity in a variety of systems, such as the synthesis of vinyl acetate on Pd-Au bimetallic catalysts\textsuperscript{24}. To determine if ensemble effects alone may be responsible for the enhanced selectivity of thiol coated catalysts, EpB hydrogenation experiments were conducted using a feed containing a variable amount of CO. Unlike sulfur, CO primarily blocks olefin hydrogenation sites without significantly impacting electronic structure\textsuperscript{22}. Therefore, varying CO exposure probes the impact of ensemble sizes and adsorbate mobility. In addition, at coverages up to 1/3 of a monolayer, CO adsorbs in a $(\sqrt{3} \times \sqrt{3})R30$ structure on Pd(111) hollow sites\textsuperscript{25}, which is the same structure observed for hexanethiol SAMs on Au(111)\textsuperscript{26}.

Selectivity and activity for epoxybutane formation were evaluated for CO concentrations up to 3500 ppm, at which point the catalyst activity became negligible. A modest, approximately linear, increase in selectivity to epoxybutane with CO concentration was observed, with a maximum selectivity of only \(~30\%\) when the surface was nearly saturated with CO. As the catalyst approached saturation, the reaction rate dropped suddenly at 2500 ppm CO. This step change is similar to the step change observed in activation barrier by Somorjai and coworkers for CO poisoning of ethylene hydrogenation on Pt(111) surfaces\textsuperscript{27}. A plot of these data is shown in Figure 3-5. Since the observed maximum in selectivity closely matches the selectivity of the palladium catalyst at low conversion (31 \(\pm\) 3\%), it is clear that ensemble effects alone do not play a critical role in the observed selectivity enhancement.
Because the molecular structure of the alkanethiol, rather than its function as merely a site blocking agent, appears to be key to the observation of high selectivity, we conducted experiments that independently examined the effects of the two component parts of the alkanethiol: the sulfur head group and the alkyl tail group. It is noted that separation of the two components is not rigorously possible, since they do not operate independently in formation of

Figure 3-5. Epoxybutane selectivity and EpB conversion versus concentration of CO in the reactant feed for a clean 5% Pd/Al₂O₃ catalyst. CO adsorbs onto Pd in a similar structure as SAMs, but it produces negligible electronic and geometric changes. Thus, CO serves as an excellent probe of ensemble effects for the enhanced selectivity observed with SAMs.
SAMs. However, such experiments provide key insights into the mechanism for the high selectivity provided by the SAM coatings.

To investigate the effect of the head group, we exposed the uncoated catalyst to 1000 ppm H$_2$S in nitrogen for periods between 5 s and 2 h at room temperature and then purged the residual H$_2$S in an inert nitrogen atmosphere. H$_2$S dissociates on Pd and can form ordered structures similar to SAMs$^{28}$, so it serves as a means of evaluating the effect of surface sulfur without the presence of a thiol tail. Figure 3-6 shows that the selectivity was enhanced at low sulfur exposures; however, larger exposures resulted in nearly complete deactivation. The gradual decrease in selectivity and activity with exposure may result from the formation of sub-surface sulfur, which can poison hydrogen adsorption$^{28}$. The epoxybutane formation rate on the sulfided catalysts was at best 31% of the rate observed on octadecanethiol coated catalysts and only slightly higher than the rate observed on propanethiol coated catalysts.
The impact of the alkyl tail without surface sulfur was evaluated by exposing the palladium catalyst to alkenes to produce a metal surface containing substantial coverages of alkylidyne (-C-(CH$_2$)$_n$-CH$_3$) species. Alkanethiols in SAMs adsorb on the (111) crystal plane of fcc metals in the same (√3x√3)R30 geometry$^{26}$ as alkylidynes such as ethylidyne$^{29}$. In addition, the potential energy surfaces for alkanethiols$^{30}$ and ethylidyne$^{31}$ diffusing on fcc(111) metals are similar, indicating that these adsorbates have similar mobilities at low coverage. Therefore, we aged the palladium catalyst in dilute propylene, 1-hexene, or 1-dodecene to produce catalysts

Figure 3-6. Epoxybutane selectivity and turnover frequency as a function of H$_2$S exposure on uncoated 5% Pd/Al$_2$O$_3$ catalysts. H$_2$S decomposes on the surface to form surface sulfur in a similar structure to SAMs at low coverage, so it serves as a probe of the effect of surface sulfur in SAMs on catalyst behavior.
with alkylidyne structures similar to SAMs. Catalysts aged in propylene or 1-hexene showed similar activities and selectivities for epoxybutane formation as the uncoated catalyst; however, unlike the uncoated catalyst, only trace (<1%) alcohols were produced. Thus, co-coverage of shorter-chain alkylidyynes does modify the selectivity, but not in the desired manner. The catalyst aged in 1-dodecene had an epoxybutane formation rate of $0.13 \pm 0.02 \text{ mol g}^{-1} \text{ s}^{-1}$, intermediate to the C6 and C12 alkanethiol SAM catalysts, and a selectivity of $65 \pm 5\%$.

DRIFT spectra for the alkene aged catalysts, shown in Figure 3-7, reveal the presence of disordered alkylidyynes in each case, indicated by asymmetric methylene stretching modes at 2935 and 2965 cm$^{-1}$, which were previously reported after 1-hexene adsorption on Ru(0001)$^{32}$. The 1-dodecene aged catalyst differs from its shorter counterparts due to the prevalence of an additional mode at 2860 cm$^{-1}$, which is consistent with carbonaceous deposits observed from exposure to alkynes such as acetylene$^{33}$ or hexyne$^{34}$. This mode is also present in the propylene and 1-hexene aged catalysts as a shoulder to the methyl stretching mode at 2800 cm$^{-1}$; however, it is less intense. These results indicate alkylidyynes cannot produce the same selectivity enhancement observed for SAMs and the observed enhancement for the 1-dodecene case likely results from the formation of significant amounts of carbonaceous deposits in larger, less mobile structures than surface alkylidyynes or alkanethiol SAMs.
Cumulatively, the results above suggest that the sulfur head group of the alkanethiol SAMs is most likely to be responsible for the high selectivity for epoxybutane formation, since high selectivity is observed for all tail lengths and atomic sulfur deposited on the surface, but is not observed after deposition of surface CO or alkylidyne. Previous studies show the effect of surface sulfur can change both geometric and electronic structure of platinum group metals\textsuperscript{35}. Geometric effects alter the crystallinity of the underlying surface, which may reduce the activity of reactions requiring multiple metal atoms and tightly bound intermediates, such as epoxide.

Figure 3-7. DRIFT spectra of 5% Pd/Al\textsubscript{2}O\textsubscript{3} catalysts aged in 1-dodecene, 1-hexene, or propylene to produce alkylidyne. Peaks in the speak show evidence of these species in each case; however, for 1-dodecene, a significant peak at 2860 cm\textsuperscript{-1} appeared indicating the presence of more tightly bound carbonaceous deposits.
hydrogenolysis. Electronic effects that may occur from surface sulfur have been observed for the synthesis of vinyl acetate on palladium. At high coverage, lateral interactions and electron withdrawing effects destabilize adsorbates, favoring bond making reactions over bond breaking reactions, which require more tightly bound species. Identical adsorbate-adsorbate interactions have been demonstrated using DFT for single atom adsorbates such as oxygen, so it is likely adsorbed sulfur could perform a similar function. Unlike the uncoated catalyst, the SAM coated catalysts did not effectively catalyze the hydrogenolysis of EpB to form alcohols or the formation of deoxygenation or decarbonylation products, possibly due to the destabilization of the tightly bound intermediate required for break a C-O or C-C bond. Also, the isomerization of the epoxide ring to an aldehyde, which is usually facile on transition metal surfaces, exhibited a high activation barrier of $65 \pm 4$ kJ/mol on the C18 SAM coated catalyst.

This mechanism for SAM enhanced selectivity (i.e., the destabilization of adsorbates to favor bond-making over bond-breaking) is supported by temperature programmed desorption (TPD) studies on single crystal Pd surfaces, which will be briefly overviewed here and discussed in more detail in the following chapters. We found that EpB adsorbed on uncoated Pd(111) through its olefin function and underwent irreversible epoxide ring opening at temperatures below 200 K, consistent with a low energy barrier for epoxide ring opening. This reaction was confirmed by the observation that no desorption of intact EpB was detected as the temperature was increased. However, on Pd(111) coated with a C6 SAM, intact EpB was observed to desorb at 260 K, suggesting that the barrier for epoxide ring-opening was increased significantly in the presence of the SAM. In addition, the saturated analog, epoxybutane, desorbed at 190 K, suggesting epoxide interactions with the surface are significantly destabilized. The presence of the SAM did not appear to limit EpB adsorption to Pd via the olefin moiety since EpB was observed to desorb at a temperature similar to that observed for ethylene and propylene on
Figure 3-8. TPD spectra for moderate doses of EpB and epoxybutane adsorbed onto C6 SAM coated Pd(111) in ultra-high vacuum. Unlike clean surfaces, the epoxide ring of these two species did not open on the SAM coated surface.

Pd(111) was used for TPD experiments in this work, and this crystal plane is most commonly used when characterizing SAMs. Although the low dispersion of the catalyst employed in this study ensures that a large fraction of the surface will consist of this crystal
plane, the supported Pd catalyst does not present a purely (111) surface, but rather many surface facets. These additional facets predominantly include (100) surface facets and corner and edge sites. Studies of SAMs on Au(100) suggest the formation of a c(2x2) structure, which has a higher coverage than its (111) counterpart. Similarly, studies of SAMs gold nanoparticles show thiol coverages greater than 60%, likely due to higher coverage on corner and edge sites, as model studies show sulfur binds more tightly at these locations. Thus, the precise ensemble of metal sites left available for reaction by the SAM will differ on the different facets of the crystal, and SAM coated catalysts are likely sensitive to dispersion. Ongoing investigations of the role of Pd particle morphology can shed further light on the role of crystallite morphology.

Although the sulfur head group of alkanethiol SAMs appears to control selectivity modification, the tail groups do appear to have an influence on activity. Figure 3-3 and the DRIFTS results show that longer, more ordered tails have the highest activity. The decrease in activity with decreasing order does not appear to result from mass transfer limitations through the tail; such effects would result in a decrease in apparent activation energy. Instead, we propose that disordered tails reduce activity in the near surface region through one of two possible mechanisms. Disordered tails can physically block access to active sites or reduce the mobility of adsorbed thiols. Such a blockage would result in the identical (within experimental uncertainty) activation barriers and product distributions observed for each tail length. It is also possible that disordered tails may increase the entropic barrier to adsorption, which would also leave the activation barrier for epoxybutane formation unchanged; however, all reaction pathways would have to be affected equally to retain the same product distribution. Differences in activity between metals that exhibit identical activation barriers for olefin hydrogenation reactions are commonly attributed to such entropic effects. Regardless, the significant reaction rates observed even for relatively long SAM tails suggest the potential to use a wide variety of
complex SAM structures, even those that significantly crowd the surface, to modify selectivity of supported metal catalysts.

The results for EpB are supported by similar experiments performed using an α-β unsaturated aldehyde, crotonaldehyde (2-buten-1-al). Experiments testing crotonaldehyde hydrogenation at 313 K on a C6 thiol coated catalyst showed 100% selectivity for butyraldehyde, the product formed by reduction of the C=C double bond. Although achieving high selectivity for this reaction is facile on Pd catalysts\textsuperscript{44}, the thiol coated catalyst continued to achieve 100% selectivity for butyraldehyde regardless of conversion or reactor residence time, whereas the uncoated catalyst produced 1-butanol at high conversions and residence times. This result indicates selectivity promotion with thiol SAMs and supported catalysts may be applicable to a variety of reactions of importance with similar reaction pathways, such as the selective hydrogenation of a double bond over other functional groups including aldehydes, acids, nitriles, or alkynes.

Since surface sulfur is primarily responsible for enhanced selectivity and disordered thiol tails can reduce activity, it is reasonable to conclude that exposure to alternate forms of sulfiding could be superior to SAMs. However, SAMs provide significant advantages over more traditional means of sulfur exposure. Despite the prominent influence of sulfur on the enhanced selectivity, catalysts sulfided by exposure to dilute H\textsubscript{2}S or sulfur containing molecules that can easily crack, such as thiophene, are not the same as catalysts with alkanethiol SAM coatings. Surface sulfur forms a wide variety of structures on Pd that can hinder hydrogenation. Similar to alkanethiol SAMS, the (√3x√3)R30 geometry of adsorbed sulfur is observed on Pd(111); however, the (√7x√7)R19 geometry is also observed and preferentially forms in ultra high vacuum on Pd(111) after annealing above 400 K\textsuperscript{45}. Temperature programmed desorption experiments show the latter structure prevents the dissociative adsorption of hydrogen and
effectively poisons the catalyst, likely through the formation of subsurface sulfur, which changes both the geometric and electronic structure of the surface\textsuperscript{28}. Although the deposition of alkanethiol SAMs does result in some surface sulfur through S-C bond cracking, depth profiling Auger electron spectroscopy experiments have shown this sulfur does not measurably penetrate into the bulk\textsuperscript{14} and is thus less likely to poison hydrogen dissociation than surface sulfur. It is worth noting that surface restructuring effects caused by deposition of alkanethiols—as has been shown for the “herringbone” reconstruction of the Au(111) surface\textsuperscript{46}—may have some influence on the observed reactivity, but such restructuring effects are expected to be far more subtle than is observed following extensive sulfidation by H\textsubscript{2}S. Therefore, alkanethiol coatings provide a facile method of restricting sulfur coverage to the more favorable (\(\sqrt{3}\times\sqrt{3}\))R30 geometry on fcc(111) surfaces, preventing such deleterious effects. These effects manifest themselves in the facile deposition method for SAMs, unlike the comparatively difficult procedure for depositing controlled quantities of surface sulfur, which in this work produced an inferior result.

3.5 Conclusions

In summary, the selective hydrogenation of unsaturated epoxides such as EpB is a considerable challenge on traditional supported metal catalysts. Unlike uncoated palladium catalysts that showed selectivities to epoxybutane at 313 K of 11\%, coated catalysts greatly improved selectivity to up to 94\% at the same EpB conversion. Mechanistic studies suggested the enhancement in selectivity was caused by metal-sulfur interactions and the thiol tail controlled sulfur coverage and improved activity over systems using only sulfur. This work shows that the precise control of surface structure by well-organized alkanethiol self-assembled monolayer coatings can dramatically improve the catalytic selectivity of hydrogenation reactions,
and that the reactivity of these SAM-modified catalysts is sensitive to subtle differences in the molecular organization within the molecular layer.

3.6 References


CHAPTER 4
Common decomposition pathways of 1-epoxy-3-butene and 2-butenal on Pd(111)

4.1 Abstract

High resolution electron energy loss spectroscopy (HREELS) and temperature programmed desorption (TPD) were employed to study the decomposition of 1-epoxy-3-butene (EpB) and 2-butenal (crotonaldehyde, CrHO) on Pd(111). HREELS investigations indicate that both EpB and CrHO decompose through a common surface aldehyde intermediate that is distinct from molecular CrHO. The surface aldehyde intermediate decomposes to yield the gas phase decarbonylation products CO and propylene, as well as H₂. Comparison with previous studies suggests that Pd is unique compared to previously-studied surfaces in its reactivity with EpB and CrHO.

4.2 Introduction

As stated in the previous chapters, improving selectivity in reactions of unsaturated oxygenates represents a major challenge in heterogeneous catalysis. Selective hydrogenation of either the olefin or oxygenate functions of 1-epoxy-3-butene (EpB)\textsuperscript{1-2} or 2-butenal (crotonaldehyde, CrHO)\textsuperscript{3-5} yields value-added products (saturated oxygenates or unsaturated alcohols, respectively). However, achieving high selectivity to a particular product is a significant challenge, especially given that a number of competing hydrogenation and
isomerization reactions can occur\textsuperscript{2}. One strategy for improving selectivity in these reactions is to design catalysts such that the primary surface-adsorbate interaction is with one of the key functional groups, whereas the other functional group remains unbound and thus less prone to reaction. For example, in hydrogenation of EpB to 1-epoxybutane, a catalyst that preferentially binds EpB through the olefin function is hypothetically desired.

Bimetallic PtAg catalysts have recently been reported to be highly active and selective for hydrogenation of EpB to 1-epoxybutane\textsuperscript{6}. In a recent contribution, this improved performance has been attributed to a bifunctional mechanism in which the olefin function binds to the reactive Pt surface, whereas the oxygenate function preferentially binds to Ag, which is much less reactive for hydrogenation\textsuperscript{7}. Despite the promise of the PtAg catalysts, there is considerable room for improvement in reaction selectivity, and improved catalysts for other high-value products such as unsaturated alcohols also need to be identified. One interesting recent report explored the hydrogenation of EpB on PdCu catalysts, and found that the selectivity for unsaturated oxygenated products (including alcohols) dramatically increased as small amounts of Cu were added to a Pd catalyst\textsuperscript{8}. The identification of mechanisms by which these catalysts—or other catalysts explored for hydrogenation of functional epoxides and aldehydes—promote selectivity requires a detailed understanding of how unsaturated oxygenates interact with key metal surfaces.

The adsorption and reaction of EpB has been previously explored on Ag(110) and Pt(111) surfaces. On Ag(110), EpB undergoes activated ring opening to produce a surface oxametallacycle intermediate; this intermediate can react at ca. 500 K to produce EpB and 2,5-dihydrofuran\textsuperscript{9}. In contrast, epoxide ring opening of EpB on Pt(111) is accompanied by C-H bond dissociation so that a surface aldehyde intermediate is formed\textsuperscript{7}. While there are some commonalities in the structures of the aldehyde intermediates derived from EpB and CrHO
adsorption on Pt(111), the structures exhibit clear differences as indicated by numerous discrepancies in their vibrational spectra. Both EpB and CrHO ultimately proceed through a decarbonylation pathway on Pt(111), yielding propylene, CO, and hydrogen as the only desorbing products. An interesting observation for the EpB- and CrHO-derived aldehyde intermediates is that both exhibit a highly intense C-O stretching vibration that is not detectably redshifted relative to unbound CrHO, suggesting a relatively weak surface-aldehyde interaction\(^\text{10}\). This result is somewhat unexpected, since previous studies of unsaturated oxygenates such as acrolein have generally shown strong interactions between the aldehyde and Pt group metal surfaces\(^\text{11-14}\). Crotonaldehyde adsorption has also been studied on PtSn bimetallic surfaces, which show improved selectivity for carbonyl hydrogenation\(^\text{15-16}\).

To understand the interaction of unsaturated oxygenates with clean surfaces, here we explore the adsorption and decomposition of EpB and CrHO on Pd(111) using high resolution electron energy loss spectroscopy (HREELS) and temperature programmed desorption (TPD). These studies reveal that EpB and CrHO go through nearly identical decomposition channels on Pd(111), in contrast to Pt(111) where differences in both HREEL and TPD spectra of intermediate structures are apparent. As on Pt(111), CO, hydrogen, and propylene are detected as desorbing products, though at some coverages small amounts of additional C\(_4\) products are detected. In comparison with studies of EpB and CrHO chemistry on other surfaces, these results suggest that EpB and CrHO interact with Pd(111) in a markedly different way than the C\(_3\) unsaturated oxygenate acrolein. This work provides a foundation for work in following chapter examining self-assembled monolayer coated surfaces.

**4.3 Experimental methods**
All experiments were conducted in one of two ultra-high vacuum chambers described in detail elsewhere\textsuperscript{16}. High resolution electron energy loss spectroscopy (HREELS) experiments were conducted in a stainless steel ultra-high vacuum chamber with an LK3000 high resolution electron energy loss spectrometer (LK technologies) and a model 981-2046 sputter gun for cleaning (Varian). All HREELS experiments were conducted at a specular angle of $60^\circ$ with respect to the surface normal and beam energy of 6.32eV. Thermal chemistry experiments with HREELS were conducted by raising the temperature of the sample to 190, 250, and 350K for two minutes each and taking scans in between each increment. The sample was allowed to cool following each temperature increase. All HREEL spectra were normalized to the elastic peak height to enable objective comparison. Temperature programmed desorption (TPD) experiments were conducted in a separate chamber equipped with a Smart-IQ+ quadrupole mass spectrometer (VG Scienta) and a model NGI3000-SE sputter gun for cleaning (LK Technologies). Cracking patterns for all relevant species were obtained by backfilling the TPD chamber to a pressure of approximately $10^{-8}$ torr ($10^{-6}$ Pa). In both chambers, EpB and crotonaldehyde were dosed to the sample using a direct dosing line facing the sample except where specified otherwise. The coverages of EpB and CrHO that underwent decarbonylation to CO and other products were determined by integration of the CO desorption peak at 485 K and comparison to the area of the CO desorption peak for a 3L (0.67ML, saturation\textsuperscript{17}) dose of CO applied to a clean surface. Cooling below room temperature was accomplished through a liquid nitrogen reservoir located in thermal contact with the sample. Both chambers had a base pressure of $\sim 10^{-10}$ torr ($10^{-8}$ Pa).

The Pd(111) crystal (Princeton Scientific) was cleaned primarily through cycles of cooling and heating in $5 \times 10^{-8}$ torr O\textsubscript{2} ($7 \times 10^{-6}$ Pa) between 400K and 1000K for TPD experiments. When this cleaning method was insufficient, mild sputtering with Ar\textsuperscript{+} ions (1-3 keV) and annealing was utilized. In HREELS experiments, sputtering, annealing, and oxygen
treatments were used for each cleaning cycle. The Pd(111) crystal was mounted on a 1.5mm tantalum disc and held onto a copper stage within each chamber using two metal clips. In the TPD chamber, temperature was measured using a thermocouple welded to the tantalum disc. In the HREELS chamber, temperature was measured by a thermocouple within the copper stage.

EpB and trans-crotonaldehyde were obtained at 98% purity from Sigma-Aldrich and purified using repeated freeze-pump-thaw cycles. Ultra-high purity H₂ and O₂ were obtained from Matheson Trigas. Ultra-high purity CO and Ar were obtained from Airgas.

4.4 Results and discussion

TPD experiments were conducted after various exposures of EpB at 173 K. Figure 4-1 shows a summary of the desorption spectrum at moderate exposure. The dominant desorption products are CO and hydrogen, consistent with decarbonylation and dehydrogenation pathways. Propylene (m/z=41), the expected decarbonylation product for the C₄H₆O EpB molecule, is also detected at 315 K, although with significantly less intensity than CO or hydrogen. Though there is also a peak in the m/z=41 trace at 245 K, small differences in the intensities of other masses, particularly m/z=29, indicate that this peak is attributable to 1-butene and smaller quantities of 1,3-butadiene rather than propylene. It is noted that 1-butene has been observed to form from hydrogenation of 1,3-butadiene near 230 K in previous work on Pd(111), indicating that the detected butylene may arise from surface hydrogenation of 1,3-butadiene¹⁸. The simultaneous desorption of significant quantities of other C₄ hydrocarbons and oxygenates such as butylene oxide, butanal, or CrHO was ruled out based on the measured fragmentation patterns of those compounds.
Figure 4A2 shows similar TPD spectra for a moderate exposure of CrHO adsorbed at 173K. Hydrogen and CO features in these spectra are similar to Figure 4A1: hydrogen desorbs in three peaks at 325, 410, and 500K and CO desorbs at 485K. There are subtle differences, however. The m/z=41 trace is broader and less distinct for CrHO compared to EpB, so that individual peaks become more difficult to detect. The very broad peak centered near 375 K is attributed to propylene based on alignment of numerous m/z traces with the fragmentation pattern for propylene. The low temperature peak near 220 K originates from unreacted CrHO, and the additional broad peak in the 41 signal at 480K is attributed to desorption of CrHO from the sample mount.

Figure 4-1. Example TPD Spectra for EpB adsorbed on Pd(111) at 173 K. Reported spectra are for a direct dose that led to desorption of 0.17 ML CO.
Figures 4A3 and 4A4 show several key desorption spectra as a function of CO desorption yield for EpB and CrHO respectively. CO yield was employed as a measure of the coverage of surface species that undergo decarbonylation, since each molecule of EpB and CrHO that undergoes decarbonylation will produce one molecule of CO. Saturation CO desorption yields were significantly higher for CrHO than EpB. For both species at low exposures, only hydrogen and CO are observed to desorb from the surface during TPD. The production of hydrocarbon products becomes detectable only at higher exposures, consistent with previous studies of EpB thermal chemistry on Pt(111)\textsuperscript{7}. At the very high direct exposures used to generate saturation EpB coverages (top trace in Figure 4-3), large amount of EpB were observed to desorb from the sample mount, resulting in the initially high values of the m/z=28 and m/z=41 traces.

Figure 4-2. Example TPD Spectra for CrHO adsorbed on Pd(111) at 173 K. Reported spectra are for a direct dose that led to desorption of 0.41 ML CO.
Figure 4-3. Effect of increasing EpB exposure on m/z=(a) 2, (b) 28, and (c) 41 traces. Doses were performed at 173 K, and CO desorption yields in ML corresponding to each spectrum are reported.
The hydrogen desorption spectra evolve dramatically upon increasing exposure. For EpB (Figure 4-3), a second hydrogen desorption peak initially appears at 366K (0.037ML dose) and

Figure 4-4. Effect of increasing CrHO exposure on m/z = (a) 2, (b) 28, and (c) 41 traces. Doses were performed at 173 K, and CO desorption yields in ML corresponding to each spectrum are reported.
shifts to a maximum of 423K (0.260ML dose). A third peak evolves with the second peak at a relatively constant temperature of 500K. Similar, though not identical, results are observed for CrHO (Figure 4-4). These results indicate that C-H scission on surface intermediates becomes more activated as surface coverage is increased; this observation is again consistent with studies of similar chemistry on Pt(111)\(^7\).

For both EpB and CrHO, low temperature peaks before 200K were observed at higher exposures (not shown in figures). The distribution of masses in these peaks corresponds to the desorption of EpB and CrHO from multilayers adsorbed to the sample and sample holder.

To summarize the TPD results, both EpB and CrHO are observed to undergo decarbonylation and dehydrogenation to form H\(_2\) and CO as volatile products. In addition, propylene is produced as a volatile product at higher exposures of both compounds, although the desorption temperature differs. Butylene and 1,3-butadiene are observed after higher EpB exposures, indicating some direct abstraction of the oxygen atom, though desorption of these species occurs by 250 K.

HREELS experiments were conducted to probe the surface chemistry of EpB and CrHO on Pd(111) as a function of temperature and exposure. Figure 4-5 shows an overview of the thermal chemistry for a surface pre-covered by a large direct dose of EpB equivalent to the largest observed dose in the TPD experiments, which yielded a coverage of 0.26 monolayers. In the corresponding TPD spectra, multilayer desorption was noted below 200K, so Figure 4-5(a) represents a multilayer HREEL spectrum. Major features in this spectrum are noted in Table 4-1. Frequency assignments were made based on previous studies of EpB, CrHO, and other relevant species on similar surfaces\(^7,19\), and values reported for pure gases\(^13\). As the surface is heated from 140K to 190K, the O-C-C bond deformations at 819 cm\(^{-1}\) consistent with the epoxide ring are reduced in intensity and a new peak arises at 1717 cm\(^{-1}\) indicative of aldehyde C=O bond
formation. By 250K, the C=O peak becomes more prominent, strongly indicating aldehyde formation. Upon further annealing to 350K, the C=O loss peak shifts toward higher frequencies more in line with adsorbed carbon monoxide\textsuperscript{19}, consistent with the decarbonylation pathway observed during TPD. This experiment was also conducted with a smaller initial coverage from a 0.75L dose of EpB and the same trends in the C=O peak intensity were noted.

![HREEL spectra](image)

**Figure 4-5.** HREEL spectra collected after (a) adsorption of EpB at 140 K and subsequent annealing to (b) 190 K, (c) 250 K, (d) 350K.
Table 4-1. Observed vibrational modes of EpB.

<table>
<thead>
<tr>
<th>Mode</th>
<th>Liquid EpB</th>
<th>EpB on Pt(111) at 140K</th>
<th>EpB on Pd(111) at 140K</th>
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<tbody>
<tr>
<td>$\nu(C_{2}-H)/C_{3}^{+}-H)$</td>
<td>2995</td>
<td>3051</td>
<td>2995</td>
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<tr>
<td>$\nu(C_{1}^{+}-H)/(C_{3}^{+}-H)$</td>
<td>2918</td>
<td>2951</td>
<td>2995</td>
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<tr>
<td>$\nu(C_{2}^{+}-C_{4}^{+})$</td>
<td>1644</td>
<td>1654</td>
<td>1643</td>
</tr>
<tr>
<td>$\chi(C_{4}^{+}-H_{2})$</td>
<td>1440</td>
<td>1433/1452</td>
<td>1475</td>
</tr>
<tr>
<td>$\nu(C_{1}^{+}-C_{2}^{+})$</td>
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<td>1256</td>
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<tr>
<td>$\rho(C_{1}^{+}-H_{2})$</td>
<td>1131</td>
<td>1138</td>
<td>1145</td>
</tr>
<tr>
<td>B(C_{1}^{+}H)</td>
<td>988</td>
<td>996</td>
<td>976</td>
</tr>
<tr>
<td>$\tau_{\omega}(C_{1}^{+}-H_{2})/\rho(C_{4}^{+}-H_{2})$</td>
<td>915</td>
<td>917</td>
<td>929</td>
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<td>$\delta_{s}(O-C_{1}^{+}-C_{6})$</td>
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<td>819</td>
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<tr>
<td>$\tau_{\omega}(C_{4}^{+}-H_{2})$</td>
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<td>683</td>
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<tr>
<td>$\tau(C_{2}^{+}-C_{3}^{+})$</td>
<td>363</td>
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</table>
It is instructive to compare the thermal chemistry of EpB to that observed for CrHO. Figure 4-6 shows the vibrational spectrum of a surface pre-covered with a large direct exposure of CrHO and subjected to increasing annealing treatments. This exposure, similar to Figure 4-5, corresponds to the maximum coverage observed in TPD experiments or 0.484 monolayers for CrHO. Figure 4-6(a) represents a multilayers spectra, indicated by the large intensity with respect to the elastic peak which results from the reduced intensity of specularly scattered electrons on the coated surface.

![HREEL spectra collected after (a) adsorption of CrHO at 140 K and subsequent annealing to (b)190K, (c) 250K, (d) 350K.](image)

**Figure 4-6.** HREEL spectra collected after (a) adsorption of CrHO at 140 K and subsequent annealing to (b)190K, (c) 250K, (d) 350K.
Table 4-2. Observed vibrational modes of CrHO

<table>
<thead>
<tr>
<th>Mode</th>
<th>Gas Phase $trans$-CrHO$^+$</th>
<th>CrHO Condensed on Pt(111)$^{13,20}$</th>
<th>CrHO on Pd(111) at 140K</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\nu$(C-H)$_{aldehyde}$</td>
<td>2728</td>
<td>2805</td>
<td>3021 (broad peak)</td>
</tr>
<tr>
<td>$\nu$(C=O)</td>
<td>1720</td>
<td>1696</td>
<td>1720</td>
</tr>
<tr>
<td>$\nu$(C=C)</td>
<td>1649</td>
<td></td>
<td>1686</td>
</tr>
<tr>
<td>$\delta_a$(CH$_3$)</td>
<td>1455</td>
<td></td>
<td>1442</td>
</tr>
<tr>
<td>$\delta_s$(CH$_3$)</td>
<td>1391</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\delta_{ip}$(CH)$_{aldehyde}$</td>
<td>1375</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\delta_{ip}$(CH)$_{vinyl}$</td>
<td>1304</td>
<td></td>
<td></td>
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<tr>
<td>$\nu$(C-C)</td>
<td>1147</td>
<td>1158</td>
<td>1144</td>
</tr>
<tr>
<td>$\nu$(C-CH$_3$)</td>
<td>1074</td>
<td></td>
<td>1019</td>
</tr>
<tr>
<td>$\rho$(CH$_3$), $\tau$(CH$_2$)</td>
<td>973</td>
<td></td>
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<tr>
<td>$\delta_{oop}$(CH)$_{aldehyde}$</td>
<td>928</td>
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<tr>
<td>$\delta_{oop}$(CH)</td>
<td></td>
<td></td>
<td>798</td>
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</tbody>
</table>
At 190K, the CrHO spectrum shares many of the same features as the EpB spectrum, and by 250K the two spectra are nearly indistinguishable (Figure 4-7). These results indicate that a C-O bond in the epoxide of EpB is broken on Pd(111), opening the epoxide C-O-C ring and forming an aldehyde species that is also produced during the thermal chemistry of CrHO. The aldehyde intermediate is characterized by a highly intense C=O stretching frequency; furthermore, the frequency of this mode is similar to solution-phase aldehydes\textsuperscript{13}. These observations strongly suggest that the aldehyde function in the intermediate common to EpB and CrHO interacts weakly with the metal surface, and that surface binding is therefore predominantly through the hydrocarbon end of the molecule.

![Figure 4-7](image)

**Figure 4-7.** Comparison of HREEL spectra from EpB and CrHO at two annealing temperatures (from data in figures 5 and 6).

As a preliminary probe of the role of surface coverage on adsorbate orientation at low temperatures, Figure 4-8 shows the spectrum of a surface treated with lower exposures of EpB at 160 K. 160K was utilized in this case instead of 140K as before because the contact of the
sample to the liquid nitrogen reservoir varied between these two experiments, leading to a higher baseline temperature. Nevertheless, both of these temperatures are sufficiently below the desorption temperature of the relevant species noted in TPD experiments, so the chemistry in both experiments is the same. The smallest exposure results in a spectrum that is significantly different from the multilayers spectrum in Figure 4-5(a). The most intense feature of this spectrum is near 770 cm$^{-1}$, which is not a major peak in the multilayers spectrum. This mode could be consistent with a perturbed O-C-C deformation and is also in the general range of CH$_2$ twisting and CH bending modes. As exposure is increased, there is a clear enhancement in the intensity of modes closest in frequency with C$_4$H$_2$ and C$_3$H deformations of the EpB molecule. It is noted that in neither spectrum is a clear signature for a C=C stretching mode observed, although this mode is weak even in the multilayers spectrum (Figure 4-5(a) and Table 4-1). While the poorly resolved trends in Figure 4-8 are not sufficient to interpret the detailed orientation of the molecule, it is clear that the orientation changes as coverage is increased.

**Figure 4-8.** HREEL spectra as a function of exposure of EpB at 160 K (a: 0.5 L, b: 2.0 L)
The exposure-dependent HREELS of a CrHO-dosed surface offers a somewhat clearer view of orientation, and is summarized in Figure 4-9. At low exposures, a peak near 800 cm\(^{-1}\) predominates and no peak near 1720 cm\(^{-1}\) is observed. As the exposure is increased, the aldehyde C=O stretching feature near 1720 cm\(^{-1}\) grows in intensity. Other features at 1040 and 1450 cm\(^{-1}\) (associated with C-CH\(_3\) stretching and CH\(_3\) deformations) grow in intensity with increasing exposure, whereas the peak at 800 cm\(^{-1}\) assigned to out-of-plane CH bending modes becomes relatively smaller. The absence of a detectable C=O aldehyde stretch (near 1720 cm\(^{-1}\)) or C=C stretch (near 1650 cm\(^{-1}\)) after the lowest CrHO exposure suggests that both functions likely experience a strong interaction with the surface at these lower surface coverages, consistent with CrHO being adsorbed in a flat-lying orientation. It is possible that this structure evolves to a more upright orientation at higher coverages (Figure 4-9(b)), though the precise exposure at which CrHO multilayers begin to be formed is not clear. The dominance of the out-of-plane bending modes in the low-exposure spectrum further suggests a relatively flat-lying molecule at low coverages.
For the purposes discussing this work, we will briefly summarize a few key results. EpB and CrHO have been observed to decompose to produce a common aldehyde intermediate beginning below 200 K. This intermediate is characterized, somewhat surprisingly, by a C-O stretching mode that indicates relatively weak interaction of the carbonyl function with the surface. This aldehyde intermediate undergoes decarbonylation and decomposition to produce CO, H₂, and propylene during TPD. The overall reaction pathway for EpB on both Pd(111) and Pt(111)⁷ is summarized in Scheme 1 and discussed below.

The primary objective of this discussion is to compare the observed decomposition of EpB and CrHO on Pd(111) with observations from previous work using related molecules and surfaces. Such comparisons may help in elucidating trends in reactions of unsaturated oxygenates for metal surfaces across the periodic table. The most direct comparison in terms of

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**Figure 4-9.** HREEL spectra as a function of CrHO exposure at 140 K (a: 0.5 L, b: 1.5 L)
adsorbates is with the decomposition of EpB\(^7\) and CrHO\(^{13}\) on Pt(111). On Pt(111), EpB and CrHO were both observed to decompose through surface aldehyde intermediates to produce the gas phase products CO, H\(_2\), and propylene. However, the structures of the EpB- and CrHO-derived aldehyde intermediates on Pt(111) are distinct as evidenced by their HREEL spectra and by differences in H\(_2\) desorption spectra during TPD. These structural differences have been traced to differences in the position of the olefin function (between the C\(^3\) and C\(^4\) atoms in EpB, between the C\(^2\) and C\(^3\) atoms in CrHO) in the original molecules\(^7\). However, a common feature between the HREEL spectra is a highly intense C-O stretching loss near 1700 cm\(^{-1}\), indicative of an aldehyde function that interacts weakly with the Pt surface and which is oriented approximately normal to the surface.

The reactivity of EpB and CrHO on Pd(111) is similar to the case on Pt(111)—intermediates with a strong vibrational feature near 1700 cm\(^{-1}\) are produced in both cases, and decarbonylation is the overall preferred pathway—but also have some noticeable differences. Comparison of the detailed HREEL spectra from Pd(111) and Pt(111)\(^7\) show that both EpB and CrHO proceed through structurally different intermediates on the two surfaces. Furthermore, on Pt(111) the EpB- and CrHO-derived intermediates are distinctly different aldehydes, whereas on Pd(111) they are practically identical (Figure 4-7). As discussed below, other work suggests that the difference between the Pt(111) and Pd(111) aldehyde intermediates could be from a greater extent of dehydrogenation in production of the intermediate on the latter surface, which is consistent with EpB and CrHO (which have different locations of the C=C bond) proceeding through a similar intermediate on Pd(111). Unfortunately, comparison of the HREEL spectrum of the EpB-derived aldehyde intermediate on Pd(111) with similar spectra of EpB- and CrHO-derived intermediates on Pt(111) does not permit a straightforward assignment of the structural differences. The peaks in the 600-1100 cm\(^{-1}\) range (corresponding primarily to C-C stretches and
CH/CH₂ deformations)⁷ are in obvious disagreement, but there is no clear absence or presence of a particular peak that identifies (for example) a distinct stoichiometry. It is also worth noting that even similar molecular connectivity can lead to somewhat different vibrational fingerprints: for example, Valcarcel et al. have used theoretical calculations to find that 1,3-butadiene is preferentially adsorbed on both Pd(111) and Pt(111) in a flat-lying η⁴ coordination, but that the detailed molecular structures are nonetheless quite different²¹. In any case, on both surfaces EpB and CrHO proceed through decarbonylation to produce CO, H₂, and propylene.

The decomposition of EpB and CrHO can also be compared to that of similar molecules on Pd(111) and other metal surfaces. For example, the decomposition of acrolein on Pd(111) has previously been studied by Davis and Barteau¹¹, who also found decarbonylation to CO, H₂, and an olefin (ethylene) to be the predominant surface pathway. Adsorbed acrolein was characterized by strong rehybridization of the carbonyl function as evidenced by a weak C-O stretching band of decreased frequency, suggesting an η⁴ adsorption mode. (Such an intermediate was also observed for acrolein on Rh(111)¹¹.) Interestingly, upon heating from 170 to 210 K, a significant loss feature at 1685 cm⁻¹, corresponding to a relatively unperturbed aldehyde state, was observed; this feature was tentatively attributed to propionaldehyde, which is formed through self-hydrogenation and observed during TPD.

At low temperatures (Figure 4-6(a)), CrHO appears to adopt a flat-lying η⁴ geometry similar to that adopted by adsorbed acrolein. However, upon annealing to 250 K, a strong aldehyde feature near 1720 cm⁻¹ becomes apparent, suggesting that the aldehyde function becomes more upright in the formation of the aldehyde intermediate common to EpB and CrHO. As discussed immediately above, a relatively lower-intensity peak at a similar position is apparent in acrolein decomposition. One possible explanation for the subtle differences in surface chemistry between acrolein and CrHO is that the methyl group significantly affects the
adsorbate-adsorbate interactions on the surface, causing the carbonyl to prefer a more upright geometry. However, experiments in which lower initial coverages of EpB or CrHO were employed prior to annealing to 250 K indicated that the loss feature near 1700 cm\(^{-1}\) predominated even at initial coverages below half-saturation.

Another interesting difference is that self-hydrogenation of CrHO to produce butyraldehyde during TPD was not observed in this work; in fact, even exploratory experiments in which the surface was predosed with D\(_2\) failed to yield any desorbing products in which D was incorporated, suggesting intramolecular decomposition pathways dominate. While the differences in chemistry between acrolein and CrHO may seem surprising, they are not unique; acrolein and CrHO have also been found to decompose through different intermediates and with different TPD products on Pt(111)\(^{13}\).

The chemistry of saturated aldehydes and epoxides has been studied on a variety of metal surfaces, including Pd(111). Ethylene oxide undergoes ring-opening and decarbonylation on Pd(111) through a proposed oxametallacycle intermediate to yield ethylene and acetaldehyde\(^{22}\). On Rh(111), Brown and Barteau found that ethylene oxide and propylene oxide decarbonylate through a proposed oxametallacycle intermediate around 230 K to yield CO and H\(_2\)\(^{23}\). On Pd(110) Shekhar et al. found ethylene oxide adsorbed molecularly onto the surface at 120 K ring-opened between 120 and 260 K through a proposed oxametallacycle intermediate to produce methylene and formyl/formaldehyde groups, which then decompose into CO and H\(_2\)\(^{24\text{-}25}\). Decomposition of simple aldehydes such as acetaldehyde is also generally characterized by a strong interaction of the carbonyl group with the surface\(^{26\text{-}28}\); in the case of Pd(111), decarbonylation is mediated by a surface acyl intermediate\(^{29}\). Clearly, the multifunctional nature of EpB and CrHO significantly perturb decomposition of these molecules, although decarbonylation is observed on Pt-group metal surfaces.
Finally, it is worth comparing the chemistry of the functional epoxide EpB on the three transition metals studied to date, Ag(110), Pt(111), and Pd(111). On all three surfaces, EpB undergoes ring-opening that is initiated below 200 K, presumably through an oxametallacycle intermediate. On Ag(110), this ring-opening reaction produces an oxametallacycle that is stable to nearly 500 K\(^9\). On Pd(111) and Pt(111)\(^7\), however, ring-opening is accompanied by at least one rapid C-H bond scission to produce a surface aldehyde. The trends observed in thermal chemistry on the three surfaces may help explain observations in catalysis of EpB; both Pt and Pd have been associated with strong affinities for isomerization of EpB to CrHO, whereas the role of Ag in bimetallic PtAg catalysts appears to be to interact with the O atom to retain an oxametallacycle structure. However, Pt and Pd are different in that Pd tends to produce a higher proportion of unsaturated products\(^8\). A greater extent of dehydrogenation in the adsorbed aldehyde intermediate on Pd(111) thus may be responsible for the observed differences between the aldehyde intermediates on Pd(111) and Pt(111). (The observation of peaks in 1400-1500 cm\(^{-1}\) region appear to indicate retention of some CH\(_2\) functionality, however.) Further studies of EpB chemistry on Cu and bimetallic surfaces are necessary to more fully understand the mechanisms by which selectivity toward particular products can be optimized.

4.5 Conclusions

The thermal chemistry of 1-epoxy-3-butene and crotonaldehyde has been investigated on Pd(111). Temperature programmed desorption studies reveal that both molecules proceed through decarbonylation pathways to produce CO, hydrogen, and (at higher coverages) small amounts of propylene. High resolution electron energy loss spectroscopy studies reveal that the principal surface intermediate produced by both 1-epoxy-3-butene and crotonaldehyde is nearly
identical by 250 K. This common surface intermediate is an aldehyde that appears to be oriented such that interaction between the aldehyde function and the surface is relatively weak. The surface reaction pathways for the two isomers differ somewhat on Pd(111) compared to Pt(111). Though aldehyde intermediates with similar C-O stretching loss features are produced in both cases, on Pt(111) the intermediates produced from 1-epoxy-3-butene and crotonaldehyde are distinct from each other and from the intermediate produced on Pd(111).

4.6 References


CHAPTER 5
Mechanistic insights into the chemoselective hydrogenation of unsaturated oxygenates on palladium functionalized with self-assembled monolayers

Abstract

The chemistry of 1-epoxy-3-butene (EpB) and similar molecules on Pd(111) coated with self-assembled monolayers (SAMs) was studied using temperature programmed desorption (TPD) and Auger electron spectroscopy (AES). Unlike clean Pd(111), EpB does not undergo ring opening on SAM covered surfaces. Comparison of EpB desorption spectra to similar molecules suggests EpB binds through its olefin functionality and interactions between the epoxide ring and the surface are significantly destabilized. EpB desorption spectra on less well-ordered SAMs show the presence of weakly bound states not observed on well-ordered surfaces. These results support previous hypotheses that the origin of selectivity and activity on SAM coated catalysts is related to the selective poisoning of epoxide ring-opening reactions.

5.1 Introduction

In the previous chapter, reaction pathways of 1-epoxy-3-butene (EpB) and crotonaldehyde were explored on clean metal surfaces to form a foundation for fundamental studies on SAM coated surfaces. In this chapter, we explore the chemistry of EpB on Pd(111) surfaces coated with a subset of the SAMs used in chapter 3.
To review, on clean Pd(111) EpB adsorbs initially through its olefin functionality with its epoxide ring intact. This adsorption structure is confirmed by HREELS experiments which show a lack of a C=C stretching mode and the presence of an epoxide ring deformation mode. By 200 K, EpB ring opens to form an aldehyde-like intermediate, indicated by a strong C=O stretching in HREEL spectra. Above 200 K, this species decarbonylates to form CO and propylene, as observed in TPD experiments and shown in Figure 5-1.

![Figure 5-1](image)

**Figure 5-1.** Reaction pathways of EpB observed on Pd(111) during TPD and HREELS experiments. (a): initial adsorption through olefin functionality; (b): decomposition to an aldehyde-like intermediate by 200 K; (c) decarbonylation to form propylene and CO.

As stated previously, selectively converting EpB to epoxybutane is difficult; however, some systems that perform this reaction effectively have been reported. Falling and colleagues invented a process achieving 84-90% selectivity for epoxybutane by using a combination of rhodium catalysts and hydrogen pressures up to 5.6 MPa, far from the mild conditions commonly employed in olefin hydrogenation reactions. More recently, Monnier and colleagues reported 55% selectivity for epoxybutane using a platinum-silver bimetallic catalyst under mild conditions. Fundamental studies suggest this catalyst achieves high selectivity through a bifunctional effect by forming a reversible oxametallacycle intermediate with silver atoms, which protects the epoxide ring from further reaction. A third example is a binuclear palladium homogeneous catalyst with (t-butyl)$_2$phosphide ligands. This catalyst hydrogenates a variety of unsaturated epoxides with selectivities as high as 95% by controlling the electronic
and steric environment around the central metal atoms\textsuperscript{7}. Fundamental knowledge of the interaction of unsaturated epoxides with the catalytic material has aided the design of these systems and predictions for future areas of research. Here, we glean similar information for the interaction of EpB with SAM coated surfaces using fundamental surface science techniques.

5.2 Experimental Methods

Experiments were conducted in a stainless steel ultra-high vacuum (UHV) system described in detail elsewhere\textsuperscript{5}. The chamber had a base pressure of \(~10^{10}\) torr. The same Pd(111) crystal (Princeton scientific) was used for all experiments. The crystal was spot welded to a 1.5 mm Ta disk that was held in the chamber on the copper stage using two clips. This sample was cooled using liquid nitrogen in thermal contact with the sample through the copper stage and heated using a resistive heater. The crystal was cleaned using cycles of heating in 5 x 10\textsuperscript{-8} torr O\textsubscript{2} (research grade, Airgas) between 700 and 1000 K, sputtering with Ar\textsuperscript{+} ions at low temperature (1-3 keV, NGI3000-SE sputter gun by LK technologies), and annealing between 700 and 1000 K. Cleanliness was verified using oxygen TPD and Auger electron spectroscopy. The Pd(111) sample was removed and reinserted into vacuum for SAM deposition and characterization using a wobble stick and a separate load-lock chamber.

Pd(111) was used for experiments in this work, and this crystal plane is most commonly used when characterizing SAMs and is the most thermodynamically stable. Nevertheless, heterogeneous catalysts exhibit many different crystal planes. These additional facets predominantly include (100) surface facets and corner and edge sites. Studies of SAMs on Au(100) suggest the formation of a c(2x2) structure, which has a higher coverage than its (111)
counterpart\textsuperscript{8}. Similarly, studies of SAMs gold nanoparticles show thiol coverages greater than 60\%\textsuperscript{9}, likely due to higher coverage on corner and edge sites, as model studies show sulfur binds more tightly at these locations\textsuperscript{10}. Thus, the precise ensemble of metal sites left available for reaction by the SAM will differ on the different facets of the crystal, and SAM coated catalysts are likely sensitive to dispersion. Nevertheless, the (111) surface of Pd serves as a good model for developing initial fundamental understanding of this system.

SAM deposition was achieved by removing the sample from vacuum and immediately inserting it into a 1 mM solution of propanethiol, hexanethiol, dodecanethiol, octadecanethiol, or thioglycerol in ethanol (Sigma Aldrich). All thiol purities were > 97\% and ethanol was 200 proof HPLC grade. SAMs were deposited over a period greater than 12 hours, after which the sample was removed from solution and rinsed with ethanol. The quality of the SAM was characterized by taking an advancing water contact angle using a goniometer (CVI Melles Griot).

The SAM coated crystal was then reinserted into the UHV chamber through an attached load-lock chamber separated by a gate valve. The load-lock chamber was pumped by a turbomolecular pump (Pfeiffer Vacuum) to a pressure less than 10\textsuperscript{-6} torr. The sample was moved into the main chamber and inserted into the sample stage with a magnetic sample transfer arm and a wobble stick. This procedure eliminates the need for baking the chamber after inserting the sample, which would result in the decomposition of the SAM coating.

1-Epoxy-3-butene (Alfa Aesar, >98\%), 1-epoxybutane (Sigma Aldrich, >99\%), crotonaldehyde (2-butenal, Sigma Aldrich, >99.5\%), and butyraldehyde (butanal, Sigma Aldrich, >99\%) were dosed directly to the sample by sending a pulse of vapor through a 1/16” OD tube.
approximately 2-3” from the sample. Size of dose was controlled by varying the pressure of the source for the vapor pulse.

Temperature programmed desorption (TPD) experiments were conducted using a Smart-IQ+ quadrupole mass spectrometer (VG Scienta) equipped with a stainless steel shroud. Auger electron spectroscopy (AES) experiments were conducted using a RVL2000 LEED/AES apparatus including an electron gun (LK Technologies) and a model CMA 2000 (LK Technologies) mounted at a right angle to the electron gun.

5.3 Results and Discussion

Studying the chemistry of a surface covered with organic ligands is more complicated than studying a clean surface, as SAM functionalized surfaces can decompose at elevated temperatures. Figure 5-2 shows a TPD spectrum for the m/z = 27 trace for a hexanethiol SAM coated surface. Other masses were observed in the desorption spectra for this SAM; however, they typically mirrored the m/z = 27 trace or showed desorption peaks at higher temperatures. The data in Figure 5-2 show that SAM decomposition occurs on the Pd(111) surface at temperatures above ~ 325 - 350 K. In the experiments below, the temperature of the sample did not exceed 323 K to prevent SAM decomposition. In addition, experiments were repeated for each SAM preparation to ensure there were no changes to the behavior of the SAM coating from thermal decomposition or exposure to adsorbates.

The behavior observed here for SAMs on Pd(111) is similar to studies on polycrystalline Au surfaces. Alkanethiol SAMs on Au change slightly in structure and order with heating up to 350 K. These changes are reversible and cooling results in a structure identical to the original.
However, when the SAM coated surface is heated above 350 K, defects form in the structure of the SAM that do not disappear on cooling\textsuperscript{11}. The onset of decomposition appears slightly lower for Pd(111). This effect may be due to the higher activity of Pd for bond breaking reactions. Significant intensity is observed even at high temperatures due to the high background pressure that persists in the vacuum chamber due to the large quantity of material desorbing from the surface and the limited pumping speed.

![Figure 5-2. TPD spectrum for the m/z = 27 trace during decomposition of a hexanethiol SAM on Pd(111). SAM decomposition was observed to begin between 325 and 350 K. Other mass traces appeared similar to m/z = 27 or showed peaks at higher temperatures.](image)

To determine the nature of EpB binding on the SAM coated surface, experiments were performed using a variety of analog molecules that contained similar functional groups, as shown
Crotonaldehyde has a similar structure to EpB, except the oxygenate functionality is different. Epoxybutane is similar to EpB, but lacks the olefin functionality. Finally, butyraldehyde has a different oxygenate functionality and lacks the olefin functionality.

Figure 5-3. Diagram of the analogs of EpB tested in TPD experiments. The identities of both the olefin and epoxide functionalities of EpB were varied to test the importance of these functionalities in generating selectivity.

TPD spectra for equivalent doses of EpB and its analogs on a hexanethiol SAM coated surface are shown in Figure 5-4. As noted in previous chapters, on clean Pd(111) EpB ring opens to form aldehyde-like intermediate around 190 K\textsuperscript{12}. On SAM coated surfaces, EpB and epoxybutane desorb intact, indicating epoxide ring opening reactions are significantly poisoned. In the previous chapter, the decomposition of EpB produced hydrogen, which desorbed around 300 K. In this case, no hydrogen desorption was observed. In addition, EpB behaves similarly to crotonaldehyde and both molecules desorb at significantly higher temperatures than their saturated counterparts. This result indicates that EpB and crotonaldehyde likely bind through their shared functionality: the olefin group. In addition, the saturated analogs adsorbed in
quantities far smaller than EpB or crotonaldehyde, indicating interactions between monofunctional oxygenates and the surface were weaker and fewer sites existed to bind these molecules. Similar experiments were performed on the other SAM coatings used in this work and the same trends were observed.

Figure 5-4. TPD spectra of EpB and analogs on hexanethiol SAM coated Pd(111). The intact desorption of EpB and the sharp contrast between unsaturated and saturated oxygenates suggests EpB and crotonaldehyde bind through their shared olefin functionality. (Epoxybutane and butyraldehyde spectra magnified 5x due to low yield)

Since the behavior of olefin hydrogenation reactions on platinum metal surfaces can vary with coverage\textsuperscript{13-14}, it is useful to examine the effect of increasing dose on EpB desorption. Experiments were performed using a range of dose sizes varying from those that produces very
little adsorbed EpB to those that produced multilayer adsorption (physisorption) of EpB. Spectra for sub-multilayer doses of EpB on each SAM coated surface are shown in Figure 5-5.
These spectra reveal interesting details of EpB chemistry on the SAM coated surfaces. First, on all surfaces the desorption temperature decreases with increasing coverage. This change results from destabilizing lateral interactions between adsorbates and through-surface effects. A similar coverage dependent desorption temperature has been observed for ethylene desorbing from clean Pd(111)\textsuperscript{15}. On Pd(111) covered with a full monolayer of adsorbates such as H or O, the desorption temperature of olefins such as ethylene or propylene shifts from over 300 K to a desorption temperature below 250 K\textsuperscript{15-16}. Infrared spectroscopy studies show this shift corresponds to a change in binding state from a di-σ bound species to the more active π-bound species\textsuperscript{17}. The maximum desorption temperature of EpB on the alkanethiol coated surfaces was below 300 K. This result is consistent with ethylene desorbing from surfaces pre-dosed with a hydrogen coverage similar to the full SAM coverage of 0.33 monolayers\textsuperscript{15}. Similar

\textbf{Figure 5-5.} TPD spectra of increasing doses of EpB on the SAM coated surfaces. All doses are submonolayer, indicated by the lack of a physisorption peak ~150 K. (C3: propanethiol, C6: hexanethiol, C12: dodecanethiol, C18: octadecanethiol, TG: thioglycerol)
destabilization of C=C adsorption has been reported for adsorption of benzene on sulfur coated Pt(111)\textsuperscript{18}, and has been attributed to steric effects\textsuperscript{19}. Small differences in peak temperature between cases may be due to small variations in the thermal contact of the sample with the stage resulting from its removal and reinsertion or small differences in dose size. As a whole, these results suggest the mechanism of binding for olefin functionality of EpB is relatively unperturbed by the addition of the SAM coating.

The shape of the peaks in the TPD spectra suggest differences between the thioglycerol SAM and the alkanethiol SAMs. The thioglycerol spectra show sharp peaks, consistent with a more uniform EpB adsorption energy; however, the alkanethiol SAMs show peaks with trailing tails. These tails may result from diffusion limitations to desorption that aren’t present in the thioglycerol case. Differences in the observed spectra for thioglycerol may also result from the order and thermal stability of phases formed by the thiol tails. Interactions between tails in SAMs with functionalized thiols can be stronger than alkanethiols due to hydrogen bonding between tail groups. Such hydrogen bonds can increase the temperature at which SAMs decompose in TPD experiments by close to 100 K\textsuperscript{20}. These effects could result in a more rigid and crystalline thioglycerol SAM at higher temperatures at which tail groups of alkanethiol SAMs tend to become disordered and more mobile\textsuperscript{21}. Changes in the alkanethiol SAM structure with temperature may result in a deviation from the Temkin isotherm-like behavior previously observed on uncoated Pd(111)\textsuperscript{15}, whereas the rigidity of the thioglycerol SAM may confer a more uniform desorption energy.

One prominent difference in the spectra is between the longer, well-ordered alkanethiol SAMs and the less well-ordered propanethiol SAM. An additional desorption peak is observed for the propanethiol case around 200 K. This peak is at a lower temperature than the desorption
peak of π-bound olefins, yet at a higher temperature than physisorbed species observed in spectra showing multilayers. This result indicates a fraction of adsorbates on less well-ordered SAMs are incapable of accessing the more tightly states universally occupied on well-ordered SAMs. Reasons for and the implications of this effect will be discussed in detail below.

Prior to any TPD experiments, SAMs were characterized outside of vacuum by measuring an advancing water contact angle, and inside of vacuum with AES. SAMs change the hydrophobicity of the metal surface and the angle an advancing droplet of water forms with the metal serves as a good measure of surface order. For alkanethiols, increasing order presents a more hydrophobic surface resulting in a larger contact angle; for hydroxylated thiols like thioglycerol, increasing order presents a more hydrophilic surface resulting in a smaller contact angle.

The contact angles observed for the propanethiol, hexanethiol, dodecanethiol, and octadecanethiol SAMs were 95, 115, 114, and 117 respectively. Based on the values reported in chapter 2 for MIS sensors, these results indicate that hexanethiol, dodecanethiol, and octadecanethiol form well-ordered SAMs on the Pd surface; whereas propanethiol formed a less-well ordered SAM. The advancing contact angle for the thioglycerol SAM was 14°. This contact angle indicates a significant amount of thioglycerol coated the surface; however, determining the relative order of the SAM with respect to the alkanethiols is not possible with this method.

The quality of the SAM coatings was also evaluated using AES. In addition to providing surface composition, AES is sensitive to changes in electronic structure. Significant changes in the local electronic structure of an atom, such as a change in oxidation state, can lead to a shift in
the AES feature for that species\textsuperscript{24}. AES spectra for the coatings employed are shown in Figure 5-6.

![AES spectra](image)

**Figure 5-6.** AES spectra of SAM coated Pd(111). The negative lobes of the S, C, and Pd features are noted by vertical lines. (C3: propanethiol, C6: hexanethiol, C12: dodecanethiol, C18: octadecanethiol, TG: thioglycerol)

The AES spectra shown in Figure 5-6 provide key details regarding the relative state and order of these surfaces. First, the negative lobe of the palladium feature is present at 330 eV for every coating, which is consistent with the clean Pd surface. This result indicates that Pd retains its typical electronic character and is not oxidized like the metal atoms in some organometallic homogeneous catalysts\textsuperscript{25}. This result does not necessarily indicate that sulfur doesn’t change the
electronic character of the underlying Pd, instead the surface has not undergone a significant change such as a change in oxidation state.

The position of the carbon feature is similar in all the coatings except the disordered propanethiol coating, where it has shifted to higher energy. This result likely indicates that the thioglycerol SAM is well ordered like its longer alkanethiol counterparts and reinforces the result that propanethiol is disordered, since shifts in the Auger feature indicate carbon has a slightly different character on the propanethiol SAM compared to the well-ordered SAMs. Thioglycerol, however, appears different than its alkanethiol counterparts in the position of the sulfur feature, which is shifted to lower energy by 2.5 eV. This shift is not as large as the ~ 10 eV shift observed in sulfates \(^\text{26}\) or the oxidation of species such as silicon \(^\text{24,27}\); however, it does indicate some change in the electronic state of S. The relative size of the S feature compared to the Pd feature is also much larger for thioglycerol than for the alkanethiols, indicating a larger fraction of the surface is covered by sulfur.

Although sulfur and Pd features are smaller in the longer alkanethiol coatings due to the shielding effect of thiol tails, sulfur and Pd exist in a similar plane with respect to the surface normal, so their relative feature size provides a means of comparing coatings. If anything, this simple analysis may underestimate the amount of surface sulfur on the thioglycerol coating, since on shorter SAMs electrons used in AES may penetrate further into the metal layer and cause subsurface atoms to contribute more to the intensity of the Pd feature. The larger amount of surface sulfur on the thioglycerol SAM coated surface may result from cracking of S-C bonds to form surface sulfur, which has been observed on Pd using x-ray photoelectron spectroscopy (XPS) \(^\text{9,23}\). These results indicate adding functional groups to the SAM tail may result in subtle changes to the surface structure that may affect catalyst behavior compared to similar size tails.
5.4 Conclusions

In chapter 3, two main hypotheses were presented to explain the behavior of SAM coated catalysts. They were:

- High selectivity results from the presence of surface sulfur. Thiol tails do not interact with adsorbates in a manner that confers selectivity.
- Activity decreases with increasing disorder because disordered tails either physically block surface sites or create entropic barriers to adsorption onto active sites.

The TPD and AES work above provides additional evidence for the refinement of these hypotheses. First, TPD spectra for saturated and unsaturated analogs of EpB help identify the mechanism by which surface sulfur improves selectivity. The weak adsorption and low yield of the saturated oxygenates (butyraldehyde and epoxybutane) shows epoxide ring ring opening reactions are significantly poisoned on the SAM coated surfaces compared to uncoated Pd(111), where ring opening reactions occur by 200 K. Also, fewer sites exist for the adsorption of the epoxide ring than sites for binding the olefin functionality. The similarity between the desorption spectra of EpB and crotonaldehyde and the higher desorption temperature of these molecules compared to their saturated counterparts strongly suggests surface sulfur causes preferential binding through the olefin functionality. The similarity between different SAM coated surfaces is consistent with the observation that tail functionality has little impact on selectivity.
Second, results of EpB desorption spectra as a function of dose size support the hypothesis for catalyst activity. The observation of weaker adsorption states on the propanethiol SAM coated surface indicates reduced activity results from a fraction of adsorbates being unable to bind in active sites. Since the techniques used in this chapter are temperature programmed, they only probe enthalpic contributions to binding, which indicates less well-ordered coatings must produce additional enthalpic barriers to binding as well as potential entropic barriers. Such effects could result from either electronic or geometric changes to the surface structure. In either case, these results suggest the exact reason for changes in catalyst activity with order may be a complex combination of factors.

5.5 References


CHAPTER 6
Conclusions and future directions

6.1 Conclusions

This work has demonstrated the considerable potential of self-assembled monolayer (SAM) coated surfaces for modifying the catalytic behavior of palladium surfaces and particles. SAMs provide significant improvements in the selective detection of acetylene in metal-insulator-semiconductor (MIS) sensors and the chemoselective hydrogenation of 1-epoxy-3-butene (EpB) to 1-epoxybutane on supported catalysts. Detailed conclusions of each set of experimental studies are provided at the end of each chapter, so here we will examine core principles elucidated from this work.

**Surface sulfur imparts selectivity.** Both studies on MIS sensors and supported palladium catalysts suggest surface sulfur performs a prominent role in the observed enhancement. On MIS sensors, this result was observed by the increase in acetylene sensitivity upon exposing devices to H$_2$S and suggested by the similar response when alkyl tails of thiols were switched for hydrophilic poly-ethylene-glycol units. In palladium catalysts, the importance of sulfur was similarly observed by experiments varying dosages of H$_2$S and in experiments aging catalysts in olefins or co-feeding CO to exclude the influence of alkyl tails or ensemble effects. The importance of surface sulfur in catalysts was also exhibited by the uniformly high selectivity in thiols with different alkyl tail lengths or added hydroxyl groups.
Comparing the work performed with EpB on clean and SAM coated Pd(111) suggests sulfur destabilizes interactions between adsorbates and the palladium surface. For acetylene detection by MIS sensors, this effect may result in a reduction in the acetylene adsorption energy, which can increase the rate of acetylene hydrogenation\textsuperscript{1,2}. For EpB hydrogenation on Pd catalysts, this effect results in a reduced ability to produce tightly bound structures required for ring opening reactions. Sulfur also has a greater destabilizing influence on oxygenates over olefins, leading to preferred binding through EpB’s olefin functionality.

**SAMs are superior to other forms of sulfiding.** Studies of sulfur poisoning on platinum group metals were first conducted over 150 years ago\textsuperscript{3}, so it is reasonable to wonder why the effects examined in this thesis have not been previously reported. Although surface sulfur deposited through means such as H\textsubscript{2}S decomposition bears some resemblance to the behavior of SAMs, in both MIS sensors and Pd catalysts, well-ordered SAMs significantly outperformed their sulfided counterparts prepared from H\textsubscript{2}S exposure. These results suggest thiol tails are instrumental in organizing and maintaining ordered overlayers on the palladium surface.

A review of existing work suggests SAM tails help prevent the formation of deleterious surface structures from sulfur. At sufficient coverage, sulfur preferentially forms a ($\sqrt{7}x\sqrt{7}$)R19 overlayer with significant subsurface absorption on Pd(111)\textsuperscript{4}. Temperature programmed desorption (TPD) experiments show this structure prevents the dissociative adsorption of hydrogen and effectively poisons the surface through changes in both the geometric and electronic structure\textsuperscript{5}. Although the deposition of alkanethiol SAMs does result in some surface sulfur through S-C bond cracking, depth profiling Auger electron spectroscopy (AES)
experiments show this species does not measurably penetrate into the bulk\textsuperscript{6} and is thus less likely to poison hydrogen dissociation than sulfur alone.

**Greater surface order correlates with better performance.** A common trend between MIS sensor and heterogeneous catalysts is the variation of behavior with surface order. On MIS sensors, contact angle measurements showed increasing surface order led to increasing acetylene response. Similarly, on heterogeneous catalysts, characterization of SAM coatings with vibrational spectroscopy showed well-ordered coatings exhibit higher activity than less-well ordered coatings. The uniform activation barriers observed for EpB hydrogenation, lack of mass transfer or diffusion limitations on the catalysts, and similar behavior between thiol coatings having different functional groups suggests changes in the near surface environment are responsible for this trend.

TPD experiments of EpB on SAM coated Pd(111) identify reasons for this trend. On less well-ordered surfaces, EpB adsorbs in a weakly bound state in addition to the state observed on well-ordered surfaces. The new state adsorbs more weakly than active states of ethylene\textsuperscript{7} or propylene\textsuperscript{8}, so it is unlikely to be active for hydrogenation. These results suggest a fraction of sites on less well-ordered surfaces are unavailable for reaction, while a number of additional sites behave similarly to well-ordered surfaces.

6.2 Future directions

**Poisoning or promotion.** As mentioned in chapter 3, the actual number of active sites on thiol SAM coated catalysts is unknown. The turnover frequencies reported in that chapter are based off the number of sites on the uncoated catalyst, determined by CO chemisorption. These
results show the catalyst activity evaluated on a per gram basis has been reduced; however, if the number of sites on the SAM coated catalysts is significantly reduced, activity at the site level could be higher than the uncoated catalyst and the true turnover frequency could be larger.

Determining the true turnover frequency of SAM coated catalysts requires a measurement of the number of active sites. CO chemisorption is the most common method used to acquire this information, but it will not work for SAM coated catalysts because CO does not stick on the catalyst surface at temperatures above ambient. Instead, chemisorption experiments using olefins could be employed. Another method is steady state isotope transient kinetic analysis (SSITKA).

In this technique the system is allowed to reach a steady state under normal conditions and then a reactant is switched to an isotopomer, such as a deuterated hydrocarbon. The non-labeled reactant concentration in the effluent flow is measured using a mass spectrometer and corrected for any gas holdup (determined by a similar experiment with an inert). Integration of the corrected signal provides the average reactant residence time of the reactant on the catalyst surface. Multiplying the residence time by the reaction rate provides the number of adsorption sites on the catalyst. The information provided by SSITKA can be used to compute reaction turnover frequencies under operating conditions. This method is more difficult than chemisorption; however, it enables the user to account for changes to the catalyst under operating conditions and adsorption states that may not be active for hydrogenation and thus provides a more accurate result.

**Structure sensitivity.** Work described in chapter 3 utilized only one, 5% Pd/Al_{2}O_{3}, catalyst. However, initial experiments performed using a 1% Pd/Al_{2}O_{3} catalyst show different behavior. When coated with an octadecanethiol SAM and tested for EpB hydrogenation under
the same conditions as the catalyst described in chapter 3, this catalyst exhibited a selectivity equivalent to other SAM coated catalysts; however, the rate of epoxybutane production (moles produced per gram of catalyst per second) was only 5% of the rate on the octadecanethiol coated catalyst presented in chapter 3. The 1% Pd catalyst likely differs from the 5% Pd catalyst in the structure and size of metal particles, so one possible interpretation of these results is that SAM chemistry may be dependent on the crystallinity of catalysts particles. This sensitivity may result from higher coverages of SAM that could completely poison reaction on planes with high Miller indices or the (100) plane\textsuperscript{10-11}. However, these data are preliminary and more experiments will need to be conducted to examine this sensitivity.

First, the structure of the 1% Pd/Al\textsubscript{2}O\textsubscript{3} catalyst must be evaluated. Although lower weight loadings typically indicate more disperse particles\textsuperscript{12}, the preparation of catalysts is far from an exact science. CO chemisorption data will provide the average metal particle size and the number of metal sites on the uncoated catalyst. This data will enable the calculation of a turnover frequency (similar to chapter 3), which is a more informative method of comparing activity than rate since it is evaluated on a per site basis. If the turnover frequencies are the same, then SAM chemistry is not sensitive to structure. If the particle size of the 1% Pd catalyst is smaller and the turnover frequency is smaller, activities are lower on planes other than the (111) plane. Conversely, if the turnover frequency is larger, activities are lower on the (111) plane compared to other planes. It is also possible that the average particle size on the 1% Pd catalyst is larger than the 5% Pd catalyst. In this case, a smaller turnover frequency on the 1% Pd catalyst indicates (111) planes are less favorable than other crystal planes, and a larger turnover frequency indicates (111) planes are more favorable than other crystal planes.
Structure sensitivity can also be studied using surface science techniques. SAMs can be deposited on Pd(100) or Pd(110) single crystals and experiments similar to those in chapter 5 could be repeated. Surface science techniques are in many ways preferable to catalysis studies due to the uniformity and known composition of single crystals. Catalysts prepared separately can contain different quantities of impurities, such as Cl, that could affect the behavior of surface sulfur\(^{13-14}\). Using surface science techniques to understand structure sensitivity has been successful for a variety of chemistries\(^{15-18}\). Overall, understanding the structure sensitivity of SAM coatings will enable better choices of catalyst weight loadings for future studies.

**Changes to the catalyst during operation.** On catalysts coated with well-ordered SAMs, epoxybutane turnover frequencies increased by ~50% during the first few hours of testing, as shown in Figure 6-1. Similar rate acceleration has been reported for a variety of olefin hydrogenation reactions\(^ {15}\) and is usually attributed to changes in the catalyst resulting from the formation of carbonaceous deposits\(^ {16}\).
To understand the origin of this rate acceleration, the catalyst can be characterized to determine how SAM structure changes with time on stream. One method of performing this experiment is *in situ* diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS). A SAM coated catalyst could be aged by the introduction of gas phase olefin and hydrogen species in similar conditions as under reaction conditions. Monitoring C-H stretching modes as a function of time with DRIFTS will identify the formation of carbonaceous deposits and changes to the structure of the SAM coating.

**Additional chemistries.** The potential for SAM coated catalysts extends beyond the chemistry studied in chapters 3, 4, and 5. Based on the results of the MIS studies in chapter 2, SAM coated catalysts may be effective for the selective hydrogenation of acetylene. Industrially, selective acetylene hydrogenation to ethylene is conducted in a feed stream of less than 5% acetylene and up to 75% ethylene. Effective catalysts should reduce the concentration of acetylene to a few ppm while not significantly hydrogenating ethylene. This process is difficult, as the activation barrier for acetylene hydrogenation exceeds the barrier for ethylene hydrogenation by ~20 kJ/mol\(^\text{17}\).

DFT studies show the origin of selectivity in conventional Pd and Pd-Ag catalysts lies with the adsorption energy of acetylene and ethylene. On Pd and Pd-Ag bimetallic surfaces, the adsorption energy of ethylene is smaller than the activation barrier for hydrogenation, so ethylene tends to desorb. Acetylene, however, binds tighter than the activation barrier for hydrogenation, so it preferentially hydrogenates. Weakening the binding of acetylene can...
improve hydrogenation rates yet results in lower selectivity, and ideal catalysts balance activity and selectivity\textsuperscript{1-2}.

SAM coatings offer another means of tuning the adsorption energy of acetylene and ethylene. Unlike the relatively immobile ad-atoms of bimetallic catalysts, the mobility of SAMs on metal surfaces may provide a different mechanism for altering the stability of these reactants that could provide high selectivity and high activity compared to conventional catalysts.

Another chemistry in which SAM coatings may be effective is the conversion of $\alpha$-$\beta$ unsaturated aldehydes on sulfur promoted Cu catalysts. This chemistry, described in detail in chapter 1, has suffered from an inability to apply sulfurous species’ in a controlled manner. The precise structure and facile deposition of SAMs may enable the reproducible preparation of effective catalysts for these reactions.

SAM coated catalysts may be effective for many other chemistries; however, there are some significant limitations. As shown in chapter 5 on model surfaces, alkanethiol SAMs decompose at temperatures above 373 K, which makes them ineffective coatings for high temperature chemistries such as cracking\textsuperscript{18}. The maximum operating temperature may be enhanced by up to 100 K by introducing thiols with tails that form strong hydrogen bonding networks. Also, thiol based SAMs can degrade in the presence of oxidizing agents\textsuperscript{6}, so their use must be limited to reducing environments such as those employed under hydrogenation conditions. As suggested below, changing the nature of the SAM attached from sulfur to other species may enable operation in other chemical environments; however, such changes will also alter the behavior of the catalyst.

**Changing thiol coverage with tail functionality.** Alkanethiols uniformly adsorb with a $(\sqrt{3} \times \sqrt{3})$R30 structure in well-ordered SAMs\textsuperscript{19}. This structure is preferable to the subsurface
structures formed by sulfur that can poison hydrogen adsorption; however, it may not be the optimal structure for achieving high activity and high selectivity. One possible means of controlling surface coverage is through the use of thiols with more bulky organic tails. These tails could sterically hinder adsorption and produce surfaces with coverages less than the 33% coverage observed for well-ordered alkanethiol SAMs. For example, SAMs formed from benzenethiol on Au(111) substrates can form a (2 x 3√2)R23 structure that has a coverage less than 20%. Using thiols such as benzenethiol may enable further improvements in SAM coated catalysts and may be essential for extending this technology to other chemistries, although fabrication and characterization of SAMs from these thiols is more difficult.

**Surface templating.** This work has shown SAM coated catalysts are effective for olefin hydrogenation reactions; however, many reactions, including hydrogenolysis, cracking, or aldehyde hydrogenation, require more tightly bound intermediates and larger ensembles. The high surface coverages of sulfur formed in SAMs may prevent adsorption of these reactants. One possible method of overcoming this challenge is by templating the surface during the deposition of the SAM.

Surface templating has been successfully deployed in chemical sensors for the selective adsorption and detection of aromatic compounds. SAMs of benzenethiol were deposited on the sensor surface using a deposition procedure similar to those employed in this thesis; however, the deposition was performed in a benzene solution instead of an ethanol solution. When the deposition was halted before the formation of a complete monolayer, the sensor showed high selectivity for benzene over ethanol and sucrose. Depositing incomplete SAMs from solutions containing compounds with specific functional groups may enhance chemoselectivity for
conversion of reactants with the same functionality. Potential applications could include the
conversion of unsaturated aldehydes to unsaturated alcohols or the hydrogenation of alkynes.

**Beyond sulfur.** Since surface sulfur is largely responsible for enhanced chemoselectivity
in the systems studied to date, alkanethiol SAM coatings may be limited to chemistries in which
sulfur improves performance. Although, as this work illustrates, the range of chemistries for
which thiol SAMs may be effective could be far more numerous than one might expect, forming
SAMs with linkages other than sulfur would extend the potential of this technology. A variety of
other linkages can be used to form SAMs, including phosphonates\textsuperscript{22}, selenides\textsuperscript{23}, siloxanes\textsuperscript{24}, and
silanes\textsuperscript{25}. Whereas alkanethiols break down in oxidizing environments\textsuperscript{6}, some of these linkages
will not and would thus extend the range of chemistries that can be conducted on SAM coated
surfaces.

### 6.3 Final remarks

Heterogeneous catalysis is in many ways the modern equivalent of alchemy. To the
outside observer the complexity and specificity of catalysts can be daunting or appear magical.
Nevertheless, the field today emerged from simple catalysis experiments first conducted on
macroscopic pure metals. Subsequent research has provided many variables that can be tuned to
improve performance including metal composition, alloy formation, crystallinity, support
material, and promoters. In this thesis, we have examined a new means of modifying catalyst
and thus introduced a new variable in the ever growing toolset of the modern catalysis
researcher.
6.4 References


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APPENDIX A

List of abbreviations used in this work

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>AES</td>
<td>Auger electron spectroscopy</td>
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<tr>
<td>C12 / C12SH</td>
<td>1-dodecanethiol</td>
</tr>
<tr>
<td>C18 / C18SH</td>
<td>1-octadecanethiol</td>
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<td>C3 / C3SH</td>
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<td>1-mercapto-3-propanol</td>
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<tr>
<td>C6 / C6SH</td>
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<td>carbon monoxide</td>
</tr>
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<td>CrHO</td>
<td>crotonaldehyde (2-butenal)</td>
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<td>capacitance-voltage</td>
</tr>
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<td>DFT</td>
<td>density functional theory</td>
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<td>DNA</td>
<td>deoxyribonucleic acid</td>
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<td>DRIFTS</td>
<td>diffuse reflectance infrared Fourier transform spectroscopy</td>
</tr>
<tr>
<td>EpB</td>
<td>1-epoxy-3-butene</td>
</tr>
<tr>
<td>EPRI</td>
<td>Electric Power Research Institute</td>
</tr>
<tr>
<td>GAANN</td>
<td>Graduate Assistantshis in Areas of National Need</td>
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<tr>
<td>GC</td>
<td>gas chromatography</td>
</tr>
<tr>
<td>HPLC</td>
<td>high pressure liquid chromatography</td>
</tr>
<tr>
<td>Acronym</td>
<td>Description</td>
</tr>
<tr>
<td>---------</td>
<td>--------------------------------------------------</td>
</tr>
<tr>
<td>HREELS</td>
<td>high resolution electron energy loss spectroscopy</td>
</tr>
<tr>
<td>LEED</td>
<td>low energy electron diffraction</td>
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<tr>
<td>MIS</td>
<td>metal-insulator-semiconductor</td>
</tr>
<tr>
<td>ML</td>
<td>monolayer</td>
</tr>
<tr>
<td>NIST</td>
<td>National Institute of Standards and Technology</td>
</tr>
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<td>PEG</td>
<td>polyethylene-glycol</td>
</tr>
<tr>
<td>PEM</td>
<td>proton exchange membrane</td>
</tr>
<tr>
<td>ppm</td>
<td>parts per million</td>
</tr>
<tr>
<td>RASEI</td>
<td>Renewable and Sustainable Energy Institute</td>
</tr>
<tr>
<td>SAM</td>
<td>self-assembled monolayer</td>
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<td>SFG</td>
<td>sum frequency generation</td>
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<tr>
<td>SSITKA</td>
<td>steady state isotope transient kinetic analysis</td>
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<td>scanning-tunneling microscopy</td>
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<td>thioglycerol</td>
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<td>temperature programmed desorption</td>
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<td>UHV</td>
<td>ultra-high vacuum</td>
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