Investigation of Diesel Engine Emissions Oxidation and Sulfation Mechanisms

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Investigation of Diesel Engine Emissions Oxidation and Sulfation Mechanisms

Hom Nath Sharma, PhD

University of Connecticut, 2015

Noble metal (Pt/Pd) based diesel oxidation catalysts (DOCs) represent the most widely used aftertreatment catalysts to treat emissions from diesel engine exhaust. Due to increasingly stringent regulations to control emissions, the DOCs need to be robust and efficient, which in turn requires a complete understanding of the catalytic reactions taking place inside those units. Despite the excellent activity of currently used DOCs towards engine emissions, they are susceptible to deactivation due to sulfur oxides (SO\textsubscript{x}) in the diesel engine exhaust. Interactions of SO\textsubscript{x} with the catalyst metal and support can result in sulfate formation which leads to the release of untreated toxic emissions to the air. In this thesis, aforementioned two issues are investigated. Specifically, our study is targeted to (a) fundamental understanding of the emissions oxidation chemistry on DOC, and (b) Identification of mechanism of sulfation of DOC. In the first strand, a comprehensive microkinetic model for primary emissions oxidation (e.g., CO, NO, NH\textsubscript{3}, HCN, and CH\textsubscript{2}O) is developed on Pt DOC. The developed microkinetic model was validated against multiple monolith and fixed bed experiments conducted in practically more relevant operating conditions such as dilute emissions concentrations, atmospheric pressure, and short residence times. This approach is extended to explore the reaction kinetics of SO\textsubscript{x} on the Pt surface. The second part of the work undertaken in this thesis focuses on understanding the sulfation mechanism of DOC utilizing state-of-the-art first principles computations. A systematic study is conducted for SO\textsubscript{x} interactions on Pt(111) and Pd(111) surfaces using density functional theory (DFT). To understand the surface reaction mechanism involving
various SO$_x$ species, we investigate the minimum energy pathways and estimated the oxidation barriers for SO$_x$ oxidation on both surfaces. As a stepping stone towards understanding sulfation, we successfully implement our first principles computed parameters as inputs into the SO$_2$ oxidation microkinetic model to predict DOC relevant experimental results. Going forward, we explored the SO$_x$ interactions with Pt and Pd surfaces in realistic temperature and pressure conditions, and under oxidizing and sulfating environments using first principles thermodynamics approach. For the first time we are able to explain why Pd behaves so differently towards sulfation compared to Pt. Few critical descriptors are identified which can be useful for the future quest of sulfur resistant catalysts materials.
Investigation of Diesel Engine Emissions
Oxidation and Sulfation Mechanisms

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B.Sc., Tribhuvan University, 2004
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Doctor of Philosophy Dissertation

Investigation of Diesel Engine Emissions Oxidation and Sulfation Mechanisms

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I would like to dedicate this thesis to my loving parents Agni Prasad Gyawali and Til Kumari Gyawali...
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Chapter 1

Introduction and Background

1.1 Diesel Engine Emissions

Diesel engines are an essential part of the modern society and backbone of the global economy. Diesel is the predominant source of power used in trucks, railroads, shipping, agriculture, public transportation, airport operations, mining as well as homeland security and defense. [1] Diesel provides better fuel economy, greater power density, better performance, unmatched durability, and longer engine life than many other energy sources. Diesel engines offer significantly higher efficiency than current gasoline spark-ignition engines; in some vehicles, fuel efficiency can be improved by 20% to 50% compared to gasoline. This provides the potential for reduced greenhouse gas emissions and reduced petroleum demand in the U.S., improving energy security. [2, 3] More than 13 million diesel vehicles are responsible for transportation of 94% of the goods in the U.S. and use ~ 4 million barrels of diesel per day [4–6]. In the European market, 53% of the passenger cars run on diesel and the global market share of diesel passenger vehicles is expected to double in the next 10 years [2, 7], However, diesel engines are responsible for producing toxic compounds such as carbon monoxide (CO), carbon dioxide (CO\(_2\)), nitrogen
1.2 Emissions Standards and Regulations

oxides (NO\textsubscript{x}), hydrocarbons (HC), sulfur oxides (SO\textsubscript{x}), volatile organic compounds (VOCs), [8–10] poly aromatic hydrocarbons (PAHs), [11, 12] soluble organic fractions (SOF), and particulate matter (PM). [3, 13, 14] Furthermore, solid emissions such as metals, inorganic compounds, sulfates and solid hydrocarbons, [14, 15] nitrogen containing emissions such as hydrogen cyanide (HCN) and ammonia (NH\textsubscript{3}) as well as aldehydes such as formaldehyde (CH\textsubscript{2}O) and acetaldehyde (CH\textsubscript{3}CHO) have also been observed in the diesel engine exhaust. [16–20] These emissions are known to cause cancer, premature death, acute and chronic respiratory injury, asthma attacks, ground level ozone formation, acid deposition, particulate haze, visibility impairment; and they can damage plants, animals, crops, and water resources. [3, 20–24] According to a US-based study by the Clean Air Task Force, toxic emissions from diesel engine exhaust claim 21,000 lives per year due to respiratory and cardiovascular diseases (∼3,000 from lung cancer); result in 27,000 heart attacks and 400,000 asthma attacks per year; lead to ∼139 billion in monetized damages or losses per year; and cause an enormous threat to the environment. [4, 6] Major emission components and their ranges from a typical diesel engine exhaust are shown in Table 1.

1.2 Emissions Standards and Regulations

The year 1970 brought major changes to air pollution regulation. The Clean Air Act amendments of 1970 established the basic approach to mobil sources that continues today. The statute mandated reductions in mobile-source emissions by 90 percent for hydrocarbon, carbon monoxide, and nitrogen oxides, with an initial target date of 1975. The diesel engine emission standards were set by the EPA and California Air Resources Board (CARB) from the mid-1980s. Diesel oxidation catalysts (DOC) and Exhaust gas recirculation (EGR) were introduced to meet the emissions standard set by the EPA. Since 1990, engine manufacturers have reduced the diesel
Table 1.1 Typical diesel engine exhaust composition at an equivalence ratio ($\lambda$) of 1.1–6 [3, 7, 25–31]. $\lambda$ is 1, when the air to fuel ratio (A/F) is 14.7.

<table>
<thead>
<tr>
<th>Species</th>
<th>Concentration range</th>
<th>Unit</th>
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<tbody>
<tr>
<td>CO</td>
<td>100-10000 ppm</td>
<td>ppm</td>
</tr>
<tr>
<td>NO$_x$</td>
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<td>ppm</td>
</tr>
<tr>
<td>HC</td>
<td>50-500 ppm C$_1$</td>
<td>ppm</td>
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<td>SO$_x$</td>
<td>Proportional to fuel sulfur [3], 10-100$^a$ [25], $\sim$1.0$^b$</td>
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<td>PM</td>
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<td>%</td>
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<td>Aldehydes</td>
<td>0.0131-0.1244 mg/km</td>
<td>mg/km</td>
</tr>
</tbody>
</table>

$^a$ Based on the information that fuel with 500 ppm of sulfur produces $\sim$20 ppm SO$_x$.

$^b$ Based on current EPA regulations for fuel sulfur level (15 ppm maximum).

particulates (soot) significantly. With new regulation set in 2007 requires all US heavy-duty diesel vehicles must have a diesel particulate filter (DPF) in the exhaust system to reduce the particulate matter (PM) level to below 0.01 g/bhp-hr. Similarly, catalytic devices were introduced in 1990s to meet the more stricter NO$_x$ reduction standards. In Europe, the standards set by the EU were first established as Euro 1 standards in 1993. Euro 6 standard, comparable in stringency to the US 2010 standards, became effective in 2013, for diesel engine emissions in Europe. Since 2010, the PM, NO$_x$, and the non-methyl hydrocarbon (NMHC) standards are 0.01 g/bhp-hr, 0.2 g/bhp-hr, and 0.14 g/bhp-hr, respectively. Figure 1.1 shows the PM and NO$_x$ standards over the years for heavy-duty diesel engines in the USA.
1.3 Exhaust Aftertreatment Components

Many changes have been made to engine design and fuel composition to reduce emission production, whilst aftertreatment units have been developed to capture emissions or convert them into less harmful components. Due to a higher air to fuel (A/F) ratio compared to traditional gasoline engines (A/F = 14.7), the traditional Three Way Catalyst (TWC) for gasoline exhaust (Three way converter works under stoichiometric condition to oxidize CO and HC and reduce NO\textsubscript{x} simultaneously) is unable to effectively control emissions from diesel engine exhaust; and therefore, the diesel engine exhaust aftertreatment system is quite complex. [22, 32] Multiple aftertreatment units are needed to control various components of diesel engine emissions, as shown in Figure 1.2.

Fig. 1.1 Emission regulations over the years from EPA for heavy-duty trucks in the US.
### 1.3 Exhaust Aftertreatment Components

Fig. 1.2 Schematic of DOC, DPF, DeNO\(_x\), and Ammonia Slip Catalyst (ASC) components in a typical diesel engine exhaust aftertreatment system. Position of the aftertreatment component units can vary according to the manufacturer, type of DeNO\(_x\) unit used, and the regulations.

#### 1.3.1 Diesel Particulate filters (DPFs)

Diesel Particulate Filters (DPF) are the most popular aftertreatment technology to control particulates/soot and to meet the stringent PM emissions standards. [8, 33] DPFs are made of porous materials and consist of channels which are alternately plugged, [2] so the exhaust gas is forced through the channel walls, but the PM is trapped on the filter wall. [34] Even though DPFs are efficient in removing particulates from the engine exhaust, periodic regeneration of DPF is necessary to avoid any plugging/back-pressure. Oxygen (10-15% of exhaust stream) is the main oxidant to burn off the soot particles typically at high temperature (~600 °C); however, presence of NO\(_2\) in the exhaust stream (from NO oxidation on DOC) can enhance the DPF efficiency significantly by reducing the required temperature (~300 °C) along with catalytic coating (in catalytic DPF (cDPF)). [30, 35–38] The schematic DPF with channels is shown in Figure 1.3.

The oxidation of diesel soot, represented here as carbon, by oxygen can be described by one of the following reactions:

$$\text{C} + \frac{1}{2}\text{O}_2 \rightarrow \text{CO} \quad (1.2)$$
In the case of soot oxidation by \( \text{NO}_2 \), the reaction is:

\[
\text{C} + \text{NO}_2 \rightarrow \text{CO}_2 + \text{NO}
\]  

(1.3)

### 1.3.2 DeNO\(_x\) Technologies

It is extremely difficult to reduce NO\(_x\) from the diesel engine exhaust under excess oxygen conditions. [40] To reduce/remove NO\(_x\) from the diesel engine exhaust, two common strategies are considered, viz., Selective Catalytic Reduction (SCR) and NO\(_x\) Storage and Reduction (NSR). SCR selectively reduces the nitrogen oxides (NO and NO\(_2\)) to N\(_2\) using either NH\(_3\)/Urea (typically V\(_2\)O\(_5\)-WO\(_3\)/TiO\(_2\) catalyst) or hydrocarbons (Ag/Al\(_2\)O\(_3\) based catalyst). [22, 41–46] On the other hand, NSR catalysts (also known as Lean NO\(_x\) Traps (LNT)) first remove NO\(_x\) from a lean gas stream by reversible chemical adsorption onto a catalyst (typically Pt/BaO/Al\(_2\)O\(_3\)) in the form of nitrates/nitrites, followed by reduction under stoichiometric or rich conditions. [47–49]
1.3 Exhaust Aftertreatment Components

Urea/NH$_3$-SCR is a popular technology for NO$_x$ reduction. However, it is also associated with excess/unreacted NH$_3$ in the downstream, typically $\sim$10 ppm. [50] A Pt/Al$_2$O$_3$ coated oxidation catalyst–Ammonia Slip Catalyst (ASC)–is often installed after the NH$_3$/Urea-SCR to control the excess NH$_3$. [51–54] ASC oxidizes NH$_3$ to N$_2$ with high selectivity, allows high NH$_3$/urea dosing without increasing NH$_3$ emissions, and avoids undesirable products such as NO$_x$ and N$_2$O. [54, 55]

The selective catalytic reduction involves the following set of reactions which are divided into three categories.

Standard SCR Reaction: This reaction involves reduction of NO by NH$_3$ in the presence of O$_2$ and is given as:

$$4\text{NH}_3 + 4\text{NO} + \text{O}_2 \rightarrow 4\text{N}_2 + 6\text{H}_2\text{O} \quad (1.4)$$

Fast SCR Reaction: When both NO and NO$_2$ in the feed react simultaneously to produce N$_2$ and H$_2$O; it is called as a fast SCR reaction, which is faster than the standard SCR reaction and given as:

$$2\text{NH}_3 + \text{NO} + \text{NO}_2 \rightarrow 2\text{N}_2 + 3\text{H}_2\text{O} \quad (1.5)$$

NO$_2$ SCR Reaction: When NO$_2$ reacts with NH$_3$, it is called as the NO$_2$ SCR reaction and it can be written as:

$$4\text{NH}_3 + 3\text{NO}_2 \rightarrow 3.5\text{N}_2 + 6\text{H}_2\text{O} \quad (1.6)$$

1.3.3 Diesel Oxidation Catalysts

Diesel Oxidation Catalysts (DOCs) represent the most predominant technology to oxidize the toxic emissions/byproducts from diesel engine exhaust. [32, 56–62] Typical DOCs are Platinum (Pt)/Palladium (Pd)/Pt-Pd alloy coated honeycomb like structures, as shown in Figure 1.4. Pd is essential to prevent the sintering of Pt particles at high temperature, which improves the
1.4 Role of DOC in Exhaust Aftertreatment

The primary function of the DOC is to oxidize HC, NO, CO, and byproducts from upstream components to less/non toxic compounds. Furthermore, DOC also provides NO\textsubscript{2} for a downstream urea-SCR, which operates efficiently at an equimolar ratio of NO and NO\textsubscript{2}. [32] NO\textsubscript{2} produced from DOC can also be used to oxidize soot in the DPF at lower temperature than with O\textsubscript{2} alone.[32, 65, 66] Finally, DOC may be needed downstream of a hydrocarbon (HC)-SCR to oxidize the SCR byproducts (or unreacted species), such as CO, HC, NO, NH\textsubscript{3}, HCN, CH\textsubscript{2}O, N\textsubscript{2}O, acetonitrile (CH\textsubscript{3}CN), and CH\textsubscript{3}CHO. [16, 17, 67, 68] Figure 1.5 shows couple of representative configurations of aftertreatment components where DOC plays an important role.
Major catalytic reactions on the DOC can be summarized as follows. [60, 61, 69, 70]

\[ CO + \frac{1}{2}O_2 \rightarrow CO_2 \]  \hspace{1cm} (1.7)

\[ [HC] + O_2 \rightarrow CO_2 + H_2O \]  \hspace{1cm} (1.8)

\[ NO + \frac{1}{2}O_2 \rightarrow NO_2 \]  \hspace{1cm} (1.9)

\[ NH_3 + O_2 \rightarrow N_2 + NO_x + H_2O \]  \hspace{1cm} (1.10)

\[ HCN + O_2 \rightarrow NO_x + CO_2 + H_2O \]  \hspace{1cm} (1.11)

\[ [Aldehydes] + O_2 \rightarrow CO_2 + H_2O \]  \hspace{1cm} (1.12)

\[ [SOF] + O_2 \rightarrow CO_2 + H_2O \]  \hspace{1cm} (1.13)

\[ SO_2 + \frac{1}{2}O_2 \rightarrow SO_3 \]  \hspace{1cm} (1.14)

Despite the versatile nature and utility of DOC, its deactivation due to sulfur is a major challenge in diesel engine exhaust aftertreatment, which is the primary focus of the sections to follow.
1.5 Impact of Sulfur on DOC

Most catalysts deactivate over time, as reflected by decreased conversion/selectivity, thereby requiring catalyst regeneration/replacement and/or process shutdown. Typical catalyst deactivation mechanisms include (i) poisoning, (ii) fouling, (iii) thermal degradation, (iv) vapor formation, (v) vapor-solid and/or solid-solid reactions, and (vi) attrition/crushing. [71, 72] Here, we focus on the deactivation of DOC due to sulfur (poisoning).

Sulfur is present in the diesel fuel and it also comes from the lubricants used. [15, 49, 60] Due to the United States Environmental Protection Agency (EPA) regulations, the currently used ultra low sulfur diesel (USLD) contains up to 15 ppm sulfur. [49, 73–75] Despite the sulfur regulations, typical diesel engine exhaust contains ∼1 ppm of sulfur in oxide form [9] which can deactivate the DOC after long term exposure as well as increase the PM emissions. [9, 15, 76, 77] An example of DOC deactivation due to sulfur in the fuel is shown in Figure 1.6, where the NO oxidation performance decreases significantly in a few hours in the presence of sulfur. [9] Lubricant oil can also adversely impact the sulfur level in exhaust leading to catalyst deactivation. [78]

Sulfur in the diesel fuel and lubricants is oxidized to sulfur dioxide (SO$_2$) in the engine. [60] Due to the excess oxygen in the exhaust, SO$_2$ can be further oxidized to sulfur trioxide.
(SO$_3$) on the DOC or cDPF above 300 C. [15, 60, 79–81] SO$_3$ has been reported to be stable up to 700 C. [32, 82] Both sulfur oxides interact with the DOC, resulting in its deactivation. In general, catalyst deactivation due to sulfur is a complex phenomena, associated with changes in structural, morphological, and electronic properties. [83] For simplicity, DOC deactivation due to sulfur can be divided into three major categories, viz., metal oxide sulfation, support sulfation, and species sulfate formation (through interactions with species in the exhaust), as described next.

Fig. 1.6 Effect of fuel sulfur level on NO conversion on commercial DOCs. [9] Reprinted from Kröcher, O. et al., Adsorption and Desorption of SO$_x$ on Diesel Oxidation Catalysts. Ind. Eng. Chem. Res. 48(22), 2009, 9847-9857, with permission from American Chemical Society (ACS).

### 1.5.1 Metal Oxide Sulfation

The sensitivity order of sulfation of oxidation catalysts used in diesel engine exhaust aftertreatment is Pd > Pt > Rh, [84] i.e., Pd is more likely to be sulfated compared to Pt DOCs. Pd is
typically converted to PdO due to the high oxygen content in the diesel engine exhaust, whereas Pt remains in the metallic form. [63] Pt is highly active for SO$_2$ oxidation [79, 85, 86] but Platinum sulfate (PtSO$_4$) formation is not favored. [15, 31] On the other hand, palladium sulfate (PdSO$_4$) formation is widely reported in the literature. [78, 87] Under lean-burn Natural Gas Vehicles (NGV) operating conditions (in the presence of SO$_2$), deactivation of Pd catalysts due to formation of inactive PdSO$_4$ has also been observed. [81, 87] Overall reaction for the metal oxide sulfation can be written as follows. [60, 88]

$$\text{PdO} + \text{SO}_3 \rightarrow \text{PdSO}_4$$

(1.15)

### 1.5.2 Support Sulfation

In Pt-Pd based DOCs, the precious metal catalysts are dispersed on a support (wash-coat) to increase the catalyst surface area which in turn provides higher catalytic activity. Supports can also provide thermal/mechanical stability. [25, 60] Typically, $\gamma$-Al$_2$O$_3$, SiO$_2$, or ZrO$_2$ are used as support materials as they are highly porous inorganic oxides and ideal for gas diffusion; among these, $\gamma$-Al$_2$O$_3$ is most common support for DOCs. [25, 32, 60, 69] However, presence of sulfur oxides in the diesel engine exhaust can be detrimental to the Al$_2$O$_3$ support, which ultimately deteriorates the DOC activity. [60, 78, 79, 89, 90] Studies show that SO$_3$ strongly interacts with the Al$_2$O$_3$ support in DOC. [91] Once SO$_3$ is formed on the catalyst, there is a reaction with Al$_2$O$_3$ to form aluminum sulfate (Al$_2$(SO$_4$)$_3$) [91–93], which blocks the alumina pores or covers its surface, resulting in decreased surface area [32, 56, 94] and decreased catalytic activity. [92] Even though the support sulfation reaction is reversible, i.e., Al$_2$(SO$_4$)$_3$ forms Al$_2$O$_3$ and SO$_3$ upon heating [84], this decomposition reaction requires a very high temperature ($\sim 727$ °C). [95] The overall reaction of Al$_2$O$_3$ support sulfation can be
written as follows. [69]

\[
\text{Al}_2\text{O}_3 + 3\text{SO}_3 \rightarrow \text{Al}_2(\text{SO}_4)_3
\]  

(1.16)

### 1.5.3 Species Sulfate Formation

Diesel engine exhaust contains significant water vapor (1.4 -7%, see Table I); therefore, SO\(_3\) can also react with the water vapor to form sulfuric acid (H\(_2\)SO\(_4\)), thus creating tremendous challenges for emissions aftertreatment. [9, 60] H\(_2\)SO\(_4\) contributes to the increase in particulates formation; ultra-fine particles in diesel exhaust are considered especially hazardous because of their ability to penetrate deeply into the lungs. [15, 96, 97] H\(_2\)SO\(_4\) can desorb at 350- 400 °C or decompose back to SO\(_3\) and H\(_2\)O at > 250 °C. [9] The overall reaction of sulfuric acid formation from SO\(_3\) and water vapor can be written as follows.

\[
\text{H}_2\text{O} + \text{SO}_3 \leftrightarrow \text{H}_2\text{SO}_4
\]  

(1.17)

Presence of NH\(_3\), e.g., through urea injection in SCR of NO\(_x\) or through NH\(_3\) formation in HC-based SCR of NO\(_x\), could also result in ammonium (bi)sulfate ((NH\(_4\))\(_2\)SO\(_4\)) formation, which increases the catalyst deactivation rate. [95, 98, 99] The overall reaction of (NH\(_4\))\(_2\)SO\(_4\) formation can be written as follows.

\[
2\text{NH}_3 + \text{SO}_3 + \text{H}_2\text{O} \leftrightarrow (\text{NH}_4)_2\text{SO}_4
\]  

(1.18)

### 1.6 Research Objectives and Outline

The primary objective of this thesis to investigate the diesel engine emissions oxidation and sulfation mechanism. To achieve these goals, we investigate the soot oxidation kinetics on
the diesel particulate filter, primary emissions and sulfur oxides oxidations, and sulfation mechanism in the diesel oxidation catalysts. The soot oxidation kinetics study is mostly an experimental work using thermogravimetric analysis (TGA) method. The comprehensive study is performed with multiple samples including carbon black and diesel engine soot samples. This study provides many insights on the kinetics parameters of soot oxidation. Details of this work and results are provided in the Appendix A. The core of this thesis encompasses the work on DOC, which involves the development of fundamental understandings of emissions oxidation (i.e. CO, NO, CH₂O, NH₃ and HCN) and SOₓ oxidation mechanism study and sulfation study to identify descriptors for sulfur deactivation of DOCs. Hydrocarbon emissions oxidation (i.e. C₂H₄ oxidation) is provided the appendix K. In essence, the soot oxidation kinetics information along with the structure-activity correlations will provide design guidelines for DPF and optimal temperature of operations to make it more economical and produce less emissions. The study of emissions oxidation chemistry will give information about the primary DOC chemistry, important reaction pathways and catalysts sizing. Such information will be crucial for efficient and economical design of DOC. On the other hand, study of the underlying molecular level sulfation mechanism will help to understand the fundamentals of DOC deactivation in the presence of sulfur oxides, identify key features of sulfation and provide some guidelines to identify new sulfur resistant catalyst materials. Next, the thesis organization is briefly discussed.

Chapter 2 provides a brief introduction to the methodologies utilized in this work. First, experimental setup is discussed for the BenchCAT reactor experiments using powder and monolith catalysts. Then, a brief description is provided for the microkinetic modeling with plug flow reactor model. At last, density functional theory and other first principles computations based methods (e.g. the first principles thermodynamics, structure prediction method called USPEX) are discussed.
Chapter 3 focus on developing a detailed mechanistic understanding of the catalytic reaction kinetics for the oxidation of five major emissions species (C$_1$ and N$_1$ components) on Pt-based DOCs. Those emissions species include CO, NO, CH$_2$O, NH$_3$, and HCN. The chapter addresses development of elementary step reaction mechanism, kinetics and thermodynamic parameter estimation using various techniques, and the model validation using plug flow reactor modeling coupled with detailed reaction mechanism.

Chapter 4 surveys the challenging problem of SO$_x$ interactions with DOC. It provides a brief background on the past work and focuses on the development of detailed microkinetic modeling of SO$_2$ oxidation of Pt based DOC.

Chapter 5 discusses the development of microkinetic model for H$_2$SO$_4$ formation on DOC due to SO$_x$ and H$_2$ interactions. Two possible pathways for the H$_2$SO$_4$ formation is analyzed and the most favorable pathway is proposed.

Chapter 6 covers the first principles based investigation of SO$_x$ interactions with Pt(111) and Pd(111) surfaces. Thermodynamics, kinetics of SO$_x$ oxidation are compared to understand the interactions of Pt and Pd with SO$_x$. This chapter also discusses how DFT can be coupled with microkinetic modeling to study the SO$_x$ oxidation process.

Chapter 7 focuses on a comprehensive analysis of sulfation behaviors of Pt and Pd DOC. The first principles thermodynamics is employed to study the phases under oxidizing and sulfating environments. From this study, few important descriptors are identified which could help us to design future sulfur resistant catalysts for DOC.

In the last Chapter, I provide a summary of this work, few key achievements, and a broad outlook for the future directions to further this research.
Chapter 2

Methods

2.1 Introduction

In this work, microkinetic modeling, density functional theory, and experimental approaches have been implemented to understand the oxidation and sulfation mechanism of diesel oxidation catalysts (DOCs). In this chapter, a brief review of the methodologies is provided. Primary emissions oxidation chemistry (e.g., CO, NO, CH₂O, NH₃, HCN) and SOₓ oxidation chemistry are studied using microkinetic modeling technique coupled with steady state plug flow reactor model. More complex SOₓ interactions on the Pt or Pd surfaces are studied using the first principles DFT. The first principles thermodynamics was implemented to understand temperature and pressure dependent behavior under oxidizing and sulfating environments. Fixed bed and monolith scale experiments in the BenchCAT reactor were used to study the selected emissions species oxidation on Pt based DOCs. Figure 2.1 shows a overall approach using multiple techniques to understand fundamentals of emissions oxidations and sulfation mechanism of DOCs.
2.2 Experiments

Altamira BenchCAT reactor is used to conduct the oxidation experiments of CO and C\textsubscript{2}H\textsubscript{4}. Both monolith and fixed bed type experiments were conducted. The fixed bed reaction was carried out on 1-5 mg of catalyst loaded in a 0.34 cm i.d. quartz tube reactor inside a temperature controlled furnace. Dycor Dymaxion mass spectrometer and Agilent Micro GC were used for the gas species analysis in the product stream. Oxidation study was carried out in a temperature range relevant to the DOC operating conditions. 1% CO oxidation experiments were carried out with 10% oxygen and balance Ar. For C\textsubscript{2}H\textsubscript{4} experiments, effects of O\textsubscript{2} partial pressure (6 -14 %), C\textsubscript{2}H\textsubscript{4} concentration (500 - 3000 ppm), and space velocity (20000 - 60000 h\textsuperscript{-1}) on catalytic performance were tested for the temperature range of 50-300 °C. Ar was used as a balance gas in the experiments. All experiments were performed at near atmospheric pressure condition.
2.3 Microkinetic Modeling

Microkinetic modeling approach was introduced by Dumesic et al. in 90s. [100] Ever since it has been successfully implemented to study variety of reactions in different environments. [101–106] Microkinetic modeling typically involves setting up a network of elementary-step reactions for a given reaction based on the information on reactants, products and the possible intermediates. Microkinetic modeling can be used to predict surface coverages, most abundant reaction intermediate(s) (MARI), conversion, and rate-determining steps without any a priori assumptions about the reactions RDS, PE, QSS, or MARI. In this thesis, microkinetic modeling is performed to study the oxidation mechanism of various emissions species. Next, a brief description of the steps is provided.

Fig. 2.2 Experimental Setup. (a) Schematic of the experimental setup used for CO and C₂H₄ oxidation experiments. (b) Picture of the BenchCAT reactor and catalyst holder.
2.3.1 Mechanism Development

A set of elementary step surface reactions mechanism is developed for a particular reaction. The reaction steps are considered based on the experimental or theoretical information on the possible intermediates and products for a given initial reactants. For example, CO oxidation can be expressed into a set of elementary reaction as:

\[
\begin{align*}
\text{CO}_{(g)} + * & \leftrightarrow \text{CO}^* & (2.1) \\
\text{O}_2(g) + * & \leftrightarrow 2\text{O}^* & (2.2) \\
\text{CO}^* + \text{O}^* & \leftrightarrow \text{CO}_2^* & (2.3) \\
\text{CO}_2^* & \leftrightarrow \text{CO}_{2(g)} & (2.4)
\end{align*}
\]

2.3.2 Kinetic Parameters Estimation

Kinetic parameters for the proposed mechanism were estimated/extracted using various methods, i.e. simulations of UHV temperature programmed surface science experiments in literature, semi-empirical UBI-QEP method [107, 108], and first principles DFT calculations. For each stable species in the reaction mechanism, we have considered multiple TPD experimental data on Pt facets to extract the species binding energies (Q) and adsorbate-adsorbate interactions (\(\alpha\)). Various TPR experimental data sets in the literature are used to extract the activation energies (Ea and bond indices (BI) for the reactions. DFT calculations are carried out to estimate binding energies (Q) and adsorbate-adsorbate interactions (\(\alpha\)) parameters of various intermediates and
2.3 Microkinetic Modeling

radicals along with stable species. Such calculations will reduce the inherent error introduced to the model due to parameters, as all parameters are computation with same level of theory and accuracy. The semi-empirical UBI-QEP method is used to estimate the coverage and temperature dependent activation energies on-the-fly in these simulations. Functional forms to compute the activation energies using UBI-QEP formalism are discussed in the Appendix B. In UBI-QEP formalism, temperature and coverage dependence to compute activation barriers are introduced through binding energy as shown in equation.

\[ Q(T) = Q_o - \alpha \theta - \gamma R(T - T_o) \]  

(2.5)

where, \( \alpha \) is the coverage dependence coefficient (kcal/mol/ML), \( \theta \) is the coverage of species (ML), \( \gamma \) is the temperature dependence coefficient for binding energies (unit-less), \( R \) is the universal gas constant (kcal/mol/K), and \( T \) is the temperature (K). ML stands for monolayer. \( T_o \) is taken as 300 K. The temperature dependence (\( \gamma \)) is derived from the statistical mechanics based calculations for degrees of freedom lost/gained upon adsorption.[26] Bond index represents the position of the transition state along the reaction coordinate, which is also used to compute the activation energies in the UBI-QEP formalism. [107, 108] It is defined for a reaction pair in the forward direction only. It ranges between 0 and 1, with a typical initial estimate of 0.5 is used here. Pre-exponential factors are taken either from literature (if available) or taken as initial estimates based on transition state theory (TST), e.g., \( 10^{13} \) s\(^{-1} \) for desorption and \( 10^{11} \) s\(^{-1} \) for Langmuir-Hinshelwood type surface reactions. Sticking coefficients for the adsorption reactions are taken from values reported in literature, otherwise taken as unity. Site density \( \sigma \) of \( 1 \times 10^{15} \) sites/cm\(^2\) (2.5 \times 10^9 \) mol/cm\(^2\)) is used in the simulations based on the typical estimate for the most stable Pt(111) facet.
2.3 Microkinetic Modeling

2.3.3 Reactor Modeling

Steady state isothermal plug flow reactor (PFR) modeling was used to simulate the monolith scale experiments conducted in various operating conditions. Isothermal assumption is based on the very small amount of heat generated during the oxidation of very dilute concentration levels of the emissions in the exhaust. The governing equations for steady state PFR are given as:

$$\frac{dY_z}{dz} = \frac{G_k M_k}{\rho \mu} + \left( \frac{A_c}{V_R} \right) \frac{S_k M_k}{\rho \mu}, \quad \text{fork} = 1, \ldots, g_{\text{gas}}$$  (2.6)

$$S_k = 0, \quad \text{fork} = n_{\text{gas}} + 1, \ldots, n_{\text{gas}} + n_{\text{surf}}$$  (2.7)

$$\sum \theta_k = 1, \quad \text{fork} = n_{\text{gas}} + 1, \ldots, n_{\text{gas}} + n_{\text{surf}}$$  (2.8)

where, k indicates the species index, $n_{\text{gas}}$ is the number of gas phase species, $n_{\text{surf}}$ is the number of surface species, z is the reactor length variable, $Y_k$ is the mass fraction of gas phase species, $G_k$ is rate of gas phase species, $M_k$ is the molecular weight of species, $S_k$ is the catalytic rate of gas phase species (through adsorption and desorption), $\rho$ is the mass density, $\mu$ is the velocity, and $A_c/V_R$ is the catalyst area per unit reactor volume.

The surface coverages at the reactor inlet are estimated using transient simulations until it reaches steady state coverage. The GRI Mech 3.0 gas phase reaction mechanism [109] was used to account for the gas phase chemistry. The resulting set of differential and algebraic (DAE) equations was solved using the DDASPK solver. [110]
2.4 Density Functional Theory (DFT)

A parameter free, in principles, method which takes the electronic and ionic charges and masses as inputs to perform the quantum mechanical calculations is referred to as "first-principles" or "ab-initio" method. Among the currently practiced electronic structure methods, density functional theory (DFT) provides the best tradeoff between computational cost and accuracy. There are many flavors of ab-initio methods, which are being used to compute the properties of the material. In this thesis, the main focus will be on one particular flavor, or more correctly, combination of methodologies and approximations. That is the plane-wave pseudopotential method, within density functional theory, employing a gradient corrected functional to describe the exchange-correlation energy.

Kohn and Sham [111] extended the work of Hohenberg and Kohn [112] and showed how the intractable many-body problem of interacting electrons in a static external potential is reduced to a tractable problem of non-interacting electrons moving in an effective potential. The effective potential includes the external potential and the effects of the Coulomb interactions between the electrons, e.g., the exchange and correlation interactions. This resembles aspects of the Hartree-Fock approximation of one-electron wavefunctions. As in Hartree-Fock theory, the n-electron system is reduced to a set of n non-interacting one-electron systems. In Hartree-Fock theory this is the basic approximation upon which the solution is built, but in DFT it is simply a tool to calculate the exact component of an unknown term. The Kohn-Sham equation is defined by a local effective external potential in which the non-interacting particles move, typically denoted as $V_{\text{eff}}(\vec{r})$, called the Kohn-Sham potential.

$$\left[ -\frac{1}{2}\nabla^2 + V_{\text{eff}}(\vec{r}) \right] \phi_i = \varepsilon_i \phi_i \quad i = 1, 2, ...., n \quad (2.9)$$
2.4 Density Functional Theory (DFT)

Here, $\varepsilon_i$ is the orbital energy of the corresponding Kohn-Sham orbital, $\phi_i$, and the density for an n-particle system is:

$$\rho = \sum_{i}^{n} \langle \phi_i | \phi_i \rangle$$  \hspace{1cm} (2.10)

The DFT is a SCF theory as Kohn-Sham equations are solved iteratively where $V_{\text{eff}}(\vec{r})$ depends on the electron density, therefore on the orbitals. Everything except the functional form of $E_{XC}$ is known exactly. The fact that the exact functional for exchange and correlation is not known results in an intrinsic limitation of, otherwise exact, current DFT and practical implementations need to rely on approximate functionals. The two approximate functional used in the present work are the local density approximation (LDA) and the generalized gradient approximation (GGA). While in LDA the functional depends only on the density at the local coordinate where the functional is evaluated, GGA also takes into account the gradient of the density at the local coordinate. A brief history about the DFT has been provided in the Appendix J. More details and background can be found elsewhere.

DFT is capable of predicting electronic structure and geometrical details of periodic and non-periodic systems, vibrational frequencies of molecules, phonon frequencies of solids, elastic constants of solids, and relative energies of different phases and surface/interface energies of solids, static and optical dielectric constants, etc. Here brief description of the computations performed using DFT.

2.4.1 Computational Details

For all DFT calculations described in this work (otherwise stated), we used the Vienna ab-initio simulation package (VASP) code [113] with the PBE implementation of the generalized gradient approximation (GGA) exchange-correlation functional.[114]
2.4.2 Pt or Pd

The structure of bulk FCC Pt/Pd (see Figure 2.3) is calculated within a primitive face-centered cubic (FCC) cell using a Monkhorst-Pack K-point mesh. The calculated bulk lattice constant of Pt and Pd were 3.97 Å and 3.95 Å respectively, which are in good agreement with previous theoretical calculations (Pt, $a_0 = 3.96$ Å–4.0 Å[115–117] and Pd, $a_0 = 3.94$ Å–3.97 Å[117–119] as well as experimental (Pt, $a_0 = 3.92$ Å[118, 120] and Pd, $a_0 = 3.89$ Å[117, 121]) results. The calculated cohesive energies were 5.6 eV/atom (experimental $E_{\text{cohesive}} = 5.8$ eV/atom [122]) and 3.7 eV/atom (experimental $E_{\text{cohesive}} = 3.89$ eV/atom [121]) for Pt and Pd respectively.

Fig. 2.3 Schematics of the FCC bulk model of Pt/Pd used in this study.

2.4.2.1 Surface Slab Models

In this work, the (111) surface of Pt and Pd metals is used. Most of the calculations were performed using a 5-layer slab model (see Figure 2.4) with the bottom two layers frozen. Typically, an intervening vacuum layer of 10-15 Å was applied. For the k-point sampling, a Monkhorst-Pack scheme was used. Surface work function ($\phi$) calculated for Pt and Pd
slabs were 5.78 eV and 5.05 eV, respectively, which are consistent with the corresponding experimental values of 5.8 eV [122] and 5.0 eV [123], respectively. Furthermore, the calculated surface energies were 97.9 meV/Å\(^2\) and 82.4 meV/Å\(^2\) for Pt(111) and Pd(111), which are in agreement with previous DFT studies. [124]
2.4.2.2 Surface Energy

Surface energy can be defined as the energy required to create one unit of surface area. The surface energy can be calculated for a symmetric slab as:

\[ \gamma = \frac{1}{2} \left[ \frac{E_{\text{slab}} - N_{\text{atom}} E_{\text{bulk}}}{A} \right] \] (2.11)

where \( E_{\text{slab}} \) is the total energy of the slab with \( N \) atoms, \( E_{\text{bulk}} \) is the energy per atom of the bulk metal, \( A \) is the cross-section area of the surface of the slab. The factor of 1/2 is to account for the two surfaces of the slab.

2.5 First Principles Thermodynamics

DFT computations can be utilized to compute many properties and compare the stability of various systems. However, the 0 K DFT can not provide accurate information of the systems at the elevated temperature and pressure conditions. The stability and physical properties of surfaces and interfaces can depend strongly on their detailed chemical composition and change with the surrounding environment. Identification of relevant compositions of these systems requires a thermodynamic treatment at the DFT computations are only enthalpies in nature. Thus, at finite temperatures, however, both configurational and vibrational entropy can be significant and must be accounted for. The temperature and pressure dependence are incorporated to the first principles DFT computations, also referred to as a first principles thermodynamics.

This recently developed approach of the first principles thermodynamics and have been successfully applied to a variety of systems, aimed at addressing problems from diverse fields; spanning from catalysis design to alloy optimization, and from study of corrosion phenomena...
to investigation of materials in the earth’s mantle. [125–128] The FPT approach is primarily employed to use information pertaining to the potential energy surface calculated at the level of electronic structure theory, for a system in equilibrium (or in a meta stable state), to calculate an appropriate thermodynamic potential function such as the Gibbs free energy $G$. The Gibbs free energy of any system decomposed in terms of various contributing factors can be given as follows:

$$G(T, P) = E^{\text{total}} + F^{\text{vib}} - TS^{\text{conf}} + pV \tag{2.12}$$

where $E^{\text{total}}$, $S^{\text{conf}}$, $P$ and $V$ represent the total energy of the system, configurational entropy, pressure, and volume terms respectively. The contribution to Gibbs free energy from $pV$ term and configurational entropy are negligible for the adsorption process, hence discarded in this study. Thus, we incorporate this contribution through harmonic normal mode analysis of the adsorbates and the substrate layers involved in the case of surface models using Bose-Einstein model approximations. The approximation is computed as, [129]

$$F^{\text{vib}} = \frac{1}{2} \sum_i 3N\epsilon_i + k_B T \sum_i 3N \ln(1 - e^{-\beta \epsilon_i}) \tag{2.13}$$

where $\epsilon_i = h\nu$ represents the phonon energy at different vibrational modes, $\nu_i$ represents the vibrational frequency and $\beta = (k_B T)^{-1}$.

When a surface is exposed to a reservoir, it tries to establish the equilibrium state as guided by the partial pressure of the surrounding. Figure 2.5 shows such scenario of a surface in oxygen environment. The surface energy of the slab with adsorbates will be stable compared to the clean slab if the surface energy of the former is lower (i.e. $\gamma_{\text{slab+adsorbates}} < \gamma_{\text{slab}}$) and change in Gibbs free energy, $\Delta G^{\text{ads}} \geq 0$. In general, surface energy of a surface model system
in equilibrium with the surrounding gas phase reservoir can be expressed as follows.

\[
\gamma(T, p\{i\}) = \frac{1}{A} \left[ G^{\text{surf}} - \sum_{i=1}^{n} N_i \mu_i(T, p_i) \right]
\]  

(2.14)

where, \(G^{\text{surf}}\), \(A\), \(\mu_i\), \(n\), and \(N_i\) represent the Gibbs free energy, surface area of the slab, individual gas species in the system, number of gas species, number of atoms/molecules of gas species, respectively. More details are provided in the Appendix.

### 2.6 Universal Structure Predictor: Evolutionary Xtallography (USPEX)

USPEX is a method developed by the Oganov laboratory since 2004, which is mostly famous for crystal structure prediction. [130, 131] The code/method, predicts the crystal packing from only a knowledge of chemical species, compositions, or the molecular geometries, has met tremendous success in correctly identifying and predicting the crystal structures of various classes of systems (bulk crystals, [132, 133] nanoclusters, [134] 2D crystals, [135] surfaces, [136] and new polymers [137, 138]). In this work, we explored the structural space of experi-
mentally unknown PtSO$_4$ and known PdSO$_4$, with a fixed stoichiometric composition, allowing up to four formula units per unit cell. Details of the USPEX methodology and background can be found elsewhere. [130, 131]
Chapter 3

Oxidation of C_1 and N_1 Species on Diesel Oxidation Catalysts (DOCs)

3.1 Introduction

In this chapter, we focus on developing a detailed mechanistic understanding of the catalytic reaction kinetics for the oxidation of five major emissions species (C_1 and N_1 components) on Pt-based DOCs. The five chemistries include oxidation of CO, NO, CH_2O, NH_3, and HCN (see Table 3.1). Even though CO and NO oxidation chemistries are well studied, [7, 103, 139–148] this work presents the first comprehensive reaction mechanism for a Pt-based DOC that can be used to predict the oxidation behavior of five key primary or secondary emissions. The chapter is organized as follows. First, we discuss the methodology for the development of emissions oxidation chemistry in Section 3.2. In Section 3.3, we discuss the estimation of kinetic parameters from ultra-high vacuum (UHV) temperature programmed desorption/reaction (TPD/TPR) experiments in literature. Performance of the reaction mechanism is demonstrated in Section 3.4 at practically more relevant operating conditions. Preliminary mechanism reduction
is discussed in Section 3.5. Finally, we discuss the overall limitations of this work in Section
3.6, followed by conclusions.

3.2 Emissions Oxidation Chemistry Development

The overall approach for the development of a comprehensive microkinetic model for the
oxidation of five emissions consists of three major steps. First, an elementary step reaction
mechanism is proposed for the oxidation of each of the five emissions. Second, the kinetic
parameters associated with various species and reactions are extracted from literature surface sci-
ence experiments or estimated from theory. Finally, the surface reaction mechanism, combined
with reactor modeling, is validated against multiple monolith and fixed bed experiments con-
ducted in practically more relevant operating conditions such as dilute emissions concentrations,
atmospheric pressure, and short residence times.

Table 3.1 Overall chemistry for the oxidation of engine exhaust emissions.

<table>
<thead>
<tr>
<th>Emission component</th>
<th>Chemistry</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td>CO + $\frac{1}{2}$O$_2$ → CO$_2$</td>
</tr>
<tr>
<td>NO</td>
<td>NO + $\frac{1}{2}$O$_2$ → NO$_2$</td>
</tr>
<tr>
<td>CH$_2$O</td>
<td>CH$_2$O + O$_2$ → CO, CO$_2$, H$_2$, and H$_2$O</td>
</tr>
<tr>
<td>NH$_3$</td>
<td>NH$_3$ + O$_2$ → NO, NO$_2$, N$_2$O, N$_2$, H$_2$, and H$_2$O</td>
</tr>
<tr>
<td>HCN</td>
<td>HCN + O$_2$ → CO, CO$_2$, NO, NO$_2$, N$_2$O, C$_2$N$_2$, H$_2$, and H$_2$O</td>
</tr>
</tbody>
</table>

3.2.1 Development of the Surface Reaction Mechanism

Elementary surface reactions for the oxidation of CO, NO, NH$_3$, HCN, and CH$_2$O on Pt are
shown in Table 3.3. The complete oxidation products include CO$_2$, NO$_2$, and H$_2$O, whereas
the incomplete oxidation products include CO, NO, and N$_2$O. Additional stable species, such
as O$_2$, N$_2$, H$_2$, and C$_2$N$_2$ (cyanogen), as well as intermediates such as, C, H, OH, COOH, N,
Table 3.2 List of species binding energies (or activation energies for associative desorption) and adsorbate interactions extracted from various TPD simulations (see Section 3.3.1 for details of the TPD simulations). If the extracted adsorbate interactions are insignificant based on the experiments at multiple initial coverages, they are explicitly indicated with zeros (for NO$_2$, HCN, and C$_2$N$_2$).

<table>
<thead>
<tr>
<th>Species</th>
<th>Q or E [kcal/mol]</th>
<th>Catalyst and reference</th>
<th>Q or E range from literature [kcal/mol]</th>
</tr>
</thead>
<tbody>
<tr>
<td>O$_2$ (asso. des.)</td>
<td>49.5-34$\theta_O$</td>
<td>Pt(111) [149]</td>
<td>40-60</td>
</tr>
<tr>
<td></td>
<td>55 - 29$\theta_O$</td>
<td>Pt(111) [150]</td>
<td>[145, 149, 151–153]</td>
</tr>
<tr>
<td></td>
<td>52.6 - 34$\theta_O$</td>
<td>Pt(111) [151]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>36 - 6.1$\theta_{CO}$</td>
<td>Pt(100) [154]</td>
<td></td>
</tr>
<tr>
<td>CO</td>
<td>34.9 - 7.5$\theta_{CO}$</td>
<td>Pt(111) [155]</td>
<td>29-54</td>
</tr>
<tr>
<td></td>
<td>37 - 7.7$\theta_{CO}$</td>
<td>Pt(111) [139]</td>
<td>[145, 147, 157–162]</td>
</tr>
<tr>
<td></td>
<td>35.8 - 12$\theta_{CO}$</td>
<td>Pt(111) [156]</td>
<td></td>
</tr>
<tr>
<td>H$_2$ (asso. des.)</td>
<td>21 - 5$\theta_H$</td>
<td>Pt(111) [163]</td>
<td>13-34</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>11.4 - 2.8$\theta_{H_2O}$</td>
<td>Pt(111) [154]</td>
<td>6-15</td>
</tr>
<tr>
<td></td>
<td>10.9 - 1.9$\theta_{H_2O}$</td>
<td>Pt(111) [172]</td>
<td>[154, 173–178]</td>
</tr>
<tr>
<td></td>
<td>20.7 - 9.9$\theta_{NH_3}$</td>
<td>Pt(111) [179]</td>
<td></td>
</tr>
<tr>
<td>NH$_3$</td>
<td>21.2 - 10$\theta_{NH_3}$</td>
<td>Pt(111) [180]</td>
<td>14-23</td>
</tr>
<tr>
<td></td>
<td>20.1 - 8.8$\theta_{NH_3}$</td>
<td>Pt(111) [181]</td>
<td>[182–189]</td>
</tr>
<tr>
<td>NO</td>
<td>29.5 - 9.7$\theta_{NO}$</td>
<td>Pt(111) [148]</td>
<td>18-43</td>
</tr>
<tr>
<td></td>
<td>29.8 - 7.6$\theta_{NO}$</td>
<td>Pt(111) [190]</td>
<td>[49, 146–148, 184, 191, 192]</td>
</tr>
<tr>
<td></td>
<td>28.4 - 6.8$\theta_{NO}$</td>
<td>Pt(111) [152]</td>
<td></td>
</tr>
<tr>
<td>NO$_2$</td>
<td>19 - 0$\theta_{NO_2}$</td>
<td>Pt(111) [193]</td>
<td>17-38</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>[191–197]</td>
</tr>
<tr>
<td>HCN</td>
<td>26.1 - 0$\theta_{HCN}$</td>
<td>Pt(112) [198]</td>
<td>14-30</td>
</tr>
<tr>
<td></td>
<td>16.6</td>
<td>Pt(111) [199]</td>
<td>[184, 200]</td>
</tr>
<tr>
<td>CH$_2$O</td>
<td>14.7</td>
<td>Pt(111) [201]</td>
<td>11-16</td>
</tr>
<tr>
<td></td>
<td>21</td>
<td>Pt(111) [202]</td>
<td>[165, 168]</td>
</tr>
<tr>
<td>C$_2$N$_2$</td>
<td>22.3 - 0$\theta_{C_2N_2}$</td>
<td>Pt(111) [203]</td>
<td>12-42</td>
</tr>
<tr>
<td></td>
<td>19.7</td>
<td>Pt(111) [202]</td>
<td>[204, 205]</td>
</tr>
</tbody>
</table>

NH, NH$_2$, CN, and HCO, are also considered. Inclusion of various cross-interactive reaction pathways, such as (i) CO and H$_2$ oxidation, (ii) NO and H$_2$ oxidation, (iii) CO oxidation and carbon formation/oxidation, and (iv) HCN oxidation and C$_2$N$_2$ formation, is a unique and
novel feature of this comprehensive mechanism. The overall reaction mechanism consists of 21 surface species and 124 irreversible surface reactions (62 reversible pairs).

3.3 Parameter Estimation From UHV Experiments

As mentioned previously, UHV-TPD simulations of various species are carried out to extract the species binding energies and adsorbate-adsorbate interactions (see Table 3.2). Similarly, UHV-TPR simulations are carried out for various systems to extract the bond indices (related to activation energies). First, we discuss representative TPD simulations, and follow up with the TPR simulations, along with reaction path analysis (RPA) to provide mechanistic insights.

3.3.1 UHV-TPD Simulations

In this work, we have studied desorption of multiple species included in the reaction mechanism. For each species, multiple TPD data sets (>25 experimental data sets in total) on Pt surface are used to extract species binding energies and adsorbate-adsorbate interactions (see Figure 3.1 for a few representative TPD simulations and comparison to experimental data). All desorption rates are shown in mol/cm$^2$/s, but turn-over frequencies (s$^{-1}$) can be obtained by dividing with the site density (mol/cm$^2$). Extracted kinetic parameters from the TPD simulations are given in Table 3.2. Even though this analysis is fairly straightforward, next we briefly discuss a few important parameters and features.

From multiple CO TPD experiments (see Figure 3.1a for an example), we have extracted $Q_{CO}$ (35-37 kcal/mol) and CO*-CO* adsorbate interactions (6-12 kcal/mol/ML). Our estimates are within the reported heat of CO chemisorption range of 29-54 kcal/mol. [103, 157–162] We note that the binding energies and adsorbate interactions for the CO oxidation chemistry are similar to the ones reported by Mhadeshwar and Vlachos. [103] The extracted $Q_{NO}$
Fig. 3.1 UHV-TPD analysis of (a) CO, (b) NO, (c) H₂, (d) O₂, (e) NO₂, and (f) HCN on Pt. Symbols represent the experimental data, whereas lines represent our simulations. Panel a: CO TPD; [139] initial high and low CO* coverages are 0.82 ML and 0.05 ML, respectively; ramp rate=13 K/s. Panel b: NO TPD; [148] initial high and low NO* coverages are 0.55 ML and 0.05 ML, respectively; ramp rate=10 K/s. Panel c: H₂ TPD; [169] initial high and low H* coverages are 0.8 ML and 0.05 ML, respectively; ramp rate=7.9 K/s. Panel d: O₂ TPD; [151] initial high and low O* coverages are 0.25 ML and 0.04 ML, respectively; ramp rate=8 K/s. Panel e: NO₂ TPD; [195] initial high and low NO₂* coverages are 0.5 ML and 0.25 ML, respectively; ramp rate=10 K/s. Panel f: HCN TPD; [198] initial HCN* coverage is 0.5ML; ramp rate=2 K/s. See Table 3.2 for the extracted kinetic parameters from these simulations.
based on multiple NO TPD experiments (see Figure 3.1b for an example) is in the range of 28-30 kcal/mol with NO*-NO* adsorbate interactions of 6-10 kcal/mol/ML. These estimates are well aligned with the reported \( Q_{NO} \) (18-43 kcal/mol [49, 146, 148, 206]). Based on the work of Hauptmann et al., \( Q_{NO} \) depends on the O* coverage as well; and these repulsive interactions are taken as 16 kcal/mol/ML. [147] The H*-H* adsorbate interactions are small (1.9 kcal/mol/ML), as seen from the relatively smaller shift in peak temperatures (see Figure 3.1c). O*-O* adsorbate interactions of 13.3 kcal/mol/ML are taken from the literature [147] and are also consistent with our TPD simulations shown in Figure 3.1d. Based on our TPD simulations (not shown), the estimated \( Q(\text{NH}_3) \) of 20-22 kcal/mol is also within the reported range of 14-23 kcal/mol. [182–185, 207] Based on the peak shift with initial coverage, the \( \text{NH}_3^*\text{NH}_3^* \) adsorbate interactions are estimated to be 9.5 kcal/mol/ML. \( Q(\text{NO}_2) \) is estimated to be 19 kcal/mole, which is consistent with literature estimates of 17-38 kcal/mol; [191–197] but no significant adsorbate interactions are observed in the experimental data [193] and the TPD simulations (see Figure 3.1e). \( Q(\text{CH}_2\text{O}) \) is estimated as 14.7 kcal/mol (not shown), which is consistent with the reported range of 11-16 kcal/mol. [165, 166, 208]

Compared to other species, the TPD behavior of HCN is different (see Figure 3.1f), as it shows decomposition and formation of \( \text{H}_2 \) and \( \text{C}_2\text{N}_2 \) as products along with typical HCN desorption. From TPD experiments [209], \( Q_{\text{HCN}} \) is estimated to be 26.1 kcal/mol. This is consistent with the literature reported range of 14-30 kcal/mol. [184, 200] Experimental data suggest that desorption of HCN from Pt is independent of the surface coverage, i.e., the adsorbate interactions are insignificant [210]. \( Q(\text{C}_2\text{N}_2)_{\text{avg}} \) is estimated to be 21 kcal/mol from the TPD simulations of \( \text{C}_2\text{N}_2 \) on \( \text{Pt}(111) \) surface. [202, 203, 211] To correctly capture the peak location of \( \text{C}_2\text{N}_2 \) formation from the HCN TPD (670 K), bond index of the reaction pair \( R_{123}-R_{124}: \text{C}_2\text{N}_2^* + * \leftrightarrow 2\text{CN}^* \) is modified to 0.73 (starting from 0.5). With this modification,
our model shows good agreement with the peak locations for all three products (HCN, H₂, and C₂N₂), as shown in Figure 3.1.

These and many other kinetic parameters estimated from the UHV-TPD simulations (see Table 3.2) form the basis of the UHV-TPR simulations described next, and also of the fixed bed and monolith simulations described in Section 3.4.

### 3.3.2 UHV-TPR Simulations

#### 3.3.2.1 CO Oxidation

Figure 3.2a shows the peaks for CO₂ formation rate and excess CO desorption rate from the CO oxidation UHV-TPR experiments on Pt(111) by Gerrard et al. [140] Initial coverages include 0.29 ML of CO* and 0.25 ML of O*. As CO* oxidation to CO₂* (R₁₀) is the most important reaction, bond index of that reaction pair R₉-R₁₀: CO₂*+* ↔ CO*+O* is adjusted to 0.73 (starting from 0.5) to correctly capture the location of the CO₂ desorption peak. The bond index modification implemented here is similar to the earlier work (bond index = 0.8) by Mhadeshwar and Vlachos [103] for this reaction based on DFT-derived Polanyi-type relations in literature. The small difference originates from our use of TPR experimental data to extract the bond index. Figure 3.2b shows the simulated coverage profiles. CO* and O* react on the surface at ~340 K to produce CO₂*, which desorbs. The excess CO* desorbs at ~500 K. A small modification of CO binding energy to 40 kcal/mol (Q_{CO^{avg}} ~36 kcal/mol from TPD in Table 3.2), within the reported range in literature (29-54 kcal/mol), is carried out to correctly capture the experimental data. To validate the bond index modification, another set of TPR experimental data for CO oxidation on Pt (initial coverages: 0.82 ML of CO* and 0.17 ML of O*) by Gland and Kollin [139] is also simulated without any parameter adjustment (Figures 3.2c and 3.2d).
Fig. 3.2 Rate (panels a and c) and coverage (panels b and d) for UHV-TPR analysis of CO oxidation on Pt(111). Symbols represent the experimental data, [139, 140] whereas lines represent our simulations. Operating conditions for panels a and c: initial surface coverages O* and CO* are 0.25 ML and 0.29 ML, respectively; ramp rate=1 K/s. [140] Operating conditions for panels b and d: initial surface coverages of O* and CO* are 0.17 ML and 0.82 ML, respectively; ramp rate=13 K/s. [139] Simulations are in close agreement with the experimental data.
The mechanism predictions are in excellent agreement with the experimental data. Overall, the reaction mechanism captures the CO oxidation chemistry well at UHV conditions.

### 3.3.2.2 NO Oxidation

To extract some of the kinetic parameters for the NO oxidation chemistry, we have used the UHV-TPR experiments conducted on Pt(111) by Mudiyanselage et al. [212] Initial coverages include 0.15 ML of NO* and 0.75 ML of O*. Bartram et al. [213] reported that NO oxidation to NO$_2$ is not favored on Pt(111) at low O* coverage (∼0.25 ML) due to the larger activation barrier for NO oxidation compared to NO desorption; however, they suggested the possibility of NO$_2$ formation at higher oxygen coverage (∼0.75 ML). A DFT study of NO oxidation on Pt(111) by Ovesson et al. suggested that the oxidation is oxygen coverage ($\theta_O$) dependent; and $\theta_O$ needs to be more than 0.25 ML for the reaction to be favorable. [192] Along the similar lines, Mudiyanselage et al. reported NO oxidation to NO$_2$ with high $\theta_O$ (∼0.75 ML) on Pt(111). [212] Without any adjustment of the kinetic parameters, we observe N$_2$ formation due to NO* decomposition; however, N$_2$ formation was not reported in the TPR experiments.

To slow down the NO* decomposition chemistry, we have adjusted the bond index of the NO* decomposition reaction pair $R_{71}$-$R_{72}$: NO*+* $\leftrightarrow$ N*+O* to 0.89 (starting from 0.5). This adjustment is consistent with the bond index modification reported earlier in Section 3.1.1 for decomposition reactions, where the increase in bond index typically results in increased activation energy. A minor adjustment of NO binding energy to 30.5 kcal/mol ($Q_{NO_{\text{avg}}} \sim 29.2$ kcal/mol from TPD in Table 3.2) is made to correctly capture the experimental data. As shown in Figure 3.3a, the NO oxidation mechanism captures the experimental peaks for all three species (NO*, NO$_2$*, and O*) very well.

Simulated coverage profiles, shown in Figure 3.3b, indicate that NO* oxidation starts immediately at low temperatures (>100 K) under the UHV conditions. This feature is also
Fig. 3.3 Rate (panel a) and coverage (panel b) profiles for UHV-TPR analysis of NO oxidation on Pt(111). Symbols represent the experimental data, [212] whereas lines represent our simulations. Operating conditions: initial surface coverages of O* and NO* are 0.75 ML and 0.15 ML, respectively; ramp rate=2 K/s. Simulations are in close agreement with the experimental data.
3.3 Parameter Estimation From UHV Experiments

reported by Mieher et al. [181] in their NO oxidation experiments, where they observed exchange of oxygen between labeled NO and O2. Above 200 K, we observe that NO2* decomposition to NO* and O* also becomes significant, therefore all of the NO* is not oxidized to NO2*. At ~300 K, NO* desorption results in the NO peak. At this temperature, most of the NO* is re-generated from NO2* decomposition, which is also consistent with the increase in O* coverage. Furthermore, NO2 desorption also competes with NO2* decomposition, resulting in a smaller NO2 desorption peak, consistent with the experimental observation by Mudiyanselage et al. [212] Finally, the excess O* desorbs at higher temperature (400-800 K), consistent with the experiments. Overall, the surface reaction mechanism captures the NO oxidation chemistry very well as UHV conditions.

3.3.2.3 CH2O Oxidation

UHV-TPR experimental data of Attard et al. [214] for CH2O oxidation on Pt(111) is used to simulate the CH2O oxidation chemistry. Here, the initial coverages include 0.5 ML of CH2O* and 0.3 ML of O*. As shown in Figure 3.4a, the simulated peak temperatures of the gaseous products are in close agreement with the reported experimental data, without any modification of the initial kinetic parameters. We note that the model predicted peak for CH2O desorption (198 K) is higher than the experimentally reported value (134 K); however the model predicted peak and the corresponding binding energy of CH2O (see Table 3.2) are consistent with other CH2O TPD experiments [201, 208] (see Section 3.1) as well as literature DFT estimates. [165, 166]

Simulated coverage profiles, shown in Figure 3.4b, indicate that at ~150 K, CH2O* and O* coverages start to decrease, resulting in the formation of CO*, H*, and OH*. RPA shows that reaction R99: CH2O* +* ↔ HCO* + H* is dominant in this region. Once formyl (HCO*) is produced, it rapidly oxidizes to CO* and OH* through reaction R108: HCO* + O* ↔ CO* + OH*. With further increase in the temperature, formyl oxidizes to H2O* through reaction R110:
Fig. 3.4 Rate (panel a) and coverage (panel b) profiles for UHV-TPR analysis of CH₂O oxidation on Pt(110). Symbols represent the experimental data, [214] whereas lines represent our simulations. Operating conditions: initial surface coverages of O* and CH₂O* are 0.3 ML and 0.5 ML, respectively; ramp rate=10 K/s. Simulations are in good agreement with the experimental data.
HCO* + OH* ↔ H₂O* + CO*, which subsequently results in H₂O desorption at ≈200 K. This is also consistent with the decrease in OH* coverage at this temperature. The second water peak at ≈250 K (much smaller and not observed experimentally) is due to the reaction between OH* and H*. The model predictions also show a very small CO₂ desorption peak at ≈260 K (magnified by a factor of 10,000), consistent with the experiments. This peak is due to reaction R₂₈: CO*+OH* → CO₂* + H*.

With further increase in the temperature, H* (primarily formed from CH₂O* decomposition) associatively desorbs (R₁₄: 2H* → H₂ + 2*) at ≈280 K, similar to the experimentally observed peak. Finally, the only species left on the surface is CO*, which desorbs at ≈495 K, consistent with the experiments. Overall, the CH₂O oxidation mechanism shows excellent agreement with the experimentally observed peaks for multiple products under the UHV conditions, without any adjustment of the kinetic parameters.

### 3.3.2.4 NH₃ Oxidation

Some of the kinetic parameters for NH₃ oxidation are extracted from the UHV-TPR experimental data on Pt(111) reported by Mieher and Ho. [181] Initial coverages include 0.12 ML of NH₃* and 0.25 ML of O*. The mechanism predictions for rates and coverages are shown in Figures 3.5a and 3.5b, respectively. Even though there is some discrepancy in the H₂O desorption peak (238 K vs. 350 K), we have verified the H₂O binding energy from additional TPD experiments [154, 172] (see Section 3.1) and literature DFT calculations. [167, 215] The mechanism predictions for other gaseous products (NO and N₂) are in excellent agreement with the experimental data. Increasing the NH₃ binding energy from 20.7 kcal/mol to ≈33.5 kcal/mol helps in capturing the H₂O desorption peak at 350 K (as it delays reaction R₆₂: NH₃* + OH* ↔ NH₂* + H₂O*), but such modification is beyond the accepted literature range reported in Table 3.2; hence, it is not carried out. Decreasing the binding energy of NH₂ to 39-47 kcal/mol [184, 187, 188, 216], which has been reported in literature using UBI-QEP and DFT
calculations for less stable configurations (top sites), has a similar effect of shifting the water peak to higher temperature. However, such modification is also inconsistent with the literature binding energy values for stable configurations (bridge sites) using DFT calculations (54-58 kcal/mol [184, 187, 187, 216]) (see Table 3.2); hence, it is not carried out.

Simulated coverage profiles in Figure 3.5b provide some insights about the surface chemistry, but RPA is required to understand the dominant reactions in the NH$_3$ oxidation chemistry. RPA at 150 K shows that NH$_3^*$ undergoes oxidative dehydrogenation through reaction R$_{55}$: NH$_3^*$ + O* $\leftrightarrow$ NH$_2^*$ + OH*. As soon as OH* is formed, both OH* and O* participate in the oxidative dehydrogenation reactions R$_{62}$: NH$_3^*$ + OH* $\leftrightarrow$ NH$_2^*$ + H$_2$O* and R$_{58}$: NH$_2^*$ + O* $\leftrightarrow$ NH* + OH*, resulting in the formation of NH*. Water formed in reaction R$_{62}$ desorbs, which is also observed in the experiments. RPA at 400 K and 450 K shows that there are four competing pathways for NH* consumption, viz., reaction R$_{76}$: NH* + O* $\leftrightarrow$ NO* + H* that subsequently results in the NO desorption peak, as well as reactions R$_{60}$: NH*+O* $\leftrightarrow$ N* + OH*, R$_{53}$: NH* + * $\leftrightarrow$ N* + H*, and R$_{66}$: NH* + OH* $\leftrightarrow$ N* + H$_2$O* that eventually lead to the N$_2$ desorption peak. The second water peak (much smaller and not observed experimentally) at higher temperature (∼450 K) is due to reactions R$_{22}$ : OH* + H* $\leftrightarrow$ H$_2$O* + * and R$_{24}$: 2OH* $\rightarrow$ H$_2$O* + O*. We have adjusted the bond indices of reaction pairs R$_{75}$-R$_{76}$, R$_{53}$-R$_{54}$, R$_{59}$-R$_{60}$, and R$_{65}$-R$_{66}$ to 0.23, 0.57, 0.65, and 0.71 (starting from 0.5), respectively, to improve the agreement with experimental data. The bond index modification, although brute-force, is necessary to ensure that both NO and N$_2$ peaks are observed in the simulations and to capture the correct kinetics for the formation of multiple products. Finally, excess oxygen, albeit negligible (∼0.02 ML), desorbs at higher temperatures (∼820 K). The O$_2$ peak was not reported by Mieher and Ho, [181] as the experiments were carried out only up to 700 K.
Fig. 3.5 Rate (panel a) and coverage (panel b) profiles for UHV-TPR analysis of NH$_3$ oxidation on Pt(111). Symbols represent the experimental data, [181] whereas lines represent our simulations. Operating conditions: initial surface coverages of O* and NH$_3$* are 0.25 ML and 0.12 ML, respectively; ramp rate=2 K/s. Simulations are in good agreement with the experimental data. Discrepancy in the peak locations for H$_2$O and O$_2$ is discussed in the text.
3.3 Parameter Estimation From UHV Experiments

3.3.2.5 HCN oxidation

UHV-TPR simulations for HCN oxidation are compared against the experimental data on Pt(112) reported by Guo et al. [209] Here, the initial coverages include 0.67 ML of HCN* and 0.25 ML of O*. Simulated rate and coverage profiles are shown in Figures 3.6a and 3.6b, respectively. A number of products are observed in the TPR experiment, viz., unreacted HCN, CO, CO₂, H₂O, H₂, N₂, and C₂N₂. We have modified the bond index of the reaction pair R₈₇-R₈₈: HCN* + O* ↔ CN* + OH* to 0.44 (starting from 0.5) to correctly capture most of the product peak temperatures.

RPA at low temperature shows that HCN* oxidizes to CN* via reaction R₈₇: HCN* + O* → CN* + OH*. As soon as OH* is formed, it oxidizes HCN* to CN* and H₂O* via reaction R₈₉: HCN* + OH* → CN* + H₂O*. Water desorbs immediately after the formation at ~260 K, consistent with the experiments. At the same temperature, CN* is oxidized to produce CO* and N* via reaction R₉₄: CN* + O* → CO* + N*. CO* reacts with O* to form CO₂* via reaction R₁₀: CO* + O* → CO₂* + *, which desorbs at ~260 K, whereas N₂ desors at ~280 K. We note that our model predictions show CO₂ and N₂ formation at significantly lower temperatures than those reported in the experiments. In case of CO₂, we have rigorously validated the CO oxidation activation energy (and temperature) from other TPR experiments reported in Sections 3.2.1 and 3.2.3. The discrepancy in N₂ formation peak could be due to potentially missing reaction pathways in our reaction network. However, under the practical operating conditions of emissions oxidation to partially and fully oxidized products, the formation of N₂ (a reduction product) is less important for a DOC. Nonetheless, it is certainly a limitation of the proposed surface reaction mechanism. The model correctly captures the H₂ desorption peak at ~415 K, which originates from the decomposition reaction R₈₅: HCN* + * → H* + CN*. The unreacted HCN desorbs at ~425 K and the remaining CO* desorbs at ~500 K, consistent with the experiments. Finally, a small quantity of cyanogen (C₂N₂*), formed from reaction R₁₂₄: 2CN* → C₂N₂* + * desorbs at a much higher temperature (~675 K), consistent with the experiments. As seen from this analysis, HCN oxidation is a very complicated chemistry, and it is quite challenging to capture the formation of all the products. Our surface reaction
Fig. 3.6 Rate (panel a) and coverage (panel b) profiles for UHV-TPR analysis of HCN oxidation on Pt(112). Symbols represent the experimental data [209], whereas lines represent our simulations. Operating conditions: initial surface coverages of O* and HCN* are 0.25 ML and 0.67 ML, respectively; ramp rate=2 K/s. Simulations are in reasonable agreement with the experimental data. Discrepancy in the peak locations for CO$_2$ and N$_2$ is discussed in the text.
mechanism shows the formation of all important products observed in the UHV conditions, and captures most of the product desorption peak locations.

Table 3.3 Surface reaction mechanism for oxidation of CO, NO, CH$_2$O, NH$_3$, and HCN on Pt. Activation energies in the last column are temperature and coverage dependent, but only representative values are shown at 300 K. Coverage dependence originates from the use of UBI-QEP [107] for the estimation of activation energies, whereas the temperature dependence is derived from the statistical mechanics based calculations for degrees of freedom lost/gained upon adsorption. [101] Further details on the functional form f are given in Appendix B. Shaded reactions in the second column are the least important ones for typical DOC conditions, and can be ignored during the simulations.

<table>
<thead>
<tr>
<th>No.</th>
<th>Reactions</th>
<th>Bond index (BI)</th>
<th>Sticking coefficient [unitless]</th>
<th>Pre-exponential factor [s$^{-1}$]</th>
<th>Activation energy at 300 K [kcal/mol]</th>
</tr>
</thead>
<tbody>
<tr>
<td>R$_1$</td>
<td>O + * → O$^*$</td>
<td>0.5</td>
<td>1</td>
<td></td>
<td>0.0</td>
</tr>
<tr>
<td>R$_2$</td>
<td>O$^*$ → O + *</td>
<td>0.5</td>
<td>1×10$^{13}$</td>
<td></td>
<td>86 - 13.3θ$_O$ - 1.5RΔT[173]</td>
</tr>
<tr>
<td>R$_3$</td>
<td>O$_2$ + 2* → 2O$^*$</td>
<td>0.5</td>
<td>0.05[151, 217]</td>
<td></td>
<td>0.0</td>
</tr>
<tr>
<td>R$_4$</td>
<td>2O$^<em>$ → O$_2$ +2</em></td>
<td>0.5</td>
<td>1×10$^{13}$</td>
<td></td>
<td>52.9 - 26.6θ$_O$ + f(T)</td>
</tr>
</tbody>
</table>

*Oxygen adsorption/desorption*

| R$_5$ | CO + * → CO$^*$ | 0.5 | 0.5[218] | | 0.0 |
| R$_6$ | CO$^*$ → CO + * | 0.5 | 5.7×10$^{16}$ | | 40 - 8.3θ$_{CO}$ - 2RΔT[147, 219] |
| R$_7$ | CO$_2$ + * → CO$_2^*$ | 0.5 | 1 | | 0.0 |
| R$_8$ | CO$_2^*$ → CO$_2$ + * | 0.5 | 1×10$^{13}$ | | 3.6 - 2RΔT |
| R$_9$ | CO$_2^*$ + * → CO$^*$ + O$^*$ | 0.73$^b$ | 1×10$^{11}$ | | 23.4 + f(θ$_O$.θ$_{CO}$.T) |

$^a$Based on CO oxidation atmospheric pressure simulations (Section 3.4.1).
$^b$Based on CO oxidation UHV-TPR simulations (Section 3.3.2.1).
### Water promoted CO oxidation

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate Expression</th>
<th>Rate Constant</th>
<th>Activation Energy</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>R25 COOH + * → COOH*</td>
<td>0.5</td>
<td>1</td>
<td>0.0</td>
<td></td>
</tr>
<tr>
<td>R26 COOH* → COOH + *</td>
<td>0.5</td>
<td>1×10^{13}</td>
<td>56.3 - 2.5\Delta T</td>
<td></td>
</tr>
<tr>
<td>R27 CO₂* + H* → CO* + OH*</td>
<td>0.5</td>
<td>1×10^{11}</td>
<td>5.4 + f(\theta_O,\theta_{CO,H},T)</td>
<td></td>
</tr>
<tr>
<td>R28 CO* + OH* → CO₂* + H*</td>
<td>0.5</td>
<td>1×10^{11}</td>
<td>19 + f(\theta_O,\theta_{CO,H},T)</td>
<td></td>
</tr>
<tr>
<td>R29 COOH* + * → CO* + OH*</td>
<td>0.5</td>
<td>1×10^{11}</td>
<td>5.8 + f(\theta_O,\theta_{CO,T})</td>
<td></td>
</tr>
<tr>
<td>R30 CO* + OH* → COOH* + *</td>
<td>0.5</td>
<td>1×10^{11}</td>
<td>18.7 + f(\theta_O,\theta_{CO,T})</td>
<td></td>
</tr>
<tr>
<td>R31 COOH* + * → CO₂* + H*</td>
<td>0.5</td>
<td>1×10^{11}</td>
<td>2.1 + f(\theta_H,T)</td>
<td></td>
</tr>
<tr>
<td>R32 CO₂* + H* → COOH* + *</td>
<td>0.5</td>
<td>1×10^{11}</td>
<td>1.3 + f(\theta_H,T)</td>
<td></td>
</tr>
<tr>
<td>R33 CO* + H₂O* → COOH* + H*</td>
<td>0.5</td>
<td>1×10^{11}</td>
<td>23.9 + f(\theta_{CO,H},T)</td>
<td></td>
</tr>
<tr>
<td>R34 COOH* + H* → CO* + H₂O*</td>
<td>0.5</td>
<td>1×10^{11}</td>
<td>5.4 + f(\theta_{CO,H},T)</td>
<td></td>
</tr>
<tr>
<td>R35 CO₂* + OH* → COOH* + O*</td>
<td>0.5</td>
<td>1×10^{11}</td>
<td>25.8 + f(\theta_O,T)</td>
<td></td>
</tr>
<tr>
<td>R36 COOH* + O* → CO₂* + OH*</td>
<td>0.5</td>
<td>1×10^{11}</td>
<td>8.2 + f(\theta_O,T)</td>
<td></td>
</tr>
<tr>
<td>R37 CO₂* + H₂O* → COOH* + OH*</td>
<td>0.5</td>
<td>1×10^{11}</td>
<td>17.3 + f(\theta_O,T)</td>
<td></td>
</tr>
</tbody>
</table>
3.3 Parameter Estimation From UHV Experiments

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate Expression</th>
<th>Preexponential Factor</th>
<th>Rate Constant</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>R_{38}</td>
<td>COOH(^+) + OH(^+) → CO(_2)(^+) + H(_2)O(^+)</td>
<td>0.5</td>
<td>(1 \times 10^{11})</td>
<td>(12.4 + f(\theta_{O,T}))</td>
</tr>
<tr>
<td><strong>NH(_3) Oxidation</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R_{39}</td>
<td>N(^+) + * → N(^+)</td>
<td>0.5</td>
<td>1</td>
<td>0.0</td>
</tr>
<tr>
<td>R_{40}</td>
<td>N(^+) → N(^+) + *</td>
<td>0.5</td>
<td>(1 \times 10^{13})</td>
<td>(107.4 - 1.5R\Delta T[105])</td>
</tr>
<tr>
<td>R_{41}</td>
<td>N(_2) + 2* → 2N(^*)</td>
<td>0.5</td>
<td>1</td>
<td>27.9 + f(T)</td>
</tr>
<tr>
<td>R_{42}</td>
<td>2N(^+) → N(_2) + 2*</td>
<td>0.5</td>
<td>(1 \times 10^{13})</td>
<td>16.7 + f(T)</td>
</tr>
<tr>
<td>R_{43}</td>
<td>NH(_3) + * → NH(_3)(^+)</td>
<td>0.5</td>
<td>1</td>
<td>0.0</td>
</tr>
<tr>
<td>R_{44}</td>
<td>NH(_3)(^+) → NH(_3) + *</td>
<td>0.5</td>
<td>(1 \times 10^{13})</td>
<td>(20.7 - 9.5\theta_{NH_3} - 2.5R\Delta T)</td>
</tr>
<tr>
<td>R_{45}</td>
<td>NH(_2) + * → NH(_2)(^+)</td>
<td>0.5</td>
<td>1</td>
<td>0.0</td>
</tr>
<tr>
<td>R_{46}</td>
<td>NH(_2)(^+) → NH(_2) + *</td>
<td>0.5</td>
<td>(1 \times 10^{13})</td>
<td>54.6 - 2.5R\Delta T[187]</td>
</tr>
<tr>
<td>R_{47}</td>
<td>NH(^+) + * → NH(^+)</td>
<td>0.5</td>
<td>1</td>
<td>0.0</td>
</tr>
<tr>
<td>R_{48}</td>
<td>NH(^+) → NH(^+) + *</td>
<td>0.5</td>
<td>(1 \times 10^{13})</td>
<td>83 - 2R\Delta T[184]</td>
</tr>
<tr>
<td>R_{49}</td>
<td>NH(_3) + * → NH(_2)(^+) + H(^+)</td>
<td>0.5</td>
<td>(1 \times 10^{11})</td>
<td>21.5 + f((\theta_{H,T})),(\eta_{NH_2,T}))</td>
</tr>
<tr>
<td>R_{50}</td>
<td>NH(_2)(^+) + H(^+) → NH(_3) + *</td>
<td>0.5</td>
<td>(1 \times 10^{11})</td>
<td>7.3 + f((\theta_{H,T})),(\eta_{NH_2,T}))</td>
</tr>
<tr>
<td>R_{51}</td>
<td>NH(_2)(^+) + * → NH(^+) + H(^+)</td>
<td>0.5</td>
<td>(1 \times 10^{11})</td>
<td>18.7 + f((\theta_{H,T}))</td>
</tr>
<tr>
<td>R_{52}</td>
<td>NH(^+) + H(^+) → NH(_2) + *</td>
<td>0.5</td>
<td>(1 \times 10^{11})</td>
<td>16.5 + f((\theta_{H,T}))</td>
</tr>
<tr>
<td>R_{53}</td>
<td>NH(^+) + * → N(^+) + H(^+)</td>
<td>0.57(^c)</td>
<td>(1 \times 10^{11})</td>
<td>19 + f((\theta_{H,T}))</td>
</tr>
<tr>
<td>R_{54}</td>
<td>N(^+) + H(^+) → NH(^+) + *</td>
<td>0.57(^c)</td>
<td>(1 \times 10^{11})</td>
<td>24.5 + f((\theta_{H,T}))</td>
</tr>
<tr>
<td>R_{55}</td>
<td>NH(_3) + O(^+) → NH(_2) + OH(^+)</td>
<td>0.5</td>
<td>(1 \times 10^{11})</td>
<td>12.5 + f((\theta_{O,T})),(\eta_{NH_3,T}))</td>
</tr>
<tr>
<td>R_{56}</td>
<td>NH(_2) + OH(^+) → NH(_3) + O(^+)</td>
<td>0.5</td>
<td>(1 \times 10^{11})</td>
<td>16.7 + f((\theta_{O,T})),(\eta_{NH_3,T}))</td>
</tr>
<tr>
<td>R_{57}</td>
<td>NH(^+) + OH(^+) → NH(_2) + O(^+)</td>
<td>0.5</td>
<td>(1 \times 10^{11})</td>
<td>24.8 + f((\theta_{O,T}))</td>
</tr>
<tr>
<td>R_{58}</td>
<td>NH(_2) + O(^+) → NH(^+) + OH(^+)</td>
<td>0.5</td>
<td>(1 \times 10^{11})</td>
<td>8.6 + f((\theta_{O,T}))</td>
</tr>
<tr>
<td>R_{59}</td>
<td>N(^+) + OH(^+) → NH(^+) + O(^+)</td>
<td>0.65(^c), 0.6(^d)</td>
<td>(1 \times 10^{11})</td>
<td>39.6 + f((\theta_{O,T}))</td>
</tr>
<tr>
<td>R_{60}</td>
<td>NH(^+) + O(^+) → N(^+) + OH(^+)</td>
<td>0.65(^c), 0.6(^d)</td>
<td>(1 \times 10^{11})</td>
<td>15.8 + f((\theta_{O,T}))</td>
</tr>
<tr>
<td>R_{61}</td>
<td>NH(_2) + H(_2)O(^+) → NH(_3) + OH(^+)</td>
<td>0.5</td>
<td>(1 \times 10^{11})</td>
<td>3.5 + f((\theta_{O,T})),(\eta_{NH_2,T}))</td>
</tr>
<tr>
<td>R_{62}</td>
<td>NH(_3) + OH(^+) → NH(_2) + H(_2)O(^+)</td>
<td>0.5</td>
<td>(1 \times 10^{11})</td>
<td>12 + f((\theta_{O,T})),(\eta_{NH_3,T}))</td>
</tr>
<tr>
<td>R_{63}</td>
<td>NH(^+) + H(_2)O(^+) → NH(_2) + OH(^+)</td>
<td>0.5</td>
<td>(1 \times 10^{11})</td>
<td>16.4 + f((\theta_{O,T}))</td>
</tr>
<tr>
<td>R_{64}</td>
<td>NH(_2) + OH(^+) → NH(^+) + H(_2)O(^+)</td>
<td>0.5</td>
<td>(1 \times 10^{11})</td>
<td>12.9 + f((\theta_{O,T}))</td>
</tr>
</tbody>
</table>

\(^{c}\)Based on NH\(_3\) oxidation UHV-TPR simulations (Section 3.2.4).
\(^{d}\)Based on NH\(_3\) oxidation atmospheric pressure simulations (Section 3.4.4).
3.3 Parameter Estimation From UHV Experiments

\[
\begin{align*}
R_{65} & \quad N^* + H_2O^* \rightarrow NH^* + OH^* \quad 0.71^c \quad 1 \times 10^{11} \quad 33.4 + f(\theta_O, T) \\
R_{66} & \quad NH^* + OH^* \rightarrow N^* + H_2O^* \quad 0.71^c \quad 1 \times 10^{11} \quad 22.2 + f(\theta_O, T)
\end{align*}
\]

**NO oxidation**

\[
R_{67} \quad NO + * \rightarrow NO^* \quad 0.5 \quad 0.88 \quad 0.0
\]

\[
R_{68} \quad NO^* \rightarrow NO + * \quad 0.5 \quad 1 \times 10^{16} \quad 30.5^c - 8\theta_{NO} - 16\theta_O - 2\Delta T[106]
\]

\[
R_{69} \quad NO_2 + * \rightarrow NO_2^* \quad 0.5 \quad 1 \quad 0.0
\]

\[
R_{70} \quad NO_2^* \rightarrow NO_2 + * \quad 0.5 \quad 1 \times 10^{13} \quad 23.5^c - 2.5\Delta T[194]
\]

\[
R_{71} \quad NO^* + * \rightarrow N^* + O^* \quad 0.89^f \quad 1 \times 10^{11} \quad 31.7 + f(\theta_O, \theta_{NO}, T)
\]

\[
R_{72} \quad N^* + O^* \rightarrow NO^* + * \quad 0.89^f \quad 1 \times 10^{11} \quad 43.8 + f(\theta_O, \theta_{NO}, T)
\]

\[
R_{73} \quad NO^* + H^* \rightarrow N^* + OH^* \quad 0.5 \quad 1 \times 10^{11} \quad 4.6 + f(\theta_O, \theta_H, \theta_{NO}, T)
\]

\[
R_{74} \quad N^* + OH^* \rightarrow NO^* + H^* \quad 0.5 \quad 1 \times 10^{11} \quad 35.1 + f(\theta_O, \theta_H, \theta_{NO}, T)
\]

\[
R_{75} \quad NO^* + H^* \rightarrow NH^* + O^* \quad 0.23^c \quad 1 \times 10^{11} \quad 8.2 + f(\theta_O, \theta_H, \theta_{NO}, T)
\]

\[
R_{76} \quad NH^* + O^* \rightarrow NO^* + H^* \quad 0.23^c \quad 1 \times 10^{11} \quad 14.9 + f(\theta_O, \theta_H, \theta_{NO}, T)
\]

\[
R_{77} \quad NO^* + OH^* \rightarrow NO_2^* + H^* \quad 0.5 \quad 1 \times 10^{11} \quad 38.2 + f(\theta_O, \theta_H, \theta_{NO}, T)
\]

\[
R_{78} \quad NO_2^* + H^* \rightarrow NO^* + OH^* \quad 0.5 \quad 1 \times 10^{11} \quad 0.0 + f(\theta_O, \theta_H, \theta_{NO}, T)
\]

\[
R_{79} \quad NO_2^* + * \rightarrow NO^* + O^* \quad 0.5 \quad 1 \times 10^{11} \quad 1.4 + f(\theta_O, \theta_{NO}, T)
\]

\[
R_{80} \quad NO^* + O^* \rightarrow NO_2^* + * \quad 0.5 \quad 3 \times 10^{12^c} \quad 21.2 + f(\theta_O, \theta_{NO}, T)
\]

**HCN oxidation**

\[
R_{81} \quad HCN + * \rightarrow HCN^* \quad 0.5 \quad 1 \quad 0.0
\]

\[
R_{82} \quad HCN^* \rightarrow HCN + * \quad 0.5 \quad 1 \times 10^{13} \quad 21.3^g - 2.5\Delta T
\]

\[
R_{83} \quad CN + * \rightarrow CN^* \quad 0.5 \quad 1 \quad 0.0
\]

\[
R_{84} \quad CN^* \rightarrow CN + * \quad 0.5 \quad 1 \times 10^{13} \quad 78.2 - 2\Delta T[184]
\]

\[
R_{85} \quad HCN^* + * \rightarrow H^* + CN^* \quad 0.5 \quad 1 \times 10^{11} \quad 21.1 + f(\theta_H, T)
\]

\[
R_{86} \quad H^* + CN^* \rightarrow HCN^* + * \quad 0.5 \quad 1 \times 10^{11} \quad 13.2 + f(\theta_H, T)
\]

\[
R_{87} \quad HCN^* + O^* \rightarrow OH^* + CN^* \quad 0.44^h, 0.7^g \quad 1 \times 10^{11} \quad 17.1 + f(\theta_O, T)
\]

\[
R_{88} \quad OH^* + CN^* \rightarrow HCN^* + O^* \quad 0.44^h, 0.7^g \quad 1 \times 10^{11} \quad 27.6 + f(\theta_O, T)
\]

\[
R_{89} \quad HCN^* + OH^* \rightarrow CN^* + H_2O^* \quad 0.5 \quad 1 \times 10^{11} \quad 5.7 + f(\theta_O, T)
\]

\[
R_{90} \quad CN^* + H_2O^* \rightarrow HCN^* + OH^* \quad 0.5 \quad 1 \times 10^{11} \quad 3.4 + f(\theta_O, T)
\]

^cBased on NO oxidation atmospheric pressure simulations (Section 3.4.2).
^fBased on NO oxidation UHV-TPR simulations (Section 3.3.2.2).
### 3.3 Parameter Estimation From UHV Experiments

<table>
<thead>
<tr>
<th>R &amp;</th>
<th>Reaction</th>
<th>Rate Constant</th>
<th>Exponent</th>
<th>Expression</th>
</tr>
</thead>
<tbody>
<tr>
<td>R91</td>
<td>CN* + O* → C* + NO*</td>
<td>0.3</td>
<td>$1 \times 10^{11}$</td>
<td>$8.9 + f(\theta_O,T)$</td>
</tr>
<tr>
<td>R92</td>
<td>C* + NO* → CN* + O*</td>
<td>0.3</td>
<td>$1 \times 10^{11}$</td>
<td>$4.7 + f(\theta_O,T)$</td>
</tr>
<tr>
<td>R93</td>
<td>CO* + N* → CN* + O*</td>
<td>0.7</td>
<td>$1 \times 10^{11}$</td>
<td>$76.5 + f(\theta_O,\theta_{CO},T)$</td>
</tr>
<tr>
<td>R94</td>
<td>CN* + O* → CO* + N*</td>
<td>0.7</td>
<td>$1 \times 10^{11}$</td>
<td>$15.4 + f(\theta_O,\theta_{CO},T)$</td>
</tr>
</tbody>
</table>

**CH$_2$O oxidation**

| R95 | CH$_2$O + * → CH$_2$O* | 0.5 | 1 | 0.0 |
| R96 | CH$_2$O* → CH$_2$O + * | 0.5 | $1 \times 10^{13}$ | 14.7 - 2.5RΔT |
| R97 | HCO + * → HCO* | 0.5 | 1 | 0.0 |
| R98 | CHO* → HCO + * | 0.5 | $1 \times 10^{13}$ | 54.4 - 2.5RΔT [168] |
| R99 | CH$_2$O* + * → HCO* + H* | 0.5 | $1 \times 10^{11}$ | 8.1 + f(θ$_H$,T) |
| R100 | HCO* + H* → CH$_2$O* + * | 0.5 | $1 \times 10^{11}$ | 20.7 + f(θ$_H$,T) |
| R101 | HCO* + OH* → CH$_2$O* + O* | 0.5 | $1 \times 10^{11}$ | 30.9 + f(θ$_O$,T) |
| R102 | CH$_2$O* + O* → HCO* + OH* | 0.5 | $1 \times 10^{11}$ | 0.0 + f(θ$_O$,T) |
| R103 | HCO* + H$_2$O* → CH$_2$O* + OH* | 0.5 | $1 \times 10^{11}$ | 18.3 + f(θ$_O$,T) |
| R104 | CH$_2$O* + OH* → HCO* + H$_2$O* | 0.5 | $1 \times 10^{11}$ | 0.0 + f(θ$_O$,T) |
| R105 | HCO* + * → H* + CO* | 0.5 | $1 \times 10^{11}$ | 0.0 + f(θ$_{CO},\theta_H$,T) |
| R106 | H* + CO* → HCO* + * | 0.5 | $1 \times 10^{11}$ | 30.8 + f(θ$_{CO},\theta_H$,T) |
| R107 | CO* + OH* → HCO* + O* | 0.5 | $1 \times 10^{11}$ | 49.2 + f(θ$_O,\theta_{CO}$,T) |
| R108 | HCO* + O* → CO* + OH* | 0.5 | $1.5 \times 10^{12}$ | 0.0 + f(θ$_O,\theta_{CO}$,T) |
| R109 | CO* + H$_2$O* → HCO* + OH* | 0.5 | $1 \times 10^{11}$ | 36.5 + f(θ$_O,\theta_{CO}$,T) |
| R110 | HCO* + OH* → CO* + H$_2$O* | 0.5 | $1 \times 10^{11}$ | 0.0 + f(θ$_O,\theta_{CO}$,T) |

**C formation and oxidation**

| R111 | C + * → C* | 0.5 | 1 | 0.0 |
| R112 | C* → C + * | 0.5 | $1 \times 10^{13}$ | 158.2 - 1.5RΔT [222, 223] |
| R113 | CO* + * → C* + O* | 0.5 | $1 \times 10^{11}$ | 54.4 + f(θ$_O,\theta_{CO}$,T) |
| R114 | C* + O* → CO* + * | 0.5 | $1 \times 10^{11}$ | 1.3 + f(θ$_O,\theta_{CO}$,T) |
| R115 | 2CO* → C* + CO$_2$* | 0.5 | $1 \times 10^{11}$ | 48.3 + f(θ$_{CO}$,T) |
| R116 | C* + CO$_2$* → 2CO* | 0.5 | $1 \times 10^{11}$ | 0.0 + f(θ$_{CO}$,T) |

$^8$Based on CH$_2$O oxidation atmospheric pressure simulations (Section 3.4.3).
3.4 Mechanism Performance and Validation

Most of the kinetic parameters in our emissions oxidation surface reaction mechanism are extracted from UHV-TPD/TPR experiments on single crystal surfaces, but it is also important to assess the mechanism performance at practically relevant operating conditions. Such conditions include monolith and fixed bed experiments conducted at atmospheric pressure with dilute levels of emissions in the feed at short residence times. As the typical concentration levels of emissions considered in this paper are very low (few tens to hundreds of ppm), we have selected relevant literature experiments consistent with such levels. To simulate the steady state experimental data, here we use an isothermal plug flow reactor (PFR) model. The assumption about isothermality is based on the very small amount of heat generated during the oxidation of dilute concentration levels for the emissions components (except for 1% CO, but here the experimental data is reported at controlled steady state temperatures). Finally, it is important to note that the kinetic parameters extracted from UHV conditions on single crystal surfaces

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$N_2O$ and $C_2N_2$

formation/decomposition

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Equation</th>
<th>Rate Constant</th>
<th>Activation Energy</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>R_{117}</td>
<td>$N_2O + * \rightarrow N_2O^*$</td>
<td>0.5</td>
<td>1</td>
<td>0.0</td>
</tr>
<tr>
<td>R_{118}</td>
<td>$N_2O^* \rightarrow N_2O + *$</td>
<td>0.5</td>
<td>$1 \times 10^{13}$</td>
<td>$6.7 - 2.5R \Delta T$[194]</td>
</tr>
<tr>
<td>R_{119}</td>
<td>$N_2O^* + * \rightarrow NO^* + N^*$</td>
<td>0.5</td>
<td>$1 \times 10^{11}$</td>
<td>$3.9 + f(\theta_{NO}, T)$</td>
</tr>
<tr>
<td>R_{120}</td>
<td>$NO^* + N^* \rightarrow N_2O^* + *$</td>
<td>0.5</td>
<td>$1 \times 10^{11}$</td>
<td>$19.8 + f(\theta_{NO}, T)$</td>
</tr>
<tr>
<td>R_{121}</td>
<td>$C_2N_2 + * \rightarrow C_2N_2^*$</td>
<td>0.5</td>
<td>1</td>
<td>0.0</td>
</tr>
<tr>
<td>R_{122}</td>
<td>$C_2N_2^* \rightarrow C_2N_2 + *$</td>
<td>0.5</td>
<td>$1 \times 10^{13}$</td>
<td>$21 - 2.5R \Delta T$</td>
</tr>
<tr>
<td>R_{123}</td>
<td>$C_2N_2^* + * \rightarrow 2CN^*$</td>
<td>$0.73^b$</td>
<td>$1 \times 10^{11}$</td>
<td>$29.6 + f(T)$</td>
</tr>
<tr>
<td>R_{124}</td>
<td>$2CN^* \rightarrow C_2N_2^* + *$</td>
<td>$0.73^b$</td>
<td>$1 \times 10^{11}$</td>
<td>$28.1 + f(T)$</td>
</tr>
</tbody>
</table>

---

$^b$Based on HCN oxidation UHV-TPR simulations (Section 3.3.2.5).
provide an excellent estimate for the simulations discussed in this section. However, some minor parameter tuning is expected given the pressure (UHV vs. atmospheric) and materials (single crystals vs. polycrystalline and supported catalysts) gap.

### 3.4.1 CO oxidation

Simulations using our CO oxidation reaction mechanism from Table 3.3 are compared against three sets of experiments conducted with monolith catalysts. The first comparison, shown in Figure 3.7a, is against the experiments conducted with a Pt/γ-Al₂O₃ monolith. [224] The support and catalyst details are as follows [224]: monolith length = 2.3 cm, monolith diameter = 1.3 cm, monolith cell density = 400 cells per square inch (CPSI), washcoat loading = 0.15 g, Pt content = 0.3 mg, and BET surface area = 151 m²/g of washcoat.

Only two kinetic parameters (pre-exponential factor for reactions R₁₆: CO* desorption and R₁₀: CO* oxidation) were slightly modified to $5.7 \times 10^{16} \text{ s}^{-1}$ (starting from $1 \times 10^{16} \text{ s}^{-1}$ [219]) and $1 \times 10^{10} \text{ s}^{-1}$ (starting from $1 \times 10^{11} \text{ s}^{-1}$), respectively, to capture the experimental data. Surface coverages in Figure 3.7b show that the surface is poisoned by CO* at low temperatures, consistent with the previous literature studies [141, 226, 227]. With increase in temperature, CO* starts to desorb, freeing up the vacancies for O₂ dissociative adsorption and subsequent CO* oxidation. At higher temperatures, as CO* is completely consumed, O* is the most abundant reaction intermediate (MARI) on the catalyst surface. We note that the pre-exponential factors proposed here for CO oxidation are different (approximately by an order of magnitude) from the ones reported by Mhadeshwar and Vlachos [103], but such discrepancy is expected given the different types of experimental data selected (ignition and molecular beam data in the earlier paper vs. monolith and fixed bed data in this work).

We also validated the CO oxidation mechanism against experimental data on a Pt/Al₂O₃ monolith reported by Carlsson and Skoglundh [225] as well as against our BenchCAT [228]
3.4 Mechanism Performance and Validation

Fig. 3.7 Performance (panel a), analysis (panel b), and validation (panels c and d) of the microkinetic model for CO oxidation on Pt monoliths. Symbols represent the experimental data, whereas lines represent our simulations. Operating conditions for panels a and b: Pt/Al₂O₃ monolith; [224] feed of 1% CO, 10% O₂, and 89% Ar; space velocity of 17,000 hr⁻¹; and catalyst area per unit reactor volume of 32.6 cm⁻¹. Operating conditions for panel c: Pt/Al₂O₃ monolith: [225] feed of 1% CO, 9% O₂, and 90% N₂; space velocity of 75,000 hr⁻¹; and catalyst area per unit reactor volume of 32.6 cm⁻¹. Operating conditions for panel d: Pt/ZnO monolith (this work); feed of 1% CO, 10% O₂, 9% N₂, and 80% Ar; space velocity of 30,000 hr⁻¹, and catalyst area per unit reactor volume of 30 cm⁻¹. A Dycor Dymaxion mass spectrometer and Agilent Micro GC 3000A were used for identification and quantification of the gaseous species in the product stream. Simulations are in close agreement with the experimental data.
experiments on a Pt/ZnO monolith. In the experiments conducted by Carlsson and Skoglundh, [225] support and catalyst details are as follows: monolith length = 1.5 cm, monolith diameter = 1.2 cm, monolith cell density = 400 CPSI, washcoat loading = 0.2 g, and catalyst coating = 0.12 g/cm$^3$. On the other hand, support and catalyst details for the experiments carried out in our lab are as follows: monolith length = 1 cm, channel size = 1 mm × 1 mm, total channels = 6, BET surface area = 6.4 m$^2$/g, Pt particle diameter = 2.6 nm, Pt loading = 2%, and monolith cell density = 400 CPSI. The mechanism predictions, without any parameter modification, are shown in Figures 3.7c and 3.7d, for the respective experiments. Overall, the proposed reaction mechanism captures the CO oxidation chemistry well against multiple experimental data sets at practically relevant operating conditions.

3.4.2 NO oxidation

Figure 3.8 shows the comparison of our model predictions with monolith and fixed bed reactor experiments for NO oxidation on Pt. [145, 229] The literature experiments reported by Bhatia et al. [229] were carried out using practically relevant NO and O$_2$ concentration levels (482 ppm and 5%, respectively) on a Pt/Al$_2$O$_3$ coated monolith (Figures 3.8a and 3.8b). Similarly, fixed bed reactor experiments were carried out by Crocoll et al. [145] using 500 ppm of NO and 3% O$_2$ (Figure 3.8e). Support and catalyst details for the experiments by Bhatia et al. [93] are as follows: monolith length = 1.5 cm, monolith diameter = 1.7 cm, monolith cell density = 400 CPSI, Pt loading = 70 g/ft$^3$, Pt loading = 2.63 wt.%, Pt dispersion = 20.3%, Pt area = 2.21 m$^2$/g of washcoat, and Pt particle size = 5.59 nm. Similarly, the support and catalyst details for the NO oxidation experiment by Crocoll et al. [145] are as follows: Pt/γ-Al$_2$O$_3$ powder catalyst, Pt loading = 2%, BET surface area = 175 m$^2$/g, total pore volume = 0.70 cm$^3$/g, pore diameter = 8.6 nm, active Pt surface area = 5.3 m$^2$/g(Pt), and catalyst weight = 1 g.
Fig. 3.8 Performance (panel a and b), analysis (panels c and d), and validation (panel e) of the microkinetic model for NO oxidation on Pt monolith and fixed bed. Symbols represent the experimental data; solid lines represent our simulations; and dashed lines represent the equilibrium calculations using GASEQ software. [230] Panel b shows the improvement in mechanism predictions after ensuring thermodynamic consistency (see text for details). Operating conditions for panels a-d: Pt/Al$_2$O$_3$ monolith; [229] feed of 482 ppm NO, 5% O$_2$, and $\sim$95% N$_2$; space velocity of 49,000 hr$^{-1}$; and catalyst area per unit reactor volume of 36.3 cm$^{-1}$. Operating conditions for panel e: Pt/Al$_2$O$_3$ fixed bed [145]; feed of 500 ppm NO, 3% O$_2$, and $\sim$97% N$_2$, space velocity 96,000 h$^{-1}$, and catalyst area per unit reactor volume of 5 cm$^{-1}$. Simulations are in close agreement with the experimental data.
Unlike CO oxidation, the experimental data show that NO conversion decreases after \( \sim 250 \) °C. Equilibrium calculations conducted using GASEQ software [230] at the high temperature conditions indicate that the experimental data for NO oxidation are equilibrium limited. RPA indicates that the oxidation of NO\(^*\) via \( R_{80} \): NO\(^*\) + O\(^*\) → NO\(_2\)\(^*\) + \(^*\) is the most important step in the kinetically controlled low temperature region; and its pre-exponential factor was slightly tuned from \( 1 \times 10^{11} \text{ s}^{-1} \) to \( 3 \times 12^{11} \text{ s}^{-1} \) to improve the agreement with the experimental data. Minor adjustment of NO\(_2\) binding energy to 23.5 kcal/mol (\( Q_{NO_2}^{TPD} = 19 \) kcal/mol, literature range 17-38 kcal/mol [191, 192, 194, 196, 197, 206, 213]) is also carried out to improve the low temperature (kinetically controlled region) NO conversion predictions. Despite such modifications, the model predictions severely under predict the higher temperature equilibrium limited data in Figure 3.8a.

The origin of this discrepancy at high temperature is associated with the lack of thermodynamic (primarily entropic) consistency of kinetic parameters, as discussed by several previous papers [101, 143, 229, 231, 232]. Maintaining thermodynamic consistency is critical, especially for correctly capturing the equilibrium limited data. In our reaction mechanism, this is accomplished by a modified Arrhenius equation with temperature exponent \( \beta \) of -0.93 (forward) and +0.93 (backward) for reaction pair \( R_{79} - R_{80} \): NO\(_2\)\(^*\) + \(^*\) ↔ NO\(^*\) + O\(^*\), (where

\[
k = A \left( \frac{T}{T_o} \right)^{\beta} e^{-\frac{E_a}{RT}}
\]

and \( T_o \) is 300 K). This allows one to match the entropy values for gas phase NO oxidation to NO\(_2\) (NO + O \( \rightarrow \) NO\(_2\)) with the overall catalytic pathway for NO oxidation to NO\(_2\) (NO adsorption, oxygen adsorption, NO\(^*\) + O\(^*\) \( \rightarrow \) NO\(_2\)\(^*\) + \(^*\), and NO\(_2\) desorption). Including temperature exponents through a modified Arrhenius equation is a standard practice in gas phase reaction mechanism development community; [109] and it is also consistent with the
approach for catalytic reaction mechanisms to fulfill the thermodynamic constraints determined by Hess’s law, as described by Mhadeshwar et al. [101] Performance of the thermodynamically consistent NO oxidation reaction mechanism is shown in Figure 3.8b. The agreement with experimental data is significantly improved under the equilibrium limited high temperature conditions.

Simulated coverage profiles along the catalyst length at two different temperatures (240 °C and 420 °C corresponding to kinetically controlled and equilibrium limited regions, respectively) are shown in Figures 3.8c and 3.8d. Under both conditions, the catalyst surface is pre-dominantly covered by O*, which is consistent with the high O₂ concentration in the feed compared to that of NO. NO₂* coverage is non-negligible in the kinetically controlled region due to NO* oxidation, but it is negligible in the equilibrium limited region due to NO₂* desorption. The thermodynamically consistent NO oxidation mechanism is further validated against fixed bed experimental data of Crocoll et al. [145] without any further modification of the kinetic parameters. As shown in Figure 3.8e, the NO oxidation mechanism predicts the conversion profile well in both kinetically controlled and equilibrium limited regions.

3.4.3 CH₂O Oxidation

The CH₂O oxidation reaction mechanism is compared against two sets of experimental data, [233, 234] as shown in Figures 3.9a and 3.9d. Some of the operating conditions in the first set of experiments (CH₂O concentration of 100 ppm, space velocity of 50000 hr⁻¹) on Pt/TiO₂ fixed bed are reasonably close to the typical conditions in diesel engine exhaust aftertreatment; however, the O₂ level is much higher (20%). In the second set of experiments, the space velocity is so high (1,250,000 hr⁻¹) that it does not represent practically relevant operating conditions (extremely short catalyst length). Under such conditions, we believe that mass transfer limitations will dominate over the surface kinetics, but we have still included this data
set as a validation of our mechanism under extreme conditions. Support and catalyst details for the experiments by Zhang et al. [233] are as follows: Pt/TiO$_2$ powder catalyst, Pt loading = 1 wt.%, Pt particle size = $\sim$1 nm, and BET surface area = 47.4 m$^2$/g. Similarly, the support and catalyst details for the experiments by Peng and Wang [234] are as follows: Pt/TiO$_2$ powder catalyst, BET surface area = 61.5 m$^2$/g, pore volume = 0.24 cm$^3$/g, average pore diameter = 11.5 nm, support particle size = 15.4 nm, Pt dispersion = 68.5%, Pt metal size = 1.5 nm, and catalyst weight = 0.25 g.

In the first set of experiments (Figure 3.9a), it is observed that CH$_2$O oxidation is close to 100% even at room temperature. The surface coverage profiles along the catalyst length at 40 $^\circ$C (Figure 3.9b) show that O* is the MARI, whereas CO* (produced from CH$_2$O*) is rapidly consumed at the catalyst entrance. Decrease in CO* coverage is consistent with increase in H* coverage due to reaction $R_{28}$: CO* + OH* $\rightarrow$ CO$_2$* + H*. RPA in Figure 3.9c shows that CH$_2$O* oxidation leads to the formation of formyl, which is further oxidized to CO* and OH* via reaction $R_{108}$: HCO* + O* $\rightarrow$ CO* + OH*. The intermediates CO* and OH* react via reaction $R_{28}$ to produce CO$_2$* and H*. Finally, H* is completely oxidized to H$_2$O* via reaction $R_{22}$: H* + OH* $\rightarrow$ H$_2$O* + *. This is consistent with the CH$_2$O oxidation experiments of McCabe and McCready, [235] who suggested that CO and H are reaction intermediates that subsequently oxidize to form CO$_2$ and H$_2$O. Based on the RPA, we have modified only one pre-exponential factor for the most important reaction $R_{108}$ from $1 \times 10^{11}$ s$^{-1}$ to $1.5 \times 10^{12}$ s$^{-1}$ to improve the agreement with the experiments. For the second set of experiments, despite the severe mass transfer limitations, our CH$_2$O oxidation mechanism reasonably predicts the experimental data at temperatures higher than 60 $^\circ$C without any further parameter modification. The evaluation of mass transfer limitations in this specific experiment is beyond the scope of the current work.
Fig. 3.9 Performance (panel a), analysis (panels b and c), and validation (panel d) of the microkinetic model for CH₂O oxidation on Pt fixed beds. Symbols represent the experimental data, whereas lines represent our simulations. Panel b shows the coverage profiles of dominant surface species along the catalyst length (actual length=0.47 cm) at 40 °C. Panel c shows the dominant reaction pathways in the CH₂O oxidation chemistry at 40 °C (at the entrance of the catalyst). Operating conditions for panels a-c: Pt/TiO₂ fixed bed; [233] feed of 100 ppm CH₂O, 20% O₂, and ~80% He; space velocity of 50,000 hr⁻¹; and catalyst area per unit reactor volume of 30 cm⁻¹. Operating conditions for panel d: Pt/TiO₂ fixed bed; [234] feed of 81.4 ppm CH₂O, 22% O₂, and ~78% N₂; space velocity of 1,250,000 hr⁻¹; and catalyst area per unit reactor volume of 100 cm⁻¹. Simulations are in reasonable agreement with the experimental data. Discrepancy in panel d due to high space velocity is discussed in the text.
3.4.4 \textbf{NH}_3 \textit{Oxidation}

Figure 3.10a compares the performance of our NH$_3$ oxidation reaction mechanism against the fixed bed reactor experiments on Pt/Al$_2$O$_3$ [236]. The support and catalyst details are as follows [236]: Pt/Al$_2$O$_3$ powder catalyst, BET surface area = 120 m$^2$/g, catalyst pore volume = 0.81 cm$^3$/g, Pt loading = 2\%, and catalyst weight = 0.3 g. Here, 700 ppm of NH$_3$ was oxidized using 8\% O$_2$ in N$_2$ at atmospheric pressure. The surface coverage profiles along the catalyst length (Figure 3.10b) at 300 $^\circ$C show that NH$_3^*$ species are depleted close to the entrance, while NO$_2^*$ is produced. Most of the surface ($\sim$90\%) is covered with O$^*$ (not shown). RPA in Figure 3.10c shows that NH$_3^*$ is sequentially oxidized to N$^*$ via reactions R$_{55}$: NH$_3^*$ + O$^*$ $\rightarrow$ NH$_2^*$ + OH$^*$, R$_{58}$: NH$_2^*$ + O$^*$ $\rightarrow$ NH$^*$ + OH$^*$, R$_{53}$: NH$^*$ + * $\rightarrow$ N$^*$ + H*, and R$_{60}$: NH$^*$ + O$^*$ $\rightarrow$ N$^*$ + OH$^*$. The alternate path for NH$^*$ oxidation is via R$_{76}$: NH$^*$ + O$^*$ $\rightarrow$ NO$^*$ + H* to form NO*. This is consistent with the work of Bradley et al. [237], who suggested that the oxidation of NH intermediate could lead to the formation of NO and N$_2$. N$^*$ formed in reactions R$_{60}$ and R$_{53}$ desorbs as N$_2$, whereas NO$^*$ formed in reaction R$_{76}$ further oxidizes through reaction R$_{80}$: NO$^*$ + O$^*$ $\rightarrow$ NO$_2^*$ + *. Most of the NO$_2^*$ desorbs, but some of it is converted back to NO$^*$ through reaction R$_{78}$: NO$_2^*$ + H* $\rightarrow$ NO$^*$ + OH$. RPA at 275 $^\circ$C shows that the H$_2$O originates from reactions R$_{62}$: NH$_3^*$ + OH$^*$ $\rightarrow$ NH$_2^*$ + H$_2$O*, R$_{64}$: NH$_2^*$ + OH$^*$ $\rightarrow$ NH$^*$ + H$_2$O*, R$_{24}$: 2OH$^*$ $\rightarrow$ H$_2$O$^*$ + O$, and R$_{22}$: H$^*$ + OH$^*$ $\rightarrow$ H$_2$O$^*$ + *

With a minor adjustment of only one bond index for reaction pair R$_{59}$-R$_{60}$: N$^*$ + OH$^*$ $\rightarrow$ NH$^*$ + O$^*$ from 0.5 to 0.6, the model is able to capture the experimental data over the entire temperature range. We note that this bond index was earlier set to 0.65 in the TPR analysis presented in Section 3.2.4. Even though the UHV-TPR experiments conducted on single crystal surfaces typically provide decent initial estimates of kinetic parameters, some further refinement is typically necessary to capture the practically more relevant atmospheric pressure data on polycrystalline or supported catalysts (this again points to the pressure and materials gap).
Fig. 3.10 Performance (panel a) and analysis (panels b and c) of the microkinetic model for NH₃ oxidation on Pt/Al₂O₃ fixed bed. Symbols represent the experimental data, whereas lines represent our simulations. Panel b shows the coverage profiles of dominant surface species (O* ≈90%, not shown) along the catalyst length at 275 °C. Panel c shows the dominant reaction pathways in the NH₃ oxidation chemistry at 275 °C (at the entrance of the catalyst). Operating conditions: Pt/Al₂O₃ fixed bed reactor; [236] feed of 300 ppm NH₃, 6% O₂, and ∼94% N₂; space velocity of 820,000 hr⁻¹; and catalyst area per unit reactor volume of 190 cm⁻¹. Simulations are in close agreement with the experimental data.
3.4 Mechanism Performance and Validation

3.4.5 HCN oxidation

The final comparison for model predictions vs. experimental data is for HCN oxidation on Pt, as shown in Figure 3.11a. The experimental data is taken from fixed bed reactor experiments conducted with 30 ppm of HCN and 6% O$_2$ on a Pt/Al$_2$O$_3$ catalyst. [16] The support and catalyst details are as follows [16]: Pt/Al$_2$O$_3$ pellet catalyst (cylindrical extrudates), catalyst volume $= 2$ cm$^3$, pellets length $= 0.13$ inch, pellets diameter $= 0.13$ inch, Pt loading $= 0.5\%$, and catalyst weight $= 2.1$ g. Axial surface coverage profiles at 225 $^\circ$C (Figure 3.11b) show that HCN* decreases along the catalyst length, while NO$_2$* increases. Similar to NH$_3$ oxidation, most of the surface ($\sim 97\%$) is covered with O* (not shown). RPA, shown in Figure 3.11c, indicates that under these operating conditions, HCN oxidation path via reaction $R_{87}$: HCN* + O* $\rightarrow$ CN* + OH* dominates the alternative path of HCN decomposition via reaction $R_{85}$: HCN* + * $\rightarrow$ H* + CN*.

We have adjusted the bond index of reaction pair $R_{87}$-$R_{88}$ from 0.5 to 0.7 to capture the low temperature HCN conversion data. We note that this bond index was earlier set to 0.44 in the TPR analysis presented in 3.2.5. As mentioned earlier, some parameter refinement is generally required for the transition from UHV simulations to practically more relevant atmospheric pressure simulations on polycrystalline or supported catalysts. Once CN* is formed, it is oxidized via two major pathways, viz., reactions $R_{91}$: CN* + O* $\rightarrow$ C* + NO* and $R_{94}$: CN* + O* $\leftrightarrow$ CO* + N*, producing NO* and N*, respectively. Bond indices of these two reaction pairs ($R_{91}$-$R_{92}$ and $R_{93}$-$R_{94}$ are modified from 0.5 to 0.3 and 0.7, respectively, to facilitate NO* formation and subsequent oxidation to NO$_2$ and N$_2$O, which were reported as oxidation products by Zhao et al. in their experiments. [16] Binding energy of HCN was slightly adjusted to 21.3 kcal/mol ($Q_{HCN}^{TPD} = 26.1$ kcal/mol, $Q_{HCN}^{avg} = 21.4$ kcal/mol from Table 3.2, literature range 14-30 kcal/mol [184, 200]) to capture the experimental data. Our HCN oxidation reaction mechanism shows good agreement with the experimental data, albeit with some parameter
3.4 Mechanism Performance and Validation

Fig. 3.11 Performance (panel a) and analysis (panels b and c) of the microkinetic model for HCN oxidation on Pt fixed bed. Symbols represent the experimental data, whereas lines represent our simulations. Panel b shows the coverage profiles of dominant surface species (O* ~97%, not shown) along the catalyst length at 225 °C. Panel c shows the dominant reaction pathways in the HCN oxidation chemistry at 225 °C (at the entrance of the catalyst). Operating conditions: Pt/Al₂O₃ fixed bed reactor [16]; feed of 30 ppm HCN, 6% O₂, and ~94% N₂; space velocity of 30,300 hr⁻¹; and catalyst area per unit reactor volume of 32 cm⁻¹. Simulations are in close agreement with the experimental data.
modification. In general, the HCN oxidation experiments are rare in literature, due to its high toxicity and lethal nature. Additional validation of this reaction mechanism will be carried out in the future, as more data becomes available for HCN oxidation under practically relevant operating conditions.

Fig. 3.12 Schematic of the important reaction pathways, intermediates, reactants, and products from the microkinetic model for oxidation of emissions on Pt. The reactants and products in gas phase are shown in shaded boxes.

3.5 Preliminary Mechanism Reduction

Based on RPA, some reactions in the detailed surface reaction mechanism are identified as the least important ones. These include the adsorption/desorption steps for radicals, viz., H, O, OH,
3.6 Limitations of the Overall Approach

COOH, HCO, N, NH, NH₂, C, and CN, as these species are more dominant on the catalyst surface than in the gas phase. Based on the HCN-TPD (Section 3.1) and HCN-TPR (Section 3.2.5) simulations, the C₂N₂ adsorption/desorption and formation/decomposition chemistry is important only at high temperatures (∼700 K); therefore, it can be ignored from the simulations at typical DOC conditions. Finally, some of the reactions in the COOH* chemistry (e.g., reactions of COOH* with H*, O*, and OH* are found to be less important than its formation from CO* + OH* and its decomposition to CO₂* + H*. This preliminary model reduction results in a shorter surface reaction mechanism with 94 steps (47 reversible) and 20 surface species. The unimportant reactions are listed in Table 3.3 (shaded reactions in the second column). Finally, the schematics of the major oxidation reaction pathways for all five emissions species are shown in Figure 3.12.

3.6 Limitations of the Overall Approach

To our knowledge, the reaction mechanism presented in this work is the first comprehensive microkinetic model on Pt that simultaneously captures five major emissions oxidation chemistries on Pt under UHV as well as practically more relevant operating conditions. Nonetheless, it is important to acknowledge the key limitations of the overall approach along with the future work needed to improve the mechanism presented here.

3.6.1 Limitations associated with the reaction mechanism and the uncertainty in kinetic parameters

Current work focuses on the oxidation of five emissions (CO, NO, CH₂O, NH₃, and HCN) only. These species contain only 1 C and/or N atom. After HC-SCR, the exhaust can contain additional secondary
• emissions, such as non-methane hydrocarbons (C$_2$H$_4$), aldehydes (CH$_3$CHO), and nitrogen-containing species (CH$_3$CN). The emissions oxidation mechanism should be expanded to include such species with more C atoms.

• Beyond the C- and N-containing species, the exhaust also contains S-species, such as SO$_2$, which originate from the oxidation of sulfur in the diesel fuel. SO$_2$ can be oxidized on the DOC to SO$_3$, which in turn could be hydrated (due to the steam in the exhaust) to sulfuric acid. Both, metal and support in the DOC, can interact with the sulfur oxides and sulfuric acid, resulting in catalyst deactivation due to sulfation. [9, 56, 78] The Schneider research group has conducted significant work in sulfur oxide chemistry on Pt using DFT. [238, 238–240] Future work should include such chemistry in the emissions oxidation mechanism.

• Uncertainty in the kinetic parameters originates from the use of various estimation methods and their accuracy. For example, species binding energies and adsorbate-adsorbate interactions estimated using the UHV-TPD experiments can vary to some extent among different experiments. Activation energies for the surface reactions are calculated using the semi-empirical UBI-QEP method. [107] Even though the UBI-QEP method is highly convenient in accounting for coverage effects and ensuring enthalpic consistency, the calculated activation energies need to be verified with first-principles DFT calculations. A number of bond indices are modified in this work to improve the agreement with the experimental data. Agreement between the UBI-QEP and DFT values can be improved by adjusting the bond indices. [241] However, accurate estimates of activation energies and location of transition state along the reaction coordinate are needed to verify the modifications conducted here. Finally, uncertainty in the experimental
measurements (if any) may be translated to the surface reaction mechanism through the adjustment of kinetic parameters.

- The reaction mechanism proposed here utilizes a single temperature exponent to account for equilibrium limitations of NO oxidation in the considered temperature range. As all reactions are theoretically reversible, temperature exponents could be considered for the entire reaction mechanism, consistent with the approaches presented in literature. [101–103] However, out of the five emissions oxidation chemistries studied here, only NO oxidation is reversible in the considered temperature range, whereas all other reactions are practically irreversible. Presence of a large amount of O$_2$ (~10-15%) in the diesel exhaust compared to the dilute levels of emissions also drives most of the emissions oxidation reactions toward the oxidized products. To ensure simplicity and practical applicability of the reaction mechanism, we have chosen to include only a single temperature exponent that is necessary for capturing the equilibrium limitations for NO oxidation.

- The mechanism reduction presented here is preliminary compared to more rigorous approaches based on principal component analysis and small parameter asymptotic. [104, 218]

### 3.6.2 Limitations Associated With the Catalyst and Reactor Modeling

- Catalyst site density used in the simulations ($1.5 \times 10^{15}$ sites/cm$^2$) is calculated from Pt(111), which is one of the most stable facets of the Pt crystal. However, the actually utilized catalysts are polycrystalline in nature. Multiple types of sites and facets - which may be relevant to the real-life catalyst operation - are not taken into account. Active site density could vary with the catalyst loading, type of support, and catalyst life (deactivation/poisoning); however these effects are not considered in this work.
• Catalyst supports, such as Ceria and zirconia, can play an active role in the emissions oxidation kinetics along with Pt. This work primarily focuses on relatively inert supports, such as alumina and titania. Nonetheless, our simplified approach for microkinetic modeling on Pt does not account for the role of support in emissions oxidation kinetics.

• A steady state isothermal PFR model is employed in the simulations. The assumption about isothermality is based on the very small amount of heat generated during the oxidation of dilute concentration levels for the emissions components. Future work will focus on investigating the performance of emissions oxidation mechanism under transient operating conditions for an exhaust containing multiple emissions.

3.7 Conclusion

In this chapter, we have reported the first microkinetic model for the oxidation of five major emissions (CO, NO, CH$_2$O, NH$_3$, and HCN) on a Pt-based DOC. The comprehensive microkinetic model contains 124 irreversible (62 reversible) steps and 21 surface species (94 steps and 20 species for the reduced version). Kinetic parameters are extracted using multiple techniques, such as the semi-empirical UBI-QEP method, literature DFT calculations, and simulations of various UHV temperature programmed experiments (TPD/TPR). Parameters extracted/estimated from such techniques are very good initial estimates, but they still require some adjustment to capture and predict the experimental data at practically more relevant operating conditions (atmospheric pressure, high O$_2$ concentration, dilute level of emissions, high space velocity, monolith- or powder-scale setups, etc.). The microkinetic model shows very good agreement with various sets of experimental data focused on emissions oxidation. The surface reaction mechanism developed in this work provides an excellent starting point for
3.7 Conclusion

DOC design and optimization, and could be further expanded by including the chemistry of additional C₂-C₃ species and sulfur impurities in the exhaust.
Chapter 4

Sulfur Oxides Interactions with Diesel Oxidation Catalysts (DOCs)

4.1 Introduction

Sulfur oxides (SO\textsubscript{x}) in the diesel engine exhaust are one of the major factors contributing toward deactivation of emissions aftertreatment catalysts. Interactions of SO\textsubscript{x} with the catalyst metals and supports can result in sulfate formation. In this chapter, we review various experimental and computational studies regarding SO\textsubscript{x} interaction on Pt-Pd/alumina catalysts, which are typically used in Diesel Oxidation Catalysts (DOCs). In addition, we propose a novel microkinetic model for SO\textsubscript{2} oxidation on Pt as a first step toward understanding the DOC-SO\textsubscript{x} interactions. The proposed model contains 24 elementary steps (12 reversible) with five surface species. The microkinetic model is validated against experimental data for SO\textsubscript{2} oxidation on Pt. Finally, we discuss the challenges of incorporating sulfur-based deactivation in kinetic modeling, and propose potential directions that could lead to the development of sulfur resistant materials for DOCs.
4.2 Literature Review of DOC-SO$_x$ Interactions

More than 98% of the sulfur in diesel is oxidized to SO$_2$ during combustion. [71, 72, 242] H$_2$S has been reported during fuel rich conditions; [242] but in fuel lean conditions for diesel engines, H$_2$S (if any) would be further oxidized to SO$_2$ and SO$_3$ above 300 °C in the presence of a Pt/Pd catalyst. [15, 32, 60] SO$_2$ and SO$_3$ subsequently interact with the DOC components, metal oxide and support. DOC sulfation has been widely studied and discussed in the literature. [15, 32, 60, 71, 72, 86, 87, 89, 242] In this section, we present a brief review of the experimental and computational investigations regarding the interactions of sulfur with DOC, that is, metal, metal oxides, as well as the alumina support.

4.3 Experimental Studies

4.3.1 Interaction of SO$_x$ with Pt

Compared to other noble metals, Pt remains in metallic form in the typical oxidizing environment. [243] Pt is very active towards SO$_2$ oxidation; [79, 243] and various techniques such as Temperature Programmed Desorption (TPD), X-ray Photoelectron Spectroscopy (XPS), Ultraviolet Photoelectron Spectroscopy (UPS), High Resolution Electron Energy Loss Spectroscopy (HREELS), Near Edge X-ray Absorption Fine Structure (NEXAFS) spectroscopy, and Low Energy Electron Diffraction (LEED), have been used to study the interaction of SO$_2$ with Pt metal. [244–252]

Ultra High Vacuum (UHV) studies show that SO$_2$ binds strongly (molecular adsorption with a sticking coefficient of $\sim$0.5) on the Pt surface with S and O atoms in $\eta^2$-SO$_2$ configuration (where $\eta^2$ represents the number of atoms of adsorbate coordinated to the surface). [245, 246] Astegger and Bechtold [246] reported that SO$_2$ desorbs at 400, 480, and 580 K (multiple
peaks) in their TPD experiments on Pt(111); however, the peaks at 480 and 580 K were due to molecularly adsorbed SO$_2$, whereas the peak at 400 K was due to saturated SO$_2$ surface. The peak at 400 K appeared only at higher initial coverages suggesting that the peak is from multilayered SO$_2$ adsorption. In the case of co-adsorbed SO$_2$ and O$_2$ on Pt(111), a SO$_3$ desorption peak was observed at 580 K. [246] The SO$_2$ desorption peak at 480 K decreased and the SO$_3$ peak at 580 K increased while increasing the oxygen surface coverage. From XPS and HREELS studies, Sun et al. [245] observed that SO$_2$ also forms sulfur monoxide (SO) and sulfate (SO$_4$) on Pt at 300 K.

Streber et al. [250] studied the adsorption and reaction of SO$_2$ on clean and oxygen pre-covered Pt(111) surfaces by in situ high resolution XPS and suggested that SO$_2$ reacts with oxygen to form SO$_3$ at 130 K, and subsequently to SO$_4$, which is stable up to 500 K. The sulfate ions impact the metal sites by deteriorating the chemisorption ability. [251] Many studies suggest that Pt metal is not converted to PtSO$_4$; however, it helps migrating the sulfur species to the support, which subsequently gets sulfated. [32, 252, 253] Based on these studies, the generalized sulfur chemistry on Pt can be summarized as follows.

\[
\text{SO}_2(g) \rightarrow \text{SO}_2^* \tag{4.1}
\]

\[
\text{SO}_2^* \rightarrow \text{SO}^* + \text{O}^* \tag{4.2}
\]

\[
\text{SO}^* \rightarrow \text{S}^* + \text{O}^* \tag{4.3}
\]

\[
\text{SO}_2^* + \text{O}^* \rightarrow \text{SO}_3^* \tag{4.4}
\]
Here, subscript \((g)\) and superscript \(\ast\) represent the gas phase and the surface species, respectively.

### 4.3.2 Interaction of SO\(_x\) with PdO

Unlike Pt, in a typical oxidizing environment, Pd is converted to more active oxidized form of PdO. \([60, 243, 254]\) Studies using Scanning Tunneling Microscopy (STM), LEED, Auger Electron Spectroscopy (AES), and TPD suggest a three-step mechanism of PdO formation, that is, chemisorption of oxygen on Pd, diffusion of chemisorbed oxygen into the Pd metal, and formation of the stoichiometric PdO structure. \([254]\) In atmospheric conditions, PdO phase is stable up to \(\sim 800{\degree}C\), whereas metallic Pd is stable above \(\sim 800{\degree}C\). \([61, 254–258]\)

Based on Fourier Transform Infrared (FT-IR) spectroscopy, Mowrey and McCormick \([87]\) suggested that PdO is active in converting SO\(_2\) to SO\(_3\), which further reacts with PdO to form PdSO\(_4\). This is also consistent with the findings of Lampert et al. \([81]\) based on fixed bed and monolith scale experiments. According to Lampert et al. \([81]\), Pd on a sulfating \((\gamma\text{-Al}_2\text{O}_3)\) support deactivates more slowly than a non-sulfating \((\text{SiO}_2)\) support. The slower deactivation is due to a reservoir type of action of the sulfating support to take SO\(_2\)/SO\(_3\). On the other hand, PdO deactivation is faster on a non-sulfating support due to the inability of the support to take SO\(_2\)/SO\(_3\) leaving PdO as the only target. Furthermore, they suggested the formation of PdO-SO\(_3\) complex for the decreased activity of the catalyst. Mowrey and McCormick \([87]\) studied PdO sulfation with and without support and suggested that the sulfation was faster in
4.4 Kinetic Modeling for SO$_2$-Based Deactivation

the absence of a support. Their XPS and FTIR studies showed sulfation of the PdO surface layer and activity loss for methane oxidation.

$$\text{Pd}^0 + \frac{1}{2} \text{O}_2 \rightarrow \text{PdO}$$  \hspace{1cm} (4.6)

$$\text{PdO} + \text{SO}_2 \rightarrow \text{Pd}^0_{\text{surface}} + \text{SO}_3$$  \hspace{1cm} (4.7)

$$\text{PdO}_{\text{interior}} + \text{Pd}^0_{\text{surface}} \rightarrow \text{Pd}^0_{\text{interior}} + \text{PdO}_{\text{surface}}$$  \hspace{1cm} (4.8)

4.4 Kinetic Modeling for SO$_2$-Based Deactivation

Kinetic modeling of sulfur interactions with Pt has received increased attention over the last decade or so [239, 240, 259–262], mostly for Pt-based LNT/NSR applications. [261, 262] Nonetheless, the findings specific to Pt could be relevant for understanding the DOC-SO$_x$ interactions. Olsson et al. [261] developed a global kinetic model for LNT deactivation due to sulfur, which consists of interaction of SO$_2$ (poisoning and regeneration) on two types of sites, namely, Barium (Ba) and Al$_2$O$_3$. For both types of sites, the kinetic model contained two steps, namely, adsorption/binding of SO$_2$ and subsequent oxidation. Furthermore, the model also contained steps for the formation of sulfates on both types of sites during the lean phase and regeneration in the presence of hydrogen. The authors suggested that sulfur poisoning occurs on both types of sites (Ba and Al$_2$O$_3$), consistent with the observations by Matsumoto et al. [263]. As all alumina sites are not covered by NO$_x$, SO$_2$ adsorption is possible. Similarly, Dowdy et al. [262] developed a global mean field kinetic model for SO$_2$ interaction with NSR (Pt/BaO/Al$_2$O$_3$ and BaO/Al$_2$O$_3$), which consists of SO$_2$ storage on NO$_x$ storage sites,
4.5 Microkinetic Modeling for Emissions and SO$_2$ Oxidation on Pt

SO$_2$ storage on bulk sites, SO$_2$ oxidation, SO$_2$ interaction with Pt in the presence of H$_2$, and oxidation of accumulated sulfur compounds on Pt by NO$_2$. The model is able to predict the decrease in NO$_x$ storage performance due to sulfur accumulation and accumulation of bulk sulfates in Pt/BaO/Al$_2$O$_3$ after exposure of SO$_2$ and oxygen. Except for a few studies of sulfur interactions with NO$_x$ reduction/storage catalyst discussed above, details of sulfation kinetics are not available; and therefore, there is an urgent need to understand the complex nature of sulfation kinetics. Along these lines, next we briefly mention the main gaps and challenges in the understanding of DOC-SO$_x$ interactions.

4.5 Microkinetic Modeling for Emissions and SO$_2$ Oxidation on Pt

In this section, we present a new microkinetic model for SO$_2$ oxidation on Pt to address the first challenge mentioned in the previous section. It mainly focuses on the development, validation, and analysis of the microkinetic model for SO$_2$ oxidation on Pt.

4.5.1 Approach for Kinetic Model Development

The overall approach for kinetic model development of SO$_2$ oxidation on Pt-DOC consists of three major steps, namely, (i) estimation/extraction of kinetic parameters in the surface reaction mechanism, (ii) performance and analysis of the microkinetic model, and (iii) additional validation. In a typical diesel engine exhaust with high O$_2$ concentration, the primary reaction for SO$_2$ is its oxidation to SO$_3$; however, some additional reactions between S and SO$_x$ species are also considered in the reaction mechanism. Based on the information for possible reaction intermediates, pathways, and final products, we have considered 24 irreversible (12 reversible)
4.5 Microkinetic Modeling for Emissions and \(\text{SO}_2\) Oxidation on Pt

catalytic reactions (see Table 4.1) and five surface (adsorbed) species (\(\text{O}^*\), \(\text{S}^*\), \(\text{SO}^*\), \(\text{SO}_2^*\), and \(\text{SO}_3^*\)). The overall approach used in microkinetic modeling has some limitations associated with the reaction mechanism, uncertainty in the kinetic parameters, as well as catalyst and reactor modeling, which have been discussed in our earlier work. [264]

Table 4.1 Surface reaction mechanism for \(\text{SO}_2\) oxidation on Pt. * indicates an empty (vacant) site, whereas superscript * indicates an adsorbed species. Activation energies in the last column are reported at 300 K; the functional dependence on coverage and temperature originates from Equation 2.1 in the text. \(\Delta T = T - T_o\), where \(T_o\) is taken as 300 K. Activation energies are computed on-the-fly using the UBI-QEP formalism, as the surface coverages changes in the simulations. Bond index represents the position of the transition state along the reaction co-ordinate. It ranges between 0 (transition state similar to reactants) to 1 (transition state similar to products). Bond index is also used to compute the activation energies according to the UBI-QEP formalism. Additional calculation details are presented in the supplementary material of our earlier work on emissions oxidation on Pt. [264] Shaded reactions in the second column are the least important ones for typical DOC conditions, and can be ignored during the reactor simulations.

<table>
<thead>
<tr>
<th>No.</th>
<th>Reactions</th>
<th>Bond index (BI)</th>
<th>Sticking coefficient</th>
<th>Activation energy at 300 K [kcal/mol]</th>
</tr>
</thead>
<tbody>
<tr>
<td>(R_1)</td>
<td>(\text{O} + * \rightarrow \text{O}^*)</td>
<td>0.5</td>
<td>1</td>
<td>0.0</td>
</tr>
<tr>
<td>(R_2)</td>
<td>(\text{O}^* \rightarrow \text{O} + *)</td>
<td>0.5</td>
<td>(1 \times 10^{13})</td>
<td>(86 - 13.3 \theta_O - 1.5 R \Delta T) [173]</td>
</tr>
<tr>
<td>(R_3)</td>
<td>(\text{O}_2 + 2* \rightarrow 2\text{O}^*)</td>
<td>0.5</td>
<td>(0.05 [151, 217])</td>
<td>0.0</td>
</tr>
<tr>
<td>(R_4)</td>
<td>(2\text{O}^* \rightarrow \text{O}_2 + 2*)</td>
<td>0.5</td>
<td>(1 \times 10^{13})</td>
<td>(52.9 - 26.6 \theta_O + f(T))</td>
</tr>
<tr>
<td>(R_5)</td>
<td>(\text{S} + * \rightarrow \text{S}^*)</td>
<td>0.5</td>
<td>1</td>
<td>0.0</td>
</tr>
<tr>
<td>(R_6)</td>
<td>(\text{S}^* \rightarrow \text{S} + *)</td>
<td>0.5</td>
<td>(1 \times 10^{13})</td>
<td>(119.53 - 1.5 R \Delta T) [265]</td>
</tr>
</tbody>
</table>
4.5.2 Kinetic Parameters for SO₂ Oxidation Mechanism

Kinetic parameters such as species binding energies (Q) are taken from literature experimental and/or DFT data, [151, 239, 240, 246, 259, 260] whereas the reaction activation energies are calculated using the semi-empirical Unity Bond Index-Quadratic Exponential Potential (UBI-QEP) method [107, 108]. Binding energies are coverage and temperature dependent.

\[ R_7 \quad \text{SO} + \ast \rightarrow \text{SO}^\ast \quad 0.5 \quad 1 \quad 0.0 \]
\[ R_8 \quad \text{SO}^\ast \rightarrow \text{SO} + \ast \quad 0.5 \quad 1 \times 10^{13} \quad 70.99 - 2R\Delta T[265] \]
\[ R_9 \quad \text{SO}_2 + \ast \rightarrow \text{SO}_2^\ast \quad 0.5 \quad 0.5 \quad 0.0 \]
\[ R_{10} \quad \text{SO}_2^\ast \rightarrow \text{SO}_2 + \ast \quad 0.5 \quad 1 \times 10^{16} \quad 30.98 - 2.5R\Delta T[265] \]
\[ R_{11} \quad \text{SO}_3 + \ast \rightarrow \text{SO}_3^\ast \quad 0.5 \quad 1 \quad 0.0 \]
\[ R_{12} \quad \text{SO}_3^\ast \rightarrow \text{SO}_3 + \ast \quad 0.5 \quad 1 \times 10^{13} \quad 36.01 - 2.5R\Delta T[265] \]

\[ \text{SO}_x \text{ oxidation/reduction} \]
\[ R_{13} \quad \text{SO}_3^\ast + \ast \rightarrow \text{SO}_3^* + \text{O}^* \quad 0.95^a \quad 1 \times 10^{11} \quad 23.7 + f(\theta_O,T) \]
\[ R_{14} \quad \text{SO}_2^* + \text{O}^* \rightarrow \text{SO}_3^* + \ast \quad 0.95^a \quad 2 \times 10^{12}^b \quad 21.5 + f(\theta_O,T) \]
\[ R_{15} \quad \text{SO}_2^* + \ast \rightarrow \text{SO}^* + \text{O}^* \quad 0.5 \quad 1 \times 10^{11} \quad 22.3 + f(\theta_O,T) \]
\[ R_{16} \quad \text{SO}^* + \text{O}^* \rightarrow \text{SO}_2^* + \ast \quad 0.5 \quad 1 \times 10^{11} \quad 16.6 + f(\theta_O,T) \]
\[ R_{17} \quad \text{SO}^* + \ast \rightarrow \text{S}^* + \text{O}^* \quad 0.5 \quad 1 \times 10^{11} \quad 20.0 + f(\theta_O,T) \]
\[ R_{18} \quad \text{S}^* + \text{O}^* \rightarrow \text{SO}^* + \ast \quad 0.5 \quad 1 \times 10^{11} \quad 30.0 + f(\theta_O,T) \]
\[ R_{19} \quad 2\text{SO}_2^* \rightarrow \text{SO}_3^* + \text{SO}_2^* \quad 0.5 \quad 1 \times 10^{11} \quad 13.7 + f(T) \]
\[ R_{20} \quad \text{SO}^* + \text{SO}_3^* \rightarrow 2\text{SO}_2^* + \ast \quad 0.5 \quad 1 \times 10^{11} \quad 10.2 + f(T) \]
\[ R_{21} \quad \text{S}^* + \text{SO}_2^* \rightarrow 2\text{SO}^* \quad 0.5 \quad 1 \times 10^{11} \quad 25.6 + f(T) \]
\[ R_{22} \quad 2\text{SO}^* \rightarrow \text{S}^* + \text{SO}_2^* \quad 0.5 \quad 1 \times 10^{11} \quad 9.9 + f(T) \]
\[ R_{23} \quad \text{SO}^* + \text{SO}_2^* \rightarrow \text{S}^* + \text{SO}_3^* \quad 0.5 \quad 1 \times 10^{11} \quad 7.7 + f(T) \]
\[ R_{24} \quad \text{S}^* + \text{SO}_3^* \rightarrow \text{SO}^* + \text{SO}_2^* \quad 0.5 \quad 1 \times 10^{11} \quad 19.9 + f(T) \]
Coverage dependent parameters (adsorbate interactions) are taken from the literature. [173] The temperature dependence is derived from the statistical mechanics based calculations for degrees of freedom lost/gained upon adsorption on the catalyst surface. [101] Coverage and temperature dependent activation energies are calculated on-the-fly using the UBI-QEP method. Sticking coefficients for O$_2$ and SO$_2$ are taken from the literature, [151, 217, 246] whereas those for the other species are assumed to be unity. Initial values of pre-exponential factors (A) are taken from Transition State Theory (TST) estimates, which include $10^{13}$ s$^{-1}$ and $10^{11}$ s$^{-1}$ for desorption and the Langmuir-Hinshelwood (L-H) type surface reactions, respectively. [100] For SO$_2$ desorption, a pre-exponential factor of $1 \times 10^{16}$ s$^{-1}$ used in this mechanism, which is based on the typically reported high values. [260, 266] A site density of $1.5 \times 10^{15}$ sites/cm$^2$ (2.5$\times 10^{-9}$ mol/cm$^2$) corresponding to the Pt(111) surface [148] is used in the simulations.

4.5.3 Mechanism Performance and Analysis

Steady state isothermal PFR simulations were carried out using the SO$_2$ oxidation mechanism to compare its SO$_2$ conversion performance against experiments conducted with Pt/SiO$_2$ coated monolith catalysts. The GRI Mech 3.0 gas phase reaction mechanism [109] was used to account for the gas phase chemistry. Transient simulations were performed at the reactor inlet to get the initial surface species coverages. The resulting set of differential and algebraic (DAE) equations were solved using the DDASPK solver. [110]

Figure 4.1 shows that the SO$_2$ oxidation reaction mechanism captures the experimental data fairly well over the entire temperature range. At high temperatures, the experimental data are limited by SO$_2$ oxidation equilibrium, which is well captured by our simulations. Only two parameters were adjusted to capture the experimental results. These include (i) pre-exponential of reaction R$_{14}$ (SO$_2$* + O* → SO$_3$* + *), which was modified to $2 \times 10^{12}$ s$^{-1}$ (starting from $1 \times 10^{12}$ s$^{-1}$), and (ii) bond index of reaction pair R$_{13}$-R$_{14}$ (SO$_3$* + * ↔ SO$_2$* + O*), which
Fig. 4.1 Performance of the microkinetic model for \( \text{SO}_2 \) oxidation on Pt. Symbols represent experimental data; solid lines represent our simulations; and dashed lines represent the equilibrium calculations using GASEQ software. [230] Operating conditions [262]: Pt/SiO\(_2\) monolith; feed of 40 ppm \( \text{SO}_2 \), 8% \( \text{O}_2 \), and \(~92\% \text{ N}_2 \); space velocity of 33,000 h\(^{-1}\); and catalyst area per unit reactor volume of 81.2 cm\(^{-1}\). Simulations are in close agreement with the experimental data.
was modified to 0.95 (starting from 0.5). The bond index modification implemented here is similar to previous work for CO oxidation reaction. [103]

The reaction pair $R_{13}$-$R_{14}$ ($SO_3^* + * \leftrightarrow SO_2^* + O^*$) was identified as the most important reaction based on sensitivity analysis. The normalized sensitivity coefficient is defined as $\frac{d\ln R}{d\ln P}$ (i.e., $(dR/dP) \times (P/R)$), where $dP$ is the change in parameter $P$ (pre-exponential factors) and $dR$ is the change in model response $R$ (conversion). Surface reactions with the highest normalized sensitivity coefficients are shown in Figure 4.2. At low temperature (250 °C), $SO_3$ adsorption/desorption pair $R_{11}$-$R_{12}$ showed the largest sensitivity, but the conversion was very low at this temperature. At 350 °C, $SO_2$ oxidation step $R_{13}$-$R_{14}$ showed the highest sensitivity. As moderate levels of $SO_2$ conversion were observed around 350 °C, kinetic parameters for the reaction pair $R_{13}$-$R_{14}$ were adjusted to capture the experimental data in Figure 4.1. At even higher temperatures (e.g., 450 °C), as the data become equilibrium limited, none of the reaction pre-exponentials were sensitive as expected.

Simulated surface coverages at the reactor exit (which are also very close to the average coverage over the reactor length) are shown in Figure 4.3a, whereas Figures 4.3b and 4.3c show the axial coverage profiles of dominant surface species at two representative temperatures: low (350 °C) and high (550 °C), respectively. At most of the conditions (> 300 °C), $O^*$ is the most abundant reaction intermediate (MARI), which is expected given its high concentration in the feed (and also in a typical diesel engine exhaust). The high coverage of $O^*$ also justifies the inclusion of repulsive adsorbate?adsorbate ($O^*$-$O^*$) interactions (coverage effects) in our reaction mechanism. At low temperature, the simulations predict some $SO_3^*$ coverage, but negligible coverage of $SO_2^*$, $SO^*$, and $S^*$. This is because $SO_2^*$ is oxidized to $SO_3^*$ even at low temperature, but it is difficult to desorb $SO_3^*$. At high temperature, $SO_3^*$ desorption becomes easier, resulting in more vacancies and less $SO_3^*$ coverage. Finally, above 500 °C, even oxygen also starts to desorb resulting in an increase in vacancies.
Fig. 4.2 Sensitivity analysis for SO$_2$ oxidation model responses with respect to the pre-exponential factor pairs in the surface reaction mechanism. Pre-exponentials are modified pairwise without perturbing the equilibrium constant. Only those reaction pairs with the highest normalized sensitivity coefficients (dlnR/dlnP, i.e., (dR/dP)×(P/R)) are shown here. The sensitivity coefficients above 400 °C are negligible (not shown here). Operating conditions are the same as in Figure 4.1.
The reaction path analysis (RPA) is shown in Figure 4.4 at two representative temperatures: low (350 °C, Figure 4.4a) and high (450 °C, Figure 4.4b). At low temperature, SO$_2^*$ reacts with oxygen via reaction R$_{14}$: SO$_2^*$ + O$^*$ → SO$_3^*$ + * to form SO$_3^*$, which subsequently desorbs, resulting in SO$_2$ conversion (oxidation). This RPA also aligns with the sensitivity analysis in Figure 4.2 and the coverage profiles in Figure 4.3. This observation, albeit on Pt, is also consistent with the experimental results reported by Luckas et al (156) in their HR-XPS studies of SO$_2$ oxidation on Pd(100) surface. At high temperature, SO$_3^*$ readsorbs on the surface, and decomposes via the reverse reaction R$_{13}$: SO$_3^*$ + * → SO$_2^*$ + O$^*$, which is consistent with the equilibrium limitations. SO$_2^*$ on the surface then follows two separate reaction pathways. The primary pathway (∼94%) is desorption to gas phase SO$_2$ via reaction R$_{10}$, whereas the secondary pathway (∼6%) is decomposition to SO$^*$ and O$^*$ via reaction R$_{15}$. However, instead of desorbing, SO$^*$ further reacts with SO$_3^*$ to regenerate SO$_2^*$ via reaction R$_{20}$: SO$^*$ + SO$_3^*$ → 2SO$_2^*$. Thus, the secondary minor pathway is not important in terms of the overall reaction of SO$_3$ decomposition at high temperature.

**4.5.4 Mechanism Validation**

Despite showing good agreement with the monolith experiments, two kinetic parameters in the surface reaction mechanism had to be adjusted to improve the agreement with the experimental data. Therefore, to assess the fidelity of the surface reaction mechanism, we carried out further validation against additional SO$_2$ oxidation experimental data on Pt/TiO$_2$ fixed bed, [86] without any further modification of kinetic parameters. Predictions using the microkinetic model are shown in Figure 15, along with the experimental data. This set of experimental data is not very relevant to the DOC operating conditions, as the feed contained an extremely high SO$_2$ concentration (11%) instead of few ppm, along with an extremely high space velocity.
Fig. 4.3 (a) Simulated steady state coverage profiles at reactor exit, (b) simulated axial coverage profiles at 350 °C, and (c) simulated axial coverage profiles at 550 °C. Operating conditions are the same as in Figure 4.1.
4.5 Microkinetic Modeling for Emissions and SO₂ Oxidation on Pt

Nonetheless, a fair agreement with experimental data demonstrates the robustness of our SO₂ oxidation surface reaction mechanism on Pt, even under extreme operating conditions.

4.5.5 Mechanism Reduction

Based on the sensitivity analysis, coverage profiles, and RPA, a preliminary mechanism reduction is carried out. Adsorption/desorption of some radicals (O*, S*, SO*) and some surface reactions involving SO* are not important (shaded reactions in Table 4.1); hence, they can be removed from the mechanism without affecting the simulation results. Finally, a 12-step SO₂ oxidation model is proposed after the mechanism reduction.
Fig. 4.5 Validation of the microkinetic model for SO$_2$ oxidation on Pt/TiO$_2$ fixed bed. Operating conditions [86]: Pt/TiO$_2$ fixed bed, feed of 11% SO$_2$, 10% O$_2$, and 79% N$_2$, space velocity 690,000 h$^{-1}$, and catalyst area per unit reactor volume of 350 cm$^{-1}$. 

Symbols: Experiments [Koutsopoulou et al.]
Line: Simulations [this work]
4.6 Conclusions

Sulfation of DOC is a challenging and complex phenomena. Very limited information of this complex chemistry is available in the literature. Details of the SO\textsubscript{x} interaction mechanism and kinetics on bimetallic DOC are not available. Similarly, SO\textsubscript{x} interaction with supports adds more challenges to the chemistry and kinetics. Therefore, a complete understanding of the sulfation mechanism and kinetics is necessary to predict the DOC deactivation and design sulfur resistant materials, thereby ultimately reducing the cost of operation. Here, we have extended the recently developed microkinetic model for five major emissions oxidation chemistries on Pt to include the SO\textsubscript{2} oxidation chemistry on Pt. The developed mechanism correctly captures experimental data for SO\textsubscript{2} oxidation relevant to DOC operating conditions. This is the first step towards understanding SO\textsubscript{x} interactions with Pt-Pd/alumina DOCs. In the future, understanding the sulfation mechanism using various approaches discussed here can be crucial to design sulfur resistant catalysts and to make the DOC an efficient and economical component of the diesel engine aftertreatment system.
Chapter 5

SO\textsubscript{x} and H\textsubscript{2}O Interactions on Pt

5.1 Introduction

Sulfuric acid (H\textsubscript{2}SO\textsubscript{4}) formation in the diesel engine exhaust is a highly favored phenomenon due to interactions of sulfur oxides (mainly SO\textsubscript{3}, in \textasciitilde 1 ppm level due to currently used ultra-low sulfur diesel) and water vapor (concentration up to \textasciitilde 7%) in the engine exhaust. [9, 31, 32] Sulfur in the diesel fuel and lubricants is oxidized to SO\textsubscript{2} in the engine and further oxidized to SO\textsubscript{3} due to the excess oxygen (\textasciitilde 12%) in the exhaust. Once formed, sulfuric acid creates tremendous challenge to the noble metal (Pt and/or Pd) based diesel oxidation catalysts (DOC), increases particulate formation in the engine exhaust and contributes to toxic acid rain formation. [15, 97] Therefore, a complete understanding of the reaction kinetics and pathways of H\textsubscript{2}SO\textsubscript{4} formation is required for a better design of the emission aftertreatment catalysts. The overall reaction of H\textsubscript{2}SO\textsubscript{4} formation can be given as:

\[ \text{SO}_3 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4 \quad \Delta H = -90\text{kJ mol}^{-1} \] (5.1)
Earlier experimental studies have shown that the reaction of SO$_3$ and H$_2$O is the primary step for H$_2$SO$_4$ formation. [266–269] Phillips et al. suggested the existence of a SO$_3$-H$_2$O complex in the gas phase using microwave spectroscopy. [267] Further, the reaction kinetics was reported to be a complex one with rate of the reaction influenced by the H$_2$O concentration. [268] DFT based studies suggested a decrease in the activation energy for SO$_3$ and H$_2$O reaction with an increase in water coverage on the surface. On the other hand, in an ab-initio method based electro-oxidation study of SO$_2$, Kriek et al. [270] proposed H$_2$SO$_4$ formation through an HSO$_3$ intermediate (SO$_2$ + OH → HSO$_3$) in addition to the SO$_3$ pathway (SO$_2$ + O → SO$_3$). Prior kinetic modeling attempts have been limited to the oxidation mechanism of SO$_2$ only to form SO$_3$. [260, 266, 269] Thus, a complete reaction mechanism and pathways are not fully understood when a complex reaction mechanism involving H$_2$O and oxygen and sulfur oxides.

In this chapter, we develop a microkinetic model for H$_2$SO$_4$ formation on Pt surface with oxidation and H$_2$O interaction of sulfur oxides (SO$_2$ and SO$_3$). We extend our previously developed SO$_2$ oxidation microkinetic model [31, 271] on Pt to include SO$_3$ and H$_2$O interactions and develop a detailed understanding of the reaction pathways en route to the sulfuric acid formation. Furthermore, we analyze the HSO$_3$ route of H$_2$SO$_4$ formation proposed by Kriek et al. [270] Overall, our model predictions show good agreement with the results from experiments operated under practically relevant DOC conditions such as low emissions concentrations (ppm level), high flow rate, and high oxygen and water concentrations.

5.2 Microkinetic Model Development

The reduced surface reaction mechanism for SO$_2$ oxidation from our previous work was adapted as a starting point. [31, 271] We further extended the reaction mechanism to include the H$_2$O interactions with SO$_4$ to form H$_2$SO$_4$. Based on the information from literature, [270, 272–274]
one can potentially have two paths involving SO$_3^*$ or HSO$_3^*$ intermediate as shown below. Here, * indicates adsorbed species.

**PATH A:**

\[
SO_2^* + O^* \leftrightarrow SO_3^* + *
\]  \hspace{1cm} (5.2)

\[
SO_3^* + H_2O^* \leftrightarrow H_2SO_4^* + *
\]  \hspace{1cm} (5.3)

**PATH B:**

\[
SO_2^* + OH^* \leftrightarrow HSO_3^* + *
\]  \hspace{1cm} (5.4)

\[
HSO_3^* + OH^* \leftrightarrow H_2SO_4^* + *
\]  \hspace{1cm} (5.5)

Initially, we considered the following 7 surface species in this mechanism: SO$_2^*$, SO$_3^*$, O*, H$_2$O*, OH*, HSO$_3^*$ and H$_2$SO$_4^*$. Based on our previous study, [31] surface species S* and SO* and their reactions were deemed insignificant. Hence, the reactions involving those surface species are not taken into account here. We considered adsorption/desorption steps of gas phase species (i.e., O$_2$, SO$_2$, SO$_3$, H$_2$O, and H$_2$SO$_4$) and surface reactions for SO$_2$ oxidation and SO$_3$ hydration. Our analysis based on the Unity Bond Index-Quadratic Exponential Potential (UBI-QEP) [107] method (see Appendix B) showed that the HSO$_3$ formation (SO$_2^*$ + OH$^*$ → HSO$_3^*$ + *) activation barrier is too high (E$_a = \sim 33$ kcal/mol at 300 K) to compete with SO$_3$ formation (SO$_2^*$ + O$^*$ → SO$_3^*$ + *, E$_a = \sim 22$ kcal/mol) pathway in the highly oxidizing environment and in the temperature range (< 400 °C) of interest in this study. Thus, inclusion of this pathway has no effect on the mechanism performance for the temperature range and emissions...
exhaust conditions considered here. Furthermore, no evidence of formation of HSO$_3$ and H$_2$ was reported during the experiments conducted under practically relevant conditions.[275] Similarly, our analysis show that the reaction for water dissociation using oxygen (H$_2$O$^*$ + O$^*$ → 2OH$^*$) also has no effect on the overall model performance even though the reaction is feasible (activation energy, $E_a = 9.4$ kcal/mol at 300 K [264]) in the temperature range studied here. Therefore, these reactions are not included in our final proposed mechanism. Overall, the reactions considered in this mechanism are chosen based on the reactants, possible intermediates, products, and the experimentally observed/proposed [268, 270] pathways. The proposed final reaction mechanism consists of 14 elementary steps (7 reversible) reactions as listed in Table 5.1.

Parameter estimation was performed using the methodology discussed in Chapter 2 and in previous chapters. Here, the binding energies of HSO$_3$ and H$_2$SO$_4$ on Pt (111) were estimated in this work using DFT implemented in VASP (see Appendix 1 for details). Steady state isothermal plug flow reactor (PFR) modeling was used to simulate the monolith scale experiments conducted in various operating conditions. Isothermal assumption is based on the very small amount of heat generated during the oxidation of very dilute concentration levels of the emissions (ppm levels) in the exhaust. Details of PFR modeling is discussed in Chapter 2.

### 5.3 Model Performance

It is expected that the microkinetic model should perform well against the experiments operated under practically relevant conditions such as atmospheric pressure, dilute emissions concentrations (ppm level), and short residence times. However, some minor parameter tuning is expected given the pressure gap (UHV vs. atmospheric), materials gap (single crystals vs. polycrystalline and supported catalysts), and uncertainty/error associated with the experimental
Table 5.1 Elementary step reaction mechanism considered to study SO$_2$ oxidation and H$_2$SO$_4$ formation on Pt

<table>
<thead>
<tr>
<th>No.</th>
<th>Reactions</th>
<th>Bond index$^b$ (BI) [unitless]</th>
<th>Sticking coefficient or Pre exponential factor [s$^{-1}$]</th>
<th>Activation energy at 300 K [kcal/mol]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adsorption/desorption</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R$_1$</td>
<td>O$_2$ + 2* → 2O*</td>
<td>0.5</td>
<td>0.05 [151, 217]</td>
<td>0.0</td>
</tr>
<tr>
<td>R$_2$</td>
<td>2O* → O$_2$ +2*</td>
<td>0.5</td>
<td>1 × 10$^{13}$</td>
<td>52.9 - 26.6$\theta$$_O$ + f(T)</td>
</tr>
<tr>
<td>R$_3$</td>
<td>SO$_2$ + * → SO$_2$*</td>
<td>0.5</td>
<td>0.5</td>
<td>0.0</td>
</tr>
<tr>
<td>R$_4$</td>
<td>SO$_2$* → SO$_2$ + *</td>
<td>0.5</td>
<td>1 × 10$^{16}$</td>
<td>29.3 - 2.5$\Delta$T [265]</td>
</tr>
<tr>
<td>R$_5$</td>
<td>SO$_3$ + * → SO$_3$*</td>
<td>0.5</td>
<td>0.5</td>
<td>0.0</td>
</tr>
<tr>
<td>R$_6$</td>
<td>SO$_3$* → SO$_3$ + *</td>
<td>0.5</td>
<td>1 × 10$^{13}$</td>
<td>34.2 - 2.5$\Delta$T [265]</td>
</tr>
<tr>
<td>R$_7$</td>
<td>H$_2$SO$_4$ + * → H$_2$SO$_3$*</td>
<td>0.5</td>
<td>1</td>
<td>0.0</td>
</tr>
<tr>
<td>R$_8$</td>
<td>H$_2$SO$_4$* → H$_2$SO$_4$ + *</td>
<td>0.5</td>
<td>1 × 10$^{13}$</td>
<td>2.8 - 3.0$\Delta$T</td>
</tr>
<tr>
<td>R$_9$</td>
<td>H$_2$O + * → H$_2$O*</td>
<td>0.5</td>
<td>1</td>
<td>0.0</td>
</tr>
<tr>
<td>R$_{10}$</td>
<td>H$_2$O* → H$_2$O + *</td>
<td>0.5</td>
<td>1 × 10$^{13}$</td>
<td>10.27 - 2.5$\Delta$T</td>
</tr>
<tr>
<td>SO$_x$ oxidation</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R$_{11}$</td>
<td>SO$_3$* + * → SO$_2$* + O*</td>
<td>0.97</td>
<td>1.2 × 10$^{11}$</td>
<td>23.2 + f($\theta$$_O$,T)</td>
</tr>
<tr>
<td>R$_{12}$</td>
<td>SO$_2$* + O* → SO$_3$* + *</td>
<td>0.97</td>
<td>5 × 10$^{12}$</td>
<td>21.3 + f($\theta$$_O$,T)</td>
</tr>
<tr>
<td>H$_2$O reactions</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R$_{13}$</td>
<td>SO$_3$* + H$_2$O* → H$_2$SO$_4$* + *</td>
<td>0.5</td>
<td>1 × 10$^{11}$</td>
<td>0.0 + f(T)</td>
</tr>
<tr>
<td>R$_{14}$</td>
<td>H$_2$SO$_4$* + * → SO$_3$* + H$_2$O*</td>
<td>0.5</td>
<td>1 × 10$^{11}$</td>
<td>19.1 + f(T)</td>
</tr>
</tbody>
</table>

$^a$ $\theta$$_O$ represents the oxygen surface coverage; * indicates a vacant site; whereas the superscript * indicates an adsorbed species. The functional form ‘f’ in the activation energy includes coverage and temperature dependence. Coverage dependence originates from the use of UBI-QEP for the estimation of activation energies; whereas the temperature dependence is derived from the statistical mechanics based calculations for degrees of freedom lost/gained upon adsorption. $\Delta$T = T - T$_0$, where T$_0$ is taken as 300 K.

$^b$ Bond index represents the position of the transition state along the reaction coordinate, which is also used to compute the activation energies in the UBI-QEP formalism. It is defined for a reaction pair in the forward direction only. It ranges between 0 and 1, with a typical estimate of 0.5.
data. Here, monolith scale experimental data [269, 275] reported in the literature are used to check the microkinetic model performance. Specifically, monolith scale experiments with 3 different types of reactor feed conditions are used: (a) SO\(_2\) and O\(_2\), (b) SO\(_2\), O\(_2\), and SO\(_3\), and (c) SO\(_2\), O\(_2\), and H\(_2\)O. Details of the mechanism performance and analysis of reaction paths are presented in next section.

### 5.3.1 SO\(_2\) Oxidation

Our microkinetic model was validated against experiments [275] conducted using Pt/Al\(_2\)O\(_3\) monolith under isothermal and steady state reactor conditions. The model predictions, surface species coverages and reaction path analysis (RPA) at different temperatures are shown in Figure 5.1. Overall, the model captures the experimental data very well over the entire range of temperature considered. At elevated temperature regions (> 350 °C), the conversion of SO\(_2\) decreases (panel a, Figure 5.1), due to equilibrium limited conditions, consistent with the decrease in calculated equilibrium conversion.

Simulated coverage profiles at the reactor exit over a temperature range of 200-500 °C are shown in panel b, Figure 5.1. While SO\(_3^*\) coverage is dominant only at low temperature, O\(^*\) is the most abundant surface species over wide temperature range (as expected due to high concentration of O\(_2\) in the diesel engine exhaust). In panels c and d in Figure 5.1, we show low temperature (320 °C) and high temperature (520 °C) surface coverage profiles over the reactor length, respectively. In both temperature cases, O\(^*\) is the dominant surface species which justifies the inclusion of repulsive adsorbate?adsorbate (O\(^*\)-O\(^*\)) interactions (coverage effects) in our reaction mechanism. RPA is shown (panel c, Figure 5.1) for two representative temperatures (i.e., 320 oC and 520 oC). It shows that the oxidation of SO\(_2\) (R\(_{12}\), SO\(_2^*\) + O\(^*\) → SO\(_3^*\) + *) occurs to form SO\(_3^*\) on the surface at low temperature which desorbs afterwards.
5.3 Model Performance

(i) RPA at 320 °C

\[ \text{O}_2(\text{g}) \rightarrow \text{SO}_2^* \rightarrow \text{SO}_3^* + \text{O}^* \]

(ii) RPA at 520 °C

\[ \text{SO}_2(\text{g}) \rightarrow \text{SO}_2^* \rightarrow \text{SO}_3^* - \text{O}^* \]

Fig. 5.1 Performance (panel a) and analysis (panels b-e) of the microkinetic model for \( \text{SO}_2 \) oxidation on Pt/Al\(_2\)O\(_3\) monolith. Symbols represent the experimental data, whereas lines represent our simulations. Panel a shows the experimental data, model performance, and the calculated equilibrium conversion profile. Panel b shows the simulated steady state coverage profiles at the reactor exit. Panel c shows the reaction path analysis at 320 °C and 520 °C. Panels d and e show the simulated axial coverage profiles at 320 °C and 520 °C, respectively. Operating conditions: [269, 275] feed of 200 ppm \( \text{SO}_2 \), 10% \( \text{O}_2 \), balance \( \text{N}_2 \); space velocity of 25 000 h\(^{-1}\); Pt loading = 50 g/ft\(^3\) with 6% dispersion; catalyst length = 3.86 cm with a cell density of 325 channels/in\(^2\); and catalyst area per unit reactor volume of 46.8 cm\(^{-1}\); total gas flow rate = 4.6 L/min.
However, SO$_3$ readsorption and decomposition occurs via reverse reaction (R$_{11}$, SO$_3^\ast$ + * $\rightarrow$ SO$_2^\ast$ + O$^\ast$), consistent with equilibrium limitations, at higher temperature.

### 5.3.2 Effect of SO$_3$ on SO$_2$ Oxidation

Experimental results suggested that the presence of SO$_3$ in the feed has negative effect on the oxidation of SO$_2$, which is accompanied by the increase in apparent activation energy and negative reaction order for SO$_3$. [269] Due to SO$_3$ in the feed, the light off temperature of SO$_2$ oxidation is pushed to higher temperature. Furthermore, SO$_2$ conversion decreases sharply at the equilibrium-limited region. The phenomenon is well captured by our model as it correctly predicts the experimental conversion profile of SO$_2$ oxidation in the presence of SO$_3$ in feed. The model performance against two sets of experimental data [269, 275] (obtained from two different feed concentrations of SO$_2$ and SO$_3$) is shown in Figure 5.2 (panel a).

To further evaluate the effect of SO$_3$ on SO$_2$ conversion in a highly oxidizing environment, we simulated both experimental data sets without SO$_3$ in the inlet feed (i.e., hypothetical conditions). The conversion profiles are shown in Figure 5.2 (panel a), as represented by blue and red dotted lines. From the results, we clearly see two distinct features. First, SO$_2$ concentration has minimal effect on the light off temperature, which is displayed by negligible change in the conversion profiles for 100 ppm (red dotted line) and 149 ppm (blue dotted line) of SO$_2$ in the feed. Second, the increase in SO$_3$ concentration results in a large shift in the light off temperature. Furthermore, negative impact on SO$_2$ conversion was observed in the equilibrium limited region due to presence of SO$_3$ in the feed.

Panels b and c (Figure 5.2) show the surface coverage profile on the catalysts length at two different temperature scales (at 320 °C and 520 °C). These profiles are very similar to the one without SO$_3$; however, SO$_3^\ast$ coverage is slightly higher on the surface for both temperatures and
5.3 Model Performance

![Equilibrium conversion graph](image)

**Fig. 5.2** Performance (panel a) and analysis (panels b and c) of the microkinetic model for SO\(_2\) oxidation on Pt/Al\(_2\)O\(_3\) monolith. Symbols represent the experimental data, whereas lines represent our simulations. Panel a shows the experimental data, model performance (solid blue and red lines), model simulations without considering SO\(_3\) in the experimental feed compositions (dotted blue and dotted red lines), and the calculated equilibrium conversion profiles. Panels b and c show the simulated axial coverage profiles for the feed composition of 100 ppm SO\(_2\), 75 ppm SO\(_3\), 10% O\(_2\), balance N\(_2\) at 320 °C and 520 °C, respectively. Operating conditions: [269, 275] feed of 100 ppm SO\(_2\), 75 ppm SO\(_3\), 10% O\(_2\), and balance N\(_2\) (red symbols); 149 ppm SO\(_2\), 106 ppm SO\(_3\), 10% O\(_2\), balance N\(_2\) (blue symbols). Reactor and catalysts details are same as in Figure 5.1.
Fig. 5.3 Comparison of the experimental SO\textsubscript{2} conversion and reactor outlet concentrations (at 351 °C) with the predictions of the microkinetic model on Pt/Al\textsubscript{2}O\textsubscript{3} monolith. Symbols represent the experimental data, whereas lines represent our simulations. Dotted blue and red lines represent the effect of A/V parameter on the model performance for the prediction of SO\textsubscript{2} conversion data. Experimental data for the reactor outlet concentration of SO\textsubscript{2} and SO\textsubscript{3}+H\textsubscript{2}SO\textsubscript{4} at 351 °C (symbols) and the model simulated values (horizontal lines) are shown with a y-axis on the right. Operating conditions: [275] feed of 98 ppm SO\textsubscript{2}, 5% H\textsubscript{2}O, 5% O\textsubscript{2}, and balance N\textsubscript{2}. Reactor and catalysts details are same as in Figure 5.1.
O* still remains as the most dominant species on the surface. Overall, the reaction pathways and mechanism remains the same in the presence or absence of SO\textsubscript{3} in the feed.

Fig. 5.4 Sensitivity analysis for the microkinetic model responses with respect to the pre-exponential factor pairs in the surface reaction mechanism shown in Table 5.1. Pre-exponentials are modified pairwise without perturbing the equilibrium constant. Only those reaction pairs with the highest normalized sensitivity coefficients \([d\ln R/d\ln P, \text{i.e.,} \,(dR/dP)\times(P/R)]\) are shown here. The sensitivity coefficients at four representative temperatures (i.e. 200 °C, 250 °C, 300 °C, and 350 °C) are shown. Sensitivity analysis at the equilibrium-limited regions is not shown here. Operating conditions are the same as in Figure 5.3.
5.3 Model Performance

5.3.3 H\textsubscript{2}SO\textsubscript{4} Formation

Very limited experimental data are available in the literature for H\textsubscript{2}SO\textsubscript{4} formation in the presence of H\textsubscript{2}O in engine exhaust conditions due to corrosive and toxic nature of H\textsubscript{2}SO\textsubscript{4}. Here, we used monolith scale experiments reported by Hamzehlouyan et al. on Pt/Al\textsubscript{2}O\textsubscript{3} catalysts. Experimental results showed significant decrease in SO\textsubscript{2} conversion in the presence of H\textsubscript{2}O. The decrease in the conversion is also associated with the catalysts poisoning due to H\textsubscript{2}SO\textsubscript{4}. Our model captures the experimental results; however, with a minor adjustment in the catalyst area per unit volume (A/V) parameter. We also show the simulated conversion profiles using a range of A/V numbers in Figure 5.3. We clearly see the impact of A/V parameters on the SO\textsubscript{2} conversion profile especially at the higher temperature. This observation fits well with the experimental evidence of catalysts active site reduction due to H\textsubscript{2}SO\textsubscript{4} poisoning. Furthermore, the plug flow reactor model used here cannot inherently capture any effect due to catalysts poisoning. Thus, the parameter adjustment in our model is reasonable. To further validate the model, we computed the selectivity and compared the model-simulated results against experimentally observed concentrations of the reactants and products as shown in Figure 5.3. Our model captures the reactant (SO\textsubscript{2}) concentration and the total product concentration (SO\textsubscript{3} and H\textsubscript{2}SO\textsubscript{4}) reported at 351 °C. [275]

Next, we looked at the sensitivity of the reaction mechanism. Sensitivity analysis allows us to identify the most sensitive and important reactions. The normalized sensitivity co-efficient is defined as dlnR/dlnP, where dlnP is the change in parameter P (pre-exponential factor) and dlnR is the change in model response R (SO\textsubscript{2} conversion). We performed a pairwise sensitivity analysis by perturbing the pre-exponential factors (of both forward and backward reactions) with same factor. In Figure 5.4, the surface reaction pairs with highest sensitivity coefficients are shown at four different temperatures (range from 200 °C to 350 °C). At low temperature (200 °C), the reaction R\textsubscript{5}-R\textsubscript{6} (SO\textsubscript{3} + * ⇌ SO\textsubscript{4}\textsuperscript{2-}) shows largest sensitivity. At the range of 250
Fig. 5.5 Simulated axial coverage profiles at 250 °C (panel a), 300 °C (panel b), and 350 °C (panel c), respectively. Operating conditions are the same as in Figure 5.3.
°C to 300 °C, reaction pairs R$_5$-R$_6$ (SO$_3$ + * ↔ SO$_3^*$) and R$_{11}$-R$_{12}$ (SO$_3^*$ + * ↔ SO$_2^*$ + O*) show the largest impact on the mechanism. The reaction pair R$_{13}$-R$_{14}$ (H$_2$ SO$_4^*$ + * ↔ SO$_3^*$+H$_2$ O*) is also one of the important reaction pairs over the range of temperature considered here.

**Fig. 5.6** Reaction path analysis at 250 °C (panel a) and 350 °C (panel b) using our microkinetic model for SO$_2$ oxidation on Pt. Operating conditions are the same as Figure 5.3.

Model simulated surface coverage profiles at three different temperatures (i.e. at 250 °C, 300 °C, and 350 °C) are shown in Figure 5.5 (panels a-c). We observed that the SO$_3^*$ is the most abundant reaction intermediate (MARI) at low temperature (250 °C) which is mainly due to its high sticking coefficient (0.5) compared to that of oxygen (0.05). With the increase in temperature, the SO$_3^*$ coverage gradually decreases while O* coverage takes over and becomes the MARI. This effect is partly due to the SO$_3^*$ desorption and H$_2$SO$_4^*$ formation (discussed in
the next paragraph). Furthermore, the binding energy of oxygen is relatively larger than that of SO$_3^*$ which translates to higher temperature desorption phenomena.

Figure 5.6 shows RPA at 250 °C (panel a) and 350 °C (panel b). The lower temperature RPA (at 250 °C) is dominated by the SO$_2$ oxidation (SO$_2^*$ + O$^*$ → SO$_3^*$ + *) and SO$_3$ desorption (SO$_3^*$ → SO$_3^+$ *) steps. However, the higher temperature RPA (at 350 °C) shows the H$_2$SO$_4$ formation (SO$_3^*$ + H$_2$O$^*$ → H$_2$SO$_4^*$ + *) reaction is one of the major pathway and competing reaction with SO$_3$ desorption which is also consistent with the sensitivity analysis in Figure 5.4.

5.4 Conclusions

In this chapter, we developed a microkinetic model for H$_2$SO$_4$ formation on Pt. The model contains 16 elementary steps (8 reversible pairs) and 5 surface species (i.e. O$^*$, H$_2$O$^*$, SO$_2^*$, SO$_3^*$, and H$_2$SO$_4^*$). Our model captures the available experimental data (from the experiments conducted under realistic DOC conditions such as low emissions concentrations, high oxygen concentrations with presence of water, atmospheric pressure, and high space velocity) and shows good agreement in kinetically and thermodynamically controlled regions. We show the impact of SO$_3$, consistent with experimental observations, on the SO$_2$ oxidation light off temperature. Our sensitivity analysis further shows the important reactions in the proposed mechanism. Finally, we show that the interaction of SO$_3$ and H$_2$O is the pathway to form H$_2$SO$_4$ on the Pt surface.
Chapter 6

SO\textsubscript{x} Oxidation Kinetics on Pt(111) and Pd(111)

6.1 Introduction

Sulfur oxides (SO\textsubscript{x}) from diesel engine and gas turbine exhaust are detrimental to noble metal (Pt/Pd) based aftertreatment catalysts. [60, 81] For instance, SO\textsubscript{2} can undergo oxidation to SO\textsubscript{3} over the catalyst, and these oxides react with the active catalyst sites, preventing reactant access and modifying the catalyst surface chemistry. [9, 31, 32] More importantly, such interactions lead to the formation of stable sulfates and subsequent deactivation of the catalyst [81, 87]. In addition, reactions of SO\textsubscript{x} with steam in the engine exhaust can produce H\textsubscript{2}SO\textsubscript{4}, which can cause severe catalyst damage. [276] Clearly, fundamental insights on SO\textsubscript{x} thermodynamics and kinetics on relevant catalyst surfaces are essential for the development of sulfur-resistant catalysts.

Past work has attempted to uncover the surface chemistry of SO\textsubscript{x} on Pt and Pd. [89, 245, 250, 265, 277–280] Experimental studies have confirmed a few stable configurations of SO\textsubscript{2},
and have noted SO$_3$ and SO$_4$ formation in the presence of oxygen. Analysis based on the unity bond index-quadratic exponential potential (UBI-QEP) method suggests that SO$_2$ oxidation, but not decomposition, is favored on various metal surfaces under typical engine exhaust conditions. Available first principles computational studies have also provided critical insights concerning SO$_2$ binding and oxidation, although predominantly on Pt.

In this chapter, we aim to develop a comprehensive understanding of SO$_x$ ($x = 0 – 4$) chemistry (adsorption/desorption and oxidation) on Pt(111) and Pd(111) surfaces using density functional theory (DFT) calculations coupled with microkinetic modeling. Firstly, a detailed investigation was performed to uncover the binding patterns, coverage dependence of binding strength, charge transfer and redistribution, and orbital interactions upon SO$_x$ adsorption. Secondly, we analyzed several possible reaction pathways and estimated kinetic parameters, including activation barriers and pre-exponential factors of SO$_2$ and SO$_3$ oxidation on both metal surfaces. Finally, the kinetic parameters computed using DFT were fed into a microkinetic model developed earlier to predict SO$_2$ conversion as a function of temperature under several different operating conditions. The predicted conversion compares favorably with available experimental data. The present work thus significantly extends insights that have emerged from past experimental and computational work, and provides a quantitative scheme for the prediction of the performance of catalysts with respect of SO$_x$ chemistry.

6.2 Methods

Our spin-polarized first principles DFT calculations were performed using the Vienna ab initio simulation package (VASP), utilizing the Perdew–Burke–Ernzerhof (PBE) functional, and the projector augmented wave (PAW) frozen–core potentials with the
O 2s, 2p, the S 3s, 3p, the Pt 5d, 6s and the Pd 4d, 5s states treated as the valence states. A plane–wave cut–off energy of 400 eV was used for the plane–wave expansion of the wave functions. The energy of a single atom or molecule was calculated using a 14×14×14 Å³ cell. Both the Pt(111) and Pd(111) surfaces were represented by a 5–layer slab, and (2×2), (3×3), and (4×4) surface unit cells. The two bottom layers of the slab were fixed and the other layers were allowed to relax. To avoid any periodic image interactions, an intervening 12–14 Å vacuum region was introduced. Monkhorst–Pack [285] grids of 5×5×1, 4×4×1, and 3×3×1 were used for Brillouin zone integration for slabs with (2×2), (3×3), and (4×4) surface unit cells, respectively. For the bulk calculations, Monkhorst-Pack mesh of 10×10×10 was used. The climbing-image nudged elastic band (CI-NEB) [286] method (with a spring constant of -5.0 eV/Å²) was used to estimate the activation barriers. The true transition states in all activation barrier calculations were confirmed by the identification of a single imaginary frequency, which corresponds to a saddle point on the potential-energy surface.

The binding energy, $E_b$, of an atom or a molecule on the slab is defined as.

$$E_b = -[E_{\text{slab}+\text{ads}} - E_{\text{slab}} - E_{\text{ads}}] \quad (6.1)$$

where $E_{\text{slab}+\text{ads}}$, $E_{\text{slab}}$, and $E_{\text{ads}}$ represent the energy of the slab with the atom/molecule, energy of the clean slab, and the energy of an isolated atom/molecule, respectively. The $E_b$ values are positive numbers, where the increase in positive number indicates the strong binding to the surface.

For each minimum energy path (MEP) from the CI-NEB [286], we calculated the activation energy barrier, $E_{\text{act}}$ as.

$$E_{\text{act}} = E_{\text{TS}} - E_{\text{IS}} \quad (6.2)$$
where $E_{TS}$ and $E_{IS}$ represent the energy of the transition state, and energy of initial state (reactants) respectively.

# 6.3 Results and Discussion

## 6.3.1 Geometric and electronic structure

Many stable configurations of atomic O and SO$_x$ on Pt(111) and Pd(111) were considered in this work (see Figure 6.1), similar to the past literature studies. [259, 265, 276, 283] Typically, the metal to sulfur bond lengths were relatively shorter on the Pd(111) surface. However, no such pattern was observed for metal-O and S-O bonds. The increase in interatomic bond length was quite large (~10 %) relative to the gas phase values (1.42–1.43 Å), when both the S and O atoms directly attached to the surface. A decrease in bond angle ($\angle$OSO), typically by 8–10 %, was observed relative to the gas phase values of $\angle$OSO = 119°–120° (detailed geometry information of all species considered is provided in Appendix D).

Bader charge analysis suggested that the charge transfer between SO$_x$ and the Pd(111) surface was slightly larger than that on Pt(111). The increase in the number of O atoms in a molecule increased the total charge transfer (i.e. SO$_4$ acquired the largest negative charge) which explains the larger coverage dependence on binding energy for this case. A molecule with more O atoms attached directly to the metal rendered a larger negative charge on it, a larger positive charge on the attached metal atoms, and a decrease in the net charge on the S atom. This behavior is potentially due to the larger electronegativity of O compared to S. In general, metal surfaces acquired a positive charge while the charge was being accumulated in the adsorbate, which is likely to accelerate catalyst poisoning by depleting the charge from the metal surface and repelling other molecules. [283] Larger charge transfer in Pd systems
6.3 Results and Discussion

Fig. 6.1 The representative stable configurations of SO\textsubscript{x} molecules at the fcc position (unless otherwise stated) of Pt(111) or Pd(111): (a) S ($\eta^1$), (b) SO ($\eta^1$), (c) SO ($\eta^2$), (d) SO\textsubscript{2} ($\eta^2$), (e) SO\textsubscript{2} ($\eta^3$), (f) SO\textsubscript{2} (bridge, $\eta^1$), (g) SO\textsubscript{3} ($\eta^3$), (h) SO\textsubscript{3} ($\eta^3$), and (i) SO\textsubscript{4} ($\eta^3$). The number super-scripted to $\eta$ represents the number of atoms in a molecule coordinated to the metal (111) surface. Binding energies (in kcal/mol) for the given configurations are shown for a 0.11 ML coverage. Pt(or Pd), S, and O atoms are represented by blue, yellow, and red colors, respectively.
Fig. 6.2 Difference electron density maps highlighting the electron charge density redistribution due to the O and SO$_x$ adsorption at the fcc site (unless otherwise stated) of Pd(111) surface: (a) O (atop, $\eta^1$), (b) S ($\eta^1$), (c) SO ($\eta^1$), (d) SO ($\eta^2$), (e) SO$_2$ ($\eta^3$), (f) SO$_2$ ($\eta^2$), (g) SO$_2$ (bridge, $\eta^1$), (h) SO$_3$ ($\eta^3$), (i) SO$_3$ ($\eta^3$), and (j) SO$_4$ ($\eta^3$). An isosurface corresponding to an electron charge density of 0.02 e/Å$^3$ is shown in each of the panels. Blue and red colors have been used to represent depletion and accumulation of charge, respectively. Silver, yellow, and red spheres represent the Pd, S, and O atoms, respectively.

relative to Pt suggests that the Pd surface is more susceptible to SO$_x$ poisoning, which has been shown in previous experimental investigations. [31] Details of Bader analysis are provided in the Appendix D.

To visualize the charge rearrangements upon SO$_x$ adsorption, we carried out difference electron density. [287] analyses (see 6.2) Hybridization between the $d_{z^2}$ orbital of Pt/Pd atoms with the 3$p$ orbital of S and the 2$p$ orbitals of O atoms can be noted. Metal $d_{xz}$ and $d_{yz}$ orbitals created charge accumulations, which indicated the presence of a forward-donation and back-donation mechanisms between SO$_x$ and metal surfaces. [265] The charge accumulation between the metal atom and the $sp^3$ hybridized S atom suggests the presence of some covalent bonding.

To understand the orbital interactions, we examined the density of states (DOS) as shown in Figure 6.3. The DOS analyses revealed the shifting of the active metal $d$-band to lower energy, creating bonding and anti-bonding orbitals. The $d$-band shifting was found to be larger for metal-S interaction compared to metal-O interaction. A remarkable broadening of S and O $p$
orbitals into the metal $d$-band region below the Fermi level was due to back-donation. [259] The S and O $p$ orbitals above the Fermi level almost disappeared and shifted to the metal $d$-band region. However, the presence of some residual states suggested the electronic charge donations from the metal, i.e. forward-donation. [259] Generally, the lower energy of S ($3p$) orbitals as compared to O ($2p$) orbitals and the larger shift in the metal $d$-band suggest the strength of metal-S interactions compared to metal-O interactions (see figures and details in Appendix D).

6.3.2 Thermodynamics and kinetics

Binding energy patterns of SO$_x$ was similar on both surfaces, with the order of the binding strength as follows: S > O > SO > SO$_4$ > SO$_3$ > SO$_2$. This result suggests that if S sticks to the surface, which is typically not the case in diesel engine exhaust, it would be extremely difficult to remove. Further, the tetrahedrally coordinated and upright standing molecules at the fcc position exhibited the largest binding energy, which is attributed to the weaker influence from the relatively distant subsurface metal layer. The effect is stronger for the atoms close to the surface. Binding energies of the most stable configurations of SO$_x$ species were in close agreement with other DFT-based studies (see Appendix D). [119, 265, 276, 283, 288]

Moreover, we observed a coverage dependence of the binding energy. Figure 6.4 shows the computed binding energies of the most stable species of SO$_x$ and O for coverages of 0.06–0.25 ML. We considered (2×2), (3×3), and (4×4) surface unit cells with one molecule leading to surface coverages of 0.25 ML, 0.11 ML, and 0.06 ML, respectively. The results suggest that SO$_4$ and O display the strongest and weakest coverage dependence, respectively. This feature may be associated with the size of the adsorbate and the charge transfer between the surface and the adsorbates.

Figure 6.5 shows a complete picture of the relative energy of SO$_x$* + (4–$x$) O* (for $x$ = 0–4) on both surfaces (* indicates that the species is adsorbed on the metal surface). Our
Fig. 6.3 Projected density of states (P-DOS) analysis of adsorbed SO$_x$ species on metal surface and comparison to the atomic components in isolated states: (a) S (fcc)$\eta^{1}$$\text{-S}_f$, (b) SO (fcc)$\eta^{1}$$\text{-S}_f$, (c) SO (fcc)$\eta^{2}$$\text{-S}_b\text{O}_a$, (d) SO$_2$ (fcc)$\eta^{2}$$\text{-S}_b\text{O}_a$, (e) SO$_2$ (fcc)$\eta^{3}$$\text{-S}_a\text{O}_a\text{O}_a$, (f) SO$_3$ (fcc)$\eta^{3}$$\text{-S}_a\text{O}_a\text{O}_a\text{O}_a$, (g) SO$_3$ (fcc)$\eta^{3}$$\text{-O}_a\text{O}_a\text{O}_a\text{O}_a$, and (h) SO$_4$ (fcc)$\eta^{3}$$\text{-O}_a\text{O}_a\text{O}_a\text{O}_a$ on Pd(111) surface and (i) S (fcc)$\eta^{1}$$\text{-S}_f$ on Pt(111) and Pd(111) surfaces. The lower part each panel (a-h) represents the projected DOS of Pt, S and O atomic orbitals in isolated atomic/molecular/pure slab state and the upper part represents the same in adsorbed state. The O-1 and O-2 represent the oxygen atom attached to Pt (with S) and S atom only. Similarly, Pd-1 and Pd-2 represent the Pd atom attached to S atom and O atom respectively. The Fermi energy ($E_{\text{Fermi}}$) is adjusted to zero in the plot.
6.3 Results and Discussion

Fig. 6.4 Coverage dependent binding energies (in kcal/mol) of the most stable SO$_x$ species and O atom adsorbed on Pt(111) and Pd(111) surfaces.

thermodynamic analyses based on the binding energies of individual species (i.e., when lateral interactions are excluded) suggest that the relative stability order is as follows: S$^+$+4O$^*$ > SO$^*$+3O$^*$ > SO$_2$$^*$+2O$^*$ > SO$_3$$^*$+O$^*$ on the Pt(111) surface and S$^+$+4O$^*$ > SO$^*$+3O$^*$ > SO$_2$$^*$+2O$^*$ > SO$_4$$^*$ on the Pd(111) surface. SO$_4$$^*$ has lower energy compared to SO$_3$$^*$+O$^*$, which suggests that the sulfates are more stable on the metal surface. The higher exothermicity of SO$_3$ oxidation suggests that the sulfate, once formed on the catalyst surface, will not decompose easily. Nevertheless, we note that lateral interactions should be taken into consideration when making conclusions regarding energetics. Such interactions were implicitly included in our CI-NEB computations (discussed next) and are reflected in the offset in the energy position of the SO$_2$$^*$+2O$^*$ and SO$_3$$^*$+O$^*$ cases with respect to the positions of the start of the CI-NEB energy profiles.

In addition to thermodynamics, reaction kinetics is critical to understand the sulfation process. Therefore, we investigated the minimum energy paths (MEPs), and estimated activation
energy barriers of the Langmuir-Hinshelwood (L-H) type surface reactions involving SO$_2$ oxidation to form SO$_3$, and subsequently SO$_4$ formation on both surfaces. The MEP analysis revealed three possible pathways (viz. paths A, B, and C) of SO$_2$ oxidation and 2 pathways (viz. paths A and B) of SO$_3$ oxidation as shown in Figure 6.6. In both cases, path A represents the diffusion of the O atom, whereas paths B and C for SO$_2$ oxidation and path B for SO$_3$ oxidation involve SO$_2$ and SO$_3$ movements, respectively. Our finding pertaining to the SO$_2$ oxidation reaction MEP (path C) is consistent with the previously reported DFT–based study on the Pt(111) surface. [289]

The activation barriers for paths B and C of SO$_2$ oxidation were lower ($\geq 7–10$ kcal/mol) than that for path A and were very similar for both surfaces (see Table 6.1 for activation energies). Hence, neither path can be ruled out from the possible reaction mechanism. As expected, path B of SO$_3$ oxidation was significantly lower for both surfaces; however the activation barrier was relatively small on the Pd(111) surface. The lower activation barrier may explain the higher sulfation susceptibility of the Pd(111) surface as seen in experimental studies. [32, 276, 277] We note that the binding energy of the O was significantly larger compared to SO$_2$ and SO$_3$. Hence, it is easier for those molecules to diffuse towards O and form products on the surface, which is consistent with previous observations. [289]

Our DFT activation barrier for SO$_2$ oxidation on Pt(111) is in close agreement with experimental results ($\sim 23$ kcal/mol) [260, 290–292] and with our previous estimate based on the UBI-QEP method (21.5 kcal/mol). [31] Unfortunately, no direct comparison to experimental data can be made for SO$_2$ oxidation on Pd(111). Nonetheless, similar oxidation behavior of SO$_x$ on the Pd(111) surface is expected and observed as well. [276] The UBI-QEP activation energy estimated using the binding energies from the present work for SO$_2$ oxidation on the Pd(111) surface is 22.2 kcal/mol, which is close to the DFT estimate. The UBI-QEP procedure to compute the activation energy using a thermodynamic loop is provided in Appendix B. In Table
6.3 Results and Discussion

Fig. 6.5 Relative energy of $SO_x$ species on Pt(111) and Pd(111) surfaces without lateral interactions along with CI-NEB computed activation barriers (which include the $SO_x$ + O lateral interactions) for the Langmuir-Hinshelwood type surface reactions ($SO_2^* + O^* \leftrightarrow SO_3^* + *$ and $SO_3^* + O^* \leftrightarrow SO_4^* + *$) on Pt(111) (a) and on Pd(111) (b). * indicates an adsorbed surface species.
6.3 Results and Discussion

6.1, we also list the pre-exponential factors of both oxidation reactions and the zero-point energy corrections (ΔZPE) to the activation, which are estimated from the vibrational frequencies of the transition state (TS) and initial state (IS).[168] The pre-exponential factor values ($10^{13}$ s$^{-1}$) suggest a tight TS. [264] Calculation details are provided in Appendix E.

Fig. 6.6 Minimum energy pathways (MEPs) for SO$_2$ and SO$_3$ oxidation on the Pt(111) surface. Panel (a–c): SO$_2$ oxidation paths A, B, and C; panel (c–d): SO$_3$ oxidation paths A and B. The middle image in each panel represents the transition state. Blue, yellow, and red spheres represent Pt, S, and O atoms, respectively.
6.3 Results and Discussion

Table 6.1 Pre-exponential factors, activation energies, zero-point ($\Delta$ ZPE) corrections, and the corrected activation energies (kcal/mol) of SO$_2$ and SO$_3$ oxidation on Pt(111) and Pd(111) surfaces computed using DFT for the paths shown in Figure 6.6.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Path</th>
<th>Pt(111)</th>
<th>Pd(111)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$A_o$</td>
<td>$E_a$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(s$^{-1}$)</td>
<td>(kcal/mol)</td>
</tr>
<tr>
<td>SO$_2^<em>$ + O</em> $\rightarrow$ SO$_3^*$</td>
<td>Path A</td>
<td>2.4 $\times$ 10$^{11}$</td>
<td>33.8</td>
</tr>
<tr>
<td></td>
<td>Path B</td>
<td>7.9 $\times$ 10$^{11}$</td>
<td>23.1</td>
</tr>
<tr>
<td></td>
<td>Path C</td>
<td>5.0 $\times$ 10$^{11}$</td>
<td>22.5</td>
</tr>
<tr>
<td>SO$_3^<em>$ + O</em> $\rightarrow$ SO$_4^*$</td>
<td>Path A</td>
<td>7.1 $\times$ 10$^{12}$</td>
<td>30.3</td>
</tr>
<tr>
<td></td>
<td>Path B</td>
<td>9.6 $\times$ 10$^{12}$</td>
<td>22.4</td>
</tr>
</tbody>
</table>

6.3.3 Microkinetic Modeling

The thermodynamic (e.g., binding energies) and kinetic (e.g., activation barriers, pre-exponential factors) information that emerges from DFT computations needs to be coupled with techniques such as microkinetic modeling to assess the relative importance of reaction pathways at various operating conditions. Microkinetic modeling can be used to predict surface coverages, most abundant reaction intermediate(s) (MARI), conversion, and rate determining steps without any a priori assumptions about the reactions. [31, 101, 264] Here, we use the present results for the thermodynamic and kinetic parameters as input to our microkinetic model developed earlier. [264] Temperature correction was applied to 0 K DFT binding energies before using in the model at 300 K (given in the last column of Table 6.2). A total of 8 elementary steps (listed in Table 6.2) involving 3 surface species, O*, SO$_2^*$, and SO$_3^*$, are used in this microkinetic model, and the conversion of SO$_2$ (to SO$_3$) is predicted at different conditions previously probed experimentally. The model also involved parameters not directly addressed in the DFT part of this work. These include the bond indices, [281] sticking coefficients, desorption pre-exponential factors, and the coverage and temperature dependence of the activation energy
Results and Discussion

(estimated using the UBI-QEP method), all of which are also listed in Table 6.2. We note that the lateral interactions of the SO₃ species are not taken into the microkinetic model. In our previous work, [264] we show that the coverage of SO₃ species (particularly SO₃*) on the catalyst's surface was relatively small compared to the oxygen. This is also consistent with the typical operating conditions for emissions oxidation, where the gas phase oxygen concentration is ~12%, and the SO₃ concentration is only a few ppms. The SO₃* coverage was observed to be slightly higher (~0.3 ML) at low temperature (~300°C), but the coverage was negligible (~0.045 ML) at higher temperature (~500°C). In fact, for most of the conditions, the surface is dominated by oxygen. Therefore, we have included the lateral interactions between oxygen molecules only. Furthermore, the UBI-QEP based activation barriers vary with coverage; however, the variation is negligible if the coverage is low. Activation barriers for R₃ and R₅ (see Table 6.2) are taken as zero, i.e., the adsorption reactions are assumed to be non-activated. Details are provided in Appendix B. The rationale for these choices have been described elsewhere. [31, 264]

Figure 6.7 shows the comparison of microkinetic model predictions against experimental data obtained at 3 different sets of experimental conditions (labeled as Set-A, Set-B, Set-C). [264, 275] Overall, good agreement is observed between the experimental data and the model predictions. In particular, Set-C in Figure 6.7 shows the model performance with SO₃ in the feed. The experimental results show a slight shift of the light-off curve towards high temperature in the presence of SO₃ in the feed. This explains the inhibition effect of SO₃ during SO₂ oxidation, [275] which is also well captured by the model. At high temperature, the presence of SO₃ in the feed further decreases SO₂ conversion due to equilibrium limitations. These results indicate that combining DFT predictions with microkinetic modeling provides a viable way to validate reaction kinetics and experiments.
Fig. 6.7 Minimum energy pathways (MEPs) for SO$_2$ and SO$_3$ oxidation on the Pt(111) surface. Panel (a–c): SO$_2$ oxidation paths A, B, and C; panel (c–d): SO$_3$ oxidation paths A and B. The middle image in each panel represents the transition state. Blue, yellow, and red spheres represent Pt, S, and O atoms, respectively.
### 6.3 Results and Discussion

Table 6.2 Elementary steps considered to study SO<sub>2</sub> oxidation on Pt. θ<sub>o</sub> represents the oxygen surface coverage, * indicates a vacant site, whereas superscript * indicates an adsorbed species. Barriers reported in the fourth and fifth columns correspond to the DFT–computed quantities at 0 K and the temperature and pressure dependent UBI-QEP estimates, respectively.

<table>
<thead>
<tr>
<th>No.</th>
<th>Reactions</th>
<th>Sticking coefficient</th>
<th>Activation energy [kcal/mol]</th>
<th>Bond index&lt;sup&gt;b&lt;/sup&gt;</th>
<th>pre-exponential factor [s&lt;sup&gt;−1&lt;/sup&gt;] at 0 K</th>
</tr>
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<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>at 0 K</td>
</tr>
<tr>
<td></td>
<td>O&lt;sub&gt;2&lt;/sub&gt; adsorption/desorption [31, 264]</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R₁</td>
<td>O&lt;sub&gt;2&lt;/sub&gt; + 2* → 2O*</td>
<td>0.05&lt;sup&gt;c&lt;/sup&gt;</td>
<td>0.0</td>
<td>0.0</td>
<td>0.5</td>
</tr>
<tr>
<td>R₂</td>
<td>2O* → O₂ + 2*</td>
<td>1.0 × 10&lt;sup&gt;13&lt;/sup&gt;d</td>
<td>52.2 – 34.6θ&lt;sub&gt;o&lt;/sub&gt;</td>
<td>52.2 – 34.6θ&lt;sub&gt;o&lt;/sub&gt; + f(T)</td>
<td></td>
</tr>
<tr>
<td>R₃</td>
<td>SO₂ + * → SO₂⁺</td>
<td>0.5&lt;sup&gt;c&lt;/sup&gt;</td>
<td>0.0</td>
<td>0.0</td>
<td>0.5</td>
</tr>
<tr>
<td>R₄</td>
<td>SO₂⁺ → SO₂ + *</td>
<td>1 × 10&lt;sup&gt;16&lt;/sup&gt;d</td>
<td>30.8</td>
<td>29.3 – 2.5ΔT</td>
<td></td>
</tr>
<tr>
<td>R₅</td>
<td>SO₃ + * → SO₃⁺</td>
<td>0.5&lt;sup&gt;c&lt;/sup&gt;</td>
<td>0.0</td>
<td>0.0</td>
<td>0.5</td>
</tr>
<tr>
<td>R₆</td>
<td>SO₃⁺ → SO₃ + *</td>
<td>1 × 10&lt;sup&gt;13&lt;/sup&gt;d</td>
<td>35.6</td>
<td>34.1 – 2.5ΔT</td>
<td></td>
</tr>
<tr>
<td>R₇</td>
<td>SO₃⁺ + * → SO₃⁺ + O⁺</td>
<td>1.2 × 10&lt;sup&gt;14&lt;/sup&gt;d</td>
<td>26.8</td>
<td>23.2 + f(θ&lt;sub&gt;o&lt;/sub&gt;,T)</td>
<td>0.97</td>
</tr>
<tr>
<td>R₈</td>
<td>SO₃⁺ + O⁻ → SO₃ + O⁺</td>
<td>5.0 × 10&lt;sup&gt;14&lt;/sup&gt;d</td>
<td>22.3</td>
<td>21.3 + f(θ&lt;sub&gt;o&lt;/sub&gt;,T)</td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup> DFT-based binding energies at 0 K are used as inputs to calculate the binding energies at a given temperature. The functional form ‘f’ includes coverage and temperature dependence. Coverage dependence originates from the use of UBI-QEP for the estimation of activation energies, whereas the temperature dependence is derived from the statistical mechanics based calculations for degrees of freedom lost/gained upon adsorption [101] (details are discussed in Appendix B). ΔT = T – T<sub>o</sub>, where T<sub>o</sub> is taken as 300 K. Activation energies are computed on-the-fly using the UBI-QEP formalism, as the surface coverages changes in the simulations. Difference in activation energies for reactions R<sub>7</sub>–R<sub>8</sub> primarily originates from the use of UBI-QEP vs. DFT.

<sup>b</sup> Bond index represents the position of the transition state along the reaction coordinate, which is also used to compute the activation energies in the UBI-QEP formalism. It is defined for a reaction pair in the forward direction only (details are discussed in Appendix B). It ranges between 0 and 1, with a typical estimate of 0.5. Bond index for reaction pair R<sub>7</sub>–R<sub>8</sub> was adjusted to 0.97 in the UBI-QEP calculations in order to closely emulate the DFT-computed barriers.

<sup>c</sup> Sticking coefficients for O<sub>2</sub> and SO<sub>2</sub> are taken from Refs. [151] and [246], respectively, whereas that of SO<sub>3</sub> is assumed to be the same as SO<sub>2</sub>.

<sup>d</sup> Pre-exponential factors for R<sub>2</sub> and R<sub>6</sub> are based on the typical order-of-magnitude estimate based on Transition State Theory (TST). [101] Pre-exponential factor for R<sub>4</sub> is based on high values (10<sup>15</sup>–10<sup>17</sup> s<sup>−1</sup>) reported in literature. [260, 262] Finally, pre-exponential factors for R<sub>7</sub> and R<sub>8</sub> are based on the DFT calculations from this work.
6.4 Conclusions

In summary, we investigated and compared the stability, morphology, thermodynamics and kinetics of various $\text{SO}_x$ species on Pt(111) and Pd(111) surfaces. Our analysis revealed 3 important pathways for $\text{SO}_2$ oxidation and 2 major pathways for $\text{SO}_3$ oxidation, where the lowest activation barrier for both oxidation reaction was due to the diffusion of $\text{SO}_2$ or $\text{SO}_3$ towards an O atom on the surface. In general, oxidation of $\text{SO}_x$ and ultimately $\text{SO}_4$ formation is a favorable process on both surfaces, although it appears that Pd is more likely to be sulfated compared to Pt (consistent with experimental findings). Quantities computed using DFT were incorporated in a previously developed microkinetic model to predict $\text{SO}_2$ conversion as a function of temperature for three sets of operating conditions, one of which included $\text{SO}_3$ in the feed. The favorable agreement of the computed results with experiments is indicative of the applicability of the present strategy to obtain quantitative insights pertaining to $\text{SO}_x$ chemistry on catalyst surfaces. This can thus lead to the rational design of sulfur-resistant emissions aftertreatment catalysts.
Chapter 7

Why Pt Survives but Pd Suffers From SO\textsubscript{x} Poisoning?

7.1 Introduction

Oxides of sulfur, predominantly SO\textsubscript{3} generated from the oxidation of SO\textsubscript{2}, poison the noble metal based emissions aftertreatment catalysts such as the Diesel Oxidation Catalysts (DOCs) by altering metal surface properties, blocking other emissions species/adsorbates, changing the reaction selectivity, and forming stable metal sulfates. [9, 31, 32, 72, 276, 277, 293, 294] Traditionally, Pt-based oxidation catalysts have been the most preferred option for the oxidation of diesel engine emissions due to their superior capability to resist sulfation (i.e., formation of PtSO\textsubscript{4} or other sulfates). [15, 283, 295] However, the high cost of Pt and its tendency to sinter at the high operating temperatures encountered have forced the inclusion of Pd in the currently used state-of-the-art oxidation catalysts. [31, 32] While Pd by itself is a good oxidation catalyst, has low cost, and resists sintering (unlike Pt), it suffers from sulfur poisoning. [31, 32, 84, 87] Indeed, many experimental and computational studies [9, 15, 87, 283, 293–295] directly point to
the heightened tendency for Pd sulfation—especially, formation of PdSO$_4$. On the other hand, no evidence exists for the formation of PtSO$_4$ even under highly oxidizing and sulfating conditions. Given the chemical similarity between Pt and Pd, the radical divide in their tendencies for sulfation remains a puzzle. A clear understanding of the circumstances (environment, chemical attributes, descriptors, etc.) that contribute to the different sulfation tendencies of Pt and Pd will guide us in rationally designing potentially lower-cost higher-performance sulfur resistant catalysts.

This work aims to provide fundamental insights pertaining to the intrinsic tendency (or lack thereof) of Pt and Pd to undergo sulfation via a comprehensive first principles thermodynamics study. The thermodynamic analysis has resulted in accurate and feature-rich bulk and surface phase diagrams of Pt and Pd when exposed to reservoirs of O$_2$ and SO$_3$. This has also aided in the identification of descriptors or key features that make Pt different from Pd. Owing to the complex nature of the sulfation process, capturing a large spectrum of possible bulk and surface phases as a function of the environmental conditions is critical. Figure 7.1 collects the anticipated and known stable phases when Pt or Pd is exposed to oxidizing and/or sulfating conditions (i.e., O$_2$ and SO$_3$ environments). This collage of possible phases includes pure bulk metals, bulk oxides and bulk sulfates as well as surface metallic forms, surfaces partially or wholly covered with O and/or SO$_3$, surface oxides, and surface sulfates. When prior experimental or computational information was available for a particular phase, it was used in our calculations. But, when such information was not available (e.g., in the case of PtSO$_4$), we determined the atomic level structure using a structure search algorithm in the Universal Structure Predictor: Evolutionary Xtallography (USPEX) method. [130, 131]
7.2 Computational Details

Our first principles calculations were carried out using density functional theory (DFT) \cite{111, 296} as implemented in the VASP code \cite{113} with the electronic wave functions expanded in a plane wave basis with a cutoff energy of 400 eV. All calculations were performed utilizing the Perdew-Burke-Ernzerhof (PBE) functional, \cite{114} the projector augmented wave (PAW) frozen-core potentials, and spin polarization method. The structures were relaxed using a conjugate-gradient algorithm until the forces on all atoms were < 0.01 eV/Å. Both the Pt(111) and Pd(111) surfaces were represented by a 5-layer slab, and (2×2), (3×3), and (4×4) surface unit cells. Two bottom layers of the slab were fixed and the remaining top 3 layers were allowed to relax. To avoid any interactions between periodic images, a 12-14 Å thick vacuum region was introduced. Monkhorst-Pack grids of 3×3×1, 4×4×1, and 5×5×1 were used for Brillouin zone integration for slabs with (4×4), (3×3), and (2×2) surface unit cells, respectively. For the Pt surface-oxide models, PtO$_2$-Pt(111) and Pd surface oxides, PdO-Pd(111), Monkhorst-Pack grids of 5×5×1 and 1×3×1 were used, respectively. Similarly, a Monkhorst-Pack grid of 4×5×1 was used for both Pt and Pd surface-sulfate models with (3×√3) supercell. To search the possible PtSO$_4$ structures, evolutionary structure prediction was performed using the USPEX code \cite{130, 131} in conjunction with \textit{ab-initio} structure relaxations using DFT and methodology as mentioned above.

7.3 First Principles Thermodynamics and Gibbs Free Energy

Once the catalog of possible phases was assembled, the Gibbs free energy of formation of each of the phases with respect to the appropriate reference states was computed using the
density functional theory (DFT) total energies, DFT phonon density of states, and the statistical mechanics of ideal diatomic (O$_2$) and polyatomic (SO$_3$) gases. [149, 297, 298] The Gibbs free energy inherently contains temperature and pressure dependence. While the pressure dependence comes entirely through the chemical potentials of the gas phase species (µ(O$_2$) and (µ(SO$_3$) of O$_2$ and SO$_3$, respectively), the temperature dependence arises due to the gas phase species as well as due to the vibrational degrees of freedom of the condensed phases. The latter is generally ignored due to the severe computational expense of phonon computations, but it is computed and shown to have no significant impact on outcome of the present work. Hence, the contribution is not included in the phase diagrams shown in this paper. Furthermore, this formulation neglects the configurational entropic contributions since it was found in the past to have no significant impact on the results, especially features of the phase diagrams. [299] The free energies were then used to construct bulk and surface phase diagrams, revealing clear differences between Pt and Pd insofar as their thermodynamic tendencies for both oxidation and sulfation are concerned. Details of the DFT calculations are described later in Computational Methods section. Vibrational modes computations and surface free energy computations are given in the Appendix F.

7.4 Bulk Thermodynamics

A simple yet effective starting point is to consider the bulk phases (metal, oxide and sulfate) shown in panels 1-3 of Figure 7.1. Both Pt and Pd metals are fcc structures (space group 225, Fm3m) with very similar lattice parameters. However, the experimentally known most stable bulk oxides of Pt and Pd are quite different from each other. [300] A dioxide compound PtO$_2$ (space group 164, P-3m1) is the most stable oxide of Pt, whereas a monoxide compound PdO (space group 131, P4$_2$/mmc) is the only known stable oxide of Pd. In the case of metal
7.4 Bulk Thermodynamics

Fig. 7.1 Schematics of the representative stable structures of various bulk and surface phases in the thermodynamic equilibrium containing O$_2$ and SO$_3$ for the temperature and pressure range considered in this study. The middle region (inside the circular boundary) represents a catalyst surface exposed to wide ranges of temperature and pressure conditions, where gas phase O$_2$, SO$_3$ along with adsorbed O and SO$_3$ on Pt or Pd surface are also shown. Panels 1-3 at the top represent the bulk phases (i.e., bulk metal, metal oxides, and bulk sulfates), and panels 4-10 represent various possible surface phases of Pt and Pd (i.e., pristine surfaces, O and/or SO$_3$ on the metal surfaces, surface oxides, SO$_3$ on the surface oxides, and surface sulfates) in an anti-clockwise order to the ultimate sulfate phase. The blue, brown, and black colors represent the clean metal surface, surface oxide, and the surface sulfate layer, respectively. Similarly, the silver, red, and yellow spheres represent the Pt or Pd, Oxygen, and Sulfur respectively.
sulfates, PdSO₄ (space group 15, C2/c) is well known experimentally; however, no information is available about PtSO₄ to the best of our knowledge. Therefore, we have used the USPEX method [130, 131] and have identified a tetragonal PtSO₄ phase (space group 84, P4₂/m). The dynamical stability of this phase was confirmed via a phonon band structure calculation, which revealed no modes with imaginary frequencies. In order to validate the veracity of the USPEX method for this class of systems, the structure of PdSO₄ was also predicted using USPEX. It is reassuring to note that the correct experimentally known ground state structure of PdSO₄ is indeed recovered. Details concerning the structure prediction results, as well as the predicted geometries of the selected phases along with comparisons to past experimental and computation work are provided in the Appendix G.

The free energies of the bulk metals, oxides, and sulfates were then used to compute the phase diagrams for both Pt and Pd, which are shown in Figure 7.2. As noted earlier, the free energy depends on the temperature and the O₂ and SO₃ partial pressures. Essentially, this figure shows the most stable phase (i.e., the one with the lowest free energy) for a given choice of the temperature and pressure dependent parts of the O₂ and SO₃ chemical potentials (represented using ΔµO₂ and ΔµSO₃). For convenience, the O₂ and SO₃ partial pressure ranges for two choices of temperatures (300 K and 700 K) are also shown. It is evident that PdO formation is more favored than PtO₂ formation as the onset of the PdO phase region occurs at less oxidizing conditions (ΔµO₂ = −1.88 eV) compared to PtO₂ (ΔµO₂ = −1.42 eV). More importantly, the PdSO₄ phase region is a lot more prominent than the PtSO₄ phase region for the same range of chemical potentials or temperature-pressure ranges. In fact, the stability range of PtSO₄ lies outside of normal pressure conditions at ambient (300 K) or higher temperatures. This may explain why there is no experimental information available for PtSO₄ thus far. [301] The clear thermodynamic resistance for PtSO₄ formation (compared to PdSO₄) in the bulk form is
Fig. 7.2 Bulk phase diagrams showing metal, metal oxide and metal sulfate (structures are shown in Figure 7.1) in the given ranges of $\Delta \mu_{SO_3}$ and $\Delta \mu_{O_2}$. Panel a: bulk phase diagram with Pd, PdO and PdSO$_4$; and panel b: bulk phase diagram with Pt, PtO$_2$ and PtSO$_4$. Chemical potential ranges are translated into a pressure range for two representative temperatures (300 K and 700 K). The stability regions of bulk sulfates show the most prominent differences.
indicative of Pt’s resistance to sulfur poisoning, and could be used as a screening criterion to identify potentially sulfur resistant catalysts.

7.5 Surface Thermodynamics

While bulk thermodynamics provides a good starting point, catalytically more realistic conditions involve surface phenomena. Therefore, we investigated the possible surface phases on both metal surfaces in oxidizing and sulfating environments. In panels 4-6 of Figure 7.1, we show the stable surface phases while increasing the oxygen partial pressure. Results (discussed later in more details) show greater affinity of Pd surface towards oxygen with highly favored surface oxide formation. Similarly, we show the stable phases of SO\textsubscript{3} on clean surface and co-adsorbed oxygen and SO\textsubscript{3} in panels 7 and 8, respectively. Panel 9 shows a more interesting phase of SO\textsubscript{3} on the oxidized surfaces of Pt and Pd. We observed that the affinity of SO\textsubscript{3} is significant on PdO only. Further interaction of SO\textsubscript{3} and the surface oxide could potentially result in a surface sulfate as shown in panel 10, and ultimately in the bulk sulfate in panel 3. These phases are discussed next, resulting in the surface phase diagrams for Pt and Pd surfaces when exposed to O\textsubscript{2} and SO\textsubscript{3}.

7.5.1 Oxygen on Pt(111) and Pd(111) Surfaces

Due to significantly high oxygen concentration (~10%) in realistic exhaust conditions [31, 32], a natural step here is to investigate the oxygen interactions on the surfaces. Experimentally observed stable phases of O on Pt(111) and Pd(111) due to O\textsubscript{2} exposure involve \textit{p}(2\times2) and \textit{c}(2\times2) configurations with possibility of higher coverage (\(\theta \text{O} \sim 1 \text{ ML}\)) when the Pt(111) surface is exposed to NO\textsubscript{2} or O\textsubscript{3}. [149, 297] Hence, we investigated the entire range (0 - 1 ML) of O coverage on both surfaces (higher O coverage is possible in surface oxides, as discussed
in the next paragraph). By considering a variety of configurational possibilities (as described in the Appendix H), this approach allowed us to fully capture lateral or adsorbate-adsorbate interactions. In general, we observed very similar oxygen interaction behavior (binding strength and lateral interaction patterns) on both Pt(111) and Pd(111) surfaces. Binding energies of oxygen on both metal surfaces are given in Appendix H.

### 7.5.2 Surface Oxides

An elevated oxygen concentration on the metal surface can proceed to a partially oxidized phase (i.e., the surface oxide phases shown in panel 6 of Figure 7.1). The surface oxide models for Pt(111) and Pd(111) surfaces considered here are guided by HRCLS, STM, LEED, and XRD experimental observations. [298, 302, 303] Experimental and computational results suggest that the surface oxide layer formation on Pt(111) and Pd(111) surfaces results in different types of arrangements of metal and oxygen atoms. 22-24 Å (O-Pt-O) trilayer structure of Pt surface oxide on a (2\times2) surface contains only three Pt atoms (unlike four Pt atoms on a clean surface) and six O atoms. LEED patterns show $\alpha$-PtO$_2$(0001) (2 × 2) overlayers on the Pt(111) surface. 25 On the other hand, a distinct Pd$_5$O$_4$ type (with repetitive structure pattern of five Pd and four O) stable surface oxide layer on Pd(111) was represented by 7\times(Pd$_5$O$_4$) model. This unique structure corresponds to a 0.67 ML oxygen coverage; it has two types of Pd atoms which are either 2- or 4-fold coordinated to O atoms and two types of O atoms which are either 3-fold (bonded to in-plane Pd atoms) or 4-fold (bonded to in-plane and subsurface Pd atoms) coordinated to Pd atoms. The LEED pattern shows that the structure is commensurate in the [2\bar{T} \bar{T} ] direction. [304]

We note the existence of possible sub-surface oxygen configurations on both metals. Todorova et al. showed that sub-surface oxygen on transition metals is initially always less stable than on-surface oxygen adsorption. However, with increasing coverage this preference vanishes, and
a. $\theta_o = 0.25$ ML tetra-I

b. $\theta_o = 0.5$ ML fcc/tetra-I

c. $\theta_o = 0.75$ ML fcc/tetra-I

d. $\theta_o = 1.0$ ML fcc/tetra-I

Fig. 7.3 Representative on-surface/sub-surface (fcc/tetra-I) models for oxygen adsorption on the (111) surface with a $(2 \times 2)$ surface supercell. Panel a: 0.25 ML of oxygen in sub-surface (tetra-I), panel b: 0.5 ML of oxygen with one O atom in on-surface (fcc) and the other on sub-surface (tetra-I) positions, panel c: 0.75 ML of oxygen with two O atoms in on-surface (fcc) and the other on sub-surface (tetra-I) positions, and panel d: 1.0 ML of oxygen with three O atoms in on-surface (fcc) and the one in sub-surface (tetra-I) positions. Silver and red spheres represent the Pt or Pd, and oxygen, respectively.
7.5 Surface Thermodynamics

Oxygen incorporation becomes more favorable above coverages of \(~0.5\ \text{ML}\). \[118, 305\] We considered the most stable/favored sub-surface site tetra-I 29 (i.e. the site directly below the 3-fold hcp position on (111) surface as shown in Figure 7.3) to compute the energetics of the on-surface and sub-surface oxygen adsorption. Our results show that on-surface (fcc)/sub-surface (tetra-I) configuration favors only after on-surface fcc coverage of 0.5 ML on Pd(111), whereas it favors only above the on-surface fcc coverage of 0.75 ML on Pt(111) (in Figure 7.4). The sub-surface only oxygen adsorption ($\theta_O = 0.25\ \text{ML}$) at tetra-I site was highly endothermic for both Pt(111) and Pd(111). However, the sub-surface/on-surface combination becomes exothermic on/above $\theta_O = 0.5\ \text{ML}$. This observation clearly shows the favorability of the on-surface oxygen adsorption at the lower coverage. In general, the adsorption of oxygen on the metal surface is followed by the on-surface/sub-surface oxygen configurations, which finally transforms to the fully oxidized metal oxide layers.

While evaluating the stability based on thermodynamics, we observed that the surface oxides phases are thermodynamically more stable than any sub-surface oxygen configurations and even the experimentally known c($2 \times 2$)-O (0.5ML) configuration. \[306\] Thus, they do not appear on the phase diagrams constructed based on thermodynamics. Utilizing the information from oxygen adsorption and surface oxides formation, we created detailed phase diagram of oxygen on both (Pd (111) and Pt(111)) surfaces. Our calculated phase boundaries for various phases of oxygen adsorption on both surfaces are in good agreement with known experimental results. \[151, 307–310\] Details of the on-surface/sub-surface oxygen adsorption, and phase diagrams are shown in Appendix H.

### 7.5.3 SO$_3$ on Pt(111) and Pd(111) Surfaces

Another spectrum of stable phases may arise due to the presence of SO$_3$ on the surface (panel 7 of Figure 7.1). SO$_3$ shows a strong affinity towards both surfaces, albeit slightly stronger
Fig. 7.4 DFT computed average binding energy $E_b$ as a function of total $O^*$ coverage with on-surface fcc and sub-surface tetra-I sites of Pt(111) and Pd(111) shown in panels a and b, respectively. The blue symbols represent the binding energies of oxygen for on-surface fcc sites of (111) surface. The red symbols represent the binding energies of oxygen for fcc/tetra-I combinations. A $(2 \times 2)$ surface supercell was used for the computations. The red symbol at $\theta_O = 0.25$ ML represents the oxygen on sub-surface tetra-I site only and higher coverages ($> \theta_O = 0.25$ ML) represent the combination of $O^*$ with one oxygen in sub-surface tetra-I and rest of oxygen on surface fcc sites. Dotted lines are drawn to guide the eyes. On-surface fcc $O^*$ coverage below 0.5 ML is always stable on both surfaces.
on Pt(111) as shown by the binding energy numbers in Figure 7.5. An upright standing chair-shaped configuration on fcc sites is the preferred one in both cases. [31, 271] Given the bulky nature of the SO$_3$ molecule, the maximum coverage on the (111) surface could only reach up to 0.33 ML in a (3×3) surface supercell. Size of the molecule is responsible for the significant lateral interactions between adjacent SO$_3$ molecules (note the sharp decrease of SO$_3$ binding energy with coverage in Figure 7.5). We note that the configurational space can be large for a higher coverage; however, the overall outcome due to the selection of our surface models will not change. Four representative stable configurations corresponding to a coverage range of 0.06 ML to 0.33 ML are considered for the generation of phase diagrams (panels 7a-d of Figure 7.6). Computed binding energies and the phase diagrams of SO$_3$ adsorption in Pt(111) and Pd(111) surfaces are given in the Appendix H.

### 7.5.4 Co-Adsorption of Oxygen and SO$_3$ on Pt(111) and Pd(111) Surfaces

A more interesting condition involves the co-adsorbed environment of SO$_3$ and oxygen on the metal surfaces as shown in panels 8a-c of Figure 7.6. In a (3×3) surface supercell, we investigated two SO$_3$ coverages (i.e., $\theta_{SO_3} = 0.11$ ML and $\theta_{SO_3} = 0.22$ ML) and possible O coverages (i.e., up to 0.89 ML). For the condition with 1 SO$_3$ molecule (i.e., $\theta_{SO_3} = 0.11$ ML) on the surface, the maximum stable oxygen coverage was 0.33 ML, whereas the maximum coverage of O decreased to 0.22 ML with 2 SO$_3$ molecules (i.e., $\theta_{SO_3} = 0.22$ ML) on the surface. Further addition of O on the surface caused destabilization and desorption of the SO$_3$ molecule from the surface. This is due to the larger binding strength of O on metal (Pt and Pd) surfaces and also due to lateral adsorbate-adsorbate interactions between O and SO$_3$ as shown in Figure 7.5. It shows the change in binding energies of SO$_3$ due to oxygen addition on the
Pt(111) and Pd(111) surfaces. Computational details of the co-adsorption and the SO$_3^*$-O$^*$ cross interactions are given in the Appendix H.

Fig. 7.5 DFT computed heat of chemisorption of SO$_3$ versus SO$_3^*$ and SO$_3^*$ + O$^*$ coverages on Pt(111) and Pd(111) surfaces shown in panels a and b, respectively. The red lines represent a linear fit to SO$_3^*$ - SO$_3^*$ interactions. The blue lines represent a linear fit for the SO$_3^*$ - O$^*$ interactions as a function of O$^*$ coverage at a fixed $\theta_{SO_3} = 0.11$ ML. A (3×3) surface supercell was used for the energy computations. For the cross-interactions calculations, a fixed surface coverage of SO$_3$ (at $\theta_{SO_3} = 0.11$ ML) was used while varying the O$^*$ coverage.

### 7.5.5 Adsorption of Oxygen and SO$_3$ on the Surface Oxides

With no experimental or computational information on the interactions of O and SO$_3$ on the oxidized surfaces, it remains an unfamiliar and unexplored territory. This study examined the possible interactions of O and SO$_3$ on the surface oxides of both Pt and Pd. As expected, both
surface oxides show no affinity towards further O addition. However, we observed a significant difference in the interaction of SO$_3$ with the oxidized surfaces. The molecular binding energy of SO$_3$ on Pd vs. Pt surface oxide layers was $-0.91$ eV and $-0.12$ eV, respectively, i.e., SO$_3$ prefers to adsorb on PdO than on PtO$_2$. This large difference indicates that such interaction is a key descriptor and a pre-requisite for the higher sulfation tendency of Pd than Pt. As expected, our results showed that the co-adsorption SO$_3$ and O was not favored by both oxidized surfaces, due to the unwelcoming nature of the oxidized metal surface towards additional oxygen. Further details are given in Appendix H.

7.5.6 Surface Sulfates

Interaction of SO$_3$ and oxidized metal surface could lead to the formation of a surface sulfate layer and ultimately to the bulk sulfate phase. Unlike surface oxide phases of Pt and Pd, we do not have experimental information about the structure/morphology of the surface sulfate phases. Hence, we utilized the structural information of bulk sulfates to create surface sulfate models for both Pt and Pd. From the known structure of PdSO$_4$ and the predicted most stable structure of PtSO$_4$, we created a sulfate layer and placed this on the $(3 \times \sqrt{3})$ surface supercell of the (111) surface of Pt or Pd to minimize the lattice strain. The choice of this surface supercell was the best possible compromise considering the size and computational cost restrictions. The structural model of the Pd surface sulfate is shown in panel 10 of Figure 7.6. Further details and other models are provided in the Appendix H.

7.6 Surface Phase Diagram

Assembling the information about the entire spectrum of stable phases discussed above, we have constructed phase diagrams for oxidizing and sulfating conditions on Pd(111) and Pt(111)
surfaces as shown in Figure 7.6. Since the entropic contribution to free energy due to vibrations is negligible and only temperature dependent, we have neglected the contribution to construct the phase diagrams. In this work, the inclusion of vibrational contributions does not alter the outcome of the phase diagram, as the relative magnitude is < 25 meV/Å² for the practically relevant temperature range of below 700 K. The impact of including the maximum vibrational contributions results in rather minor changes (up to 0.07 eV shift in O adsorbed phase boundaries and up to 0.16 eV shift in SO₃ adsorbed phase boundaries) to the features of the phase diagrams (most notably, a small shift in the phase boundaries in the phases with SO₃ adsorption). For example: at 300 K, the change of $\Delta \mu_{O_2}$ from −2.64 eV to −2.59 eV corresponds to an incredibly small pressure change of about $-2.2 \times 10^{-36}$ atm. Hence, none of the new stable structures disappears (or appears) from (or into) the phase diagram. While this analysis provides a justification for neglecting the vibrational contribution in many prior studies, [299, 306] we note that the inclusion of such contributions may be useful for complex systems. The computed vibrational contributions for various adsorbed phases are shown in Appendix I.

The surface phase diagram, as portrayed in Figure 7.6, is fairly complex due to possible existence of many phases. The chemical potentials of O₂ and SO₃ (using $\Delta \mu_{O_2}$ and $\Delta \mu_{SO_3}$) represent the x- and y- axes, respectively. Two more intuitive pressure scales (at representative temperatures of 300 K and 700 K) are shown opposite to the chemical potential range. Starting from the lower left corner of the phase diagram (i.e., low chemical potential region of O₂ and SO₃), we observe a stable clean metal surface phase in both cases (Pd and Pt). We clearly see a tendency to get oxidized easily in the case of Pd surface due to the oxygen chemical potential demarcation ($\Delta \mu_{O_2} = -2.52$ eV for Pd and $\Delta \mu_{O_2} = -2.21$ eV for Pt in the case of experimentally known $p(2 \times 2)$ phase) favoring the O adsorption (panel 5b of Figure 7.6). While keeping the SO₃ concentration low and moving towards higher O₂ chemical potential (horizontal direction), we encounter an experimentally observed stable phase of $p(2 \times 2)$-O overlayer [311] (i.e., $\theta_O =$...
0.25 ML, panel 5b of Figure 7.6) on both surfaces after the low coverage phase of $\theta_O = 0.06$ ML. We note that the experimentally observed $c(2 \times 2)$-O overlayer (i.e., $\theta_O = 0.5$ ML)– most likely a metastable phase before transforming to a more stable surface oxide phase– was not identified as a stable phase in our study. Furthermore, the kinetics will also play a role [306] for the transformation of the $c(2 \times 2)$-O overlayer structure to the surface oxide phase. Further increase in O$_2$ chemical potential leads to the formation of stable surface oxide phases (panel 6 of Figure 7.6) on both surfaces. Besides the experimentally observed morphological differences, these two phases deeply contrast in oxidation affinity. The onset of surface oxide formation on Pd(111) surface is from $\Delta \mu_{O_2} = -2.38$ eV, whereas the onset point for the same on Pt(111) surface is from $\Delta \mu_{O_2} = -1.32$ eV. As seen experimentally, [31] our results suggest that the oxidized phase of Pd, unlike the more stable metallic state of Pt, is the most prevalent state in relevant catalytic conditions (P $\sim$ 1 atm and T $\sim$ 200-500 °C).

Moving toward higher SO$_3$ chemical potential region while keeping the O$_2$ chemical potential low (vertical direction), we observed multiple stable phases of SO$_3$ (represented by a range of $\theta_{SO_3} = 0.11$–0.33 ML, panels 7a-d of Figure 7.6) on both metal surfaces. Further increase in coverage of SO$_3$ on the metal surface is not stable due to the bulky nature of the molecule, and it falls beyond the realistic temperature and pressure ranges. Stronger binding strength of SO$_3$ with Pt (111) translates to the higher coverage favorability of SO$_3$ on Pt(111) than on Pd(111) surface ($\Delta \mu_{SO_3} = -0.64$ eV for Pd and $-1.0$ eV for Pt in the case of $\theta_{SO_3} = 0.33$ ML).

Towards the higher chemical potential region along the diagonal (i.e., higher chemical potential for both O$_2$ and SO$_3$), we observed quite different behaviors on both metal surfaces. Unlike a single co-adsorbed phase in case of Pd (panel 8a of Figure 7.6), multiple such phases were stable on the Pt surface (panels 8a-c of Figure 7.6). We observed a stable phase of SO$_3$ on the surface oxide of Pd (panels 9a-e of Figure 7.6), but this feature was absent in the case of Pt
Fig. 7.6 Surface phase diagrams of Pd(111) (top panel) and Pt(111) (bottom panel) surfaces in a constrained thermodynamic equilibrium with SO₃ and O₂. The given chemical potential range of oxygen ($\Delta \mu_{O_2}$) and SO₃ ($\Delta \mu_{SO_3}$) are translated into a pressure range for two representative temperatures (300 K and 700 K). The numbering of the phases in each panel and structural models is adapted according to Figure 7.1. Common structural models for both Pt and Pd phases are represented by a single structure and corresponding structural number, whereas the different structural models of the same phase of Pt and Pd are subscripted (Pt or Pd) in the panel number (e.g., structures 6 and 9a). Structural models for 9b, 9c, and 9d of the top panel are not shown here for brevity, whereas the final structure 9e is shown. Dotted lines represent the bulk phase boundaries. Bulk phases numbering are shown with black arrows showing the respective regions. Bulk structural models are not shown here. Silver, red, and yellow spheres represent the Pt or Pd, Oxygen, and Sulfur respectively. Blue spheres represent the Pt or Pd in the surface oxide or surface sulfate models.
surface oxide at practically relevant temperature and pressure conditions (the phase boundary starts at $\Delta \mu_{SO_3} = -1.15$ eV for Pd and $-0.1$ eV for Pt). This result aligns well with the idea of a pre-requisite state to proceed towards the surface sulfate and ultimately the bulk metal sulfate of Pd. We note that the surface sulfate phase (panel 10 of Figure 7.6) for Pd(111) appears at a reasonably low chemical potential, which agrees with the experimental observation of PdSO$_4$ formation under typical operating conditions. In the case of Pt, surface sulfate phase does not appear to be a stable phase. In realistic temperature and pressure conditions, we expect to have co-adsorbed phases of O and SO$_3$, surface-oxides phases of Pd, surface sulfate phase of Pd, and eventually the bulk sulfate phase of Pd.

Based on the observations so far, we briefly discuss the key insights and outcomes of this study. Figure 7.7 shows a comparison of the key features of the Pd(111) and Pt(111) surfaces. (a) Panel a shows the O$_2$ chemical potential difference in bulk oxide formation. Clearly, PdO formation is preferred over PtO$_2$ even at low oxygen chemical potential. (b) Panel b compares the O$_2$ chemical potential for surface oxide formation. We observe that the surface oxide formation is favored on Pd than Pt. (c) Panel c shows a rather indistinguishable O binding strength on both surfaces. This behavior aligns well with our natural belief of both metals being rather similar due to other physical/morphological properties such as metal-oxygen bond length ($\sim 2$ Å), most stable adsorption sites (3-fold fcc), nature of charge transfer between metal-oxygen during adsorption [271] (d) On the other hand, the sulfation behavior is quite different for the two metals. Panel d compares the phase boundary onset of bulk sulfate formation in terms of O$_2$ and SO$_3$ chemical potentials (also see Figure 7.2). It is clearly observed that PdSO$_4$ formation is highly favored, unlike PtSO$_4$, under typical operating conditions. (e) Panel e displays the significant difference in SO$_3$ binding strength on both surface oxide layers. SO$_3$ binds more strongly to PdO than PtO$_2$. (f) Panel f shows the surface energy comparison of pristine Pt(111) and Pd(111) surfaces. As observed experimentally, [312, 313] lower surface
### Key Features of Pt and Pd for Possible Sulfation Descriptors

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<tr>
<th>(a) Bulk oxide</th>
<th>(b) Surface oxide</th>
<th>(c) O adsorption</th>
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<tr>
<td><img src="image" alt="Bulk oxide formation" /></td>
<td><img src="image" alt="Surface oxide formation" /></td>
<td><img src="image" alt="O binding strength" /></td>
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<tr>
<td>Bulk PdO is highly favored</td>
<td>Surface oxidation is highly favored on Pd(111)</td>
<td>Pd(111) &gt;&gt; Pt(111) O binding may not be a descriptor</td>
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<th>(d) Bulk sulfates</th>
<th>(e) SO$_3$ on surf. oxide</th>
<th>(f) Clean surf. energy</th>
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<tr>
<td><img src="image" alt="Bulk sulfate formation phase boundary" /></td>
<td><img src="image" alt="SO$_3$ binding strength" /></td>
<td><img src="image" alt="Surface energy" /></td>
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<tr>
<td>Bulk PdSO$_4$ is highly favored; however, PtSO$_4$ formation may not be seen in typical T and P conditions</td>
<td>Pd(111) &gt;&gt; Pt(111) SO$_3$ binds more strongly to Pd</td>
<td>Pt(111) &gt; Pd(111) Pt is prone to sintering</td>
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Fig. 7.7 Key descriptors for metal oxidation and sulfation. Panel a: $\Delta \mu_{O_2}$ onset point for bulk oxide formation, panel b: $\Delta \mu_{O_2}$ onset point for surface oxide formation, panel c: oxygen binding energy on the pristine (111) surfaces, panel d: bulk sulfate phase boundary onset point on $\Delta \mu_{O_2}$ and $\Delta \mu_{SO_3}$ scales, panel e: SO$_3$ binding strength on the surface oxides, and panel f: surface energy of pristine (111) surfaces. Significant differences are seen between Pt and Pd for all features, except in case of panel c (O binding energy).
energy of Pd compared to Pt is associated with the higher stability against sintering. This explains, along with the cost factor, why modern DOCs are bimetallic (Pt/Pd) in nature. Except for oxygen binding, all other key features can serve as descriptors for catalyst sulfation and the resulting deactivation, and hence we believe that they can be utilized for faster and effective screening of the potential sulfur resistant catalysts.

### 7.7 Limitations and Assumptions

We note that a few assumptions have been made in our work. First, our choice of surface plane is the (111) facet of Pt and Pd. Even though the catalyst nanoparticles contain many types of facets due to polycrystalline nature, the (111) facet is known to be the dominant, most stable and one of the most active surfaces. [314, 315] Second, we do not consider metal-support interactions in this study. The support can have a significant influence in some catalytic systems; however the Al₂O₃ support, typically used in emissions oxidation catalysts, is relatively inert. [264] Hence, we do not expect the support to impact or alter the main conclusions of this work. Third, we have constructed the surface sulfate model by placing bulk sulfate on the metal surface. Nevertheless, we believe our model captures the essence of a surface sulfate phase. Fourth, accuracy of the results presented here will depend on the choice of functional. However, given the number of cases considered and the sizes of systems for each case, considering nonlocal exchange-correlation functionals (e.g., hybrid functionals) would be computational cost prohibitive. Furthermore, we found that the PBE functional is also adequate to address the structure of van der Waals bonded PtO₂ layers. We calculated the energetics of the PtO₂-Pt(111) system with van der Waals interactions using the DFT-D2 functional. [316] The difference in total energy was < 2.2 meV/atom when van der Waals interactions were included. Thus, only the PBE functional was used throughout, and all conclusions were consistently reached using
this functional. It is expected that the qualitative aspects of our results and our main conclusions will not be impacted by the usage of a higher level functional. Finally, we have only considered the thermodynamic aspects in this study. While kinetics also plays an important role during phase transformations, the stability and possibility of the formation of such phases is controlled by thermodynamics, and should be considered first, before kinetic aspects are explored.

7.8 Conclusions

In summary, we have investigated the bulk and surface sulfation phenomena of Pt and Pd under catalytically relevant temperature and pressure conditions using first principles thermodynamics. Bulk and surface phase diagrams were constructed and possible stable phases en route to sulfation were identified. The bulk phase diagrams clearly suggested that the oxidation and sulfation of Pd is highly favored whereas metallic form of Pt is favored under catalytically relevant conditions. The surface phase diagrams clearly showed some remarkable differences between Pt (111) and Pd(111) surfaces in oxidizing and sulfating environments. Our results showed that the oxidized metal surfaces (i.e., surface oxides) are the key to understand sulfation. Pd showed a great affinity to form the surface oxide phase and showed significant $\text{SO}_3$-to-surface oxide binding strength. On the other hand, surface oxide layer formation is relatively less favored and $\text{SO}_3$-to-surface oxide binding strength was significantly smaller for Pt. Furthermore, the surface sulfate phase formation was favored only on Pd(111) in catalytically relevant conditions. The aforementioned key features can be used to screen materials to identify potential candidates for sulfur resistant catalysts.
Chapter 8

Conclusions and Future Work

8.1 Summary

Despite the widespread use and importance of diesel engines, toxic emissions from the diesel engine exhaust create a huge challenge for human health and environment. Some of the important emissions present in the diesel engine exhaust are CO, NO, CO₂, NO₂, SO₂, NH₃, HCN, CH₂O, CH₃CHO, PAHs, SOF, and PM. Many aftertreatment units, such as DOC, DPF, and DeNOₓ systems, are being used to control these emissions. Due to increasing stringent regulations to control emissions, the aftertreatment units need to be robust and efficient.

DOC is mainly responsible for oxidation of emissions from the engine as well as toxic byproducts. However, the deactivation of DOC due to sulfur present in the diesel fuel and lubricants creates a tremendous challenge, as DOC is a very expensive unit. Sulfur present in the fuel and lubricants is converted to SO₂ in the diesel engine. This SO₂ is converted to SO₃ due to high oxygen concentration in the engine exhaust. Formation of SO₃ triggers many interactions with metal oxides and supports which leads to the formation of sulfates and subsequent deactivation of the DOC. In addition to the metal and support sulfation, the
presence of H\textsubscript{2}O and NH\textsubscript{3} also leads to the production of sulfuric acid and ammonium sulfate, respectively, to hasten the DOC deactivation.

This work mainly focuses on developing a fundamental understanding of the emissions oxidation chemistry and sulfation mechanism. To achieve the main goal, multidimensional and multi-scale approaches have been employed using various research techniques including experimental, microkinetic modeling and the first principles density functional theory methods.

To understand the primary oxidation chemistry on DOC, a detailed 124-step (62 reversible) microkinetic model is developed for five major emission species (i.e. CO, NO, NH\textsubscript{3}, CH\textsubscript{2}O, and HCN). Kinetic parameters for the detailed microkinetic model are extracted from ultra-high vacuum (UHV) temperature programmed desorption/reaction (TPD/TPR) experiments in literature. Starting with these kinetic parameters as initial estimates, the surface reaction mechanism is extensively tested against practically more relevant operating conditions, such as atmospheric pressure, dilute emissions concentrations, and short residence times, typically experienced by the Diesel Oxidation Catalysts (DOCs). In each of the five oxidation cases, mechanistic analysis is presented to uncover the most important reaction chemistry. The microkinetic model shows very good agreement with multiple experimental data sets on monolith and fixed bed reactor scale, for the oxidation of all five components. For practical implementation, the mechanism is further reduced to 94 steps (47 reversible) using preliminary model reduction.

Next, the model is extended to study SO\textsubscript{2} oxidation on Pt DOC. The developed mechanism correctly captures experimental data for SO\textsubscript{2} oxidation relevant to DOC operating conditions. This is the first step towards understanding SO\textsubscript{x} interactions with Pt-Pd/alumina DOCs. This work has been extended further to include more complex chemistry of H\textsubscript{2}SO\textsubscript{4} formation in the presence of H\textsubscript{2}O and SO\textsubscript{x} species.

Given the complexity of the SO\textsubscript{x} chemistry with the Pt/Pd catalysts, a DFT based investigation is performed to understand how exactly these SO\textsubscript{x} species interact with metal surfaces.
While Pt is more active in SO$_2$ oxidation than Pd; and no sulfate formation is observed on Pt. Unlike Pt, Pd metal remains in oxidized form (PdO) in the presence of oxygen and forms sulfate on the surface. This work tries to unravel these mysteries about vastly different behaviors of Pt and Pd towards SO$_x$ and sulfation. First, thermodynamic study is performed to understand the binding patterns, binding strengths, and lateral interactions. Then SO$_x$ oxidation minimum energy pathways are identified and the activation barriers are calculated. Here, we are able to show the different behaviors from Pt and Pd towards SO$_x$.

To understand the sulfation phenomena in realistic situation, temperature and pressure factors need to be considered. Thus, going beyond the traditional zero temperature and pressure DFT computations, this work introduced the first principles thermodynamics approach to mimic the oxidization and sulfation environment for Pt and Pd surfaces. For the first time, the possible sulfation mechanism is discovered which showed drastically different behavior on Pt and Pd. In practically relevant temperatures and O$_2$ and SO$_3$ partial pressures, our results show that Pt and Pd show significantly different behavior towards oxidation and sulfation. PdO formation is favored even at low oxygen chemical potential; however, PtO$_2$ formation is not favorable in catalytically relevant conditions. Similarly, PdSO$_4$, and adsorbed SO$_3$ and oxygen species on clean and oxidized surfaces are highly favored, whereas PtSO$_4$ formation does not occur at typical temperature and pressure conditions. Finally, several descriptors are identified that correlate to heightened sulfation tendencies, such as the critical O chemical potential for bulk oxide and surface oxide formation, chemical potentials O and SO$_3$ for bulk sulfate formation, and SO$_3$ binding strength on metal surface-oxide layers, which can be used to explore promising sulfur resistant catalysts.
8.2 Future Directions

8.2.1 Microkinetic Model Extension

Higher number nitrogen and carbon containing emissions species like acetonitrile and the oxygenates like acetaldehyde can be the immediate extension of our model. While this work lays the foundation of the reactions and mechanism for the mono carbon and nitrogen containing species, the inclusion of those higher C and N containing species should be straightforward using bottom up modeling strategy.

Another aspect of the thesis is to lay out the foundation to include the Hydrocarbons oxidation mechanism on the DOCs. Although this work only involves in the oxidation of $C_2$ HC species ($C_2H_4$), many different HCs exist in diesel exhaust, including aromatics, saturated (paraffin), and unsaturated (olefin) components. Generally, ethylene, propylene, ethane and propane are used to model unsaturated HCs and saturated HCs, respectively. Different HCs and mixtures of HCs show different rates of reaction. For example, alkanes tend to show slower reaction rates as the carbon chain length increases because more adjacent sites are required to achieve adsorption of the hydrocarbon chains. While monometallic Pt catalysts have the most efficient light-off performance for hydrocarbons, one can plan to investigate $C_3$ HC oxidation on Pt to understand the fundamental chemistry on Pt based DOCs and extend the $C_2$ oxidation chemistry. Further, this mechanism can be expanded easily to include higher hydrocarbon species by utilizing bottom-up mechanism development technique. [317]

8.2.1.1 Support Sulfation

The diffusion of $SO_3$ species into the bulk alumina initiates the support sulfation process. This process is accelerated due the oxidizing environment in the engine exhaust. Kinetics of alumina support sulfation needs be included in the emissions-oxidation model to correctly simulate
DOC deactivation. In this future work, one can investigate the alumina sulfation mechanism and kinetics using DFT. Furthermore, one can conduct Nudged Elastic Band (NEB) calculations using VASP to estimate the activation energy for alumina sulfation. Pre-exponential factor for alumina sulfation can be estimated using vibrational frequency calculations combined with transition state theory (TST). These first-principles DFT calculations involving SO$_3$, alumina support and aluminum sulfate will provide the theoretical estimates for the kinetic rate constant for alumina support sulfation. Reactor modeling with the support sulfation mechanism will provide more realistic estimation of the DOC sulfation process.

8.2.1.2 Reactor Modeling with Sulfation Kinetics

Predicting DOC performance over time will require a kinetic and reactor modeling framework to incorporate the extent of metal and support sulfation coupled with the emissions-oxidation kinetics. After combining the emissions-oxidation model with the kinetic parameters for catalyst sulfation, one can proceed with PFR modeling to predict the DOC activity/performance over time. Incorporation of catalyst sulfation in reactor modeling is a challenging task, as the extent of metal and support sulfation needs to be coupled with the emissions-oxidation kinetics. We can utilize two prior experimental observations to overcome this challenge: (i) deactivation of metal oxide results in inactive metal sulfate sites and (ii) alumina sulfation results in decreased surface area. Consistent with the first observation, one can propose to implement two types of sites: sulfated inactive sites and non-sulfated active sites. As the extent of metal sulfation increases, the sulfated inactive sites increase relative to the non-sulfated active sites; however, the total site density is conserved. Consistent with the second observation, the overall surface area available for emissions-oxidation chemistry decreases, as the extent of alumina support sulfation increases.
8.2 Future Directions

8.2.2 Emissions Oxidation and Sulfation on Bimetallic Pt-Pd Catalysts

The next level of this work may be the exploration of bimetallic nature of the catalysts in DOCs. This can be proceeded with the identification of the stable bimetallic composition under realistic conditions. The first step would be the structure prediction of bimetallic Pt-Pd alloy using USPEX. Then, the stability of the bimetallic catalysts under various condition can be studied using the first principles thermodynamics. Once, thermodynamic stability of the phases are established, the kinetics investigation can be done.
References


[75] ENVIRONMENTAL PROTECTION AGENCY, Environmental protection agency: Technical amendments to the highway and nonroad diesel regulations, Federal Register Volume 71, Number 83 (Monday, May 1, 2006), 2006.


References


References


Appendix A

Experimental Study of Carbon Black and Diesel Engine Soot Oxidation Kinetics Using Thermogravimetric Analysis
Experimental Study of Carbon Black and Diesel Engine Soot Oxidation Kinetics Using Thermogravimetric Analysis

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ABSTRACT: Non-catalytic oxidation kinetics of diesel engine soot and more than a dozen commercial carbon black samples was investigated using non-isothermal and isothermal thermogravimetric analysis (TGA) experiments. The effect of various operating parameters, such as oxygen flow rate, initial sample mass, oxygen partial pressure, crucible type, and ramp rate, on the oxidation rate was investigated. Three types of TGA experiments (non-isothermal single-ramp rate, non-isothermal multiple-ramp rates, and isothermal) were conducted and analyzed to extract the kinetic parameters for oxidation. Activation energies for oxidation of carbon black samples ranged from 125 to 257 kJ/mol, whereas that for soot oxidation was ∼155 kJ/mol. Furthermore, oxidation rate trends were explained on the basis of structural characteristics, such as scanning electron microscopy (SEM)-based average particle size and Brunauer–Emmett–Teller (BET) surface area. In general, a low particle size and high surface area were associated with a higher oxidation rate and vice versa. A thorough understanding of the non-catalytic oxidation kinetics developed in this work along with the correlation of the oxidation rate with the structural parameters may assist in efficient oxidation of diesel engine soot during the regeneration of diesel particulate filters.

1. INTRODUCTION

More than 13 million diesel vehicles are responsible for transportation of 94% of the goods in the U.S. and use ∼4 million barrels of diesel per day.1–3 In the European market, 53% of the passenger cars run on diesel.4 Diesel engines are the workhorses for industrial, commercial, and personal transportation and also play a vital role in power generation, because of the highly efficient combustion, excellent fuel economy, torque, durability, reliability, and low operating costs.5–7 However, emissions from diesel engines contain fine particles produced during high-temperature pyrolysis or combustion. Diesel particulate matter (PM), also known as soot, is primarily composed of carbon along with some organic compounds, inorganic compounds (ash), sulfur compounds, and traces of metals from unburnt fuel and lubricating oil. PM formation is a complex phenomenon, which depends upon the engine operating conditions, fuel type, and lubricating oil, resulting in a wide range of particle sizes and chemical compositions.8–17 PM emissions are responsible for various human health and environmental problems, such as asthma, bronchitis, lung cancer, air pollution, and global warming.5,12,13 Diesel particulate filter (DPF) is the most popular aftertreatment technology to meet the stringent PM emission standards.14,15 DPFs need to be periodically regenerated through oxidation of soot; otherwise, the accumulated soot can cause backpressure, resulting in decreased fuel economy and possible engine and/or filter failure.16,17 Given the complexity and variability in the soot structure as well as the need for periodic DPF regeneration, there is an urgent need to develop a comprehensive understanding for the kinetics of soot oxidation.

This work focused on developing such an understanding through a comprehensive investigation of 15 carbonaceous samples (diesel engine soot provided by Corning, 13 commercial carbon black samples, and graphite). The effect of various parameters, such as the oxidizer flow rate, initial sample mass, partial pressure of oxygen, crucible type, and ramp rate, was studied using temperature-programmed oxidation (TPO) thermogravimetric experiments. The paper is organized as follows. First, experimental details are provided in section 2, followed by a description of the data analysis methods in section 3. In section 4, we discuss the effect of various operating conditions in non-isothermal experiments, followed by kinetic parameter extraction. The results are compared to isothermal experiments presented in section 5. Summary and concluding remarks are presented in the end.

2. EXPERIMENTAL SECTION

2.1. Materials. A total of 15 different samples studied included a diesel engine soot sample provided by Corning, 13 commercial carbon black samples obtained from various manufacturers, and a graphitic carbon sample. The samples were as follows: (1) diesel soot (Corning), (2) graphite (Fisher Scientific), (3) Mogul-E (Cabot), (4) Monarch 1300 (Cabot), (5) Monarch 1400 (Cabot), (6) Monarch 280 (Cabot),...
isothermal steps. Instrumental specifications and experimental protocols are given in Table 1.

Table 1. Details of the TGA Instrument and Experimental Protocols

<table>
<thead>
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<td>special heating mode</td>
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Experimental Protocol for Non-isothermal Tests

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<th>description</th>
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<tr>
<td>2</td>
<td>ramp to 800 °C with ramp rate β = 5–20 °C/min</td>
</tr>
<tr>
<td>3</td>
<td>hold at 800 °C for 15 min</td>
</tr>
<tr>
<td>4</td>
<td>cool to room temperature</td>
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</tbody>
</table>

Experimental Protocol for Isothermal Tests

<table>
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<tr>
<th>step</th>
<th>description</th>
</tr>
</thead>
<tbody>
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<td>1</td>
<td>flow of nitrogen (balance and purge gases)</td>
</tr>
<tr>
<td>2</td>
<td>ramp to T_nonisothermal with β = 20 °C/min</td>
</tr>
<tr>
<td>3</td>
<td>flow of oxidant gas with nitrogen</td>
</tr>
<tr>
<td>4</td>
<td>hold at T_nonisothermal for 120 min</td>
</tr>
<tr>
<td>5</td>
<td>cool to room temperature</td>
</tr>
</tbody>
</table>

In all of the experiments, the oxidizer gas (UHP air or 10% O₂ in Ar from Airgas) flow rate was 60 mL/min and N₂ was used as a purge gas with a flow rate of 40 mL/min. The initial mass of the carbon black samples was ~10–12 mg. However, because of the low density of diesel soot, an initial mass of only ~2.5 mg was used. For the non-isothermal experiments, the samples were heated in a platinum (Pt) crucible (the Pt crucible was inert, as discussed later in section 2.3.4) from room temperature to 800 °C at a chosen ramp rate (5–20 °C/min), followed by a 15 min hold at 800 °C, and then cooling back to room temperature. For the isothermal experiments, first, the samples were heated to the desired temperature with a ramp rate of 20 °C/min, and then, the samples were kept at the isothermal point for 2 h under oxidizing environment, followed by cooling back to room temperature. Non-isothermal tests are typically preferred over isothermal tests for two reasons: (i) an isothermal test always consists of a finite non-isothermal heating time, as a result of which strictly isothermal tests are not possible, and (ii) multiple experiments are required for extraction of kinetic parameters from isothermal tests. On the other hand, isothermal tests provide information about the characteristic profile of the reaction and, hence, provide an idea about the appropriate kinetic model. In this work, we conducted isothermal tests for selected samples to extract the kinetic parameters and to validate the parameters obtained from the non-isothermal experiments. Finally, the oxidation rate is defined on the basis of the temperature required for a certain level of fractional conversion. For example, T₁₀, T₅₀, and T₉₀ represent the temperatures required to achieve 10, 50, and 90% mass loss, respectively. T₉₀ is also referred to as the light-off temperature.

2.3. Factors Affecting TGA Experiments. 2.3.1. Oxygen Flow Rate. The overall efficiency of the gas–solid reactions can be greatly affected by the gas flow rate and, hence, mass-transfer limitations or limiting reactants. For the oxidation of carbon black or soot, the availability of oxygen is critical; otherwise, the observed oxidation efficiency may be lower because of the lack of sufficient oxygen. This is particularly important at high temperatures, where the soot oxidation rate is high and the lack of oxygen can limit the overall soot oxidation rate. To ensure that the TGA experiments reported here were not affected by such limitations because of insufficient availability of oxygen in the oxidizer gas, we conducted a series of experiments with various oxidizer gas flow rates while maintaining other parameters the same. Figure 1 shows the mass loss profile of Printex-U for various levels of air flow rates (20–80 mL/min). The oxidation rate at a gas flow rate of 20 mL/min was lower than that at a gas flow rate of 40 mL/min or higher, but the rate stayed constant for gas flow rates of 40 mL/min and higher. Therefore, the oxidizer gas flow rate must be at least 40 mL/min to avoid the scenario in which oxygen becomes the limiting reactant. On the basis of these experiments, we used an oxidizer gas flow rate of 60 mL/min in all of the TGA experiments reported in this paper.
panel d, 4−19 mg). We observed that large initial masses were affected by diffusional limitations, as evident from the delayed oxidation rate. On the basis of these experiments, we selected moderate initial masses of 10−12 mg for each sample, except for diesel soot (∼2.5 mg), which had a much lower density.

2.3.3. Ramp Rate. The effect of the ramp rate on gas−solid reactions is well-documented in the literature.20−34 High ramp rates are typically associated with heat- and mass-transfer limitations.33 On the other hand, experiments conducted with low ramp rates are not influenced by such limitations.35 Our results in Figure 2 for different initial masses and ramp rates showed delayed oxidation rates in the case of large initial masses and high ramp rates as a result of their combined effect (e.g., Figure 2d). However, in general, the effect of the initial mass was negligible in the considered initial mass range, with a ramp rate of 5−15 °C/min. On the basis of these experiments, we have chosen a low ramp rate of 5 °C/min for most of the experiments.

2.3.4. Crucible. The crucible shape in the TGA experiments can significantly influence the oxidation kinetics because of mass-transfer limitations.20,23,26,27,36 A large crucible height can lead to a large stagnant volume (space available in the crucible above the sample) and, hence, diffusion limitations.20,23,26,27,36 Therefore, short and wide crucibles are typically recommended for such studies.23,37 In this work, we used short and wide crucibles (D = 10 mm, h = 2 mm, and h/D = 0.2, with actual sample h/D < 0.2) to avoid such limitations. Furthermore, to ensure that the Pt crucible is inert in the oxidation experiments, we conducted additional experiments with an alumina crucible in identical operating conditions. As shown in Figure 3, results with both crucibles were almost identical for two samples (panel a, Printex-XE2B; panel b, Printex-U); hence, the Pt crucible could be considered as inert in the subsequent experiments.

2.3.5. Diffusion Limitations. Diffusion limitations in soot oxidation kinetics during TGA experiments have been discussed in the literature,20,23−25,27,30,36−43 and such limitations can impact kinetic parameter estimation.24,27,36,40,43 As discussed earlier, diffusion limitations can be avoided or minimized by selecting an appropriate initial sample mass, ramp rate, crucible shape, sample packing, bed height, and stagnation volume.23,24,27,36,44 Internal mass-transfer limitations could also be important and could differ for each sample because of different pore sizes. Such limitations have been estimated in the literature using the effectiveness factor and Thiele modulus,40,45,46 however, they were not considered in the scope of our work presented here.

2.4. Experimental Reproducibility. Prior to discussing the results and data analysis from the TGA experiments for multiple samples and various operating conditions, it was important to ensure that the experiments had good reproducibility. Figure 4 shows an example of the experimental reproducibility over three runs for the oxidation of diesel soot (panel a) and Printex-XE2B (panel b). As observed from the overlapping profiles, the TGA experiments were highly reproducible.

3. DATA ANALYSIS FOR KINETIC PARAMETER EXTRACTION

Three methods were used for the TGA data analysis: (a) non-isothermal single-ramp rate, (b) non-isothermal multiple-ramp rates, and (c) isothermal. A majority of the results presented in this work are focused around the non-isothermal single-ramp rate method, whereas the other two methods are demonstrated for additional validation or comparison. Next, we discuss the details of the data analysis for the three methods.
3.1. Method A: Non-isothermal Single-Ramp Rate Method. Estimation of kinetic parameters from TGA data can be performed using various approaches, as recommended by the Kinetics Committee of the International Confederation for Thermal Analysis and Calorimetry (ICTAC).18 However, the most widely used approach for kinetic parameter estimation from soot or carbon black oxidation is based on the Arrhenius equation format:20,47,48

\[
\frac{dm}{dt} = km^ap_{O_2}^r = A \exp\left(-\frac{E_a}{RT}\right)m^aP_{O_2}^r
\]

where \(m\) is the instantaneous sample mass at time \(t\), \(k\) is the reaction rate constant, \(A\) is the pre-exponential factor, \(E_a\) is the activation energy, \(T\) is the operating temperature, \(P_{O_2}\) is the partial pressure of oxygen, and \(n\) and \(r\) are the reaction orders for carbon and oxygen, respectively. It is known that the surface area of the carbonaceous samples increases during oxidation. However, any change in the surface area and pore size effects is not accounted for in the simplified kinetic expression. Furthermore, most literature studies for carbon black or soot oxidation show reaction orders close to unity.20,25,39,40 (see section 5 for the validity of this assumption). In that case, the above equation can be rearranged as

\[
\ln\left(\frac{dm}{mdt}\right) = \ln(Ap_{O_2}) - \frac{E_a}{RT}
\]

where \(E_a\) and \(A\) can be estimated from the slope and intercept of a \(\ln(-dm/mdt)\) against \(1/T\) plot. In this method, TGA data at a single-ramp rate are sufficient for the analysis and kinetic parameter extraction.

3.2. Method B: Non-isothermal Multiple-Ramp Rate Method. To delineate the effect of the ramp rate from the kinetic parameters, they can also be estimated using a fractional conversion \(\alpha\) [where \(\alpha = 1 - (m/m_0)\)] in the non-isothermal experiments conducted at different ramp rates \(\beta\). This analysis is based on the Flynn–Wall–Ozawa method49–52 and Doyle’s approximation.53,54 Equation 1 can be written in terms of fractional conversion \(\alpha\) as

\[
\frac{da}{d\beta} = -\frac{1}{m_0} \frac{dm}{dt}
\]

\[
= A \exp\left(-\frac{E_a}{RT}\right)m_0P_{O_2}
\]

\[
= A \exp\left(-\frac{E_a}{RT}\right)(1 - \alpha)P_{O_2}
\]

With a linear ramp rate \(\beta = d\beta/dt\), eq 3 can be written as

\[
\frac{da}{d\beta} = \frac{A}{\beta} \exp\left(-\frac{E_a}{RT}\right)(1 - \alpha)P_{O_2}
\]

Integrating this equation from a very low temperature (zero conversion) to the final temperature \(T_f\) corresponding to a final degree of conversion \(\alpha\), and using \(x = E_a/RT\) gives

\[
-ln(1 - \alpha) = \frac{Ap_{O_2}E_a}{\beta R} \int_0^{\alpha} x^{1-x}dx = \frac{Ap_{O_2}E_a}{\beta R} I(x)
\]
The integral $I(x)$ is approximated as 28,51

$$\log I(x) \approx -2.315 - 0.457x$$

(6)

When eqs 5 and 6 are combined and rearranged, we obtain

$$\log \beta = \log \left( \frac{AP_{O_2} E_a/R}{-\ln(1-\alpha)} \right) - 2.315 - 0.457 \times \frac{E_a}{RT}$$

(7)

The activation energy $E_a$ for different conversion values $\alpha$ can be calculated from the slope of a log $\beta$ versus $1/T$ plot.

### 3.3. Method C: Isothermal Method

Isothermal tests provide another way of studying the kinetics of gas–solid reactions occurring in carbon black or soot oxidation.12,23,30,55–57

Starting from eq 1, under isothermal conditions, one can write

$$\ln(1-\alpha) = \ln\left(\frac{m}{m_0}\right) = \int_{m_0}^{m} \frac{dn}{m} = \int_{0}^{t} -A \exp\left(-\frac{E_a}{RT}\right) dp_{O_2} dt = -A \exp\left(-\frac{E_a}{RT}\right)p_{O_2} t$$

(8)

When eq 8 is rearranged, we obtain

$$-\ln t = \ln\left(\frac{AP_{O_2}}{-\ln(1-\alpha)}\right) - \frac{E_a}{RT}$$

(9)

A plot of $-\ln t$ versus $1/T$ at a chosen value of $\alpha$ gives the activation energy $E_a$ from the slope and pre-exponential factor $A$ from the intercept.28

Given the assumptions associated with eqs 1 and 2, the kinetic parameters (activation energies and pre-exponential factors) estimated using the aforementioned methods should be treated as apparent parameters only.

### 4. OXIDATION KINETICS USING NON-ISOTHERMAL EXPERIMENTS

#### 4.1. Effect of the Oxygen Partial Pressure

Soot could be oxidized using the oxygen present in the diesel engine exhaust (5–15% oxygen18,59) or using air. Although the oxygen content in air is higher than that in the typical diesel engine exhaust, literature studies have commonly used air to test the oxidation of soot samples.20,55,60

Therefore, we conducted the TGA experiments with both oxidizers: (i) 10% $O_2$ in Ar and (ii) air. Experimental protocol details are provided in Table 1.

Mass loss profiles for all 15 samples with these two oxidizers are shown in Figures 5 and 6, respectively, with a constant ramp rate of $5 \, ^\circ C/min$. The diesel soot sample in this study was collected under real diesel engine exhaust conditions [engine type, light duty; engine swept volume, 2 L; revolutions per minute (rpm), 3250 min$^{-1}$; torque, 50 N m; power, 17 kW; and exhaust gas flow rate, 253 kg/h]. It contained metal oxides and ash particles, which were not burnt off during the oxidation experiments. A very small amount of ash particles was observed in the crucible after the diesel soot experiments, which was not the case with other carbon black samples. Therefore, the diesel soot conversion was not 100%, even at high temperatures, as observed in Figures 5 and 6. The negligible deviation from 100% conversion for other samples and the slight increase in diesel soot mass with the temperature (at high temperatures) could be associated with experimental uncertainty in measuring very small quantities.

Details of $T_{10^f}, T_{90^f}$, and $T_{90}$ are reported in Table 2. The $T_{50}$ values for the most commonly studied samples, such as Printex-U and VulcanXC72R, were in close agreement with the literature data (e.g., reported $T_{50}$ of Printex-U = 606 $^\circ C$ and $T_{50}$ of VulcanXC72R = 683 $^\circ C$ by Atrimak et al.61 and reported $T_{50}$ of Printex-U = 607 $^\circ C$ and $T_{50}$ of VulcanXC72R = 667 $^\circ C$ by Hinot62). In general, there were three major groups in the considered samples: (i) Monarch 1300, Monarch 1400, and Printex-XE2B had low light-off temperatures ($T_{10^f} < 500 \, ^\circ C$) and, hence, the highest oxidation rate; (ii) Printex-G, Monarch 280, VulcanXC72R, and graphite showed high light-off temperatures ($T_{10^f} > 600 \, ^\circ C$) and, hence, the lowest oxidation rate; and (iii) all other samples had a moderate oxidation rate, with a $T_{10^f}$ ranging between 500 and 600 $^\circ C$. The trend was similar for $T_{90}$ and $T_{90}$ (see Table 2). Monarch 1300 and Monarch 1400 contained 7% moisture, as compared to...
negligible moisture (0−0.6%) in the other samples. Therefore, oxidation data for Monarch 1300 and Monarch 1400 are reported with and without considering the moisture content (see Table 2). To calculate the conversion without considering the moisture content, the conversion (∼4−5%) of those two samples just before reaching 200 °C was used to compute the "corrected" initial mass without moisture. As expected, the $T_{10}$ values were significantly affected by the moisture content, but the $T_{50}$ and $T_{90}$ values were not.

Figure 7 compares the $T_{10}$, $T_{50}$, and $T_{90}$ values for all samples with 10% O$_2$ and air. Oxidation is faster with air. The operating conditions are the same as in Figures 5 and 6.

![Figure 7](https://example.com/figure7.png)

**Table 2. Light-Off Temperature Data from Non-isothermal Experiments**

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<th>sample number</th>
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<th>$T_{50}$ (°C)</th>
<th>$T_{90}$ (°C)</th>
<th>$T_{10}$ (°C)</th>
<th>$T_{50}$ (°C)</th>
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$^a$Data without moisture (see the text for details).

![Figure 8](https://example.com/figure8.png)

**Figure 8.** (a) Mass loss profiles and (b) Arrhenius plots for diesel soot and Printex-U samples using method A. The operating conditions are the same as in Figure 5.
Table 3. Apparent Kinetic Parameters from Non-isothermal and Isothermal Experiments

| Sample number | Samples | \(E\) (kJ/mol) | \(k_{300}\) (Pa\(^{-1}\) s\(^{-1}\)) | \(k_{900}\) (Pa\(^{-1}\) s\(^{-1}\)) | \(k_{1200}\) (Pa\(^{-1}\) s\(^{-1}\)) | \(A\) (Pa\(^{-1}\) s\(^{-1}\)) | \(R^2\) range | \(E\) (kJ/mol) | \(k_{300}\) (Pa\(^{-1}\) s\(^{-1}\)) | \(k_{900}\) (Pa\(^{-1}\) s\(^{-1}\)) | \(k_{1200}\) (Pa\(^{-1}\) s\(^{-1}\)) | \(A\) (Pa\(^{-1}\) s\(^{-1}\)) | \(R^2\) range |
|---------------|---------|---------------|-----------------|-----------------|-----------------|-----------------|----------------|---------------|-----------------|-----------------|-----------------|-----------------|-----------------|----------------|
| 1             | diesel soot | 1.0 \(\times\) 10\(^3\) – 9.4 \(\times\) 10\(^2\) | 1.1 \(\times\) 10\(^{-8}\) | 8.8 \(\times\) 10\(^{-8}\) | 1.7 \(\times\) 10\(^{-7}\) | 10 – 90 | 0.985 | 152 – 169 | 1.0 \(\times\) 10\(^3\) – 8.5 \(\times\) 10\(^2\) | 1.6 \(\times\) 10\(^{-8}\) | 6.6 \(\times\) 10\(^{-8}\) | 2.3 \(\times\) 10\(^{-7}\) |
| 2             | graphite   | 3.3 \(\times\) 10\(^{-1}\) – 2.6 \(\times\) 10\(^{-1}\) | 2.3 \(\times\) 10\(^{-7}\) | 6.9 \(\times\) 10\(^{-7}\) | 1.8 \(\times\) 10\(^{-6}\) | 20 – 90 | 0.683 | 133 – 155 | 6.2 \(\times\) 10\(^{-1}\) – 1.8 \(\times\) 10\(^{-2}\) | 2.2 \(\times\) 10\(^{-8}\) | 7.9 \(\times\) 10\(^{-8}\) | 2.4 \(\times\) 10\(^{-7}\) |
| 3             | Mogul-E    | 1.1 \(\times\) 10\(^{-3}\) | 1.1 \(\times\) 10\(^{-9}\) | 5.9 \(\times\) 10\(^{-9}\) | 20 – 90 | 0.999 | 189 | 0.816 | 1.6 \(\times\) 10\(^{-3}\) | 1.3 \(\times\) 10\(^{-6}\) | 1.3 \(\times\) 10\(^{-6}\) |
| 4             | Monarch 1300 | 1.9 \(\times\) 10\(^{-2}\) | 4.3 \(\times\) 10\(^{-3}\) | 9.6 \(\times\) 10\(^{-3}\) | 1.5 \(\times\) 10\(^{-3}\) | 40 – 90 | 1.5 \(\times\) 10\(^{-7}\) | 0.945 | 189 | 0.816 | 1.6 \(\times\) 10\(^{-3}\) | 5.8 \(\times\) 10\(^{-3}\) | 1.3 \(\times\) 10\(^{-6}\) |

\(^a\)The kinetic parameters correspond to method A with ramp rate \(\beta = 5 \degree C/min\), unless specified otherwise. Method A was applied for different ramp rates \((\beta = 5 – 20 \degree C/min)\). For the given range, the first value is for 20 \degree C/min experiments and the second value is for 5 \degree C/min experiments. Method B: non-isothermal experiments with multiple-ramp rates. Activation energies and pre-exponential factors are given for the fractional conversion \(\alpha\) range of 0.1 – 0.9, whereas the rate constants \(k\) are reported for \(\alpha\) of 0.5. Method C: isothermal experiments. Activation energies and pre-exponential factors are given for the fractional conversion \(\alpha\) range of 0.2 – 0.9, whereas the rate constants \(k\) are reported for \(\alpha\) of 0.5. Without moisture (see the text for details).
Therefore, the oxidation of carbon black and soot samples with air was faster than with 10% O2. Because the oxidation profiles in Figures 5 and 6 showed similar trends for both cases, the decrease in $T_{10-90}$ values for air was due to the higher concentration of O2 in air (21%).

Method A discussed in section 3.1 was used to extract the apparent activation energies and pre-exponential factors. Figure 8 shows an example of data analysis for diesel soot and Printex-U. First, data in panel a confirmed that the oxidation behavior of diesel soot and Printex-U was quite similar, which explains why Printex-U is commonly used as a surrogate for diesel soot.30,40,42,59,63–65 Second, we used a much wider range of conversion profile (from 10 to ~90%) for data analysis in panel b compared to the literature studies,42,66 which ensured the validity of the estimated kinetic parameters over almost the complete oxidation process. Third, as shown in panel b, the ln(−dm/dt) versus 1/T plots for diesel soot and Printex-U are almost straight lines with $R^2 > 0.99$, which agrees with the assumption of first-order kinetics. A similar analysis was conducted for all samples for both oxidizer gases (10% O2 and air), and the kinetic parameters (along with the considered conversion ranges and $R^2$ values) are reported in Table 3. Oxidation reaction rate constants at different temperatures ($k_{300}$, $k_{500}$, and $k_{600}$) are also given in Table 3 for both cases (10% O2 and air), which indicated that oxidation with air was faster than with 10% O2.

In general, the range of activation energies reported in the literature for the oxidation of carbon black and soot samples is 100–300 kJ/mol.21,30,34,40,42,43,47,60,64,66–69 However, the typically reported activation energies for diesel engine soot oxidation are in the range of 120–180 kJ/mol.30,59,80,68,70–72 Neet et al.59 suggested that the activation energy increased in the following sequence: soot < activated carbon < carbon and chars < graphite, which was also observed in our experiments, with graphite showing the largest activation energy and the smallest rate constant. Given the comprehensive nature of our study, literature data were not available for direct comparisons for all of the samples studied; however, the activation energies estimated from our TGA experiments were in close agreement with those reported in the literature. For example, the activation energy for diesel soot oxidation with oxygen was reported to be 164 kJ/mol by Higgins et al.60 and Darcy et al.,68 and 177 kJ/mol by Lee et al.,60 which compare well to our estimate of 172 kJ/mol. Similarly, the activation energy for Printex-U oxidation was reported to be 168 kJ/mol by Neet et al.59 and 161 kJ/mol by Tang et al.42 with 10% O2 and 160 kJ/mol by Hinot62 with 20% O2, which compare well with our estimates of 165 kJ/mol with 10% O2 and 182 kJ/mol with air. Despite the agreement with the literature, it is important to note that the estimated kinetic parameters should ideally not change with the O2 partial pressure. As alluded to earlier, this fundamental limitation most likely stems from the simplified kinetic expressions (eqs 1 and 2), where the change in the surface area during oxidation and the pore size effects were ignored and the reaction order with respect to O2 was assumed to be unity. Therefore, we emphasize that the estimated activation energies (and pre-exponential factors) should be considered as apparent kinetic parameters only.
To understand the variation of the oxidation rate for the different carbon black and soot samples, they were characterized using scanning electron microscopy (SEM) and Brunauer–Emmett–Teller (BET) surface area. SEM analysis indicated that the average particle size (over ~200 particles) varied over a wide range (20.9–74 nm). Similarly, the BET surface area varied over a wide range as well (43–1005 m²/g). The oxidation rate of carbon black and soot samples is a complex function of various structural factors and operating conditions; however, the large variations in average particle size and surface area may be used to explain some of the trends in the oxidation rate. Monarch 1400, Monarch 1300, and Printex-XE2B had the smallest average particle size (20.9–26.7 nm), whereas Printex-G, Monarch 280, and Mogul-E had the largest particle size (69.7–74 nm). Surface areas of Monarch 1400, Monarch 1300, and Printex-XE2B were in the higher range of 342–1005 m²/g, whereas those of Printex-G, Monarch 280, and Mogul-E were in the lower range of 45–49 m²/g. The higher rate of Monarch 1400, Monarch 1300, and Printex-XE2B (T = range of 547–616 °C) could be attributed to the smaller particle size and higher surface area. Similarly, the lower rate of Printex-G, Monarch 280, and Mogul-E (T = range of 630–674 °C) could be attributed to the larger particle size and lower surface area.

4.2. Effect of the Ramp Rate. The ramp rate β is another operating parameter that typically shows a large impact on the oxidation profile. To validate the activation energies estimated in the previous section, we conducted TGA experiments with 10% O₂ and air using four ramp rates (5, 10, 15, and 20 °C/min) for diesel soot and Printex-U samples. Experimental protocol details are provided in Table 1. As shown in Figure 9, the oxidation rate shifted to higher temperatures with an increase in the ramp rate. A higher ramp rate reduces the overall reaction time in an experiment for a given temperature range, and less mass loss occurs at the same temperature point compared to a lower ramp rate case. For example, for heating from 600 to 800 °C, it takes only 10 min with 20 °C/min, whereas it takes 40 min with 5 °C/min. Kalogirou and Samaras suggested that the higher ramp rates could also be associated with diffusional limitations, which are more prominent in the case of low oxygen concentrations. Our experimental results with different ramp rates and oxygen partial pressures were consistent with this observation. For example, when the 10% O₂ versus air profiles in Figure 9 are compared, the delay in the oxidation rate with an increased ramp rate was higher for 10% O₂ compared to that for air. This also justifies the 5 °C/min ramp rate used in section 4.1 (method A) for kinetic parameter estimation. On the other hand, data analysis presented in this section could be affected by diffusional limitations to some extent at higher ramp rates but provide a reasonably good validation of the kinetic parameters.

Results obtained from diesel soot and Printex-U oxidation with 10% O₂ and air for various ramp rates (5–20 °C/min) were analyzed using method B discussed in section 3.2. Figure 10 shows a plot of log β versus 1/T for diesel soot and Printex-U for both 10% O₂ (panel a) and air (panel b) for a selected fractional conversion α of 0.5. The estimated kinetic parameters are reported in Table 3. With 10% O₂, the estimated activation energies for diesel soot and Printex-U oxidation were in the range of 155–198 and 78–142 kJ/mol, respectively (these ranges were based on applying method B at different fractional conversions),

![Figure 11. Flynn–Wall–Ozawa plot for diesel soot (initial mass of 2.5 mg) and Printex U (initial mass of 10 mg) oxidation. (a) Diesel soot with 10% O₂, (b) diesel soot with air, (c) Printex-U with 10% O₂ and (d) Printex-U with air, using method B for a fractional conversion α range of 0.1–0.9. Operating conditions are the same as in Figure 9.](dx.doi.org/10.1021/ef3009025)
which were comparable to the numbers estimated from method A (154–172 and 87–165 kJ/mol, respectively; these ranges were based on applying method A at different ramp rates). Similarly, with air, the estimated activation energies for diesel soot and Printex-U oxidation were in the range of 121–163 and 136–170 kJ/mol, respectively (these ranges were based on applying method B at different fractional conversions), which were also comparable to the numbers estimated from method A (152–169 and 143–182 kJ/mol, respectively; these ranges were based on applying method A at different ramp rates). A larger deviation was observed in the case of 10% O\textsubscript{2} than air, which could be due to the diffusional limitations associated with larger ramp rates and a low oxygen concentration. However, the rate constants calculated using method B at any particular temperature (see \(k\) values in Table 3 for \(\alpha = 0.5\)) showed excellent agreement with the rate constants calculated using method A.

Before moving on to the isothermal experiments in the next section, we note that the kinetic parameters estimated using method B are dependent upon the fractional conversion \(\alpha\). For example, parameter estimation analysis was carried out for a wider range of fractional conversion values (\(\alpha = 0.1–0.9\)), as shown in Figure 11 for diesel soot and Printex-U. The activation energies varied with the fractional conversion (diesel soot, 155–198 kJ/mol for 10% O\textsubscript{2} and 121–163 kJ/mol for air; Printex-U, 78–142 kJ/mol for 10% O\textsubscript{2} and 136–170 kJ/mol for air). Overall, the analysis based on method B provided excellent validation for the kinetic parameters estimated using method A. Nonetheless, we recommend experiments with lower ramp rates to avoid any influence of heat- and mass-transfer limitations.

5. KINETICS FROM ISOTHERMAL TESTS

Apart from the non-isothermal experiments reported thus far, we also conducted isothermal tests for selected samples (diesel soot, Printex-U, Monarch 1300, and VulcanXC72R) to further validate the kinetic parameters. The four samples were selected to cover the range from low to high oxidation rates from the non-isothermal experiments. For each sample, we conducted isothermal experiments at multiple temperature points with the same initial mass. After reaching the set point (isothermal temperature), the sample was kept at the set point for 2 h. Experimental protocol details are provided in Table 1. Method C discussed in section 3.3 was used for the analysis of the isothermal experiments.

Figure 12 shows the mass loss profiles of the four selected samples. Plots of conversion \(\alpha\) versus time \(t\) suggest that the reaction profiles or kinetic curves of diesel soot and commercial carbon black samples are of the decelerating type, in which the rate is maximum at the beginning and decreases continuously with the extent of conversion.\(^{18}\) Reaction order models are generally used for gas–solid reactions of the decelerating type. First-order reaction kinetics was used for the analysis of these data to extract the kinetic parameters, consistent with the methods A and B discussed earlier. The estimated kinetic parameters are reported in Table 3.

In general, the activation energies estimated using method C (isothermal) were slightly lower than those estimated using

![Figure 12](https://example.com/figure12.png)

**Figure 12.** Isothermal conversion profiles of (a) diesel soot (initial mass of 2.5 mg), (b) Printex-U (initial mass of 10 mg), (c) VulcanXC72R (initial mass of 5 mg), and (d) Monarch 1300 (initial mass of 12 mg). Operating conditions: isothermal experiment, 10% O\textsubscript{2} oxidant, flow rate at 60 mL/min, and ramp rate to reach isothermal temperature at 20°C/min.
methods A and B (non-isothermal). Similarly, the pre-exponential factors calculated using method C (isothermal) were lower than those estimated using methods A and B (non-isothermal). On the other hand, the reaction rate constants computed at 550, 600, and 650 °C for α of 0.5 showed good agreement with the corresponding rate constants estimated from the non-isothermal experiments. This indicated that the activation energies estimated using method C could be affected by the compensation effect between activation energies and pre-exponential factors. The compensation effect is a commonly reported phenomenon, in which change in the activation energy is compensated by change in the pre-exponential factor.

Analysis conducted at different fractional conversion values for diesel soot oxidation with 10% O₂ and air is shown in Figure 13a. The activation energy varied with fractional conversion, consistent with literature reports on solid-state reaction kinetics. For example, the estimated activation energy ranged over fractional conversion α of 0.2−0.9 for diesel soot (112−142 kJ/mol for 10% O₂ and 133−155 kJ/mol for air) and Printex-U (107−136 kJ/mol for 10% O₂ and 135−153 kJ/mol for air), and corresponding variation in pre-exponential factors confirmed the existence of the compensation effect. Figure 13b shows the variation in activation energy with the pre-exponential factor. Complex or multiple-step reaction kinetics of soot oxidation was ruled out because of the absence of multiple peaks and/or shoulders in the reaction rate curve.

Despite this limitation, method C (isothermal) provided a reasonably good validation of the kinetic parameters estimated using methods A and B (non-isothermal).

To verify the assumption of first-order kinetics with respect to O₂, we estimated the reaction order (nO₂) based on the isothermal experiments with 10% O₂ and air for the four samples studied here (diesel soot, Printex-U, Monarch 1300, and VulcanXC72R). The estimated nO₂ was 1 for diesel soot, whereas it was close to 1 for the other carbon black samples (0.95 for Printex-U, 0.88 for Monarch 1300, and 0.90 for VulcanXC72R). Finally, to demonstrate the validity of effective models used here, Figure 14 shows how the apparent kinetic parameters extracted at nominal conditions (fractional conversion α = 0.5) along with first-order kinetics with respect to O₂ can adequately capture the entire range of experimental data; i.e., the compensation effect between the apparent activation energy and pre-exponential factors was not critical for the effective models considered here.

6. CONCLUSION

In this work, we conducted non-isothermal and isothermal TGA experiments for more than a dozen carbon black samples and a diesel engine soot sample with 10% O₂ and air to...
investigate the effect of operating conditions on the oxidation rate and to extract the corresponding apparent kinetic parameters. Limitations associated with the availability of oxygen were avoided by conducting experiments in sufficient oxidizer gas flow rate conditions. The partial pressure of oxygen and ramp rates showed significant effects on the oxidation rate. Oxidation with air was faster than with 10% O<sub>2</sub> because of the higher concentration of oxygen in air. The activation energy for the oxidation of carbon black samples ranged from 125 to 257 kJ/mol, whereas that for soot oxidation was ~155 kJ/mol. Oxidation rate trends were explained on the basis of structural characteristics, such as SEM-based average particle size and BET surface area. In general, a small particle size and high surface area were associated with a higher oxidation rate and vice versa. Kinetic parameters extracted using the non-isothermal experiments at a single-ramp rate (method A) were further validated using additional non-isothermal experiments with multiple-ramp rates (method B) and isothermal experiments (method C). The overall agreement for kinetic parameters estimated using the three methods (consisting of separately conducted experiments) was remarkable; however, the analysis in methods B and C indicated that the extracted parameters could be affected by a compensation effect between activation energies and pre-exponential factors as they change with the extent of conversion. Overall, the comprehensive understanding developed in this work for oxidation of carbon black and soot samples could be beneficial for the improved design and optimization of DPF operation and regeneration protocols.

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**Notes**

The authors declare no competing financial interest.

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**REFERENCES**


Appendix B

Functional Dependence of Activation Energies

Fig. B.1 Schematic of a reaction loop with gas phase and surface reactions.
To calculate activation energies using the UBI-QEP method [107], a reaction loop with gas phase and surface reactions is considered here for all reactions. The gas phase bond dissociation energy $D_{gas}$ is calculated from enthalpies of the reactants and the products as,

$$D_{gas} = \sum \text{H}_{\text{products}} - \sum \text{H}_{\text{reactants}}$$ (B.1)

The reaction is written in the endothermic direction (for gas phase), i.e., $D_{gas} \geq 0$. Here, the standard state molar enthalpy is temperature dependent and it is given by,

$$H^o = \int_0^T C_p^o dT$$ (B.2)

The specific heats $C_p$ can be calculated using Eq. C.4 in Appendix C. Alternatively, polynomial form of Eq. C.5 in Appendix A can be used to compute the enthalpy. The polynomial coefficients for each species are used from thermodynamic databases (e.g., GRI-Mech 3.0 thermodynamic database) [109].

For the reaction loop considered, heat of surface reaction can be calculated as,

$$\Delta H_{surf} = D_{gas} + Q_A + Q_B - Q_C - Q_D$$ (B.3)

Here, $Q$ is the binding energy, which is temperature dependent based on the calculations for degrees of freedom lost/gained upon adsorption, as described by Mhadeshwar et al. [101]. $Q$ can also be species coverage dependent, as described in Chapter 2. This makes the heat of surface reaction coverage and temperature dependent.
UBI-QEP formalism is then used to compute the forward ($E_f$) and backward ($E_b$) activation energies for the reactions. Note that activation energies are related to the heat of surface reaction as,

$$\Delta H_{\text{surf}} = E_f - E_b$$  \hspace{1cm} (B.4)

Therefore, the activation energies are coverage and temperature dependent as well. Formulas for the activation energy calculation vary depending on the reaction type [101, 107]. Only the types relevant to our surface reaction mechanism are discussed next.

### B.1 Non-activated Atomic or Non-dissociative Mol. Adsorption

Here, the adsorption is non-activated; hence the forward activation energy is zero. As there is no bond breaking, the gas phase dissociation energy is also zero. Example:

$$\text{CO} + * \leftrightarrow \text{CO}^*,$$  \hspace{1cm} (B.5)

here, $E_f = 0$,

$D_{\text{gas}} = 0$,

$\Delta H_{\text{surf}} = -Q_{\text{CO}}$, and

$$E_b = Q_{\text{CO}}.$$ \hspace{1cm} (B.6)
**B.2 Non-activated Dissociative Adsorption**

Here, the adsorption is non-activated; hence the forward activation energy is zero. However, the bond dissociation energy is non-zero. Example:

\[ \text{O}_2 + 2^* \leftrightarrow 2^O^* , \quad (B.7) \]

Here, \( E_f = 0 \),

\[ \Delta H_{surf} = D_{gas} - 2 Q_O , \quad \text{and} \]

\[ E_b = -\Delta H_{surf}. \quad (B.8) \]

**B.3 Activated Dissociative Adsorption**

Here, the adsorption is activated; hence the forward activation energy is non-zero. Furthermore, the bond dissociation energy is also non-zero. Example:

\[ \text{N}_2 + 2^* \leftrightarrow 2^N^* , \quad (B.9) \]

\[ \Delta H_{surf} = D_{gas} - 2 Q_N , \]

\[ E_f = \omega \left[ \Delta H_{surf} - Q_{N_2} + 0.5 Q_N \right] , \quad \text{and} \]

\[ E_b = E_f - \Delta H_{surf}. \quad (B.10) \]

Here, \( \omega \) is the bond index.
B.4 Surface Dissociation

Here, the surface species undergoes dissociation. Example:

\[
\text{OH} + \ast \leftrightarrow \text{O}^\ast + \text{H}^\ast, \tag{B.11}
\]

\[
\Delta H_{\text{surf}} = D_{\text{gas}} + Q_{\text{OH}} - Q_{\text{O}} - Q_{\text{H}},
\]

\[
E_f = \omega \left[ \Delta H_{\text{surf}} + (Q_{\text{O}} Q_{\text{H}})/(Q_{\text{O}}+Q_{\text{H}}) \right], \text{ and}
\]

\[
E_b = E_f - \Delta H_{\text{surf}}. \tag{B.12}
\]

B.5 Surface Disproportionation

Here, the surface species undergo disproportionation. Example:

\[
\text{CO}_2 + \text{H}^\ast \leftrightarrow \text{CO}^\ast + \text{OH}^\ast, \tag{B.13}
\]

\[
\Delta H_{\text{surf}} = D_{\text{gas}} + Q_{\text{CO}_2} + Q_{\text{H}} - Q_{\text{CO}} - Q_{\text{OH}},
\]

\[
E_f = \omega \left[ \Delta H_{\text{surf}} + (Q_{\text{CO}} Q_{\text{OH}})/(Q_{\text{CO}}+Q_{\text{OH}}) \right], \text{ and}
\]

\[
E_b = E_f - \Delta H_{\text{surf}}. \tag{B.14}
\]

B.6 Temperature Dependence on Binding energy

Next, we discuss the generalized assumptions to calculate the temperature dependence to the binding energy of a molecule due to degrees of freedom lost/gained during adsorption: (a) Each translational, rotational, and vibrational degree of freedom (DOF) corresponds to 0.5R_g T,
0.5R_g T, and R_g T, respectively. (b) Upon adsorption, all translational and rotational DOF are converted into vibrational DOF. For example, in SO_2 and SO_3 molecules, with a vertical axis through the adsorbed atom, one of the gained vibrational DOF is assumed to be a free internal rotor (rigid rotor (RR) approximation) and counts as 0.5R_g T. [317] So, the total change in degrees of freedom (2.5R_g T) of SO_2 and SO_3 for the temperature dependence can be calculated as:

\[-3F_T - 3F_R + F_{RR} + 4F_V\]  \hspace{1cm} (B.15)

Here F_T, F_R, and F_V represent the translational, rotational, and vibrational degrees of freedom. F_{RR} represents that the vibrational DOF is assumed to be a free internal rotor. The "+" and "−" signs indicate gain and loss of DOF, respectively.
Appendix C

Thermodynamic data for cyanogen (C$_2$N$_2$)

HCN oxidation chemistry on Pt contains C$_2$N$_2$ as a recombination product, as reported by Guo et al. [209]. In order to conduct reactor simulations, thermodynamic data of specific heat coefficients are determined here in ChemKin format, based on the thermodynamic data reported on the NIST webbook website. The website reports gas phase heat capacity data using Shomate equation, as given below.

\[
C_p^o = A + Bt + Ct^2 + Dt^3 + \frac{Et}{t^2}
\]  

(C.1)

\[
H^o - H_{298.15}^o = A + B \frac{t^2}{2} + C \frac{t^3}{3} + D \frac{t^4}{4} - \frac{Et}{t} + F - H
\]

(C.2)

\[
S^o = A \ln(t) + Bt + C \frac{t^2}{2} + D \frac{t^3}{3} - \frac{Et}{2t^2} + G
\]

(C.3)

Here, $C_p^o$ is the Heat capacity (J/molK), $H^o$ is the standard enthalpy (kJ/mol), $S^o$ is the standard entropy (J/molK), and $t$ is the normalized temperature (K)/1000. Table C.1 shows the reported thermodynamic coefficients $A$ to $H$. 
Table C.1 Reported coefficients for \( \text{C}_2\text{N}_2 \) thermodynamic data.

<table>
<thead>
<tr>
<th>Temperature [K]</th>
<th>Low-Mid temperature range 298-1300 K</th>
<th>Mid-High temperature range 1300-6000 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>51.6929</td>
<td>83.01014</td>
</tr>
<tr>
<td>B</td>
<td>36.79351</td>
<td>2.209166</td>
</tr>
<tr>
<td>C</td>
<td>-12.46154</td>
<td>-0.419735</td>
</tr>
<tr>
<td>D</td>
<td>0.701803</td>
<td>0.027676</td>
</tr>
<tr>
<td>E</td>
<td>-0.428743</td>
<td>-9.308648</td>
</tr>
<tr>
<td>F</td>
<td>290.6951</td>
<td>264.0342</td>
</tr>
<tr>
<td>G</td>
<td>291.2884</td>
<td>315.7192</td>
</tr>
<tr>
<td>H</td>
<td>309.0725</td>
<td>309.0725</td>
</tr>
</tbody>
</table>

The thermodynamic data was fitted with the following equations, separately at the low and high temperature ranges.

\[
\frac{C^0_p}{R} = a_1 + a_2 T + a_3 T^2 + a_4 T^3 + a_5 T^4 \tag{C.4}
\]

\[
\frac{H^0}{RT} = a_1 + \frac{a_2}{2} T + \frac{a_3}{3} T^2 + \frac{a_4}{4} T^3 + \frac{a_5}{5} T^4 + \frac{a_6}{6} T \tag{C.5}
\]

\[
\frac{S^0}{R} = a_1 \ln T + a_2 T + \frac{a_3}{2} T^2 + \frac{a_4}{3} T^3 + \frac{a_5}{4} T^4 + a_7 \tag{C.6}
\]

Here, \( T \) is the temperature (K) and \( a_1 \) to \( a_7 \) are the polynomial coefficients. Table C.2 shows the calculated coefficients.
Table C.2 Calculated coefficients for C2N2 thermodynamic data in ChemKin format.

<table>
<thead>
<tr>
<th>Coefficients</th>
<th>Low-Mid temperature range</th>
<th>Mid-High temperature range</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>298-1300 K</td>
<td>1300-6000 K</td>
</tr>
<tr>
<td>a1</td>
<td>4.00801541E+00</td>
<td>7.65682428E+00</td>
</tr>
<tr>
<td>a2</td>
<td>1.33682724E-02</td>
<td>2.33702677E-03</td>
</tr>
<tr>
<td>a3</td>
<td>-1.57983027E-05</td>
<td>-7.77839287E-07</td>
</tr>
<tr>
<td>a4</td>
<td>1.03107335E-08</td>
<td>1.17450503E-10</td>
</tr>
<tr>
<td>a5</td>
<td>-2.71547695E-12</td>
<td>-6.64325037E-15</td>
</tr>
<tr>
<td>a6</td>
<td>3.54050000E+04</td>
<td>3.42500000E+04</td>
</tr>
<tr>
<td>a7</td>
<td>2.85184990E+00</td>
<td>-1.61912162E+01</td>
</tr>
</tbody>
</table>
Appendix D

Adsorption of SO$_x$ on Pt and Pd surfaces

D.1 Binding energy and adsorption geometry

Table D.1 contains the computed structural parameters of SO$_x$ ($x = 0–4$) species on both surfaces. In the conformation notation, the number super-scripted to $\eta$ represents the number of atoms in a molecule coordinated to the metal (111) surface, and the subscripts $a$, $b$, $f$, and $h$ stand for the atoms on atop sites, bridge sites, fcc hollow sites, and hcp hollow sites, respectively. The $\eta^1$–S⊥ notation represents the S atom in SO$_2$ molecule with 2 O atoms attached only with S atom (unbound to the metal surface). From Table S1, it has been observed that the metal to sulfur (M-S) bond lengths were relatively shorter in for the Pd(111) surface. However, no such pattern was observed for metal to oxygen (M-O) and sulfur to oxygen (S-O) bonds. The increase in interatomic bond length was quite large when both atoms directly attached to the surface compared to the case when one atom is attached. The shortest metal sulfur bond (2.20 Å) was for SO molecule where S is attached to 3 metal atoms in fcc position. The S-O bond (O unbound to the metal) increased slightly (1.43 Å – 1.46 Å) from the gas phase bond length of 1.42 Å; however, the bond length increased tremendously (1.51 Å – 1.55 Å).
Å) in the case when both S and O atoms are attached. The bond angle ($\angle$OSO) decreased from the gas phase values ($\text{SO}_2(\angle\text{OSO}) = 119.5^\circ$ and $\text{SO}_3(\angle\text{OSO}) = 120^\circ$). An interesting configuration, SO$_2$(bridge)$\eta^1$–S$\perp$, has both oxygen atoms unbonded to the metal surface, showed the minimal decrease in bond length ($\angle$OSO) = 117$^\circ$) from the gas phase $\angle$OSO bond angle. Furthermore, the computed binding energies of various SO$_x$ species are compared with the available DFT based results (see Table D.2).

Table D.1 Bond lengths (Pt/Pd-S, Pt/Pd-O, S-O), bond angles (OSO), and binding energies of the stable configurations of oxygen (O), and sulfur oxides (SO$_x$) adsorbed on Pt(111) and Pd(111) Surfaces. Total number of identical bond lengths and bond angles of that particular configuration are reported in parentheses, which arises from the symmetry of the adsorbed molecule.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Configuration</th>
<th>Pt(111) surface</th>
<th>Pd(111) surface</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Bond length(Å)</td>
<td>Bond angle(°)</td>
<td>Bond energy</td>
</tr>
<tr>
<td>S$_2$O</td>
<td>$\eta^1$–O$_2$O$_2$O$_2$</td>
<td>2.09(±3)</td>
<td>1.43</td>
</tr>
<tr>
<td></td>
<td>$\eta^2$–O$_2$O$_2$O$_2$</td>
<td>2.10(±3)</td>
<td>1.43</td>
</tr>
<tr>
<td>S$_2$O$_2$</td>
<td>$\eta^1$–S$_2$O$_2$O$_2$</td>
<td>2.16(±3)</td>
<td>1.44</td>
</tr>
<tr>
<td>S$_2$O$_3$</td>
<td>$\eta^1$–S$_2$O$_2$O$_2$</td>
<td>2.13(±3)</td>
<td>1.44</td>
</tr>
<tr>
<td></td>
<td>$\eta^2$–S$_2$O$_2$O$_2$</td>
<td>2.13(±3)</td>
<td>1.44</td>
</tr>
<tr>
<td>S$_2$O$_4$</td>
<td>$\eta^1$–O$_2$O$_2$O$_2$</td>
<td>2.11(±3)</td>
<td>1.55(±3)</td>
</tr>
<tr>
<td>S$_2$O$_5$</td>
<td>$\eta^1$–O$_2$O$_2$O$_2$</td>
<td>2.11(±3)</td>
<td>1.55(±3)</td>
</tr>
<tr>
<td>S$_2$O$_6$</td>
<td>$\eta^1$–O$_2$O$_2$O$_2$</td>
<td>2.11(±3)</td>
<td>1.55(±3)</td>
</tr>
<tr>
<td>S$_2$O$_7$</td>
<td>$\eta^3$–O$_2$O$_2$O$_2$</td>
<td>2.30(±3)</td>
<td>1.45</td>
</tr>
<tr>
<td>S$_2$O$_8$</td>
<td>$\eta^3$–O$_2$O$_2$O$_2$</td>
<td>2.30(±3)</td>
<td>1.45</td>
</tr>
<tr>
<td>S$_2$O$_9$</td>
<td>$\eta^3$–O$_2$O$_2$O$_2$</td>
<td>2.30(±3)</td>
<td>1.45</td>
</tr>
<tr>
<td>S$<em>2$O$</em>{10}$</td>
<td>$\eta^4$–O$_2$O$_2$O$_2$</td>
<td>2.29(±3)</td>
<td>1.46</td>
</tr>
<tr>
<td>SO</td>
<td>$\eta^1$–S$_2$O$_2$O$_2$</td>
<td>2.16(±3)</td>
<td>1.46</td>
</tr>
<tr>
<td>SO</td>
<td>$\eta^2$–S$_2$O$_2$O$_2$</td>
<td>2.17(±3)</td>
<td>1.50</td>
</tr>
<tr>
<td>SO</td>
<td>$\eta^3$–S$_2$O$_2$O$_2$</td>
<td>2.16(±3)</td>
<td>1.51</td>
</tr>
<tr>
<td>SO</td>
<td>$\eta^4$–S$_2$O$_2$O$_2$</td>
<td>2.16(±3)</td>
<td>1.51</td>
</tr>
<tr>
<td>SO</td>
<td>$\eta^5$–S$_2$O$_2$O$_2$</td>
<td>2.16(±3)</td>
<td>1.51</td>
</tr>
<tr>
<td>S</td>
<td>$\eta^1$–S$_2$O$_2$O$_2$</td>
<td>2.27(±3)</td>
<td>1.57</td>
</tr>
<tr>
<td>S</td>
<td>$\eta^2$–S$_2$O$_2$O$_2$</td>
<td>2.27(±3)</td>
<td>1.57</td>
</tr>
<tr>
<td>S</td>
<td>$\eta^3$–S$_2$O$_2$O$_2$</td>
<td>2.27(±3)</td>
<td>1.57</td>
</tr>
<tr>
<td>S</td>
<td>$\eta^4$–S$_2$O$_2$O$_2$</td>
<td>2.27(±3)</td>
<td>1.57</td>
</tr>
<tr>
<td>O</td>
<td>$\eta^1$–O$_2$O$_2$O$_2$</td>
<td>2.05(±3)</td>
<td>1.46</td>
</tr>
<tr>
<td>O</td>
<td>$\eta^2$–O$_2$O$_2$O$_2$</td>
<td>2.04(±3)</td>
<td>1.46</td>
</tr>
<tr>
<td>O</td>
<td>$\eta^3$–O$_2$O$_2$O$_2$</td>
<td>1.82(±3)</td>
<td>1.46</td>
</tr>
</tbody>
</table>

Typically, the increase in surface coverage of an adsorbate decreases the binding strength of that adsorbate on the metal surface. In this work, we explored the effect of coverage on
Table D.2 Comparison of binding energies (kcal/mol) for the most stable configurations of SO\(_x\) species on Pt(111) and Pd(111) surfaces. Surface coverage of 0.11 ML is considered for the comparison.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Conformation</th>
<th>Pt(111) surface</th>
<th>Pd(111) surface</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>This work</td>
<td>Other DFT</td>
<td>This work</td>
</tr>
<tr>
<td>SO(_4)</td>
<td>(\eta^3)-O(_a)O(_a)O(_a) (87.2 \quad 86.5)(^{[283]}) (81.6)(^{[265]})</td>
<td>(85.1 \quad )–</td>
<td>(85.1 \quad )–</td>
</tr>
<tr>
<td>SO(_3)</td>
<td>(\eta^3)-S(_a)O(_a)O(_a) (30.3 \quad 27.5)(^{[283]}) (33.0)(^{[265]})</td>
<td>(27.4 \quad )–</td>
<td>(27.4 \quad )–</td>
</tr>
<tr>
<td>SO(_2)</td>
<td>(\eta^2)-S(_a)O(_a) (27.2 \quad 24.4)(^{[283]}) (28.1)(^{[265]})</td>
<td>(26.7 \quad 28.9)(^{[276]})</td>
<td>(26.7 \quad 28.9)(^{[276]})</td>
</tr>
<tr>
<td>SO</td>
<td>(\eta^1)-S(_f) (69.5 \quad 68.1)(^{[283]}) (68.0)(^{[265]})</td>
<td>(66.8 \quad )–</td>
<td>(66.8 \quad )–</td>
</tr>
<tr>
<td>S</td>
<td>(\eta^1)-S(_f) (122.2 \quad 118.7)(^{[283]})</td>
<td>(115.1 \quad 111.8)(^{[119]})</td>
<td>(115.1 \quad 111.8)(^{[119]})</td>
</tr>
<tr>
<td>O</td>
<td>(\eta^1)-O(_f) (98.6 \quad 100.6)(^{[283]})</td>
<td>(99.7 \quad 108.1)(^{[288]})</td>
<td>(99.7 \quad 108.1)(^{[288]})</td>
</tr>
</tbody>
</table>

Table D.3 Coverage dependent binding energy (kcal/mol) of the most stable SO\(_x\) species and O atom adsorbed on Pt(111) and Pd(111) surfaces.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Conformation</th>
<th>Pt(111) surface</th>
<th>Pd(111) surface</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(p(2\times2))</td>
<td>(p(3\times3))</td>
<td>(p(4\times4))</td>
</tr>
<tr>
<td></td>
<td>0.25 ML</td>
<td>0.11 ML</td>
<td>0.06 ML</td>
</tr>
<tr>
<td>SO(_4)</td>
<td>(\eta^1)-O(_a)O(_a) (81.4 \quad 87.2 \quad 90.3 \quad 92.8)</td>
<td>(80.1 \quad 85.1 \quad 87.6 \quad 89.8)</td>
<td>(80.1 \quad 85.1 \quad 87.6 \quad 89.8)</td>
</tr>
<tr>
<td>SO(_3)</td>
<td>(\eta^1)-S(_a)O(_a) (25.8 \quad 30.8 \quad 33.3 \quad 35.6)</td>
<td>(24.7 \quad 27.6 \quad 28.4 \quad 29.8)</td>
<td>(24.7 \quad 27.6 \quad 28.4 \quad 29.8)</td>
</tr>
<tr>
<td>SO(_2)</td>
<td>(\eta^1)-S(_a)O(_a) (23.6 \quad 27.2 \quad 29.1 \quad 30.8)</td>
<td>(24.4 \quad 26.7 \quad 28.1 \quad 29.1)</td>
<td>(24.4 \quad 26.7 \quad 28.1 \quad 29.1)</td>
</tr>
<tr>
<td>SO</td>
<td>(\eta^1)-S(_f) (65.7 \quad 69.5 \quad 70.6 \quad 72.4)</td>
<td>(65.5 \quad 66.8 \quad 68.1 \quad 68.7)</td>
<td>(65.5 \quad 66.8 \quad 68.1 \quad 68.7)</td>
</tr>
<tr>
<td>S</td>
<td>(\eta^1)-S(_f) (114.6 \quad 122.2 \quad 123.4 \quad 126.9)</td>
<td>(109.8 \quad 115.1 \quad 115.8 \quad 118.3)</td>
<td>(109.8 \quad 115.1 \quad 115.8 \quad 118.3)</td>
</tr>
<tr>
<td>O</td>
<td>(\eta^1)-O(_f) (96.1 \quad 98.6 \quad 99.3 \quad 100.4)</td>
<td>(98.6 \quad 99.6 \quad 99.9 \quad 100.5)</td>
<td>(98.6 \quad 99.6 \quad 99.9 \quad 100.5)</td>
</tr>
</tbody>
</table>

binding energies of SO\(_x\) and O on both surfaces. The computed binding energies of the most stable species of SO\(_x\) are given for the coverage range from 0.25 ML to zero coverage (see Table D.3). The zero coverage binding energies are estimated from linear interpolation of the DFT–computed binding energies.
D.2 Bader Charge Analysis

Bader charge analysis, purely based on the electronic charge density, was performed to calculate the net charge transfer from/to molecules to/from catalysts surface. The Bader analysis results are presented in Table D.4, where we report the net charge transfer to the molecule from the slab ($Q_{mol}$), the net charge acquired by the metal atoms ($Q_{Pt}$ or $Q_{Pd}$) directly attached to the atom/molecule, and the net charge acquired by the sulfur atom ($Q_{S}$) in the molecule.

Among the different configurations of a molecule, the one with higher number of O atoms attached directly to the metal rendered larger negative charge on the molecule and larger positive charge on attached Pt atoms; however, it exhibited decrease in the net charge on S atom. For example, the $Q_{mol}$, $Q_{Pd}$, and the $Q_{S}$ of $SO_3$ (fcc)$\eta^3$–$S_{a}$O$_a$O$_a$ on Pd(111) were -0.696, +0.424, and +4.714 respectively; however, those for $SO_3$ (fcc)$\eta^3$–O$_a$O$_a$O$_a$ changed to -0.957, +0.585, and +4.316 respectively producing ~27% difference in charge transfer between two configurations of a molecules. An interesting behavior was observed for $SO_2$ (bridge)$\eta^1$–$S_{\perp}$ molecule, where $Q_{mol}$ and $Q_{Pt}$ (or $Q_{Pd}$) were remarkably low but the $Q_{S}$ was higher compared to other $SO_2$ configurations.

D.3 Density of states analysis

We decomposed the electron density and wave function into contributions from atomic orbitals, i.e. $s$, $p$ and $d$ orbitals centered on each atom. Figure 6.3 shows the $p$-DOS of various $SO_x$ molecules on Pd(111) and Pt(111) surfaces. In Figure 6.3, each panel (a-h) shows the projected atomic DOS of atom/molecule in a isolated state along with the pure slab surface in the lower part and the adsorbed states of those in the upper part. Further, comparison of DOS of S adsorption on Pd(111) and Pt(111) surfaces is given in Figure 6.3(i). We observed the shifting of active metal $d$ band to lower energy after adsorption of atom/molecule in all cases. The
Table D.4: Bader charge analysis of O and \( \text{SO}_x \) adsorption on Pt(111) and Pd(111) surfaces. Charge (au) in the molecule (\( Q_{\text{mol}} \)), surface metal atoms (\( Q_{\text{Pt}} \)), and sulfur atom (\( Q_{\text{S}} \)) represents the total charge acquired after adsorption.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Conformation</th>
<th>Pt(111) surface</th>
<th>Pd(111) surface</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{SO}_4 )</td>
<td>(fcc)( \eta^3 )-O(_a)O(_a)O(_a)</td>
<td>(-1.010 +0.700 +6.000 )</td>
<td>(-1.070 +0.670 +6.000 )</td>
</tr>
<tr>
<td>( \text{SO}_4 )</td>
<td>(hcp)( \eta^3 )-O(_a)O(_a)O(_a)</td>
<td>(-1.000 +0.690 +6.000 )</td>
<td>(-1.070 +0.671 +6.000 )</td>
</tr>
<tr>
<td>( \text{SO}_3 )</td>
<td>(fcc)( \eta^3 )-S(_a)O(_a)O(_a)</td>
<td>(-0.656 +0.412 +4.60 )</td>
<td>(-0.696 +0.424 +4.714 )</td>
</tr>
<tr>
<td>( \text{SO}_3 )</td>
<td>(hcp)( \eta^3 )-S(_a)O(_a)O(_a)</td>
<td>(-0.652 +0.414 +4.614 )</td>
<td>(-0.694 +0.411 +4.697 )</td>
</tr>
<tr>
<td>( \text{SO}_3 )</td>
<td>(hcp)( \eta^3 )-O(_a)O(_a)O(_a)</td>
<td>(-0.920 +0.685 +4.263 )</td>
<td>(-0.937 +0.466 +4.313 )</td>
</tr>
<tr>
<td>( \text{SO}_2 )</td>
<td>(fcc)( \eta^2 )-S(_a)O(_a)</td>
<td>(-0.330 +0.189 +3.325 )</td>
<td>(-0.369 +0.258 +3.334 )</td>
</tr>
<tr>
<td>( \text{SO}_2 )</td>
<td>(hcp)( \eta^2 )-S(_a)O(_a)</td>
<td>(-0.327 +0.157 +3.336 )</td>
<td>(-0.373 +0.201 +3.361 )</td>
</tr>
<tr>
<td>( \text{SO}_2 )</td>
<td>(bridge)( \eta^1 )-S(_\perp)</td>
<td>(-0.272 +0.023 +3.475 )</td>
<td>(-0.353 +0.114 +3.403 )</td>
</tr>
<tr>
<td>( \text{SO}_2 )</td>
<td>(fcc)( \eta^3 )-S(_a)O(_a)O(_a)</td>
<td>(-0.439 +0.341 +2.997 )</td>
<td>(-0.471 +0.362 +3.095 )</td>
</tr>
<tr>
<td>( \text{SO} )</td>
<td>(fcc)( \eta^1 )-S(_f)</td>
<td>(-0.196 +0.152 +1.693 )</td>
<td>(-0.195 +0.152 +1.693 )</td>
</tr>
<tr>
<td>( \text{SO} )</td>
<td>(hcp)( \eta^1 )-S(_b)</td>
<td>(-0.163 +0.142 +1.700 )</td>
<td>(-0.151 +0.202 +1.701 )</td>
</tr>
<tr>
<td>( \text{SO} )</td>
<td>(fcc)( \eta^2 )-S(_h)O(_a)</td>
<td>(-0.236 +0.057 +1.434 )</td>
<td>(-0.267 +0.165 +1.469 )</td>
</tr>
<tr>
<td>( \text{SO} )</td>
<td>(hcp)( \eta^2 )-S(_b)O(_a)</td>
<td>(-0.232 +0.056 +1.451 )</td>
<td>(-0.303 +0.163 +1.146 )</td>
</tr>
<tr>
<td>( \text{S} )</td>
<td>(fcc)( \eta^1 )-S(_f)</td>
<td>(-0.125 +0.076 -0.125 )</td>
<td>(-0.256 +0.244 -0.256 )</td>
</tr>
<tr>
<td>( \text{S} )</td>
<td>(hcp)( \eta^1 )-S(_b)</td>
<td>(-0.081 +0.060 -0.081 )</td>
<td>(-0.256 +0.228 -0.256 )</td>
</tr>
<tr>
<td>( \text{O} )</td>
<td>(fcc)( \eta^1 )-O(_f)</td>
<td>(-0.772 +0.622 )</td>
<td>(-0.773 +0.752 )</td>
</tr>
<tr>
<td>( \text{O} )</td>
<td>(hcp)( \eta^1 )-O(_b)</td>
<td>(-0.757 +0.633 )</td>
<td>(-0.764 +0.714 )</td>
</tr>
<tr>
<td>( \text{O} )</td>
<td>(atop)( \eta^1 )-O(_a)</td>
<td>(-0.599 +0.484 )</td>
<td>(-0.604 +0.386 )</td>
</tr>
</tbody>
</table>
$d$ band shifting was larger in the case of sulfur metal interaction compared to oxygen metal interaction. Panel c, d, e, and f (in Figure 6.3) show the difference in $d$ band shifting, where Pd-1 shows larger shift (M-S interaction) then Pd-2 (M-O interaction). Along the same line, we found very similar characteristics of DOS in the case of Pt(111) surface. Nonetheless, we showed the DOS of S adsorption (see Figure 6.3(i)) on both surfaces for the comparison. We note that the oxygen 2$p$ orbitals attached to metal and sulfur atom (denoted as O-1 in Figure 6.3) showed more broadening with a spike at -7 eV, whereas the oxygen 2$p$ orbitals attached only with sulfur atom (denoted as O-2 in Figure 6.3) showed relatively smaller broadening with a spike at -6eV. Furthermore, we observed strong interactions of $p$ orbitals of S and O with each other and with metal $d$ band in this reason (-5 to -8 eV) We note that the $d$ band was larger and extend to lower energy in Pt(111) along with broadening and larger separation of bonding and antibonding states of $p$ orbitals, which can be assigned to comparatively stronger SO$_x$ binding to Pt(111) surface observed in this study. Finally, we also observed diffused metal $s$ orbitals and provided some contribution to total DOS (not shown here); however, the contribution was negligible compared to metal $d$ orbitals. [318].
Appendix E

Computation of Pre-exponential Factors

From Vibrational Modes

Pre-exponential factors are important kinetics parameters for the study of various catalytic process, which can be calculated rigorously using DFT. For an example, the elementary step surface reaction of SO\textsubscript{2} oxidation on the Pt/Pd surfaces, the reaction rate constant \( k \) is given as:

\[
  k_i = A_o \exp\left(\frac{-E_{a,i}}{K_B T}\right) \quad (E.1)
\]

Where \( A_o, E_{a,i}, K_B, \) and \( T \) represent the pre-exponential factor, reaction activation energy, Boltzmann’s constant, and temperature respectively. The pre-exponential factor \( A_o \) can be given as:

\[
  A_o = \frac{K_B T}{\hbar} \exp\left(\frac{\Delta S_{i}^{\ddagger}}{K_B}\right) \quad (E.2)
\]
Where $h$ is the Planck’s constant and $\Delta S^o_{i\dagger}$ represents the standard state entropy change accompanying the formation of transition state and calculated as:

$$\Delta S^o_{i\dagger} = S^o_{TS\dagger} - S^o_{IS} \quad (E.3)$$

Where $S^o_{TS\dagger}$ and $S^o_{IS}$ represent the transition state entropy and the initial state entropy. The entropies can be calculated from the analysis of vibrational modes of the species as follows, [168, 319]

$$S_{vib} = K_B \sum_{i}^{\text{no.of modes}} \left( \frac{x_i}{e^{v_i} - 1} - \ln(1 - e^{-x_i}) \right) \quad (E.4)$$

Where $x_i$ represents the each vibrational mode and calculated from the vibrational frequency $v_i$ as:

$$x_i = \frac{h v_i}{K_B T} \quad (E.5)$$

The lowest possible energy at ground state, zero-point energy (ZPE) accounts for the energy at zero Kelvin. The difference in zero-point energy, i.e. $\Delta ZPE$ can be calculated as: [319]

$$\Delta ZPE = \left( \sum_{i}^{\text{no.of modes}} \frac{h v_i}{2} \right)_{TS} - \left( \sum_{i}^{\text{no.of modes}} \frac{h v_i}{2} \right)_{IS} \quad (E.6)$$

The vibrational frequencies, except the single imaginary mode in each transition state, are utilized to compute the pre-exponential factors and zero-point energy. The frequencies are listed in Table E.1.
Table E.1 List of the vibrational frequencies (cm\(^{-1}\)) of initial state and transition state of SO\(_2\) oxidation (SO\(_2^* + O^* \rightarrow SO_3^*\)) and SO\(_3\) oxidation (SO\(_3^* + O^* \rightarrow SO_4^*\)) on Pt(111) and Pd(111) surfaces.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Path</th>
<th>Frequencies (cm(^{-1}))</th>
<th>Pt(111)</th>
<th>Pd(111)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Initial-state</td>
<td>Transition state</td>
<td>Initial-state</td>
</tr>
<tr>
<td>SO(_2^* + O^* \rightarrow SO_3^*)</td>
<td>Path A</td>
<td>1173, 957, 491, 434, 347</td>
<td>1197, 809, 496, 479, 312, 268</td>
<td>1167, 953, 482, 414, 365</td>
</tr>
<tr>
<td></td>
<td></td>
<td>306, 149, 87, 81, 44, 21</td>
<td>194, 156, 155, 87, 50</td>
<td>361, 175, 120, 96, 81, 63, 27</td>
</tr>
<tr>
<td></td>
<td>Path B</td>
<td>1220, 1017, 486, 476, 370, 197</td>
<td></td>
<td>1224, 1096, 490, 443, 364, 165</td>
</tr>
<tr>
<td></td>
<td></td>
<td>140, 108, 98, 62, 58</td>
<td></td>
<td>154, 144, 92, 60, 53</td>
</tr>
<tr>
<td></td>
<td>Path C</td>
<td>1261, 1063, 505, 482, 365, 200</td>
<td></td>
<td>1247, 1053, 493, 446, 408, 165</td>
</tr>
<tr>
<td></td>
<td></td>
<td>183, 127, 100, 53, 41</td>
<td></td>
<td>162, 150, 125, 46, 42</td>
</tr>
<tr>
<td>SO(_3^* + O^* \rightarrow SO_4^*)</td>
<td>Path A</td>
<td>1219, 871, 802, 592, 504, 457, 439</td>
<td>1213, 876, 741, 592, 485, 440, 416</td>
<td>1198, 914, 823, 561, 488, 439, 434</td>
</tr>
<tr>
<td></td>
<td></td>
<td>410, 360, 285, 259, 217, 148, 103, 92</td>
<td>329, 232, 183, 156, 153, 127, 112</td>
<td>401, 352, 258, 228, 150, 127, 82, 53</td>
</tr>
<tr>
<td></td>
<td></td>
<td>323, 183, 163, 149, 94, 66</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Appendix F

First Principles Thermodynamics

F.1 Surface and Bulk Free Energy

Surface energy of a surface model system in equilibrium with the surrounding gas phase reservoir can be expressed as follows.

\[
\gamma(T, p\{i\}) = \frac{1}{A} \left[ G_{\text{surf}} - \sum_{i=1}^{n} N_{i}\mu_{i}(T, p_{i}) \right] \quad (F.1)
\]

where, \(G_{\text{surf}}\), \(A\), \(\mu_{i}\), \(n\), and \(N_{i}\) represent the Gibbs free energy, surface area of the slab, individual gas species in the system, number of gas species, number of atoms/molecules of gas species, respectively. For the stability comparison between multiple models (with \(\text{SO}_{3}\) and \(\text{O}\) on the surface), we take the clean slab as a common reference. Then, the relative surface energy can be computed as:

\[
\Delta\gamma_{(T, \text{SO}_{3}, \text{O})} = \frac{1}{A} \left[ G_{\text{surf, SO}_{3}, \text{O+slab}} - G_{\text{surf, slab}} - \frac{N_{\text{O}}}{2}\mu_{\text{O}_{2}} - N_{\text{SO}_{3}}\mu_{\text{SO}_{3}} \right] \quad (F.2)
\]
The Gibbs free energy can be further simplified in terms of DFT computed energy \[299\]
and expressed as:

\[
\Delta \gamma(T, SO_3, O) = \frac{1}{A} \left[ \Delta E_{\text{DFT}}^{SO_3, O} + \Delta E_{\text{Vib}}^{SO_3, O} - \frac{N_O}{2} \Delta \mu_{O_2} - N_{SO_3} \Delta \mu_{SO_3} \right] \tag{F.3}
\]

where \(\Delta E_{\text{Vib}}^{SO_3, O} (\Delta E_{\text{Vib}}^{SO_3, O} = F_{\text{Vib}}^{SO_3, O+\text{slab}} - F_{\text{Vib}}^{\text{slab}})\) represents the vibrational contributions to the free energy. \(\Delta E_{\text{DFT}}^{SO_3, O}\) is the average binding energy of SO\(_3\) and O (the DFT energy difference slab+adsorbates and clean slab) which can be obtained from DFT calculations as follows:

\[
\Delta E_{\text{DFT}}^{SO_3, O} = \left[ E_{\text{DFT}}^{SO_3, O+\text{slab}} - E_{\text{slab}}^{\text{slab}} - \Delta N_{\text{Pt/Pd}} E_{\text{Pt/Pd}} - \frac{N_O}{2} E_{\text{DFT}}^{O_2} - N_{SO_3} E_{\text{DFT}}^{SO_3} \right] \tag{F.4}
\]

where \(E_{\text{DFT}}^{SO_3, O+\text{slab}}\) and \(E_{\text{slab}}^{\text{slab}}\) represent the total energy of the slab+adsorbates and the slab only, respectively. The \(\Delta N_{\text{Pt/Pd}}\) represents the condition if the number of Pt/Pd atoms of the slab+adsorbates are not equal to the one in clean slab, i.e. \(N_{\text{slab+ads}}^{\text{slab}} \neq N_{\text{Pt/Pd}}\) as in the case of surface oxides of Pt and Pd. The excess/deficiency of metal atoms are taken from/ put into a bulk reservoir can be represented by the bulk phase chemical potential \(\mu_{\text{Pt/Pd}}^{\text{bulk}}\). The chemical potential of the gas species (i.e. \(\mu_{SO_3}\) and \(\mu_{O_2}\)) can be represented as a combination of total energy and the temperature and pressure dependent function as:

\[
\mu_{O_2}(T, P_{O_2}) = E_{O_2}^{\text{DFT}} + \Delta \mu_{O_2}(T, P_{O_2}) \tag{F.5}
\]

where \(E_{O_2}^{\text{DFT}}\) represents the DFT energy of an isolated O\(_2\) molecule and the \(\Delta \mu_{O_2}(T, P_{O_2})\) represents the temperature and pressure dependent chemical potential term (computation details are given in supporting information). Similarly, chemical potential of SO\(_3\) can be calculated as:

\[
\mu_{SO_3}(T, P_{SO_3}) = E_{SO_3}^{\text{DFT}} + \Delta \mu_{SO_3}(T, P_{SO_3}) \tag{F.6}
\]
Which also contains the DFT computed energy of an isolated SO$_3$ molecule and chemical potential with temperature and pressure dependence. Computations details and results are shown in supporting information. Further, we define the binding energy per atom (or molecule) O (or SO$_3$) on the surface as:

\[ E_{\text{bind}}^{\text{O}} = \frac{1}{N_\text{O}} \left[ E_{\text{DFT}, \text{O}+\text{slab}} - E_{\text{DFT, slab}} - \frac{N_\text{O}}{2} E_{\text{DFT}, \text{O}_2} \right] \]  

(F.7)

Adsorption of O (or SO$_3$) on the surface oxides of Pt/Pd is slightly different case compared to the adsorption on the clean surface. Here, we define the binding energy taking the oxidized surface as a reference. For example, the adsorption of SO$_3$ on the surface oxide is given as:

\[ E_{\text{bind}}^{\text{SO}_3} = \frac{1}{N_{\text{SO}_3}} \left[ E_{\text{DFT}, \text{SO}_3+\text{surf.oxd.}} - E_{\text{DFT, surf.oxd.}} - N_{\text{SO}_3} E_{\text{DFT, SO}_3} \right] \]  

(F.8)

The Phase diagrams are created by plotting the relative surface energy vs. the chemical potentials of oxygen and SO$_3$ ($\Delta \mu_\text{O}_2$ and $\Delta \mu_\text{SO}_3$) in x and y-axis respectively. As mentioned in the main text, we see little effect of the vibrational contributions to the free energy; however, the outcome and stability of the phases do not change.

To establish the stability of bulk phases, Gibbs free energy is computed which can be written as:

\[ \Delta G = \left[ E_{\text{DFT, \text{SO}_3+surf.oxd.}}^{\text{DFT}} - \frac{N_\text{O}}{2} \Delta \mu_\text{O}_2 - N_{\text{SO}_3} \Delta \mu_\text{SO}_3 \right] - E_{\text{DFT, bulk(metal)}}^{\text{DFT}} \]  

(F.9)

where $E_{\text{DFT, bulk(sulfate oxide)}}^{\text{DFT}}$ and $E_{\text{DFT, bulk(metal)}}^{\text{DFT}}$ represent the DFT computed energy of the bulk sulfate or oxide species and the corresponding bulk metal. The $\mu_\text{O}_2$ and $\mu_\text{SO}_3$ are computed as shown above.
F.2 Vibrational Contributions to the Free Energy

The Gibbs free energy consists of the contribution from atomic/molecular vibration as:

\[
G(T, P) = E^{\text{total}} + F^\text{vib} - TS^{\text{conf}} + pV \tag{F.10}
\]

where \(E^{\text{total}}, S^{\text{conf}}, p, \text{and } V\) represent the total energy of the system, configurational entropy, pressure, and volume terms respectively. The contribution to Gibbs free energy from \(pV\) term and configurational entropy are negligible for the adsorption process, hence discarded in this study. Thus, we incorporate this contribution through harmonic normal mode analysis of the adsorbates and the substrate layers involved in the case of surface models using Bose-Einstein model approximations. The approximation is computed as, [129]

\[
F^\text{vib} = \frac{1}{2} \sum_i 3N\varepsilon_i + K_B T \sum_i 3N \ln(1 - e^{-\beta \varepsilon_i}) \tag{F.11}
\]

where \(\varepsilon_i = h\nu\) represents the phonon energy at different vibrational modes, \(\nu_i\) represents the vibrational frequency and \(\beta = (K_B T)^{-1}\).
Appendix G

Bulk Parameters and USPEX Predictions

G.1 Bulk Parameters of Oxides and Sulfates of Pt and Pd

We considered various bulk structures (clean metals, metal oxides, and metal sulfates) in this study. In Table G.1, we show the computed lattice parameters of the structures considered.

G.2 USPEX Predictions

In this study, we predict the structure of PtSO₄ using an evolutionary algorithm based method USPEX. [131] We explored the configurational space of PtSO₄ using up to 4 formula unit supercell. Multiple independent USPEX run were performed to avoid confining in a local minimum. The most stable structure of PtSO₄ was predicted to be a tetragonal structure with space group P42/m (84). To validate our prediction, we performed the USPEX calculation on PdSO₄, which showed the P42/m (84) structure is the lowest energy phase along with the previously known monoclinic C2/c (15) structure [301] being a competing structure. We show the relative energies and atomic arrangements of a few USPEX predicted structures of PtSO₄.
Table G.1 Structural parameters of the various bulk phases considered in this study. Available experimental parameters are given inside brackets below the computed values. Space groups were determined using FINDSYM software.

<table>
<thead>
<tr>
<th>S.N.</th>
<th>Structure</th>
<th>Lattice parameters</th>
<th>Space group</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Pt</td>
<td>a [Å] 3.97, (3.92)&lt;sup&gt;a&lt;/sup&gt;</td>
<td>Fm3m (225)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>b [Å] 3.97, (3.92)&lt;sup&gt;a&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>c [Å] 3.97, (3.92)&lt;sup&gt;a&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Pd</td>
<td>a [Å] 3.94, (3.89)&lt;sup&gt;b&lt;/sup&gt;</td>
<td>Fm3m (225)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>b [Å] 3.94, (3.89)&lt;sup&gt;b&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>c [Å] 3.94, (3.89)&lt;sup&gt;b&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>PtO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>a [Å] 3.12, (3.10)&lt;sup&gt;c&lt;/sup&gt;</td>
<td>P-3m1 (164)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>b [Å] 3.12, (3.10)&lt;sup&gt;c&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>c [Å] 3.60, (3.10)&lt;sup&gt;c&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>PdO</td>
<td>a [Å] 3.05, (3.03)&lt;sup&gt;d&lt;/sup&gt;</td>
<td>P42/mmc (131)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>b [Å] 3.05, (3.03)&lt;sup&gt;d&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>c [Å] 5.40, (5.33)&lt;sup&gt;d&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>PtSO&lt;sub&gt;4&lt;/sub&gt;</td>
<td>a [Å] 4.14</td>
<td>P42/m (84)&lt;sup&gt;e&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td></td>
<td>b [Å] 4.14</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>c [Å] 8.89</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>PdSO&lt;sub&gt;4&lt;/sub&gt;</td>
<td>a [Å] 7.49</td>
<td>C2/c (15)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>b [Å] 6.32</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>c [Å] 7.77</td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup> references [117, 120]  
<sup>b</sup> references [117, 121]  
<sup>c</sup> references [320, 321]  
<sup>d</sup> references [322]  
<sup>e</sup> predicted structure

and PdSO<sub>4</sub> in Figure G.1. Results suggested that many structures are common in both PdSO<sub>4</sub> and PtSO<sub>4</sub>. We used Density Functional theory (DFT) [111] implemented in VASP [113] for the first principles computations with the USPEX. Relative energetics of the four selected structures is shown in Figure G.1 and lattice parameters information for the structures given in Table G.2.

Table G.2 DFT computed lattice parameters of USPEX predicted bulk PtSO<sub>4</sub> and PdSO<sub>4</sub>.

<table>
<thead>
<tr>
<th>S.N.</th>
<th>Structure</th>
<th>Lattice parameters</th>
<th>Space group</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>PtSO&lt;sub&gt;4&lt;/sub&gt;</td>
<td>a [Å] 4.15</td>
<td>Tetragonal, P42/m (84)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>b [Å] 4.15</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>c [Å] 8.86</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>α [°] 90</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>β [°] 90</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>γ [°] 90</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>PdSO&lt;sub&gt;4&lt;/sub&gt;</td>
<td>a [Å] 6.19</td>
<td>Tetragonal, P4/n (85)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>b [Å] 6.19</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>c [Å] 4.94</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td></td>
<td>α [°] 90</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>β [°] 90</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>γ [°] 90</td>
<td></td>
</tr>
</tbody>
</table>
Fig. G.1 Relative energetics and structures predicted using USPEX method. Panel a: relative energetics of PdSO$_4$ structures and panel b: relative energetics of PtSO$_4$ structures, compared to the most stable P4$_2$/<i>m</i>, 84. Predicted structural models for both sulfates are shown in the respective panels. Space-group of the structure was determined using FINDSYM [323] software.
Appendix H

Oxygen and SO\textsubscript{3} on Pt(111) or Pd(111) Surfaces and Sub-Surfaces

H.1 Oxygen on Pt/Pd Surfaces and Sub-Surfaces

Experimental studies suggest that the adsorption of oxygen is favored on 3-fold hollow fcc sites on both Pt(111) and Pd(111) surfaces. Most commonly reported structures include a \(p(2\times2)\) and a \(c(2\times2)\) configurations corresponding the coverage of 0.25 ML and 0.5 ML, respectively. In this study, we considered a coverage range of 0.06 ML to 1 ML coverage of oxygen on both surfaces. For 0.06 ML (in a \((4\times4)\) surface supercell) and 0.25 ML (in a \((2\times2)\) surface supercell) coverage of oxygen, all fcc sites (most stable sites) are equivalent; however, adsorption of further oxygen on the surface could produce hundreds of possible surface configuration combinations. To avoid the calculation for all possible configurations, we employ few constrains to our models. First, we only consider fcc sites for the configuration. Second, too close positions of the atom/molecule on the surface are unphysical due to immense lateral interactions. Hence, we avoid such close unphysical combinations by considering the distance
between two atoms/molecules greater than the two adjacent fcc sites. Our results shows that the 3-hold hollow fcc sites are in fact the most stable adsorption sites even for higher oxygen coverages.

To study the sub-surface oxygen adsorption favorability and transition over on-surface adsorption, we considered the most stable/favored sub-surface site tetra-I (site directly below 3-fold hcp site on (111) surface). A (2×2) surface supercell was considered and the coverage was varied from 0.25 ML to 1 ML (see Figure S2). The 0.25 ML coverage of sub-surface oxygen corresponds to an only O at sub-surface tetra-I position. Then, the rest of the oxygen coverage for sub-surface/on-surface combination contain one sub-surface oxygen at tetra-I site and rest on the on-surface fcc sites.

The adsorption behavior is similar for both Pt(111) and Pd(111) surfaces considered here; however, the binding strength of oxygen on Pd(111) is slightly greater compared to the same on Pt(111) surface. This is also true for on-surface/sub-surface oxygen configurations. Binding energies for the most stable and metastable configurations considered are given in the Table H.1. The decrease in the binding energy, computed as given by Equation H.1, with the increase the oxygen coverage indicates the presence of lateral interaction.

\[
E_{\text{bind}}^{\text{O}} = \frac{1}{N_O} \left[ E_{\text{DFT,O+slab}} - E_{\text{DFT,slab}} - \frac{N_O}{2} E_{\text{DFT,O}_2} \right] \tag{H.1}
\]

Figure H.1 shows a comparative picture of the oxygen adsorption on Pt(111) and Pd(111) surfaces. The upper panels (panel a and b, Figure H.1) show the change of surface energy with respect to the oxygen chemical potential. We provide more intuitive quantity (i.e. \( p_{O_2} \)) corresponding to the oxygen chemical potential at 300 K and 900 K. At very low chemical potential \( \Delta \mu_{O_2} \approx -2.5 \text{ eV} \), clean surface is stable in both cases. With the increase in oxygen chemical potential, various surface structures can be seen as stable phases before a surface
Fig. H.1 Relative surface energy as a function of $\Delta \mu_{O_2}$ and phase diagrams of oxygen adsorption on Pt(111) and Pd(111) surfaces. Pressure scales (in atm) at two representative temperatures (300K and 900K) are given opposite to the chemical potential scale in two upper panels. Symbols in the lower panels represent the experimental data available for the various phases in the given temperature-pressure conditions. Panel a: relative surface energy ($\Delta \gamma$) vs relative oxygen chemical potential ($\Delta \mu_{O_2}$) for Pt(111); panel b: relative surface energy ($\Delta \gamma$) vs relative oxygen chemical potential ($\Delta \mu_{O_2}$) for Pd(111); panel c: phase diagram of O adsorption on Pt(111) for the range of temperature and pressure conditions. Symbol $\star$ represents the experimentally observed [309] clean slab condition, symbol $\times$ represents the temperature and pressure conditions [151] for surface coverage of 0.25 ML, symbols $\bullet$ represent the pressure conditions [324] at constant temperature (425 K) where surface coverage of 0.25 ML was observed, and symbol $\blacksquare$ represents the surface oxide condition [324] observed; panel d: phase diagram of O adsorption on Pd(111) for the range of temperature and pressure conditions. Symbol $\blacklozenge$ represents the experimentally observed [310] clean slab condition, symbols $\bullet$ represent the experimental condition of constant pressure and range of temperatures for the surface coverage of 0.25 ML, and symbols $\blacksquare$ and $\star$ represent the condition of surface oxide phase (PdO on Pd(111)) observed experimentally [307, 308]. Sub-surface oxygen phases were not shown in panel a and b.
Table H.1 DFT computed binding energies per atom of the most stable phases of O for on-surface and on-surface/sub-surface combinations on Pt(111) and Pd(111) surfaces using Equation 3.2.

<table>
<thead>
<tr>
<th>Structure (fcc)</th>
<th>Coverage (ML)</th>
<th>Binding energy (eV) Pt(111)</th>
<th>Binding energy (eV) Pd(111)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 O on (4×4)</td>
<td>0.06</td>
<td>-1.25</td>
<td>-1.29</td>
</tr>
<tr>
<td>1 O on (2×2)</td>
<td>0.25</td>
<td>-1.15</td>
<td>-1.26</td>
</tr>
<tr>
<td>2 O on (2×2)</td>
<td>0.50</td>
<td>-0.87</td>
<td>-1.00</td>
</tr>
<tr>
<td>3 O on (2×2)</td>
<td>0.75</td>
<td>-0.52</td>
<td>-0.63</td>
</tr>
<tr>
<td>4 O on (2×2)</td>
<td>1.00</td>
<td>-0.17</td>
<td>-0.21</td>
</tr>
<tr>
<td>Tetra-I, 1 O on (2×2)</td>
<td>0.25</td>
<td>0.76</td>
<td>0.48</td>
</tr>
<tr>
<td>Tetra-1/fcc, 2 O on (2×2)</td>
<td>0.5</td>
<td>-0.57</td>
<td>-0.92</td>
</tr>
<tr>
<td>Tetra-1/fcc, 3 O on (2×2)</td>
<td>0.75</td>
<td>-0.49</td>
<td>-0.74</td>
</tr>
<tr>
<td>Tetra-1/fcc, 4 O on (2×2)</td>
<td>1.00</td>
<td>-0.26</td>
<td>-0.43</td>
</tr>
</tbody>
</table>

oxide becomes more stable. Results show that the surface oxides become more stable before the oxygen surface coverage of 0.5 ML; however, the Pd surface oxide formation is highly favored. The thermodynamic stability range of bulk oxides are also marked on the plot for corresponding metal bulk oxides. Furthermore, we show the surface phase diagrams (panel c and d, Figure H.1) of oxygen on Pt(111) and Pd(111) surfaces in a wide range of temperature and pressure conditions. The surface phase diagram confirms the higher oxidation affinity of Pd(111) surface compared to Pt(111) surface. For the comparison, we plotted various experimental data obtained from literature to our phase diagrams. Various experimental points fall on the stable phase regions predicted in this study. In general, we observed a larger oxygen affinity and lower surface energy of Pd(111) surfaces suggesting that the Pd(111) surface is more stable.

**H.2 SO₃ on Pt/Pd Surfaces**

The upright standing chair-shaped configuration was the most stable SO₃ configuration on the surface plane considered here. The binding energies of the most stable phases are given in the
H.3 SO₃ and O on Pt(111) or Pd(111) Surfaces

Table H.2. Unlike oxygen, results suggest that the binding strength of SO₃ on Pt(111) surface is stronger compared to SO₃ on Pd(111) surface.

We compared the SO₃ adsorption behavior on both Pt(111) and Pd(111) surfaces in Figure H.2. In panels a and b, we show the change in surface energy vs. SO₃ chemical potential. Results show that the SO₃ adsorption is favored more on Pt(111) surface. Unlike oxygen, adsorbed SO₃ phases are not stable in 1 atm pressure and at 600 K conditions. Further, we show the phase diagram of SO₃ adsorption on both surfaces for a wide temperature and pressure range (see panel c and d in Figure H.2). The surface phase diagram also shows a relatively higher affinity of Pt(111) towards SO₃.

Table H.2 DFT computed binding energies per molecule of the most stable phases of SO₃ on Pt(111) and Pd(111).

<table>
<thead>
<tr>
<th>Structure (fcc)</th>
<th>Coverage (ML)</th>
<th>Binding energy (eV) Pt(111)</th>
<th>Binding energy (eV) Pd(111)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 SO₃ on (4×4)</td>
<td>0.06</td>
<td>-1.45</td>
<td>-1.23</td>
</tr>
<tr>
<td>1 SO₃ on (3×3)</td>
<td>0.11</td>
<td>-1.33</td>
<td>-1.16</td>
</tr>
<tr>
<td>2 SO₃ on (3×3)</td>
<td>0.22</td>
<td>-1.22</td>
<td>-1.07</td>
</tr>
<tr>
<td>3 SO₃ on (3×3)</td>
<td>0.33</td>
<td>-1.15</td>
<td>-0.90</td>
</tr>
</tbody>
</table>

H.3 SO₃ and O on Pt(111) or Pd(111) Surfaces

Two SO₃ coverages (i.e. 0.11 ML and 0.22 ML) were considered along with a range of oxygen coverages on (3×3) surface. As mentioned earlier, we contained the possible configurations of SO₃ and oxygen to the most stable fcc sites and avoided unphysical adsorption condition. For the 0.11 ML SO₃ condition, oxygen coverage up to 0.33 ML found to be stable; however, oxygen coverage up to 0.22 ML was found to be stable for the 0.22 ML SO₃ condition. Total binding energy of the adsorbates (SO₃ and O) is computed for those stable cases are given in Table H.3.
Fig. H.2 Relative surface energy as a function of $\Delta \mu_{SO_3}$ and phase diagrams of SO$_3$ adsorption on Pt(111) and Pd(111) surfaces.
Table H.3 DFT computed total binding energies of the most stable phases of SO$_3$ and O on Pt(111) and Pd(111).

<table>
<thead>
<tr>
<th>Structure (fcc)</th>
<th>Coverage (ML)</th>
<th>Binding energy (eV) Pt(111)</th>
<th>Binding energy (eV) Pd(111)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 SO$_3$ + 1 O on (4×4)</td>
<td>0.22</td>
<td>-2.49</td>
<td>-2.44</td>
</tr>
<tr>
<td>1 SO$_3$ + 2 O on (3×3)</td>
<td>0.33</td>
<td>-3.42</td>
<td>-3.49</td>
</tr>
<tr>
<td>1 SO$_3$ + 3 O on (3×3)</td>
<td>0.44</td>
<td>-3.77</td>
<td>-3.97</td>
</tr>
<tr>
<td>2 SO$_3$ + 1 O on (3×3)</td>
<td>0.33</td>
<td>-3.47</td>
<td>-3.16</td>
</tr>
<tr>
<td>2 SO$_3$ + 2 O on (3×3)</td>
<td>0.44</td>
<td>-3.48</td>
<td>-3.21</td>
</tr>
</tbody>
</table>

H.4 Estimation of Cross-interactions of SO$_3$* and O*

In this work, we used a surface unit cell of (3×3) to investigate the cross-interactions (inter-species lateral interactions) between SO$_3$* and O* on Pt(111) and Pd(111) surfaces. For a generalized surface supercell (p×q), the maximum occupancy (available sites) for 1ML coverage can be written as pq(=N). For a (3×3) surface supercell, the maximum occupancy is 9. At the given all adsorbates coverage of $\theta$, we can define the adsorption energy as,

$$E_{\theta}^{\text{ads}} = E_{\theta=0}^{\text{slab}} + \sum_{i=1}^{N} E_{\text{gas},i} - E_{\theta}^{\text{total}}$$  \hspace{1cm} (H.2)

where,

$E_{\theta}^{\text{ads}}$ = Total adsorption energy of all adsorbates at a coverage $\theta$

$E_{\theta=0}^{\text{slab}}$ = Energy of the slab

$E_{\text{gas},i}$ = Gas phase energy

$E_{\theta}^{\text{total}}$ = Energy of the slab + adsorbates

Adsorbate-adsorbate interactions and zero-coverage heat of chemisorption are denoted as $I_{\theta}^{\text{ads}}$ and $Q_{\theta}^{\text{ads}}$, respectively and can be extracted by fitting heat of chemisorption $Q_{\theta}^{\text{ads}}$ (Adsorption energy $E_{\theta}^{\text{ads}}$ per adsorbate) as a function of surface coverages $\theta$. $I_{\theta}^{\text{ads}}$ and $I_{\theta}^{\text{ads}}$ denote self-interactions and cross-interactions, respectively. For different species adsorption, we use $E_{(j,k)}^{\theta}$
and $Q_{(j,k)}$ representing $E_{\text{ads}}^{\theta_j}$ and $Q_{\text{ads}}^{\theta_k}$, respectively, where $j$ and $k$ are the kinds of adsorbates. For a simple case of self-interactions, heat of chemisorption $Q_{\text{ads}}^{\theta_m}$ is computed as,

$$Q_{\text{ads}}^{\theta_m} = \frac{E_{\text{ads}}^{\theta_m}}{m}, \quad \text{form} = 1, \ldots, N. \quad (H.3)$$

For the cross interactions $I_{AB}$ computations, $A$ is fixed at the minimum coverage (i.e. $\theta_A = 1/N$ ML) and $B$ is varied from 0 to the maximum occupancy of $(1-N)$. We assume a pairwise additivity in the case of effects in energy due to adsorption. For example, 1 atom/molecule of $B$ is added next to 1 atom/molecule of $A$, the interactions result due to ?the change in energy of $A$ due to $B$? and ?the change in energy of $B$ due to $A$?. Similarly, if another atom/molecule of $B$ is added next to $A$ and $B$ system, the interactions result from ?change in energy of $A$ due to second $B$?, ?change in energy of 1st $B$ due to 2nd $B$?, and ?change in energy of 2nd $B$ due to $A$ and 1st $B$?. We further assume that the effect of $A$ on $B$ is equivalent to the effect of $B$ on $A$. Hence, a generalized formula for the heat of chemisorption at any coverage of $B$ is given as [317]

$$Q_{(1,k)} = Q_{(1,k-1)} - \frac{E_{(1,k-1)} + E_{(0,1)} - E_{(1,k)} - 2 \times (k-1)I_{BB}}{2} \quad (H.4)$$

Here, we keep occupancy of $A$ to a minimum (i.e. 1), and $k$ varies form 1 to $(1-N)$. We estimate the $E_{(1,k-1)}$, $E_{(0,1)}$, and $E_{(1,k)}$ using DFT. When we fit $Q$ as a function of $?B$, we can estimate the cross-interaction $I_{AB}$. Table H.4 shows the calculated parameters for Pt(111) and Pd(111) surfaces.
Table H.4 computations of SO$_3\ast$-O$\ast$ interactions on Pt(111) and Pd(111). For Pt(111): O$\ast$-O$\ast$ interactions of 30.44 kcal/mol/ML and $E_{ads}^{(θ_O=0.11)} = E(0,1)$ of 98.6 kcal/mol are used and for Pd(111): O$\ast$-O$\ast$ interactions of 32.49 kcal/mol/ML and $E_{ads}^{(θ_O=0.11)} = E(0,1)$ of 99.7 kcal/mol are used.

<table>
<thead>
<tr>
<th>$θ_O$ML (at $θ_{SO_3}=0.11$)</th>
<th>0</th>
<th>0.11</th>
<th>0.22</th>
</tr>
</thead>
<tbody>
<tr>
<td>k</td>
<td>0</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>E(1,k) (kcal/mol) Pt(111)</td>
<td>30.85</td>
<td>127.22</td>
<td>218.02</td>
</tr>
<tr>
<td>E(1,k) (kcal/mol) Pd(111)</td>
<td>27.87</td>
<td>125.53</td>
<td>217.14</td>
</tr>
<tr>
<td>Q(1,k) (kcal/mol) Pt(111)</td>
<td>30.85</td>
<td>29.73</td>
<td>29.21</td>
</tr>
<tr>
<td>Q(1,k) (kcal/mol) Pd(111)</td>
<td>27.87</td>
<td>26.85</td>
<td>26.40</td>
</tr>
</tbody>
</table>

H.5  \textbf{SO$_3$ and O on the Surface Oxides of Pt(111) or Pd(111) Surfaces}

As expected, PtO$_2$/Pt(111) surface seems to be relatively passive. In this passive structure, each Pt is coordinated to 6 O atoms and each O atom is coordinated to 3 adjacent Pt atoms. Further addition of O atom on top position of Pt on the surface was not favored. A SO$_3$ molecule on the O atom of the surface oxide layer was barely stable. Higher coverages of SO$_3$ or O, and co-adsorption conditions were not stable. Surface oxide model of Pd showed significant affinity towards SO$_3$. Here, co-adsorption of SO$_3$ and O was not favored. We explored possible adsorption configurations of O and/or SO$_3$ on the surface. For SO$_3$, a 3-fold coordinated O on the surface was the most favored site. Co-adsorption configuration was constructed based on the information about the most stable sites for each species. Higher coverage configurations were not explored due to extremely large supercell size. The binding energy of O (or SO$_3$) adsorption on the surface oxides is given as:

$$E_{bind}^{O} = \frac{1}{N_O} \left[ E_{O+surf-oxd}^{DFT} - E_{surf-oxd}^{DFT} - \frac{N_O}{2} E_{O_2}^{DFT} \right]$$  \hspace{1cm} (H.5)
The binding energy definition here is different from the Equation H.1 since this is referenced with the surface oxide (not the clean surface) and also contains the energetic changes due to the formation of the surface oxides. The binding energies are given in Table H.5.

Table H.5 DFT computed binding energies of O/SO$_3$ adsorption on PtO$_2$-Pt(111) and PdO-Pd(111) surfaces. Binding energy per atom/molecule is given in case of mono species adsorption. Total binding energies are given for the co-adsorption (mixed O and SO$_3$) cases.

<table>
<thead>
<tr>
<th>Structure</th>
<th>Binding energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PtO$_2$-Pt(111)</td>
</tr>
<tr>
<td>1 O</td>
<td>2.55 (top, Pt)</td>
</tr>
<tr>
<td>1 SO$_3$</td>
<td>-0.12 (top, O)</td>
</tr>
<tr>
<td>2 SO$_3$</td>
<td>Unstable</td>
</tr>
<tr>
<td>3 SO$_3$</td>
<td>-</td>
</tr>
<tr>
<td>4 SO$_3$</td>
<td>-</td>
</tr>
<tr>
<td>5 SO$_3$</td>
<td>-</td>
</tr>
<tr>
<td>1 SO$_3$ + 1 O</td>
<td>Unstable</td>
</tr>
</tbody>
</table>

H.6 Surface Sulfate Models

To create the surface sulfate model on the (111) surface of Pt and Pd, we choose the (3×√3) surface supercell. Then, bulk structures of PtSO$_4$ and PdSO$_4$ (both P4$_2$/m and C2/c phases) are used to create an overlayer of sulfate on the clean slab. We observed no significant difference in energetics of the surface sulfate model created using two bulk sulfates phases. For example, the surface sulfate model of Pt(111) using P4$_2$/m bulk PtSO$_4$ was lower in energy by -0.05 eV compared to the model created using C2/c bulk PtSO$_4$. Hence, the choice of the model had no real impact on the phase diagrams. The surface sulfate models used in this work are shown in Figure H.3.
Fig. H.3 Representative surface sulfate models from bulk sulfates on the (111) surface with a $(3 \times \sqrt{3})$ surface supercell. Silver, red, and yellow spheres represent the Pt or Pd, Oxygen, and Sulfur respectively. Blue spheres represent the Pt or Pd in the surface sulfate models.
Appendix I

Computation of Free Energies due to Vibrational Contributions

Here the relative vibrational contributions are shown, taking clean surface as a reference, to free energy due to oxygen adsorption (see Figure I.1) and SO\(_3\) adsorption (see Figure I.2) on Pt(111) and Pd(111) surfaces. Only adsorbates and the top metal surface layer are allowed, as appropriate, to vibrate since the vibration of atoms away from the surface (sub-surface atoms) are assumed to cancel out in the computation of \(\Delta F^V\). We observed that the adsorption of SO\(_3\) shows slightly larger impact on free energy change compared to O adsorption on both surfaces. In oxygen adsorption, the relative free energy (\(\Delta F^V/A\)) remains positive below \(\sim 750\) K and it goes to negative range at higher temperature. The shift from positive to negative values of relative free energy occurs at \(\sim 580\) K in the case of SO\(_3\) adsorption. Overall, the vibrational contribution to free energy remains < 25 meV/Å for the catalytically important range of temperature. Hence, it will not have any significant impact on the overall results.
Fig. I.1 Vibrational contributions to the relative free energy ($\Delta F^V/A$) due to oxygen adsorption on Pt(111) and Pd(111) surfaces. Panel a: O adsorption on Pt(111) surface; panel b: O adsorption on Pd(111) surface. Relative change in free energy due to adsorption for a range of 0.25 ML to 1ML surface coverage and the surface oxide models are shown here.
Fig. I.2 Vibrational contributions to the relative free energy ($\Delta F^V/A$) as a function of temperature due to $\text{SO}_3$ adsorption on Pt(111) and Pd(111) surfaces. Panel a: $\text{SO}_3$ adsorption on Pt(111) surface; panel b: $\text{SO}_3$ adsorption on Pd(111) surface. Relative change in free energy due to adsorption for a range of 0.11 ML to 0.33 ML surface coverage and the surface sulfate models are shown here.
Appendix J

Density Functional Theory: Background

J.1 Density Functional Theory (DFT)

There are many flavors of ab-initio methods, which are being used to compute the properties of the material. In this thesis, the main focus will be on one particular flavor, or more correctly, combination of methodologies and approximations. That is the plane-wave pseudopotential method, within density functional theory, employing a gradient corrected functional to describe the exchange-correlation energy. Few key concepts are given below, which is required for the practical implementation of the DFT.

J.1.1 The Schrödinger Equation

The Schrödinger’s equation is the fundamental equation of physics for describing quantum mechanical behavior of a given non-relativistic physical system. The time independent Schrödinger equation is:

\[ \hat{H}\psi_i = E_i\psi_i \]  \hspace{1cm} (J.1)
where \( \hat{H} \) is the hamiltonian operator for a system of nuclei and electrons in the absence of electric and magnetic fields. \( \psi_i \) represents the wave function of the \( i^{th} \) state of the system and contains the sum of all information about the system. \( E \) is the energy of the state described by the \( \psi_i \). Virtually all of the physical properties of the interest can be obtained by the identification of the ground state energy \( E_0 \).

The wavefunction depends on the three spatial coordinates of each electrons and the nuclei, and one spin coordinate of each electron (i.e. \( \pm \frac{1}{2} \)). The wavefunction is not a observable quantity, but the square of the wavefunction \( \int |\psi(\vec{r})|^2 \, d\vec{r} \) is the probability of the electron with wave function \( \psi(\vec{r}) \) that will be found within a given volume element \( d\vec{r} \). The complete hamiltonian \( \hat{H} \) for a system with \( N \) nuclei and \( n \) electrons can be written as:

\[
\hat{H} = -\frac{1}{2} \sum_{i=1}^{n} \nabla_i^2 - \frac{1}{2} \sum_{A=1}^{N} \frac{1}{M_A} \nabla_A^2 - \sum_{i=1}^{n} \sum_{A=1}^{N} \frac{Z_A}{r_{iA}} + \sum_{i=1}^{n} \sum_{j=1, j \neq i}^{n} \frac{1}{r_{ij}} + \sum_{A=1}^{N} \sum_{A \neq B}^{N} \frac{Z_A Z_B}{R_{AB}}
\]

where the subscripts \( i \) and \( j \) represent the \( n \) electrons in the system and the subscript \( A \) and \( B \) represent the \( N \) nuclei in the system. \( M_A \) and \( Z_A \) are the mass and the charge, respectively, of the nucleus \( A \). The spatial coordinates of the electrons and nuclei ate \( \vec{r}_i \) and \( \vec{R}_A \), and the distance between particles \( i \) and \( A \), is \( r_{iA} = |\vec{r}_i - \vec{R}_A| \). the first two terms representing the kinetic energy \( \hat{T} \) of the electrons and nuclei, respectively, and the last three terms representing the electrostatic potential energy due to electron-nucleus attraction \( \hat{V}_{Ne} \), electron-electron repulsion \( \hat{V}_{ee} \), and nucleus-nucleus repulsion \( \hat{V}_{NN} \), respectively.

### J.1.2 The Born-Oppenheimer Approximation

Since the nuclei are much heavier than the electrons, their motion will be relatively much slower than the electrons. In the limit of stationary nuclei (referred to variously as the Born-Oppenheimer, adiabatic, or clamped-nuclei approximation) the electrons are thought of as
moving in the field of fixed nuclei. The result of this is that the kinetic energy terms can be separated and \( \hat{V}_{NN} \) becomes a constant. Then a simplified electronic Schrödinger equation is solved for the electronic wavefunction,

\[
\hat{H}_{\text{elec}} = \hat{T} + \hat{V}_{\text{Ne}} + \hat{V}_{\text{ee}}, \text{and}
\]

\[
\hat{H}_{\text{elec}} \psi_{\text{elec}} = E_{\text{elec}} \psi_{\text{elec}}
\]

The total energy of the system is:

\[
E_{\text{total}} = E_{\text{elec}} + E_{\text{nuc}}
\]

where

\[
E_{\text{nuc}} = \sum_{A=1}^{N} \sum_{A \neq B}^{N} \frac{Z_A Z_B}{R_{AB}}
\]

The Born-Oppenheimer approximation does not capture certain features like electronic conduction where electronic and nuclear dynamics are important. Time dependent Schrödinger equation can be solved precisely for single electron systems like Hydrogen atom. The introduction of another electron creates the complexity due to electrostatic interactions between them.

### J.1.3 Hartree-Fock Approximation

In 1930’s, Douglas Hartree and Vladimir Fock developed a method called Hartree-Fock approximation which assumes the total wavefunction is separable by the coordinates of each individual electron. Even though this assumption is not absolutely correct, it is able to approximately solve
for the individual one-electron wavefunctions $\psi_i$, which are then combined to obtain the total electronic wavefunction,

$$\psi(x_1, x_2, \ldots, x_n) = \psi_1(x_1) \psi_2(x_2) \ldots \psi_n(x_n) \quad (J.7)$$

It ignores all the important effects of exchange symmetry and so, instead of a simple product, an antisymmetrized product is used. The antisymmetrized product of $n$ one-electron wavefunctions is approximately equal to the true $n$-electron wavefunction $\psi_0$ (called Slater determinant $\Phi_{SD}$).

The individual one electron wave function which consists it are called spin orbitals. Because the instantaneous electrostatic repulsion does not enter into one electron potential $V_{HF}(i)$, electrons get too close to one another, and this causes the energy ($E_{HF}$) to be higher than the true ground state energy ($E_0$). This energy is termed as the correlation energy, $E_C$.

$$E_C = E_0 - E_{HF} \quad (J.8)$$

### J.1.4 Development of DFT

The wavefunction itself is not directly observable. The attraction of density functional theory is that it depends on the observable electron density, $\rho(\vec{r})$, with only three spatial coordinates regardless of the size of the system. The electron density is the square of the wavefunction.

### J.1.5 Hohenberg-Kohn Theorems

In 1964 Hohenberg and Kohn presented a mathematical proof that the electron density could uniquely determine the Hamiltonian, and hence the ground state energy. According to the first theorem, there is a one to one mapping between the electronic wavefunction, $\psi$, and the electron density, $\rho$. The second theorem states that the ground state electron density corresponds
to the density that minimizes the energy of the system. Thus the electron density contains all
the necessary information (uniquely, as the proof demonstrates) to determine $\hat{H}$. So, the ground
state energy $E_0$ can be written as the function of ground state electron density, $\rho_0$.

$$E_0[\rho_0] = T[\rho_0] + E_{ee}[\rho_0] + E_{ne}[\rho_0]$$  \hspace{1cm} (J.9)

where the components and their subscripts have the same meaning as above and are themselves
functionals of the electron density. This expression is separable into components which depend
on the system under consideration (i.e., on $\vec{R}_A$, $Z_A$ and $n$), the electrostatic attraction between
nuclei and electrons, and the non-system-specific components, $T[\rho_0]$ and $E_{ee}[\rho_0]$. These
system-independent components are grouped together into a single term, the Hohenberg-Kohn
functional, $F_{HK}[\rho_0]$. Hohenberg and Kohn did not provide specific guidance for how to actually
solve the problem and the functional form of $F_{HK}[\rho]$ is a total mystery. Later, Kohn and Sham
introduced an approach to solving for the electron density and ground state energy that was
more general, beginning with the next landmark paper in DFT history by Kohn and Sham (1965).

### J.1.6 Kohn-Sham Equations

Kohn and Sham extended the work of Hohenberg and Kohn and showed how $F_{HK}[\rho]$ can be
calculated. This was done by calculating $F_{HK}[\rho]$ exactly as much as possible, and leaving
the remainder in one smaller unknown term. This resembles aspects of the Hartree-Fock
approximation of one-electron wavefunctions. As in Hartree-Fock theory, the $n$-electron system
is reduced to a set of $n$ non-interacting one-electron systems. In Hartree-Fock theory this is
the basic approximation upon which the solution is built, but in DFT it is simply a tool to
calculate the exact component of an unknown term. For this non-interacting electron system, the
wavefunction is a Slater determinant and the kinetic energy for this \(T_{HF}\) is known exactly. The Slater determinant, \(\Phi_S\), consists of orbitals, \(\phi_i(\vec{x}_i)\), termed Kohn-Sham orbitals (to distinguish them from the spin orbitals of Hartree-Fock theory).

\[
\hat{f}^{KS} \phi_i = \varepsilon_i \phi_i \quad i = 1, 2, \ldots, n \tag{J.10}
\]

where \(\varepsilon_i\) are the energies of the Kohn-Sham orbitals, \(\phi_i\), and the Kohn-Sham operator, \(\hat{f}^{KS}\), is the one-electron Hamiltonian of the fictitious non-interacting system of electrons, which depends on the kinetic energy of the electrons and an effective one-electron potential, \(V_S\).

\[
\hat{f}^{KS} = -\frac{1}{2} \nabla^2 + V_S(\vec{r}) \tag{J.11}
\]

\(V_S\) is chosen to make the connection between model and reality by obtaining the electron density, \(\rho_S(\vec{r})\), same as the ground state density \(\rho_0(\vec{r})\), in the true system of interacting electrons.

\(F_{HK}[\rho]\) also contains the term \(V_{ee}[\rho]\) and can be split into a Coulomb term, \(J[\rho]\), which is known exactly, and another term, \(E_{ncl}[\rho]\), which describes all of the non-classical interaction between electrons, such as exchange and correlation. So, the Coulomb terms, \(J[\rho]\), and the noninteracting part of the kinetic energy, \(T_C[\rho]\), have been found exactly. A small part of the kinetic energy, \(T_C\), is influenced by correlation effects, and cannot be found by the method described above. The remainder, which cannot be treated exactly, is called the Exchange correlation energy, \(E_{XC}\), equal to \(T_C[\rho] + E_{ncl}[\rho]\). Then the \(V_S(\vec{r})\) is now \(V_{eff}(\vec{r})\)

\[
V_{eff}(\vec{r}) = \int \frac{\rho(\vec{r}_2^2)}{r_{12}} d\vec{r}_2 + V_{XC}(\vec{r}_1) - \sum_\Lambda \frac{Z_A}{r_{1A}} \tag{J.12}
\]

where

\[
V_{XC} = \frac{\delta E_{XC}}{\delta \rho} \tag{J.13}
\]
and the final Kohn-Sham equation becomes,

\[
\left[ -\frac{1}{2} \nabla^2 + V_{\text{eff}}(\vec{r}) \right] \phi_i = \varepsilon_i \phi_i \quad i = 1, 2, \ldots, n \tag{J.14}
\]

with the electron density,

\[
\rho = \sum_i^n < \phi_i | \phi_i > \tag{J.15}
\]

The DFT is a SCF theory as Kohn-Sham equations are solved iteratively where \( V_{\text{eff}}(\vec{r}) \) depends on the electron density, therefore on the orbitals. Everything except the functional form of \( E_{XC} \) is known exactly, and this is the major difference between density functional theory and wavefunction theory. In wavefunction theory, the approximation appears at the outset, in the assumption that the real wavefunction is a Slater determinant. In density functional theory, the approximation appears in the final step - the search for a suitable expression for the exchange-correlation energy.

### J.1.7 Exchange-Correlation Functionals

The Exchange-Correlation Functionals provide the estimate for exchange and exchange and correlations energies of electrons. The physical contributions are: kinetic energy correction due to the hypothetical, non-interacting electron system, exchange interaction for electrons of like spin, due to Pauli exclusion principle, which forbids electrons of like spin from occupying the same orbital, correlation of electrons of different spin, due to Coulomb interactions that prevent electrons of unlike spin from coinciding in space, which is otherwise allowed by the Pauli exclusion principle, and correction for the interaction of each electron with itself (self-interaction) artificially created by use of the classical Coulomb potential for a point charge (electron) with the entire electron density, \( \rho(r) \), including itself. Much of the work has been
done over the years to find reasonable estimates to the "true" functional, without which DFT cannot provide exact solutions.

The simplest way of approximating the exchange-correlation energy, introduced by Kohn and Sham, is called the local-density approximation (LDA). In this scheme the value of $E_{XC}$ per electron is taken to be the same as that of an electron in a uniform 'gas' of electrons. The use of the term 'local' means that the exchange-correlation energy at $\vec{r}$ in this approximation depends only on the electron density at $\vec{r}$. In other words, contributions to $E_{XC}$ from inhomogeneities in the real electron density at a distance from $\vec{r}$ (i.e., non-local contributions) are not considered.

$$V_{XC} = f[(\rho(\vec{r})]$$

(J.16)

Their performance in most areas of solid state studies was a significant improvement over the Hartree-Fock approximation. However, some of the poor performances are: binding energies are almost always overestimated, the wrong ground state is sometimes predicted to be stable (e.g. a non-magnetic hcp structure of iron), insulating systems which exhibit strong correlation effects (e.g., NiO) are predicted to be metallic, and weak bonds, such as hydrogen bonds, are not well described, and van der Waals forces are not accounted for.

Incorporating non-local correlation effects partially achieved by introducing a dependence on the gradient in the electron density around the location $r$, and this is known as the generalized gradient approximation (GGA):

$$V_{XC} = f[(\rho(\vec{r}), \nabla(\rho(\vec{r}))]$$

(J.17)

GGA tend to undo the overbinding effect, though in some cases this leads to severe underbinding. Noble gas cryocrystals, and molecular cryocrystals like $N_2$, are not predicted to be bound at all by some GGA’s. However, the correct magnetic and structural ground state is found for
metals like iron, chromium and manganese. Further extension of the XC functional are the Hybrid functionals which incorporate aspects of the Hartree-Fock method and does calculate the electron exchange energy exactly. New functionals are proposed and tested frequently to address specific shortcomings of the standard LDA and GGA approaches. In this work, we mostly use PBE GGA functional.

### J.1.8 Self-Consistency and Basis Functions

Kohn-Sham equations must be solved with a self-consistent, iterative approach as the Hamiltonian requires knowledge of the electron density where an initial electron density (usually some type of guess based on the particular atoms involved) is applied, then solutions for a new electron density obtained. This is then used to update the Hamiltonian to solve for yet another, improved electron density and it is repetitive. The self-consistency is reached when the energy (typically) fall below a predetermined threshold, or convergence criterion. Since the actual functional form of the electron density and electron wavefunctions are unknown, these are approximated by linear combinations of known functions, known as basis functions.

\[
\psi_i = \sum_{j} c_{i,j} \phi_{i,j}
\]

The weighting coefficient, \( c_{i,\sigma} \) of each basis function, \( \phi_{i,\sigma} \) determines the contribution to the overall wavefunction, \( \psi_i \). The optimal set of coefficients for a given choice of basis functions are solve rather than solving for the actual functional from. The cost of obtaining a solution increases with the number of basis functions used. Thus, it is most efficient to use basis functions that behave similarly to the wavefunction they are being used to approximate. For atom-centered basis functions, gaussian functions are commonly used due to their computational efficiency, but more expensive exponential functions are also used as basis functions because of
their similarities to actual wavefunctions, thus requiring fewer basis functions to achieve the same level of accuracy.

### J.1.9 Periodic Supercell Implementation

In this case, by the implementation of periodic boundary condition, a relatively smaller supercell is repeated infinitely in directions. Due to the periodic nature of the system, basis functions are chosen which are also periodic and will therefore be able to capture the correct behavior more efficiently. An infinite system means infinite number of electrons and wavefunctions. Wavefunctions can be indexed based on a measure of the periodicity of the system, called the reciprocal lattice vector, $k$. The $k$ vector can take on any value, but only a small set of values are unique, and these are referred to as the first Brillouin zone. Bloch’s theorem states that for periodic systems the wavefunction can always be written as the combination of a periodic part, indexed by $k$ and a part internal to the supercell, $\chi$.

\[
\psi^k = \sum_n e^{ika} \chi_n \tag{J.19}
\]

where the integer $n$ indexes an infinite sum over all multiples of the lattice constant, $a$, and $k$ ranges between $\pm a$. In DFT calculations, integration over values of $k$ numerically done, and the specification of reciprocal-space grid points for this integration is referred to as the $k$-point grid. An automatically generating an evenly-spaced $k$-point grid was developed by Monkhorst and Pack.

Planewave basis functions are essentially combinations of sine and cosine functions of the form

\[
\phi_p(x) = e^{i p x} \tag{J.20}
\]
where $p$ is chosen accordingly to make the periodicity of the basis function commensurate with the supercell. These are used to expand the supercell-invariant portion of Bloch's theorem in terms of periodic functions. The planewave expansion must be truncated at some point. This cutoff can be expressed in terms of an energy and it is termed as cutoff energy. By setting a cutoff energy, the basis set is completely specified for a given supercell geometry.
Appendix K

Hydrocarbon Emissions Oxidation on Platinum Based Diesel Oxidation Catalysts (DOC): A Combined Study Using Experiments and Microkinetic Modeling
Hydrocarbon Emissions Oxidation on Platinum Based Diesel Oxidation Catalysts (DOC): A Combined Study Using Experiments and Microkinetic Modeling

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Abstract

In this work, a comprehensive 52-step (26 reversible) microkinetic model is developed for C$_2$H$_4$ oxidation on Pt. Kinetic parameters for the detailed microkinetic model are extracted from ultra-high vacuum (UHV) temperature programmed desorption/reaction (TPD/TPR) experiments in literature and calculated using density functional theory (DFT). Starting with these kinetic parameters as initial estimates, the surface reaction mechanism is extensively tested against the experiments conducted under practically more relevant operating conditions, such as atmospheric pressure, dilute emissions concentrations, and short residence times, typically experienced by the Diesel Oxidation Catalysts (DOCs). C$_2$H$_4$ oxidation experiments are conducted using a fixed bed reactor for various operating conditions. Mechanistic analysis is presented to uncover the most important reaction chemistry. The microkinetic model shows very good agreement with multiple experimental data sets on monolith and fixed bed reactor scale.
1. Introduction

Hydrocarbons (HC) emission from fossil fuel based engines including diesel engines pose a serious threat to human health and environment. [1-4] Wide range of HC species (i.e. unsaturated, saturated, aromatic, and poly-aromatic hydrocarbons (PAH)) are present in the diesel engine exhaust. [1, 3, 5] A typical range of HC emission from diesel engines is 50–500 ppm C\textsubscript{1}. [4] To meet mandatory HC emissions standards set by the Environment Protection Agency (EPA) in the USA and European commission in Europe, Pt/Pd/Pt-Pd blend based diesel oxidation catalysts (DOCs) are employed in the engine emissions aftertreatment units. [3, 4] However, tremendous challenge lingers in optimal and robust design of DOC due to increasingly stringent emissions standards and exponential price hike of noble metal catalysts over the years. Thus, a fundamental understanding of HC oxidation chemistry on DOC is paramount.

Many experimental and computational studies in the past investigated the oxidation of C\textsubscript{2}H\textsubscript{4} on Pt. [6-14] Some notable experimental studies involve the ultra-high vacuum (UHV) TPD/TPR studies on various single crystal plane, [15, 16] X-ray based studies, [10] and fixed bed reactor type experiments [8, 13] to understand the oxidation mechanism. Steininger et al. suggested that H\textsubscript{2}O and CO\textsubscript{2} are the final oxidation products along with H\textsubscript{2} and CO formation. [16] Further, no indication for reaction intermediates containing carboxyl or hydroxyl groups was found from their high-resolution electron energy loss spectroscopy (EELS) and temperature programmed thermal desorption spectroscopy (TPDS) experiments. However, ethylidyne (CH\textsubscript{3}CH) intermediate was observed during C\textsubscript{2}H\textsubscript{4} only TPD experiments. [16] Similar observations about the oxidation products and intermediates were reported by Berlowitz et al. Stable
intermediates as a decomposition and oxidation products.[7, 14, 17] On the other hand, in fixed a bed type experiments in atmospheric pressure condition, Imanaka et. al.[13] observed complete conversion of C₂H₄ at 120 °C on Pt/Al₂O₃ catalysts.

Kinetic modeling of C₂H₄ oxidation has been reported by Sant et al. [6] on Pt based catalysts; however, the model consisted some global reactions without detailed intermediate steps and radical species. An oxidation mechanism at relatively high temperature (600 K - 900 K) and high pressure (60 bar) conditions was proposed by Lopez et al. [18] On the other hand, Stegelmann and Stoltze proposed a microkinetic model of C₂H₄ oxidation on Ag catalysts with ethylene oxide (C₂H₄O) and acetic acid (CH₃CHO) species as intermediates. [19] In general, previously reported kinetic models were unable to include many intermediate species and elementary steps, which can be crucial to capture reaction pathways correctly. Furthermore, a detailed mechanism of C₂H₄ oxidation on DOC, particularly relevant to the diesel engine exhaust condition, is not available and requires an attention.

This work investigates the detail mechanism of C₂H₄ oxidation, as representative HC oxidation from diesel engine exhaust, on Pt based DOC using a combinatorial approach including experiments, density functional theory (DFT), and microkinetic modeling. More specifically, we consider practically relevant operating conditions experienced by a typical DOC, i.e. ppm level of emissions concentration, high oxygen concentration (10 - 15 %), short residence time, and atmospheric pressure environment. Microkinetic modeling is used to predict surface coverages, most abundant reaction intermediate(s) (MARI), conversion, and rate determining steps without any a priori assumptions; however, it requires good initial parameters. Those parameters can come
either from experiments or from first principle DFT computations. In this study, we extract the kinetic parameters from the simulations of TPD/TPR experiments and from DFT calculation. Parameters, mostly for the radicals and reaction intermediates, are not always available from experimental studies. In that case, DFT studies can provide those parameters; however, the temperature/pressure dependent kinetic parameters cannot be obtained. Thus, we implement semi-empirical unity bond-index quadratic exponential potential (UBI-QEP) [20] method to compute coverage and temperature dependent quantities such as activation barriers. Finally, we conducted fixed bed reactor experiments in practically realistic DOC operating conditions for the validation of our model. The global reaction mechanism of C2H4 oxidation on Pt is given as:

\[ C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O. \]  

[1]

This paper is organized as follows. First, we discuss the methodology for the development of emissions oxidation chemistry in Section 2. In Section 3, we discuss the estimation of kinetic parameters from ultra-high vacuum (UHV) temperature programmed desorption/reaction (TPD/TPR) experiments in literature. Performance of the reaction mechanism is demonstrated in Section 4 at practically more relevant operating conditions. Preliminary mechanism reduction is discussed in Section 5. Finally, we discuss the overall limitations of this work in Section 6, followed by conclusions.

2. Methodology

2.1 DFT calculation

Our first principles DFT calculations were performed using the Vienna ab initio simulation package (VASP) [21, 22] utilizing the Perdew-Burke-Ernzerhof (PBE) [23]
functional, and the projector augmented wave (PAW) [24] frozen-core potentials. Plane-wave cut-off energy of 500 eV was used for the plane-wave expansion of the wave functions. The energy of a single atom or molecule was calculated using a $14 \times 14 \times 14$ Å$^3$ cell. A 5-layer slab and a $3 \times 3$ surface unit cell was considered to represent a Pt(111) surface. The two bottom layers of the slab were fixed and the other layers were allowed to relax. To avoid any periodic image interactions, an intervening 12-14 Å vacuum region was introduced. Monkhorst-Pack grids[25] of $4 \times 4 \times 1$ were used for Brillouin zone integration for the slab with $3 \times 3$ surface unit cell. For the Pt bulk calculations, Monkhorst-Pack mesh of $10 \times 10 \times 10$ was used. The binding energy $E_b$ of an atom or a molecule on the slab is defined as:

$$E_b = -[E_{\text{slab+adsorbate}} - E_{\text{slab}} - E_{\text{adsorbate}}]$$  [2]

where $E_{\text{slab+adsorbate}}$, $E_{\text{slab}}$, and $E_{\text{adsorbate}}$ represent the energy of the slab with the atom/molecule, energy of the clean slab, and the energy of an isolated atom/molecule, respectively. $E_b$ values are positive numbers, where an increase in positive number indicates the strong binding to the surface.

### 2.2 Experimental

#### 2.2.1 Catalysts characterization

Powder Pt/Al$_2$O$_3$ catalysts with 1% Pt loaded on alumina was purchased directly from Sigma-Aldrich. Platinum loading in the range of 0.70 - 1.30 % was confirmed by the company through ICP. The catalytic oxidation performance data was tested after a simple pretreatment. Figure 1 shows the characterization of Pt/Al$_2$O$_3$ using N$_2$ adsorption/desorption and SEM analysis. The isothermal N$_2$ adsorption and desorption
analysis of the Pt/Al₂O₃ powder catalysts is shown in Figure 1a. The BET surface area was calculated in the linear relative pressure range from 0.05 to 0.3. The typical hysteresis loop between the adsorption and desorption branches in figure 1a indicates that the existence of large amount of mesopores in the powder catalysts. The BJH desorption pore size distribution was also shown in Figure 1b, which revealed that the mesopores in the catalysts have a narrow size distribution with an average pore size around 10 nm. In panel c and d (Figure 1), SEM image and the elemental composition are shown confirming the Pt loading in the catalyst sample used in this study.

2.2.2 Catalytic performance tests

A fixed-bed type reactor, BenchCAT reactor from Altamira Instruments, was used for C₂H₄ oxidation experiments using Pt/Al₂O₃ powder catalysts. The reaction was carried out on 100 mg of Pt/Al₂O₃ catalyst loaded in a 0.34 cm i.d. quartz tube reactor inside a temperature-controlled furnace. Dycor Dymaxion mass spectrometer and Agilent Micro GC were used for the gas species analysis in the product stream. Effects of O₂ partial pressure (6 – 14 %), C₂H₄ concentration (500 – 3000 ppm), and space velocity (20000 – 60000 h⁻¹) on catalytic performance were tested for the temperature range of 50-300 °C. Ar was used as a balance gas in the experiments. All experiments were performed at near atmospheric pressure condition.

2.3 C₂H₄ oxidation chemistry development strategy

Microkinetic modeling of C₂H₄ oxidation consists of three major steps. First, elementary step reaction mechanism is developed for the oxidation chemistry based on reactants, intermediates, possible reaction pathways, and final products. Second, kinetic parameters
for the proposed reactions are extracted/estimated from literature surface science experiments, semi-empirical methods, and DFT calculations. Third, the surface reaction mechanism, combined with reactor modeling, is validated against multiple fixed bed experiments conducted in practically relevant operating conditions of DOC.

We note that some uncertainty may be associated with the microkinetic modeling due to various factors such as choice of reaction mechanism, kinetic parameters, experimental methods, and reactor modeling. Uncertainties due to the choice of reactions and species may be reduced with mechanism complexity; however, it reduces the practical usability. A good set of initial kinetic parameters is crucial for the microkinetic modeling. However, the kinetic parameters are inherently associated with some uncertainty due to the accuracy of estimation methods. Similarly, uncertainty may come from experimental methods due to products and intermediate identification techniques, availability of range of temperature, and species concentration profiles etc. On the other hand, reactor model uncertainty involves the role of diffusion vs. kinetics, representation of experimental non-uniformity with uniform mean field performance. [26] In general, many uncertainties come from various sources; nonetheless, provide justification for some parameter adjustment in the model.

2.3.1 Surface reaction mechanism development

Elementary step surface reaction mechanism of \( \text{C}_2\text{H}_4 \) oxidation consists of following 15 surface species: \( \text{H}^* \), \( \text{O}^* \), \( \text{OH}^* \), \( \text{H}_2\text{O}^* \), \( \text{C}^* \), \( \text{CO}^* \), \( \text{CO}_2^* \), \( \text{COOH}^* \), \( \text{CH}^* \), \( \text{CH}_2^* \), \( \text{CH}_3^* \), \( \text{C}_2\text{H}_2^* \), \( \text{C}_2\text{H}_3^* \), \( \text{C}_2\text{H}_4^* \), \( \text{C}_3\text{H}^* \), and \( \text{CCH}_2^* \). We considered the complete oxidation products such as \( \text{CO}_2 \) and \( \text{H}_2\text{O} \) as well as the other stable products such as \( \text{CO} \), \( \text{H}_2 \), and \( \text{C}_2\text{H}_2 \).
Various cross-interactive reaction pathways such as CO and H₂ oxidation, CO oxidation and carbon formation/oxidation, C₂H and CCH₂ oxidation chemistries are included in this work. In total, 52 elementary step reactions (26 reversible pairs) are considered in this study. Detail reaction mechanism is given in Table 2.

2.3.2 Kinetic parameter estimation/extraction

Kinetic parameters for the proposed mechanism were estimated/extracted using various methods, i.e. simulations of UHV temperature programmed surface science experiments in literature, semi-empirical UBI-QEP method[20], and first principles DFT calculations. For each stable species in the reaction mechanism, we have considered multiple TPD experimental data on Pt facets to extract the species binding energies (Q) and adsorbate-adsorbate interactions (α). Resulting parameters from the TPD simulations are shown in Table 1 and Figure 3. Detailed information about the experimental conditions and the experimental vs. model predicted peak temperatures is given in Section 3. Various TPR experimental data sets in the literature are used to extract the activation energies (E_a and bond indices (BI) for the reactions. Details of the TPR simulations are discussed in Section 3.

DFT calculations are carried out to estimate binding energies (Q) and adsorbate-adsorbate interactions (α) parameters of various intermediates and radicals along with stable species. Such calculations will reduce the inherent error introduced to the model due to parameters, as all parameters are computation with same level of theory and accuracy. The semi-empirical UBI-QEP method is used to estimate the coverage and temperature dependent activation energies on-the-fly in these simulations. Functional
forms to compute the activation energies using UBI-QEP formalism are discussed elsewhere. [2] In UBI-QEP formalism, temperature and coverage dependence to compute activation barriers are introduced through binding energy as shown in equation 3.

\[ Q(T) = Q_o - \alpha \theta - \gamma R (T - T_o) \]  

where, \( \alpha \) is the coverage dependence coefficient (kcal/mol/ML), \( \theta \) is the coverage of species (ML), \( \gamma \) is the temperature dependence coefficient for binding energies (unitless), \( R \) is the universal gas constant (kcal/mol/K), and \( T \) is the temperature (K). ML stands for monolayer. \( T_o \) is taken as 300 K. The temperature dependence (\( \gamma \)) is derived from the statistical mechanics based calculations for degrees of freedom lost/gained upon adsorption. [27] Bond index represents the position of the transition state along the reaction coordinate, which is also used to compute the activation energies in the UBI-QEP formalism. [27, 28] It is defined for a reaction pair in the forward direction only. It ranges between 0 and 1, with a typical initial estimate of 0.5 is used here.

Pre-exponential factors are taken either from literature (if available) or taken as initial estimates based on transition state theory (TST), e.g., \( 10^{13} \text{s}^{-1} \) for desorption and \( 10^{11} \text{s}^{-1} \) for Langmuir-Hinshelwood type surface reactions. Sticking coefficients for the adsorption reactions are taken from values reported in literature, otherwise taken as unity. Site density \( \sigma \) of \( 1 \times 10^{15} \text{sites/cm}^2 \) (\( 2.5 \times 10^9 \text{mol/cm}^2 \)) is used in the simulations based on the typical estimate for the most stable Pt(111) facet.[29]

2.3.3 Mechanism performance and validation at more realistic conditions
Validation of the developed model is crucial as the operating conditions experienced by the DOCs are significantly different from the UHV conditions for temperature programmed experiments or the zero-temperature conditions used in first principles calculations. Therefore, it is important to ensure that the microkinetic model developed with such parameters also works in the practically more relevant conditions, such as atmospheric pressure, dilute emissions concentrations (few tens to hundreds of ppm), and short residence times. In this work, fixed bed reactor experiments were conducted to obtain C_2H_4 oxidation data in realistic DOC conditions. The results obtained from our experiments are used to validate the developed model. Details of the mechanism performance and analysis of reaction paths are presented in Section 4.

Gas phase chemistry is taken into account through the GRI-Mech 3.0[30] reaction mechanism. Steady state isothermal PFR simulations were carried out using the developed oxidation mechanism performance against experimental results. Transient simulations were performed at the reactor inlet to get the initial surface species coverages. The resulting set of differential and algebraic (DAE) equations was solved using the DDASPK solver.

3. Results and discussions

3.1 C_2H_4 oxidation experiments

Figure 2 shows the essence of experimental results obtained for the C_2H_4 oxidation on Pt/Al_2O_3 catalyst. In panel a, we show the effect of C_2H_4 concentration on light off temperature. With the total flow rate of 50 sccm, we considered four different concentration (500 ppm – 3000 ppm) of C_2H_4 and 10% O_2 to see the effect. We clearly
see a huge shift in light off temperature ($T_{50}$, 50% conversion) as it moves from ~80 °C (for 500 ppm of C$_2$H$_4$) to ~140 °C (for 3000 ppm of C$_2$H$_4$). Our results are consistent with the experimental results of C$_2$H$_4$ complete conversion at 145 °C by Imanaka et al.[13], while considering 1% C$_2$H$_4$ and 4% O$_2$. The effect of O$_2$ concentration is shown in panel b (Figure 2). Unlike the C$_2$H$_4$ effect, we observed significantly lesser impact on light of temperature due to oxygen concentration considered here (6-14%). This is due to the fact that even 6% oxygen is already in excess compared to the ppm level of C$_2$H$_4$ concentrations considered here. In the light of oxygen concentration information on diesel engine exhaust, we see no significant impact of O$_2$ alone. We note that the outcome may be different while the concentration of oxygen is being relatively low (for example, engine in rich conditions). To depict the change in driving conditions (accelerating/decelerating), we conducted experiments with varying total flow rate (50 – 150 sccm) for 1000 ppm C$_2$H$_4$ and 10% O$_2$. Surprisingly, the effect on light off temperature was small even with the large variation in space velocity (~20000 - 60000 h$^{-1}$) (see Panel c, Figure 2).

### 3.2 TPD simulations

From TPD simulations, we extracted the binding energy of C$_2$H$_4$ (17.9 kcal/mol) and C$_2$H$_6$ (8.1 kcal/mol) along with adsorbate interactions $\alpha_{C_2H_4} = 1.9$ kcal/mol/ML and $\alpha_{C_2H_6} = 0.9$ kcal/mol/ML). The estimated binding energies are within the range of values reported in the literature (range of $Q_{C_2H_4} = 14 - 20$ kcal/mol and $Q_{C_2H_6} = 6 - 10$ kcal/mol). We have used the binding energies and adsorbate interactions of other stable species (for example: CO, H$_2$O, H$_2$, O$_2$ etc) obtained from TPD simulations in our previous work.[2]
Here, we discuss the C\textsubscript{2}H\textsubscript{4} TPD, which results in decomposition and formation of various products. Heating of C\textsubscript{2}H\textsubscript{4} to higher temperature leads to the decomposition and formation of C\textsubscript{2}H\textsubscript{6} and H\textsubscript{2} along with molecular desorption of C\textsubscript{2}H\textsubscript{4}. Our simulations correctly capture the products peaks as well as the molecular desorption of C\textsubscript{2}H\textsubscript{4}. In order to capture the experimental results, bond index of C\textsubscript{2}H\textsubscript{4}* + * $\leftrightarrow$ C\textsubscript{2}H\textsubscript{3}* + H* and C\textsubscript{2}H\textsubscript{3}* + * $\leftrightarrow$ C\textsubscript{2}H\textsubscript{2}*+ H* were modified to 0.75 and 0.76 respectively (starting from 0.5). With these minor adjustments, Figure 3c shows the agreement of model simulations and experimental peaks. Further, the simulated coverage profile in Figure 3d shows the dominant surface species. At low temperature, we see the decomposition of C\textsubscript{2}H\textsubscript{4}* and formation of H\textsubscript{2} and C\textsubscript{2}H\textsubscript{3}*. The C\textsubscript{2}H\textsubscript{3}* is stable up to 500 K and further decomposes to form CH* on the surface. The decomposition of CH* was not seen, although expected, due to the range of temperature considered. The kinetic parameters estimated from these TPD simulations are incorporated in the mechanism for further investigations through TPR and PFR simulations.

### 3.3 TPR simulations

Ultra high vacuum TPR experimental data from Steininger et al.[16] was taken to simulate the oxidation mechanism of C\textsubscript{2}H\textsubscript{4} on Pt(111) surface. Figure 4a shows the peaks for C\textsubscript{2}H\textsubscript{4} oxidation products (i.e. CO, CO\textsubscript{2}, H\textsubscript{2}, and H\textsubscript{2}O) and excess C\textsubscript{2}H\textsubscript{4} desorption rate from the C\textsubscript{2}H\textsubscript{4} oxidation TPR on Pt(111) and Figure 4b shows the model simulated coverage profiles with various surface species such as C\textsubscript{2}H\textsubscript{4}*, C\textsubscript{2}H\textsubscript{3}*, OH*, C\textsubscript{2}H*, and CH* over the range of temperature. The initial coverage include 0.35 ML of C\textsubscript{2}H\textsubscript{4}* and 0.23 ML of O* on the surface. Bond index (UBI-QEP parameter) of the reaction pair Rx
(C₂H₄* + O* ⇔ C₂H₃* + OH*) was modified to 0.9 (starting from 0.5) to correctly capture the experimental peak temperature.

RPA suggests that the oxidation and decomposition starts at low temperature with the formation of C₂H₃*, H*, and OH* on the surface as seen in figure 4b. Excess of C₂H₄* starts desorbing at ~200 K (peak at ~280 K, Figure 4a). At the same time, H₂O formation and simultaneous desorption occurs due to the reactions H₂O* + * ⇔ OH* + H* and H₂O* + O* ⇔ 2OH* resulting in a peak at ~290 K. At ~ 400 K, two experimental peaks of H₂O and CO₂ were observed. RPA shows that the H₂O formation is mostly due to the reactions C₂H₂* + H₂O* ⇔ C₂H₃* + OH* and C₂H₂* + OH* ⇔ C₂H* + H₂O*(~80 % combined) and partly due to the reactions H₂O* + * ⇔ OH* + H* and H₂O* + O* ⇔ 2OH* (~20% combined). The CO₂ formation is mainly due to the reactions COOH* + * ⇔ CO₂* + H* and CO₂* + H* ⇔ CO* + OH*, where CO* formation is primarily due to the reaction CH* + CO* ⇔ C₂H* + O*. Once CO₂* is formed on the surface, it desorbs immediately resulting a peak at ~400 K (Figure 4a). Finally, the last two peaks appear at ~500 K, i.e. experimental desorption peaks of CO and H₂. RPA suggests that the CO peak at this temperature range is primarily due to desorption of CO* from the surface due to sufficient energy at the elevated temperature. Formation of H* on the surface is due to the reaction C₂H₃* + * ⇔ C₂H₂* + H*, which desorbs as H₂ immediately. The C₂H₂* species further decompose into CH* on the surface, which can be seen in the coverage profile (Figure 4b). With no oxygen on the surface, the increase in temperature will leads to the decomposition of CH* species into C* and H* (not shown here).

3.4 Model performance under practically relevant operating conditions
The developed mechanism performed well against the experimental data from UHV conditions. However, the realistic condition (i.e. DOC operating condition) is significantly different as discussed in Section 2.3.3. Thus, we performed \( \text{C}_2\text{H}_4 \) oxidation experiments (discussed earlier in Section 3.1). Next, we discuss the validation/performance of the model using the data obtained from our fixed-bed reactor experiments.

### 3.4.1 Effect of \( \text{C}_2\text{H}_4 \) concentration

First, we show the model performance to capture the concentration effect of \( \text{C}_2\text{H}_4 \) (concentration 500-3000 ppm) on the light off temperature using 10% \( \text{O}_2 \). As discussed earlier, the impact of increasing \( \text{C}_2\text{H}_4 \) concentration on the light off temperature was quite large, which is captured by our model nicely for the entire temperature range. As expected, the conversion profile reaches complete conversion quite rapidly. The model performance is shown in Figure 6. We show the simulated coverage profile for different initial \( \text{C}_2\text{H}_4 \) feed concentrations at 100 °C. we clearly see the dominant coverage of \( \text{CH}^* \) and \( \text{CO}^* \) species on the surface. \( \text{O}^* \) coverage was not seen at lower temperature range; however, it becomes a MARI above \( \sim 150 \) °C (not shown here).

We have adjusted the bond index of the reaction pair \( R_{29}-R_{30}(\text{C}_2\text{H}_4^* + \text{O}^* \leftrightarrow \text{C}_2\text{H}_3^* + \text{OH}^*) \) to 0.65 to capture the low temperature profile correctly. We note that the adjustment was slightly different in TPR simulations. This modification is justified as some parameter refinement is generally required for the transition from UHV simulations to practically more relevant atmospheric pressure simulations on polycrystalline or supported catalysts. At higher temperature, abrupt change in coverage profiles was
observed while achieving the complete conversion state. This aligns well with the experimental observation as the complete conversion occurred in few degrees range after achieving ~50% C$_2$H$_4$ conversion.

3.4.2 Effect of O$_2$ concentration

The effect of O$_2$ concentration of the light off temperature was predicted without modifying any kinetic parameters of the model. This model was able to capture our experimental data well. The effect of oxygen concentration was not as big as compared to the effect of C$_2$H$_4$ concentration. Our model performance against the experimental data is shown in Figure 6.

3.4.3 Effect of flow rates

Our microkinetic model performed well and captured our experimental data well. In this case, varying the flow rate up to 300% showed no such drastic impact on the light off temperature. Our model performance against the experimental data is shown in Figure 7.

3.5 Sensitivity analysis

Sensitivity analysis was performed to identify the important reaction in the mechanism. The normalized sensitivity coefficient is defined as dlnP/dlnR (i.e., (dP/dR)×(R/P)), where dP is the change in parameter P (pre-exponential factors) and dR is the change in model response R (conversion). Figure 8 shows the most sensitive reaction pairs (10 pairs are shown here). The reaction pair R$_{29}$-R$_{30}$ (C$\_2$H$_4^\ast$ + O$^\ast$ ↔ C$\_2$H$_3^\ast$ + OH$^\ast$) was the most sensitive reaction in our analysis.
4. Conclusions

In this study, we performed a detailed study of C\textsubscript{2}H\textsubscript{4} oxidation on Pt based DOC using multiple methods including fixed bed experiments, DFT computations, and microkinetic modeling. Our experimental results suggested that the concentration of C\textsubscript{2}H\textsubscript{4} has the most impact on the light off temperature. This suggests that the slight fluctuation on the O\textsubscript{2} concentration and the total exhaust flow rate have no significant impact on the DOC performance. DFT computations are performed to obtain the kinetic parameters for our microkinetic model for C\textsubscript{2}H\textsubscript{4} oxidation on Pt. Our model performs well against all the experimental data. Finally we propose a 52 elementary step model for the oxidation of C\textsubscript{2}H\textsubscript{4} on Pt.

5. Acknowledgements

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References


Figures

**Figure 1:** Surface characterization of Pt/Al\(_2\)O\(_3\) powder catalysts: (a) N\(_2\) adsorption/desorption analysis; (b) BJH desorption pore size distribution; (c) Elemental analysis acquired under SEM; (d) ICP analysis. The weight percentage of Pt is found to be 1\%. 

<table>
<thead>
<tr>
<th>Element</th>
<th>O-K</th>
<th>Al-K</th>
<th>Pt-M</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wt. %</td>
<td>61.3</td>
<td>37.1</td>
<td>1.6</td>
</tr>
</tbody>
</table>
Figure 2: Experimental conversion profiles of C₂H₄ oxidation on Pt/Al₂O₃ catalyst showing the effect of C₂H₄ concentration (in panel a), effect of oxygen concentration (in panel b), and the effect of total flow rate (in panel c) on the light off temperature.
**Figure 3:** UHV-TPD analysis of (a) C$_2$H$_6$ desorption, (b) C$_2$H$_4$ desorption, (c) C$_2$H$_4$ decomposition, (d) C$_2$H$_4$ simulated coverage profiles, on Pt. Symbols represent the experimental data, whereas lines represent our simulations. Panel a: C$_2$H$_6$ TPD; [31] initial high and low C$_2$H$_6$* coverages are 0.3 ML and 0.07 ML, respectively; ramp rate =
5 K/s. Panel b: C\textsubscript{2}H\textsubscript{4} TPD\textsuperscript{[16]}; initial high and low C\textsubscript{2}H\textsubscript{4}* coverages are 0.5 ML and 0.16 ML, respectively; ramp rate = 2 K/s. Panel c: C\textsubscript{2}H\textsubscript{4} decomposition TPD\textsuperscript{[32]}; initial C\textsubscript{2}H\textsubscript{4}* coverage is 0.25ML; ramp rate = 2 K/s. Panel d: simulated surface coverage profile of C\textsubscript{2}H\textsubscript{4}* decomposition TPD; experimental conditions are same as Panel c. See Table 2 for the extracted kinetic parameters from these simulations.
Figure 4: UHV-TPR analysis of C₂H₄ oxidation on Pt(111). Panel a shows the rate of desorption of species and panel b shows the model simulated coverage profiles of surface species over a range of temperature. Symbols represent the experimental data, [16]
whereas lines represent the simulations. Operating conditions: initial surface coverages of O* and C2H4* are 0.23 ML and 0.35 ML, respectively; ramp rate=15.5 K/s. Simulations are in good agreement with the experimental data.
Figure 5: Model performance for prediction of C$_2$H$_4$ concentration impacts on light off temperature. Lines are the simulations and symbols are the experimental data points. Operating conditions are same as in Figure 2.
Figure 6: Model performance for prediction of $O_2$ concentration effects on light off temperature. Lines are the simulations and symbols are the experimental data points. Operating conditions are same as in Figure 2.
Figure 7: Model performance for prediction of flow rate effects on light off temperature. Lines are the simulations and symbols are the experimental data points. Operating conditions are same as in Figure 2.
Figure 8: Sensitivity analysis for the microkinetic model responses with respect to the pre-exponential factor pairs in the surface reaction mechanism shown in Table 2. Pre-exponentials are modified pairwise without perturbing the equilibrium constant. Only those reaction pairs with the highest normalized sensitivity coefficients \( \left[ \frac{d \ln R}{d \ln P}, \text{i.e.,} \left( \frac{dR}{dP} \right) \times \frac{P}{R} \right] \) are shown here. The sensitivity coefficients at three representative
temperatures (i.e. 90 °C, 100 °C, and 110 °C) are shown. Operating conditions are the same as in Figure 3.

**Table 1:** Species binding energies along with the coverage dependence.

<table>
<thead>
<tr>
<th>SN</th>
<th>Surface species</th>
<th>Extracted/calculated binding energy $Q$ (kcal/mol)</th>
<th>Coverage dependence $\alpha$ (kcal/mol)</th>
<th>Source /Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>O*</td>
<td>86.01</td>
<td>13.3$\theta_O$</td>
<td>TPD[2]</td>
</tr>
<tr>
<td>2</td>
<td>H*</td>
<td>60.89</td>
<td>1.9$\theta_H$</td>
<td>TPD[2]</td>
</tr>
<tr>
<td>3</td>
<td>OH*</td>
<td>63.0</td>
<td>33$\theta_O$</td>
<td>DFT[2]</td>
</tr>
<tr>
<td>4</td>
<td>H$_2$O*</td>
<td>10.27</td>
<td>-</td>
<td>TPD[2]</td>
</tr>
<tr>
<td>5</td>
<td>CO*</td>
<td>40.0</td>
<td>8.3$\theta_{CO}$</td>
<td>TPD[2]</td>
</tr>
<tr>
<td>6</td>
<td>CO$_2$*</td>
<td>3.6</td>
<td>-</td>
<td>TPD[2]</td>
</tr>
<tr>
<td>7</td>
<td>C*</td>
<td>158.20</td>
<td>-</td>
<td>DFT[2]</td>
</tr>
<tr>
<td>8</td>
<td>CH*</td>
<td>157.73</td>
<td>-</td>
<td>DFT (this work)</td>
</tr>
<tr>
<td>9</td>
<td>CH$_2$*</td>
<td>93.62</td>
<td>-</td>
<td>DFT (this work)</td>
</tr>
<tr>
<td>10</td>
<td>C$_2$H$_2$*</td>
<td>50.0</td>
<td>-</td>
<td>DFT (this work)</td>
</tr>
<tr>
<td>11</td>
<td>C$_2$H$_3$*</td>
<td>67.5</td>
<td>-</td>
<td>DFT (this work)</td>
</tr>
<tr>
<td>12</td>
<td>C$_2$H$_4$*</td>
<td>17.9</td>
<td>1.8$\theta_{C_2H_4}$</td>
<td>TPD simulation (this work)</td>
</tr>
<tr>
<td>13</td>
<td>C$_2$H*</td>
<td>103.6</td>
<td>-</td>
<td>DFT (this work)</td>
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<tr>
<td>14</td>
<td>CCH$_2$*</td>
<td>107.1</td>
<td>-</td>
<td>DFT (this work)</td>
</tr>
<tr>
<td>15</td>
<td>COOH*</td>
<td>56.26</td>
<td>-</td>
<td>DFT[2]</td>
</tr>
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</table>
Table 2: Activation energies in the last column are temperature and coverage dependent, but only representative values are shown at 300 K. Coverage dependence originates from the use of UBI-QEP for the estimation of activation energies, whereas the temperature dependence is derived from the statistical mechanics based calculations for degrees of freedom lost/gained upon adsorption. Further details on the functional form ‘f’ are given in Appendix B.

<table>
<thead>
<tr>
<th>No.</th>
<th>Reactions</th>
<th>Bond index (BI) [unitless]</th>
<th>Sticking coefficient [unitless] or Pre exponential factor [s⁻¹]</th>
<th>Activation energy at 300 K [kcal/mol]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Oxygen adsorption/desorption</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R₁</td>
<td>O₂ + 2* → 2O*</td>
<td>0.5</td>
<td>0.05</td>
<td>0</td>
</tr>
<tr>
<td>R₂</td>
<td>2O* → O₂ + 2*</td>
<td>0.5</td>
<td>1×10¹³</td>
<td>52.9 − 26.6θ₀ + f(T)</td>
</tr>
<tr>
<td><strong>CO oxidation</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R₃</td>
<td>CO + * → CO⁺</td>
<td>0.5</td>
<td>0.5 [29]</td>
<td>0</td>
</tr>
<tr>
<td>R₄</td>
<td>CO⁺ → CO + *</td>
<td>0.5</td>
<td>5.7×10¹⁶</td>
<td>40 − 8.3θ₃₀ − 2RΔT</td>
</tr>
<tr>
<td>R₅</td>
<td>CO₂ + * → CO₂⁺</td>
<td>0.5</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>R₆</td>
<td>CO₂⁺ → CO₂ + *</td>
<td>0.5</td>
<td>1×10¹³</td>
<td>3.6 − 2RΔT</td>
</tr>
<tr>
<td>R₇</td>
<td>CO₂⁺ + * → CO⁺ + O⁺</td>
<td>0.73</td>
<td>1×10¹¹</td>
<td>23.4 + f(θ₀, θ₀, T)</td>
</tr>
<tr>
<td>R₈</td>
<td>CO⁺ + O⁺ → CO₂⁺ + *</td>
<td>0.73</td>
<td>1×10¹⁰</td>
<td>18.6 + f(θ₀, θ₀, T)</td>
</tr>
<tr>
<td><strong>H₂ oxidation</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R₉</td>
<td>H₂ + 2* → 2H⁺</td>
<td>0.5</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>R₁₀</td>
<td>2H⁺ → H₂ + 2*</td>
<td>0.5</td>
<td>1×10¹³</td>
<td>17.6 − 3.8θ₃₀ + f(T)</td>
</tr>
<tr>
<td>R₁₁</td>
<td>H₂O + * → H₂O⁺</td>
<td>0.5</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>R₁₂</td>
<td>H₂O⁺ → H₂O + *</td>
<td>0.5</td>
<td>1×10¹³</td>
<td>10.3 − 2.5RΔT [120, 121]</td>
</tr>
<tr>
<td>R₁₃</td>
<td>OH⁺ + * → H⁺ + O⁺</td>
<td>0.5</td>
<td>1×10¹¹</td>
<td>27 + f(θ₀, θ₀, T)</td>
</tr>
<tr>
<td>R₁₄</td>
<td>H⁺ + O⁺ → OH⁺ + *</td>
<td>0.5</td>
<td>1×10¹¹</td>
<td>8.6 + f(θ₀, θ₀, T)</td>
</tr>
<tr>
<td>R₁₅</td>
<td>H₂O⁺ + * → OH⁺ + H⁺</td>
<td>0.5</td>
<td>1×10¹¹</td>
<td>18.3 + f(θ₀, θ₀, T)</td>
</tr>
<tr>
<td>R₁₆</td>
<td>OH⁺ + H⁺ → H₂O⁺ + *</td>
<td>0.5</td>
<td>1×10¹¹</td>
<td>12.6 + f(θ₀, θ₀, T)</td>
</tr>
<tr>
<td>R₁₇</td>
<td>H₂O⁺ + O⁺ → 2OH⁺</td>
<td>0.5</td>
<td>1×10¹¹</td>
<td>9.4 + f(θ₀, T)</td>
</tr>
<tr>
<td>R₁₈</td>
<td>2OH⁺ → H₂O⁺ + O⁺</td>
<td>0.5</td>
<td>1×10¹¹</td>
<td>22.1 + f(θ₀, T)</td>
</tr>
</tbody>
</table>
### Water promoted CO oxidation

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Stoichiometry</th>
<th>Preexponential Factor</th>
<th>Arrhenius Factor</th>
<th>Other Terms</th>
</tr>
</thead>
<tbody>
<tr>
<td>R19</td>
<td>CO$_2^<em>$ + H$^</em>$ → CO$^<em>$ + OH$^</em>$</td>
<td>0.5</td>
<td>$1 \times 10^{11}$</td>
<td>$5.4 + f(\theta_O, \theta_{CO}, \theta_H, T)$</td>
</tr>
<tr>
<td>R20</td>
<td>CO$^<em>$ + OH$^</em>$ → CO$_2^<em>$ + H$^</em>$</td>
<td>0.5</td>
<td>$1 \times 10^{11}$</td>
<td>$19 + f(\theta_O, \theta_{CO}, \theta_H, T)$</td>
</tr>
<tr>
<td>R21</td>
<td>COOH$^<em>$ + * → CO$^</em>$ + OH$^*$</td>
<td>0.5</td>
<td>$1 \times 10^{11}$</td>
<td>$5.8 + f(\theta_O, \theta_{CO}, T)$</td>
</tr>
<tr>
<td>R22</td>
<td>CO$^<em>$ + OH$^</em>$ → COOH$^*$ + *</td>
<td>0.5</td>
<td>$1 \times 10^{11}$</td>
<td>$18.7 + f(\theta_O, \theta_{CO}, T)$</td>
</tr>
<tr>
<td>R23</td>
<td>COOH$^<em>$ + * → CO$^</em>$ + H$^*$</td>
<td>0.5</td>
<td>$1 \times 10^{11}$</td>
<td>$2.1 + f(\theta_H, T)$</td>
</tr>
<tr>
<td>R24</td>
<td>CO$_2^<em>$ + H$^</em>$ → COOH$^*$ + *</td>
<td>0.5</td>
<td>$1 \times 10^{11}$</td>
<td>$1.3 + f(\theta_H, T)$</td>
</tr>
</tbody>
</table>

### C$_2$H$_4$ oxidation

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Stoichiometry</th>
<th>Preexponential Factor</th>
<th>Arrhenius Factor</th>
<th>Other Terms</th>
</tr>
</thead>
<tbody>
<tr>
<td>R25</td>
<td>C$_2$H$_4$ + * → C$_2$H$_4^*$</td>
<td>0.5</td>
<td>1</td>
<td>0.0</td>
</tr>
<tr>
<td>R26</td>
<td>C$_2$H$_4^*$ → C$_2$H$_4$ + *</td>
<td>0.5</td>
<td>$1 \times 10^{13}$</td>
<td>$17.9 - 1.8\theta_{C_2H_4} - 3\Delta T$</td>
</tr>
<tr>
<td>R27</td>
<td>C$_2$H$_4^<em>$ + C$_2$H$_3^</em>$ + H$^*$</td>
<td>0.5</td>
<td>$1 \times 10^{11}$</td>
<td>$16.35 + f(\theta_H, \theta_{C_2H_4}, T)$</td>
</tr>
<tr>
<td>R28</td>
<td>C$_2$H$_3^<em>$ + H$^</em>$ → C$_2$H$_4^*$ + *</td>
<td>0.5</td>
<td>$1 \times 10^{11}$</td>
<td>$15.6 + f(\theta_H, \theta_{C_2H_4}, T)$</td>
</tr>
<tr>
<td>R29</td>
<td>C$_2$H$_4^<em>$ + O$^</em>$ → C$_2$H$_3^<em>$ + OH$^</em>$</td>
<td>0.75</td>
<td>$1 \times 10^{11}$</td>
<td>$11.2 + f(\theta_H, \theta_{OH}, T)$</td>
</tr>
<tr>
<td>R30</td>
<td>C$_2$H$_3^<em>$ + OH$^</em>$ → C$_2$H$_4^<em>$ + O$^</em>$</td>
<td>0.75</td>
<td>$1 \times 10^{11}$</td>
<td>$28.8 + f(\theta_H, \theta_{OH}, T)$</td>
</tr>
<tr>
<td>R31</td>
<td>C$_2$H$_2^<em>$ + OH$^</em>$ → C$_2$H$_3^<em>$ + O$^</em>$</td>
<td>0.5</td>
<td>$1 \times 10^{11}$</td>
<td>$32.27 + f(\theta_H, \theta_{OH}, T)$</td>
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<tr>
<td>R32</td>
<td>C$_2$H$_3^<em>$ + O$^</em>$ → C$_2$H$_2^<em>$ + OH$^</em>$</td>
<td>0.5</td>
<td>$1 \times 10^{11}$</td>
<td>$5.54 + f(\theta_H, \theta_{OH}, T)$</td>
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<tr>
<td>R33</td>
<td>CCH$_2^<em>$ + OH$^</em>$ → C$_2$H$_3^<em>$ + O$^</em>$</td>
<td>0.5</td>
<td>$1 \times 10^{11}$</td>
<td>$39.23 + f(\theta_H, \theta_{OH}, T)$</td>
</tr>
<tr>
<td>R34</td>
<td>C$_2$H$_3^<em>$ + O$^</em>$ → CCH$_2^<em>$ + OH$^</em>$</td>
<td>0.5</td>
<td>$1 \times 10^{11}$</td>
<td>$0.0 + f(\theta_H, \theta_{OH}, T)$</td>
</tr>
<tr>
<td>R35</td>
<td>C$_2$H$_2^<em>$ + H$_2$O$^</em>$ → C$_2$H$_3^<em>$ + OH$^</em>$</td>
<td>0.5</td>
<td>$1 \times 10^{11}$</td>
<td>$23.32 + f(\theta_{OH}, T)$</td>
</tr>
<tr>
<td>R36</td>
<td>C$_2$H$_3^<em>$ + OH$^</em>$ → C$_2$H$_2^<em>$ + H$_2$O$^</em>$</td>
<td>0.5</td>
<td>$1 \times 10^{11}$</td>
<td>$9.26 + f(\theta_{OH}, T)$</td>
</tr>
<tr>
<td>R37</td>
<td>CO$^<em>$ + CH$_2^</em>$ → CCH$_2^<em>$ + O$^</em>$</td>
<td>0.5</td>
<td>$1 \times 10^{11}$</td>
<td>$39.77 + f(\theta_O, \theta_{CO}, T)$</td>
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<tr>
<td>R38</td>
<td>CCH$_3^<em>$ + O$^</em>$ → CO$^<em>$ + CH$_2^</em>$</td>
<td>0.5</td>
<td>$1 \times 10^{11}$</td>
<td>$7.92 + f(\theta_O, \theta_{CO}, T)$</td>
</tr>
<tr>
<td>R39</td>
<td>C$_2$H$_2^<em>$ + O$^</em>$ → C$_2$H$_3^<em>$ + OH$^</em>$</td>
<td>0.5</td>
<td>$1 \times 10^{11}$</td>
<td>$19.61 + f(\theta_O, \theta_{OH}, T)$</td>
</tr>
<tr>
<td>R40</td>
<td>C$_2$H$_3^<em>$ + OH$^</em>$ → C$_2$H$_2^<em>$ + O$^</em>$</td>
<td>0.5</td>
<td>$1 \times 10^{11}$</td>
<td>$19.56 + f(\theta_O, \theta_{OH}, T)$</td>
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<tr>
<td>R41</td>
<td>C$_2$H$_2^<em>$ + OH$^</em>$ → C$_2$H$_3^<em>$ + H$_2$O$^</em>$</td>
<td>0.5</td>
<td>$1 \times 10^{11}$</td>
<td>$12.7 + f(\theta_{OH}, T)$</td>
</tr>
<tr>
<td>R42</td>
<td>C$_2$H$_3^<em>$ + H$_2$O$^</em>$ → C$_2$H$_2^<em>$ + OH$^</em>$</td>
<td>0.5</td>
<td>$1 \times 10^{11}$</td>
<td>$0.0 + f(\theta_{OH}, T)$</td>
</tr>
<tr>
<td>R43</td>
<td>CH$^<em>$ + CO$^</em>$ → C$_2$H$_2^<em>$ + O$^</em>$</td>
<td>0.5</td>
<td>$1 \times 10^{11}$</td>
<td>$86.64 + f(\theta_O, \theta_{CO}, T)$</td>
</tr>
<tr>
<td>R44</td>
<td>C$_2$H$_2^<em>$ + O$^</em>$ → CH$^<em>$ + CO$^</em>$</td>
<td>0.5</td>
<td>$1 \times 10^{11}$</td>
<td>$0.0 + f(\theta_O, \theta_{CO}, T)$</td>
</tr>
<tr>
<td>R45</td>
<td>CO$^<em>$ + H$^</em>$ → CH$^<em>$ + O$^</em>$</td>
<td>0.5</td>
<td>$1 \times 10^{11}$</td>
<td>$44.7 + f(\theta_O, \theta_H, \theta_{CO}, T)$</td>
</tr>
<tr>
<td>R46</td>
<td>CH$^<em>$ + O$^</em>$ → H$^<em>$ + CO$^</em>$</td>
<td>0.5</td>
<td>$1 \times 10^{11}$</td>
<td>$10.94 + f(\theta_O, \theta_H, \theta_{CO}, T)$</td>
</tr>
<tr>
<td>R47</td>
<td>CH$^<em>$ + OH$^</em>$ → CH$_2^<em>$ + O$^</em>$</td>
<td>0.5</td>
<td>$1 \times 10^{11}$</td>
<td>$43.5 + f(\theta_O, \theta_{OH}, T)$</td>
</tr>
<tr>
<td>R48</td>
<td>CH$_2^<em>$ + O$^</em>$ → CH$_2^<em>$ + OH$^</em>$</td>
<td>0.5</td>
<td>$1 \times 10^{11}$</td>
<td>$1.28 + f(\theta_O, \theta_{OH}, T)$</td>
</tr>
<tr>
<td>R49</td>
<td>CH$^<em>$ + H$_2$O$^</em>$ → CH$_2^<em>$ + OH$^</em>$</td>
<td>0.5</td>
<td>$1 \times 10^{11}$</td>
<td>$33.6 + f(\theta_{OH}, T)$</td>
</tr>
<tr>
<td>R50</td>
<td>CH$_2^<em>$ + OH$^</em>$ → CH$^<em>$ + H$_2$O$^</em>$</td>
<td>0.5</td>
<td>$1 \times 10^{11}$</td>
<td>$4.06 + f(\theta_{OH}, T)$</td>
</tr>
<tr>
<td>R51</td>
<td>C$_2$H$_2^<em>$ + * → C$_2$H$_3^</em>$</td>
<td>0.5</td>
<td>1</td>
<td>0.0</td>
</tr>
<tr>
<td>R52</td>
<td>C$_2$H$_2^*$ → C$_2$H$_2$ + *</td>
<td>0.5</td>
<td>$1 \times 10^{13}$</td>
<td>$50 - 3\Delta T$</td>
</tr>
</tbody>
</table>