SIMULATION OF NO OXIDATION CATALYSIS OVER
OXYGEN-COVERED TRANSITION METAL SURFACES

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Doctor of Philosophy

by

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Abstract
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Lean burn (excess O$_2$) automobile engines are more energy efficient than their stoichiometric or rich (O$_2$ starved) burn counterparts, but technologies do not exist to effectively remediate harmful NO$_x$ ($x=1,2$) compounds from lean exhaust. Current removal strategies rely in part on the catalytic oxidation of NO to NO$_2$

\[ \text{NO} + \frac{1}{2}\text{O}_2 \rightarrow \text{NO}_2 \]

Pt is the most active metal, but there is a strong drive to use less expensive materials. Understanding how Pt functions is a key step in catalyst design.

Prior experiments and theory indicate the catalysis is promoted at high O coverage ($\theta_O = N_O/N_{Pt}$), but too much O is inhibitive: Pt is prone to oxidative deactivation. The rate is promoted by high O$_2$ pressures and inhibited by product NO$_2$. The latter is true even after correcting for approach to equilibrium, suggesting NO$_2$ hinders the reaction kinetics.

In this work, we attempt to understand these phenomena with molecular simulation. We use density functional theory, first principles thermodynamics, and mean field microkinetic modeling to elucidate the catalysis under actual reaction conditions. We find the reaction occurs at 0.25–0.50 monolayer O. At these $\theta_O$,
the kinetics of O₂ dissociation (O₂ + 2* → 2O*) are strongly inhibited due to repulsive interactions on the surface, but the O–NO bond formation (NO* + O* ⇌ NO₂ + 2*) kinetics are facile. In contrast to prior reports, we show O₂ dissociation is rate limiting, and O–NO bond formation is equilibrated. The rate is strongly dependent on pO₂, and the O coverage is governed by pNO₂/pNO, leading to the observed rate inhibition by NO₂. These observations are in excellent agreement with experiment.

We apply our models to other transition metals and transition metal alloys to facilitate new catalyst design. Analysis indicates such materials should exhibit nearly identical behavior to Pt, offering no improvements in rate or propensity to oxidize. Screening the catalytic properties of Au nanoparticles and the O buffering properties of Co₃O₄/metal oxide supports is recommended for future work.
This dissertation is dedicated to all my family, friends, teachers, mentors, coaches, and colleagues who have pushed me to achieve.
“An inventor is a man who asks ‘Why?’ of the universe and lets nothing stand between the answer and his mind.”

-Ayn Rand
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SYMBOLS

\( a \)  lattice constant
\( A \)  surface area
\( C \)  concentration
\( d \)  distance
\( E \)  energy
\( F \)  Helmholtz free energy
\( \vec{F} \)  force
\( \mathcal{F} \)  gas flux
\( G \)  Gibbs free energy
\( \hat{\mathcal{H}} \)  Hamiltonian operator
\( H \)  enthalpy
\( h \)  Planck’s constant
\( k \)  reaction rate constant
\( k_B \)  Boltzmann’s constant
\( k^a \)  spring force constant
\( K \)  equilibrium constant
\( L \)  number of surface sites
\( m \)  mass
\( N \)  number
$N_A$  Avogadro’s number

$p$  partial pressure

$P$  pressure

$\mathcal{P}$  probability

$q$  partial charge

$Q$  canonical ensemble partition function

$r$  reaction rate

$\vec{r}$  vector, distance

$R$  ideal gas constant

$R^2$  coefficient of determination

$S$  entropy

$S$  sticking coefficient

$T$  temperature

$\mathcal{T}$  kinetic energy

$U$  internal energy

$V$  volume

$\vartheta$  potential energy

$X$  conversion

$X$  configuration

$X_{rc}$  degree of rate control

$y$  mole fraction (gas phase)

$Z$  nuclear charge

$\alpha$  reaction order

$\beta$  approach to equilibrium, reversibility
\( \gamma \) surface energy
\( \Gamma \) k-point at (0,0,0)
\( \epsilon \) error
\( \zeta \) slope
\( \theta \) coverage
\( \mu \) chemical potential
\( \nu \) vibrational frequency
\( \xi \) y-intercept
\( \rho \) density
\( \tau \) residence time
\( \phi \) Bloch function
\( \psi \) wavefunction
\( \omega \) degeneracy

‡ transition state
<table>
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<td>act</td>
<td>activation</td>
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<tr>
<td>ads</td>
<td>adsorption, adsorbate</td>
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<td>AES</td>
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form formation
FPT first principles thermodynamics
GGA generalized gradient approximation
HC hydrocarbon
HCP hexagonal close packed
HREELS high resolution electron energy loss spectroscopy
indep independent
int interacting, integral
kMC kinetic Monte Carlo
LDA local density approximation
LEED low energy electron diffraction
LNT lean NO\textsubscript{x} trap
M metal
max maximum
MEP minimum energy path
ML monolayer
NEB nudged elastic band
NEXAFS near edge X-ray absorption fine structure
nn nucleus-nucleus
NN nearest neighbor
NSC NO\textsubscript{x} storage catalyst
NSR NO\textsubscript{x} storage and reduction
PAW projector augmented wave
PES potential energy surface
PM particulate matter
<table>
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<th>Abbreviation</th>
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<td>PW91</td>
<td>Perdew-Wang GGA implementation from 1991</td>
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<tr>
<td>RAIRS</td>
<td>reflection absorption infra red spectroscopy</td>
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<tr>
<td>RDS</td>
<td>rate determining step</td>
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<tr>
<td>rxn</td>
<td>reaction</td>
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<tr>
<td>SCR</td>
<td>selective catalytic reduction</td>
</tr>
<tr>
<td>STM</td>
<td>scanning tunneling microscope</td>
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<td>surf</td>
<td>surface</td>
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<td>TBT</td>
<td>atop-bridge-atop geometry</td>
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<td>TFB</td>
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<td>THB</td>
<td>atop-HCP-bridge geometry</td>
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<tr>
<td>TOF</td>
<td>turn over frequency</td>
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<td>TPD</td>
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<td>temperature programmed reaction</td>
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<td>TS</td>
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<td>TWC</td>
<td>three way catalyst</td>
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<td>UHV</td>
<td>ultra high vacuum</td>
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<td>exchange correlation</td>
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<td>X-ray photoelectron spectroscopy</td>
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<td>ZP</td>
<td>zero point</td>
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ACKNOWLEDGMENTS

This project has been funded by the Department of Energy National Energy Technology Laboratory through the University Computational Materials Consortium, the Department of Energy Basic Energy Sciences grant number DE-FG02-06ER15830-001, and the University of Notre Dame.

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1.1 NO\textsubscript{x}: Harmful By-Products of Combustion

The global demand for energy is steadily increasing, and combustion of fossil fuels for energy is increasing concomitantly \[6\]. One of the primary concerns with fossil fuel burning in air is that it releases harmful pollutants into the atmosphere. CO\textsubscript{2} contributes strongly to global warming \[6, 106\], and unspent hydrocarbons (HCs) and CO released in incomplete combustion deteriorate air quality and cause health problems \[6, 106\]. NO\textsubscript{x} \((x = 1, 2)\) compounds are also formed from N\textsubscript{2} at high \(T\). NO\textsubscript{x} are metastable to their molecular constituents N\textsubscript{2} and O\textsubscript{2} at standard conditions \((T = 298 \text{ K}, P = 1 \text{ bar})\),

\[
\frac{1}{2}N_2 + \frac{1}{2}O_2 \rightarrow NO \quad \Delta H_{\text{rxn}}^\circ = +90\text{kJ mol}^{-1} \quad (1.2)
\]

\[
NO + \frac{1}{2}O_2 \rightarrow NO_2 \quad \Delta H_{\text{rxn}}^\circ = -60\text{kJ mol}^{-1} \quad (1.3)
\]

but they form readily in air at high temperature \[176, 217\]. “Thermal” NO\textsubscript{x} represent the majority of NO\textsubscript{x} in combustion exhaust and form via the Zel’dovich
mechanism

\[ \text{O + N}_2 \rightarrow \text{NO + N} \quad (1.4) \]

\[ \text{N + O}_2 \rightarrow \text{NO + O} \quad (1.5) \]

“Prompt” NO\textsubscript{x} form via reaction of hydrocarbon radicals with N\textsubscript{2} at high temperature, and “fuel” NO\textsubscript{x} form by oxidation of N-containing molecules in fuel\[220\]. Rapid cooling of exhaust gases leaves NO\textsubscript{x} kinetically trapped in air\[217\].

NO\textsubscript{x} inflows to the troposphere from natural processes are exactly balanced by outflows from precipitation\[214\]. In contrast, tropospheric inflows from anthropogenic sources are unbalanced because there is no available outflow medium.

Fuel combustion in the US alone accounts for more than 20 million short tons of NO\textsubscript{x} inflows to the troposphere annually, with nearly half that coming from transportation sources\[6\]. There are several adverse effects of tropospheric NO\textsubscript{x}.

They interact with sunlight to produce ozone\[214, 220\]

\[ \text{NO}_2 + h\nu \rightarrow \text{NO + O} \quad (1.6) \]

\[ \text{O + O}_2 + \text{CM} \rightarrow \text{O}_3 + \text{CM} \quad (1.7) \]

\[ \text{O}_3 + \text{NO} \rightarrow \text{NO}_2 + \text{O}_2 \quad (1.8) \]

( where CM is a carrier molecule such as N\textsubscript{2} or O\textsubscript{2}), a component of photochemical smog. They also react with water to form HNO\textsubscript{3}, which leads to acid rain\[6\].

NO\textsubscript{x} has a four day residence time in the troposphere\[214\], so if all anthro-
pogenic releases ceased, tropospheric NO\textsubscript{x} concentrations would rapidly decrease to their balanced levels (about 0.1 teragrams) \cite{214}. Combustion strategies that minimize NO\textsubscript{x} release, particularly in the transportation sector, will contribute significantly to reducing anthropogenic NO\textsubscript{x} release. “Lean” (excess O\textsubscript{2}) burn processes are attractive options because they operate at lower temperatures, are more fuel efficient, and emit fewer HCs, CO, and NO\textsubscript{x} than stoichiometric or rich (O\textsubscript{2}-starved) burn processes \cite{68, 106, 123, 133}. However, exhaust treatment strategies do not exist to effectively remediate NO\textsubscript{x} from lean exhaust \cite{217}. One of the major outstanding challenges in designing lean combustion engines is effective remediation of NO\textsubscript{x} from emissions \cite{217}. Catalytic technologies promise to facilitate this problem \cite{68, 106, 123, 217}.

1.2 Catalysis for NO\textsubscript{x} Remediation in Lean-Burn Vehicles

1.2.1 NO\textsubscript{x} Storage Catalysts

NO\textsubscript{x} storage catalyst (NSC) strategies are rooted in the so-called Three Way Catalyst (TWC), which is comprised of Pt and/or Pd and Rh supported on Al\textsubscript{2}O\textsubscript{3} and CeO\textsubscript{2} \cite{106, 223}. TWCs effectively oxidize HCs and CO (on Pt and Pd) and reduce NO\textsubscript{x} (on Rh) in stoichiometric Otto engine exhaust \cite{123, 223}, but they are much less effective for lean burn Otto engines. Lean burn Otto engines operate in alternating lean and rich cycles, and TWCs cannot effectively reduce NO\textsubscript{x} in the lean (i.e. oxidizing) cycles \cite{68, 217}. NO\textsubscript{x} storage catalysts, such as the NO\textsubscript{x} Storage and Reduction Catalyst (NSR), or Lean NO\textsubscript{x} Trap (LNT), were developed to address this \cite{63, 78, 165, 223, 237}. The basic composition of NSCs is the same as TWCs in that they are comprised of a metal catalyst on a metal oxide support. However NSCs use different metals for different functions. NSCs
are comprised of Pt/BaO/Al₂O₃. In lean conditions, NO is oxidized to NO₂ on the Pt component [165],

$$\text{NO} + \frac{1}{2}\text{O}_2 \xrightarrow{\text{Pt}} \text{NO}_2$$  \hspace{1cm} (1.9)

and product NO₂ is stored as a nitrate (NO₃⁻) on the BaO component. In stoichiometric conditions stored NO₃⁻ is released as NO₂, and NO₂ is reduced to N₂ by HCs and CO on the Pt component [165]

$$\text{NO}_2 + \text{H}_2 + \text{CO} \xrightarrow{\text{Pt}} \text{Pt} \xrightarrow{\text{Pt}} \text{N}_2 + \text{H}_2\text{O} + \text{CO}_2$$  \hspace{1cm} (1.10)

NSCs effectively reduce up to 85% of NOₓ emissions in lean burn Otto engine exhaust [165, 237].

1.2.2 Particulate Matter and NOₓ Reduction Systems

Exhaust from continuous lean burn operation is more difficult to control because there is no stoichiometric cycle in which to reduce NOₓ. Diesel engines operate in this manner. Further, they release particulate matter (PM, primarily soot), which must also be remediated [223]. Typical NOₓ and PM releases from diesel combustion are roughly inversely proportional to each other, so an engine operating point can be chosen such that the releases are optimal for the available catalyst system [17]. Simultaneous PM and NOₓ remediation systems are comprised of a Pt catalyst upstream of a PM filter [17, 181]. The filter is a channeled monolith that has half the channels sealed off at the inlet and the other half sealed off at the outlet. Inlet gases are thus forced through the channel walls, leaving PM stranded in the filter. PM is oxidized to CO₂ within the monolith by NO₂ formed
via oxidation of exhaust NO on the upstream Pt catalyst (Equation 1.9). \[ PM + NO_2 \rightarrow CO_2 + NO \] (1.11)

More efficient variations use monoliths coated with NO\textsubscript{x} storage material, allowing continuous reduction of NO\textsubscript{x} [18] or NO oxidation catalyst material, promoting further NO and thus PM oxidation.

1.2.3 Selective Catalytic Reduction Catalyst

Selective Catalytic Reduction (SCR) catalysts are also used to remediate NO\textsubscript{x} from diesel and lean burn gasoline engine exhaust. These catalysts do not treat PM, so diesel engines with SCRs operate under conditions which minimize PM and maximize NO\textsubscript{x} emissions. SCR catalysts promote NO\textsubscript{x} reduction by CO + H\textsubscript{2}, HCs, or, most commonly, NH\textsubscript{3} [105]. NH\textsubscript{3} is commonly supplied to the catalyst through liquid urea, which hydrolyzes in vehicle exhaust [105].

\[ CO(NH_2)_2 + H_2O \rightarrow 2NH_3 + CO_2 \] (1.12)

SCRs for vehicles are comprised of metal-substituted zeolites [68]. They effectively reduce NO\textsubscript{x} to N\textsubscript{2} and H\textsubscript{2}O [105].

\[ NH_3 + NO_x + oxidant \rightarrow N_2 + H_2O \] (1.13)

where traditionally the “oxidant” is O\textsubscript{2} (g). Recent studies show the rate of reduction is faster and more effective at low T when the reactants include an equimolar mixture of NO:NO\textsubscript{2} [128, 131, 244], and the most effective SCR catalysts
are located downstream of an oxidation catalyst, which promotes NO oxidation to NO₂ (Reaction 1.9).

1.3 NO Oxidation in the Gas Phase

Pt-catalyzed NO oxidation to NO₂ (Reaction 1.9) is a key step in all the NOₓ remediation technologies discussed in the previous section. To understand the surface phase thermodynamics and kinetics, i.e. the catalysis, it is useful to first understand the gas phase thermodynamics and kinetics. The reaction is 1st order in O₂ and 2nd order in NO [175]. The rate constant, \( k_{NO₂} \), at standard T is on the order of \( 10^3 L^2 mol^{-2} s^{-1} \) [175]. The rate is

\[
\frac{d[NO₂]}{dt} = \frac{1}{2} k_{NO₂} [NO]^2 [O₂]
\]

A typical untreated lean burn exhaust stream may contain 100 ppm NO and 5% O₂ [106]. The NO₂ formation rate at 298 K and 1 bar total pressure with \( y_{NO} = 100 \) ppm and \( y_{O₂} = 5\% \) (\( y \) denotes mole fraction) is \( 10^{-10} \) mol L⁻¹ s⁻¹. The rate is small despite the reasonably large \( k_{NO₂} \). The kinetics of gas phase NO oxidation are inhibited by “termolecularity,” that is, the requirement that two NO collide simultaneously with an O₂ in order to break the O=O bond and form two O–NO ones. Catalysts alleviate the termolecularity by activating the O=O bond

\[
O₂ + 2* \rightarrow 2O*
\]

and “trapping” O, therefore facilitating the O–NO collision. In Equation 1.15, * is a binding site, and O* is catalyst-bound O. The catalyzed rate is up to 10 orders of magnitude greater than the gas phase rate.
Figure 1.1. Temperature-dependent equilibrium NO conversion for NO oxidation given 100 ppm NO and 0 ppm NO$_2$ initially in 50 ppm, 500 ppm, 0.5%, and 5% O$_2$ in a balance of inerts (total pressure of 1 bar).

The standard heat ($\Delta H_{\text{rxn}}^\circ$) and entropy ($\Delta S_{\text{rxn}}^\circ$) of NO oxidation are $-57.19$ kJ mol$^{-1}$ ($-0.5927$ eV) and $-73.26$ J mol$^{-1}$ K$^{-1}$ ($-0.7592$ meV K$^{-1}$), respectively [176]. Due to the small $\Delta H_{\text{rxn}}^\circ$, the gas phase equilibrium switches from products to reactants at relatively low $T$ (Figure 1.1). Temperature programmed reaction (TPR) experiments of Pt-catalyzed NO oxidation [182] show that the reaction is equilibrium limited. Pt “lights off” for NO$_2$ formation at approximately 600 K. Below that, the realizable NO conversion is near 0.

The thermodynamics of NO oxidation are much different than for the more familiar CO oxidation

$$\text{CO} + 1/2\text{O}_2 \rightarrow \text{CO}_2 \quad (1.16)$$

The latter is much more exothermic, $\Delta H_{\text{rxn}}^\circ = -2.93$ eV, and it therefore achieves
CO conversions near unity up to 2000 K. Pt-catalyzed CO oxidation has been studied extensively over the years and is now well characterized [37, 41, 64, 65, 67, 186, 192, 239], but much work is needed to fully understand catalyzed NO oxidation.

1.4 Transition Metals as Oxidation Catalysts

Oxidation catalysts perform two tasks effectively: breaking an O=O bond (Reaction 1.15) and forming O–reductant bonds

\[
\text{reductant} + O^* \rightarrow \text{reductant} - O + *
\] (1.17)

Because they have partially filled d-electron shells\(^1\) that readily mix with O p, transition metals make excellent oxidation catalysts. Early transition metals have such high affinities for oxygen that they readily form bulk oxides [39], which tend to be inactive for O\(_2\) activation. Late transition metals are less reactive and more common.

O binding energy

\[
M + O \rightarrow M - O \quad \Delta E = E_{M-O} - E_M - E_O
\] (1.18)

where M is a bulk transition metal with an exposed surface, is an important property of oxidation catalysts [177]. Binding energies calculated with Density Functional Theory (DFT) for many late transition metals are shown in Table [1.1].

In general metals further to the left of a period and further up in a family in

\(^1\)Exceptions are Cu, Ag, Au

\(^2\)Energies are average integral binding energies at 1/4 ML O, computed with ultrasoft pseudopotentials and the generalized gradient approximation exchange correlation functional.
TABLE 1.1

DFT-CALCULATED OXYGEN BINDING ENERGIES (in eV) WITH RESPECT TO O ON FLAT TRANSITION METAL SURFACES

<table>
<thead>
<tr>
<th></th>
<th>Fe</th>
<th>Co</th>
<th>Ni</th>
<th>Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>−6.9</td>
<td>−5.3</td>
<td>−5.4</td>
<td>−4.3</td>
</tr>
<tr>
<td>Ru</td>
<td>−5.6</td>
<td>−4.9</td>
<td>−4.1</td>
<td>−3.3</td>
</tr>
<tr>
<td>Os</td>
<td>−5.5</td>
<td>−4.6</td>
<td>−3.9</td>
<td>−2.5</td>
</tr>
</tbody>
</table>

the Periodic Table have stronger (more negative) O binding energies \[98, 150, 247\]. Recent theoretical work indicates activity for O\(_2\) activation is correlated to O binding energy \[177\]. Ru, for example, binds O relatively strongly and is commonly used for CO oxidation \[22, 41, 91–93, 192, 202, 203, 205–207, 232\] (although to date there is controversy as to whether Ru metal or RuO\(_2\) is the active phase for the catalysis \[92, 187\].) Experimental evidence shows that it is much more active at low \(T\) than Pd, Pt, and Ir \[41\].

The optimal catalyst for NO oxidation must maximize facility for O=O bond activation subject to the constraint that O–NO bond formation

\[
\text{NO} + \text{O}^* \longrightarrow \text{NO}_2 + *
\]

is exothermic. Pt is commonly used \[33, 44, 48, 53, 54, 56, 103, 140, 148, 171\].
because it binds O more weakly than many metals but substantially enough to promote activity. In contrast, Au is inactive for \( \text{O}_2 \) activation because it is too noble \cite{257}.

Despite its good redox properties, Pt catalysts are very expensive. Over the last 10 years the price of Pt has risen steadily, selling at 342 United States Dollars (USD)/troy oz in early 1998 and peaking at over 2200 USD/troy oz in early 2008 \cite{130}, nearly a 650% increase. For comparison, Au went from 250 USD/troy oz to 1000 USD/troy oz, a 400% increase, in the same time span\footnote{The purchasing power of the USD dropped 32% between 1998 and 2008 \cite{179}, so one troy oz of Pt (Au) would have cost 451 (330) 2008-USD in 1998.}. Automotive catalysts consume approximately 40% of the Pt produced worldwide, and this will increase as European and Asian auto markets grow \cite{123}, heightening the demand and thus conceivably the price. A key consideration in catalyst design is reducing cost while maintaining emission control quality. For NO oxidation, this means either reducing the amount of Pt necessary or using a less expensive material altogether.

1.5 Experimental Observations of Pt-Catalyzed NO Oxidation

The ultimate goal of this work is to propose an alternative to pure Pt for NO oxidation catalysis. To do this, it is important to first understand how Pt functions. The kinetics and mechanism of Pt-catalyzed NO oxidation have been the subject of many experimental investigations \cite{44,48,53,54,103,140,148,171,172,173,180,182,184,263,264}. The rate on supported Pt is observed to increase with increasing particle size \cite{172,264}, suggesting the flat, low index surfaces to be the most active for the catalysis. Further, activity is associated with high surface coverages of O (\( \theta_\text{O} = \text{N}_\text{O}/\text{N}_\text{Pt} \)) \cite{48,54,148,171,173,182,183}. However, too
much oxygen leads to deactivation, likely due to the formation of inactive surface oxides [54, 148, 172, 182, 183]. NO conversion is kinetically controlled below the catalyst light-off temperature, observed to be around 500 - 700 K [48, 54, 103, 182, 183].

Kinetic experiments typically strive to measure reaction rate derivatives in order to construct the rate equation. Reaction rate orders (derivatives with respect to partial pressure $p$) and apparent activation energy (derivative with respect to temperature $T$) are sensitive to the conditions under which they are measured. At low NO conversion ($X_{NO} < \approx 20\%$), where the product NO$_2$ concentration is low, observed rate orders are $+0.3$, $+0.5$, and $0$ for NO, O$_2$, and NO$_2$, respectively [103, 148], and activation energies are a modest 35 - 50 kJ mol$^{-1}$ [48, 103, 148, 182, 183]. At higher NO conversion ($X_{NO} > \approx 25\%$) and thus higher background NO$_2$ concentrations, observed rate orders increase to $+1.0$ and $+0.7$ for NO and O$_2$, respectively, while the NO$_2$ order becomes $-1.0$, indicating that the reaction product inhibits reaction, even after correcting for the effect of the reaction equilibrium on rate [171, 172]. The activation energy increases to 80 kJ mol$^{-1}$ [171, 172] at these higher conversion conditions.

1.6 Empirical Models of Pt-Catalyzed NO Oxidation

Several empirically-based models of Pt-catalyzed NO oxidation have been reported [48, 103, 148, 148, 171, 172, 182, 183, 229]. They each assume a reaction mechanism and parameterize it using experimental data, such as from temperature programmed desorption and/or NO reaction. These models are successful at predicting some of the general features of the catalysis, such as the catalyst light-off between 200 - 300°C or rate inhibition by NO$_2$. However, they are somewhat
limited in the steps considered, and none of them explains all of the observed behavior.

A number of reaction mechanisms have been proposed to explain the observed kinetics, but there are a number of inconsistencies, such as whether $O_2$ adsorbs associatively \[ O_2 + \ast \leftrightarrow O_2\ast \] (1.20)
or dissociatively \[ O_2 + 2\ast \leftrightarrow 2O\ast \] (1.21),
as well as which features are rate limiting. To best fit the experimental observations, the studies observing +0.5 order in $O_2$ propose $O$–$NO$ bond formation
\[ NO\ast + O\ast \rightarrow NO_2\ast + \ast \] (1.22)
is rate limiting and $O_2$ dissociative adsorption (Equation 1.21) is in quasi-equilibrium, and the ones observing closer to +1.0 order propose $O_2$ associative adsorption (Equation 1.20) is the rate determining step (RDS) and $O$–$NO$ bond formation is in quasi-equilibrium. These inconsistencies, as well as the incomplete description of the kinetic behavior indicate the importance of applying theoretical modeling to elucidate the underlying mechanism and rate-limiting features.

1.7 Atomistic Models of Pt-Catalyzed NO Oxidation

Atomistic simulations based on density functional theory (DFT) have also been used to characterize the intermediates and reaction steps involved in Pt-catalyzed NO oxidation \[ 50, 129, 159, 188 \]. Calculations show that the reaction of
an isolated NO adsorbate with an O adsorbate is 0.8 eV endothermic on a clean Pt(111) surface [188], and even more endothermic on a finite Pt cluster [262], because pristine Pt binds O and NO too strongly to promote reaction. Consistent with experimental observation, Pt promotes NO$_2$ decomposition [12, 13, 189]. Catalytic NO oxidation relies on a catalytic material that can promote both O$_2$ dissociation (Reaction 1.21) and O–NO bond formation (Reaction 1.22). The optimal catalyst binds O strongly, but more weakly than O–NO: its O binding energy is just less than $-0.6$ eV. O-covered Pt surfaces achieve this binding energy through destabilizing lateral interactions [188, 241]. These have been shown to be dominated by first (1NN) and second (2NN) nearest neighbor repulsions of 0.2 and 0.1 eV [188, 241]. Prior work shows NO and O each surrounded by two 1NN and two 2NN are bound weakly enough to promote reaction [188].

Atomistic simulations show the influence of adsorbate coverage on surface reactions is critical to Pt-catalyzed NO oxidation catalysis [56, 129, 159, 188]. Ovesson et al. [188] computed the kinetics of O–NO bond formation and O and NO diffusion on pristine Pt(111) and used a two-body lateral interaction model to estimate coverage effects on the rate expression. Kinetic Monte Carlo (kMC) simulations performed at different initial O coverages show that a minimum of 0.25 ML O is necessary to promote NO oxidation and that the rate increases with increasing coverage. Mei et al. [159] and Kieken et al. [129] calculated the barrier to O–NO bond formation on clean Pt(100) and used a bond order conservation model [101] to describe coverage effects. KMC simulations show the rate of NO oxidation, measured by counting the number of NO$_2$ molecules that desorb from the surface in a given amount of time, increases with $T$ up to about 700 K before decreasing due to equilibrium limitations. The activation energy within the increasing $T$
regime was computed by fitting to an Arrhenius expression to be 40 kJ mol$^{-1}$. Disselkamp et al. [56] assumed a constant activation energy based on the work of Mei et al. [159] for O–NO bond formation on Pt(100) and computed reaction probabilities between O and NO in different adsorption sites. Calculated “reaction velocities” indicate meta-stably bound atop O and bridge NO contribute primarily to NO$_2$ formation. These models successfully capture some of the observed behavior, such as sensitivity to O coverage and $T$. However, they make assumptions about O$_2$ equilibration with the surface, the RDS, and the effect of coverage on the catalysis. Further, they are unsuccessful in capturing some of the key observables, such as the inverse rate order in NO$_2$.

O$_2$ dissociation [1.21] is the canonical route for breaking the O=O bond, but experiment and theory [83] indicate the reaction is strongly kinetically inhibited at high $\theta_O$. One way to circumvent the increasingly unfavorable energetics of this route with increasing surface O coverage, and to account for the observed first-order dependence on O$_2$, is through an NO “assisted” dissociation pathway [82, 229]:

\[
\begin{align*}
\text{NO} + O_2^* & \longrightarrow OONO^* \quad (1.23) \\
\text{OONO}^* & \longrightarrow \text{NO}_2 + O^* \quad (1.24)
\end{align*}
\]

This assisted pathway is similar to that proposed to account for the high CO oxidation activity of nanoscale Au particles [141, 146, 147, 168, 169, 201, 208, 267, 269] and in other contexts [221]. In each case, simultaneous formation of one O-reductant and one O-M bond is energetically favorable to the formation of two O-M bonds. While this pathway may help account for some of the observed NO oxidation kinetics, its relevance under realistic surface and reaction conditions
remains to be established [229].

A first-principles model based on calculations that more directly interrogate surface coverage is necessary to describe the broader features of Pt-catalyzed NO oxidation. In this work, we report DFT calculations of the structures and binding energies of the potential surface intermediates in NO oxidation over Pt(111) as a function of O surface coverage. We show that the adsorption sites and configurations are sensitive to coverage, that the binding energies uniformly decrease with increasing coverage, and that the coverage dependence can be correlated to the coverage-dependent O adsorption energies [82]. We also describe the coverage-dependent transition states for O₂ dissociation, ON−O bond formation, [83] and NO-assisted O₂ dissociation. The results are incorporated into a coverage-dependent microkinetic model and solved over a range of conditions similar to those probed experimentally [229]. The model predicts steady-state coverages similar to those inferred from energy arguments, predicts O₂ dissociative adsorption to be rate limiting, and finds O−NO bond formation to be in quasi-equilibrium. This last reaction is found to control O coverage and to introduce the inverse NO₂ order observed experimentally. Assisted dissociation is found not to contribute significantly to overall activity at these conditions. The model reasonably reproduces the observed TOF, rate orders, and catalyst light-off temperature. The results confirm the general mechanistic features inferred from experiment [171–173] and show that kinetic models must incorporate explicit coverage dependence to reproduce observation.
CHAPTER 2

RESEARCH METHODOLOGY

The goal of this work is to develop an atomistically detailed kinetic model for Pt-catalyzed NO oxidation that is consistent with the experimentally observed behavior. It will contain $\theta_O$-dependent thermodynamics and kinetics obtained from DFT and first-principles thermodynamics (FPT) and be used to understand how Pt promotes NO oxidation so that an alternative catalyst can be proposed. The research methodology relies heavily on density functional theory calculations, estimation of thermodynamic properties, and kinetic modeling.

2.1 Density Functional Theory

2.1.1 Theory

DFT is a powerful tool that can be used to compute the electronic energies of systems with large numbers of electrons at relatively small computational expense. Its basis is the electronic Hamiltonian for an N-electron molecule [142]:

$$\hat{H} = -1/2 \sum_{i=1}^{N} \nabla_i^2 + \sum_{i=1}^{N} \vartheta(\vec{r}_i) + \sum_{j>i} \sum_{i,j} 1/|\vec{r}_{ij}|$$ (2.1)
which describes the kinetic motions of the electrons subject to the nuclear ($\alpha$) potentials \[142\]

$$\vartheta (\vec{r}_i) = - \sum_\alpha Z_\alpha / |\vec{r}_i\alpha|$$ \hspace{1cm} (2.2)

The potential is a function of the spatial positions of all the electrons relative to the nuclei $\vec{r}_{i\alpha}$. The electronic energies ($E_i$) and wavefunctions ($\psi_i$) are obtained by solving the Schrödinger equation

$$\hat{H} \psi_i (\vec{r}_1, \ldots, \vec{r}_N) = E_i \psi_i (\vec{r}_1, \ldots, \vec{r}_N)$$ \hspace{1cm} (2.3)

As the system size gets very large, as for a large metal slab, the dimensionality and thus expense of finding the N-electron wavefunctions becomes very large. The wavefunctions are not direct observables, but they are useful for computing the electron probability density,

$$\rho_0 (\vec{r}_1) = \int \ldots \int \psi^* (\vec{r}_1, \ldots, \vec{r}_N) \psi (\vec{r}_1, \ldots, \vec{r}_N) d\vec{r}_2 \ldots d\vec{r}_N$$ \hspace{1cm} (2.4)

where * indicates the complex conjugate \[216, 227\]. The electron probability density is measurable, and it is arguably the most important property of an N-electron molecule. DFT was built upon this notion \[216\] in an attempt to decrease computational expense associated with understanding the electronic structures of large systems. It was first developed by Hohenberg and Kohn, who showed that \[116, 142, 227\]

1. The ground state energy is a unique functional of the ground state electron probability density.

2. The electron probability density that minimizes the energy is the true ground
state electron probability density.

From this, they were able to write the Hamiltonian in terms of \( \rho_0 (\vec{r}) \) rather than \( \psi (\vec{r}_1, \ldots, \vec{r}_N) \), reducing the 3N-dimensional problem into a 3-dimensional problem. The DFT energy is [142, 227]

\[
E_0 = \int \rho_0 (\vec{r}) \partial \theta (\vec{r}) \, d\vec{r} + T[\rho_0] + E_{ee}[\rho_0 (\vec{r})] + E_{nn} \tag{2.5}
\]

where \( T, E_{ee}, \) and \( E_{nn} \) are the total kinetic energy, total potential energy from electron-electron interaction, and potential energy from nucleus-nucleus interaction, respectively. The latter term is found classically using Coulombic potentials [227], but \( T \) and \( E_{ee} \) are not as straightforward. Their forms were determined by Kohn and Sham [132, 142, 216], who separated the problem into two pieces: an interacting part and a non-interacting part [142, 227]

\[
E_0 = \int \rho_0 (\vec{r}) \theta (\vec{r}) \, d\vec{r} - \frac{1}{2} \sum_{i=1}^{n} \left\langle \psi_i^* (\vec{r}_i) \left| \nabla_i^2 \psi_i (\vec{r}_i) \right| \psi_i (\vec{r}_i) \right\rangle + T^{\text{int}}[\rho_0 (\vec{r})] + E_{Coulomb}^{ee} + E_{xc}[\rho_0 (\vec{r})] + E_{nn} \tag{2.6}
\]

where \( T^{\text{int}} \) and \( E_{xc} \) are the kinetic energy difference between the interacting and non-interacting systems and potential energy difference between the actual and Coulombic electron-electron interactions, respectively. Kohn and Sham combined these into the exchange-correlation energy functional \( \theta_{xc}[\rho_0] \), thus collapsing all indeterminable quantities into a single functional [132, 216]. The Kohn-Sham solution gives a set of one-electron wavefunctions as a function of the electron density [216, 227]

\[
\left[-\frac{1}{2} \nabla_i^2 + \theta (\vec{r}_i) + E_{Coulomb}^{ee} (\vec{r}_i) + \theta_{xc}[\rho_0 (\vec{r})]\right] \psi_i = E_i \psi_i \tag{2.7}
\]
While this provides for a much more efficient calculation of the electronic energy, to date the true form of $\varphi_{xc}[\rho_0]$ is unknown. The quality of DFT calculation strongly depends on the accuracy of $\varphi_{xc}[\rho_0]$ approximation.

There are many varieties of $\varphi_{xc}[\rho_0]$ available [196]. Some popular ones are the local density approximation (LDA), which uses only information about the local electron probability density to define $\varphi_{xc}[\rho_0]$, and the generalized gradient approximation (GGA), which uses information about the local electron density and its gradient [196, 227]. Beyond that, meta-GGAs use information about the local density, its gradients, and its Laplacians, and hyper-GGAs use information about the local density, its gradients, and the exact N-electron exchange energy [196].

Today, the primary constraint in selecting $\varphi_{xc}$ is computational expense. Meta-GGA calculations on small systems comprised of less than a dozen atoms can take several hours on a typical high performance computing cluster, and large systems with the same level of theory could conceivably take days, weeks, or even months. For large systems, even on state-of-the-art computers, the GGA is typically the most feasible level of theory.

We use the GGA in this work. Comparison with experiment in the following chapters shows that the GGA is quite accurate for computing properties of the Pt surface, given its continuous and relatively homogeneous electron probability density. However, because the GGA is a relatively “local” method, there are errors associated with computing the properties of gas phase atoms and molecules, which have non-continuous and inhomogeneous electron densities. In this work this primarily affects descriptions of molecule/surface bond energies. There are few experimental measurements of these energies, and the available ones vary widely. It is thus difficult to exactly quantify these energies. We consider this as
we report results throughout this work.

2.1.2 Electronic and Vibrational Energies from DFT

DFT calculations are performed using the periodic supercell, plane wave basis approach as implemented in the Vasp code. Periodic approaches are extremely useful for calculating the electron densities of periodic and “infinitely large” systems. In these methods atoms are arranged in a “supercell” defined by lattice vectors \( \vec{a}_i \), and supercells are repeated infinitely many times in all three \( \vec{a}_i \) directions, filling all of three-dimensional space. Bloch functions are convenient solutions

\[
\phi_{\vec{k}}(\vec{r}) = \exp\left( i\vec{k} \cdot \vec{r} \right) u_{\vec{k}}(\vec{r}) \tag{2.8}
\]

They are constructed under Bloch’s theorem as the products of an oscillatory part (\( \exp\left( i\vec{k} \cdot \vec{r} \right) \)) and a cell-invariant function (\( u_{\vec{k}}(\vec{r}) \)) with the same periodicity as the supercell. They are represented as plane waves. The \( \vec{k} \) are electron wavevectors in reciprocal space, defined in each dimension by \( k_j \leq |\pi/\vec{a}_j| \), and are related to the electron’s momentum. Functionally, they describe bonding between periodic supercell images. For a good description of this, see Ref. [216]. The collection of \( \vec{k} \) comprise the band structure. For Vasp calculations, \( \vec{k} \) are specified directly as \( \mathbf{k} \)-points. In any calculation, plane waves are included up to a specified “cut-off” energy, and we use 400 eV in this work. The highest occupied energy level is the Fermi level. The DFT solution is the sum of

\[
\psi_i^{\vec{k}}(\vec{r}) = \exp\left( i\vec{k} \cdot \vec{r} \right) u_i^{\vec{k}}(\vec{r}) \tag{2.9}
\]

In this work we use plane waves to calculate the electronic energies of periodic bulk Pt as well as “infinitely large” Pt slabs.
The computational expense of all electronic structure calculations scales with the number of electrons. We are interested in understanding how atoms bond, so we are most interested in interactions among valence electrons. Electron cores contribute negligibly to bonding, and they are difficult to describe with plane waves. To decrease computational expense, they are described by the projector augmented-wave (PAW) \([21, 136]\) method, which is a frozen core method that projects actual core wavefunctions onto plane waves. Electronic energies of the valence electrons are computed with the PW91 implementation of the GGA \([194, 195]\). The solutions are determined self-consistently: first, a trial electron density is introduced. The density defines a potential, which defines a new density. If the computed density does not match the trial density, the two are “mixed” to create a new trial density, which defines a new potential, and so on, until the trial density and the computed density are within the prescribed convergence criteria \([227]\). In this work the electronic structure is converged when the energy difference between subsequent iterations is 0.00001 eV.

The ultimate goal of these calculations is to locate stationary structures on the potential energy surface (PES). We start by specifying a trial geometry and computing its electronic structure. The forces on the atoms are then evaluated by taking the gradient of the total energy, and the atomic positions are updated pursuant to the forces. Structures are relaxed in this manner until the prescribed structural convergence criteria are achieved \([47]\). We use two convergence criteria in this work. In the earlier chapters, which detail “low coverage,” or bonding in the presence of just a few atoms, ionic relaxations are performed until the energy difference between subsequent iterations is less than 0.0001 eV. In the later chapters, which detail bonding in the presence of many atoms, ionic relaxations
are performed until forces on the atoms are less than 0.05 eV Å\(^{-1}\). The former method provides much tighter convergence at a higher computational expense.

2.1.2.1 Atoms and Molecules

Gas-phase atoms and molecules are simulated in supercells 12 Å on a side, large enough to ensure negligible interactions between neighboring cells. Similarly, they are performed as Γ-point calculations (k-points = 1×1×1). Spin-polarization is applied as appropriate, electronic states have integer occupancies, and in order to capture their asymmetric electronic ground states, the NO molecule and O atom are computed with no symmetry.

2.1.2.2 Bulk Pt

The structure of bulk FCC Pt is calculated within a primitive face-centered cubic (FCC) cell using a 10 × 10 × 10 Monkhorst-Pack \textsuperscript{170} k-point mesh, Γ-centered to yield 8000 total k-points, of which 35 are symmetry unique. With this k-point mesh energies are converged to within 1 meV per Pt atom. The lattice parameter is calculated to be 3.9861 Å, in excellent agreement with previous reports \textsuperscript{74}. The calculated lattice parameter exceeds the experimental value by 0.063 Å \textsuperscript{200}, or 2%, consistent with the general tendency of the GGA to overestimate internuclear distances \textsuperscript{47}. The computed equilibrium volume is \(\hat{V} = 15.833\) Å\(^3\) per Pt. This value is used in all slab calculations.

To decrease computational expense associated with populating states near the Fermi level, a Gaussian smearing profile with a smearing parameter of 0.10 eV is imposed at the Fermi levels for bulk and slab calculations, and reported energies are extrapolated to zero smearing. Smearing introduces finite temperature and
hence an entropy contribution to the electronic energy; the maximum contribution observed here is for the clean Pt(111) surface, which is 0.010 eV/atom.

2.1.2.3 Pt Slabs

To model NO oxidation over a Pt catalyst, we need a sufficient Pt catalyst model. Experimental evidence indicates that activity is associated with large Pt particles [172], suggesting the low surface energy, low index faces to be the most active. Experiments on a (111) single crystal produce the highest observed rate [229], and we perform calculations over this face. The atoms in the (111) face on a FCC crystal form a close-packed hexagonal structure [149]. Surface atoms are “bound” to their nine closest Pt neighbors, meaning they have just three “dangling” bonds. NO oxidation is therefore promoted by a stable surface rather than a more reactive stepped, kinked, or defect-rich surface. The latter surfaces tend to bind adsorbates more strongly than close-packed (111). Recalling from Chapter 1, moderating the O–catalyst binding energy is important to NO oxidation catalysis.

Platinum(111) supercells are constructed of four layers of 2 Pt $\times$ 2 Pt, 3 Pt $\times$ 3 Pt, 4 Pt $\times$ 4 Pt (Figure 2.1), and 5 Pt $\times$ 5 Pt surface planes and separated from vertical images by five layers (14 Å) of vacuum space. Monkhorst-Pack [170] k-point samplings of 10$\times$10$\times$1, 8$\times$8$\times$1, 6$\times$6$\times$1, and 4$\times$4$\times$1, respectively, are used to sample the first Brillouin zone. Comparison of these meshes with larger and smaller even and odd meshes indicates that slab electronic energies are converged to within 0.1 meV per Pt. The atoms in the bottommost layers of the supercells are fixed in the calculated bulk locations, and the atoms in the remaining three layers are allowed to relax. We find the atoms in the first (topmost) and second
layers of the bare slab relax inward from their bulk positions by approximately 0.06 and 0.07 Å respectively, and the third layer atoms relaxed by 0.01 Å. Supercell calculations are performed non-spin-polarized.

To obtain a precise estimate of the Pt(111) surface energy, fully relaxed calculations were performed on slabs of increasing thickness from three to eighteen layers, using a 2 Pt × 2 Pt supercell. Surface energies were computed for the slabs by:

\[
E_{\text{surf}} = \frac{\left(E_{\text{slab}}^{\text{DFT}} - N_{\text{Pt,slab}}E_{\text{Pt,bulk}}^{\text{DFT}}\right)}{2A_{\text{slab}}} 
\]  

(2.10)

The surface energy fluctuates within 1.4 meV Å\(^{-2}\) between ten and eighteen Pt layers. The fourteen layer model, which has a surface energy of 93.327 meV Å\(^{-2}\), is representative of an infinitely thick slab: the topmost Pt layer on each side of the slab vertically expands to a separation of 2.836 Å from the second layer; the spacing between the second and third and third and fourth layers are 2.810 Å, or just slightly compressed from the bulk, and the subsequent interlayer separations are 2.819 Å, within 0.001 Å of the calculated bulk separation. For comparison,
the first two interlayer separations are reported to be 2.80 and 2.79 Å based on a low-energy diffraction (LEED) analysis \[152\], consistent with an expansion of the outermost layer relative to the bulk separation.

The surface free energy depends in part on the bulk and surface phonon spectra, computed by two-sided finite differencing within the harmonic oscillator approximation and using Cartesian displacements of ±0.01 Å. The bulk Pt spectrum was calculated within a 32 atom cubic supercell and a $3 \times 3 \times 3$ \(k\)-point mesh. The surface phonon spectrum was determined using a four-layer 4 Pt $\times$ 4 Pt model and a $3 \times 3 \times 1$ \(k\)-point mesh.\(^1\) Atoms in the bottommost layer were held fixed in calculated bulk positions. Modes resulting from third layer atoms pushing against the frozen bottom layer were neglected. The primary difference between the bulk and surface spectra is a grouping of modes in the surface spectrum blue-shifted from 100 to 147 cm\(^{-1}\) on Pt atoms near the solid/vacuum interface. This shift is used to compute the vibrational quantities of the free surface.

2.1.2.4 Molecule/Pt(111) Systems: Adsorption

Adsorption energies are calculated for atoms and molecules adsorbed to the relaxed surface of a supercell, for example:

\[
\text{B} + \ast \rightarrow \text{B} \ast \quad \Delta E^{\text{ads}} = E_{\text{B} \ast}^{\text{DFT}} - E_{\ast}^{\text{DFT}} - E_{\text{B}}^{\text{DFT}}
\] (2.11)

\(^1\)Ideally, we would calculate the surface phonon spectra using the 14-layer 2$\times$2 supercell discussed above. However, displacing 56 atoms by ±0.01 Å in all three Cartesian directions ($56 \times 2 \times 3 = 336$ total displacements) is far more time consuming than displacing the 48 non-frozen atoms in the 4-layer 4$\times$4 model (= 288 displacements.) If it becomes important to know the surface phonon spectra very accurately, I recommend re-calculating it with the 14-layer 2$\times$2 model.
In this notation * denotes an adsorption site and B* denotes chemisorbed gas atom/molecule B. Spin polarization is negligible for all adsorbates considered except for O₂, for which the maximum effect on the adsorption energy is 0.07 eV/O₂. Spin polarization is thus neglected in all reported energies unless indicated. Test calculations indicate dipole interactions between vertical slab images have negligible effects on the adsorption energies at all O coverages considered. The adsorption energy is sensitive to the number of metal layers included in the Pt(111) slab and the lateral dimensions of the supercell, the latter of which determines the effective inter-adsorbate spacing. All the adsorbates considered here interact repulsively, such that their adsorption energies decrease with increasing coverage. The number of metal layers used also affects the Pt–Pt interactions within the slab and thus indirectly affects adsorbate–substrate bonding. At 1/16 ML we observe that the adsorption energies exhibit even-odd oscillations that attenuate with the number of metal layers. This phenomenon has been noted previously [26, 29] with respect to other adsorbate properties. We estimate the absolute adsorption energy to be systematically exaggerated by 0.06 eV in the four layer slabs. Other sources of error, such as the finite plane wave energy cut-off and the finite effective temperature at the Fermi level, are expected to be on the order of a few meV.

Two approaches are used to analyze the charge transfer accompanying chemisorption. The total density of states (DOS), that is the number of energy states within the interval $E$ to $dE$ [216], is decomposed into atom-centered contributions, or atomic DOS, by integrating the charge around each atom within cut-off radii of 1.74, 0.74, and 0.82 Å for Pt, N, and O respectively. The atomic DOS are also projected onto spherical harmonics over the entire span of states to provide total s, p, and d partial DOS on each atom. In addition, a Bader [9] charge analysis
is applied, taking advantage of a recent implementation of the Bader method for Vasp. The Bader analysis partitions space into non-spherical atomic regions defined by local minima in the charge density. Atom charges are obtained by integrating the local charge density over the volume of each region. The Bader regions are disjoint and space filling and thus give a unique partitioning of charge. Because the regions are not spherical, however, they do not lend themselves to decomposition into angular contributions. The Bader and DOS methods were used in conjunction to compliment each other. While the results differ numerically, qualitative trends are in agreement.

Adsorbate vibrational frequencies are calculated by two-sided finite differences in the DFT gradients. All the atoms in the admolecule and its immediate neighbor Pt are included in the finite differences and are perturbed by \( \pm 0.01 \) Å. Diagonalization of the second derivative matrix provides the harmonic vibrational frequencies and eigenmodes. All vibrational frequency calculations are performed for one adsorbate in a 4 Pt \( \times \) 4 Pt supercell.

2.1.2.5 Molecule/Pt(111) Systems: Reaction

Activation barriers were computed for the following reactions

\[
O_2 * + * \rightarrow 2O*
\]  
\( (2.12) \)

\[
NO * + O* \rightarrow NO_2 * + *
\]  
\( (2.13) \)

\(^2\)Coverage can have a significant effect on adsorbate vibrational frequencies. If it is important to understand the exact adsorbate frequencies under certain coverage conditions, vibrational frequencies should be calculated at the right coverage.
on 4 Pt × 4 Pt cells using the Climbing Image Nudged Elastic Band (CI-NEB) method \[109, 111, 126\]. CI-NEB is a gradient-based method that relaxes discrete images to the minimum energy path (MEP), with the highest energy “climbing” image relaxing to a saddle point. For a tutorial on gradient based methods, see References \[42, 49, 60, 84, 109, 111, 126, 199, 246\]. Images are connected with springs, ensuring that all images relax to the same MEP. Forces perpendicular to the MEP on all images except the climbing-image (CI) are relaxed to zero persuant to the spring forces as defined by Hooke’s Law,

\[
\vec{F}_i = -\nabla \vartheta_i|_\perp + k^s_i (\vec{r}_{i+1} - \vec{r}_i) - k^s_i (\vec{r}_{i} - \vec{r}_{i-1})
\]

(2.15)

where \(k^s\) are spring force constants, and perpendicular and parallel forces on the CI are relaxed to zero. The CI relaxes to a saddle point without any spring forces,

\[
\vec{F}_{CI} = -\nabla \vartheta_{CI}
\]

(2.16)

so it is important to include enough images between the initial image and CI and the CI and final image to ensure the CI relaxes to the saddle point on the MEP connecting the initial and final images. The only interaction between the CI and its adjacent images are the spring force interactions on the adjacent images.

Coverage-dependent \(O_2\) dissociation (Reaction [2.12]) and O–NO bond formation (Reaction [2.13]) barriers were determined by relaxing images along the MEP until forces perpendicular to the path fell below 0.05 eV Å\(^{-1}\). Initial and final images were converged to 0.03 eV Å\(^{-1}\). The initial (Reaction [2.12]) or final (Re-
action 2.13) image contained one $O_2$ or $NO_2$ adsorbed to Pt(111), $p(2\times2)$-O, and $p(2\times1)$-O, configurations which have been shown theoretically \cite{241} and observed experimentally \cite{55} to be stable under increasing O chemical potential. The maximum root-mean-squared separation between images was kept to less than 1 Å. Activation barriers for NO-assisted $O_2$ dissociation (Reaction 2.14) were obtained by first relaxing images along the MEP until forces perpendicular to the path fell below 0.50 eV Å$^{-1}$ and then using Henkelman’s CI-NEB-based dimer method \cite{110} to relax two images near the transition state (TS) until forces on the atoms were less than 0.05 eV Å$^{-1}$. The obtained TS image was used in a normal CI-NEB run to ensure it is on the path connecting the initial and final images. The vibrational modes of all TSs were computed to ensure they have one imaginary mode in the correct degree of freedom. To ensure accurate vibrational frequencies, in these calculations the electronic structure is converged until the difference in energy between subsequent iterations is less than $10^{-8}$ eV.

2.2 Thermodynamic Modeling

2.2.1 Theory

Thermodynamic analysis is performed within a first-principles thermodynamics (FPT) framework \cite{207}, which takes electronic and vibrational data from quantum mechanics calculations to estimate $T$-dependent properties. Finite $T$ can theoretically induce electronic and vibrational excitations in the molecule/metal systems explored in this work. The probabilities of such excitations are computed using statistical mechanics \cite{158}. The electronic states exhibit quantum behavior
and can be described by Fermi-Dirac statistics \[ \text{[158]} \]

\[
\mathcal{P}(E) = \frac{1}{1 + \exp \left( \frac{E - E_{\text{Fermi}}}{k_B T} \right)} \tag{2.17}
\]

where \( \mathcal{P} \) is the probability that a given state is occupied and \( E_{\text{Fermi}} \) is the Fermi energy of the metal at 0 K. At 0 K, Equation 2.17 is a step function, and \( \mathcal{P} = 1 \) for \( E \leq E_{\text{Fermi}} \), and \( \mathcal{P} = 0 \) for \( E > E_{\text{Fermi}} \). \( \mathcal{P}(E) \) vs. \( T \) are shown in Figure 2.2. Even at 1273 K, \( \mathcal{P}(E) \) resembles a step function. Electronic excitations in the slab systems are thus ignored in this work. Vibrational states can be considered classically at much lower \( T \), above about 100 K, and thus can be described by Boltzmann statistics. Boltzmann statistics,

\[
\mathcal{P}(E) = \frac{\exp \left( \frac{-E}{k_B T} \right)}{Q} \tag{2.18}
\]

where \( Q \) is the partition function, are relevant when the number of available states far exceeds the number of particles 158. In this work Boltzmann statistics are used in conjunction with the harmonic oscillator approximation to interrogate vibrational excitations in the slab systems to compute vibrational free energies. These are used to evaluate the stabilities of different compositions of molecule/metal systems under a variety of gas atmospheres. This stability analysis is integral to understanding the catalyst composition under actual reaction conditions.

### 2.2.2 Coverage Dependent Surface Energies

Thermodynamic analysis is performed in Chapters 4 and 6 with the majority performed in Chapter 4. Chapter 4 is the basis for exploring the properties of
Figure 2.2. Fermi-Dirac distribution vs. $T$ in units of $E/E_{\text{Fermi}}$.

Figure 2.3. Computational approach for calculating the surface free energy of an oxygen-covered surface in equilibrium with an oxygen reservoir.
the Pt catalyst under actual reaction conditions. There we seek to determine the thermodynamics of different O coverages on Pt(111) in equilibrium with an oxygen reservoir by comparing the surface free energy at constant temperature $T$ and oxygen potential $\mu_O$. The Legendre transform of the Helmholtz free energy with respect to $N_O$, or $F^{(1)}_X [242]$, is an appropriate thermodynamic potential for the oxygen-covered surface with constant Pt composition:

$$F^{(1)}_X(T, V, \mu_O) = F_X - \mu_O N_O$$

(2.19)

Here $X_O$ denotes a particular arrangement and coverage of O on a slab. Since the volume is fixed at a value consistent with equilibrium bulk Pt in all calculations, we drop $V$ from the list of thermodynamic variables. It is computationally convenient to decompose the surface free energy into contributions from the formation of the bare surface and from subsequent oxygen adsorption, as shown in Figure 2.3:

$$\gamma^{(1)}_{X_O} = \gamma_{Pt(111)}(T) + \Delta \gamma^{(1)}_{X_O}(T, \mu_O)$$

(2.20)

The first term can be calculated reliably from the fourteen layer slab results and the second from the four layer slab models. This approach helps to reduce errors caused by the finite thickness of the slabs used to calculate the O-adsorbed configurations.

The Pt(111) surface free energy is calculated from the Pt bulk and fourteen layer slabs according to

$$\gamma_{Pt(111)} = \frac{F_{slab}(T, N_{Pt}) - N_{Pt} F_{bulk}(T)}{2A}$$

(2.21)
\[ F(T) = E^{\text{DFT}} + E^{\text{ZP}} + \Delta F(T) \quad (2.22) \]

where \( \Delta F(T) = F(T) - F(0\text{K}) \). The zero point energy, \( E^{\text{ZP}} \), for the bulk is calculated from an average over the harmonic vibrational modes to be \( E^{\text{ZP}}_{\text{bulk}} = 0.0189 \text{ eV per Pt} \). For the slab, the shift from 100 to 147 cm\(^{-1}\) contributes an additional 0.004 eV to the surface energy. This contribution is small because the number of “bulk-like” Pt is much larger than the number of “surface” Pt. Vibrational degrees of freedom are the only contribution to \( \Delta F \), calculated according to Boltzmann statistics [158]:

\[ \Delta F^{\text{vib}} = -k_B T \ln Q^{\text{vib}} \quad (2.23) \]

where \( Q^{\text{vib}} \) is the vibrational contribution to the canonical ensemble partition function. Again we use the harmonic oscillator approximation and average over all the vibrational modes of the bulk:

\[ \Delta F^{\text{vib}}_{\text{bulk}} = \frac{1}{N_{\text{Pt}}} \left( \frac{k_B T}{N_{\text{Pt}}} \sum_j \ln \left[ 2 \sinh \left( \frac{\hbar \nu_j}{2k_B T} \right) \right] \right) \quad (2.24) \]

and the slab vibrational free energy is adjusted by the free energy change due to the 47 cm\(^{-1}\) shift. We find \( \gamma_{\text{Pt(111)}}(0\text{K}) = 93.5 \text{ meV \AA}^{-2} (1.50 \text{ J m}^{-2}) \) and \( \gamma_{\text{Pt(111)}}(300\text{K}) = 93.7 \text{ meV \AA}^{-2} (1.50 \text{ J m}^{-2}) \). The surface energy is insensitive to variations in \( T \) because the slab vibrational spectrum differs only slightly from the bulk. Our calculated result is in excellent agreement with results from other models [75].

The change in surface free energy upon O adsorption per unit surface area \( (A) \)
of $X_O$ is similarly

$$\Delta \gamma_{X_O}^{(1)} = \frac{F_{X_O}(T, N_{Pt}, N_O) - F_{Pt(111)}(T, N_{Pt}) - N_O \mu_O}{A}$$

$$= \left( E_{X_O}^{DFT} - E_{Pt(111)}^{DFT} \right) + \left( E_{X_O}^{ZP} - E_{Pt(111)}^{ZP} \right) + (\Delta F_{X_O} - \Delta F_{Pt(111)}) - \mu_O N_O$$

For a given configuration, the DFT energy difference is calculated using identical four layer Pt(111) supercells. We assume that the only contribution to the zero-point (ZP) and vibrational free energy differences ($\Delta F_{vib}$) is due to the oxygen vibrational modes and, for FCC-bound oxygen, can be approximated using the vibrational modes of an isolated O atom and scaled by $N_O$. Test calculations indicate that, in agreement with experimental observation [125], the Pt(111)-O vibrational modes are insensitive to O coverage, shifting 22 cm$^{-1}$ or less. Such small changes have at most 0.5 meV Å$^{-2}$ effect on $\Delta \gamma_{X_O}^{(1)}$. In principle $\Delta F_{X_O}(T)$ also has a contribution from configurational entropy associated with the surface oxygen ordering. For an ordered oxygen overlayer, this contribution is given by

$$F_{X_O} = -k_B T \ln \omega_0$$

where $\omega_0$ is the number of symmetry equivalent arrangements of $X_O$.

2.3 Microkinetic Modeling

The reaction mechanism and RDS are explored using microkinetic modeling. In this method, one or more reaction mechanisms are proposed, and their rate constants are computed using inputs from DFT and FPT. Microkinetic modeling is at the forefront of theoretical methods for kinetic analysis [1, 7, 8, 19, 20, 45, 58].
### TABLE 2.1

**CATALYZED REACTION MECHANISM FOR** $A_2 + 2B \rightarrow 2AB$

<table>
<thead>
<tr>
<th>i</th>
<th>$A_2 + 2* \leftrightarrow 2A*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>ii</td>
<td>$A* + B* \leftrightarrow AB* + *$</td>
</tr>
<tr>
<td>iii</td>
<td>$B + * \leftrightarrow B*$</td>
</tr>
<tr>
<td>iv</td>
<td>$AB* \leftrightarrow AB + *$</td>
</tr>
</tbody>
</table>

88, 95, 107, 119, 120, 127, 177, 206. It has been successfully employed to elucidate the mechanisms of Pt-catalyzed methanol decomposition [95, 127] and dimethyl ether combustion [120], RuO$_2$-catalyzed CO oxidation [206], Pt-catalyzed water gas shift [94], and transition metal-catalyzed ammonia synthesis [50, 107, 236], as well as many other reactions. In this work we combine results from thermodynamic stability analysis with microkinetic modeling to capture the Pt-catalyzed NO oxidation reaction mechanism under actual gas phase conditions. In collaboration with experimental observation, the results illustrate how Pt promotes NO oxidation.

Kinetic modeling is performed assuming the reaction takes place in a continuously stirred tank reactor (CSTR). The gas phase is assumed to be well mixed so that there are no concentration or temperature gradients. The reactions are modeled as elementary steps, and their rates are written as functions of their reversibilities ($\beta_j$)

$$r_j = r_j^{\text{forward}} - r_j^{\text{reverse}} = r_j^{\text{forward}} (1 - \beta_j) \quad (2.27)$$
The reversibilities for each step, also known as the approaches to equilibrium, are equal to the reaction quotient divided by the equilibrium constant and are related to the reversibility of the overall gas reaction. For example, for the simple reaction

\[ A_2 + 2B \rightarrow 2AB \quad (2.28) \]

\[ \beta = \frac{p_{AB}^2}{p_{A_2}p_B^2K_{rxn}} \quad (2.29) \]

If the catalyzed mechanism is as given in Table 2.1 then

\[ \beta = \beta_i\beta_{ii}\beta_{iii}\beta_{iv} \quad (2.30) \]

The steady state solution is that where the net rates of all reactions weighted by their stoichiometric numbers are equal

\[ r_i = 2r_{ii} = 2r_{iii} = 2r_{iv} \quad (2.31) \]

It is determined in the method of DeDonder relations \[58\] by solving for \( \beta_j \). Steps with \( \beta_j \) near unity are in quasi-equilibrium, and steps with \( \beta_j \approx \beta \) are rate limiting.

This methodology allows solution of a reaction mechanism without making any assumptions about the RDS. The computed RDS is verified using the Degree of Rate Control \[34, 36, 57\]. This method takes the derivative of the overall rate with respect to the rate constants of the individual reactions

\[ \chi_{rc,i} = \frac{k_i}{r} \left( \frac{\partial r}{\partial k_i} \right)_{k_{j \neq i}, K} \quad (2.32) \]
to see which rate constants have the largest impact. This purely kinetic method more generally finds the RDS than the thermodynamics-based method of De-Donder relations.

Coverage-dependent surface reaction rate constants are developed using transition state theory (TST) \[45, 88\]. For example, the forward rate constant for \( \text{ii} \) is

\[
k_{\text{ii}}^{\text{forward}}(\theta) = \frac{k_B T}{\hbar} \exp \left( -\frac{E^\dagger(\theta) - E_{A^*+B^*}(\theta)}{k_B T} \right)
\]

(2.33)

where \( E \) are modeled coverage-dependent energies and \( ^\dagger \) indicates the transition state complex. Surface reaction prefactors are taken to be constant. These quantities rely on changes in vibrational entropies, which are expected to be less than 0.1 meV per K. The backward rate constant is simply

\[
k_{\text{ii}}^{\text{reverse}} = \frac{k_{\text{ii}}^{\text{forward}}}{K_{\text{ii}}}
\]

(2.34)

Rate constants for molecule/surface reactions are parameterized using collision theory \[45, 62, 88\] and are written as the product of the molecular flux impinging on the surface and a sticking coefficient. For example, for \( \text{i} \)

\[
k_{\text{i}}^{\text{forward}}(\theta) = \mathcal{F}_{A_2} S_{A_2}(\theta)
\]

(2.35)

The molecular flux is calculated from the translational partition function of the impinging gas \[45, 62, 88\]

\[
\mathcal{F}_{A_2} = \frac{P_{y_{A_2}}}{[L] \sqrt{2\pi m_{A_2} k_B T}}
\]

(2.36)

where \([L]\) is the concentration of surface sites and \( y_{A_2} \) is the mole fraction of \( A_2 \) in
the gas phase. \( F \) has units of site\(^{-1}\) s\(^{-1}\). For unactivated adsorption the sticking coefficient is taken to be unity and for activated adsorption is described using an Arrhenius model:

\[
S_{\text{gas}}(\theta) = \exp\left(\frac{-\Delta E_{\text{act}}(\theta)}{k_B T}\right)
\]

(2.37)

The activation energy, \( \Delta E_{\text{act}} \), of adsorption is equal to the energy of the adsorption transition state relative to the energy of the gas phase \(^{[88]}\).

TSs for dissociative adsorption are approximated with the computed TSs for surface dissociation. For example, the TS for \( i \) is approximated with the TS for

\[
A_2 + \rightarrow 2A^*
\]

(2.38)

which can be reliably calculated with DFT as described above. To calculate the TS for \( i \) exactly requires classical dynamics calculations in addition to DFT in order to describe the effects of energy transfer between \( A_2 \) and the surface due to the collision \(^{[139]}\). Such collisions can excite vibrational, rotational, translational, and even electronic modes within the molecule or local surface phonons (For a summary of recent theoretical attempts to describe these phenomena, see Ref. \(^{[139]}\)). We expect the energy transfer effects are small on metallic Pt, and they are neglected in all adsorption reactions in this work. Associative adsorption is treated in a similar manner. Adsorption events are summarized in Figure 2.4.

The prefactors for molecule/surface reactions capture the change in entropy in going from a gas molecule, with three degrees of freedom (DOF) in translation, to a “trapped” transition state complex \(^{[149]}\), with two lateral degrees of translational freedom. In reality, the trapped state may have anywhere between 0 \( \leq \) DOF \( < 3 \)
Figure 2.4. Activation energies, $\Delta E^{\text{act}}$, for associative (left) and dissociative (right) adsorption.
DOF after collision, and determining this requires classical/quantum dynamics calculations. In this work we find approximating TS mobility with two DOF yields results in good agreement with experiment, and reverse rate constants for molecule/surface reactions are calculated by

$$k_{\text{reverse}}^{(i)} = \frac{k_{\text{forward}}^{(i)}}{K_{i}^{(i)}}$$  \hspace{1cm} (2.39)

Reaction i is a special case. In reality, dissociation could occur via molecule/surface reaction (as in i) or by adsorption and subsequent surface-moderated dissociation

$$A_2 + \star \leftrightarrow A_2 \star$$

$$A_2 \star + \star \leftrightarrow 2A\star$$  \hspace{1cm} (2.40)

In fact, both processes could occur simultaneously. The different dissociation mechanisms have different TSs with different mobilities. Appropriately describing the dissociation/recombination requires determining the relative probabilities of each. In this work, we find dissociative adsorptions via molecule/surface reactions are much more probable than associative adsorptions and subsequent surface-moderated dissociations. The latter rely on being able to generate large enough coverages so that the rate of surface dissociation is non-negligible, but as we show in Chapters 4-6, $O_2$, $NO_2$, and other coverages are negligibly small at the $O$ coverages relevant to NO oxidation. In general, though, the likelihoods of these different pathways should be carefully checked when developing microkinetic models.
CHAPTER 3

DFT-BASED CHARACTERIZATION OF THE MULTIPLE ADSORPTION MODES OF NITROGEN OXIDES ON PT(111)

3.1 Introduction

A necessary step in developing a more complete description of Pt-catalyzed NO oxidation is enumeration and description of the various surface species relevant to catalytic activity. The surface science of NO on Pt(111) has long been of interest due to its potential relevance to NO reduction catalysis [31, 86], and NO₂ adsorption on Pt(111) has garnered much attention as a low pressure route to accessing higher oxygen coverages than are possible by O₂ dissociation [12, 13]. However, the relationship of the surface species and their interconversion to NO oxidation activity remains to be clarified. As a step in this direction, in this chapter we characterize the stable and some meta-stable states of adsorbed N, O, NO, NO₂, and NO₃ on a Pt(111) surface. Charge density analysis is used to characterize the nature and extent of interactions between the adsorbates and the surface, calculated harmonic vibrational frequencies are used to correlate the adsorbates with experimental observation, and the adsorption energies of all species are compared. In the low coverage limit all adsorbates are thermodynamically unstable with respect to adsorbed NO, reinforcing the critical role of local surface coverage in promoting the conversion of NO to NO₂ on the Pt(111) surface. The work presented in this chapter comes almost directly from Reference [81].
3.2 Results

3.2.1 Gas-phase NO, NO$_2$, NO$_3$

One defining characteristic of the NO, NO$_2$, and NO$_3$ molecules is that they are all odd-electron radicals with doublet ground states, so some care must be taken in describing their electronic structures within DFT. NO has a $^2\Pi$ ground state, and the single $\pi^*$ electron can either be distributed between both components of the $\pi^*$ level, preserving $C_{\infty v}$ symmetry, or localized in one of the $\pi^*$ components in a symmetry-broken calculation. The bond length is insensitive to this choice, but the symmetry-broken molecule is 0.03 eV lower in energy and is the reference used here. Consistent with experiment, NO$_2$ has $C_{2v}$ symmetry and a spatially non-degenerate $^2A_1$ ground state. NO$_3$ is a highly reactive molecule in the gas phase and is not expected to be a significant homogeneous product of NO oxidation. However, NO$_3$ adsorbates could well be formed under strongly oxidizing conditions, and thus it is useful as a reference to consider the gas phase structure. In agreement with experiment [113, 121, 252] the GGA predicts NO$_3$ to exhibit $D_{3h}$ symmetry and a $^2A_1'$ ground state. The calculated gas-phase structures are shown in Figures 3.2a, 3.5a, and 3.7a and again as expected for the GGA uniformly overestimate experimental bond lengths by approximately 0.03 Å [113, 114]. Table 3.2 shows the calculated Bader atomic charges; the N–O bonds are uniformly polarized towards O, with the largest charge separation for NO. Table 3.3 shows the calculated harmonic frequencies and their assignments, all of which are close to the experimentally observed values.
3.2.2 Adsorbates

3.2.2.1 NO

The close-packed Pt(111) surface offers a number of potential adsorption sites for an NO molecule, including one-fold coordination atop a single Pt, two-fold coordination at a bridge site, and three-fold coordination at so-called FCC and HCP sites (Figure 3.1). While the earliest evidence suggested NO to bind at bridge sites at low coverage [14, 86], more recent evidence from NEXAFS [70], STM [153, 154], LEED [153, 155], HREELS [154], and RAIRS [155] all concur that NO prefers to adsorb in FCC three-fold hollow sites at low coverage on Pt(111). Previous DFT results [5, 31, 33, 76, 79, 145, 188, 240] also predict the three-fold hollow FCC adsorption site to be most stable at low coverage. This agreement between simulation and experiment stands in contrast to the well-documented inconsistency between experiment and DFT for the preferred site of CO binding on Pt(111) [74].

We find NO to bond N-down and normal to the Pt surface at FCC sites, with an increase in the N–O bond length of 0.046 Å over the gas-phase (Figure 3.2b).
Figure 3.2. DFT-calculated gas-phase (a), FCC-bound (b), HCP-bound (c), and atop-bound (d) NO structures.
The GGA-calculated adsorption energies at 1/16 ML and 1/4 ML are 2.00 and 1.93 eV, respectively (Table 3.1). Previously reported values at 1/4 ML range from 1.75 to 2.10 eV [5, 76, 79, 145, 240]. These differences can largely be attributed to the use of more modest three-layer slabs in most earlier work, which as noted above can have a noticeable effect on absolute adsorption energies. For example, we calculate the adsorption energy of NO at 1/16 and 1/4 ML on three-layer Pt slabs to be 2.18 and 2.06 eV, in good agreement with other recent reports [5, 240]. Differences in pseudopotentials and k-point sampling likely account for the balance of the discrepancies. We believe the methods applied here, including PAW potentials with well-converged k-point sampling and four-layer slabs, provide the best available DFT adsorption energy estimates.

Adsorption of NO, and in fact of all adsorbates considered in this work, causes the Pt atoms local to the adsorbate to relax laterally, or parallel to the surface and away from the adsorbate, as well as vertically, or normal to and upward from the surface. These relaxations can result in substantial changes in the Pt–Pt separations near the adsorbates. In Table 3.1 we report the lateral relaxation in terms of the increase in Pt–Pt separations of the atoms in the adsorption site relative to the Pt–Pt separation in clean Pt(111), and we report the vertical relaxation as the increase in height of these Pt above the Pt surface atoms remote to the adsorption site. In the case of NO adsorption in an FCC site, for instance, the three Pt atoms nearest to N separate to a Pt–Pt distance of 2.95 Å, or 0.13 Å greater than in the clean Pt(111) surface, and vertically by 0.153 Å with respect to the Pt surface plane. The vertical distance between the three local Pt and N is 1.119 Å. In general, the lateral Pt relaxations are smaller at higher surface coverage and the Pt–adsorbate distances are greater. As surface coverage increases, more
TABLE 3.1

ADSORPTION ENERGIES ($\Delta E^{ads}$, in eV), CHANGE IN LOCAL Pt SEPARATION ($\Delta$(Pt–Pt), in Å), INCREASE IN LOCAL Pt HEIGHT ($\Delta$(Pt–surf), in Å), AND LOCAL Pt–ADSORBATE VERTICAL SEPARATION ($\Delta$(Pt–ads) in Å) OF NO, NO$_2$, NO$_3$, O, AND N ON Pt(111)

<table>
<thead>
<tr>
<th>geometry</th>
<th>NO</th>
<th>FCC</th>
<th>−2.00</th>
<th>−1.93</th>
<th>0.132</th>
<th>0.153</th>
<th>1.119</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>NO</td>
<td>HCP</td>
<td>−1.86</td>
<td>0.078</td>
<td>0.136</td>
<td>1.251</td>
<td></td>
</tr>
<tr>
<td></td>
<td>NO</td>
<td>atop</td>
<td>−1.59</td>
<td>N/A</td>
<td>0.286</td>
<td>1.939</td>
<td></td>
</tr>
<tr>
<td>NO$_2$</td>
<td>μ-N,O-nitrito</td>
<td>−1.35</td>
<td>−1.29</td>
<td>0.075</td>
<td>0.140 (N)</td>
<td>1.881 (N)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>O,O’-nitrito</td>
<td>−1.25</td>
<td>0.066</td>
<td>0.097</td>
<td>2.132</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>nitro</td>
<td>−1.24</td>
<td>N/A</td>
<td>0.208</td>
<td>2.036</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NO$_3$</td>
<td>O,O’-nitrato</td>
<td>−1.67</td>
<td>−1.62</td>
<td>0.004</td>
<td>0.099</td>
<td>2.113</td>
<td></td>
</tr>
<tr>
<td></td>
<td>nitrato</td>
<td>−1.17</td>
<td>0.173</td>
<td>0.034</td>
<td>2.223</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O</td>
<td>FCC</td>
<td>−4.38</td>
<td>−4.36</td>
<td>0.212</td>
<td>0.075</td>
<td>1.075</td>
<td></td>
</tr>
<tr>
<td></td>
<td>HCP</td>
<td>−3.98</td>
<td>0.164</td>
<td>0.142</td>
<td>1.109</td>
<td></td>
<td></td>
</tr>
<tr>
<td>N</td>
<td>FCC</td>
<td>−4.89</td>
<td>−4.81</td>
<td>0.185</td>
<td>0.131</td>
<td>0.898</td>
<td></td>
</tr>
<tr>
<td></td>
<td>HCP</td>
<td>−4.71</td>
<td>0.116</td>
<td>0.144</td>
<td>0.979</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>bridge</td>
<td>−4.00</td>
<td>0.199</td>
<td>0.169</td>
<td>1.123</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
surface Pt become involved in the Pt-adsorbate bond, causing less pronounced vertical Pt relaxation.

Bader analysis (Table 3.2) indicates a net 0.50 electron transfer from Pt to the FCC-bound NO molecule. The origins of this charge transfer can be understood by reference to density of states (DOS) decompositions (Figure 3.3). Like CO \[23,98\], NO has a filled 5σ donor state, but unlike CO has one electron localized in the antibonding 2π* state. Because N is more electronegative than C, the NO 5σ and 2π* levels are lower in energy (by approximately 2 eV within the GGA) than are the corresponding CO levels. NO is thus an even stronger π acceptor than is CO \[238\], and congruent with this, the GGA-calculated NO FCC
adsorption energy is 0.13 eV greater than CO. The left side of Figure 3.3 shows the molecular NO valence orbitals and their mappings onto the surface Pt d DOS upon adsorption. The eigenvalues of both molecular and adsorbed NO are presented relative to the respective Fermi energy. Forward donation from the NO molecule 5σ level into Pt d levels stabilizes the 5σ orbital with respect to 1π and pushes some of the Pt d states above the Fermi level, resulting in weak σ bonding \[115, 238\].

Most notably, however, is the strong mixing between the NO 2π* levels and the Pt d band that splits the 2π* into occupied Pt-bonding and unoccupied antibonding levels. In agreement with the Bader calculations, charge from the Pt surface flows into these 2π states, as reflected by a 0.30 electron increase in the integrated DOS π density from the gas-phase to the surface. Occupation of this antibonding state lengthens the N–O bond, consistent with experimental observation based on NEXAFS \[70\].

The calculated FCC NO stretch frequency is red shifted 397 cm\(^{-1}\) relative to the gas phase (Table 3.3). Adsorbed NO vibrational spectra have been observed by HREELS \[154\] and RAIRS \[155\] and due to the population of multiple adsorption sites have a complicated behavior as a function of NO exposure. A band red-shifted 386 cm\(^{-1}\) relative to the gas-phase has been assigned to FCC-bound NO, in good agreement with the results here \[154, 155\].

At high NO coverages additional types of adsorption sites are reported to be populated on Pt \[5, 70, 153, 155\] and other metals, such as Pd \[255\] and Rh \[249\]. We have characterized two other isomers of surface-bound NO, both of which are meta-stable at 1/16 ML coverage. The HCP isomer bonds N-down in a three-fold hollow HCP site (Figure 3.2). The bond length variations and charge distribu-
TABLE 3.2

BADER CHARGES OF GAS-PHASE AND ADSORBED NO, NO₂,
NO₃, O, AND N IN e (Oₓ DENOTES SURFACE-BOUND O)

<table>
<thead>
<tr>
<th>structure</th>
<th>charge</th>
<th>N</th>
<th>Oₓ</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO (g)</td>
<td>0.00</td>
<td>+1.10</td>
<td>N/A</td>
<td>−1.10</td>
</tr>
<tr>
<td>NO FCC</td>
<td>−0.50</td>
<td>+0.10</td>
<td>N/A</td>
<td>−0.60</td>
</tr>
<tr>
<td>NO HCP</td>
<td>−0.50</td>
<td>+0.10</td>
<td>N/A</td>
<td>−0.60</td>
</tr>
<tr>
<td>NO atop</td>
<td>−0.15</td>
<td>+1.10</td>
<td>N/A</td>
<td>−1.25</td>
</tr>
<tr>
<td>NO₂ (g)</td>
<td>0.00</td>
<td>+0.70</td>
<td>N/A</td>
<td>−0.35</td>
</tr>
<tr>
<td>µ-N,O-nitrito</td>
<td>−0.45</td>
<td>+0.40</td>
<td>−0.45</td>
<td>−0.40</td>
</tr>
<tr>
<td>O,O’-nitrito</td>
<td>−0.40</td>
<td>+0.70</td>
<td>−0.55</td>
<td>N/A</td>
</tr>
<tr>
<td>Nitro</td>
<td>−0.35</td>
<td>+0.60</td>
<td>N/A</td>
<td>−0.48</td>
</tr>
<tr>
<td>NO₃ (g)</td>
<td>0.00</td>
<td>+0.81</td>
<td>N/A</td>
<td>−0.27</td>
</tr>
<tr>
<td>O,O’-nitrato</td>
<td>−0.50</td>
<td>+1.00</td>
<td>−0.50</td>
<td>−0.50</td>
</tr>
<tr>
<td>Nitrato</td>
<td>−0.70</td>
<td>+0.80</td>
<td>N/A</td>
<td>−0.50</td>
</tr>
<tr>
<td>O FCC</td>
<td>−0.80</td>
<td>N/A</td>
<td>−0.80</td>
<td>N/A</td>
</tr>
<tr>
<td>O HCP</td>
<td>−0.75</td>
<td>N/A</td>
<td>−0.75</td>
<td>N/A</td>
</tr>
<tr>
<td>N FCC</td>
<td>−0.75</td>
<td>−0.75</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>N HCP</td>
<td>−0.75</td>
<td>−0.75</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>N bridge</td>
<td>−0.65</td>
<td>−0.65</td>
<td>N/A</td>
<td>N/A</td>
</tr>
</tbody>
</table>
### TABLE 3.3

VIBRATIONAL FREQUENCIES OF GAS-PHASE AND ADSORBED NO, NO₂, AND NO₃ IN cm⁻¹

<table>
<thead>
<tr>
<th>Structure</th>
<th>Asym. Stretch</th>
<th>Sym. Stretch</th>
<th>In- (out-of-) Plane Bend</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO (g)</td>
<td>1899</td>
<td></td>
<td>1876 [114]</td>
</tr>
<tr>
<td>NO FCC</td>
<td>1502</td>
<td></td>
<td>1490 [155]</td>
</tr>
<tr>
<td>NO HCP</td>
<td>1529</td>
<td></td>
<td>1508 [155]</td>
</tr>
<tr>
<td>NO atop</td>
<td>1702</td>
<td></td>
<td>1715 [155]</td>
</tr>
<tr>
<td>NO₂ (g)</td>
<td>1666</td>
<td></td>
<td>1618 [113]</td>
</tr>
<tr>
<td>O,O’-nitrito</td>
<td>1274</td>
<td></td>
<td>N/A</td>
</tr>
<tr>
<td>NO₃ (g)</td>
<td>1319</td>
<td></td>
<td>1492 [252]</td>
</tr>
<tr>
<td>O,O’-nitrato</td>
<td>1510</td>
<td></td>
<td>N/A</td>
</tr>
<tr>
<td></td>
<td>1034</td>
<td></td>
<td>N/A</td>
</tr>
<tr>
<td>Nitrato</td>
<td>1123</td>
<td></td>
<td>N/A</td>
</tr>
</tbody>
</table>
tions are quite similar to the FCC result, but the adsorption energy decreases by 0.14 eV to 1.86 eV, comparable to previous reports \[5, 76\]. The calculated HCP vibrational frequency is red-shifted 370 cm\(^{-1}\) from gas-phase NO, slightly less than FCC NO and similar to the 368 cm\(^{-1}\) red-shift for an NO vibrational mode assigned to HCP-bound NO at high NO exposures \[154, 155\].

In addition, NO can bind N-down and bent atop a single Pt (Figure 3.2d) at high NO coverages, as has been observed in a variety of experiments \[14, 70, 154, 155\] and DFT calculations \[5, 33, 240\]. At 1/16 ML, we calculate the atop isomer to have an N–O bond length of 1.179 Å, an increase of 0.010 Å over the gas-phase but significantly shorter than the three-fold isomer bond lengths \[70\], and to sit at an angle of 53.8° with respect to the surface normal. Adsorption causes the atop Pt to rise a rather large 0.29 Å above the surface plane. The atop adsorption energy is 1.60 eV at 1/16 ML coverage, 0.40 eV less than the FCC isomer. Consistent with this difference, the net charge transfer to atop NO obtained from the Bader charge analysis is only 0.15 electrons, and the charge distribution between N and O is quite similar to the gas-phase molecule. In line with this small charge transfer, the low-coverage atop NO vibrational frequency is calculated to be red-shifted only 197 cm\(^{-1}\) relative to the gas-phase, consistent with the 161 cm\(^{-1}\) red-shift reported experimentally \[154, 155\].

The stability of the atop isomer with respect to the FCC isomer increases with increasing surface coverage. At 1/2 ML NO, calculated in a 2 Pt × 2 Pt supercell, we find the most stable configuration to have atop and FCC NO co-adsorbed in equal proportions, as noted previously \[5, 154, 155\]. Similarly, in agreement with experiment \[14\], we find co-adsorption of O atoms to stabilize atop NO with respect to FCC NO; this preference for atop bonding at high O
coverage could be significant in promoting the formation of NO$_2$ by reducing the NO motion necessary to form the new O–NO bond. By comparison, starting from FCC-bound NO and O, nudged elastic band calculations show that both adsorbates must migrate towards atop positions in order to form surface-bound NO$_2$.

The much greater GGA-predicted preference for FCC over atop adsorption for NO (0.40 eV) than for CO (0.15 eV), as well as the experimentally observed NO preference for FCC sites over atop, can both be traced to the $\pi$ acceptor strength of NO. Based on comparisons of the integrated DOS, $\pi$ backbonding from Pt to NO constrained to adsorb atop and perpendicular to the Pt surface (Figure 3.4 right) is 0.8 electrons less effective than in an FCC site, due to poorer overlap between the $2\pi^*$ and Pt d states in the atop position. In order to compensate for the lack of donated Pt d density, atop NO bends with respect to the Pt surface, enhancing $\sigma$ bonding at the expense of $\pi$ and increasing the binding energy by 0.5 eV. NO bending allows the $5\sigma$ and the partially filled in-plane $2\pi_y$ orbitals to hybridize into an N-centered lone pair and a half-filled orbital directed toward the atop Pt. The latter hybrid $\sigma$ bonds effectively with the Pt d$_{z^2}$ orbitals oriented normal to the Pt surface, as reflected in the enhanced mixing between the two shown on the left side of Figure 3.4. The $\pi$ back-donation is weak and localized to the out-of-plane $2\pi_x$ orbitals. The strong $\pi$ acceptor NO thus prefers FCC over atop sites at low coverage because of better $\pi$ interactions with the surface in the former. When forced to compete with other adsorbates for Pt d density, as occurs at higher coverage, bent NO $\sigma$ bonding at atop sites becomes more favorable. The weaker $\pi$ acceptor/better $\sigma$ donor CO discriminates less strongly between the two sites, and in fact the GGA appears to reverse the
actual atop over FCC site preference because it exaggerates the contributions of π backbonding [137, 151].

3.2.2.2 NO₂

At low coverage, evidence from HREELS [12, 13] and previously reported DFT calculations [188] indicate NO₂ to adsorb on Pt(111) with one N–O bond bridging two surface Pt atoms and the second N–O bond directed away from the surface, in the so-called μ-N,O-nitrito configuration. We find the same adsorption geometry
here, shown in Figure 3.5b. Adsorption lengthens the surface-bound N–O bond by 0.105 Å while leaving the free N–O distance essentially unperturbed. Further, the O–N–O angle decreases by 15.0°. These modifications are consistent with those expected for an NO\textsubscript{2} strongly reduced by interaction with the surface. For instance, the O–N–O angle in ionic NO\textsuperscript{2}\textsuperscript{−} compounds is also approximately 15° less than in free NO\textsubscript{2} \[162\]. The GGA-calculated adsorption energy of µ-N,O-nitrito is 1.35 eV, or 0.65 eV less than NO. Adsorption causes modest restructuring of the Pt surface: the Pt atoms bound to the N and O atoms move apart by 0.08 Å and rise by 0.140 Å and 0.102 Å respectively, relative to the Pt surface atoms not involved with the adsorbate–substrate bonds (Table 3.1).
As with FCC NO, Bader charge analysis indicates a substantial charge transfer from the Pt surface to adsorbed NO$_2$ (Table 3.2). The right side of Figure 3.6 shows the valence orbitals of molecular NO$_2$, which include filled non-bonding (4b$_1$) and half-filled anti-bonding (6a$_1$) orbitals of in-plane, or $\sigma$-like, symmetry, as well as lower-energy filled (1a$_2$) and higher-energy vacant (2b$_2$) orbitals of out-of-plane, or $\pi$, symmetry. The most significant bonding interactions occur between a hybridized combination of the in-plane NO$_2$ valence levels and the Pt d states. Integration of the in-plane NO$_2$ DOS indicates a charge transfer of 0.60 electrons from the Pt surface, and donation into the hybrid drives the lengthening of the N–O bond and opening of the O–N–O angle. In contrast, interactions with the out-of-plane NO$_2$ levels are more modest: the 2b$_2$ level is pushed above the Fermi level and is essentially non-interacting with the Pt d states, while approximately 0.2 electrons flow from the 1a$_2$ level to the Pt surface. Thus, as with NO, NO$_2$ bonding is dominated by donation from Pt to the adsorbate, but in-plane “$\sigma$” contributions greatly outweigh out-of-plane “$\pi$” ones.

We also located two meta-stable NO$_2$ isomers (Figures 3.5c and 3.5d), both of which have local C$_2v$ symmetry and are of comparable energy and only about 0.10 eV less stable than the global minimum $\mu$-N,O-nitrito isomer. In fact, the similarities in adsorption energies of the three isomers are quite striking given their very different adsorption configurations. The O,O$'$-nitrito, or chelating, isomer adsorbs with both O atoms down and bridging two nearest-neighboring Pt atoms (Figure 3.5c). The N–O bonds are both lengthened 0.046 Å and the O–N–O angle decreased 11.1° relative to the gas phase, slightly less strongly perturbed than the $\mu$-N,O-nitrito case. The bridged Pt atoms separate to a distance of 2.884 Å, notably larger than the O–O distance of 2.208 Å but similar to the Pt–
Figure 3.6. Orbital correlation diagram for $\mu$-N,O-nitrito NO$_2$ adsorption on Pt(111). Right: Valence NO$_2$ molecular states. Left: Contributions of NO$_2$ in-plane (blue), out-of-plane (red), and surface Pt d states to the total DOS.
Pt distance induced by $\mu$-N,O-nitrito adsorption (Table 3.1). The Pt–O distances are over 2 Å, one of the longest adsorbate–substrate distances observed in this work. The Bader-calculated charge transfer to NO$_2$ is decreased by 0.05 electrons relative to $\mu$-N,O-nitrito (Table 3.2). Bonding occurs primarily via Pt d donation into the half-filled in-plane NO$_2$ 6a$_1$ orbital, which has both the correct symmetry and orientation to interaction with surface Pt orbitals; forward donation through the out-of-plane 1a$_2$ level is negligible.

The least-strongly bound nitro isomer bonds N-down, planar and atop Pt (Figure 3.5d). The N–O bonds are lengthened by 0.020 Å and the O–N–O angle decreased by 7.8°, both less strongly modified than in the $\mu$-N,O-nitrito and O,O$'$-nitrito cases. Charge donation from Pt to NO$_2$ is weakest in the nitro isomer, as indicated by the Bader analysis (Table 3.2). Bonding again is primarily mediated through Pt d donation into the in-plane 4b$_1$ and 6a$_1$ NO$_2$ orbitals.

We have calculated the vibrational spectra of the three NO$_2$ isomers at 1/16 ML coverage. The symmetric and asymmetric N–O stretch frequencies all red-shift relative to the gas-phase in response to charge donation from the Pt surface (Table 3.3) while the O–N–O bending modes are less sensitive to adsorption. The two $\mu$-N,O-nitrito N–O stretches decouple into a higher frequency mode for the free N–O bond and a much lower frequency mode for the surface-bound N–O. In contrast, the splitting between the two stretch modes is diminished in the two C$_{2v}$ isomers.

As with NO, the relative stabilities of these various NO$_2$ isomers are sensitive to surface coverage. Koel et al. have used vibrational HREEL to characterize these adsorption modes as a function of O coverage on Pt(111) [12, 13]. A mode observed at 1560 cm$^{-1}$ has been attributed to the $\mu$-N,O-nitrito isomer, and both
the DFT adsorption energy and vibrational frequency results support this assignment. A mode at 1180 cm\(^{-1}\) has been assigned to the second N–O stretch of this isomer, and here the experiments and DFT results are in less satisfactory agreement. This discrepancy is possibly a consequence of differences in surface coverages between experiment and simulation, which could have a particularly large effect on vibrational motion parallel to the Pt surface. The observed band is also similar in energy to the calculated symmetric stretch of the \(C_{2v}\) O,O\textsuperscript{′}-nitrito isomer, and an alternative possibility is that both isomers coexist under the conditions of experimental observation. A mode at 1270 cm\(^{-1}\) that appears with increasing O coverage has been assigned to the nitro isomer. The DFT results could be interpreted to support the assignment of this mode to either \(C_{2v}\) NO\(_2\) isomer. In general, then, the DFT results are in agreement with the experimental evidence for the presence of more than one isomer of NO\(_2\) under different coverage conditions, but further calculations that explicitly take into account the effects of O coverage are necessary to provide definitive assignments.

3.2.2.3 NO\(_3\)

To our knowledge NO\(_3\) adsorbates have not been explicitly identified on Pt(111). However, NO\(_3\) adsorbates have been observed on Ag(110) \cite{185,118,185} at high NO\(_2\) exposures and have been suggested to account for some features in the temperature programmed desorption of NO\(_2\) from Pt(111) at high initial coverages \cite{12}. DFT results indicate NO\(_3\) does bond to the Pt(111) surface. The most favorable configuration is similar in orientation to the O,O\textsuperscript{′}-nitrito NO\(_2\) isomer, including a trigonal planar NO\(_3\) adsorbate with two O atoms directed toward the surface and bridging two Pt atoms with local \(C_{2v}\) symmetry.
Figure 3.7. DFT-calculated gas-phase NO₃(a), O,O'-nitrato (b), and nitrato (c) isomers.

(Figure 3.7b). This configuration is labeled O,O'-nitrato. The bond distances between N and the two bridging O atoms increase 0.054 Å from gas-phase NO₃ to 1.306 Å while the terminal N–O bond is shortened 0.030 Å. The NO₃ adsorbate is bound with respect to gas-phase NO₃ by 1.67 eV, intermediate between NO and NO₂. The Pt atoms separate negligibly in the lateral directions and rise 0.099 Å above the surface plane, and the Pt–O distances are 2.113 Å. The Pt–Pt and Pt–O distances are comparable to those of O,O'-nitrito (Table 3.1).

Bader decomposition indicates that 0.50 electrons transfer from Pt to NO₃ upon adsorption, comparable to the charge transfer found for NO and NO₂ adsorbates (Table 3.2). As shown on the right side of Figure 3.8, the NO₃ valence electronic structure is similar to NO₂ in having close lying and partially filled in-plane (3e′ and 2a₂') and filled and vacant out-of-plane (1e'' and 2a₂'') levels. Also like NO₂, the primary orbital interactions upon adsorption involve mixing and charge transfer into the in-plane states from Pt d levels. Occupation of the in-plane levels increases by 0.4 electrons, while only 0.05 electrons are transferred to NO₃ through out-of-plane interactions.
Figure 3.8. Orbital correlation diagram for O,O’-nitrato NO$_3$ adsorption on Pt(111). Right: Valence NO$_3$ molecular states. Left: Contributions of NO$_3$ in-plane (blue), out-of-plane (red), and surface Pt d states to the total DOS.
O,O'-nitrato adsorption causes the degenerate NO$_3$ asymmetric stretch to separate into higher and lower frequency modes (Table 3.3). The higher frequency mode is similar to an asymmetric stretching mode observed for a surface nitrate on Ag(111) [185]. The symmetric stretch is red-shifted 139 cm$^{-1}$.

Analogous to observations for NO$_3$ adsorption on basic metal oxides [218], a metastable NO$_3$ adsorption mode can also be found in which the adsorbate binds planar and side-on to Pt(111) with local D$_{3h}$ symmetry (Figure 3.7c). This nitrato adsorption energy is 1.17 eV, or 0.50 eV less than the perpendicular-bound O,O'-nitrato isomer. Here charge transfer from the surface to the adsorbate is a substantial 0.70 electrons and the distance between surface and adsorbate more than 2.2 Å. The bonding thus has a large electrostatic component and is likely most important, if ever, under conditions in which the Pt surface is electron-rich rather than under the oxidizing conditions relevant to NO oxidation.

3.2.2.4 O and N

In order to compare the energies of Pt–adsorbed NO, NO$_2$, and NO$_3$ it is useful to have as energy references their surface-bound atomic constituents, O and N. Both O and N atoms are well known to prefer FCC sites on Pt(111) at low coverages. The PW91-GGA binding energies referenced to gas-phase O($^3$P) and N($^4$S) are 4.38 and 4.89 eV, respectively (Table 3.1), in good agreement with previously reported results [18, 98, 188, 241]. These binding energies decrease at 1/4 ML by 0.02 and 0.08 eV, respectively, an amount commensurate with that for the various molecular adsorbates. As shown by Bader analysis, at 1/16 ML charge transfer to both atoms in these sites is substantial (Table 3.2), reflecting the large electronegativities of both atoms. Binding at HCP sites is found to be
less favorable by 0.40 and 0.18 eV for O and N, respectively, in good agreement
with previously reported results \[73\]. Bridge-bonded N is also metastable; in
contrast, the bridge site is a transition state for O diffusion between HCP and
FCC sites \[25\].

Because of ambiguities in the definition of the atomic ground states within
DFT \[10\] it is both more convenient and, due to cancellation of overbinding er-
rors between the metal–atom and atom–atom bonds, more accurate to report
these atomic binding energies with respect to the calculated gas-phase $O_2$ and $N_2$
molecules.

$$\frac{1}{2} A_2(g) \rightarrow A^* \quad \text{(3.1)}$$

On this basis the 0 K binding energies are $-1.29$ and 0.28 eV for an O and N atom,
respectively. Note that N adsorbs endothermically with respect to $N_2$. While we
are unaware of any experimental determination of the N binding energy, the O
binding energy can be compared to the observed single-crystal heat of adsorption
of $O_2$ on Pt(111) reported by King et al \[266\]. The adsorption heat was obtained
by pulsing an $O_2$ molecular beam at a Pt(111) crystal surface and measuring both
the temperature rise due to exothermic dissociative adsorption and the pressure
rise due to molecular scattering and desorption. Extrapolating to low-coverage
and ignoring adsorption likely due to surface defects, the dissociative adsorption
energy is reported to be 1.58 eV at 298.15 K. Correcting to 0 K using the tabulated
heat capacities \[176\] and removing zero point energy contributions using the DFT-
calculated O–O zero point energy decreases this to 1.46 eV. Using these estimates,
the PW91 GGA underbinds O–Pt(111) by approximately 0.17 eV with respect to
molecular $O_2$. 

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3.3 Discussion

As shown above, the likely intermediates in NO oxidation, including NO, NO₂, and NO₃, all adsorb exothermically on the Pt(111) surface, accompanied by substantial charge transfer from the surface to the adsorbates and modest surface relaxations. All three of these adsorbates have fairly large electron affinities (0.026 eV [176], 2.273 eV [69], and 3.937 eV [252], respectively) and either \( \pi \) (NO) or \( \sigma \) (NO₂, NO₃) orbitals available for accepting electron density. The observed structural changes and vibrational frequency shifts are consistent with those expected for reduced forms of the adsorbates. With respect to the gas-phase molecules the order of binding energies is found to be NO > NO₃ > NO₂.

With respect to understanding the surface thermodynamics of NO oxidation, it is useful to consider the stabilities of the NO, NO₂, and NO₃ species relative to each other and to their atomic fragments. The relative DFT energies of the various adsorbate combinations at constant NO₃ stoichiometry and 1/16 ML coverage of all species (i.e., approximately the low coverage limit) are plotted in Figure 3.9. The most stable surface composition is dilute adsorbed NO and O, which is slightly lower in energy than atomic N and O and 0.78 eV lower in energy than adsorbed NO₂. Thus, consistent with previous evidence, the present DFT results show Pt(111)-adsorbed NO to be stable both to dissociation [31, 145] as well as to oxidation to NO₂ via reaction with surface O in the absence of any lateral interaction effects [12, 13, 188]. Oxidation of adsorbed NO to adsorbed NO₃ is even more endothermic and thus energetically unfavorable at low surface coverage.

The DFT-calculated relative energies of gas-phase NO, NO₂, and NO₃ are also indicated on the same energy axis in Figure 3.9. The significant surface adsorption
Figure 3.9. DFT-calculated energies of NO, NO₂, NO₃, and N at constant NO₃ stoichiometry at low coverage.
energy of NO\textsubscript{2} likely accounts, at least in part, for the inhibiting effect of gaseous NO\textsubscript{2} on catalytic NO oxidation over Pt catalysts \cite{171, 172}. To the extent that catalytic NO oxidation does occur via a Langmuir-Hinshelwood type mechanism on the Pt(111) surface, then, it is a result of modifications of the surface energetics arising from destabilizing lateral interactions between the adsorbates that promote both the conversion of NO to NO\textsubscript{2} and the desorption of NO\textsubscript{2}.

Under practically relevant catalytic NO oxidation conditions, O\textsubscript{2} is present at partial pressures many orders of magnitude greater than NO, and thus surface O is likely to be the dominant surface species. Clearly by simple equilibrium arguments, higher O surface concentrations will tend to promote the formation of NO\textsubscript{2}. Local configurational and lateral interaction effects are of even greater importance, however. We have already noted that one significant effect of increasing surface coverage is to drive adsorbed NO and NO\textsubscript{2} to more weakly bound atop sites; the inherently larger destabilizing effect on NO compared to NO\textsubscript{2} will tend to have a promoting effect on the conversion of adsorbed NO to adsorbed NO\textsubscript{2}. Conversion of surface-bound NO to NO\textsubscript{2} involves breaking of one surface Pt–O bond and formation of one O–NO. Higher O coverages favor this transformation in two ways, by weakening the Pt–O surface bond and by locally favoring a more compact single surface species (NO\textsubscript{2}) over two species (NO and O). The magnitude of these effects must be on the order of 1 eV to reverse the low-coverage energetic preference for NO over NO\textsubscript{2}. Previous DFT results \cite{188, 241} show that lateral interactions can in the aggregate be of this order of magnitude.

While the GGA energies reported here are the best available for the surface-bound nitrogen oxide species, the GGA does significantly overestimate the exothermicity of the gas-phase reactions of NO and O\textsubscript{2} to NO\textsubscript{2} (Eq. \ref{eq:1}) and of NO\textsubscript{2} and
O$_2$ to NO$_3$. At 0 K with zero-point contributions removed from the energies, the experimental NO oxidation energy is $-0.64$ eV compared to the GGA result of $-1.18$ eV. NO$_2$ oxidation to NO$_3$ is 0.45 eV (endothermic) while the GGA predicts it to be $-0.07$ eV (exothermic). As a consequence, the GGA significantly exaggerates the gas-phase equilibrium fractions of NO$_2$ and NO$_3$ over NO at any given condition. Further, unless fortuitously compensated by errors in the GGA-calculated molecular adsorption energies, these overestimates also propagate to the surface reactions connecting NO to NO$_2$ and NO$_2$ to NO$_3$. The requirements for favorable surface catalysis, for instance in terms of the destabilizing lateral interactions induced by neighboring adsorbates, are even more stringent than indicated by the GGA. Careful treatment of these effects will be important in any quantitative model of NO oxidation catalysis on Pt(111).

3.4 Conclusions

The DFT supercell results reported here illustrate the variety of nitrogen oxide adsorption states possible on the Pt(111) surface. At low coverage, adsorption is dominated by maximization of back-donation from the Pt surface to the strong electron acceptors NO, NO$_2$, and NO$_3$. These electronic effects are apparent in the calculated charge distributions and in perturbations of the surface and adsorbate density of states. NO in particular is strongly surface bound and is stable both to dissociation and to association with dilute surface O to form NO$_2$. These results are consistent with the well-known ability of NO$_2$ to act as an O atom donor to the Pt(111) surface $^{12,13}$ and reflect the greater inherent strength of the Pt(111)–O bond than the O–NO one. NO$_3$ is relatively higher in energy and not likely to be stable in isolation on Pt(111).
NO and NO$_2$ are found to possess a number of metastable adsorption configurations at low coverage, in which they occupy lower-coordination adsorption sites and reorient with respect to the Pt surface. The lower stability of these configurations reflects less effective charge donation from the Pt surface to adsorbate. At the higher surface coverages of oxygen relevant to catalytic oxidation conditions, competition for metal surface charge density will tend to favor these metastable configurations at the expense of the electron-withdrawing low-coverage configurations. In addition, lateral interactions between adsorbates weaken Pt(111)–O bonds and thus are important in shifting the surface energetics in favor of formation of NO$_2$. Correct description of both the configurational and energetic consequences of high surface coverages are important in capturing the energetics and kinetics of the interconversion of Pt-bound NO and NO$_2$. These topics are explored further in the chapters to come.
CHAPTER 4

THERMODYNAMICS OF ENVIRONMENT-DEPENDENT OXYGEN CHEMISORPTION ON PT(111)

4.1 Introduction

Surface coverage generated by environmental conditions has a large impact on catalysis. For instance, the rate of the familiar CO oxidation reaction on metal surfaces:

\[
\text{CO(g)} + \frac{1}{2}\text{O}_2(g) \longrightarrow \text{CO}_2(g) \tag{4.1}
\]

is well known to depend on the stoichiometric ratio \( p_{\text{CO}}/p_{\text{O}_2} \), which determines whether the metal surface is in a reduced (CO dominated) or oxidized (oxygen dominated) state \([191, 192]\). Near stoichiometry, catalysts can exhibit complex spatial and temporal behavior as their surfaces oscillate between these two regimes \([66, 67, 138]\). Even under conditions in which oxygen is the predominant surface species, the actual compositional state of the active surface can be ambiguous. Oxidation activity has been associated with surface adsorbed oxygen, surface oxide films, and even the bulk metal oxides of nominally metallic catalysts ranging from Ru \([22, 186, 205, 233]\) to Ag \([160, 213, 215]\) to Pd \([77, 243]\) to Pt \([3, 108, 193]\). Even on the noblest of metals, Au, oxidized Au surfaces or islands have been implicated in observed oxidation activity \([52, 89, 157, 164]\).

One can begin to understand the complexity by first looking for simplifying
models to describe limiting regimes of behavior. Equilibrium models, while not fully faithful representations of a dynamic surface under reaction conditions, can be particularly useful for clarifying surface compositions and reaction steps relevant to observed catalysis \[207\]. In the first-principles thermodynamics approach, density functional theory calculations are used to quantify the thermodynamics of various surface compositional states and to relate them to the composition of the gas phase. This approach has been most widely applied to oxidation catalysis in which gaseous O\(_2\) is the principle source of surface oxygen. Considering the lean limit, in which oxygen is the (nearly) exclusive surface species, the catalyst surface or particle composition in equilibrium with O\(_2\) at some temperature and pressure (that is, chemical potential \(\mu_O\)) is determined by the free energy minimum over the possible oxygen compositions and configurations \(X_O\) of the catalyst M:

\[
M + \frac{1}{2}O_2(g) \rightleftharpoons M - O(X_O) \tag{4.2}
\]

As \(\mu_O\) becomes more positive, successively more highly oxygen-covered surfaces become thermodynamically stable. Further, the binding energy of oxygen to the surface—a key indicator of catalytic oxidation activity \[20\]—varies with the surface composition. Identification of the many relevant coverage states \(X_O\) is a significant challenge for any given system, but nonetheless this FPT approach has been productively applied to predict the thermodynamics of oxygen adsorbed on Ru, Pd, Pt, and Ag metal surfaces \[161, 213, 215, 233, 241, 270\] at RuO\(_2\) and Fe\(_2\)O\(_3\) oxide surfaces \[15, 202, 204, 205, 250\], competing metal, metal oxide films, and bulk oxides of Pt, Pd, and Cu \[209, 210, 222, 230\], and finite Pt clusters \[260, 261\]. Campbell has applied these concepts to establish stability limits for thin film metal oxides on metal surfaces \[35\].
In the CO oxidation reaction (4.1) carried out at temperatures and pressures of practical interest, gaseous O\(_2\) is the thermodynamically and kinetically most relevant oxidant present in the reaction mixture and equilibrium (4.2) bounds the surface oxygen coverage. Such is not necessarily the case in NO oxidation (Equation 1.3). Because the ON–O bond is relatively weak and also kinetically labile, the product NO\(_2\) can sometimes be more effective at dosing oxygen to a catalyst surface than O\(_2\):

\[
M + NO_2(g) \rightleftharpoons M - O(X_O) + NO(g) \quad (4.3)
\]

As discussed in Chapter 3, NO\(_2\) dosing is used to promote the formation of high coverages of oxygen on Pt surfaces [12, 13, 189], and this equilibrium has been proposed to control Pt surface oxygen during NO oxidation catalysis [171–173, 229]. Thus, the surface oxygen coverage, and the oxygen binding energy, can depend on the NO oxidation reactant and product concentrations.

In studying NO oxidation, it is important to take into consideration the possibility that \(\mu_O\) is not solely determined by temperature and pressure of O\(_2\) when determining the thermodynamic limits for oxygen chemisorption. In this chapter, we catalog and determine the oxygen binding energies and stabilities of a wide range of ordered Pt(111)-O configurations. We identify several distinct binding energy regimes associated with increasing oxygen coverage on the metal surface. We then use FPT methods to predict the oxygen coverages in equilibrium with a variety of oxygen sources. We identify several oxygen dosage cases arising from different assumptions about the kinetically important pathways by which oxygen adds to the surface, each providing a different representation of the equilibrium surface oxygen coverages. Finally, we present a simple diagrammatic approach to summarize coverage-dependent oxygen adsorption thermodynamics. The re-
sults help illuminate the coupling between reaction conditions, surface reactivity, and surface composition necessary to develop a complete model of NO oxidation catalysis. The work in this paper is taken almost exactly from Reference [82].

4.2 Results

4.2.1 Oxygen Adsorption Sites and Lateral Interactions

Figure 4.1 summarizes the DFT results for isolated oxygen atoms adsorbed FCC, HCP, atop, and bridge sites, here modeled using a 4 Pt × 4 Pt supercell with 0 K, non-zero point corrected binding energies reported relative to a gas-phase triplet O$_2$ molecule. As shown in Chapter 3, at low coverage, O is well-known to prefer to bind in three-fold hollow FCC sites [81], while HCP adsorption is 0.4 eV higher in energy. The bridge site is actually a transition state for O diffusion [25], while the atop site is unstable. O adsorption in the lowest-energy FCC site induces a significant amount of relaxation in the Pt(111) lattice: lateral, in-plane relaxation of the Pt atoms away from O increases the Pt separations by 0.212 Å (7.5%) [72]. By comparison to adsorption at a Pt(111) surface rigidly constrained at the clean geometry, this relaxation contributes 0.3 eV to the calculated O binding energy.

To examine the effect of co-adsorption on oxygen binding, we calculated the adsorption energies of O atom pairs at first-, second-, and third-nearest neighbor (1NN, 2NN, and 3NN, respectively) separations in FCC sites (Figure 4.2). The relaxed locations and energies relative to infinite separation are shown in Figure 4.2. The lateral interactions between O atoms are uniformly repulsive (positive in sign), are most pronounced for atoms that share a surface Pt atom, and decrease in magnitude monotonically with the O-O distance. Co-adsorption
Pt(111) + ½ O₂ (g) → Pt(111)-O( X₀)

FCC
-1.291 eV

HCP
-0.899 eV

Bridge
-0.676 eV

Atop
+0.178 eV

TS at low θ

Figure 4.1. Isolated O binding structures and energies relative to O₂ (g).

O* + O* (dₒ-O* = ∞) → 2O*

1NN
3.01 Å
Relaxed 0.203 eV
Rigid 0.243 eV

2NN
4.91 Å
Relaxed 0.099 eV
Rigid 0.015 eV

3NN
5.63 Å
Relaxed 0.009 eV
Rigid -0.023 eV

Figure 4.2. First-, second-, and third- nearest neighbor separations and interaction energies for O bound in FCC sites. The arrows indicate the directions of local Pt relaxations due to adsorption. Interaction energies are relative to two FCC-bound O in isolation and are compared with ones on a rigid Pt lattice (all Pt in clean Pt(111) positions). The rigid 1NN, 2NN, and 3NN separations are 2.82, 4.88, and 5.64 Å, respectively.
generally induces lateral lattice relaxation similar to that from single O adsorption, but modified by the mutual effect of neighbor O on some intervening Pt atoms. These mutual interactions can either reinforce or oppose each other, as illustrated in Figure 4.2. Similar effects are observed for O in other sites. For instance, a pair of FCC- and HCP-bound O separated by 3.47 Å, 4.30 Å, and 5.87 Å interact repulsively by 0.31, 0.086, and 0.043 eV, respectively, with respect to isolated FCC and HCP O.

The origins of these destabilizing O–O lateral interactions include factors such as Coulombic repulsion between adsorbates, local changes in surface electronic structure and bonding, and Pt(111) lattice strain [71]. To isolate the contributions of surface strain to the interaction energies, we re-calculated the FCC pair interactions by allowing the O atoms to relax while constraining the Pt atoms to their clean Pt(111) positions. This rigid surface model gives an indication of the “intrinsic electronic” 1NN, 2NN, and 3NN interaction energies. The rigid interaction energies are calculated to be 0.243, 0.015, and −0.023 eV, respectively, to be compared with the 0.203, 0.099, and 0.009 eV interactions on the fully relaxed surface. At 1NN separation Pt surface relaxation decreases the repulsion between O by 0.04 eV; the local relaxations about each O constructively reinforce each other and are thus attractive (Figure 4.2) because they push a common Pt atom away from each other. In contrast, at 3NN separation the O experience a slight intrinsic attractive interaction that is opposed by 0.03 eV by surface relaxation; at this separation the local relaxations about O tend to push an intervening Pt pair together. At 2NN separation the small intrinsic repulsive interaction is increased by 0.08 eV by surface relaxation: the local O relaxations push several Pt atoms together and significantly destabilize the O pair. Thus, while intrinsic electronic
effects are the major contributors to the 1NN interaction, surface relaxation is responsible for the large magnitude of the 2NN interaction and even the sign of the 3NN interaction.

The binding energy of a specific surface-bound O is thus influenced by the number and arrangement of neighbor O. This effect can be further probed by calculating binding energies for O atoms in various local arrangements using forward differencing on the slab energies:

$$\text{Pt}(111) - O(X_O) + \frac{1}{2}O_2(g) \rightarrow \text{Pt}(111) - O(X_O) + O^*$$  (4.4)

We consider a variety of configurations with all O in FCC sites and report binding energies with respect to gas-phase $O_2$, as for isolated O in Figure 4.1b. Using this reference, binding energies range from $-1.3$ eV to $+1.0$ eV, with exothermic adsorption in the limit of few neighbors and highly endothermic adsorption at the largest number of neighbors. Figure 4.3a plots the binding energies calculated this way against the number of nearest neighbor O, a simple diagnostic of local environment. Binding energy clearly decreases with neighbor number, but the influence of 2NN and other interactions introduces significant scatter and curvature. Based on the observation above that the 1NN interaction is twice as great as the 2NN interaction and that the 3NN interaction is small for a pair of O atoms, we define an effective neighbor number, $N_{\text{NN}_{\text{eff}}}$:

$$N_{\text{NN}_{\text{eff}}} = 2N_{\text{1NN}} + N_{\text{2NN}}$$  (4.5)

Binding energies are plotted against $N_{\text{NN}_{\text{eff}}}$ of O* in Figure 4.3b. The configuration-specific O binding energies correlate nearly linearly with the composite neighbor
Figure 4.3. Calculated FCC O binding energies relative to gas-phase O$_2$ as a function of the number of 1NN (a) and composite numbers of 1NN and 2NN (b) FCC O.

number at small numbers of neighbors. The scatter in energy increases substantially at high neighbor numbers. While simple neighbor number descriptors can be useful indicators of the effects of local environment on bond energy, more sophisticated parameterizations of DFT energies based on bond order conservation or cluster expansions provide greater quantitative predictability.

4.2.2 Equilibrium Oxygen Adsorption Configurations

To examine the effects of multiple surface interactions on equilibrium surface thermodynamics, we constructed 82 configurations of O adsorbed on the unreconstructed Pt(111) surface at 32 different coverages, \( \theta_O = N_O/N_{Pt} \), from 0 to 1 ML (1 ML \( \Rightarrow N_O/N_{Pt} = 1 \)). O atoms and the three top-most Pt layers in the slab are allowed to relax. The configurations include various combinations of O binding at FCC, HCP, and atop adsorption sites. The bridge site was excluded as it is a transition state for O diffusion between FCC and HCP.
sites at low coverage \cite{25}. In general, configurations were chosen iteratively with
the goal to minimize the total energy at each coverage and to include all stable
configurations identified in previous computational work \cite{241} and suggested by
experimental observation \cite{125,253}. The computed formation energy is a use-
ful measure of stability and is a function of $N_O$. It is computed by comparing
the electronic energy of a particular configuration $X_O$ with that of an arbitrarily
chosen reference. We choose the clean surface and an equivalently sized supercell
with 1 ML of FCC-bound oxygen as a reference to maximize cancellation of error:

$$\gamma_{X_O}^{\text{form}} = \left[ E_{X_O}^{\text{DFT}} - (\theta_O E_{1\text{ML}}^{\text{DFT}} + (1 - \theta_O) E_{\text{Pt}(111)}^{\text{DFT}}) \right] / A \quad (4.6)$$

Surface formation energies are shown in Figure 4.4 plotted against $\theta_O$ and labeled
by adsorption site. Consistent with the low-coverage results, Figure 4.4 shows that
O atoms prefer to bind in FCC sites at all coverages and generally order in such a
way as to minimize destabilizing 1NN and 2NN interaction combinations. The
thermodynamically stable O configurations at 0 K are those that lie on the convex
hull of surface formation energies, denoted by the solid line. All configurations
not on the hull are meta-stable to a linear combination of the two adjacent stable
configurations. Some of these configurations are close to the stability line (i.e.
within 1 meV Å$^{-2}$ of the hull) and thus may become important at finite $T$. All
the configurations on and those close to the hull are displayed in Figure 4.5. The
results here are largely consistent with previous DFT calculations of a more modest
number of chemisorbed O configurations, including in particular the appearance
of cusps in the formation energy at the 1/4 ML p(2×2)-O, 1/2 ML p(2×1)-O,
and 2/3 ML p(\sqrt{3} \times \sqrt{3})-2O configurations \cite{241} and the appearance of a 0.4 ML
configuration on the hull. In disagreement with prior work, we do not find either
Figure 4.4. DFT-calculated surface formation energies of Pt(111)–O(X₀) as a function of θ₀, labeled by the types of adsorption sites occupied in the configuration. Energies of stable configurations are circled and form the lowest-energy hull.
the 1/3 ML \( p(\sqrt{3} \times \sqrt{3}) \)-O or the 3/4 ML \((2 \times 2)\)-3O orderings to lie on the low energy hull; both are metastable to configurations not included in earlier analysis. Empirically we find that at all coverages the lowest energy configurations are those that maximize the lateral separation of O atoms. Along the formation energy line within the region \( 0 \leq \theta_O \leq 1/4 \) ML, for instance, O atoms add such that the minimum O separation is 3NN. This sequence ends in the \( p(2 \times 2) \)-O ordering, where the FCC lattice is filled up through 3NN sites, i.e. six 3NN per O. This ordering is well known to form upon exposure of a Pt(111) surface to O\(_2\) at modest temperatures and UHV pressures \([55, 85, 87, 152, 178, 235]\). The average two-body repulsive 3NN interaction is +0.010 eV per O pair in this configuration, very similar to the +0.009 eV noted above for two interacting O in isolation.

Addition of FCC oxygen beyond \( p(2\times2) \)-O occurs with the introduction of 1NN and 2NN interactions and culminates in the \( p(2\times1) \)-O ordering. This configuration has one third of the 1NN and 2NN sites filled in addition to all the 3NN ones for each O. In this ordering, the O atoms occupy alternating rows of FCC sites. This ordering may account for observations of a \((2 \times 2)\)-2O pattern observed in LEED at \( \theta_O \approx 0.5 \) ML \([125, 234, 253]\). For the \( p(2\times1) \)-O ordering to match LEED observations, O rows would be present in three degenerate orientations rotated 120° from each other on the same lattice. This rotational disordering has been observed in Monte Carlo simulations of adsorbed O ordering \([241]\).

Recent temperature-programmed desorption (TPD) and high-resolution electron energy loss spectroscopy (HREELS) experiments using isotopically labeled oxygen have been interpreted in terms of occupation of HCP O sites at coverages above 1/4 ML, and in particular a hexagonal configuration of 50% FCC and 50% HCP O at 1/2 ML (Figure 4.5) has been proposed to account for the appearance
Figure 4.5. DFT-calculated O coverages and configurations. Stable configurations are to the left of and above the topmost dotted line, nearly stable configurations are in between the dotted lines, and the 50% FCC/50% HCP configuration proposed to explain TPD results [125] is below and to the right of the bottommost dotted line.
of multiple desorption peaks in O$_2$ TPD experiments \cite{125, 253}. As shown in Figure 4.4, we find partial HCP occupancy (triangle symbols) to be energetically disfavored to FCC occupancy at all coverages \cite{55}. If such a mixed phase does form, then, it is due kinetic effects, entropic effects, or both.

Beyond p(2×1)-O, the next configuration located on the lowest energy hull is the 2/3 ML p(√3 × √3)-2O. The region in between it and p(2×1)-O is characterized by rearrangement of O from linear to hexagonal ordering in which each O has three 1NN, six 2NN, and three 3NN, i.e., an increase in 1NN and 2NN, and a decrease in 3NN compared to p(2×1)-O. Based on the two-body interaction energies estimated from calculations on O atom pairs above, this configuration would be expected to be unstable relative to configurations with a filled 3NN sub-lattice. Some combinations of more distant two-body interactions and/or multi-body interactions thus contribute to the stability of this configuration.

Beyond 2/3 ML, the 1NN, 2NN, and 3NN interactions begin to saturate, leading to sharp energy increases. We find that O maintains its preference for hexagonal ordering on the (3×3) lattice, and therefore that the 3/4 ML (2×2)-3O ordering is meta-stable to the p(√3 × √3)-2O and 7/9 ML orderings. Chemisorbed oxygen coverages have been reported up to 0.77 ML O on Pt(111) \cite{189, 190, 211, 253}, consistent at least in coverage with the calculated stable FCC-only 7/9 ML configuration.

All of these surface oxygen configurations are conceivably in competition with an oxidized surface film \cite{271}. The structures of these oxide overlayers may or may not correspond to the stable bulk oxides and can be difficult to predict, even with the aid of experimental observation \cite{24, 55, 160}. To compare the stability of one possible form of a surface oxide against the adsorbed configurations considered
here, we calculate the structure and energy of an α-PtO₂ film above Pt(111). This film has been suggested as the form of such an oxide on Pt(111) both because it has good epitaxy and because α-PtO₂ itself has a small surface energy. Our calculated structure of Pt(111)-α-PtO₂ is shown in Figure 4.6. We find that the α-PtO₂ film indeed has good epitaxy with Pt(111): its (100) direction can align against the (200) direction of Pt(111), yielding a lattice parameter within the surface oxide of 3.253 Å, just slightly exaggerated from its calculated bulk value of 3.167 Å. Because of the change in Pt stoichiometry at the surface, the formation energy of the surface oxide cannot be plotted directly on Figure 4.4. We consider the comparison of chemisorbed oxygen and surface oxide further below.

4.2.3 Coverage-dependent Oxygen Binding Energies

In order to relate surface coverage to surface reactivity, it is useful to extract from Figure 4.4 equilibrium coverage-dependent oxygen binding energies. At 0 K the integral adsorption energy at any coverage is related to the difference in energy
between a point on the formation energy hull and an equivalent amount of Pt surface and gas-phase O\(_2\). The equilibrium *differential* adsorption energy at 0 K is then related to the slope of the formation energy curve and can be written as

\[
\Delta E_{\theta O}^{\text{bind}}(0K) = \bar{A} \frac{d\gamma_{\theta O}^{\text{form}}}{d\theta_O} + \Delta E_{\theta O=1}^{\text{int}}
\]  

(4.7)

where \(\bar{A}\) is the Pt(111) surface area per Pt, and, taking gas-phase O\(_2\) as the oxygen reference, \(\Delta E_{\theta O=1}^{\text{int}} = -0.232\) eV/O is the per O DFT energy difference due to

\[
\text{Pt(111)} + \frac{1}{2}\text{O}_2(g) \rightarrow \text{p}(1 \times 1) - \text{O}
\]  

(4.8)

Four distinct coverage-dependent Pt(111) oxygen binding energy regimes are evident from the DFT-computed formation energy hull, including a low coverage regime at 0 < \(\theta_O\) ≤ 1/4 ML, a moderate coverage regime at 1/4 < \(\theta_O\) ≤ 1/2 ML, a high coverage regime at 1/2 < \(\theta_O\) ≤ 2/3 ML, and a highest coverage regime beyond 2/3 ML. The formation energies vary nearly linearly with \(\theta_O\) in the first three regimes (although the third of these is defined only by its two endpoints) and quadratically at highest coverage. The formation energies in each of the regimes are fitted using the method of least squares and differentiated to get differential adsorption energies by use of Equation 4.7. In the region 0 < \(\theta_O\) ≤ 1/4 ML, \(\Delta E_{\theta O}^{\text{bind}}\) by this analysis is −1.255 eV per O. For comparison, the calculated electronic energy difference for the reaction

\[
\text{Pt(111)} + \frac{1}{2}\text{O}_2(g) \rightarrow \text{Pt(111)} - \text{O(0.04)}
\]  

(4.9)

by forward differencing is −1.342 eV per O. In the 1/4 < \(\theta_O\) ≤ 1/2 and 1/2 < \(\theta_O\) ≤ 2/3 ML regimes the binding energies increase to −0.658 and −0.168 eV
per O, respectively. Beyond 2/3 ML O the differential binding energy increases linearly with $\theta_O$, from +0.426 eV per O at 2/3 ML to +1.076 eV per O at 0.94 ML. From these results the 2/3 ML p($\sqrt{3}$ $\times$ $\sqrt{3}$)-2O ordering is the highest surface O coverage thermodynamically accessible with O$_2$ (g). Stronger oxidants, such as O$_3$ or N$_2$O, would be necessary to achieve higher O coverages.

Experimental observations are consistent with the calculated low coverage adsorption energy and the decrease in adsorption energy with increasing coverage on Pt(111) [189]. The low-coverage adsorption energy has been estimated from single-crystal calorimetry experiments [266] to be $-1.58$ eV per O, while careful kinetic analysis of TPD spectra [38, 189] provides a value of $-1.11$ eV per O. The DFT differential adsorption energy can be approximately corrected to a finite temperature enthalpy by incorporating surface vibrational and gas-phase enthalpy corrections:

$$
\Delta H^{\text{bind}}(T) = \Delta E^{\text{bind}} + E_{O}^{\text{ZP}} + \Delta E_O(T)
$$

$$
- \frac{1}{2} \left[ E_{O_2}^{\text{ZP}} + \Delta H_{O_2}(T) + k_B T \ln \left( p_{O_2}/1 \text{ bar} \right) \right]
$$

where $E_{O}^{\text{ZP}}$ is the zero-point energy of one adsorbed O, $\Delta E_O$ is the temperature-dependent vibrational internal energy of one adsorbed O, and $E_{O_2}^{\text{ZP}}$ is determined from the DFT calculated O$_2$ vibrational stretch [81]. $\Delta H_{O_2}(T) = H_{O_2}(T) - H_{O_2}(0K)$ is calculated using values obtained by interpolating the Shomate Equation between 298 and 1200 K [176] and linearly extrapolating to 0 K. From this analysis, $\Delta H^{\text{bind}}(298K, 1\text{bar})$ is $-1.23$ eV per O for $0 < \theta_O \leq 1/4$ ML. The temperature-corrected DFT result is thus within 0.12 eV of the TPD observation but differs more significantly from the calorimetry results.

Kinetic analysis of TPD experimental results shows a gradual increase in oxy-
gen adsorption energy up to 1/4 ML, followed by a sharp increase above that coverage [189]. The TPD results are a convolution of the coverage-dependent thermodynamics and kinetics of desorption so extraction of quantitative adsorption energies is difficult. At 1/4 ML the adsorption energy is estimated to be $-0.78 \text{ eV per O}$, which can be compared with the DFT result of $-0.658 \text{ eV per O}$ ($\Delta H_{\text{bind}}^{\text{DFT}}(298K, 1\text{bar}) = -0.56 \text{ eV per O}$).

From Figure 4.4, the thermodynamically persistent configurations are those at the endpoints of the first three coverage regimes, i.e. $p(2\times2)$-O, $p(2\times1)$-O, and $p(\sqrt{3} \times \sqrt{3})$-2O. Each of these will be the thermodynamically preferred surface O ordering over some range of oxygen chemical potentials. The 0 K surface free energies $\gamma_{XO}^{(1)}(0K, \mu_0)$ of these orderings, calculated according to Equation 2.25, are plotted against oxygen chemical potential $\mu_0$ in Figure 4.7. Increasing O potential minimizes the surface energy of progressively more highly O-covered surfaces. To place the $\alpha$-PtO$_2$ overlayer on this same scale, we assume that Pt in the overlayer is in equilibrium with a bulk reservoir, i.e. that Pt can freely exchange between surface and the bulk, and transform $\gamma_{XO}^{(1)}(0K, \mu_0)$ with respect to the changes in the number of Pt at the surface, $\Delta N_{\text{Pt}}$:

$$\gamma_{XO}^{(2)}(0K, \mu_0, \mu_{\text{Pt}}) = \gamma_{XO}^{(1)}(0K, \mu_0) - (\Delta N_{\text{Pt}}/A) \mu_{\text{Pt}} \tag{4.11}$$

Taking $\mu_{\text{Pt}} = E_{\text{DFT}}^{\text{bulk}} + E_{\text{ZP}}^{\text{bulk}}$ yields the result shown in Figure 4.7. Zero point vibrational contributions to the energy are computed based on the DFT calculated vibrational spectrum of just the $\alpha$-PtO$_2$ overlayer.

The $\alpha$-PtO$_2$ thin film indeed becomes stable at O potentials similar to those in equilibrium with the moderate coverage regime, i.e. in the region where the $1/4$ and $1/2$ ML lines intersect. One cannot rule out the existence of other, even lower
energy surface oxide films. Thus, based on these DFT results, one can conclude that any surface O coverage greater than 1/2 ML is meta-stable to formation of a surface oxide, and any such coverages that do form owe their existence to kinetic resistance of the Pt(111) surface to the formation of such an oxide. In contrast, the $\alpha$-PtO$_2$ surface oxide is metastable to surface oxygen at lower oxygen chemical potentials.

An oxidized Pt surface has been observed to be formed during dosing of O atoms to the Pt(111) surface [211, 253]. The transition from chemisorbed oxygen to an oxidized surface around 0.75 ML is characterized by a shift of the O$_2$ TPD peak to higher temperature, suggesting that oxygen is more strongly bound in the oxide than on the Pt(111) surface. Consistent with this, we calculate the energy to remove one O atom from the Pt(111)-$\alpha$-PtO$_2$ overlayer to be 1.435 eV, or at least 0.18 eV greater than any surface chemisorbed O. This oxide is observed to coexist with chemisorbed oxygen down to a coverage of 0.5 ML [253], also consistent with
the crossover between oxide and surface oxygen shown in Figure 4.7. While we have not investigated the transformation from the oxide to chemisorbed oxygen, it seems quite likely from the different structures and compositions of the oxide and chemisorbed oxygen phases that such a transition is activated and contributes to the “explosive” transformation of the oxide to an oxygen-covered surface at conditions at which the oxide is meta-stable to surface oxygen.

4.3 Analysis and Discussion

Given this catalog of oxygen coverages and binding energies, the limiting equilibrium surface oxygen coverages under various reaction assumptions and conditions can be considered. To do so, it is useful to imagine a metal surface in a well-mixed reactor in which an oxidizing gas or gas mixture is fed at some fixed inlet concentrations, and to further imagine that the surface comes to an equilibrium with oxygen through some limited and prescribed reactions. The conceptually simplest case is that in which the only source of surface O is directly dissociated O$_2$ (g), but the addition of reductants or alternative oxygen sources may modify the equilibrium O coverage. Figure 4.8 illustrates several different equilibrium scenarios that we model using statistical thermodynamics. In these scenarios we consider different equilibria between bound O and an O source. The different O sources generate different O chemical potentials which can be used in coordination with Equation (12) to perform stability analyses.

4.3.1 Chemisorbed oxygen from O$_2$

In the case in which the metal surface is exposed only to a gas of O$_2$ and inerts, corresponding to 1 in Figure 4.8, the steady-state, equilibrium surface
Figure 4.8. Possible reactions between an oxygen-covered surface and gas-phase oxidants and reductants, modeled in a well-mixed flow reactor.

The surface free energy of any particular surface coverage, $\gamma^{(1)}_{\theta_0}(T, \mu_0)$, is thus determined by the gas-phase oxygen potential, which itself is related to the $O_2$ \((g)\) pressure $P$ and temperature $T$ through an equation of state. Assuming ideal gas behavior, as is appropriate for conditions of catalytic relevance, the integrated form of the Gibbs-Duhem equation gives \[27\]:

$$\mu_{M-O} = \frac{1}{2} \mu_{O_2}^0$$

\[(4.13)\]

where $\Delta G_{O_2}(T, 1\text{bar}) = G_{O_2}(T, 1\text{bar}) - G_{O_2}(0K, 1\text{bar})$ and is calculated in the same manner as $\Delta H_{O_2}(T, 1\text{bar})$ in Equation \[4.10\]. Using this method, we find $\Delta H_{O_2}(298K, 1\text{bar})$ to be 0.0975 eV, which is in excellent agreement with the
Figure 4.9. Pt(111)/O\textsubscript{2} stability diagram (a) and diminishing effect of NO + 1/2 O\textsubscript{2} ⇌ NO\textsubscript{2} equilibrium on equilibrium O coverages (b). In (b) initial mole fractions of O\textsubscript{2}, NO, and NO\textsubscript{2} are 10\%, 20\%, and 0\%, respectively, in a balance of inert gas, and the total pressure is allowed to vary with \(P_{O_2,0}: (P = 10 \times P_{O_2,0})\). In the shaded regions, chemisorbed O configurations are metastable to Pt(111)-α-PtO\textsubscript{2}.

\[ H_{O_2}(298 K, 1 \text{bar}) - H_{O_2}(10 K, 1 \text{bar}) \] of 0.0974 eV determined using the HSC database \[117\]. Notice that \(\mu_{O_2}^0 = G_{O_2}^0\), as is the thermodynamic definition of chemical potential.

In Figure 4.9a we plot the calculated O configurations that minimize the surface free energy \(\gamma_{X_O}^{(1)}(T, \mu_O)\) as a function of \(T\) greater than 300 K and \(P\) from UHV to ambient, conditions over which O\textsubscript{2} is expected to extensively dissociate over the Pt(111) surface. This stability diagram is drawn to include two types of regions: ordered configurations and intermediate regions in which one ordered configuration evolves into the next higher or lower coverage. In the latter we include the configurations that lie along the linear portions of the formation energy curve which have nearly constant oxygen binding energies and thus are unlikely
to be distinguishable as unique phases. The former are the endpoints of those regimes, where oxygen binding energies change distinctly. Within this model the 1/4 ML ordering is stable over a wide range of $T$ and $p_{O_2}$ conditions, including typical UHV conditions. Experiment 53, 85, 87, 152, 178, 235 and previous DFT-parameterized Monte Carlo simulations 99, 241 agree that at low $T$ the 1/4 ML coverage corresponds to the p(2×2)-O ordering and that the p(2×1)-O ordering becomes stable at higher coverage. The surface oxide is stable at the conditions in the shaded region, first appearing at chemical potentials in equilibrium with coverages between 1/4 and 1/2 ML. Chemisorbed oxygen regimes become metastable to this surface oxide at this point, although they are experimentally observed to persist to over 1/2 ML, again presumably reflecting the slow kinetics of transformation from chemisorbed phase to surface oxide 97, 125, 253. The highest coverage attainable with $O_2$ oxidant under representative oxidation conditions is 1/2 ML.

4.3.2 Effect of reductants on equilibrium surface oxygen

A reductant $Y$, such as $CO$, $NO$, $H_2$, or $CH_4$, added with $O_2$ to a well mixed reactor can diminish the oxygen concentration and chemical potential by (possibly catalyzed) reactions to form $YO$ ($CO_2$, $NO_2$, $H_2O$, and $CH_3OH$, respectively). The range of possible oxygen potentials in the reactor is bounded from above by the inlet $O_2$ concentration, $\mu_{max}^{M-\text{O}} = 1/2\mu_0^{O_2}$, corresponding to no $O_2$ consumption by $Y$. The minimum oxygen potential is determined by the equilibrium consumption of $O_2$ by $Y$, which is determined both by the relative amounts of reductant to oxidant and by the gas-phase chemical equilibrium 35:

$$Y(g) + \frac{1}{2}O_2(g) \rightleftharpoons YO(g) \quad (4.15)$$
\[ \mu_{M-O} = \frac{1}{2} \mu_{\text{O}_2}^{\text{eq}} = \mu_{\text{YO}}^{\text{eq}} - \mu_{\text{Y}}^{\text{eq}} \]  

(4.16)

This situation corresponds to simultaneous equilibrium of both (1) and (2) in Figure 4.8. The equilibrium values can be determined by solving the mass action expression for a given set of initial conditions and equilibrium constant. A simple and instructive case is that in which Y and O\(_2\) are introduced in stoichiometric proportions with an inert diluent to an isothermal, isobaric reactor. The minimum value of the oxygen chemical potential is then:

\[ \mu_{\text{O}_2}^{\text{eq}} = \mu_{\text{O}_2}^0 + k_B T \ln \left( \frac{y_{\text{O}_2}^{\text{eq}}}{y_{\text{O}_2}^0} \right) = \mu_{\text{O}_2}^0 + k_B T \ln (1 - X_{\text{Y}}^{\text{eq}}) \]  

(4.17)

where \( y_i \) are mole fractions and \( X_{\text{Y}}^{\text{eq}} \) is the equilibrium conversion of Y, the solution of the mass action expression:

\[ K_{\text{Y}}^{\text{eq}}(T) = \frac{X_{\text{Y}}^{\text{eq}}}{\sqrt{y_{\text{O}_2} P_{\text{P}} (1 - X_{\text{Y}}^{\text{eq}})^3}} \]  

(4.18)

Here \( P \) is the pressure within the flow reactor and \( P_{\text{P}} \) is the pressure standard of 1 bar.

The effect of strong reductants like CO or H\(_2\) on the oxygen potential is dramatically different from that of a weak reductant like NO or SO\(_2\). In the former case, the equilibria (4.15) go to completion at temperatures at least as high as 1000 K for a wide range of pressures. The equilibrium stoichiometric O\(_2\) concentration is vanishingly small and \( \mu_{\text{O}_2}^{\text{eq}} \) becomes much less than zero, so that the equilibrium O coverage on the Pt(111) surface approaches zero. In comparison, the oxidation of NO to NO\(_2\) is equilibrium limited at moderate temperatures.
Figure 4.9b illustrates the effect of a stoichiometric dose of NO on the equilibrium surface O coverage as a function of initial O$_2$ pressure, obtained from solution of Equations 4.17 and 4.18 and using the experimental NO oxidation equilibrium constant. As seen by comparison with Figure 4.9a, even at stoichiometry the oxygen chemical potential remains high enough to sustain a significant O coverage over all conditions. It is worth noting that the GGA enthalpy of the NO oxidation reaction, $-1.2$ eV, is substantially more negative than the experimental value of $-0.63$ eV at 0 K. Use of the GGA energies would thus significantly overestimate the reducing strength of NO, the extent of the NO to NO$_2$ equilibrium, and the extent to which NO would deplete the equilibrium oxygen coverage on a metal surface.

The equilibrium conversion of NO to NO$_2$ increases with increasing pressure of oxygen and decreasing temperature, and thus conditions that favor high conversions also promote high oxygen coverages. Practical NO oxidation is carried out in excess O$_2$ to promote high conversions, and the diminishing effect of the reductant on oxygen potential is then even less. Thus, even if O$_2$ dissociation is the only source of surface oxygen, equilibrium oxygen coverages upwards of 1/2 ML can be expected on a Pt(111) surface under all NO oxidation conditions, as confirmed by experimental observation [171, 172, 229]. At these high oxygen potentials, chemisorbed O is metastable to oxidized Pt; the deactivation of NO oxidation catalysts due to the formation of oxides has also been noted [172].
4.3.3 Chemisorbed oxygen from alternative sources

4.3.3.1 Oxygen from gas-phase sources

Because the slow kinetics of O$_2$ dissociation at high O coverage can limit the development of equilibrium oxygen coverages, other more kinetically facile oxidants like NO$_2$ [189, 272], O$_3$ [125], and even atomic O [16, 85, 87, 157, 190, 253, 254] are frequently employed to access high O coverage states on Pt and other metals. In principle the equilibrium thermodynamics of O atom adsorption can be modeled in the same way as O$_2$ adsorption. In practice the O chemical potential of an O atom source is much greater than of an O$_2$ source, and thus very high oxygen coverages and oxides are readily formed. To model oxygen coverage from dosage with NO$_2$, O$_3$ or other molecular sources of oxygen requires a slight modification of the thermodynamic model. This situation corresponds to considering the operation of 2 alone in Figure 4.8. Again we imagine a well-mixed reactor in which oxidant YO and reductant Y are introduced in known proportions, so that the equilibrium surface oxygen coverage is determined at steady state by

$$\text{YO} (g) + M \rightleftharpoons Y (g) + M - O(\theta_O)$$  \hspace{1cm} (4.19)

$$\mu_{M-O} = \mu_{YO}^0 - \mu_Y^0$$ \hspace{1cm} (4.20)

In principle the chemical potential difference can be related directly to the DFT energies using an expression similar to Equation 4.14:

$$\mu_{M-O} = E_{YO}^{\text{DFT}} + E_{YO}^{\text{ZP}}$$
$$+ \Delta G_{YO}(T, 1\text{bar}) - (E_Y^{\text{DFT}} + E_Y^{\text{ZP}} + \Delta G_Y(T, 1\text{bar})) + k_B T \ln \left( \frac{y_{YO}^0}{y_Y^0} \right)$$  \hspace{1cm} (4.21)

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As moles of gas are conserved in equilibrium \[4.19\] the oxygen potential is a function of \(T\) and the concentration ratio but not of the total pressure. In practice, a more reliable approach that reduces the DFT errors in the molecular energies is to relate \(\mu_{\text{M-O}}\) to \(\mu_{\text{O}_2}\) from Equation \[4.14\] using the experimentally established standard free energy of the \(Y + 1/2 \text{O}_2 \rightleftharpoons Y\text{O}\) reaction, \(\Delta G^\circ_{Y/YO}(T, 1\text{bar})\):

\[
\mu_{\text{M-O}} = \mu^0_{\text{YO}} - \mu^0_Y = \frac{1}{2} \mu_{\text{O}_2}(T, 1\text{bar}) + \Delta G^\circ_{Y/YO}(T, 1\text{bar}) + k_B T \ln \left(\frac{y^0_{\text{YO}}}{y^0_Y}\right) \tag{4.22}
\]

Y/YO pairs with \(\Delta G^\circ_{Y/YO}(T, 1\text{bar}) < 0\) thus have lower O potential than \(\text{O}_2\) at the same temperature and pressure conditions. Such is the case for the slightly exothermic NO oxidation reaction at moderate temperatures. The opposite is true for pairs with \(\Delta G^\circ_{Y/YO}(T, 1\text{bar}) > 0\), as for \(\text{N}_2/\text{N}_2\text{O}\) or \(\text{O}_2/\text{O}_3\).

Equilibrium O coverages on Pt(111) for \(\text{YO} = \text{NO}_2\), experimental \(\Delta H_{\text{NO/NO}_2}(0\text{K}) = -0.63\) eV, and \(\text{YO} = \text{O}_3\), \(\Delta H_{\text{O}_2/\text{O}_3}(0\text{K}) = +1.49\) eV, are shown in Figures \[4.10\]a and b as a function of the mixing ratio. Again, the GGA-calculated reaction energies of \(-1.2\) and \(+1.2\) eV, respectively, systematically underestimate the experimental energies and would lead to systematically lower predicted O coverages. Both YO/Y reservoirs can generate higher coverages of O on Pt(111) than \(\text{O}_2\) (g). Due to its lower effective 0 K O potential, the NO\(_2\)/NO couple can only do so for mole ratios of NO\(_2\) to NO greater than \(10^6\). There is only a small entropic contribution to the chemical potential because the number of gas phase molecules (NO + NO\(_2\)) remains constant as O is added to and taken from the surface, so as the temperature increases, there is little driving force for O to partition into the gas reservoir. Hence, the NO\(_2\)/NO phase behavior is dominated by the concentration ratio and inverts near \(p_{\text{NO}_2}/p_{\text{NO}} = 1\). Experiments show that NO\(_2\) dosing can generate O coverages on Pt(111) up to 0.7–0.8 ML \[189\]. These coverages are
greater than the highest observed coverage accessible with O_2 by over 0.2 ML. In contrast, the O_3/O_2 reservoir has a greater effective 0 K O potential than O_2 (g). It experiences similar dependencies on temperature and pressure as the NO_2/NO reservoir, but these contributions are less noticeable since it can access high O coverages even at very low O_3 to O_2 ratios. O coverages up to about 1 ML on Pt(111) as well as Pt oxidation have been observed after exposure to O_3 [211].

In these models the surface oxygen is assumed to be in a state of constrained equilibrium with respect to recombinative loss of O atoms as O_2 (1) of Figure 4.8. That is, recombinative O_2 loss is assumed to be negligibly slow compared to O adsorption and removal by YO and Y even under conditions in which O_2 desorption is energetically favored. As such, Y + 1/2 O_2 ↔ YO is not equilibrated. Such appears to be the case under at least some conditions for both the NO_2/NO and O_3/O_2 couples. Both have been observed to access higher coverages than are possible with O_2. O atom dosing has been observed to attain chemisorbed O coverages up to about 0.8 ML [253], further evidence that O recombination on Pt(111) is kinetically slow. Lastly, the observed kinetics of Pt-catalyzed NO oxidation are consistent with a model in which surface O coverage is controlled by facile reaction with NO_2, while unassisted O_2 dissociation is slow [171, 172, 229].

As direct O_2 dissociation is expected to be slow at the high oxygen coverage conditions that prevail during catalytic NO oxidation, alternative routes that effectively result in O_2 dissociation could become practically important. One plausible possibility is reductant assisted O_2 dissociation (3 in Figure 4.8):

\[
\text{NO (g) + O}_2 (\text{g}) + M \rightleftharpoons [M - \text{OONO}] \rightleftharpoons \text{NO}_2 (\text{g}) + M - \text{O} (\theta_o)
\]  (4.23)

In this model, O_2 dissociation proceeds along a pathway in which one Pt–O and
Figure 4.10. Equilibrium oxygen coverages on Pt(111) arising from different oxygen sources: (a) NO$_2$ → NO + Pt(111)-O($\theta_0$); (b) O$_3$ → O$_2$ + Pt(111)-O($\theta_0$); (c) NO + O$_2$ → NO$_2$ + Pt(111)-O($\theta_0$). Note the horizontal axis in (c) is reversed from (a). In the shaded regions, chemisorbed O configurations are metastable to Pt(111)-$\alpha$-PtO$_2$. 
one O–NO bond are formed, mitigating to some extent the unfavorable energetics (and possibly kinetics) of creating two Pt–O bonds from O₂ dissociation. Recent DFT results from our group indicate the possibility of just such a pathway through a peroxynitrite (OO–NO) intermediate \[229\], and is consistent with the observed first order dependence of reaction rate on \( p_{O_2} \). The net gas-phase reaction in this case becomes

\[
\text{NO (g) + O}_2 \text{ (g) } \rightleftharpoons \text{NO}_2 \text{ (g)} + \frac{1}{2} \text{O}_2 \text{ (g)} \quad (4.24)
\]

and the oxygen chemical potential can be written

\[
\mu_{M-O} = \mu_{NO}^0 + \mu_{O_2}^0 - \mu_{NO_2}^0 \quad (4.25)
\]

Contrary to intuition, under conditions in which reaction [4.23] contributes significantly to observed surface oxygen concentration, \( \mu_O \) actually increases with NO and decreases with NO₂ pressures. Following arguments like those above, we can write

\[
\mu_{M-O} = \frac{1}{2} \mu_{O_2}(T, 1\text{bar}) + [-\Delta G^{\circ}_{\text{NO/NO}_2}(T, 1\text{bar})] + k_B T \ln \left[ \frac{y_{\text{NOPO}_2}}{y_{\text{NO}_2}^0} \right] \quad (4.26)
\]

Because the reaction consumes one gas molecule, \( \mu_O \) is a function of the total pressure. Comparing with equation [4.22], the NO oxidation reaction free energy, \( \Delta G^{\circ}_{\text{NO/NO}_2} \), is seen to enter with a negative sign and the mole ratio of NO to NO₂ is inverted. When reaction [4.24] is at equilibrium, the second and third terms cancel and the oxygen potential reduces to that of the O₂-only case described above. Away from equilibrium, in particular at low temperatures and high reactant to product ratios, the second and third terms together become positive and actually increase the oxygen potential over that of the O₂ reservoir acting alone. As a
result, this pathway can in principle promote quite high oxygen coverages.

This effect is illustrated in Figure 4.10, where the equilibrium coverage is plotted against $y_{\text{NO}}/y_{\text{NO}_2}$ at constant $p_{\text{O}_2} = 0.1$ bar. For instance, an equimolar mixture of NO and NO$_2$ at room temperature is in equilibrium with $2/3$ ML O, and this equilibrium coverage is maintained to higher temperature under NO excess. *Ex situ* Auger electron spectroscopy (AES) measurements performed on a Pt(111) crystal after NO oxidation catalysis indicate a surface oxygen coverage of upwards of $0.76 \pm 0.06$ ML [229], greater than that expected from the dissociation of O$_2$ or NO$_2$. Reaction 4.24 may well contribute to the build up of this high O coverage during NO oxidation.

4.3.3.2 From reducible oxides

Reducible oxides are frequently employed as supports for metal-containing catalysts such as the automotive three-way catalyst [245]. One function of these supports is to buffer the oxygen content in the chemically fluctuating reactant gas by storing or releasing oxygen. Ceria-zirconia is a well known example of such an oxygen storage material, and in a series of papers [46, 197, 198, 265], Gorte and co-workers have quantified the oxygen storage capabilities of this material in terms of a reaction with approximate stoichiometry:

$$\text{ZrO}_2/\text{CeO}_3 + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{ZrO}_2/2\text{CeO}_2$$ (4.27)

The heat of this reaction is found to be approximately $-105$ kJ mol$^{-1}$ ($-1.09$ eV) at 510 K [265], and a similar value is found to characterize the energetics of oxygen transfer from the mixed oxide to a supported transition metal. Assuming that this reaction comes to a constrained equilibrium with a metal surface and following the
approach above for gas-phase redox couples, reaction 4.27 can be used to establish a chemical potential scale:

\[
\mu_{\text{M-O}} = \mu_{\text{ZrO}_2/2\text{CeO}_2} - \mu_{\text{ZrO}_2/\text{Ce}_2\text{O}_3} = \frac{1}{2} \mu_{\text{O}_2}(T, 1\text{bar}) + \Delta G^{\circ}_{\text{Ce}_2\text{O}_3/2\text{CeO}_2}(T, 1\text{bar})
\]

(4.28)

with the one key difference that composition variables do not enter for these solid materials. We estimate \(\Delta G^{\circ}_{\text{Ce}_2\text{O}_3/2\text{CeO}_2}(T, 1\text{bar})\) by combining the measured value of the reaction 4.27 enthalpy with the temperature-dependent enthalpy and entropy of the bulk cerias, as tabulated in the HSC database [117]. Mapping the resultant chemical potentials onto the chemisorbed Pt(111) surface free energies through equation 2.25 yields the stability diagram shown in Figure 4.11.

The solid oxide maintains the oxygen potential at a nearly constant value at all conditions, so that the equilibrium oxygen coverage at all temperatures is a constant 1/4 ML. Thus, to the extent that equilibrium between the metal and oxygen storage material can be maintained and that the oxygen storage material can buffer any other oxygen sources, Pt is protected from formation of surface oxides as well as from complete depletion of surface oxygen, a feature likely important, for instance, in maintaining simultaneous catalytic oxidation and reduction activity in the automotive three-way catalyst. Modifications of the oxide, for instance by adding or altering dopants, would provide one means for tailoring the oxygen coverage on Pt or any other metal to a desirable range for a particular catalytic reaction.

4.3.4 Ellingham diagram of chemisorbed O stability

As noted above, DFT results and experiments show that oxygen chemisorption on the Pt(111) surface is coverage-dependent and is characterized by several cov-
Figure 4.11. Pt(111)-O coverage in equilibrium with ceria-zirconia oxygen storage material.
verage regimes with distinct differential oxygen binding energies. If each of these different coverage regimes is treated as the formation of a distinct compound, then the thermodynamics of each can be summarized in a fashion similar to bulk oxides in an Ellingham diagram \[61\]. Ellingham diagrams are commonly applied in metallurgy to compare the free energies of oxidation of metals as a function of temperature:

\[
M(s) + \frac{1}{2}O_2(g) \rightleftharpoons M - O(s)
\]  

Here we apply the concept to differential oxygen adsorption energies.

Figure 4.12 plots the free energies of several oxidation reactions in the form \(X + 1/2 \ O_2 \rightleftharpoons X - O\) as functions of \(T\). The \(O_2\) pressure is set to 0.1 bar, a representative catalytic oxidation condition. The \(NO \rightleftharpoons NO_2\) line is calculated based on the experimental free energy of reaction at equal concentrations of \(NO\) and \(NO_2\), i.e. corresponding to 50% conversion of an \(NO\) gas. Each differential adsorption energy regime on the Pt(111) surface is indicated by a separate line. The contributions of configurational entropy are not included, but would tend to diminish the slopes of the adsorbed configurations. The point at which one of these lines crosses the 0 of free energy corresponds to the temperature at which a particular coverage regime becomes thermodynamically unstable to the next lower one in coverage. Thus at these \(O_2\) conditions the clean surface is preferred above about 1000 K, up to 1/4 ML between about 600 and 1000 K, and up to 1/2-ML below 600 K. The combination of any reaction lower on the Ellingham diagram with the reverse of one above forms a thermodynamically favored couple, and this relationship can be used to relate surface coverage to surface reactivity. For instance, CO oxidation \[4.1\] at constant pressure has a reaction free energy approximately 2 eV lower than the most stable 0 to 1/4-ML line (i.e., off-scale
Figure 4.12. Free energies (Ellingham diagram) of various oxidation reactions (\(X + 1/2 \text{O}_2 \rightleftharpoons X-O\)) at constant \(p_{\text{O}_2}\) of 0.1 bar vs. \(T\). For all free energy calculations, the activity of X–O is equal to the activity of X.
beyond the bottom of the figure), implying that CO is able to completely reduce this an any of the O chemisorption regimes. In contrast, the oxidation of O₂ to O₃ has a free energy 1.5 eV above the oxidation energy of 1/2 ML going to 2/3 ML (off-scale above the top of the figure), so ozone is able to drive the formation of any O coverage.

Most interesting are reactions with free energies similar to those of chemisorbed O on Pt(111). For instance, consistent with the analysis of the previous section, ZrO₂/2CeO₂ is capable of promoting formation of up to 1/4 ML coverage, but any higher O coverage drives the reverse ZrO₂/Ce₂O₃ oxidation to ZrO₂/2CeO₂.

Similarly, at equimolar mixing, NO oxidation to NO₂ (upward sloping line) can be driven by reaction with the 1/4 to 1/2-ML surface O above about 500 K, but below this temperature NO₂ decomposes to release oxygen to Pt. NO oxidation to NO₂ is always promoted by reaction with 1/2 to 2/3-ML O. The downward sloping line corresponds to NO-assisted O₂ dissociation. This reaction can simultaneously promote NO₂ production and formation of oxygen coverages of up to 2/3-ML to about 450 K and 1/2-ML up to about 650 K. Thus, an NO oxidation mechanism based on the two reactions

\[
\text{Pt}(111) + \text{NO}(g) + \text{O}_2(g) \rightarrow \text{NO}_2(g) + \text{Pt}(111) - \text{O}(\theta_O) \quad (4.30)
\]

\[
\text{NO}(g) + \text{Pt}(111) - \text{O}(\theta_O) \rightarrow \text{NO}_2(g) + \text{Pt}(111) \quad (4.31)
\]

has a “window” of acceptability that extends to above 500 K, is consistent with the generation of O coverages up to and beyond 1/2-ML, and circumvents the need to dissociate O₂ at high O coverage.
This approach of describing different coverage regimes with single adsorption energies is not quantitative, not the least because of uncertainties in the DFT calculated energies, and obviously says nothing about the rates of various reaction steps. It does highlight in a single diagram, however, the competing energetics of various oxidation and reduction processes. Such a diagram might be used, for instance, to screen for other combinations of metals and coverages that more favorably promote both O\textsubscript{2} dissociation and NO oxidation over a wider range of conditions.

4.4 Conclusions

In this chapter we illustrate the use of state-of-the-art supercell DFT methods and thermodynamic models to characterize the high coverage limits of chemisorbed oxygen on the Pt(111) surface and to consider the stability of the high coverage states in communication with a variety of potential reactive oxygen sources or sinks. By simulating a wide variety of oxygen coverages and configurations, we show that oxygen uniformly prefers to bind at three-fold, FCC sites. These FCC O interact repulsively with neighbors through a combination of electronic interactions and surface relaxation effects that significantly modify the Pt(111)–O bond strength. In combination, these interactions lead to distinct energetic preferences for certain oxygen orderings that minimize repulsive interactions. With respect to reaction chemistry, these configurations effectively partition into just four binding energy regimes, from the lowest-coverage regime (< 1/4 ML) in which O\textsubscript{2} dissociation at the surface is highly exothermic, to intermediate coverages, to a high coverage regime (> 2/3 ML) essentially inaccessible to molecular O\textsubscript{2}. The boundaries between these ordering regimes become blurred at elevated temperatures
where entropic effects act to counterbalance the energetic preference for ordering, but identification of these regimes is invaluable for characterizing the conditions necessary for reactivity of surface O with NO.

The actual oxygen coverage at a metal surface is a convolution of the equilibrium thermodynamics of oxygen adsorption from some source and the kinetics of the steps that transfer oxygen from a source to the surface. While molecular O$_2$ is the most common source of reactive oxygen at a surface, it is not the only or necessarily even the most important one, especially at high coverage conditions and in the presence of other strongly oxidizing gases. Constrained equilibrium calculations provide a means to compare the effect of various reaction assumptions on surface coverage. For instance, at moderate NO$_2$/NO ratios, NO$_2$ dissociation yields higher equilibrium O coverages than are attainable with O$_2$; NO-assisted O$_2$ dissociation can attain even higher O coverages, consistent with experimental observation, under conditions that prevail during NO oxidation catalysis and thus may have an important role in that chemistry. A simple plot of reaction free energy vs. temperature (an Ellingham diagram) provides a convenient way of summarizing the consequences of these various reactions on surface O coverage.

In NO oxidation the dominant surface species present during catalysis (O) likely does not arise from dissociation of the most obvious reactant (O$_2$). A similar situation prevails for catalytic ammonia synthesis from N$_2$ and H$_2$ over transition metals. In this case the surface N coverage is controlled by the concentration of labile product NH$_3$ rather than the slow-to-dissociate N$_2$ reactant [50]; within the framework described here, the N surface chemical potential is controlled by the NH$_3$/H$_2$ ratio rather than by N$_2$. The thermodynamic approach applied here would find ready application to this system.
Of course the ultimate goal of this dissertation is to quantify both the thermodynamics and kinetics of surface reactions for analysis of the statics and dynamics of reactivity. Equilibrium models have much to contribute: the pathways and rates of surface reactions are more numerous, more expensive and more difficult to calculate than equilibrium energies, especially if these pathways depend sensitively on surface coverage. The results from this chapter assist in choosing the best kinetic processes to calculate. These are discussed in detail in Chapter 6.

Finally, DFT bond energies calculated within the generalized gradient approximation can suffer significant errors, as is the case for the ON–O bond. An approach like that used here, which attempts to take maximum advantage of experimental thermodynamic data, can help mitigate the influence of these errors. We take advantage of this method in the remaining chapters of this work.
CHAPTER 5
O INTERACTIONS WITH NO$_x$ AND O$_2$: THE EFFECT OF GEOMETRIC ADAPTABILITY ON NO OXIDATION

5.1 Introduction

The results from the previous two chapters as well as prior work [188] show that NO oxidation is catalyzed by O-covered Pt. O coverage can have significant effects on the thermodynamics and kinetics of surface reactions. A quantitative picture of these effects is needed to fully understand the catalysis. In this chapter we analyze the thermodynamics of NO, NO$_2$, NO$_3$, and O$_2$ chemisorption on O covered Pt(111). We then present coverage-dependent transition barrier calculations for two dissociations important to NO oxidation catalysis: independent O$_2$ dissociation

$$O_2 + * \rightarrow 2O*$$ (5.1)

and NO$_2$ dissociation

$$NO_2 + 2* \rightarrow NO* + O*$$ (5.2)

Large sections of this chapter come directly from References [83] and [229].
5.2 Results

5.2.1 NO, NO₂, NO₃, and O₂ Adsorption

To investigate adsorbate coadsorption with O, we computed the energies of the stable and metastable isomers of NO, NO₂, NO₃, and O₂ at finite O coverages spanning from 1/16 to 15/16 ML. In reaction conditions we expect O dominates the surface, and the coverages of all other species are < 1/4 ML \[82, 188\]. We model these O-dominated surfaces using 3 Pt × 3 Pt and 4 Pt × 4 Pt and supercells with varying amounts of O and one NOₓ or O₂. The coverage of NOₓ or O₂ is limited to 1/9 and 1/16 ML in these cells, and the adsorbates are separated from each other by at least 11.3 Å. Key O orderings used are the 1/4 and 1/2 ML p(2×2)-O and p(2×1)-O surfaces (Figure 4.5) \[55\]. Binding energies are calculated relative to the O-covered surfaces

\[
\text{Pt}(111) - \text{O} (\theta) + B \rightarrow \text{Pt}(111) - \text{O} (\theta) + B^* \tag{5.3}
\]

As shown in Chapter 3, NO binds in threefold FCC and HCP sites and onefold atop sites at low coverage \[81\]. Binding in FCC sites is preferred with \( \Delta E_{\text{NO}}^{\text{bind}} = -2.00 \text{ eV} \). HCP and atop binding are 0.13 and 0.4 eV higher in energy. NO prefers threefold binding because it allows optimal π interactions with the Pt surface atoms \[81\]. These interactions are likely maximized in FCC sites, which maintain the stacking symmetry of the Pt substrate. This FCC < HCP < atop binding preference is maintained up to 1/4 ML O (Figure 5.1).

NO binds stably in atop sites on p(2×2)-O. The change in site preference is induced by O nearest neighbor interactions. There is only one FCC site available on p(2×2)-O, and it has two 1ˢᵗ and two 2ⁿᵈ nearest neighbor (NN) O. 1NN
Figure 5.1. O coverage-dependent binding energies for HCP, FCC, and atop NO.
interactions arise when an adsorbate and O share a surface Pt (Figures 4.2, 5.2). We compute isolated O/FCC NO 1\textsuperscript{st} and 2\textsuperscript{nd} interactions of +0.23 and +0.08 eV per pair, respectively (Table 5.1), nearly identical to the O/O ones discussed in Chapter 4 \cite{82, 163}. Accordingly, the calculated FCC NO binding energy on p(2\times2)-O is $-1.28$ eV, 0.72 eV weaker than on Pt(111). The optimal HCP binding site on p(2\times2)-O has three 1NN O (Figure 5.2), and its binding energy is $-1.00$ eV, 0.86 eV smaller than at 0 ML. There are two types of atop sites on p(2\times2)-O: one with one 1NN O and one with three 2NN O. 2NN interactions are much weaker than 1NN ones, and binding in the latter site is preferred by 0.4 eV. The atop NO binding energy is $-1.50$ eV at 1/4 ML, only 0.10 eV smaller than at 0 ML.

At 1/2 ML O, represented by the p(2\times1)-O ordering, FCC NO binding is accompanied by four 1NN and four 2NN O. HCP binding requires NO and O to sit less than 2 Å from each other and is unstable. Atop NO picks up a 1NN O, and its binding energy increases to $-0.8$ eV, but it is strongly preferred over threefold...
TABLE 5.1

O/NO\textsubscript{x} AND O/O\textsubscript{2} 1NN AND 2NN INTERACTIONS (in eV per pair)

BY BINDING GEOMETRY

<table>
<thead>
<tr>
<th></th>
<th>1NN</th>
<th>2NN</th>
</tr>
</thead>
<tbody>
<tr>
<td>FCC NO</td>
<td>+0.23</td>
<td>+0.08</td>
</tr>
<tr>
<td>Atop NO</td>
<td>+0.41</td>
<td>+0.02</td>
</tr>
<tr>
<td>HCP NO</td>
<td>+0.31</td>
<td>+0.09</td>
</tr>
<tr>
<td>Nitro NO\textsubscript{2}</td>
<td>+0.38</td>
<td>+0.05</td>
</tr>
<tr>
<td>O,O’-nitrito NO\textsubscript{2}</td>
<td>+0.35</td>
<td>+0.04</td>
</tr>
<tr>
<td>TBT O\textsubscript{2}</td>
<td>+0.36</td>
<td>+0.08</td>
</tr>
<tr>
<td>TFB O\textsubscript{2}</td>
<td>+0.30</td>
<td>+0.10</td>
</tr>
</tbody>
</table>

binding.

All binding geometries are destabilized by O interactions. The threefold geometries are especially affected since they form three bonds with Pt. Atop NO, which forms a single bond, is stabilized at high coverage because it can bind in a manner to minimize repulsive interactions. NO maintains strong binding to O-covered Pt because it binds in a variety of sites in order to optimize interactions with Pt and O.

NO\textsubscript{2} is coordinatively flexible like NO. At low coverage, it binds in the twofold \(\mu\)-N,O-nitrito and O,O’-nitrato and onefold nitro geometries, and \(\mu\)-N,O-nitrito is stable by 0.1 eV (Chapter 3 |81\|. Like NO, it assumes onefold binding at finite \(\theta_O\) to minimize interactions with O (Figure 5.3). The nitro isomer is preferred for
Figure 5.3. O coverage-dependent binding energies for \( \mu\)-N,O-nitrito, O,O'-nitrito, and nitro NO\(_2\).

\( \theta_O \geq 1/4 \) ML. In fact, \( \mu\)-N,O-nitrito is unstable for \( \theta \geq 1/4 \) ML, and O,O'-nitrito is strongly destabilized due to interactions with O. O,O'-nitrito is unstable for \( \theta_O \geq 1/2 \) ML. Like atop NO, nitro acquires a 1NN O at 1/2 ML O, causing a significant weakening of its adsorption energy.

NO\(_3\) binds in the twofold O,O'-nitrato geometry at low coverage, and it maintains this preference for \( \theta_O \geq 1/4 \) ML. It has one 1NN O on p(2×2)-O, and it tilts slightly so that the distance between the O closest to surface bound O is maximized. At 1/2 ML it picks up an additional 1NN O, resulting in significant weakening of the adsorption energy. Like O'O-nitrito, O,O'-nitrato is unstable beyond 1/2 ML. Unlike NO and NO\(_2\), NO\(_3\) does not geometrically adapt to minimize O interactions, and its binding energy increases dramatically with O coverage.

O\(_2\) binds in the twofold atop-bridge-atop (TBT) and atop-bridge-FCC (TFB)
geometries at low coverage [59, 235, 248, 251]. In the TBT geometry O bind atop Pt and across a bridge site, and in the TFB geometry, O bind atop Pt and in a bridge site and across an FCC site (Figure 5.5). TBT \( \text{O}_2 \) is spin polarized with a magnetic moment of 1 electron up to \( 1/2 \) ML O. TBT and TFB \( \text{O}_2 \) are nearly isoenergetic at all coverages. Both geometries bind relatively weakly on clean Pt(111) with \( \Delta E_{\text{O}}^{\text{bind}} = -0.8 \text{ eV} \). They experience significant O interactions on \( \text{p}(2\times2)\)-O and beyond. Adsorption on \( \text{p}(2\times2)\)-O is just barely exothermic, and it is endothermic on \( \text{p}(2\times1)\)-O by nearly 0.6 eV. Unlike NO and NO\(_2\), these twofold binding geometries cannot adapt to minimize O interactions, and their binding energies increase dramatically with \( \theta_O \). We do not find any onefold adsorption modes for \( \text{O}_2 \) at these higher coverages.
Figure 5.5. O coverage-dependent binding energies for TBT and TFB O$_2$. 
5.2.2 O\textsubscript{2} and NO\textsubscript{2} Dissociation

5.2.2.1 O\textsubscript{2} Dissociation

Results from the previous section show that NO and NO\textsubscript{2} maintain strong binding on Pt up to 1/2 ML due to their abilities to adapt geometrically and minimize repulsive lateral interactions with O. NO\textsubscript{3} and O\textsubscript{2} cannot adapt geometrically and thus binding is greatly weakened above 1/4 ML. In this section, we apply the same analysis to two competing dissociation reactions important to NO oxidation catalysis: independent O\textsubscript{2} dissociation\textsuperscript{5.1} and NO\textsubscript{2} dissociation\textsuperscript{5.2}. We show that NO\textsubscript{2} dissociation is much more facile than O\textsubscript{2} dissociation at finite \(\theta\textsubscript{O}\) because NO\textsubscript{2} and NO are coordinatively flexible, and O\textsubscript{2} and O are not.

We showed in Chapter\textsuperscript{4} that both O\textsubscript{2} and NO\textsubscript{2} can add O to Pt in NO oxidation\textsuperscript{82}. Additionally, our experimental collaborators have shown in \textit{in situ} XPS that, under conditions of equal \(\mu\textsubscript{O}\textsuperscript{1}\), NO\textsubscript{2} dissociation can generate higher \(\theta\textsubscript{O}\) than O\textsubscript{2},\textsuperscript{83}, suggesting the kinetics of NO\textsubscript{2} dissociation are more facile than O\textsubscript{2}. To understand this difference in dissociation rates, we computed the O\textsubscript{2} and NO\textsubscript{2} dissociation pathways at 0, 1/4, and 1/2 ML O. Minimum energy paths are shown in Figures\textsuperscript{5.6 and 5.7}.

At 0 ML, TBT O\textsubscript{2} (Figure\textsuperscript{5.6 R}) dissociates along a path in which the molecule stretches and slides sideways into neighbor FCC sites\textsuperscript{248}. O\textsubscript{2} span bridge and atop sites and are separated by 1.88 Å at the transition state (TS) (Figure\textsuperscript{5.6 S}). The low-coverage TS energy is calculated to be 0.24 eV below the O\textsubscript{2} (g) entrance channel, about 0.2 eV lower than estimated in molecular beam and TPD experiments\textsuperscript{38}.

At higher O coverage repulsive adsorbate-adsorbate interactions distort the\textsuperscript{\textit{in situ} conditions were: 518 K, 0.1 Torr O\textsubscript{2}, 0.05 Torr NO, 0.05 Torr NO\textsubscript{2}}}
Figure 5.6. Minimum energy paths referenced to $O_2(g)$ and geometries for $O_2^* \rightarrow 2O^*$. Dotted lines label 1\textsuperscript{st} nearest neighbor interactions.
initial and transition states. On the p(2×2)-O and p(2×1)-O surfaces, adsorbed O$_2$ suffers one and three 1NN interactions, respectively. At these higher coverages O$_2$ dissociation occurs by rotation about a surface normal and stretching of the O=O bond until the O occupy adjacent FCC sites. The O–O distances at the transition states increase to 1.60 and 1.76 Å on p(2×2)-O and p(2×1)-O, respectively. O$_2$ interacts with two and six neighbor O (Figure 5.6 P), increasing the energy barriers to 1.0 and 2.3 eV above O$_2$ (g).

These results are consistent with a dramatic decrease in O$_2$ dissociation rate with increasing O coverage. To circumvent errors in the absolute DFT barriers, we calculate relative dissociation rates with respect to the clean Pt(111) surface according to

$$\frac{r(\theta_O)}{r(\theta_O = 0)} = \frac{Q_{\text{vib}}^t(\theta_O)}{Q_{\text{vib}}^t(\theta_O = 0)} \exp \left[ -\frac{E^t(\theta_O) - E^t(\theta_O = 0)}{k_B T} \right]$$  \hspace{1cm} (5.4)

At 518 K and 0.1 Torr O$_2$, the conditions considered by our experimental collaborators in Reference [83], the O$_2$ dissociation rates decrease to 3×10$^{-12}$ and 6×10$^{-24}$ that of the clean surface, respectively. Like O$_2$ adsorption, O$_2$ dissociation is hindered at high $\theta_O$ due to lateral interaction effects.

5.2.2.2 NO$_2$ Dissociation

Because NO$_2$ can adapt geometrically, its dissociation pathway is much more facile at high O coverage than that of O$_2$. At 0 ML, dissociation from the $\mu_O$-N,O-nitrito configuration occurs by migration of O and NO to adjacent FCC sites [83, 159, 188]. The TS is 0.35 eV below the NO$_2$(g) entrance channel, and based on the relative energies and partition functions at the TS relative to the respective gases, we estimate the NO$_2$ dissociation rate to be 88 times that of O$_2$.
at 518 K and \( p_{O_2}/p_{NO_2} = 2 \). At higher coverage, we construct a minimum energy pathway starting from an O-down atop Pt configuration (Figure 5.7, U) that has zero and one nearest-neighbor O on p(2×2)-O and p(2×1)-O, respectively. Nudged elastic band calculations identify a pathway in which O shifts to an adjacent FCC site and product NO moves atop Pt to decrease interactions with O. Consistent with atop NO binding [81], the off-surface O–N bond is shorter in the TS and product than at low coverage. In the reactant, the on-surface O–N distance is notably larger, indicating bound NO
2 is more readily dissociable at high coverage. The dissociation barrier with respect to NO
2(g) increases with increasing O coverage, consistent with a decrease in product binding energies, but the effects are moderated by the changes in reactant, TS, and product configurations that reduce adsorbate-O interactions. The calculated NO
2 dissociation rate does decrease with O coverage, to \( 10^{-4} \) and \( 10^{-11} \) that on clean Pt(111) at p(2×2)-O and p(2×1)-O, respectively, but this decrease is not nearly as drastic as for O
2. At the highest O coverage, we estimate the rate of NO
2 dissociation to be \( 10^{12} \) times that of O
2 at \( p_{NO_2}/p_{O_2} = 1/2 \).

The results demonstrate, consistent with experiment [83], the kinetic advantages of NO
2 over O
2 in developing high O coverages on Pt(111). This kinetic facility is rooted in the ability of NO and NO
2 and the inability of O
2 and O to geometrically adapt to minimize surface interactions with O at high coverage. The results also demonstrate that in principle, the \( \theta_O \) can attain values above those at which surface oxygen is energetically unstable to associative desorption of O
2: as shown in Figure 5.6, O
2 desorption remains a highly activated process even at high O coverages.
Figure 5.7. Minimum energy paths referenced to NO\textsubscript{2} (g) and geometries for NO\textsubscript{2}\textsuperscript{*} → NO\textsuperscript{*} + O\textsuperscript{*}. Dotted lines label 1\textsuperscript{st} nearest neighbor interactions.
5.2.3 NO-Assisted O$_2$ Dissociation

The results from the previous section show how coordinative flexibility influences catalysis. In NO oxidation, O coverage is likely controlled by product NO$_2$ rather than O$_2$ because O$_2$ dissociation is strongly kinetically hindered. O=O dissociation is a necessary step in NO oxidation, and since independent O$_2$ dissociation is slow, there may be alternate, lower energy dissociation pathways. In this section, we explore an “NO-assisted” dissociation pathway. In this pathway, NO and O$_2$ combine to form a bound OONO* complex similar in connectivity but with greater OO–NO bond length (1.814 Å) than the well know peroxynitrite anion OONO$^*$ (1.37 Å calculated at the B3LYP/6-311 + G* level [144]).

\[
\begin{align*}
O_2^* + NO^* & \rightarrow OONO^* + \ast \quad (5.5) \\
OONO^* + \ast & \rightarrow NO_2^* + O^* \quad (5.6)
\end{align*}
\]

The cis OONO* conformation is 0.2 eV lower in energy than the trans. The cis-OONO* intermediate (Figure 5.8) binds O-down atop Pt in a onefold geometry that allows it to minimize interactions with FCC O at high \(\theta_O\) (Figure 5.9). Its OO portion is closest to the Pt surface, with Pt-O distances of about 2 Å. The NO fragment is located about 3 Å above the Pt surface. Formation of this intermediate is exothermic starting from both NO (g) + O$_2^*$ and NO$^*$ + O$_2$ (g), reversing, for instance, the endothermicity of isolated O$_2$ adsorption at these high coverage conditions. In contrast, on an oxygen-free surface, OONO* is unstable to dissociation to 2O$^*$ and NO$^*$ by more than 3.1 eV. A similar intermediate has been proposed to account for the observed oxidation of NO to NO$_2$ over Cu-ZSM-5.
Examination of $O_2$ adsorption and OONO* formation at O coverages intermediate to 0 ML and 0.67 ML shows similar trends in decrease in $O_2$ adsorption energy and binding enhancement by co-adsorption with NO. Coverage dependent binding energies and geometries are shown in Figure 5.8. OONO* adsorption energies vary non-linearly with O coverage in the models chosen here. OONO* adsorption is slightly diminished at 1/4 ML O and more significantly diminished at 1/2 ML O. In fact, we find OONO* (as well as NO$_2$) adsorbates to bind more weakly on the p(2×1)-O surface than the 2/3 ML p(√3 × √3)-2O one, due to stronger local interactions with surface O in the former ordering. These binding energies are clearly a sensitive function both of O coverage and local adsorption environment. Onefold OONO* binding is much more robust at high $\theta_O$ than twofold $O_2$ binding, and OONO* intermediates could play a role in catalyzed $O_2$ dissociation at high $\theta_O$.

5.2.4 Discussion

The DFT-calculated thermodynamic profiles for surface reactions of $O_2 + 2$ NO within one supercell at O coverages up to 2/3 ML are summarized in Figure 5.9. The 0 ML dashed line illustrates the unfavorable surface energetics of NO oxidation at low surface coverage: while $O_2$ is readily dissociated on Pt(111) in this limit, the intrinsic Pt-O bond strength inhibits formation and desorption of NO$_2$. In contrast, at 2/3 ML O coverage, shown by the solid line, $O_2$ dissociation is strongly disfavored in isolation but assisted by interaction with NO. The high oxygen covered surfaces are passivated towards $O_2$ dissociation, possibly opening up an NO-assisted dissociation pathway. Unlike the independent $O_2$ dissociation
Figure 5.8. $O_2$ independent adsorption (a) and co-adsorption with NO (b) as a function of coverage. Adsorption energies are given in eV and $O$ coverages in ML. $\Delta H^{\text{ads}} = \Delta E^{\text{bind}} + \Delta E^{\text{ZP}}$. 

(a) $O_2 (g) + \ast \rightarrow O_2 \ast$

\[
\begin{align*}
\theta = 0 & \quad \Delta H^{\text{ads}} = -0.89 \\
\theta = 0.25 & \quad \Delta H^{\text{ads}} = -0.25 \\
\theta = 0.5 & \quad \Delta H^{\text{ads}} = +0.47 \\
\theta = 0.66 & \quad \Delta H^{\text{ads}} = +0.82
\end{align*}
\]

(b) $NO (g) + O_2 (g) + \ast \rightarrow OONO \ast$

\[
\begin{align*}
\theta = 0 & \quad \Delta H^{\text{ads}} = -1.24 \\
\theta = 0.25 & \quad \Delta H^{\text{ads}} = -1.14 \\
\theta = 0.5 & \quad \Delta H^{\text{ads}} = -0.41 \\
\theta = 0.66 & \quad \Delta H^{\text{ads}} = -0.67
\end{align*}
\]
pathway, the energetics of the assisted pathway are minimally affected by $\theta_O$ because OONO* forms a single bond with Pt, allowing minimal interaction with surface O.

The intermediate coverage results in Figure 5.9 illustrate the greater sensitivity of the $O_2$ dissociation energetics to surface coverage than for the associative pathway. The two pathways approximately coincide in energy near 0.5 ML O, where $2O^* + NO^*$ is just slightly preferred over OONO* and NO$_2$ formation is exothermic. Thus, both pathways may contribute to observed NO oxidation catalysis depending on reaction conditions. Actual contributions depend on the relative kinetics of these two pathways and will be discussed further in the next chapter.

Figure 5.9. Comparison of NO oxidation energetics as a function of O coverage. OONO* intermediates in the associative pathway are denoted with grey bars.
5.3 Conclusions

Stability at finite $\theta_O$ for NO oxidation intermediates is a strong function of geometric adaptability. Adsorbates such as NO, NO$_2$, and OONO that can bind in onefold geometries can minimize 1NN O interactions at the $\theta_O$ relevant to NO oxidation. In contrast, adsorbates that cannot adapt to the local surface environment, such as O$_2$ and O, bind in higher coordination geometries, and their binding energies are strongly weakened due to repulsive interactions with surface O. This geometric adaptability further effects surface reactions involving these adsorbates. NO$_2$ dissociation is robust at high $\theta_O$, and in contrast, independent O$_2$ dissociation is strongly inhibited due to repulsive O interactions along the path. Independent O$_2$ dissociation is so strongly inhibited that we need to search for alternate O=O dissociation pathways. A NO-assisted O$_2$ dissociation path through a onefold OONO* species has been identified and may contribute to O$_2$ dissociation in NO oxidation. Of course, the likelihoods of these pathways depend on their relative kinetics. We investigate the relative kinetics of NO$_2$ dissociation, O$_2$ dissociation, and NO-assisted O$_2$ dissociation in Chapter 6.
CHAPTER 6

COVERAGE-DEPENDENT MICROKINETIC MODEL OF PT-CATALYZED NO OXIDATION

6.1 Introduction

In the previous chapters, we collected an extensive number of binding energies and activation energies likely to be important in Pt-catalyzed NO oxidation. In this chapter, we use these calculations to develop an atomistically detailed kinetic model. We consider two mechanisms, independent and NO-assisted \( \text{O}_2 \) dissociation. We show that the coverage dependence of adsorption and reaction can be correlated to the coverage-dependent O adsorption energies [82]. With this we develop and solve microkinetic models at realistic reaction conditions. We find the surface coverage under reaction conditions of interest is \( 1/4 \leq \theta < 1/2 \) ML. The turnover frequency (TOF) of the independent mechanism is consistent with experimental observation, and it exceeds the NO-assisted one under modeled conditions. Our model predicts \( \text{O}_2 \) dissociative adsorption is rate limiting. Further, O–NO bond formation has a small, coverage-independent barrier above \( 1/4 \) ML O and is predicted to be in quasi-equilibrium. O–NO bond formation governs the O coverage, leading to the inverse \( \text{NO}_2 \) order observed experimentally. Our model reasonably reproduces the observed TOF, rate orders, and catalyst light-off temperature. The majority of this work is contained within Reference [80].
6.2 Results and Discussion

In the following we parameterize coverage-dependent thermodynamics and kinetics using energies calculated in Chapter 5. These results are integrated into a microkinetic model, which provides steady state rates, coverages, and rate determining steps (RDS). The predictive success of the microkinetic models relies on accurate descriptions of the $\theta_O$-dependent thermodynamics and kinetics, as described below. Unless otherwise noted, all quantities are given in eV.

6.2.1 Coverage-Dependent Adsorption

We showed in Chapter 5 that NO$_x$ and O$_2$ can adsorb in a variety of geometries at a Pt metal surface [12, 13, 81, 251]. To study the sensitivity of this adsorption to surface coverage, we consider six O-precovered Pt(111) surfaces between 0 and 0.50 ML, using as models the thermodynamically stable, FCC O arrangements identified in previous work [82]. At coverages near and above 0.5 ML, the FCC-chemisorbed oxygen surface becomes unstable to a reconstructed and partially oxidized surface [55, 82, 104]. As shown below, the models predict steady state coverages under reaction conditions at or below 0.4 ML, below the coverages at which these reconstructions begin to dominate the material.

The most stable adsorption configurations on the pristine 4×4 supercell, a 1/4 ML p(2×2)-O supercell, and a 1/2 ML p(2×1) supercell are shown in Figure 6.1. Differential adsorbate binding energies (Equation 5.3) are plotted in Figure 6.2. As with O adsorption [82, 188, 241], lateral interactions between adsorbates cause adsorbate binding energies to increase with $\theta_O$.

As discussed in Chapter 5, NO prefers FCC adsorption on pristine Pt(111), and atop for $\theta_O \geq 0.25$ ML. At 0.50 ML, adsorption is accompanied by a significant
Figure 6.1. Most stable binding geometries of NO (a), NO$_2$ (b), NO$_3$ (c) and O$_2$ (d) at 0, 1/4, and 1/2 ML O.
Figure 6.2. Calculated differential binding energies for the most stable configurations of O, NO, NO$_2$, NO$_3$, and O$_2$ as functions of $\theta_O$ (left) and $\Delta E_O^{\text{bind}}$ (right).
amount of surface relaxing, similar to that observed in Pt surface oxidation above 0.5 ML O [104]. Similar to NO, NO₂ adsorbs in higher coordination sites at low coverage and onefold sites for \( \theta_O \geq 0.25 \) ML, and binding above 0.50 ML induces surface relaxation. NO₃ binds in the twofold O,O'-nitrato geometry at all \( \theta_O \), and binding at high \( \theta_O \) is accompanied by significant 1NN O repulsion. If NO₃ plays a role in the mechanism, it will be by reaction of NO₂ and O. Binding energy analysis indicates NO₃ formation from surface NO₂ and O

\[
\text{NO}_2 + O^* \rightarrow \text{NO}_3 + \gamma^*
\]  

is endothermic below 0.50 ML, \( \theta_O \) relevant to the catalysis. We therefore do not consider it in our models. O₂ binds most weakly of all adsorbates. Adsorption is nearly thermoneutral at 0.25 ML and endothermic by nearly 0.6 eV at 0.50 ML. O₂ binds in twofold geometries at all \( \theta_O \). Its O–O distance decreases from 1.37 at 0 ML to 1.30 Å at 0.50 ML, and the Pt-O distances increase from 2.0 to 2.3 Å due to weaker interaction with the surface. Bader charge partitioning [9, 81] and density of states (DOS) analyses indicate adsorption at low coverage is accompanied by significant charge transfer of more than 0.6 electrons from Pt to O via electronic interactions between Pt d and the O₂ antibonding \( 1\pi_g^* \) orbital. The charge transfer decreases with \( \theta_O \) and is 0.4 electrons at 0.50 ML due to competition for \( \pi \) electron density with O, causing the decrease in O–O bond length and the weaker binding. As shown in Figure 6.2, O₂ binding is the weakest of all the adsorbates of interest here, and NO binding is strongest. Conformational flexibility is essential to maintaining this advantage at increasing coverage.

Figure 6.2 shows that the optimal-site binding energies of all intermediates vary in similar ways with increasing surface coverage. In Figure 6.2, binding energies
of NO$_x$ and O$_2$ are plotted against atomic O binding energies \cite{82}. Nearly linear correlations are evident \cite{163}; least-squares analysis yield $R^2$ values of 0.92 and greater. For NO, the most strongly bound surface intermediate, the correlation is:

$$
\Delta E_{\text{bind}}^{\text{NO}} (\theta) = 0.92 \Delta E_{\text{bind}}^{\text{O}} (\theta) - 0.83
$$

with $R^2$ of 0.99. The slopes for NO, NO$_2$, and NO$_3$ are less than one, reflecting their greater conformational adaptability to surface coverage than that of FCC O. The slope for O$_2$ is 1.02.

6.2.2 Coverage-Dependent Activation Energies

6.2.2.1 NO* + O* → NO$_2$ + *

Coverage-dependent rate constants depend in part on the activation energies, explicitly calculated here as functions of $\theta_O$. Catalytic O–NO bond formation

$$\text{NO}^* + \text{O}^* \rightarrow \text{NO}_2 + ^*$$

is well documented at $\theta_O = 0$ \cite{83, 124, 129, 159, 174, 188}. Reaction involves bound NO and O initially in 1NN FCC sites coming together to form bridge bound NO$_2$ \cite{83, 124, 188}. The TS assumes a threefold THB-like geometry, with the NO and O fragments binding in bridge and atop sites, respectively, and straddling an HCP site (Figure 6.3). The activation barrier is 1.5 eV \cite{83}. Further, the surface reaction is $\approx 0.6$ eV endothermic, even when referenced to 1NN reactants: Pt–O binding is preferred over ON–O at this coverage \cite{81, 83, 188}. The reaction energy and barrier increase by 0.2 eV when referenced to well-separated NO* and O*.

Higher O coverage is calculated to substantially decrease the barrier to O–
Figure 6.3. NEB-calculated potential energy surfaces for O–NO bond formation at 0, 0.25, and 0.50 ML O. Distances are in Å.
NO bond formation (Figure 6.3). We identify a path in which atop-bound NO combines with a 1NN O to form O-down atop-bound NO₂. The product is a previously uncomputed NO₂ isomer that is metastable to the preferred nitro configuration by 0.6 eV, but it is geometrically closer to the TS. On the 1/4-ML O surface, the reaction passes through a transition state in which the O atom has migrated to a bridge site, the Pt–NO distance has increased to 3.0 Å, so that NO is no longer directly bound to the surface, and the O–NO distance has decreased 1.10 Å to 1.69 Å. Frequency and NEB analysis confirm that this transition state connects the reactant and product states. Despite the substantial loss of surface bonding, the reaction barrier is significantly (0.8 eV) less than on the clean surface: unfavorable adsorbate-adsorbate interactions are decreased along the reaction pathway, in part because of the adaptability of the reactants, products, and transition state to the surface coverage. This transition state has three fewer unfavorable 1NN interactions than would be found if the reaction proceeded along the same path as found at low coverage.

On the 1/2 ML surface, the entire potential energy surface is pushed up in energy, so that the reaction barrier relative to NO and O is essentially unchanged. Again atop-bound NO combines with a 1NN O to form O-down, atop-bound NO₂, but to minimize adsorbate interactions, at the transition state surface binding is through a single, atop O (Figure 6.3). The TS geometry is nearly identical to the one at 1/4 ML, except the O–NO bond is 0.2 Å longer. The transition state experiences four fewer 1NN O interactions than the NO* + O* reactant state, and seven fewer than would be predicted by extrapolation from the low coverage pathway.

In summary, above 1/4 ML the computed barrier to Reaction 1.22 is computed
to be 0.7 eV independent of surface coverage. For the purposes of kinetic modeling, we increase this reaction barrier by 0.4 eV to account for the energy cost of bringing FCC O and atop NO into 1NN proximity.

$$\Delta E_{\text{act}} = \begin{cases} 1.7 \text{ eV} & \theta < 0.25 \text{ML} \\ 1.1 \text{ eV} & \theta \geq 0.25 \text{ML} \end{cases}$$  \hspace{1cm} (6.4)

6.2.2.2 $\text{O}_2 + \ast \rightarrow 2\text{O}^*$

$\text{O}_2$ dissociation

$$\text{O}_2 + \ast \rightarrow 2\text{O}^*$$  \hspace{1cm} (6.5)

on clean Pt(111) has also been studied extensively within DFT supercell models [59, 83, 124, 248]. Figure 6.4 shows the results obtained here, which agree well with earlier reports. At low coverage, NEB calculations identify a transition state that connects bridge-bound $\text{O}_2$ to two FCC-bound O in 1NN sites. Like its low coverage O–NO bond formation counterpart, the TS occupies a THB geometry. The barrier is $-0.24$ eV with respect to $\text{O}_2 (g)$ [83]. Consistent with expectation, $\text{O}_2$ dissociation is facile at low coverage.

Unlike the NO$_x$ adsorbates, the preferred chemisorbed O and O$_2$ binding sites do not change with increasing coverage. We construct NEB pathways from bridge-bound $\text{O}_2$ to two 1NN FCC O on the higher coverage model surfaces (Figure 6.4). The TSs have O in atop and bridge sites and straddle HCP sites, similar to the low coverage TS, but at 1/4 and 1/2 ML the TS geometries are slightly distorted because of repulsion with surface O [83]. For example, at 1/4 ML, the atop O maximizes its distance from surface O and thus minimizes its distance from bridge O, resulting in a smaller O–O bond length than at 0 or 1/2 ML. Such
Figure 6.4. NEB-calculated potential energy surfaces for independent $O_2$ dissociation at 0, 0.25, and 0.50 ML O. Distances are in Å.
brønstead-evans-polyani (BEP) relationships are a convenient means of correlating the activation energies of structural similar transition states. Figure 6.5 plots the computed O₂ dissociation barrier against the computed reaction energy to 1NN products, both energies taken with respect to O₂ (g). Despite the differences in O–O bond lengths in the TS geometries (Figure 6.4), the two
energies are linearly correlated with unit slope, because the relationships between
the number of O interactions in the transition and product states at these $\theta_O$ are
identical.

$$\Delta E^\text{act}(\theta) = \Delta E^\text{bind}_\text{2O}(\theta) + 2.12$$

(6.6)

In contrast to the O–NO bond formation reaction, a lateral interaction model thus
appropriately describes the coverage-dependence of O$_2$ dissociation. For kinetic
modeling purposes, we reference the reaction barrier to the binding energies of
O atoms in their equilibrium, maximally separated, configurations, by assuming

$$\Delta E^\text{bind}_\text{2O} = 2\Delta E^\text{bind}_\text{O} + 1\text{NN interaction energy},$$

where the O/O 1NN interaction
energy is 0.2 eV [82, 188, 241]. The resulting relationship is

$$\Delta E^\text{act}(\theta) = 2\Delta E^\text{bind}_\text{O}(\theta) + 2.32.$$  

(6.7)

6.2.2.3 O$_2$ + NO* $\rightarrow$ NO$_2$ + O*

NO-assisted O$_2$ dissociation

$$\text{O}_2 + \text{NO}^* \rightarrow \text{NO}_2 + \text{O}^*$$

(6.8)

has been proposed as a lower energy route than direct dissociation, and stable
OO–NO adsorbates have been calculated to be stable to NO* + 2O* for $\theta_O >$
0.50 ML [229]. NO-assisted O$_2$ dissociation involves NO and O$_2$ combining to
form an OONO species that dissociates into NO$_2$ and O (Reactions 1.23 and
1.24). On the low coverage surface, we construct a pathway starting from FCC
bound NO and a 2NN TBT O$_2$. The products are an O-down atop NO$_2$ adsorbate,
identical to the one used to model O–NO bond formation, and FCC O. The TS is
Figure 6.6. NEB-calculated potential energy surface for NO-assisted O₂ dissociation at 0, 0.25, and 0.50 ML O. Distances are in Å.
for NO-assisted $\text{O}_2$ dissociation is a *trans*-OONO structure bound approximately in a bridge site (Figure 6.6). Its geometry is independent of $\theta_0$ and similar to those of stable *cis*- and *trans*-OONO species that can form on Pt(111) at high $\theta_0$, but its O–ONO bond is longer (1.7 vs. 1.3 Å) and its OO–NO bond is shorter (1.4 vs. 1.8 Å), consistent with simultaneous O–O dissociation and O–NO bond formation. It has zero, zero, and one 1NN O at 0, 0.25, and 0.50 ML O, respectively, identical to NO, and dissociation barriers relative to NO* + $\text{O}_2$ are independent of $\theta_0$ (Figure 6.6)

$$\Delta E^{\text{act}} = 1.0$$  \hspace{1cm} (6.9)

indicating the O/atop NO and O/OONO 1NN interaction are similar. Like NO and NO$_2$, the OONO TS species assume onefold atop binding geometries that minimize interactions with FCC O. $\text{O}_2$ dissociation through such TSs could avoid the high barrier associated with independent $\text{O}_2$ dissociation at high $\theta_0$.

### 6.2.3 Coverage-Dependent Reaction Parameters

These results show that binding energies and even reaction pathways are sensitive to but vary in distinct ways with surface coverage. A successful kinetic model must incorporate this coverage sensitivity without becoming so complex as to be unsolvable. Here we explore a mean field model that captures these coverage features by mapping all parameters to a single coverage variable, $\theta$. Such a model cannot be expected to properly capture surface reaction statistics, but will indicate relative contributions of reaction steps to the overall reaction kinetics. It will thus provide a description of the most important steps involved in Pt-catalyzed NO oxidation.
Figure 6.7 summarizes previously reported, DFT-calculated integral binding energies for FCC-chemisorbed O on Pt(111), as a function of O coverage [82].

\[ \text{Pt}(111) + \left( \theta_O / 2 \right) \text{O}_2 \rightarrow \text{Pt}(111) - \text{O} (\theta_O) \]  

They vary nearly quadratically with \( \theta_O \), as expected for interactions dominated by pair-wise adsorbate interactions. Differential energies \( \Delta E_{\text{bind}}^{\text{O}} \)

\[ \text{Pt}(111) - \text{O} (\theta_O) + 1/2\text{O}_2 \rightarrow \text{Pt}(111) - \text{O} (\theta_O) + \text{O}^* \]  

are the derivatives of the integral binding energies \( \Delta E_{\text{int}}^{\text{O}} \) and at 0 K follow a step-like function up to 0.67 ML with near constant values for \( 0 \leq \theta < 0.25 \text{ ML} \), \( 0.25 \leq \theta < 0.50 \text{ ML} \), and \( 0.50 \leq \theta < 0.67 \text{ ML} \) [82]. As a first pass at describing
the $\theta_O$-dependent $\Delta E_{O}^{\text{bind}}$, we fit the integral binding energies in the range $0 < \theta < 1$ ML to a quadratic in $\theta_O$ (Figure 6.7):

$$\Delta E^{\text{int}} = 1.39\theta_O^2 - 1.63\theta_O$$  \hspace{1cm} (6.12)

Differentiation does not reproduce the near step functions in $\Delta E_{O}^{\text{bind}}$, but it does provide a rough approximation of the continuous differential binding energy

$$\Delta E_{O}^{\text{bind}} = 2.78\theta - 1.63$$  \hspace{1cm} (6.13)

Previous equilibrium models \[82\] and preliminary kinetic modeling show that the 0.25 to 0.5 ML coverage range is the most relevant to NO oxidation, and thus to obtain an improved binding energy model, we construct a second quadratic fit within this range (Figure 6.7)

$$\Delta E^{\text{int}} = 0.58\theta_O^2 - 1.08\theta_O - 0.08$$  \hspace{1cm} (6.14)

$$\Delta E_{O}^{\text{bind}} = 1.16\theta_O - 1.08$$  \hspace{1cm} (6.15)

Additionally, we fit differential binding energies within the $0.25 \leq \theta < 0.50$ ML regime, computed by finite differencing, to a linear equation (Figure 6.7)

$$\Delta E_{O}^{\text{bind}} = 0.83\theta_O - 0.91$$  \hspace{1cm} (6.16)

Equations 6.15 and 6.16 produce $\Delta E_{O}^{\text{bind}}$ within 0.1 eV. We use Equation 6.15 in the microkinetic model since it uses only the stable O orderings. Its slope
### TABLE 6.1

**COVERAGE-DEPENDENT REACTION (ΔE) AND ACTIVATION (ΔE_{act}) ENERGIES FOR POTENTIAL NO OXIDATION MECHANISM STEPS**

<table>
<thead>
<tr>
<th>Reaction</th>
<th>ΔE (eV)</th>
<th>ΔE_{act} (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>O₂ + 2* → 2O*</td>
<td>2.32θₐₙ - 2.16</td>
</tr>
<tr>
<td>II</td>
<td>NO + * ⇌ NO*</td>
<td>1.06θₐₙ - 1.83</td>
</tr>
<tr>
<td>III</td>
<td>NO* + O* → NO₂ + 2*</td>
<td>-2.22θₐₙ + 2.31</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>IV</td>
<td>O₂ + NO* → NO₂ + O*</td>
<td>0.10θₐₙ + 0.15</td>
</tr>
<tr>
<td>V</td>
<td>O₂ + * ⇌ O₂*</td>
<td>1.17θₐₙ - 0.59</td>
</tr>
<tr>
<td>VI</td>
<td>NO₂ + * ⇌ NO₂*</td>
<td>0.76θₐₙ - 1.65</td>
</tr>
<tr>
<td>VII</td>
<td>NO₃ + * ⇌ NO₃*</td>
<td>0.92θₐₙ - 1.49</td>
</tr>
</tbody>
</table>

is similar to one recently reported to describe θₐₙ-dependent average integral O binding energies on Pt(111) \[163\].

Taking advantage of the correlations noted above between O adsorption energies and the energies of other adsorbates and of transition states, these results can be used to write all relevant parameters in terms of θₐₙ. The resulting reaction parameters, based on the correlation of Equation 6.15 are shown in Table 6.1. The O–NO bond formation and NO-assisted O₂ dissociation barriers are taken to be independent of coverage between 0.25 ≤ θ < 0.50 ML, consistent with the computed reaction profiles.
These correlations are all based on the calculated interactions between an adsorbate or transition state and neighbor adsorbed O. As shown below, at large gas-phase NO to NO\textsubscript{2} ratios, the surface NO coverage can become appreciable. We calculate a two-body O/FCC NO interaction of 0.23 eV per pair, nearly identical to an O/O interaction \cite{82, 163, 188, 241}. To within a small error, then, the $\theta_O$-dependent energies are a reasonable representation of binding and transition state energies at $\theta = \theta_{NO} + \theta_O$.

6.2.4 Microkinetic NO Oxidation Model

The data in Table 6.1 provide all the information necessary to construct equilibrium and kinetic models of the NO oxidation surface reaction. Standard-state reaction free energies, $\Delta G^\circ_{\text{rxn}}(\theta, T)$, can be constructed by including reactant and product vibrational zero-point energies ($E^{\text{ZP}}$), the finite temperature vibrational free energy of the adsorbates ($\Delta F^{\text{vib}}$), and the finite temperature total free energy of any gas-phase species ($\Delta G^\circ(T)$) \cite{82}. Free energies for Reactions I-IV in Table 6.1 are

$$\Delta G_I(\theta, T) = 2\Delta E_\text{O}^{\text{d}}(\theta) + 2E^{\text{ZP}}_\text{O}_* - E^{\text{ZP}}_\text{O}_2 + 2\Delta F^{\text{vib}}_\text{O}_*(T) - \Delta G_{\text{O}_2}(T, 1\text{bar}) \quad (6.17)$$

$$\Delta G_{II}(\theta, T) = \Delta E_\text{NO}^{\text{d}}(\theta) + E^{\text{ZP}}_{\text{NO}_*} - E^{\text{ZP}}_{\text{NO}_2} + \Delta F^{\text{vib}}_{\text{NO}_*}(T) - \Delta G_{\text{NO}}(T, 1\text{bar}) \quad (6.18)$$

$$\Delta G_{III}(\theta, T) = \Delta G_{\text{rxn}}(T, 1\text{bar}) - 1/2\Delta G_I(\theta, T) - \Delta G_{II}(\theta, T) \quad (6.19)$$

$$\Delta G_{IV}(\theta, T) = \Delta G_I(\theta, T) + \Delta G_{III}(\theta, T) \quad (6.20)$$

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\( \Delta G_{\text{rxn}}(T, \text{1 bar}) \) in Equation 6.19 is for the overall gas phase reaction NO (g) + 1/2 \( \text{O}_2 \) (g) \( \rightarrow \) NO\(_2\) (g). This formulation neglects the small surface configurational entropy. Vibrational energies use calculated harmonic vibrational spectra for adsorbates at low surface coverage \([81]\). By far the largest contribution to the free energies are the gas-phase free energies, which we take from experimental tabulations \([176]\).

In a first set of calculations, we estimated the equilibrium coverages of the various surface intermediates at representative NO oxidation conditions, \( P = \text{1 bar}, \ y_{\text{O}_2} = 10\% \ (y = \text{mole fraction}), \ y_{\text{NO}_x} = 100 \ \text{ppm}, \) and \( T = 573 \ \text{K} \). \( \theta_{\text{NO}_2} \) and \( \theta_{\text{O}_2} \) are all calculated to be less than \( 10^{-7} \) ML at all ratios of NO to NO\(_2\). Therefore, we consider NO\(_2\) and O\(_2\) to react directly from the gas phase in our models. The only species other than O that accumulates on the surface at reaction conditions is NO (Figure 6.8).

We thus focus on the contributions of Reactions I–IV in Table 6.1 to net NO oxidation. The O, NO, and free site (\( \theta_\ast = 1 - \theta \)) coverages are

\[
\theta_{\text{NO}} = \theta_\ast p_{\text{NO}} K_{\text{II}} \quad (6.21)
\]

\[
\theta_{\text{O}} = \theta_\ast \sqrt{p_{\text{O}_2} \beta_1 K_1} = \frac{p_{\text{NO}_2} \theta_\ast}{p_{\text{NO}} \beta_{\text{III}} K_{\text{II}} K_{\text{III}}} \quad (6.22)
\]

\[
\theta_\ast = \frac{1}{1 + p_{\text{NO}} K_{\text{II}} + \sqrt{p_{\text{O}_2} \beta_1 K_1}} \quad (6.23)
\]

NO adsorption is taken to be barrierless and thus equilibrated; the O and free site coverages depend on the reversibilities of the other reactions. Further, over-

\[\text{\footnotesize[1] Frequencies are provided in Appendix A.}\]
all reaction rates depend only on the rates of O₂ dissociation and O–NO bond formation.

The coverage-dependent rates of the four surface reactions are written in a mean field methodology using the calculated kinetic parameters.

\[ r_1(\theta, T) = J_{\text{O}_2} \exp \left[ -\frac{\Delta E_{\text{act}}^1(\theta)}{k_B T} \right] \theta_O^2 (1 - \beta_1) \] (6.24)

\[ r_{\text{indep}}^{\text{III}}(\theta, T) = \frac{k_B T}{h} \exp \left[ -\frac{\Delta E_{\text{act}}^{\text{III}}(\theta)}{k_B T} \right] \theta_{\text{NO}} \theta_O \left( 1 - \sqrt{\beta/\beta_1} \right) \] (6.25)

\[ r_{\text{assist}}^{\text{III}}(\theta, T) = \frac{k_B T}{h} \exp \left[ -\frac{\Delta E_{\text{act}}^{\text{III}}(\theta)}{k_B T} \right] \theta_{\text{NO}} \theta_O \left( 1 - \beta/\beta_1 \right) \] (6.26)

\[ r_{\text{IV}}(\theta, T) = J_{\text{O}_2} \exp \left[ -\frac{\Delta E_{\text{act}}^{\text{IV}}}{k_B T} \right] \theta_{\text{NO}} (1 - \beta_1) \] (6.27)

For a given set of reaction conditions and \( \beta \), the steady state solutions are the \( \beta_j \) that make \( 2r_1 = r_{\text{indep}}^{\text{III}} \) and \( r_{\text{IV}} = r_{\text{assist}}^{\text{III}} \). This approach provides solutions without requiring any assumptions about relative reaction rates.

6.2.4.1 Mechanisms and Rate Determining Steps

We separately solve an independent O₂ dissociation model, including reactions I–III in Table 6.1 and a NO-assisted O₂ dissociation model, in which reaction I is replaced by reaction IV. Rates, coverages, and \( \beta_j \) for \( P = 1 \) bar, \( y_{\text{O}_2} = 10\% \), \( y_{\text{NO}_x} = 100 \) ppm, and \( T = 573 \) K are shown in Figures 6.8 and 6.10, plotted as a function of conversion \( X_{\text{NO}} \approx 0 - 0.93 \).

As shown in Figure 6.8, the independent O₂ dissociation turnover frequency
Figure 6.8. Steady state rates (left) and $\theta$ (right) for independent and NO-assisted $O_2$ dissociation mechanisms as functions of conversion. Conditions are: $P = 1$ bar, $y_{O_2} = 0.1$, $y_{NO_x} = 100$ ppm, $T = 573$ K.

Figure 6.9. Steady state rates (left) and $O$ and NO coverages (right) for the independent and NO-assisted $O_2$ dissociation mechanisms at $P = 1$ bar, $y_{O_2} = 0.1$, $y_{NO_x} = 0.01$, $T = 573$ K.
Figure 6.10. $\beta_1$, $\beta_{III}$, and $\beta$ (left) and degree of rate control (right) for $\text{O}_2 + 2^* \rightarrow 2\text{O}^*$ and $\text{NO}^* + \text{O}^* \rightarrow \text{NO}_2 + 2^*$ vs. conversion.
Conditions are: $P = 1$ bar, $y_{\text{O}_2} = 0.1$, $y_{\text{NO}_x} = 100$ ppm, $T = 573$ K.

(TOF) is greater than the NO-assisted O$_2$ dissociation one at all conversions. The difference is maximized near $X_{\text{NO}} = 0$, where the independent route is more than 100 times faster than the assisted one, but the difference decreases with increasing conversion. The computed TOF for the independent mechanism is 0.9 site$^{-1}$ s$^{-1}$ near $X_{\text{NO}} = 0$, and it decreases with $X_{\text{NO}}$ to 0.004 site$^{-1}$ s$^{-1}$ at $X_{\text{NO}} = 0.93$. This initial TOF agrees remarkably well the experimentally observed value of 0.4 site$^{-1}$ s$^{-1}$ at the same conditions on Pt(111) [229].

NO and O coverages are the same for both models and are shown in Figure 6.8. Under these reaction conditions total surface coverage increases from 0.25 ML at low conversion up to 0.4 ML near $X_{\text{NO}} = 1$. NO is the most abundant surface species at small $X_{\text{NO}}$, where $p_{\text{NO}_x}/p_{\text{NO}}$ is small. $\theta_{\text{NO}} < 0.25$ ML for all $X_{\text{NO}}$. Oxygen becomes the most abundant surface species at $X_{\text{NO}} > 0.25$, and $\theta_{\text{NO}}$ is
less than 0.1 ML for $X_{\text{NO}} > 0.33$.

At low $X_{\text{NO}}$, where $\theta$ is at its minimum, the independent $O_2$ dissociation barrier is up to 0.15 eV smaller than the NO-assisted one, favoring independent over assisted dissociation. At higher $X_{\text{NO}}$, the independent $O_2$ dissociation barrier is at least as large as the NO-assisted one, but $\theta_{\text{NO}}$ and the NO-assisted $O_2$ dissociation rate become small. NO oxidation thus proceeds via independent $O_2$ dissociation at all $X_{\text{NO}}$. The competition between independent and assisted dissociation pathways is sensitive to the relative pressures of NO and $O_2$. Higher $NO_x$ partial pressures produce higher NO coverages and, as the assisted step is modeled as a reaction between adsorbed NO and gas-phase $O_2$, the assisted rate increases. Further, these higher coverages inhibit direct $O_2$ dissociation. Microkinetic modeling results at $P = 1 \text{ bar}$, $y_{O_2} = 10\%$, $y_{NO_x} = 1\%$, and $T = 573 \text{ K}$ are shown in Figure 6.9. NO-assisted $O_2$ dissociation becomes preferred at the higher $y_{NO_x}$.

These solutions provide insights into the reaction steps that control reaction rates. In the DeDonder formalism, reaction steps with $\beta_j$ near unity are in quasi-equilibrium, and steps with $\beta_j \approx \beta$ are rate limiting [58]. Figure 6.10 plots $\beta_j$ and $\beta$ for the independent mechanism at $y_{NO_x} = 100 \text{ ppm}$ reaction conditions. $\beta_1 = \beta$ and $\beta_{\text{III}} = 1$ at all $X_{\text{NO}}$, so that the NO ↔ NO$_2$ reaction III is quasi-equilibrated and $O_2$ dissociation is rate determining. The results are identical for the NO-assisted mechanism, since $\beta_{IV} = \beta_1 \beta_{\text{II}} \beta_{\text{III}}$.

Additionally, we calculate “degree of rate control” derivatives by finite difference, and the results are shown in Figure 6.10. $\chi_{rc,1} = 1$ at all $X_{\text{NO}}$, indicating that $O_2$ dissociation has a large positive control on overall rate. $\chi_{rc,\text{III}}$ goes from $-0.5$ at low $X_{\text{NO}}$ to $-2.0$ at high $X_{\text{NO}}$. The negative values indicate that Reaction III is an “inhibition” step [36]: faster conversion of NO to NO$_2$ actually decreases
the overall reaction rate by interfering with O\textsubscript{2} dissociation, and this effect is most pronounced at the highest NO\textsubscript{2}/NO ratios. These results are consistent with the rate inhibition by NO\textsubscript{2} observed experimentally [171, 172, 229].

Both the methods of DeDonder relations and the degree of rate control indicate O\textsubscript{2} dissociation is rate limiting at the coverages that prevail during NO oxidation over Pt. These results are a direct consequence of the differing coverage sensitivities of O\textsubscript{2} dissociation and NO reaction to NO\textsubscript{2}. Because O\textsubscript{2} dissociation is rate limiting, O coverage becomes governed by the NO\textsubscript{2}/NO equilibrium (Equation 6.22) [83, 171, 172, 229], and increases with X\textsubscript{NO}.

6.2.4.2 Temperature Dependence

Temperature-dependence for \( \beta = 0.0031 \) is shown in Figure 6.11. We calculate Pt lights off for NO oxidation around 250°C (Figure 6.11a), in excellent agreement with experiment [182]. Figure 6.11a compares the calculated rate using DFT-calculated and experimental reaction energies for NO + 1/2 O\textsubscript{2} \( \rightarrow \) NO\textsubscript{2} (a component of Equation 6.19). We use the experimental value to report results in this work. The DFT value is \(-1.18\) eV, nearly 0.6 eV different than the experimental value of \(-0.60\). Using the experimental value, the rate levels off around 350°C. In contrast, the purely DFT rate increases with \( T \) until about 700°C. \( T \)-dependent \( \theta \) are shown in Figure 6.11b. Using the experimental \( \Delta E_{\text{rxn}} \), the total coverage \( \theta \) decreases with \( T \) up to about 350°C, where \( \theta \approx 0.26 \) ML, due to entropy. Between 350 and 420°C, \( \theta \) is constant, but \( \theta_{\text{NO}} \) decreases, and \( \theta_{\text{O}} \) increases due to the release sites previously occupied by NO. When controlled by \( p_{\text{NO}_2}/p_{\text{NO}} \), the equilibrium \( \theta_{\text{O}} \) is less susceptible to changes in \( T \) than \( \theta_{\text{NO}} \) because \( \theta_{\text{O}} \) is only marginally dependent on entropy [82]. At 350°C, \( \theta_{\text{NO}} \) is 0.03 ML. The O–NO
Figure 6.11. Rate (a), total coverage (b), macroscopic $X_{\text{NO}}$ (c), and $\beta_i$ (d) vs. $T$ for the independent $O_2$ dissociation mechanism. Dotted lines indicate DFT calculated $\Delta E_{\text{rxn}}$ were used, and solid lines indicate experimental ones were used for $\text{NO (g)} + \frac{1}{2} \text{O}_2 (g) \rightarrow \text{NO}_2 (g)$. Conditions are: $P = 1 \text{ bar}$, $y_{O_2} = 0.1$, $y_{\text{NO}_x} = 100 \text{ ppm}$, $\beta = 0.0031$, except for in (c), where $\beta$ is variable.
bond formation rate, and thus reversibility, decreases with $\theta_{\text{NO}}$ (Figure 6.11d). By $420^\circ\text{C}$, $\theta_{\text{NO}}$ is on the order of $10^{-3}$, O–NO bond formation is rate limiting with $\beta_{\text{III}} = 0.15$, and $\theta_{\text{O}}$ is controlled by equilibrium with O$_2$.

Achievable $T$-dependent macroscopic conversions,

$$X_{\text{NO}}^{\text{macro}} = \frac{\tau L V_{\text{micro}}}{N_A C_{\text{NO,0}}} \quad (6.28)$$

modeled in a CSTR with residence time $\tau = 100$ s, site density $L/V = 1.5 \times 10^{15}$ sites/unit reactor volume, and $C_{\text{NO,0}} = 0.0001$ bar$/RT$ are shown in Figure 6.11, and compared with equilibrium gas phase conversions. $r_{\text{micro}}$ are calculated rates from microkinetic modeling, and $N_A$ is Avogadro’s number. Using the experimental $\Delta E_{\text{rxn}}$, $X_{\text{NO}}$ is negligible below and equilibrium-limited above the Pt light-off $T$, as observed experimentally [182]. The DFT-$\Delta E_{\text{rxn}}$ solution captures the catalyst light off $T$ but fails to capture the equilibrium limitation. It artificially stabilizes NO$_2$, promoting O–NO bond formation and inhibiting NO$_2$ dissociation, and it predicts the equilibrium switches from products to reactants at much higher $T$, starting around $700^\circ\text{C}$. At that $T$, $\theta < 0.25$ ML due to entropic effects, and the thermodynamics and kinetics are dramatically different than at $1/4 \leq \theta < 1/2$ ML. Using the experimental $\Delta E_{\text{rxn}}$ in the model allows it to capture both the high $\theta$ and equilibrium limitation relevant to NO oxidation catalysis at experimentally and industrially relevant $T$.

The apparent activation energy $\Delta E_{\text{app}}$ is another measure of $T$ sensitivity. Under conditions where $y_{\text{NO}} \ll y_{\text{O}_2}$, the rate of Pt-catalyzed NO oxidation can be described by

$$r(p_{\text{O}_2}, p_{\text{NO}}, \beta, T) = F_{\text{O}_2}P(\theta) \exp \left[ -\frac{\Delta E_{I\text{act}}^\text{act}(\theta)}{k_B T} \right] \quad (6.29)$$
where $\mathcal{P}(\theta)$ is the probability that $O_2$ impinges on the surface in a site where it can dissociate, equal to $\theta^2_s$ in the mean field approximation.

$$\Delta E^{\text{app}} = -k_B \left( \frac{\partial \ln r}{\partial (1/T)} \right) = -k_B \frac{d}{d(1/T)} \left[ \ln \mathcal{F}_{O_2} + \ln \mathcal{P}(\theta) - \frac{\Delta E_{I}^{\text{act}}(\theta)}{k_B T} \right] \quad (6.30)$$

Both the middle and latter terms depend on $\theta$, which is a function of $p_{O_2}$, $p_{NO}$, $\beta$, and $T$ (as well as $\Delta E_{O}^{\text{bind}}$ and $\Delta E_{NO}^{\text{bind}}$.) $\Delta E^{\text{app}}$ is thus strongly dependent on the conditions under which the derivative is taken as well as the model parameters.

Numerical differentiation of Equation (6.30) between 280 – 320°C at $p_{O_2} = 0.1$ bar, $p_{NO} = 2.5 \times 10^{-5}$ bar, and $\beta = 0.03$, conditions where $\theta_{NO}$ is small, and thus where dependence on $p_{NO}$ and $\Delta E_{NO}^{\text{bind}}$ is minimal, yields $\Delta E^{\text{app}} = 2$ eV, which is much higher than observed values of 0.4 – 0.8 eV [48, 103, 148, 171, 172, 182, 183, 229] and also about twice as large as $\Delta E_{I}^{\text{act}}$. The biggest contribution comes from the strongly $\theta$-dependent latter term, and the middle term contributes approximately 0.2 to $\Delta E^{\text{app}}$ in the mean field approximation. The difference between this calculated value and experimental observation could be due in part to differences in measurement conditions. For example, we hold $p_{O_2}$, $p_{NO}$, and $\beta$ constant to find $\Delta E^{\text{app}}$, but the results would be different if we substituted $X_{NO}$ or $p_{NO_2}$ for $\beta$.

The difference could also be due in part to errors in the calculated parameters. For example, our model uses $\Delta E_{I}^{\text{act}}$ that depend on $\Delta E_{O}^{\text{bind}}$ for equilibrium O configurations, but such ordered configurations are likely metastable to disordered structures with higher $\Delta E_{O}^{\text{bind}}$, and thus higher $\Delta E_{I}^{\text{act}}$, at these higher $T$. It is therefore possible that our model predicts $\Delta E_{I}^{\text{act}}$ changes too dramatically with $T$.

Further, the mean field model requires all free sites are equivalent, which in reality is likely not true. While our mean field model successfully describes properties depending on the rate, it is likely too simplistic to describe properties depending...
on rate derivatives.

6.2.4.3 Reaction Rate Orders

Reaction rate orders capture partial pressure dependence,

\[ \alpha_B = \left( \frac{\partial \ln r}{\partial \ln p_B} \right) = \frac{d}{d \ln p_B} \left[ \ln F_{O_2} + \ln \mathcal{P} (\theta) - \frac{\Delta E_{\text{act}} (\theta)}{k_B T} \right] \]  

(6.31)

and like \( \Delta E^{\text{app}} \), they are sensitive to conditions and model parameters, although not to the extent as \( \Delta E^{\text{app}} \). We therefore do not expect perfect agreement with experimental observation. There are three natural partial pressure variables: \( p_{O_2} \), \( p_{NO} \), and \( p_{NO_2}/p_{NO} \), which can be represented by \( \beta \). Numerical differentiations of Equation (6.31) with respect to these quantities are shown in Table 6.2.

The \( O_2 \) order is a sum of the contributions from the \( O_2 \) flux colliding with the Pt surface, a contribution of 1, and the extent to which \( p_{O_2} \) influences \( \theta_O \) (Equation 6.22). At constant \( \beta \), \( p_{NO_2}/p_{NO} \) varies by \( p_{O_2}^2 \), and \( \theta_O \) varies concomitantly, leading to \( \alpha_{O_2} \) between 0–1, in reasonable agreement with observed values between 0.5 and 1.0 [103, 148, 171, 172, 229]. The \( NO_2/NO \) order captures the rate inhibition caused by \( NO_2/NO \) promotion of high \( \theta_O \) [171, 172, 229]. Calculated values span from \(-0.8\) at low \( p_{NO_2}:p_{NO} \) to \(-1.6\) at high \( p_{NO_2}:p_{NO} \), in reasonable agreement with observed values between 0 and \(-2.0\) [103, 148, 171, 172, 229].

The \( NO \) order has two contributions: from the effect of \( p_{NO_2}/p_{NO} \) on \( \theta_O \) and from the effect of \( p_{NO} \) on \( \theta_{NO} \). The former influence is a positive contribution, and the latter is a negative contribution. We calculate \( \alpha_{NO} \) between \(-1.3\) at low \( p_{NO_2}:p_{NO} \) and \(-0.1\) at high low \( p_{NO_2}:p_{NO} \). These are quite different than observed values which span from 0.3 to 1.3 [103, 148, 171, 172, 229]. These differences are due in
TABLE 6.2

CALCULATED O\textsubscript{2}, NO, AND NO\textsubscript{2}/NO RATE ORDERS AT VARIOUS CONDITIONS. ALL ORDERS WERE TAKEN AT 300\textdegree C. $y_\text{O}_2$ WAS VARIED BETWEEN 5–15\% FOR $\alpha_{O_2}$, $y_\text{NO}$ WAS VARIED BETWEEN 20–105 PPM FOR $\alpha_{NO}$, AND $\beta$ WAS VARIED BETWEEN 6.3$\times$10$^{-5}$–0.076 FOR $\alpha_{NO_2/NO}$

<table>
<thead>
<tr>
<th>$y_{\text{NO}}$ (ppm)</th>
<th>$\beta$</th>
<th>$\alpha_{O_2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>87.5</td>
<td>6.3$\times$10$^{-5}$</td>
<td>0.8</td>
</tr>
<tr>
<td>75.0</td>
<td>3.4$\times$10$^{-4}$</td>
<td>0.6</td>
</tr>
<tr>
<td>50.0</td>
<td>3.1$\times$10$^{-3}$</td>
<td>0.3</td>
</tr>
<tr>
<td>25.0</td>
<td>0.03</td>
<td>0.2</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$y_{\text{NO}}$ (ppm)</th>
<th>$y_{\text{O}_2}$</th>
<th>$\alpha_{\text{NO}_2/\text{NO}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>70.0</td>
<td>0.1</td>
<td>−0.8</td>
</tr>
<tr>
<td>60.0</td>
<td>0.1</td>
<td>−1.0</td>
</tr>
<tr>
<td>40.0</td>
<td>0.1</td>
<td>−1.5</td>
</tr>
<tr>
<td>20.0</td>
<td>0.1</td>
<td>−1.6</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$y_{\text{O}_2}$</th>
<th>$\beta$</th>
<th>$\alpha_{\text{NO}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>6.3$\times$10$^{-5}$</td>
<td>−1.3</td>
</tr>
<tr>
<td>0.1</td>
<td>3.4$\times$10$^{-4}$</td>
<td>−0.9</td>
</tr>
<tr>
<td>0.1</td>
<td>3.1$\times$10$^{-3}$</td>
<td>−0.3</td>
</tr>
<tr>
<td>0.1</td>
<td>0.03</td>
<td>−0.1</td>
</tr>
</tbody>
</table>
large part to differences in measurement conditions. Here, we hold $\beta$, and thus $\theta_O$ constant, and experimental orders are typically measured holding $p_{NO_2}$ constant while allowing $\beta$ to vary. Experimental orders are thus biased toward the effect of $p_{NO_2}/p_{NO}$ on $\theta_O$. They are not, however, equal to $-1$ times the observed $\alpha_{NO_2}$ [171, 172, 229], suggesting there is an effect on the rate from $\theta_{NO}$. This is particularly true on Pt(111), where measured NO and NO$_2$ orders are 1.3 and $-2.0$ [229].

6.2.5 Model Sensitivity to $\Delta E_{O}^{\text{bind}}$

In these models we describe $\Delta E_{O}^{\text{bind}}$ using a linear function in $\theta$. The results are sensitive to both the slope and the y-intercept of this expression. The y-intercept can be compared with observed values. There are two experimental estimates of the O-Pt(111) binding energy at low $\theta$ [82]: one based on micro-calorimetry that estimates $\Delta E_{O}^{\text{bind}} = -1.6$ eV [266], and one based on kinetic analysis of TPD spectra that estimates it is $-1.1$ eV [38]. Our calculated value is $-1.3$ eV. The error in the calculated O binding energy in equilibrium with $p_{NO_2}/p_{NO}$, $\epsilon_{eq}$, is equal to the sum of the error in the calculated $\Delta E_{O}^{\text{bind}}$, $\epsilon_{\Delta E_{O}^{\text{bind}}}$, and the error in $\Delta E_{\text{rxn}}$ for the overall gas phase reaction. For $-0.2 \leq \epsilon_{\Delta E_{O}^{\text{bind}}} \leq 0.3$, $\epsilon_{eq}$ is minimized when the experimental $\Delta E_{\text{rxn}}$ is used.

The simplest way to model the slope is to set it equal to 0, but that is ineffective for NO oxidation. $\Delta E_{O}^{\text{bind}}$ is governed by $p_{NO_2}/p_{NO}$, and it adapts to reflect changes in $X_{NO}$, going from $-0.79$ eV at $X_{NO} \approx 0$ to $-0.62$ eV at $X_{NO} = 0.93$. This would be different if O$_2$ controlled $\theta_O$, since $p_{O_2}$ remains relatively constant over the course of the reaction. In that case, a slope of 0 would be appropriate. In this case, a static $\Delta E_{O}^{\text{bind}}$ is only valid near the $X_{NO}$ in equilibrium with that
particular $\Delta E_{\text{bind}}^O$. At significantly lower $X_{\text{NO}}$, the model produces $\theta < 0.25$ ML (i.e. it increases $\theta$ to compensate low $X_{\text{NO}}$), where O–NO bond formation is endothermic \[81, 188\], and at significantly higher $X_{\text{NO}}$, it produces $\theta > 0.50$ ML, where O$_2$ dissociation is activated by more than 2.2 eV. Since $\Delta E_{\text{bind}}^O$ is governed by $p_{\text{NO}_2}/p_{\text{NO}}$, which is continuous and dynamic, $\Delta E_{\text{bind}}^O$ must be continuous and dynamic as well. In this work we attempt to describe the slope as accurately as possible by using only equilibrium O orderings within the $\theta$ range most relevant to the catalysis.

### 6.3 Conclusions

In this work we parameterized a coverage-dependent mean field model to simulate Pt-catalyzed NO oxidation. The model leads to general understanding of the catalysis under relevant reaction conditions. We find that under experimental and industrial conditions, independent O$_2$ dissociation is rate limiting, and NO$_2$ dissociation is equilibrated. The catalysis occurs at high surface coverage, generated by equilibrium with $p_{\text{NO}_2}/p_{\text{NO}}$. The model reasonably reproduces observed TOF, catalyst light-off $T$, and rate orders \[48, 103, 148, 171, 172, 182, 183, 229\] (Table 6.3). This success can be attributed to key modeling design features implemented in this work:

- $\theta$-dependent thermodynamics and kinetics were explicitly calculated
- The experimental $\Delta E_{\text{rxn}}$ for NO + 1/2 O$_2$ → NO$_2$ was used to capture the observed $\theta$ and equilibrium limitations under conditions of interest
- No assumptions were made about the RDS
- $\Delta E_{\text{bind}}^O (\theta)$ was accurately calculated from an extensive set of data
TABLE 6.3

NO OXIDATION KINETICS: COMPARISON OF MICROKINETIC MODELING RESULTS AND EXPERIMENTAL OBSERVATION

<table>
<thead>
<tr>
<th></th>
<th>Model</th>
<th>Experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td>TOF (site$^{-1}$ s$^{-1}$)</td>
<td>0.9</td>
<td>0.4</td>
</tr>
<tr>
<td>Light-Off $T$ (°C)</td>
<td>250</td>
<td>200</td>
</tr>
<tr>
<td>$\Delta E_{\text{app}}$ (eV)</td>
<td>2.0</td>
<td>0.4-0.8</td>
</tr>
<tr>
<td>$\alpha_{O_2}$</td>
<td>0.2-1.0</td>
<td>0.5-1.0</td>
</tr>
<tr>
<td>$\alpha_{NO_2}$</td>
<td>$-0.8 \rightarrow -1.6$</td>
<td>$0 \rightarrow -2.0$</td>
</tr>
<tr>
<td>$\alpha_{NO}$</td>
<td>$-1.3 \rightarrow -0.1$</td>
<td>0.3-1.0</td>
</tr>
</tbody>
</table>

There are some discrepancies between the calculated and experimental values. This could be due in large part to limitations in the mean field model, which fundamentally assumes all sites are equivalent at any coverage, and that effect of coverage on rate can be captured in an average way. They could also be due to other model parameters, such as $\Delta E_{O}^{\text{bind}} (\theta (T))$. Further modeling is necessary to truly understand these effects. Qualitatively, the results from the mean field model are in excellent agreement with experimental observation and describe how Pt promotes NO oxidation. They can be used to design better catalysts for NO oxidation. The optimal material for NO oxidation maximizes facility for $O_2$ dissociative adsorption and minimizes tendency to oxidize. Unfortunately, for most transition metals, these two properties are inherently linked. $O$ affinitive metals facilely dissociate $O_2$ and tend to oxidize. We consider this in the next chapter.
CHAPTER 7

UNDERSTANDING NO OXIDATION CATALYSIS ON TRANSITION METALS: TOWARD RATIONAL CATALYST DESIGN

7.1 Introduction

The goal of rational catalyst design is to design a catalyst that improves performance and reduces cost over the existing technology. Reaction rate is the canonical measure of catalyst performance, and cost includes not only the purchase cost but also the cost of regeneration. One problem with Pt for NO oxidation is that it is poisoned by inactive surface oxides over time \[82, 172\], requiring regeneration. An optimal catalyst operates at a high rate and avoids this deactivation. Selecting a new catalyst material is difficult. Pt is one of the most noble transition metals, but it is susceptible to deactivation due to bulk oxidation under NO oxidation conditions, so surely less noble metals, such as Ir, Pd, Cu, Ru, etc. will be prone to oxidation under the same conditions. Au is the most noble transition metal, and "large" Au particles can resist oxidation even under significant O chemical potentials \[117, 224-226\]. However, because Au is not affinitive toward O, it is inactive for O\(_2\) dissociation. We calculate the O binding energy on Au(111) is \(\Delta E_{O}^{\text{bind}} = -0.21\ eV\). Approximating the binding energy of 2O* 1NN to be 2 \(\Delta E_{O}^{\text{bind}}\), an overestimate, we can approximate the dissociation barrier using a general BEP
relationship derived by Nørskov et al. [177]

\[
\Delta E^{\text{act}} = (2.07 \pm 0.07) + \Delta E_{2O^*}(0.90 \pm 0.04) \tag{7.1}
\]

The activation energy is 1.9 eV, and thus the dissociation rate is on the order of \(10^{-11}\) site\(^{-1}\) s\(^{-1}\). As documented before, Au is too noble to effectively promote O\(_2^*\) activation [257] and thus NO oxidation.

Pt is an effective NO oxidation catalyst because it binds O strongly enough to promote O\(_2\) dissociation and weakly enough that bulk oxidation slow. However, Pt is expensive, and its susceptibility to oxidation calls for improvement. The best catalyst will maximize rate and minimize tendency to oxidize, thus capturing the best features from Pt and Au. Such materials could lie on the periodic table between these two metals. In this chapter, we examine a Pt/Au mixture for NO oxidation catalysis in terms of its susceptibility to oxidize, catalytic rate, and cost. Pt/Au mixtures have previously been studied in the context of NO oxidation [124, 129]. In reaction conditions, we show Pt segregates to the surface, allowing stronger O binding than Pt or Au. We find activity and susceptibility to oxidation are nearly identical to Pt, but in a less volatile economy, Au\(_3\)Pt may be less expensive to purchase. We go on to predict that the kinetic behavior will be similar on most extended transition metal particles. As an example, we run our kinetic model over Ir and show that it exhibits the same kinetic features as Pt and Pt/Au.

7.2 Structural Details

Au\(_3\)Pt models were constructed using 4-layer 2×2 supercells and \(\mathbf{k}\)-point meshes of 10×10×1. All other DFT details are identical to those in Chapter 2. We ex-
amine two Pt/Au models: a perfectly mixed phase and a segregated phase (Figure 7.1). The perfectly mixed phase was modeled in the L1\textsubscript{2} crystal structure. We calculate its lattice constant is 4.124 Å, intermediate between that of Pt and Au. The fully segregated phase was modeled as a Pt monolayer over a Au substrate \cite{96}. We use the calculated Au lattice constant of 4.171 Å for the supercell, representing a 4.4% expansion of the Pt lattice. The surfaces are shown in Figure 7.1. The segregated phase, which we will show in the next section is stable under NO oxidation conditions, was compared with an α-PtO\textsubscript{2} thin film over a Au substrate to investigate oxidation. The thin film was modeled exactly in the manner as the one used previously to investigate Pt surface oxidation \cite{82}. 

Figure 7.1. Fully mixed (top) and segregated (bottom) surfaces of Au\textsubscript{3}Pt used to model NO oxidation.
TABLE 7.1

COVERAGE-DEPENDENT INTEGRAL O BINDING ENERGIES (in eV per metal atom) ON FULLY MIXED AND FULLY SEGREGATED AU₃PT

<table>
<thead>
<tr>
<th>θ₀</th>
<th>1/4</th>
<th>1/2</th>
<th>3/4</th>
<th>1</th>
</tr>
</thead>
<tbody>
<tr>
<td>L1₂</td>
<td>−0.12</td>
<td>−0.08</td>
<td>+0.25</td>
<td>+0.72</td>
</tr>
<tr>
<td>Segregated</td>
<td>−0.40</td>
<td>−0.67</td>
<td>−0.79</td>
<td>−0.46</td>
</tr>
</tbody>
</table>

7.3 Results

7.3.1 Susceptibility to Oxidation

Here we compute surface energies of the different phases of Au₃Pt/O to determine stability under oxidation conditions. Integral O binding energies

\[
M + (θ₀/2) O₂ \rightarrow M - O
\]  

(7.2)

on the metallic Au₃Pt models at 0, 1/4, 1/2, 3/4, and 1 ML O are given in Table 7.1. As on Pt [82], O prefers FCC binding on the segregated and mixed phases at all coverages. There are two types of FCC sites on the mixed phase model, one where O sits above Au in the third metal layer, and one where it sits above Pt. The former, which allows binding with surface Pt, is preferred by 0.44 eV. O binds more strongly to the segregated phase at all θ₀ investigated here, consistent with its preference to bind to more reactive Pt.
The surface energy is related to the integral binding energy through \[ \gamma^{(1)} = \Delta E_{\text{int}} - \frac{1}{2} \left( \Delta G_{\text{O}_2} (T, P^0) + k_B T \ln p_{\text{O}_2} \right) \tag{7.3} \]

where we have ignored vibrational contributions of bound O since we found them to be small in Chapter 4. Surface energies, plotted against $\Delta \mu_O = \mu_O(T, P) - \mu_O(0K)$, are shown in Figure 7.2. Typical $\mu_O$ for NO oxidation are indicated with vertical dotted lines. The fully mixed phase is stable at low O potentials, and the segregated phase is stable when the O potential is significant enough to induce O chemisorption. The $\alpha$-PtO$_2$-Au(111) surface oxide comes into equilibrium with the 1/2 ML coverage at the high end of $\mu_O$ for NO oxidation, similar to Pt. This result indicates Au$_3$Pt will likely experience oxidation over time in NO oxidation, so like Pt, it is susceptible to deactivation.

7.3.2 Catalytic Rate

Surface energy analysis shows the segregated phase of Au$_3$Pt is present under NO oxidation conditions. The catalyzed rate over this phase is needed to compare the performance with Pt. We showed in Chapter 6 that the key descriptor of NO oxidation activity is differential O binding energy. We estimate $\Delta E_{\text{O}}^{\text{bind}}$ by fitting integral O binding energies (Table 7.1) to a second order polynomial using the method of least squares (Figure 7.3) and differentiating

\[ \Delta E_{\text{O}}^{\text{bind}} = 3.30\theta_O - 2.16 \tag{7.4} \]

The trend is limited to four orderings, so it is not highly accurate over the entire range of $\theta$, but the difference between fitted and computed energies is minimized.
Figure 7.2. Surface energies for Au$_3$Pt as a function of O potential. The 0 ML line is for the fully mixed phase, and the remaining lines are for the fully segregated phase. Vertical dotted lines indicate the chemical potential range for NO oxidation.

at 1/2 ML, near the coverages relevant for the catalysis. At this $\theta$, $\Delta E_{\text{bind}}^\text{O} = -0.50$ eV by finite differencing and $-0.51$ eV using Equation [7.4].

Since the segregated phase of Au$_3$Pt is effectively a Pt catalyst over a Au substrate, the thermodynamics and kinetics of NO oxidation over Au$_3$Pt are likely to be quite similar to Pt. As an estimate of the kinetic behavior, we apply the kinetic model derived in Chapter 6 to Au$_3$Pt. The important inputs for the model are $\Delta E_{\text{bind}}^\text{O}$ (Equation [7.4]), $\Delta E_{\text{NO}}^{\text{bind}}$, and $\Delta E_{\text{I}}^{\text{act}}$. We assume NO binding site preferences and binding energy relationships with O are identical on Pt and Au$_3$Pt and apply Equation [6.2] to Equation [7.4]

$$\Delta E_{\text{NO}}^{\text{bind}} = 3.02\theta - 1.14$$ (7.5)
We further assume Au₃Pt operates via the independent O₂ dissociation mechanism. The activation energy is computed by combining Equations 6.7 and 7.4:

\[ \Delta E_{\text{act}}^I = 6.60\theta - 2.00 \] (7.6)

Microkinetic modeling results at 573 K, 100 ppm NOₓ, 10% O₂, and 1 bar total pressure are shown in Figures 7.4 and 7.5. Au₃Pt operates at a slightly higher θ than Pt, consistent with stronger O binding induced by the expanded Pt lattice [4, 124]. \( \Delta E_{O}^{\text{bind}} \) at the operating θ is slightly greater than on Pt (−0.74 vs. −0.71 eV, respectively, at \( \beta = 0.028 \)), and the rate on Au₃Pt is about 3 times greater. Both catalysts light off for NO oxidation at the same \( T \) of about 250°C. Aside from the slightly higher θ and rate, the general features of the catalysis are similar. The rates are within the same order of magnitude, so Au₃Pt shows no real improvement in performance.
Figure 7.4. Independent O\(_2\) dissociation rate (left) and catalytic coverages (right) vs. NO conversion on the segregated phase of Au\(_3\)Pt. Conditions are: \(P = 1\) bar, \(y_{O_2} = 0.1\), \(y_{NO_x} = 100\) ppm.

Figure 7.5. \(T\)-dependent rate for NO oxidation on fully segregated Au\(_3\)Pt. Conditions are: \(P = 1\) bar, \(y_{O_2} = 0.1\), \(y_{NO_x} = 100\) ppm.
7.3.3 Cost

On the cost axis, a Pt/Au mixture catalyst could be less expensive to purchase than a Pt one. Over the last 10 years, Au has traded for as low as half the Pt price (although at the time of writing, Au and Pt are within 100 $ per troy oz.\footnote{130}), so replacing 75% of Pt atoms with Au could be economically attractive. However, our results indicate Au$_3$Pt is just as susceptible to oxidation as pure Pt, so like Pt, it would need to be regenerated for NO oxidation. Regeneration of Au$_3$Pt could be more costly than for Pt because in reducing conditions, Au will segregate to the surface to minimize the surface energy. The regenerated catalyst would thus need to be exposed to an oxidizing atmosphere for some time to promote Pt segregation to the surface, which as shown above, induces oxidation.

7.4 Outlook for Extended Transition Metal Particles

The kinetic results for segregated Au$_3$Pt-catalyzed NO oxidation are, probably unsurprisingly, very similar to the ones on pure Pt. In this section, we show that this similarity is induced by $\theta$ and that results should be similar on any extended transition metal surface that operates at moderate $\theta$.

Results from microkinetic modeling of NO oxidation over Pt (Chapter\footnote{6} indicate the rate is a strong function of $\theta = \theta_O + \theta_{NO}$. The O coverage under reaction conditions is given by Equation\footnote{6.22} $\theta_O = p_{NO_2}\theta_*/p_{NO}K_{II}K_{III}$. Since $\theta_O$ is dictated by $p_{NO_2}/p_{NO}$, the catalyst operates at the $\theta_O$ where $K_{II}K_{III}$ satisfies $p_{NO_2}/p_{NO}$ subject to the availability of free sites

\[ K_{II}K_{III} = \frac{p_{NO_2}}{p_{NO}} \frac{\theta_*}{\theta_O} = \sqrt{\frac{K_{Rxn}}{K_I}} \]  

(7.7)
where \( K_{\text{rxn}} \) is for \( 2 \text{NO} + \text{O}_2 \rightarrow 2 \text{NO}_2 \). Assuming surface vibrational energies are nearly identical across metals, at constant \( p_{\text{NO}_2}/p_{\text{NO}} \) the O binding energy thus depends only on the ratio of \( \theta_*/\theta_O \)

\[
\Delta E^\text{bind}_O = \frac{1}{2}\Delta G_{\text{rxn}} + k_B T \ln \left( \frac{p_{\text{NO}_2}}{p_{\text{NO}}} \right) + E^\text{ZP}_O - \frac{1}{2}E^\text{ZP}_{\text{NO}_2} + \Delta E^\text{vib}_O - \frac{1}{2}\Delta G_{\text{O}_2} \left( T, P^0 \right) + k_B T \ln \left( \frac{\theta_*}{\theta_O} \right)
\]

Different materials thus operate at different \( \theta \) in order to obtain the \( \Delta E^\text{bind}_O \) required by \( p_{\text{NO}_2}/p_{\text{NO}} \), but differences in \( \Delta E^\text{bind}_O \) between materials are limited to \( k_B T \ln (\theta_*/\theta_O) + O(0.01) \). The latter term accounts for small fluctuations due to differences in surface vibrational energies. The small differences in \( \Delta E^\text{bind}_O \) lead to small differences in activation energy. Results from prior work \cite{177} and Chapter 6 indicate the activation energy is linked to \( \Delta E^\text{bind}_O \)

\[
\Delta E^\text{act}_T = \zeta \Delta E^\text{bind}_{2O* \text{1NN}} + \xi
\]

where

\[
\Delta E^\text{bind}_{2O* \text{1NN}} \approx 2\Delta E^\text{bind}_O + \text{1NN interaction energy}
\]

Differences in activation energy between metals are thus limited to \( 2\zeta k_B T \ln (\theta_*/\theta_O) + O(0.01) + \zeta \Delta (\text{1NN interaction energy}) \). Based on test calculations on a limited number of materials, we expect the last term is on the order of 0.1 eV. Therefore, the rate of \( \text{O}_2 \) dissociation on metals that operate at “moderate” \( \theta \), i.e. \( 0.1 \leq \theta \leq 0.9 \text{ ML} \) should be within an order of magnitude. Metals that operate at very low or very high \( \theta \) exhibit different behavior. For example, the barrier
on Au, which operates at a very low $\theta = 2 \times 10^{-5}$ ML at $\beta = 0.028$, is 1.9 eV, or about 1 eV greater than the barrier on Pt.

The results show that metals that follow an independent $O_2$ dissociation route for NO oxidation and operate at moderate $\theta$ should all exhibit similar kinetics. To demonstrate this further, we apply the microkinetic model from Chapter 6 to a completely different material altogether. We choose Ir since it neighbors Pt on the periodic table. Using 4-layer $4 \times 4$ and $3 \times 3$ Ir supercells (lattice parameter = 3.871 Å), we calculate $\Delta E_{O}^{\text{bind}}$ at 0, 0.25, 0.33, and 0.50 ML are $-1.84$, $-1.51$, $-1.31$, and $-0.85$ eV/O, respectively. Least-squares fitting yields

$$\Delta E_{O-Ir}^{\text{bind}} = 1.94\theta - 1.90$$  \hspace{1cm} (7.11)

with $R^2 = 0.96$. The maximum difference between fitted and calculated values is 0.1 eV. From this, assuming the binding energy of $2O^* 1\text{NN} = 2 \Delta E_{O-Ir}^{\text{bind}}$ (neglecting the O/O 1NN interaction\(^1\)), and using Equation (7.1) the $O_2$ dissociation barrier is

$$\Delta E_{I}^{\text{act}} = 3.44\theta - 1.35$$  \hspace{1cm} (7.12)

As for Au$_3$Pt, we apply Equation (6.2) to compute the NO binding energy\(^2\)

$$\Delta E_{NO}^{\text{bind}} = 1.78\theta - 2.58$$  \hspace{1cm} (7.13)

Microkinetic modeling results are given in Figures 7.6 and 7.7. As expected, they

\(^{1}\)Neglecting the 1NN interaction energy gives the maximum difference.

\(^{2}\)For this assumption to be valid, NO needs to exhibit the same binding behavior as on Pt. DFT calculations show that NO prefers atop binding on Ir(111)\(^{134}\). We thus expect some discrepancies in our results. However, since our model does not depend explicitly on $\theta_{NO}$, it is largely insensitive to $\Delta E_{NO}^{\text{bind}}$. It is more important that we capture the total coverage $\theta$. 

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are nearly identical to results on Pt and Au\textsubscript{3}Pt. Ir operates at a slightly higher \(\theta\) and thus a slightly smaller \(\Delta E^\text{bind}_O\) \((-0.77 \text{ eV at } \beta = 0.028\) and a slightly higher rate. It lights off for NO oxidation at 250°C, just like Pt and Au\textsubscript{3}Pt. The results strongly suggest since \(\Delta E^\text{bind}_O\) is dictated by gas phase conditions rather than material, it is not a tunable variable for NO oxidation catalysts, and only nominal improvements can be made to \(\Delta E^\text{act}\) and rate.

### 7.5 Conclusions

The results from this chapter show Au\textsubscript{3}Pt and Pt exhibit similar kinetic features for NO oxidation catalysis, and we predict the kinetics are similar for all extended transition metal surfaces that actively dissociate O\_2. This is a unique feature of NO oxidation catalysis that occurs because \(p\text{NO}_2/p\text{NO}\) governs the O binding energy, \(\Delta E^\text{bind}_O\), which dictates the surface kinetics, meaning the kinetics
Figure 7.7. $T$-dependent rate for NO oxidation on Ir(111). Conditions are: $P = 1$ bar, $y_{O_2} = 0.1$, $y_{NO_x} = 100$ ppm.

are governed by gas conditions, not by material. Au$_3$Pt has a similar tendency to oxidize as Pt, and we expect other less noble metals will be prone to oxidation as well. Deactivation via oxidation could be an unavoidable circumstance of NO oxidation catalysis on these materials. They may find use in exhaust control for lean burn Otto engines, which operate in alternating cycles of lean and rich conditions, but in general, efforts to design catalysts for NO oxidation should shift focus from large transition metal particles to materials that are either not susceptible to oxidation in NO oxidation or that have oxides that are reducible by NO. In the next chapter, we recommend screening Au nanoparticles as potential catalysts.
CHAPTER 8

THE FUTURE OF CATALYZED NO OXIDATION: AU NANOPARTICLES?

8.1 Summary of Conclusions

In this work, we developed a microkinetic model of Pt-catalyzed NO oxidation. The mechanism is described by a rate limiting independent $O_2$ dissociation step and an equilibrated $O$–NO bond formation step

$$O_2 + 2* \rightarrow 2O*$$

$$NO + * \rightleftharpoons NO*$$

$$NO* + O* \rightleftharpoons NO_2 + 2*$$

This model successfully captures the observed rate, rate inhibition by $NO_2$, first order rate dependence on $O_2$, catalyst light-off temperature, and sensitivity to $O$ coverage. The model is defined by several key features. The thermodynamics and kinetics are strongly sensitive to the differential $O$ binding energy on the surface, which we extensively characterize in Chapter 4. The $O$ binding energy increases dramatically with coverage due to repulsive lateral interactions between $O$. The catalysis occurs at significant surface coverage between $0.25 \leq \theta < 0.50$ ML,
and accurate modeling requires appropriate description of the catalysis within this coverage regime. These properties are thoroughly investigated in Chapters 5 and 6. Ours is the only reported model that uses explicit calculations of the coverage-dependent thermodynamics and kinetics. Prior models accounted for coverage effects by extrapolating low coverage energies into the appropriate coverage regime using some sort of lateral interaction model. In this work, we show that other factors contribute to the catalysis at high coverage, specifically the ability or inability of species to adapt to the local coverage environment. We show in Chapter 5 that NO and NO$_2$ can assume onefold binding geometries and minimize lateral repulsion from O at high coverage. Similarly, the O–NO bond formation TS adapts to the local surface environment and assumes onefold binding at high $\theta$, minimizing interactions with O. Its barrier is constant at 0.7 eV for $0.25 \leq \theta \leq 0.50$ ML. In contrast, O and O$_2$ assume threefold and twofold geometries at all coverages and interact extensively with O. The O$_2$ dissociation TS cannot adapt to the coverage environment, and its energy increases dramatically with coverage, going from 0.95 to 2.28 eV between 0.25 and 0.50 ML. Because of these features, in the $0.25 \leq \theta < 0.50$ ML regime, O–NO bond formation is equilibrated and O$_2$ dissociation is rate limiting. We show in Chapter 6 that the O coverage, and thus the O binding energy, is governed by $p_{NO_2}/p_{NO}$, which changes with $X_{NO}$. This equilibrium leads to the negative NO$_2$ order observed experimentally [171, 172, 229]. We accurately capture the O binding energy in equilibrium with $p_{NO_2}/p_{NO}$ by using the experimental reaction energy for NO + 1/2 O$_2$ → NO$_2$ instead of the GGA one. The GGA one overestimates the stability of NO$_2$ by 0.6 eV and does not capture the lability of the O–NO bond within the $T$ and $\theta$ regime of interest. The consistency between our results and experimental ob-
vation indicates the importance of including these features in the microkinetic model.

Knowledge of the mechanism can be used in rational catalyst design, which is discussed in Chapter 7. The optimal material for NO oxidation maximizes facility for $O_2$ dissociative adsorption and minimizes tendency to oxidize. Unfortunately, for most transition metals, these two properties are inherently linked. $O$ affinitive metals facilely dissociate $O_2$ and tend to oxidize. It is difficult to conceive of a material that is more active yet more noble. As a possibility, we explored a $Au_3Pt$ alloy for NO oxidation, thinking such an alloy could maintain Pt’s affinity for $O$ and inherit some of Au’s nobility. In NO oxidation conditions, $Au_3Pt$ functions as a so-called pseudomorphic monolayer catalyst [96, 124], a Pt monolayer on a Au substrate. Its activity toward NO oxidation and its tendency to oxidize are identical to Pt. In fact, the rates on most transition metals are similar. The rate is controlled by the $O_2$ dissociative adsorption activation energy, which is governed by the $O$ binding energy, which is defined by the coverage, which is dictated by $p_{NO_2}/p_{NO}$. $p_{NO_2}/p_{NO}$ equilibrates with the $O$ coverage that produces the equilibrium binding energy. Nearly all transition metals thus operate at nearly identical binding energies and thus rates. NO oxidation is thus a case where the kinetics are controlled by the gas phase conditions rather than by the material! Not to mention, most materials have stronger $O$ affinities and thus tendencies to oxidize than Pt. So how do we improve upon a Pt catalyst for NO oxidation?

8.2 Recommendations for Future Work

Au nanoparticles have garnered much attention in the last two decade due to their high reactivities relative to bulk Au [40, 102]. Particles are seemingly more
tunable for catalysis than extended surfaces because their sizes can be controlled and thus optimized for a particular reaction. In particular, Au particles sized anywhere from a couple of atoms to large bulk-like structures have found extensive use in CO oxidation. Au particles have been successfully applied to NO oxidation as well. Jang et al. [122] showed experimentally that 5% Au/Co$_3$O$_4$/Al$_2$O$_3$ is particularly active for low-$T$ NO oxidation. They showed it can achieve $X_{\text{NO}}$ on the upwards of 95% at 200°C, well above what is possible on large Pt particles [80, 182]. Further, they showed low-$T$ activity is sustainable for more than 15 hours. During this time, the only decreases in activity were due to decreases in $T$ below 150°C. It seems that these particles may avoid the high catalyst light-off $T$ that accompanies Pt and other transition metals.

One reason for this extended activity could be that the Au particles are either less susceptible to oxidation than, for example, large Pt particles, or that their oxides are active toward NO oxidation. Stampfl and co-workers have begun investigation of Au nanoparticles in oxidizing conditions [224, 225]. They have shown that Au nanoparticles do oxidize, but at the very highest $\mu_\text{O}$ relevant for NO oxidation, i.e. below 475 K in 1 atm O$_2$.

Another reason could be that Co$_3$O$_4$/Al$_2$O$_3$ buffers Au against oxidation [82]. A check of the redox properties of Co$_3$O$_4$ indicates

$$\text{Co}_3\text{O}_4 \rightarrow 3\text{CoO} + 1/2\text{O}_2$$

(8.1)

has $\Delta G = 2.1$ eV at 573 K [117], so it is unlikely an unsupported Co$_3$O$_4$/CoO
redox couple can oxidize NO,

\[
\text{NO} + \text{Co}_2\text{O}_4 \rightarrow 3\text{CoO} + \text{NO}_2 \tag{8.2}
\]

has \( \Delta G = +1.5 \text{ eV} \) at that \( T \). It is possible, however, that \( \text{Co}_2\text{O}_4 \) interactions with the \( \text{Al}_2\text{O}_3 \) support enhance the redox properties, as for the \( \text{ZrO}_2/2\text{CeO}_2 \) couple discussed in Chapter 4. In fact, metal oxide-supported \( \text{Co}_3\text{O}_4 \) has been shown to exhibit high NO oxidation activity \[268\]. Given the poor redox properties of \( \text{Co}_3\text{O}_4/\text{CoO} \) alone, this is most likely due to a modified O binding energy. It would be interesting to know if supporting \( \text{Co}_3\text{O}_4 \) on a metal oxide somehow alters its redox properties, and if so, what the modified O binding energy is, particularly if it is within the range relevant for NO oxidation. It would also be interesting to know if supported \( \text{Co}_3\text{O}_4 \) can act as an O buffer in NO oxidation.

Based on the results in this dissertation and the literature discussed in this chapter, I recommend examining materials other than large metal particles for NO oxidation catalysis. I recommend screening Au nanoparticles, which can be tuned for size to capture the optimal catalytic properties. I recommend investigating the redox properties of Au surface and bulk oxides. I further recommend screening the buffering properties of \( \text{Co}_3\text{O}_4/\text{metal oxide supports} \). If such supports can protect a material against oxidation, maintain a strong enough O binding energy to promote \( \text{O}_2 \) dissociation, and maintain a weak enough O binding energy to promote O–NO bond formation, they could conceivably be used with a variety of materials to promote NO oxidation. In that case, the catalyst material could be optimized for cost. This dissertation provides a general understanding of transition metal-catalyzed NO oxidation which can be used as a starting point for answering these questions.


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