A Design Strategy Applied to Sulfur Resistant Lean NO$_x$ Automotive Catalysts

by

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Abstract

Catalyst poisoning due to sulfur compounds derived from fuel sulfur presents a major challenge, intractable thus far, to development of many advanced technologies for automotive catalysts such as the lean NO\textsubscript{x} trap. Under lean conditions, sulfur will be oxidized to SO\textsubscript{3} and then form sulfate on the trap. The sulfate on the trap is thermodynamically very stable and, thus, difficult to purge. The NO\textsubscript{x} trap will then be deactivated over time. Our objective has been to build up a framework for the design of selective, sulfur resistant, oxidation automotive catalysts, which are active for the oxidation of NO to NO\textsubscript{2} but relatively inactive for the oxidation of SO\textsubscript{2} to SO\textsubscript{3}.

It is well known that the catalytic properties of alloys are often superior to those of pure metals, because of either the electronic effect or the ensemble effect or both. The ensemble effect is due to a change in distribution and availability of surface reaction sites, while the electronic effect is due to a change in electronic structure, leading to a change in rate constants of elementary steps. However, a very large number of possible compositions of alloys exist for any particular application. Therefore, a fundamental understanding of the relationship between the electronic structure, the composition, and the activity of alloys, which could aid in catalyst design, is first developed. This is accomplished by constructing a generalized weighted d-band center model for the prediction of the binding strength of chemisorbed molecules, in which the various atoms in the molecules bind unequally to multiple types of surface atoms. This model is then applied to estimate the adsorption energies of SO\textsubscript{2} and NO at both initial states and transition states on various surfaces. Both energetic data and electronic structure data are obtained from first principles density functional theory calculations.

Our model is found to predict well the relative stability of adsorbates on surfaces and can be used to predict the effects of different compositions on the energy of adsorption. A strong linear correlation is found between our new weighting of the positions of the d band of the surface and the molecular adsorption energy. These linear relationships are then used together with energy decomposition scheme for a
coadsorbed system on surfaces, to predict the reactivity of SO$_2$ and NO oxidation on different surfaces. A catalyst which is selective for the oxidation of NO over SO$_2$ is then developed. This study should aid in the development of more effective catalysts for an extremely important environmental application.

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Chapter 1

Introduction to Automotive Catalysts

Automotive catalysts were designed to mitigate the exhaust from the tailpipe of automobile. They have been one of the greatest successes of heterogeneous catalysis over the last three decades, having brought a tremendous benefit to our air quality. Driven by more and more stringent emission regulations, the field of automotive catalysis will perpetually stay at the very edge of technology. Research and development of this field mainly focuses on two directions: upstream direction of power plant applications, such as fuel cell vehicles, and downstream applications, such as exhaust emissions aftertreatment. The latter is especially important for the development of fuel efficient, lean-burn vehicles, both diesel and spark-ignited. In this study, we will focus on the downstream direction.

1.1 Automotive catalysts exhaust control systems

The automotive catalyst exhaust system controls: (1) the partial combustion product—carbon monoxide (CO), (2) the residual uncombusted hydrocarbons (HC), (3) nitrogen oxides (NO\textsubscript{x}), and (4) particular matter (PM). Among those, CO and HC are converted under oxidizing conditions (with excess air) while NO\textsubscript{x} is reduced to N\textsubscript{2} under reducing conditions. This can be clearly seen in Figure 1-1 which shows the
conversion efficiency for the three species (1, 2, and 3) as a function of the air/fuel ratio. Figure 1-1 shows that the conversion efficiency of the oxidation reactions (removal of CO or HC) increases with the increase of the air/fuel ratio, while that of the reduction reactions (removal of NO\textsubscript{x}) decreases with the increase of the air/fuel ratio. (Shelef & McCabe, 2000) Therefore, only when the air/fuel ratio is controlled sufficiently close to the stoichiometric value (around 14.7), can all three pollutants be converted (essentially to CO\textsubscript{2}, H\textsubscript{2}O and N\textsubscript{2}) with high efficiency over a single catalyst. (Gross et al., n.d.) The three-way automotive catalyst (TWC) operates at this value of air/fuel, being a combination of platinum, palladium, and rhodium, in which, rhodium is introduced especially for reduction of NO\textsubscript{x}. However, operating TWCs at stoichiometry precludes taking advantage of operating the vehicle under lean conditions, a condition with a large excess of air, where there is an opportunity to improve the fuel economy due to lower pumping losses, higher ratio of the constant-pressure to constant-volume specific heats of the burnt gas, and reduced heat loss to the walls of the combustion chamber. As shown in Figure 1-1, the main challenge for lean condition operation is how to remove the NO\textsubscript{x} from an exhaust stream containing a large excess of oxygen.

### 1.2 NO\textsubscript{x} control under lean condition

Two possible ways to enhance the efficiency of NO\textsubscript{x} removal under lean conditions have been developed: (1) selective catalysis, in which NO\textsubscript{x} can be reduced by a reductant, present in the exhaust or added deliberately (Shelef, 1995) and (2) NO\textsubscript{x} traps which can store NO\textsubscript{x} for a period of lean operation followed by a short duration catalytic, reductive purging of the stored NO\textsubscript{x} to N\textsubscript{2}. (Takahashi, 1995) However, catalyst poisoning due to sulfur compounds coming from sulfur in the fuel presents a major challenge, intractable thus far, to development of many of these advanced technologies. (Shelef & McCabe, 2000) We discuss the details below.
Oxidation:
\[ \text{CO} + \frac{1}{2} \text{O}_2 \rightarrow \text{CO}_2 \]
\[ (\text{HC}) + \text{O}_2 \rightarrow \text{H}_2\text{O} + \text{CO}_2 \]

Reduction:
\[ \text{NO} + \text{CO} \rightarrow \frac{1}{2} \text{N}_2 + \text{CO}_2 \]
\[ \text{NO} + \text{H}_2 \rightarrow \frac{1}{2} \text{N}_2 + \text{H}_2\text{O} \]

Figure 1-1: Conversion efficiency of CO, HC, and NO\textsubscript{x} vs. Air/fuel ratio.

1.2.1 Selective Catalysis Reduction (SCR) technology

Background on SCR technology

"Selective" is used here because the catalytic reduction of the NO\textsubscript{x} with a reductant occurs preferentially to the oxidation of the reductant with oxygen. (The commonly used reducing agents are anhydrous or aqueous ammonia NH\textsubscript{3} and aqueous urea CO(NH\textsubscript{2})\textsubscript{2}. ) Therefore, it allows the NO\textsubscript{x} reduction reaction to take place in an oxidizing atmosphere. The choice for the type of catalyst is determined by the temperature of the exhaust environment. A problem with SCR technology is that the selectivity is not as yet adequate (Shelef, 1995) and the unfavored reducing agents (ammonia or urea) are needed. Another important but unsolved issue is the catalyst poisoning by the sulfur in the exhaust, which originate in the fuel. This will be discussed in the next subsection.
Impact of fuel sulfur on SCR technology

In order to cover a wide operating temperature range while still maintaining the high NOx conversion efficiency, an SCR technology which is effective at temperature below 250°C will be needed. However, these SCR systems are very sensitive to sulfur at those low temperatures. Another adverse effect of sulfur when using SCR is the potential to form ammonia sulfates, which can then deposit on the catalyst surface.

1.2.2 Lean NOx traps (Adsorbers)

Background on lean NOx traps

Another prospective method to remove NOx from the lean exhaust is to use a NOx trap. The idea of this method is illustrated in Figure 1-2. With this technology, shown in Figure 1-2, NO is catalytically oxidized to NO2 and then stored on a chemical trap, usually made of barium or calcium oxides, as nitrates under lean conditions. Then, the system is temporarily switched to a short period of rich conditions, the stored NOx being reduced to nitrogen and released. NOx trap technology, therefore, can only be called a partial lean-burn strategy, since a periodical brief operation under rich conditions is required to remove the stored NOx. However, the fuel economy penalty due to the occasional short duration of rich operation can be offset by a gain in the conversion efficiency of NOx at the maximum fuel economy.

Impact of fuel sulfur on lean NOx traps

Given the similarities in the chemical properties of gaseous sulfur and nitrogen oxides, the NOx trap is extremely sensitive to sulfur poisoning. As mentioned in the last subsection, the material used for NOx traps is usually a basic oxide, such as BaO or CaO, which adsorb the acidic oxides of nitrogen. They adsorb not only the oxides of nitrogen, but also the oxides of sulfur. More specifically, shown in Figure 1-3, SO2 from the sulfur in the fuel can catalytically react with oxygen to form SO3. (The Pt particles incorporated within the trap promote the oxidation reaction of SO2 to SO3.) SO3 then reacts with the NOx storage components, forming the sulfates (e.g.
BaSO₄). Because the thermodynamic stability of the surface sulfates is considerably higher than that of the surface nitrates, the stable sulfates cannot be decomposed during the purging cycles and, thus, render the adsorbing capabilities of the NOₓ trap ineffective. In addition, SO₃ can also be catalytically converted to sulfate in the exhaust stream resulting in higher particulate emissions.

There are several possible approaches to solve the sulfur poisoning problem and realize a wide implementation of lean NOₓ trap technology: (1) restrict the sulfur content in the fuel to a very low level, (2) make the trapping materials more selective to NO₂ adsorption, and (3) search for new selective catalysts active in the oxidation of NO to NO₂ and relatively inactive in the oxidation of SO₂ to SO₃. (Shelef & McCabe, 2000) The last one is the main goal of this thesis.

1.3 Current approaches for catalyst design

It is well known that the catalytic properties of alloys are often superior to those of pure metals because of either the electronic effect (due to the change in electronic
structure) or the ensemble effect (due to the change in distribution and availability of surface reaction sites) or both. (Sachtler, 1973) But so far, most heterogeneous catalysts are designed via continual incremental improvements of existing catalysts. The incremental improvements are made by applying heuristics and rules of thumb to change existing catalysts and then testing these changes empirically until better catalysts are found. In many cases, this approach has been effective. For example, TWCs, based on supported Pt, Rh, and Pd together with ceria and other additives have been continually improved since the 1970's and are one of the great triumphs of catalyst design. They have led to much less pollution in the air in all cities in which they are installed in automobiles. However, a major problem with the incremental design approach is that further improvement is very hard, because decades of implementation of this approach has led to catalysts that are near their limit of optimization, and this approach does not lead to the ability to propose completely new catalysts, such as alloys.

Another, more recent approach to catalyst design is the combinatorial approach. In this approach, many catalyst formulations are synthesized and tested rapidly in order to optimize catalyst properties. This is an important approach but is limited
by the speed of the combinatorial search. The parameter space of the search is necessarily limited, and the combinatorial approach itself, cannot propose which part of parameter space to choose. For example, to choose bimetallic catalysts from 20 metals with 5 proportions of the metals, a researcher would have to perform \((20 \times \frac{19}{2} \times 5) = 950\) combinations. Certainly, it would be desirable to be able to propose a priori more limited ranges of compositions to explore.

Fortunately, there is an alternative approach—rational catalyst design based on the relationships between the intrinsic properties of materials and their catalytic activities by using molecular simulations. To the best of our knowledge, this approach has led to the design of only one new catalyst, a non-coking steam reforming catalyst by Nørskov et al. (Besenbacher et al., 1998) This catalyst design was based on the ensemble effect, adding a dopant to the surface to prevent nucleation of carbon material without affecting steam reforming.

In this thesis, Nørskov’s ideas will be used as a spring board to design new automotive catalysts based on molecular simulations.

### 1.4 Goal and objectives

The goal of this thesis is to design a new selective, sulfur resistant, oxidation automotive catalyst, which can be active for the oxidation of NO to NO₂ but relatively inactive in the oxidation of SO₂ to SO₃. Molecular simulations are employed for this purpose. Specifically, the objectives of this thesis are to:

1. Identify surface structures on the surface phase diagram of O/Pt(111) and rate limiting steps.

2. Develop and verify a generalized electronic composition–property relationship which can be applied to a complex adsorption system.

3. Propose new materials for selective, sulfur resistant catalysts.
Chapter 2

Computational Methods

In this chapter, the principles of the methodologies that are employed in this thesis are briefly summarized.

2.1 Overview of total energy calculations

Nearly all physical properties are related to total energies or to differences between total energies of matter. The matter can be in the gas phase, or in a condensed phase; it can be solid liquid or amorphous, homogeneous or heterogeneous (molecules in solution, interfaces, adsorbates on surfaces). For example, at zero K, the equilibrium lattice constant of a crystal is the one that minimizes the total energy. Therefore, if total energies can be calculated, any physical property related to a total energy or to a difference between total energies can be determined computationally. To do that, we can unambiguously describe the system as a number of nuclei and electrons interacting through Coulombic forces by a Hamiltonian in the following general form:

\[
\hat{H} = -\sum_{i=1}^{P} \frac{\hbar^2}{2M_i} \nabla_i^2 - \sum_{i=1}^{N} \frac{\hbar^2}{2} \nabla_i^2 + \sum_{i<j}^{P} \frac{Z_i Z_j}{|R_i - R_j|} + \sum_{i<j}^{N} \frac{1}{|r_i - r_j|} - \sum_{j=1}^{P} \sum_{i=1}^{N} \frac{Z_i}{|R_j - r_i|}
\]

(2.1)

Where \( R = \{R_I\}, \ I = 1...P \), is a set of nuclear coordinates, and \( r = \{r_i\}, \ i = 1...N \), is a set of electronic coordinates. \( Z_I \) and \( M_I \) are the nuclear charges and masses, respectively. Atomic units are employed here. The length unit is the Bohr radius \( a_0 (=0.5292 \text{ Å}) \);
the charge unit is the charge of the electron, e; and the mass unit is the mass of the electron, m.

Eq. (2.1) can be written in a more compact way as:

\[ \hat{H} = \hat{T}_n + \hat{T}_e + \hat{V}_{nn} + \hat{V}_{ee} + \hat{V}_{ne} \] (2.2)

Each item in Eq. (2.2) corresponds to that in Eq. (2.1). \( \hat{T}_n \) and \( \hat{V}_{nn} \) are the kinetic and potential nuclear operators. \( \hat{T}_e \) is the kinetic operator of electrons. \( \hat{V}_{ee} \) is the electron-electron interaction. \( \hat{V}_{ne} \) is the nuclear-electron interaction.

In principle, all the properties can be derived by solving the many-body Schrödinger equation in Eq. (2.3) (where \( \Psi(R,r) \) is the many-body wave function). However, in practice, this problem is intractable. Therefore, simplifying assumptions and approximations are necessary to describe the electronic structure of molecules and solids, but they still should be able to preserve accuracy to an acceptable level. These simplifications and approximations are summarized in the following sections.

\[ \hat{H}\Psi(R,r) = E\Psi(R,r) \] (2.3)

### 2.2 Born-Oppenheimer approximation

Because of the large difference in mass between the electrons and nuclei, the time scale associated with the motion of the nuclei is much shorter than that associated with the motion of the electrons. Therefore, the nuclei can be treated adiabatically, leading to a separation of electronic and nuclear coordinates in the many-body wave function, as shown in Eq. (2.4), where \( i \) can be any electronic Eigenstate. Eq. (2.4) is the so-called Born-Oppenheimer (B-O) approximation. This approximation reduces the many-body problem to the dynamics of electrons in some frozen-in configuration of the nuclei, as expressed in Eq. (2.5).

\[ \Psi_i(R,r) = \Theta_i(R)\Phi_i(R,r) \] (2.4)
\[(\hat{T}_e + \hat{V}_{ee} + \hat{V}_{ne})\Phi_i(R, r) = E_i\Phi_i(R, r)\] (2.5)

\section*{2.3 Density functional theory (DFT)}

\subsection*{2.3.1 Electron-electron interactions}

Even with B-O approximation, the many-body problem still remains formidable. One of the most difficult aspects is caused by the need to take into account the effects of the electron-electron interactions ($\hat{V}_{ee}$ in Eq. (2.2)). This includes electron-electron repulsion, due to Coulomb interaction ($\hat{V}_H$ in Eq. (2.6)), and electron exchange and correlation energy ($\hat{V}_{XC}$ in Eq. (2.6)). As we know, the wave function of a many-electron system must be antisymmetric, because electrons are Fermions. The exchange energy is the reduction of the Coulomb energy of the electronic system due to the antisymmetry of the wave function, which causes a spatial separation between electrons with the same spins. It can be included in a total energy calculations by the Hartree-Fock approximation. The correlation energy is defined as the difference between the energy in the Hartree-Fock limit and the exact nonrelativistic energy of a system. The challenge is to calculate accurately the exchange and correlation energies. The current state-of-the-art and widely used methodology that allows for modeling the electron-electron interactions with minimal simplifying assumptions is density functional theory (DFT). (Hohenberg & Kohn, 1964; Kohn & Sham, 1965)

\[\hat{V}_{ee} = \hat{V}_H + \hat{V}_{XC}\] (2.6)

\subsection*{2.3.2 Hohenberg-Kohn theorems}

The two main theorems that serve as the foundation of DFT were proved by Hohenberg and Kohn in the early sixties. (Hohenberg & Kohn, 1964) The first one says that the total electronic energy, including exchange and correlation, of a system in the ground state is uniquely determined by the electron density. This theorem thus establishes the existence of a functional that maps the electron density into energy.

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However, it does not provide the explicit form of the functional. The second one states that the exact electron density minimizes the electronic energy and also provides a variational principal to solve for the electron density, and hence energy.

### 2.3.3 Kohn-Sham energy functional and equations

Combining Eq. (2.2), Eq. (2.6) and Hohenberg-Kohn theorems, the Kohn-Sham total energy functional for a set of electronic states \( \phi_i \) can be written as:

\[
E_{KS} = -\frac{\hbar^2}{2} \sum_i \int \phi_i^* \nabla^2 \phi_i \, dr + \int \hat{V}_n(r)n(r)dr + \frac{1}{2} \int \int \frac{n(r)n(r')}{|r-r'|} \, dr \, dr' + E_{XC}[n(r)]
\]

(2.7)

where \( \hat{V}_n \) is the static total electron-nuclear (or ion) potential. All of the items in Eq. (2.7) are functions of electron density \( n(r) \) as given in Eq. (2.8). Notice that the energy associated with nuclear repulsion is not a function of electron density and can be added to the total energy as a constant for given nuclear positions.

\[
n(r) = \sum_i |\psi_i(r)|^2
\]

(2.8)

A set of wave functions \( \phi_i \) that minimize the Kohn-Sham energy functional in Eq. (2.7) can be obtained by the self-consistent solutions to the Kohn-Sham equations in Eq. (2.9) (Kohn & Sham, 1965):

\[
[-\frac{\hbar^2}{2} \nabla^2 + \hat{V}_n(r) + \hat{V}_H(r) + \hat{V}_{XC}(r)] \psi_i(r) = \varepsilon_i \psi_i(r)
\]

(2.9)

where \( \hat{V}_H \) is the Hartree potential of the electrons:

\[
\hat{V}_H(r) = \int \frac{n(r')}{|r-r'|} \, dr'
\]

(2.10)

\( \hat{V}_{XC} \) is the exchange-correlation potential given by:

\[
\hat{V}_{XC}(r) = \frac{\partial E_{XC}[n(r)]}{\partial n(r)}
\]

(2.11)
The Kohn-Sham equations in Eq. (2.9) allow one to map the interacting many-electron system onto a system of non-interacting electrons moving in an effective potential due to all the other electrons.

2.3.4 Approximations for describing the exchange-correlation energies

The calculation of exchange-correlation energies is nontrivial. Many functionals have been developed for better describing the exchange-correlation energies in recent years.

Local Density Approximation–LDA

LDA uses the form of the exchange-correlation functional for a homogeneous electron gas. For \( \tilde{V}_{XC}[n(r)] = \tilde{V}_X[n(r)] + \tilde{V}_C[n(r)] \), LDA has the exchange term adopted the form deduced by Dirac (Dirac, n.d.):

\[
\tilde{V}_X[n(r)] = \frac{3}{4} \frac{3}{\pi} n(r)^{1/3}
\]  

(2.12)

while the correlation term \( \tilde{V}_C[n(r)] \) can be determined from quantum Monte Carlo simulations. (Ceperley & Alder, 1980) LDA is successful in many systems, especially those where the electronic density is quite uniform, such as bulk metals. However, LDA fails in a number of situations, including the metallic surfaces, because the XC potential decays exponentially, whereas it should follow a power law.

Generalized Gradient Approximation–GGA

GGA is an improvement over LDA, in which not only the local electron density is considered but also the gradients in the electron density. Previous studies in our group have tested and confirmed that the Perdew-Wang '91 (PW91) GGA functional (Perdew et al., 1992) works well for our systems (Lin et al., 2001; Lin et al., 2002;
Lin et al., 2004a). The form of this exchange functional is: (Perdew & Wang, 1991)

\[
\hat{V}_X = \hat{V}_{X}^{LDA} \left( \frac{1 + a_1 s \sinh^{-1}(a_2 s) + (a_3 + a_4 e^{-100s^2}) s^2}{1 + a_1 s \sinh^{-1}(a_2 s) + a_5 s^4} \right)
\]  

(2.13)

where \(a_1 = 0.19645\), \(a_2 = 7.7956\), \(a_3 = 0.2743\), \(a_4 = -0.1508\), \(a_5 = 0.004\), and \(s = \frac{\sqrt{n}}{2k_F n}\) for \(k_F = (3\pi^2 n)^{1/3}\).

The PW91 correlation functional is given by: (Perdew & Wang, 1991)

\[
\hat{V}_C = \hat{V}_{C}^{LDA} + n\hat{H}(t, r_s, \zeta)
\]  

(2.14)

with \(\hat{H} = \hat{H}_0 + \hat{H}_1\), where,

\[
\hat{H}_0 = g^2 \beta^2 \ln[1 + \frac{2\alpha}{\beta} \frac{t^2 + 1 + At^4}{1 + 2t^2 + 2At^4}]
\]  

(2.15)

\[
\hat{H}_1 = \nu[C_c(t_s) - C_c(0) - \frac{3C_c}{7}g^2 t^2 \exp[-100g^4(\frac{k_F^2}{k_F n})t]]
\]  

(2.16)

\[g = \frac{(1+\zeta)2/3+(1-\zeta)2/3}{2}, \quad t = \frac{\sqrt{n}}{2k_F n}, \quad k_s = (\frac{4k_F}{\pi})^{1/2},\]

\[\alpha = 0.09, \quad \beta = \nu C_c(0), \quad \nu = \frac{15}{3}(3\pi^2)^{1/3}, \quad C_c(0) = 0.004235, \quad C_x = -0.001667,
\]

\[A = \frac{2\alpha}{\beta} \frac{1}{\exp[-\frac{2\alpha V_{LDA}^{LDA}}{g^2 \beta^2}] - 1}
\]  

(2.17)

In summary, DFT can be used to determine the ground state energy and the electron density while bypassing the calculation of the electronic wavefunctions. The solution is achieved variationally, by changing the electron density and solving for the electronic energy iteratively until the energy is minimized for a given configuration. The absolute error in these calculations is on the order of several kcal/mol; however, cancellation of errors allows for very accurate determination of relative energies. In this thesis, all the calculations are performed by using Dacapo (http://www.fysik.dtu.dk/CAMP/dacapo.html n.d.), a well established total energy code based on DFT, developed by Nørskov and coworkers at the Technical University of Denmark.
2.4 Periodic supercells

After the approximations in the previous two sections, it is still impossible to handle an infinite number of noninteracting electrons moving in the potential of an infinite number of nuclei or ions. This issue can be solved by applying Bloch’s theorem to the wave functions of a periodic system.

2.4.1 Bloch’s theorem

The ions in a perfect crystal are arranged periodically (at 0K). Therefore, the external potential, which acts on the electrons will also be periodic. That is, \( V(r) = V(r + l) \), where \( l \) is a lattice vector of the crystal (the length of the unit cell).

Bloch’s theorem uses the periodicity of a crystal to reduce the infinite number of one-electron wavefunctions to simply the number of electrons in the unit cell of the crystal. The wavefunction is written as the product of a wavelike part and a periodic cell part: (Aschcroft & Mermin, 1976)

\[
\psi_i(r) = \exp[ik \cdot r] f_i(r)
\]  
(2.18)

The second term is the periodic cell part. This can be expressed by expanding it into a finite number of plane waves, the wave vectors of which being reciprocal lattice vectors, \( G \), of the crystal, \( G \cdot l = 2\pi m \), where \( m \) is an integer.)

\[
f_i(r) = \sum_G c_{i,G} \exp[iG \cdot r]
\]  
(2.19)

Therefore, by submitting Eq. (2.19) into Eq. (2.18), each electronic wavefunction can be written as a sum of plane waves,

\[
\psi_i(r) = \sum_G c_{i,k+G} \exp[i(k + G) \cdot r]
\]  
(2.20)
2.4.2 k-point sampling

By the use of Bloch’s theorem, the problem of the infinite number of electronic wave functions has now been changed into the problem of calculating a finite number of wave functions at an infinite number of reciprocal space vectors within the first Brillouin zone. The first Brillouin zone can be mapped out by a continuous set of points, \( \{k : k = (k_x, k_y, k_z)\} \), throughout that region of reciprocal space (k-space). The occupied states at each k-point contribute to the electronic potential of the bulk solid. Since the set \( \{k\} \) is continuous, there are an infinite number of k-points in the Brillouin zone. Therefore, in principle, an infinite number of calculations are needed to compute this potential. However, the electronic wavefunctions at k-points that are very close together will be almost identical. It is therefore possible to represent the electronic wave functions over a region of reciprocal space at a small number of k-points. The error incurred by this approximation can be made arbitrarily small by choosing a sufficiently dense set of k-points.

Methods have been devised for obtaining very accurate approximations to the electronic potential from a filled electronic band by calculating the electronic wave functions at special sets of k-points. The two most common methods are those of Chadi and Cohen (Chadi & Cohen, 1973) and Monkhorst and Pack (Monkhorst & Pack, 1976). The method by Monkhorst and Pack is used in the course of this work. It can yield not only the sets of points identical to those given by Chadi and Cohen’s method, but also additional sets with the same properties. It is based on generating a set of periodic functions which are orthonormal on a uniformly spaced set of special points in the Brillouin zone (refer to Eq. (2.21)).

\[
S_{mn}(q) = \frac{1}{q^3} \sum_{j=1}^{P(q)} w_j A_m(\vec{k}_j) A_n(\vec{k}_j) = \delta_{mn}
\]  

(2.21)

where, \( q \) is an integer that determines the number of special points in the set. \( P(q) \) is the symmetry-dependent number of points, \( \vec{k}_j \), from the set of points in the irreducible wedge of the Brillouin zone. \( w_j \) is the weight associated with \( \vec{k}_j \) and is simply the
ratio of the order of the entire point group to the order of the group of the wave vector at \( \bar{k}_j \). For example, if \( \bar{k}_j \) is a general point in the (1,1,1) direction of the simple-cubic lattice, \( w_j = 48/6 = 8 \).

### 2.4.3 Plane wave basis sets

The electronic wave functions at each \( k \)-point are now expressed in terms of a discrete plane wave basis set. In principle, this Fourier series is infinite. However, the coefficients \( c_{i,k+G} \) for the plane waves with a smaller kinetic energy \( \frac{\hbar^2}{2} |k + G|^2 \) typically have a more important role than those with a larger kinetic energy. Therefore, we can only include the \( G \) vectors with kinetic energies lower than a maximum cutoff energy \( E_{\text{cut}} \left( \frac{\hbar^2}{2} |k + G|^2 \leq E_{\text{cut}} \right) \). The introduction of a plane wave energy cutoff reduces the basis set to a finite size.

This kinetic energy cut-off will lead to an error in the total energy of the system, but, in principle, it is possible to make this error arbitrarily small by increasing the size of the basis set by allowing a larger energy cut-off. The cut-off that is used in practice depends on the system under investigation. The \( E_{\text{cut}} \) used in this thesis is 25 Rydbergs.

Another advantage of expanding the electronic wave functions in terms of plane wave basis sets is that the Kohn-Sham equations take a particularly simple form. Substitution of Eq. (2.20) in to the Kohn-Sham equations, Eq. (2.9), gives:

\[
\sum_{G'} \left[ \frac{\hbar^2}{2} |k + G|^2 \delta_{GG'} + \hat{V}_n(G - G') + \hat{V}_H(G - G') + \hat{V}_{XC}(G - G') \right] c_{i,k+G'} = \varepsilon_i c_{i,k+G} \quad (2.22)
\]

It can be seen in this form that the reciprocal space representation of the kinetic energy is diagonal and the various potentials can be described in terms of their Fourier transforms. A usual method of solving the plane wave expansion of Eq. (2.22) is by diagonalization of the Hamiltonian matrix whose elements \( H_{k+G,k+G'} \) are given by the term in the brackets above. It follows that the size of the Hamiltonian matrix is determined by the energy cut-off \( \frac{\hbar^2}{2} |k + G_c|^2 \). This matrix size can be intractably large for systems that contain both valence and core electrons. This problem can
be overcome by the use of the pseudopotential approximation, described in the next section.

2.5 Pseudopotential approximation

2.5.1 The idea of pseudopotential approximation

It is well known that most physical properties of solids are dependent on the valence electrons to a much greater degree than that of the tightly bound core electrons. For this reason, the pseudopotential approximation is introduced. In this approximation, the core electrons and the strong nuclear potential are removed and replaced with a weaker pseudopotential, which acts on a set of pseudo wave functions, rather than the true valence wave functions.

The schematic diagram in Figure 2-1 shows these functions. The valence wave functions oscillate rapidly in the region occupied by the core electrons because of the strong ionic potential. These oscillations maintain the orthogonality between the core and valence electrons. The pseudopotential is constructed in such a way that there are no radial nodes in the pseudo wavefunction in the core region. Moreover the pseudo wave functions and pseudopotential are identical to the all-electron wave function and potential outside the cut-off radius \((r_c)\) in Figure 2-1. This condition has to be carefully checked as it is possible for the pseudopotential to introduce new non-physical states (so called ghost states) into the calculation.

The pseudopotential is also constructed such that its scattering properties for the pseudo wave functions are identical to those of the ion and core electrons for the valence wave functions. In general, this will be different for each angular momentum component of the valence wave function. Therefore, the pseudopotential must be angular momentum dependent. Pseudopotentials with an angular momentum dependence are called non-local pseudopotentials.
Figure 2-1: Schematic illustration of the all-electronic (AE) wave function and electronic potential \((Z/r)\) (solid lines) vs. distance from atomic nucleus, \(r\). The corresponding pseudo wave function and pseudopotential are also plotted (dashed lines). The radius at which all-electron and pseudoelectron values match is marked \(r_c\).
2.5.2 Vanderbilt’s ultrasoft pseudopotential

A pseudopotential is not unique, and several methods of generation exist. The one used in this thesis is called Vanderbilt’s ultrasoft pseudopotential (PP), which has a separable form well suited for plane-wave solid-state calculations and transition-metal systems. (Vanderbilt, 1990; Laasonen et al., 1993)

In Vanderbilt’s ultrasoft PP scheme, the total energy of valence electrons, described by the wave functions, $\phi_i$, can be written as:

$$E_{tot} = \sum_m \langle \phi_m | -\frac{\hbar^2}{2} \nabla^2 + V_{NL} | \phi_m \rangle + \int V_{loc}^{(r)}(r)n(r)dr + \frac{1}{2} \int \int \frac{n(r)n(r')}{|r-r'|}drdr' + E_{XC}[n(r)]$$

(2.23)

Different from Eq. (2.7), the PP contains both a local part, $V_{loc} = \sum_l V_{loc}^{(r)}(|r-R_l|)$, and a nonlocal part, $V_{NL} = \sum_{i,l} D_{ij}^{(0)}|\beta_i^l(r-R_l)|$, where the function, $\beta_i^l = \beta_i(r-R_l)$, as well as the coefficients $D_{ij}^{(0)}$, characterize the PP.

The electron density in Eq. (2.23) is given by:

$$n(r) = \sum_m |\phi_m(r)|^2 + \sum_{ij,l} Q_{ij}^l(\phi_m|\beta_i^l)\langle\beta_i^l|\phi_m]\]$$

(2.24)

where $Q_{ij}^l(r) = Q_{ij}(r-R_l)$ is the augmentation function, localized in the core regions and also part of the PP. Therefore, the electron density in Eq. (2.24) is now separated into two parts: a soft delocalized contribution given by the squared moduli of the wave functions and a hard contribution localized at the cores. The ultrasoft PP is fully determined by the qualities $V_{loc}^{(r)}$, $D_{ij}^{(0)}$, $Q_{ij}(r)$ and $\beta_i(r)$.

2.5.3 Generation procedure of Vanderbilt’s ultrasoft PP in literature

As usual, the generation of Vanderbilt’s ultrasoft PP also starts with the all-electron calculations on a free atom in some reference configuration, leading to a screened
potential $V_{AE}$ using the Schrödinger equation:

$$[T + V_{AE}(r)]\psi_i(r) = \varepsilon_i\psi_i(r)$$ \hspace{1cm} (2.25)$$

Here, $i$ is a composite index, $i=\{\varepsilon_l m\}$, and $T$ is the kinetic-energy operator.

Next, cutoff radii $r_{cl}$ are chosen, and for each $\psi_i$ obtained above, a pseudo wave function $\phi_i$ is constructed, subject only to the constraint that it joins smoothly to $\psi_i$ at $r_{cl}$. A smooth local potential $V_{loc}(r)$ is also generated in such a way that it matches $V_{AE}(r)$ at $r_{cl}$ and $r_c$. Then, local orbitals, $|\chi_i\rangle = (\varepsilon_i - T - V_{loc})|\phi_i\rangle$, are formed. (They vanish beyond $r_c$ where $V_{loc} = V_{AE}$ and $\phi_i = \psi_i$.)

Define $B_{ij} = \langle \phi_i | \chi_j \rangle$. Now, the quantities needed to specify the PP are: $Q_{ij}(r) = \psi^*_i(r)\psi_j(r) - \phi^*_i(r)\phi_j(r)$, $|\beta_i\rangle = \sum_j (B^{-1})_{ij} |\chi_j\rangle$.

Let $q_{ij} = \langle \psi_i | \psi_j \rangle_R - \langle \phi_i | \phi_j \rangle_R$, where $R$ is a diagnostic radius, which is chosen large enough that all pseudo- and AE quantities agree at and beyond $R$. $|\phi_i\rangle$ obeys the following secular equation:

$$(T + V_{loc} + \sum_{ij} D_{ij} \langle \beta_i | \beta_j \rangle )|\phi_i\rangle = \varepsilon_i (1 + \sum_{ij} q_{ij} \langle \beta_i | \beta_j \rangle )|\phi_i\rangle \hspace{1cm} (2.26)$$

where $D_{ij} = B_{ij} + \varepsilon_j q_{ij}$.

Therefore, by a "descreening" procedure, we can obtain

$$V_{n}^{loc}(r) = V_{loc}(r) - \int \frac{n(r')}{|r - r'|} dr' - \epsilon_{XC}(r) \hspace{1cm} (2.27)$$

and

$$D_{ij}^{(0)} = D_{ij} - \int V_{loc}(r') n(r') dr' \hspace{1cm} (2.28)$$

The PP generated in the procedure above obeys the criteria that any method should follow. These are: (1) The core charge produced by the pseudo wave functions must be the same as that produced by the atomic wave functions. This ensures that the pseudo atom produces the same scattering properties as the ionic core. (2) Pseudo-electron eigenvalues must be the same as the valence eigenvalues obtained from the atomic wave functions. (3) Pseudo wave functions, as well as their first and
second derivative, must be continuous at the core radius and also be non-oscillatory.

2.6 Minimum Energy Paths and the Nudged Elastic Band method

In order to understand chemical and physical processes occurring in a complicated system, it is useful to find a Minimum Energy Path (MEP) connecting two local minima on the potential energy surface of a system. The transition state of the reaction corresponds to the saddle point along this path. Many computational methods have been proposed to find the MEPs. (Elber & Karplus, 1987; Czerminski & Elber, 1990; Choi & Elber, 1991; Ulisky & Elber, 1990; Olender & Elber, 1997; Weinan et al., 2002; Jónsson et al., 1998; Henkelman & Jónsson, 2000; Henkelman et al., 2000; Maragakis et al., 2002; Chu et al., 2003) A very popular one is the Nudged Elastic Band (NEB) method. (Jónsson et al., 1998) The NEB method is based on the chain-of-states representation of a path. (Elber & Karplus, 1987) It determines the MEP by creating intermediate images along the path that represent replicas of the original system. Spring constants between the adjacent images are added to insure the continuity of the path. By minimizing the force along the path (tangential direction) and perpendicular to the path, the band will be converged to the MEP. Thus, the NEB method has provided a framework to search for a MEP and the saddle point. It has been widely applied to surface reactions and diffusion processes on surfaces. (Eichler & Hafner, 1999; Ciobica et al., 2000; Ciobica & van Santen, 2002; Fordell et al., 2002; Trushin et al., 2002; Xu & Mavrikakis, 2002; Lin et al., 2004b) Therefore, this thesis also uses the NEB method to find the MEPs.

More details about NEB are given in this paragraph. First, let a string of images be denoted by \([r_0, r_1, r_2, ..., r_N]\), where the endpoints are fixed as the initial \((r_0)\) and final states \((r_N)\), while all the other \(N-1\) intermediate images are adjusted by the
optimization algorithm. The objective function is:

\[ S(\vec{r}_0, ..., \vec{r}_N) = \sum_{i=1}^{N} V(\vec{r}_i) + \sum_{i=0}^{N-1} \frac{1}{2} k(\Delta l_i - \Delta l)^2 \] (2.29)

where \( \Delta l_i \) is defined as the distance between replica \( i-1 \) and \( i \), \( \Delta l \) is the average distance between replicas. Then, minimize the objective function with respect to the intermediate images, \( \vec{r}_0, ..., \vec{r}_N \). This mimics an elastic band, strung between two fixed endpoints, made up of \( N \) beads and \( N-1 \) springs with the spring constant \( k \) (in Eq. (2.29)).

The problem with this is that the elastic band tends to cut corners and gets pulled off the MEP by the spring forces in regions where the MEP is curved. Also, the images tend to slide down towards the endpoints. Both problems can be solved by a force projection, the so called "nudging". To do this, a tangent vector, \( \vec{t}_i \), along the path has to be defined for each replica. The forces on each replica in the framework of NEB can then be written as:

\[ \vec{F}_i = \vec{F}_i^\perp + \vec{F}_i^\parallel \] (2.30)

\[ \vec{F}_i^\perp = -\nabla V \cdot (1 - \vec{t}_i \vec{r}_i) \] (2.31)

\[ \vec{F}_i^\parallel = -\nabla (\sum_{i=1}^{N-1} \frac{1}{2} k(\Delta l_i - \Delta l)) \] (2.32)

where \( \vec{F}_i^\perp \) is the force component in the off-path direction (perpendicular to the tangent direction) and comes only from the potential energy instead of the elastic bands. \( \vec{F}_i^\parallel \) is the component in the tangent direction, and comes only from the elastic bands. As we can see in Eq. (2.31), in the off-path direction, the spring forces do not interfere with the true forces. This prevents the corner-cutting problem. Similarly in Eq. (2.32), the true forces also do not compete with the spring forces along the tangent direction, which cures the sliding-down problem. Therefore, a stationary point under the NEB forces is a MEP.

It is also important to eliminate the rigid body translation and rotation of the replicas during the optimization of the path. One flexible way is to define the distance
between replicas in the root-mean-square (RMS) best-fit space. (Chu et al., 2003) Furthermore, to ensure that the true saddle point is obtained, the climbing image (CI) algorithm (Henkelman et al., 2000), which is a slight modification of NEB, can be utilized. In the CI calculation, an image with the highest energy is selected after several iterations. For this image, other than including the perpendicular projection of the force, the inverse of the tangent component of the force is also included, instead of the spring force. Therefore, this intermediate image will move down on the potential energy surface to the MEP in the perpendicular direction and up in the direction of the reaction coordinate. As a result, this method insures rigorous convergence to the saddle point without any significant increase in the computational cost.

2.7 Monte-Carlo simulations

Chapter 3 of this thesis uses Monte Carlo methods to simulate the surface phase diagram of O/Pt(111). Different oxygen adsorption configurations are sampled with the probability given by (Landau & Binder, 2000):

\[ P_s = \frac{\exp(-H_s/k_BT)}{Z} \] (2.33)

where \( s \) is a particular state that a system is in, \( k_B \) is Boltzmann’s constant and \( Z \) is the partition function with the form:

\[ Z = \sum_s \exp(-H_s/k_BT) \] (2.34)

This is achieved by a Markov chain of configurations, where each configuration can be derived from a previous one with a proper transition probability, due to Metropolis.

The simulation starts with an arbitrary configuration which is composed of an array of lattice sites with the occupation variable +1 (occupied) or -1 (unoccupied). A new configuration is generated by selecting sites and changing their occupation variables from +1(-1) to -1(+1) according to a pre-established rule in which a transition probability \( \omega(i \rightarrow f) \) is compared to a random number between 0 and 1. \( i \)
represents the initial state, and \( f \) corresponds to the state after the transition. The criterion for the transition is the following:

If \( E(\vec{\sigma}_f) < E(\vec{\sigma}_i) \),

\[
\omega(i \to f) = 1 \tag{2.35}
\]

If \( E(\vec{\sigma}_f) \geq E(\vec{\sigma}_i) \),

\[
\omega(i \to f) = \exp\left(\frac{E(\vec{\sigma}_f) - E(\vec{\sigma}_i)}{k_BT}\right) \tag{2.36}
\]

where \( E(\vec{\sigma}) \) is the grand canonical energy of configuration \( \vec{\sigma} \) defined as

\[
E(\vec{\sigma}) = H(\vec{\sigma}) - \mu N \tag{2.37}
\]

\( H \) is the enthalpy, \( \mu \) is the chemical potential, and \( N \) is the number of oxygen atoms in the simulation. If the transition probability is larger than a chosen random number, the new configuration \( \vec{\sigma}_f \) is accepted, otherwise, the previous one \( \vec{\sigma}_i \) is kept.

Once converged, thermodynamic averages (i.e. the average enthalpy) can be obtained by

\[
H = \sum_s H_sP_s \tag{2.38}
\]

Two types of simulations can be performed: (1) vary temperature \( T \) at a constant chemical potential \( \mu \) and (2) vary chemical potential \( \mu \) at a constant temperature \( T \). At each fixed \( \mu \) and \( T \), a large number of configurations are sampled with the Metropolis algorithm. Usually, about 4000-6000 MC steps are necessary for our system to obtain the convergence after the equilibrium.

The phase transitions can be characterized by discontinuities or divergences of thermodynamic potentials. For example, first order transitions will have a discontinuity in enthalpy \( H \) vs. temperature \( T \) or coverage \( x \) vs. chemical potential \( \mu \); continuous phase transitions will have a divergence in the heat capacity \( (C_p \text{ in Eq. (2.39)}) \)
or susceptibility ($\chi_\mu$ in Eq. (2.40)) vs. chemical potential.

\[ C_p = \frac{\partial H}{\partial T} = \frac{\langle H^2 \rangle - \langle H \rangle^2}{k_B T^2} \quad (2.39) \]

\[ \chi_\mu = \frac{\partial x}{\partial \mu} = \frac{\langle N^2 \rangle - \langle N \rangle^2}{k_B T^2} \quad (2.40) \]
Chapter 3

Phase Diagram of Oxygen Adsorbed on Platinum(111)

A complete phase diagram of oxygen atoms adsorbed on a Pt(111) surface with oxygen coverages below half a monolayer has been computed for the first time, and compared with the surface phase diagrams of related systems. Effective interaction parameters of a lattice model for the triangular lattice of the fcc sites of the Pt(111) surface were determined from first principles computations. Oxygen forms on the platinum(111) surface two stable ordered phases, which persist up to high temperatures. They are the $p(2\times2)$ and $p(2\times1)$ phases, having coverages of $1/4$ and $1/2$ monolayer respectively. At the coverage of $2/5$ monolayer, another stable phase consisting of $p(2\times1)$ rows but with every two rows offset by an empty site is predicted by our model, but this phase is stable only below 250 K. All three phases undergo continuous phase transitions to the disordered state upon heating. At coverages lower than $1/4$ monolayer and at low temperatures, oxygen atoms cluster into $p(2\times2)$ islands, in agreement with observations from an STM study. The formation of $p(2\times2)$ oxygen islands is a consequence of attractive third nearest neighbors interactions, despite strong repulsion between the first and second nearest neighbors. Two regions separated by first-order phase boundaries are found at coverages between 0.26 monolayer and 0.37 monolayer and coverages between 0.43 monolayer and 0.5 monolayer.
3.1 Motivation

Ordering of adsorbates on surfaces is a fairly universal phenomenon at moderate temperatures (Masel, 1996). Knowledge of the stability of different ordered structures is important for understanding reactions, since reaction rates will be different when the reactants are condensed into different phases. Therefore, a thorough study of the phase diagrams of adsorbates on surfaces is of great importance in describing the thermodynamics and kinetics of processes on surfaces, including adsorption, desorption, diffusion, and chemical reactions.

Oxygen adsorption on metal surfaces, especially on platinum surfaces, has been extensively studied in recent years (Meinel et al., 1997; Bogicevic et al., 1998; Stipe et al., 1997; Wintterlin et al., 1996), because of its key role in various important catalytic reactions, such as the three-way and lean-NOx automobile catalysts, the manufacture of sulfuric acid, and a variety of other processes involving the oxidation of CO and other chemical species (Taylor et al., 1984; Lin et al., 2002; Lynch & Hu, 2000; Bleakley & Hu, 1999). It was found that upon adsorption of oxygen, atomic oxygen is the only species present on platinum surfaces at all but low temperatures (Stipe et al., 1997). The fcc site, which is the hollow adsorption site without a second layer metal atom directly beneath the hollow, is found to be the most stable adsorption site of an oxygen atom on Pt(111) (Bogicevic et al., 1998; Lynch & Hu, 2000). It was further observed by STM experiments that at sub-monolayer coverages, small oxygen islands of p(2x2) symmetry form and merge on a Pt(111) surface, leaving large surface areas of platinum unoccupied (Stipe et al., 1997). It would be interesting to know why islands of oxygen form. This is a fundamental question for similar, well-organized oxygen islands on other metal surfaces as well, and a thorough understanding of the formation mechanism and phase diagram of these islands can also be very valuable in determining the mechanisms of important catalytic reactions and processes. Although many studies of the adsorption of atomic oxygen on metal surfaces have been performed before, to our knowledge, only a few phase diagrams of oxygen on metal surfaces have been reported previously. These
include O/Ni(111) (Kortan & Park, 1981; Schwennicke & Pfünir, 1997), O/Rh(100) (Baraldi et al., 1997), O/Ru(0001) (De'Bell et al., 1991; Piercy et al., 1992; Xiong & Li, 2001), O/W(110) (Wang et al., 1978; Vattulainen et al., 1999), and O/Ni(100) (Taylor & Park, 1983; Piercy & Pfünir, 1987). No study of the phase diagram of O/Pt has been reported so far. In this chapter, we present a phase diagram of the O/Pt(111) surface, computed from first principles, and compare it with the phase diagrams of other systems.

The symmetry of ordered structures on surfaces is dictated by the interactions between the adsorbates. Thus, having a set of accurate lateral interaction parameters is invaluable for understanding the phase transitions on surfaces. In recent decades, quantitative experimental methods of surface science such as Scanning Tunneling Microscopy (STM) (Trost et al., 1996; Österlund et al., 1999), and Low Energy Electron Diffraction (LEED) (Schwennicke & Pfünir, 1997) have been widely used to evaluate the lateral interactions. On the other hand, first principles computations (Stampfl et al., 1999; Van der Ven et al., 1998), have also been used in some systems to evaluate the lateral interactions. Of these methods, only first principles computations can allow one to determine unambiguously the magnitude of various lateral interactions, and this approach was therefore used to determine the various lateral interactions in this study. The lateral interaction parameters extrapolated from the first principles energies were then used in grand canonical Monte Carlo (GCMC) simulations in order to calculate the phase diagram. Details about the steps used to obtain the phase diagram are described in the next section (Chapter 3.2). Then in Chapter 3.3, results are presented and discussed.

### 3.2 Details of calculations

#### 3.2.1 Density functional theory (DFT) for total energies

First-principles density functional theory (DFT), as implemented in the GNU publicly licensed software DACAPO (http://www.fysik.dtu.dk/CAMP/dacapo.html, n.d.), was
used to compute the total energies. The configuration set selected for the DFT computations was based on seven basic unit cells, as illustrated in Figure 3-1. Since the energy of adsorption of oxygen atoms on the fcc sites on Pt(111) is much larger than that on the hcp sites of Pt(111)

(Bogicevic et al., 1998; Lynch & Hu, 2000), only the fcc sites for O adsorbed on Pt(111) were treated explicitly in this study. Full coverage, also referred to as one monolayer (1ML), is defined by all the fcc sites on the Pt(111) surface being occupied by oxygen atoms. The largest unit cell chosen in Figure 3-1 is a (3x3) structure. In this cell, the largest O-O separation is equal to three Pt lattice constants and corresponds to the fifth nearest-neighbor distance of like sites. At these distances, the lateral interactions can be assumed to be negligible (Stampfl et al., 1999). The chemisorption energy of an oxygen atom at the fcc site on Pt(111) on a (2x2) unit cell with three layers was found to be 4.43 eV, which is in good agreement with the results of other theoretical studies (Bleakley & Hu, 1999; Hammer & Nørskov, 1997b). A four-layer slab model with only the bottom layer fixed was also used to check the effects of the finite thickness of the slab model for the Pt(2x2)-O configuration by comparing the formation energy of oxygen to that on the three-layer model. The difference in formation energy between these two slab model calculations is only 0.3 meV. Note that Bogicevic et al. have found that the energy change between a four-layer model (with the top two layers fixed) and a six-layer model (with the top four layers fixed) is less than 10 meV (Bogicevic et al., 1998). A three-layer Pt model has also been applied by Lynch and Hu in their study of CO and atomic oxygen chemisorption on Pt(111) (Lynch & Hu, 2000). Therefore, three-layer slab models were used for the Pt(111) surface throughout this study. All the layers were relaxed during optimization except for the bottom layer, which was fixed at the calculated Pt bulk lattice constant, 4.00 Å. [This value is close to the experimental value, 3.92 Å (Kittel, 1996; Aschcroft & Mermin, 1976).] A vacuum of ~ 10 Å was used to separate the slabs. Between these slabs, we included a point dipole in the Z direction (the direction perpendicular to the slabs) in order to eliminate the interactions among periodic images. The gradient-corrected exchange-correlation functional PW91-GGA (Perdew et al., 1992) was used.
Figure 3-1: Adsorbed oxygen configurations calculated using DFT-GGA. Large empty circles represent Pt atoms and small filled circles represent O atoms. Unit cells are marked in each configuration.
in this study, in addition to ultrasoft pseudopotentials (Vanderbilt, 1990; Laasonen et al., 1993), and planewave expansions with energy cutoffs of 25 Ry (340 eV). The geometry optimization for Pt(3x3)-O was sampled at 4x4x1 Monkhorst-Pack k-points (Monkhorst & Pack, 1976). In order to have the same precision, a larger number of k points corresponding to a larger surface Brillouin zone were used for smaller systems. In order to determine the importance of spin-polarization in the O/Pt(111) system, spin-polarization calculations were performed on several configurations. We found that spin-polarization usually lowers the formation energy by about 1.5 meV, which is well within the numerical accuracy of the pseudopotential methods. All total-energy calculations in this study were therefore nonmagnetic. The accuracy of all the models and parameters used here have been tested and confirmed in previous studies in our laboratory (Lin et al., 2002; Lin et al., 2001; Lin et al., 2004a).

3.2.2 Cluster expansion for lateral interaction parameters

Lateral interactions were modeled via cluster expansions, and the parameters in the cluster expansions were obtained from a small number of first principles calculations. The energy of any configuration could then be computed using a cluster expansion.

In order to specify a configuration, a site occupation variable is assigned to each adsorption site on the surface. Any configuration is then represented by a vector composed of all the site occupation variables. Different choices of the site occupation variables are possible and two sets of the site operators have been used in our study.

Each element in the first set of site occupation variables, $\sigma_i$, takes the value +1 if the site is occupied and -1 if a vacancy is at that site. These site occupation variables are also called spin variables, due to their correspondence with the Ising model (Flinn, 1956). It has been shown that the dependency of any property of a configuration can be expanded exactly in terms of polynomials consisting of products of discrete site occupation variables, $\sigma_i$, where $\sigma_i = \pm 1$ (Sanchez et al., 1984). For computational convenience, these occupation variables were used in the Monte Carlo simulations in our studies. A cluster expansion of the energy, with the assumption that oxygen only adsorbs on the fcc site on Pt(111), then takes the following form:
Figure 3-2: Lateral interactions between and among oxygen atoms adsorbed on Pt(111). Small circles represent oxygen atoms and large circles represent platinum atoms.

\[
E(\sigma) = V_0 + \sum_i V_i \sigma_i + \sum_{i,j} V_{i,j} \sigma_i \sigma_j + \sum_{i,j,k} V_{i,j,k} \sigma_i \sigma_j \sigma_k + \ldots, \tag{3.1}
\]

where all the coefficients (V's) are called effective cluster interactions (ECI's). The interactions up to the third nearest neighbors are illustrated in Figure 3-2, in which, the oxygen atoms marked 1 are the first nearest neighbor atoms to the oxygen atom marked 0. Similarly, those marked 2, and 3 are the second, and third nearest neighbors to the oxygen atom 0. \(V_{i,j}\) and \(V_{i,j,k}\) are pair and three-body interactions respectively. Treating interactions up to three-body and third nearest neighbors was found in our test study to be sufficient to model the system with a high degree of accuracy. With the truncation, the ECI's were fit to first principles energies of different oxygen-vacancy arrangements (Figure 3-1) and were then used to calculate the formation energy of any configuration.

A second set of site operators is also used, as these enable a more physical interpretation of the results. The occupation variables of this set, \(P_i\), have the value 0
when site $i$ is vacant, and the value $+1$ when the site is occupied. It is also called a point variable (Clap & Moss, 1966). In the case of only one adsorbed species (oxygen atoms) in the system, we can write the configurational energy of adsorbed oxygen on fcc sites of Pt (111) as:

$$E(P) = W_0 + \sum_i W_i P_i + \sum_{i,j} W_{i,j} P_i P_j + \sum_{i,j,k} W_{i,j,k} P_i P_j P_k + \ldots,$$  \hspace{1cm} (3.2)

where $P_i = 1$ (occupied) and 0 (vacant), and where the $W$'s are similar to the $V$'s of Eq. (3.1). $W$ and $V$ can be related mathematically by using the relationship between $P_i$ and $\sigma_i$:

$$P_i = \frac{1}{2}(1 + \sigma_i).$$  \hspace{1cm} (3.3)

Details can be found in Inden and Pitsch paper (Inden & Pitsch, 1991). It is worth pointing out that only the $W$'s in Eq. (3.2) can be associated with the interactions between oxygen atoms on the surface illustrated in Figure 3-2. Within this representation, we set interactions between oxygen and vacancies, vacancies and vacancies equal to zero. Thus, interactions represented by $W$'s will be used to discuss and explain island formation on the Pt surface in the Chapter 3.3.2.

3.2.3 Monte Carlo simulations

As mentioned in the last Section, lateral interactions $V_{i,j}$, $V_{i,j,k}$ between oxygen atoms on the Pt(111) surface for the first set of site operators were used in grand canonical Monte Carlo simulations to compute the phase diagram of O/Pt(111). The Monte Carlo simulations were typically performed on a 30x30 two-dimensional lattice with periodic boundary conditions, which has been shown to be sufficient for the O/W(110) system (Vattulainen et al., 1999). A lattice with the size 60x60 was used to check the finite size effect on our Monte Carlo results. We found that a 30x30 2D lattice is sufficient to simulate the surface phase diagram of the O/Pt(111) system in this study. 2000 Monte Carlo passes per lattice site were performed for equilibration, followed
by 5000 Monte Carlo passes per site for sampling at each temperature (T) and chemical potential ($\mu$). The continuous phase transition boundaries between the ordered phase and the disordered phase were determined by connecting the positions at which the heat capacity or susceptibility diverged at various chemical potentials. At first-order phase transitions (in the grand canonical ensemble), bulk properties such as the grand-canonical energy or the coverage (oxygen concentration) are discontinuous. However, the occurrence of hysteresis in numerical simulations at first-order phase transitions makes a precise determination of their location difficult. A reliable way of determining first-order phase boundaries is with the common tangent construction applied to constant temperature Gibbs free energy curves of the two phases participating in the transition. (This is equivalent to determining the location at which the grand-canonical free energies of the two phases competing for stability cross.) In a composition versus temperature phase diagram, first-order phase transitions at constant temperature appear as two phase coexistence regions. For any composition inside the two phase region, the thermodynamically stable state consists of two co-existing phases. We obtained Gibbs free energy curves at constant temperature by integrating the chemical potential versus composition from suitable reference states (Van der Ven et al., 1998; van de Walle & Asta, 2002).

At very low temperatures, the flipping probability becomes very small, and virtually nothing happens for a long time. Therefore, an event driven algorithm (the $N$-fold way (Landau & Binder, 2000)) was used for the Monte Carlo simulations at temperatures below 300 K. The $N$-fold way algorithm is similar to the kinetic Monte Carlo algorithm but without physically relevant rate constants: a list of all the events with their probabilities is built and updated during each step of the simulation, and a flip, determined by a random number, occurs at each step. At low temperatures, the net gain in performance of the $N$-fold way algorithm is dramatic, although each flip takes a considerable amount of CPU time.
3.3 Results and discussions

3.3.1 Formation energies of oxygen adsorbed on Pt(111)

For purposes of understanding phase stability, it is often convenient to consider formation energies instead of adsorption energies. The formation energy of a particular configuration at a given coverage (\( \theta \)) of oxygen on Pt(111) is defined as:

\[
\Delta_f E = E_{O-Pt} - (1 - \theta)E_{Pt} - \theta E_{Pt(1\times1)-O}
\]  

(3.4)

where, \( E_{O-Pt} \) is the total energy for a configuration of oxygen atoms adsorbed on Pt(111) with the coverage \( \theta \), \( E_{Pt} \) is the total energy for a clean Pt(111) surface, and \( E_{Pt(1\times1)-O} \) is the total energy of oxygen adsorbed on Pt(111) at full coverage. The formation energy clearly illustrates the stability of the ordered oxygen configurations relative to a mixture of a clean surface and a surface with full coverage of oxygen at the same overall composition.

Formation energies were determined by inserting DFT total energies of fifteen configurations (refer to Table 3.1 and Figure 3-1) of oxygen adsorbed on Pt(111), (with oxygen coverages ranging from zero to one) into Eq. (3.4). As plotted in Figure 3-3,
Table 3.1: Formation energies (in meV) for O on Pt(111) for various coverages. (All of the configurations can be found in Figure 3-1.)

<table>
<thead>
<tr>
<th>Label</th>
<th>Configuration</th>
<th>Coverage of O (ML)</th>
<th>Formation energy (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>clean Pt(111) surface</td>
<td>0</td>
<td>0.000</td>
</tr>
<tr>
<td>b</td>
<td>(3x3)-O</td>
<td>1/9</td>
<td>-107.670</td>
</tr>
<tr>
<td>c</td>
<td>(3x3)-2O</td>
<td>2/9</td>
<td>-189.641</td>
</tr>
<tr>
<td>d</td>
<td>(3x3)-2O</td>
<td>2/9</td>
<td>-202.428</td>
</tr>
<tr>
<td>e</td>
<td>(2x2)-O</td>
<td>1/4</td>
<td>-245.525</td>
</tr>
<tr>
<td>f</td>
<td>(√3x2)-O</td>
<td>1/4</td>
<td>-229.897</td>
</tr>
<tr>
<td>g</td>
<td>(3x1)-O</td>
<td>1/3</td>
<td>-233.265</td>
</tr>
<tr>
<td>h</td>
<td>(√3x√3)-O</td>
<td>1/3</td>
<td>-283.512</td>
</tr>
<tr>
<td>i</td>
<td>(2x1)-O</td>
<td>1/2</td>
<td>-340.318</td>
</tr>
<tr>
<td>j</td>
<td>(√3x2)-2O</td>
<td>1/2</td>
<td>-326.729</td>
</tr>
<tr>
<td>k</td>
<td>(3x1)-2O</td>
<td>2/3</td>
<td>-266.384</td>
</tr>
<tr>
<td>l</td>
<td>(√3x√3)-2O</td>
<td>2/3</td>
<td>-318.790</td>
</tr>
<tr>
<td>m</td>
<td>(2x2)-3O</td>
<td>3/4</td>
<td>-261.702</td>
</tr>
<tr>
<td>n</td>
<td>(√3x2)-3O</td>
<td>3/4</td>
<td>-260.625</td>
</tr>
<tr>
<td>o</td>
<td>(1x1)-O</td>
<td>1</td>
<td>0.000</td>
</tr>
</tbody>
</table>

Formation energies of all the configurations are negative. In order to analyze phase stability at zero Kelvin, we constructed the convex hull of the formation energies, as illustrated by the solid lines in Figure 3-3. In general, phase stability is determined by the state with the lowest free energy. In a binary system, the common tangent construction determines phase stability when two phases can simultaneously coexist. At 0 K, the free energy equals the energy and hence the convex hull can be viewed as a set of common tangents connecting the energies of the most stable phases. At any composition between two stable phases connected by a line of the convex hull, the thermodynamically most stable state consists of a phase separation of those two phases. Typically the phases on the convex hull remain stable as the temperature is increased, though phases that are marginally stable tend to disorder at low temperatures and may not appear at reasonable temperatures in a temperature composition phase diagram. We find that of the original 12 configurations considered, 5 appear on the convex hull. These stable phases are p(2x2)-O, with a coverage of 1/4 ML, p(√3x√3)-O, with a coverage of 1/3 ML, p(2x1)-O, with a coverage of 1/2 ML, p(√3x√3)-2O, with a coverage of 2/3 ML, and p(2x2)-3O, with a coverage of 3/4.
Table 3.2: Fitted ECIs by using a cluster expansion with the first set of site operators for O/Pt(111). \((i, j, k \text{ in } V_{i,j,k} \text{ or } V_{i,j,k} \text{ are marked Figure 3-2})\)

<table>
<thead>
<tr>
<th>ECI's</th>
<th>meV</th>
</tr>
</thead>
<tbody>
<tr>
<td>(V_{0,1})</td>
<td>72.367</td>
</tr>
<tr>
<td>(V_{0,2})</td>
<td>12.345</td>
</tr>
<tr>
<td>(V_{0,3})</td>
<td>2.936</td>
</tr>
<tr>
<td>(V_{0,1,1})</td>
<td>-0.684</td>
</tr>
<tr>
<td>(V_{0,1,3})</td>
<td>4.664</td>
</tr>
<tr>
<td>(V_{0,1,2})</td>
<td>1.501</td>
</tr>
</tbody>
</table>

ML. While the configuration \(p(3x3)-O\) has a formation energy close to the convex hull, it does not lie on the convex hull, and hence cannot be expected to be present in a temperature composition phase diagram. At the end of this section, we will show that \(p(2x2)-O\) and \(p(2x1)-O\) remain stable up to reasonably high temperatures.

### 3.3.2 Lateral interaction parameters

The fitted interaction parameters for both sets of site operators described in Chapter 3.2.2 are listed in Table 3.2 (spin variable set) and Table 3.3 (point variable set). As mentioned in the previous cluster expansion part, the spin variable set is convenient for computational purposes, while the point variable set offers a more physical interpretation of the interactions. With the mathematical relationship between the two sets of site operators, Eq. (3.3), the lateral interactions corresponding to the spin variable set are transformed from those corresponding to the point variable set \(W_{i,j}\) and are listed \((V-W)\) and compared to the direct fit results \((V-ECI)\) in Table 3.4. Comparison in Table 3.4 shows that the lateral the interaction parameters fitted with different sets of site operators \((V_{i,j} \text{ and } W_{i,j})\) are consistent with each other. There are some differences, which we attribute to the different number of configurations we used for fitting.

As shown in Table 3.3, the repulsion between the nearest neighbor oxygen atoms on Pt(111) is about 0.24 eV. Lynch and Hu used the DFT and generalized gradient approximation (GGA) computation and found that the energy difference between oxygen adsorption at fcc and hcp sites on Pt(111) is 0.47 eV (Lynch & Hu, 2000).
Table 3.3: Fitted ECIs by using a cluster expansion with the second set of site operators for O/Pt(111). In brackets, we list the interaction parameters fitted by Piercy et al. from the experimental O/Ru(0001) phase diagram (Piercy et al., 1992). In parenthesis, we list the interaction parameters derived by Stampfl et al. from DFT computations for O/Ru(0001) (Stampfl et al., 1999). (i, j, k in $W_{i,j}$ or $W_{i,j,k}$ are marked in Figure 3-2.)

<table>
<thead>
<tr>
<th>ECI's</th>
<th>meV</th>
<th>ECI's</th>
<th>meV</th>
</tr>
</thead>
<tbody>
<tr>
<td>$W_{0,1}$</td>
<td>237.088</td>
<td>$W_{0,2}$</td>
<td>39.498</td>
</tr>
<tr>
<td>$W_{0,3}$</td>
<td>-5.808</td>
<td>$W_{0,1,1}$</td>
<td>12.914</td>
</tr>
<tr>
<td>$W_{0,1,3}$</td>
<td>29.567</td>
<td>$W_{0,1,2}$</td>
<td>6.302</td>
</tr>
</tbody>
</table>

Table 3.4: Comparison between effective cluster interactions corresponding to the first set of site operators. The interaction parameters listed in the V-ECI column were fitted directly by the cluster expansion with the first set of site operators. Those in the V-W column were transformed from interaction parameters fitted with the second set of site operators. (i, j, k in $V_{i,j}$ or $V_{i,j,k}$ are marked in Figure 3-2.)

<table>
<thead>
<tr>
<th>ECI's</th>
<th>V-ECI/meV</th>
<th>V-W/meV</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V_{0,1}$</td>
<td>72.367</td>
<td>71.468</td>
</tr>
<tr>
<td>$V_{0,2}$</td>
<td>12.345</td>
<td>10.662</td>
</tr>
<tr>
<td>$V_{0,3}$</td>
<td>2.936</td>
<td>2.244</td>
</tr>
<tr>
<td>$V_{0,1,3}$</td>
<td>4.664</td>
<td>3.696</td>
</tr>
<tr>
<td>$V_{0,1,2}$</td>
<td>1.501</td>
<td>0.788</td>
</tr>
<tr>
<td>$V_{0,1,1}$</td>
<td>-0.684</td>
<td>1.614</td>
</tr>
</tbody>
</table>
Therefore, in the O/Pt(111) system, the binding energy difference of an oxygen atom between fcc and hcp sites is much higher than the nearest neighbor repulsive interactions between adsorbed oxygen atoms on the Pt(111) surface. This result is consistent with our assumption that the occupation of hcp sites is not very important in determining the phase diagram of O/Pt(111). It is also different from the O/Ru(0001) system, in which the hcp site is preferred over the fcc site by 0.072 eV at the DFT-GGA level of theory, much less than the first nearest neighbor repulsion between oxygen atoms on hcp sites (0.27 eV) (Stampfl et al., 1999).

We emphasized in Chapter 3.2.2 that a straightforward physical interpretation can not be assigned to the interaction parameters, $V_{i,j}$ of Eq. (3.1), but $W_{i,j}$, the coefficients of Eq. (3.2), can be physically interpreted. They are effective interactions among atoms on a Pt(111) surface. In Table 3.3, the lateral interaction parameters, $W_{i,j}$ indicate that there exists a strong repulsion between nearest neighbor oxygen atoms (0.237 eV), relatively strong repulsions between next nearest neighbor oxygen atoms (0.040 eV), and a weak attraction between third nearest neighbors (-0.006 eV). No known experimental energies of interactions for O/Pt(111) are available for comparison with our results here, but we can compare our results with those for O/Ru(0001), both of which have triangular lattices in which adsorption occurs at well defined sites [fcc for O/Pt(111) and hcp for O/Ru(0001)]. The interactions determined by Piercy et al. for their best fit to the experimental O/Ru(0001) phase diagram (Piercy et al., 1992) are given in brackets in Table 3.3. The interactions derived by Stampfl et al. for O/Ru(0001) from first-principles calculations (Stampfl et al., 1999) are given in parenthesis in Table 3.3. It is found that the pair-wise interactions that we obtained for O/Pt(111) are similar to both the experimental and theoretical interactions for O/Ru(0001).

The repulsions between the nearest- and next-nearest- neighbor oxygen atoms on Pt(111) can be explained by bond-competition concepts, which have been applied to other systems previously (Lynch & Hu, 2000; Bleakley & Hu, 1999; Shustorovich & Sellers, 1998; Lopez et al., 1980). The effects of the adsorbed oxygen atoms on the projected density of states (pDOS) of their neighbor Pt atoms are illustrated in
Figure 3-4: Comparison among the changes of projected density of states (pDOS) of Pt atoms at different distances from an adsorbed oxygen atom. (The differences are with respect to Pt atoms of the same symmetry at clean surfaces.)

Figure 3-4. The order of effects induced by the adsorbed oxygen atom to its neighbor Pt atoms is: nearest Pt neighbors $\gg$ next nearest Pt neighbors $>$ third nearest Pt neighbors. According to the bond-competition concept, if coadsorbed atoms have to compete with each other for bonding with the surface metal atoms, it would be expected that the most stable adsorption configuration involves the minimum possible amount of competition. Since the adsorbed oxygen atoms have a strong and reasonably strong effect on their first- and second- nearest neighbor Pt atoms, respectively, any coadsorbed oxygen atoms which compete for bonding with the same Pt atoms should suffer an energetic penalty to adsorb, due to the repulsions to the already adsorbed oxygen atoms. On the other hand, Table 3.3 clearly shows attraction between third nearest neighbors. We explain this using an argument similar to that of Feibelman, who studied O adsorbed on Pt(111) (Feibelman, 1997). He showed that when an oxygen atom (oxygen $a$ in Figure 3-5) is adsorbed on an fcc site on Pt(111), the $d$ electrons of its Pt nearest neighbors (Pt 1a, 1b, and 2a in Figure 3-5) are "frustrated" by two incompatible demands. The first is to get as far away from the negatively charged O atom as possible. The other one is to avoid weakening Pt-Pt
bonds by filling antibonding $d$ states. These two demands together strengthen the bond between Pt atoms 1$a$ and 2$c$, and the bond between Pt atoms 1$b$ and 2$b$ (refer to Figure 3-5). Therefore, the overall adsorption of the oxygen atom is strengthened. Similarly, in Figure 3-5, the bond between Pt atoms 1$c$ and 2$c$, and the bond between Pt atoms 1$d$ and 2$b$ are both strengthened. It turns out that these strengthening of bonds is optimized for $p(2x2)$.

3.3.3 Phase diagram of O/Pt(111)

The calculated equilibrium phase diagram of O/Pt(111) with oxygen coverages of up to half a monolayer is presented in Figure 3-6, where the solid lines are continuous phase transition boundaries and the dashed lines signify the boundaries of two-phase coexistence regions (first-order phase transitions). It can be seen that chemisorption of oxygen atoms on Pt(111) leads to two ordered phases at temperatures between about 200 K and 700 K. They are the $p(2x2)$ phase, with an oxygen coverage of 1/4 ML and the $p(2x1)$ phase, with an oxygen coverage of 1/2 ML. The corresponding configurations are shown in the insets in Figure 3-6. The presence of the two phases is similar to results in the literature for O/Ru(0001) (Piercy et al., 1992; Stampfl et al., 1999).
Figure 3-6: Phase diagram of O/Pt(111): The solid lines denote continuous phase transitions and the dotted lines denote first order phase transitions.

Also, similar to the experimental and theoretical results of O/Ru(0001) (Piercy et al., 1992), the boundaries of both the $p(2\times 2)$ and the $p(2\times 1)$ phases in our O/Pt(111) phase diagram denote continuous phase transitions. The order-disorder transition temperatures for the stoichiometric $p(2\times 2)$ phase and $p(2\times 1)$ phase are predicted to be 670 K and 480 K, respectively. We note that automotive catalysts typically run at temperatures greater than 700 K (EPA workshop on gasoline sulfur, 1998), and we would expect no ordered phases in this region. Kaburagi and Kanamori have studied the ordered ground states of the triangular lattice and found that $p(2\times 2)$-O can be stabilized if $V_{01} > 5V_{02} > 0$ which is exactly the case in our system (refer to Table 3.2) (Kaburagi & Kanamori, 1978; Kaburagi & Kanamori, 1974).

At finite temperature, defects and antiphase boundaries can occur, and due to
Figure 3-7: A sample configuration of the ordered oxygen phase having the symmetry $p(2\times1)$ on Pt(111), with $p(2\times1)$ rows rotated by 120° with respect to each other.
the symmetry of p(2x1), domains having rows with different directions, which are rotated by 120° with respect to each other, can coexist (see the zig-zag structure in Figure 3-7). Similar behavior has also been observed in the STM study of other systems, such as the O/Ru(0001) system by Meinel et al. (Meinel et al., 1997) and the Au(111) system by Barth et al. (Barth et al., 1990), but these were thought to be caused by a long-range elastic lattice strain (Besenbacher, 1996). We attribute our zig-zag structure to sluggish "kinetics" in Monte Carlo.

Our phase diagram for O/Pt(111) is quite different from the O/Ni(111) phase diagram measured by Kortan and Park (Kortan & Park, 1981). Although both systems show p(2x2) phases at a coverage of around 1/4 ML, unlike the O/Ni(111) phase diagram, our O/Pt(111) phase diagram contains no stable phase with a coverage of 1/3 ML, e.g., a p(√3x√3)-O phase at intermediate to high temperatures. Note that the p(√3x√3)-O ordered phase is marginally stable at zero Kelvin (i.e. it is on the convex hull), and therefore it should be observed at sufficiently low temperatures. At a low temperature and when the coverage equals 2/5 ML, a small phase with a continuous transition boundary appears in our phase diagram. The order-disorder transition temperature of this phase is about 250 K. In this phase, every two p(2x1) oxygen rows are offset by an empty site (see the inset between those for p(2x2) and p(2x1) phases in Figure 3-6). In other words, it is characterized by a unit cell which is a combination of p(√3x√3) and p(2x1). Since it is hard to name it in a conventional way, we denote this phase region X in Figure 3-6. Note that we found that the cluster expansion used to calculate the phase diagram predicts the X phase to be on the convex hull. Furthermore, clear thermodynamic discontinuities were observed in the Monte Carlo simulations when crossing from the X phase to the disordered phase or to the p(2x2) or p(2x1) phases. Hence the X phase is a distinct stable phase. Phase X is an unexpected phase from our original formation energy curve, since we did not include any DFT energy for a configuration at an oxygen coverage equaling to 2/5 ML in the fit of the cluster expansion. To prove that phase X is a stable phase on the 2D lattice, we performed a DFT computation with the same unit cell as marked in the inset configuration corresponding to the phase X in Figure 3-6.
Figure 3-8: Regions characterized as $p(2 \times 2)$ oxygen islands in a snapshot of a GCMC calculation ($T = 100$ K, $\mu = -979$, and $\theta = 0.09$ ML).

The formation energy of the new configuration, marked as a square in Figure 3-3, does appear on the convex hull. This not only proves that the new configuration is a stable phase, but also shows that our cluster expansion is robust enough to predict the energies for configurations that were not included in the fit of the interaction parameters. Experimental effort around an oxygen coverage of 0.4 ML is suggested in order to confirm the DFT prediction of the stability of phase $X$.

In our O/Pt(111) phase diagram, there are three regions separated by first-order phase boundaries, which means that those regions are two-phase coexistent regions. The first one appears at low temperatures and low coverages, where a first-order phase transition occurs from the $p(2 \times 2)$ phase to the disordered lattice gas phase. The coexistent region is therefore characterized by a state with $p(2 \times 2)$ islands. A typical $p(2 \times 2)$ oxygen island configuration obtained from Monte Carlo simulations at 100 K with a coverage of 0.09 ML is illustrated in Figure 3-8. At 100 K, when the oxygen atoms adsorb with a coverage of 0.09 ML, $p(2 \times 2)$ oxygen islands with different sizes are predicted to form on the Pt(111) surfaces. This is in good agreement with
the STM study of Stipe et al., in which it was found that regions of $p(2\times2)$ symmetry began to appear when the Pt(111) surface was dosed at 82 K and then warmed to 156 K (see Figure 3-9) (Stipe et al., 1997). In Figure 3-9, the island with the mark $p(2\times2)$ includes about 15 oxygen atoms, a size which is similar to those in our simulations. A tricritical point, corresponding to the intersection of boundaries of a $p(2\times2)$ phase region, a disordered phase, and a mixed phase region of $p(2\times2)$ islands surrounded by the disordered phase, was found at the coverage of 0.18 ML, when the temperature is about 270 K. This is similar to the tricritical point ($T = 300K, \theta = 0.21 \text{ ML}$) in the experimental phase diagram of O/Ni(111) (Kortan & Park, 1981). We attribute the further stabilization of $p(2\times2)$ oxygen islands to the attractions between the third nearest neighbors (refer to Table 3.3). Piercy et al. compared the phase diagrams calculated via Monte Carlo simulations with and without attractive third nearest neighbor interactions. They found that $p(2\times2)$ islands grow at a coverage below $1/4$ ML at low temperatures when an attractive third nearest neighbor pair interaction is included. However, $p(2\times2)$ islands do not form when the phase diagram was simulated without a third nearest neighbor attractive pair interaction (Piercy et al., 1992). We found that as we increase the oxygen chemical potential, the $p(2\times2)$ phase transforms to the $p(2\times1)$ phase at low temperatures by first passing through a coexistent region of $p(2\times2)$ and $X$ at coverages between 0.26 ML and 0.37 ML, followed by a single phase region $X$ around $2/5$ ML, and then another two-phase region of $X$ and $p(2\times1)$ at coverages higher than 0.43 ML.

### 3.3.4 Phase under experimental conditions

In this section, Reuter et al.’s idea (Reuter & Scheffler, 2001) is used to predict phases under the experimental conditions (Temperature is about 700 K and Pressure is around 0.1 atm).

First, a zero reference state of $\mu_O(T, P)$ is chosen to be the total energy of oxygen in an isolated molecule, i.e., $\mu_O(0K, P) = \frac{1}{2}E^{\text{total}}_{O_2} = 0$. With respect to this reference
Figure 3-9: Oxygen on Pt(111) dosed at 82 K and warmed to 152 K. Bright atoms are Pt and dark atoms are O. 70 ÅX 70 Å. Reproduced with permission from Ref. (Stipe et al., 1997)

\[
\mu_O(T, P^0) = \frac{1}{2}[H(T, P^0, O_2) - H(0K, P^0, O_2)] - \frac{1}{2}T[S(T, P^0, O_2) - S(0K, P^0, O_2)]
\]  \hspace{1cm} (3.5)

This equation allows us to obtain the temperature dependence simply from the differences in the enthalpy and entropy of an O\textsubscript{2} molecule with respect to the T=0 K limit. For standard pressure, P\textsubscript{0}=1 atm, these values have already been tabulated in thermochemical tables. (Stull & Prophet, 1971) Inserting those into Eq. (3.5) leads finally to \mu_O(T, P^0). For example, when T=700 K, \mu_O(T, P^0) = -0.73 eV.

Assuming that the surrounding O\textsubscript{2} atmosphere is ideal gas, it has been shown that the following expression applies, which gives us the temperature and pressure dependence, if we only know the temperature dependence of \mu_O(T, P^0) at one particular pressure, P\textsubscript{0} (Reuter & Scheffler, 2001):

\[
\mu_O(T, P) = \mu_O(T, P^0) + \frac{1}{2}kT\ln\left(\frac{P}{P^0}\right)
\]  \hspace{1cm} (3.6)
Therefore, at experimental conditions (T=700 K, P=0.1 atm), we have,

\[ \mu_O(700K, 0.1 atm) = -0.73 + \frac{1}{2} kT \ln\left(\frac{0.1}{1}\right) = -0.7995eV \]  (3.7)

This corresponds to the coverage of around 0.2 ~ 0.25 ML. Thus, the system will exist as the p(2x2) phase under the experimental condition (T=700 K, P=0.1 atm). (2x2) is therefore chosen as the unit cell during most of the calculations in the course of this thesis.

### 3.4 Conclusions

The surface phase diagram of the O/Pt(111) system has been computed from first-principles for the first time. This was accomplished by performing grand canonical Monte Carlo simulations on a 2D lattice, and incorporating up to next-next-nearest neighbor interactions that were determined from density functional theory computations. Our results indicate that oxygen atoms adsorbed on Pt (111) form well-ordered p(2x2) (at 1/4 ML) and p(2x1) (at 1/2 ML) phases with continuous phase boundaries. The order-disorder phase transition temperatures of these two phases are 670 K and 480 K, respectively. Oxygen atoms are shown to cluster into p(2x2) islands at coverages lower than 1/4 ML at low temperatures, which is in agreement with the STM experiments of Stipe et al.. The stabilization of oxygen p(2x2) islands on Pt(111) is a consequence of the attractive third-nearest-neighbor interactions between the adsorbed oxygen atoms. Other two phase-coexistant regions are found to exist between coverages of 0.26 ML and 0.37 ML and between coverages of 0.43 ML and 0.5 ML. At temperatures lower than 250 K, a new stable phase at the coverage of 2/5 ML consisting of two p(2x1) rows offset by an empty site was found. This phase has a continuous phase transition boundary, and we designate it phase X.
We have developed a new electronic composition-property relationship between the adsorption energy of molecules binding unequally to multiple atoms on metal surfaces and the electronic properties of the surface. This relationship allows the estimation of the relative stability of adsorbates on various surfaces, assuming that the adsorbate adopts the same local configuration on each surface, and therefore also allows the estimation of the adsorption energy of molecules through large regions of parameter space in alloy systems with data from only a few explicit calculations. We have applied this relationship to the adsorption of SO₂ on Pt surfaces alloyed with Pd, Cu, Ru, and Ni. Using a new formula for weighting the metal d-band, we found a strong linear relationship between the weighted positions of the d states of surfaces and the most stable molecular adsorption energies. The consequences of our electronic
composition-property relationship for catalyst design are also discussed.

4.1 Motivation

It is well known that the catalytic properties of alloys are often superior to those of pure metals because of either the electronic effect or the ensemble effect or both. (Sachtler, 1973) The difficulty, however, with choosing an alloy with desired properties is that the range of parameter space becomes drastically larger when alloys are explored versus pure metals. If a generally applicable approach could be found such that the properties of reactions could be predicted on different surfaces, such as monometallic surfaces, alloy surfaces, and overlayers, our ability to design catalysts would be augmented tremendously. The d-band center and weightings thereof have been found to correlate well with the chemical activity of metal surfaces, (Hammer et al., 1996; Hammer & Nørskov, 1995; Mavrikakis et al., 1998; Hammer & Nørskov, 2000) but so far the weightings are suitable only for predicting the interactions of simple adsorbates in a limited way, e.g. with a single type of metal atom on monometallic or pseudomorphic overlayer surfaces, such as the adsorption of CO at the top site of Pt(111) or Cu/Pt(111) (Mavrikakis et al., 1998) or of interactions between adsorbates and surfaces on which the adsorbates form bonds equally with more than one type of metal surface atom, such as hydrogen chemisorption on the hollow site of Pd-Re alloyed overlayers and alloyed surfaces. (Pallassana et al., 2000)

In this Chapter, we present a model that can be used to predict the binding strength of chemisorbed molecules which bind unequally to multiple types of surface atoms. The adsorption of SO$_2$ on the Pt(111) surface, alloy surfaces, and overlayers, is used as an example of such adsorption processes and a means to verify our model. The chemistry of sulfur-containing species on transition metal catalysts has been of interest to scientists for decades, since it is critical in poisoning the catalysts under both oxidizing and reducing conditions. (Rodriguez & Hrbek, 1999; Haase, 1997; Lin & Trout, 2003) A fundamental understanding of properties of metals surfaces that govern their interactions with SO$_2$ could shed light on the design of sulfur resistant
transition metal catalysts. Moreover, a successful approach to modeling SO$_2$ should lead to the ability to model a variety of molecules with significant interest to catalysis and surface physics.

### 4.2 Details of calculations

With the GNU publicly licensed software DACAPO, first principles density functional theory (DFT) methods were used to study the adsorption of SO$_2$ on various alloyed surfaces and overlayers. The initial geometries of SO$_2$ on all the surfaces were chosen from the most stable adsorbed configuration (fcc $\eta^2$-S$_8$,O$_a$) on the clean Pt (111) surface, determined in one of our previous studies. (Lin et al., 2004a) In this geometry, SO$_2$ is at an fcc site with two atoms (S and O$^2$) down and one atom (O$^1$) sticking up, as illustrated in Fig. 4-1. In order to compare the relative stability of SO$_2$ on different surfaces, a (2x2) unit cell and a three-layer slab model were used throughout the study. The use of a three-layer thick and (2x2) Pt slab model to describe accurately the properties of atomic and molecular adsorbates has been tested as explained by publications from our group and from others. (Mavrikakis et al., 1998; Pallassana et al., 2000; Lin et al., 2004a; Lin et al., 2002; Alavi et al., 1998; Li & Gewirth, 2003; Tang et al., 2004; Kitchin et al., 2004) The positions of the atoms in SO$_2$ and those in all but the bottom Pt layer in the slab model were relaxed during the optimization. The bottom Pt layer was fixed at the calculated bulk lattice constant, 4.00 Å. A vacuum of $\sim$ 10 Å was used to separate the slabs. The gradient-corrected exchange-correlation functional PW91-GGA (Perdew et al., 1992) was used, in addition to ultrasoft pseudopotentials (Vanderbilt, 1990; Laasonen et al., 1993) and planewave expansions with an energy cutoff of 25 Ry (340 eV). All the surface Brillouin zones were sampled at 4x4x1 Monkhorst-Pack k-points. (Monkhorst & Pack, 1976) Taking into account explicitly electron spin was found to change the SO$_2$ adsorption energies by only 0.1 kJ/mol on alloy surfaces, well within the numerical accuracy of the pseudopotential methods. Therefore, all the calculations were nonmagnetic in this study.
Figure 4-1: Schematic of SO$_2$ adsorbed to alloyed Pt (111) surfaces in which the surface atom labeled b is replaced by another atom, Pd in this case. (a) top view; (b) side view with bond lengths of the Pd-Pt system.

The surface alloys and overlayers, designated as $nM^x$/Pt(111), were modeled by replacing $n$ Pt atoms in the top Pt layer with other metal atoms (M) such as Pd, Cu, Ru and Ni etc. $n=1$, 2 or 3 are surface alloys with different local concentrations of M, such that $n=4$ is an overlayer; $x$ represents the sites replaced, as marked in Fig. 4-1 and Fig. 4-2.

### 4.3 Results and discussions

#### 4.3.1 Development of new weighted d-band center model

For SO$_2$ adsorbed on $nM^x$/Pt(111) surfaces, the d-band position for Pt and M atoms on the surfaces varies with the types and concentrations of M atoms. The extent of overlap between the orbitals of SO$_2$ and the d-bands of the surface atoms therefore also varies. Since SO$_2$ binds unequally to multiple surface atoms (Fig. 4-1), different arrangements ($x$ in $nM^x$/Pt(111)) of M atoms on the Pt(111) surface will have different effects on the adsorption energy of SO$_2$. Considering all these factors, we constructed a simple expression for weighting the d-band center of various alloyed surfaces or overlayers as follows:

$$E_{d-weighted} = \frac{\sum_M V_M^2 E_d^M \left( \sum_i N_i^{M-i} S_i^{M-i} \right)}{\sum_M V_M^2 \left( \sum_i N_i^{M-i} S_i^{M-i} \right)} \tag{4.1}$$
where, $V_{M}^2$ is the d-band coupling matrix for the surface metal atom $M$, which has been tabulated as a database in Ruban et al.’s work ($V_{pt}^2=3.90$, $V_{pd}^2=2.78$, $V_{Cu}^2=1.0$, $V_{Re}^2=3.87$, $V_{Ni}^2=1.16$, all relative to Cu). (Ruban et al., 1997) $E_{d}^{M}$ is the d-band center of the surface metal atom $M$. It was calculated by taking the first moment of the normalized d-projected density of states (pDOS) about the Fermi level. $N_{M-i}^{M}$ is the number of bonds between the surface metal atom $M$ and the atom $i$ in the adsorbate molecule. [M and i are considered to be bonded in two possible ways: first, when the distance between M and i is shorter than 3 Å (such as in Fig. 4-1, $N^{a-d-S}=1$, $N^{c-O}=1$); second, when the distance between M and i is long, but i has more than one geometrically equivalent atoms M (such as in Fig. 4-1, $N^{b-O}=3$).] $S_{M-i}^{M}$ represents the bond strength between the surface metal atom $M$ and the atom $i$ in the adsorbate. Inclusion of $S_{M-i}^{M}$ is an important, distinguishing element of our model. (Pallassana et al., 2000) It accounts for the differences in the interaction of different atoms in the adsorbate and different metal atoms ($x$). We chose the form of $S_{M-i}^{M}$ to be electrostatic:

$$S_{M-i}^{M} = \frac{C_{M}C_{i}}{d_{M-i}}$$

where, $C_{M}$ and $C_{i}$ are the Pauling electronegativities of the metal atom (M) and the atom (i) in the adsorbate, (Allred, 1961) and $d_{M-i}$ is the distance between these two atoms (Fig. 4-1(b)). The sum in Eq. (4.1) runs over all geometrically equivalent atoms M in the adsorbate-covered surface cell. It is found in our calculations that the change of geometry parameters $d_{M-i}$ in going from adsorption on the pure metal to adsorption on alloys is about an order of magnitude more among different series than within each series. This is due to the effects of anti-segregation. Therefore, even though we fully relaxed each system aside from the bottom layer, we used the same set of geometry parameters ($d_{M-i}$) for each $nM^{x}/Pt(111)$ series (same M). The error for $E_{d-weighted}$ caused by this approximation is less than 0.001eV, which is considered to be negligible.
4.3.2 Application of new model to SO$_2$ chemisorption on Pt(111) surfaces, alloys, and overlayers

In Fig. 4-2 are plotted the energies of adsorption of SO$_2$ on different configurations and types of surface alloys as a function of our weighted d-band center. The letters next to each point designate the surface atom or atoms that have been substituted. In Fig. 4-2(a) and 2 (b), Pd-Pt and Cu-Pt alloys, one can discern three different linear relationships. The dot-dashed lines represent the effect of different configurations of the same concentration and type of surface alloy. The dotted lines and the solid lines represent the effect of changing the concentration of alloyed species and show that this effect is linearly additive. Note that the properties of Pd-Pt and Cu-Pt are quantitatively different. These results are somewhat remarkable in that they show that given four carefully chosen points, all of the other points can be estimated to a high degree of accuracy. In particular, the configuration with the highest energy of adsorption and that with the lowest energy of adsorption can be determined.

The plot for the Ru-Pt system in Fig. 4-2 (c), looks different from the other two. Substitution of Pt for Ru on the surface does not lead to additive changes in the energy of adsorption as it does for the Pd-Pt and Cu-Pt systems. All the points fall more or less around the linear solid line in Fig. 4-2 (c). The trend is that the more substitution of Pt surface atoms by Ru, the higher is the energy of adsorption. Note that substituting Pt for Ru at site b has almost no effect except when b is the last site to be substituted. In the correlations shown here, the term for b in Eq. (4.1) is removed.

In order to show the importance of the $S^{M-i}$ term in Eq. (4.1), the weighted d-band center of various surfaces calculated by our model are compared to those calculated by Pallassana et al.'s model (Pallassana et al., 2000) in Table 4.1. In each series, the binding energy differences between x=a/d and c, ab and bc, ac and ad, abd and abc could not be captured by Pallassana et al.'s model. This deficiency is clearly illustrated in Fig. 4-2(a') by taking Pd/Pt(111) series as an example. Shown in Fig. 4-2(a'), lines a/d-c, ad-ac-b, acd-ab-bc, and abd-abc/bcd are all perpendicular to the x
Figure 4-2: Adsorption energies of SO$_2$ on different alloyed Pt (111) surfaces and overlayers vs. weighted d-band center of the surfaces: (a) Pd-Pt series; (b) Cu-Pt series; and (c) Ru-Pt series. (a') Pd-Pt series (by Pallassana et al.’s model (Pallassana et al., 2000)).
Table 4.1: Binding energies (BE) of SO₂ on nM⁺/Pt(111) and comparison of weighted d-band center of the surfaces calculated by our model and Pallassana et al.’s model (Pallassana et al., 2000)

<table>
<thead>
<tr>
<th>M</th>
<th>Pd</th>
<th>Cu</th>
<th>Ru</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>BEᵃ</td>
<td>E_dᵇ</td>
<td>E_dᶜ</td>
</tr>
<tr>
<td>a/d</td>
<td>110.87 -2.45 -2.45</td>
<td>85.83 -2.43 -2.43</td>
<td>141.84 -2.46 -2.46</td>
</tr>
<tr>
<td>b</td>
<td>131.07 -2.39 -2.36</td>
<td>142.25 -2.36 -2.36</td>
<td>115.42 -2.60 -2.60</td>
</tr>
<tr>
<td>c</td>
<td>124.22 -2.44 -2.45</td>
<td>143.12 -2.41 -2.43</td>
<td>156.33 -2.41 -2.46</td>
</tr>
<tr>
<td>ac</td>
<td>119.63 -2.34 -2.36</td>
<td>108.90 -2.28 -2.30</td>
<td>176.03 -2.29 -2.35</td>
</tr>
<tr>
<td>bc</td>
<td>139.31 -2.27 -2.26</td>
<td>166.64 -2.24 -2.22</td>
<td>173.96 -2.29 -2.34</td>
</tr>
<tr>
<td>ad</td>
<td>105.82 -2.36 -2.36</td>
<td>50.16 -2.29 -2.29</td>
<td>158.29 -2.34 -2.34</td>
</tr>
<tr>
<td>acd</td>
<td>114.60 -2.24 -2.26</td>
<td>75.25 -2.16 -2.16</td>
<td>188.51 -2.17 -2.23</td>
</tr>
<tr>
<td>abd</td>
<td>120.81 -2.19 -2.16</td>
<td>72.24 -2.14 -2.11</td>
<td>163.76 -2.15 -2.09</td>
</tr>
<tr>
<td>abc</td>
<td>134.70 -2.16 -2.16</td>
<td>133.04 -2.12 -2.11</td>
<td>202.22 -2.05 -2.08</td>
</tr>
</tbody>
</table>

ᵃPositive value is used here (Unit: kJ/mol)
ᵇCalculated by our model in this manuscript (Unit: eV)
ᶜCalculated by Pallassana et al.’s model (Pallassana et al., 2000) (Unit: eV)

axis, which means that Pallassana model can not distinguish differences within those series. Its application would lead to a qualitatively wrong prediction. The behavior of Pallassana et al.’s model will become even worse in other adsorption systems such as, NO and NO₂ on alloyed Pt(111) surface, which is currently being studied in our group. This is because different surface metal atoms interact with different atoms in the adsorbates. Therefore, incorporating the effects of the type of bond formed between the adsorbate and substrate is necessary for accurately predicting the strength of adsorption.

The difference between the Ru-Pt alloys and the other two can be explained by the difference in the local d-projected density of states (pDOS) of the surface atoms. Fig. 4-3 (a) - (c) illustrate the pDOS of d-orbitals for the surface metal atoms in which the fraction of the alloyed atom is 1/2. The pDOS for the Pt atom in the pure Pt system is also plotted in each figure for comparison. The basic features of the DOS for the surface Pt atoms in each system are similar, but the shapes of the DOS for alloyed atoms (M) in each system are very different. (Refer to the dashed lines in Fig. 4-3.) Even so, the d-band center of Pd in Pd-Pt and that of Cu in Cu-Pt are at almost the same position, ~ -2.1 eV, which is much lower than that of Ru in Ru-Pt, ~ -1.8 eV. It
Figure 4-3: Local d-projected density of state (pDOS) of different atoms of various alloyed surfaces: (a) Pd alloyed Pt(111) surface; (b) Cu alloyed Pt(111) surface; and (c) Ru alloyed Pt(111) surface. (Energy values in the legend are the d-band centers for each metal surface atom described by that legend.)
can be seen in Fig. 4-3 that the DOS of Pt atoms in Pd-Pt does not differ very much from that in the pure Pt system. However, compared to the pure Pt system, the DOS of Pt atoms in Cu-Pt shifts slightly toward the Fermi level, while that in Ru-Pt shifts in the opposite direction. In addition, the difference in the weighted d-band centers between Pd or Cu and Pt is much smaller than that between Ru and Pt in Ru-Pt. In Eq. (4.1), changes in the $E_d^M$ terms have more effect on $E_{d-weighted}$ in nRu/Pt(111) systems than in nPd/Pt(111) and nCu/Pt(111) systems in which changes in the $S^{M-i}$ terms can have more of an effect. Thus, the effect of alloying each site of the Pt(111) surface on the adsorption energy of SO$_2$ is more significant with Ru than with Pd or Cu. The higher the surface concentration of Ru, the more significant the difference will be. Other possible reasons to account for the difference between the Ru-Pt alloys and Pd-Pt or Cu-Pt alloys are: (1) the Pt-Ru bond was shown to be stronger than the Pt-Pt bond by about 1.5eV; (Koper et al., 2002) therefore the ability for adsorbing the adsorbates after replacing that site with Ru atom will be affected according to the bond energy conservation concept; (2) crystal structures of Pd, Cu and Pt are all face centered cubics (fcc) while the crystal structure of Ru is hexagonal close-packed (hcp).

The adsorption energies of the most stable configurations of SO$_2$ on each system studied (pure Pt(111), 1Pd/Pt(111), 1Pd$^c$/Pt(111), 2Pd$^{bc}$/Pt(111), 1Cu$^{b/c}$/Pt(111), 2Cu$^{bc}$/Pt(111), and all nRu$^x$/Pt(111)) are plotted in Fig. 4-4 as a function of the weighted d-band centers. Here we define the most stable configurations as those for which the energy of adsorption decreases as sites are substituted one at a time. Fig. 4-4 shows that there is a strong correlation between the adsorption energy of the most stable configuration of SO$_2$ and the weighted d-band centers for the surfaces calculated here. Several points (1Ni$^b$/Pt(111), 1Ni$^c$/Pt(111), 2Ni$^{bc}$/Pt(111), and 3Ni$^{abc}$/Pt(111)) for the nNi$^x$/Pt(111) system are included in Fig. 4-4 to test the generality of the linear relationship. The $R^2$ of the least square fitted line in Fig. 4-4 is 0.86, which is as well as the performance of simpler d-band weightings for simpler adsorbates. (Hammer et al., 1996; Pallassana et al., 2000) Among the most stable configurations, the farther the weighted d-band center is shifted toward the Fermi energy, the stronger
Figure 4-4: Linear relationship between stable SO₂ adsorption on various alloyed Pt(111) surfaces and overlayers vs. weighted d-band center of the surfaces.

is the interaction of SO₂ with the surfaces. This is in agreement with observations in the literature for simpler adsorbates, using simpler d-band weightings. (Mavrikakis et al., 1998; Pallassana et al., 2000) Applying our model to other systems such as, NO and NO₂, shows that our model can be generally applicable.

4.4 Conclusions

We conclude that our approach can model the relative stability of adsorbates on various surfaces, assuming that the adsorbate adopts the same local configuration on each surface. The types, local concentrations, and the arrangements of the surface atoms can vary. We found that using a new weighting that we have developed, the most stable molecular adsorption strength depends linearly on the weighted position of the d states of the surface relative to the Fermi level. The closer the weighted d-band center to Fermi level, the stronger the adsorption is. Our approach should be useful in general to decide which type and local concentration of surface atoms to choose for designed alloy catalysts.
Chapter 5

NO Chemisorption on Pt(111), Rh/Pt(111), and Pd/Pt(111)

The chemisorption of NO on clean Pt(111), Rh/Pt(111) alloy and Pd/Pt(111) alloy surfaces has been studied by first principles density functional theory (DFT) computations. It was found that the surface compositions of the surface alloys have very different effects on the adsorption of NO on Rh/Pt(111) versus that on Pd/Pt(111). This is due to the different bond strength between the two metals in each alloy system. A complex d-band center weighting model developed by authors in a previous study for SO₂ adsorption is demonstrated to be necessary for quantifying NO adsorption on Pd/Pt(111). A strong linear relationship between the weighted positions of the d states of the surfaces and the molecular NO adsorption energies shows: the closer the weighted d-band center is shifted to the Fermi energy level, the stronger the adsorption of NO will be. The consequences of this study for the optimized design of the three-way automotive catalysts (TWC) are also discussed.

5.1 Motivation

Alloys have attracted considerable interests in the field of heterogeneous catalysis because their catalytic properties are often superior to those of pure metals. Enhanced properties are due to either the electronic effect or the ensemble effect or
both. (Sachtler, 1973) In order to narrow down the parameter space for choosing an alloy with desirable properties in catalyst design, it is desirable to have composition-property relationships, so that the properties of reactions could be predicted on different surfaces, such as monometallic surfaces, alloy surfaces, and overlayers. An approach to this in the literature is based on the d-band center and weightings of it, which have been found to correlate well with the chemical activity of different metal surfaces. (Hammer et al., 1996; Hammer & Nørskov, 1995; Mavrikakis et al., 1998; Hammer & Nørskov, 2000; Pallassana et al., 2000; Tang & Trout, 2005a) The interactions of simple adsorbates with a single type of metal atom on monometallic or pseudomorphic overlayer surfaces, such as the adsorption of CO at the top site of Pt(111) or Cu/Pt(111), can be correlated directly to the d-band center of that metal atom. (Mavrikakis et al., 1998) A simple weighting is usually necessary to treat properly the interactions between adsorbates and surfaces on which the adsorbates form bonds equally with more than one type of metal surface atom, such as hydrogen chemisorption on the hollow site of Pd-Re alloyed overlayers and alloyed surfaces. (Pallassana et al., 2000) It is likely that a more complicated d-band center weighting would need to be used for the binding of chemisorbed molecules which bind unequally to multiple types of surface atoms, such as the adsorption of SO$_2$ on the Pt(111) surface, alloy surfaces, and overlayers. (Tang & Trout, 2005a)

The adsorption of NO on metal surfaces has been widely studied due to its importance in various heterogeneous catalytic processes. (Brown & King, 2000; Shelef & Graham, 1994; Taylor, 1993; Schmatloch & Kruse, 1992) One of the important examples is the reduction of toxic NO$_2$ gas in automobile exhaust. This reaction, along with the oxidation of CO and hydrocarbons (HC), proceeds simultaneously on the so-called three-way catalyst (TWC), which usually consists of platinum, palladium, and rhodium. The performance of the catalyst can be adjusted by changing its composition. However, hitherto no detailed and systematic studies have been carried out for the adsorption of NO on Rh or Pd alloyed Pt(111) surfaces.

Similarly, the dissociation of NO on metal surfaces has also been the subject of many experimental (Zhu et al., 2003; Delouise & Winograd, 1985; Borg et al.
and theoretical (Loffreda et al., 2003; Hammer, 2001; Loffreda et al., 1998) investigations due to its importance to environmental catalysis. It plays a key role in the catalytic transformation of NO into harmless molecules. By using high-resolution X-ray photoelectron spectroscopy (XPS) and temperature-programmed XPS, Zhu et al. found that no dissociation of NO takes place on Pt(111). (Zhu et al., 2003) NO dissociation is also found to be unfavorable on the Pd surfaces, especially the Pd(111) surface. (Loffreda et al., 2003; Hammer, 2001; Loffreda et al., 1998) The calculated dissociation barriers are found to be much smaller at Pd steps and edges compared to the values on Pd(111). (Loffreda et al., 2003; Hammer, 2001). The order of the effective dissociation activation energies on Pd surfaces is: step(511) [1.54 eV] < (100) [1.63 eV] < terrace (511) [1.77 eV] < (111) [2.44 eV]. (Loffreda et al., 2003) The dissociation therefore takes place at the step of Pd surfaces. Rh surfaces are far superior over Pd surfaces in terms of NO dissociation. (Loffreda et al., 1998) However, the dissociation of NO on Rh is strongly dependent on the structure of surfaces. Both experimental (Delouise & Winograd, 1985; Borg et al., 1994; Villarrubia & Ho, 1987) and theoretical (Loffreda et al., 2003; Hammer, 2001; Loffreda et al., 1998) studies found that the NO dissociation reaction is much faster on the open Rh(100) surface and the stepped Rh(331)/(511) surface than on the dense Rh(111) surface. Because of the low dissociation activity of NO on Pt(111), Pd(111) and Rh(111), NO dissociation is not considered to be important on Rh/Pd alloyed Pt(111) surfaces and therefore, not studied here.

In this chapter, we study the adsorption of NO on clean Pt(111) surfaces, Rh/Pd alloyed Pt(111) surfaces, and Rh/Pd overlayers with Pt(111) as the substrate. D-band center models are used to analyze the relationship between the adsorption strength of NO on surfaces and the surface compositions. Qualitatively different behaviors are found in the different systems. We explain this difference via the difference in the bonding strength between Pt atoms and the metal atoms added to form the alloy. A fundamental study of the properties of metals surfaces that govern their interactions with NO could lead a better understanding of the the reaction mechanisms and specific reaction pathways.
5.2 Details of calculations

First principles density functional theory (DFT) methods were used to study the adsorption of NO on various surfaces. (The GNU publicly licensed software DACAPO was used. (http://www.fysik.dtu.dk/CAMP/dacapo.html, n.d.)) We first studied the adsorption of NO at different sites on clean Pt(111) surfaces including: fcc, hcp, top, and bridge. The top view and side view of each adsorption configuration are plotted in Fig. 5-1. The bridge-site adsorption is not plotted since the geometry optimization ended up as the fcc adsorption. A (2x2) unit cell and a three-layer slab model were used throughout the study. The applicability of this slab model to describe accurately the properties of atomic and molecular adsorbates has been tested thoroughly by publications from our group and from others. (Mavrikakis et al., 1998; Pallassana et al., 2000; Tang & Trout, 2005a; Aizawa et al., 2002; Lin et al., 2004a; Lin et al., 2002; Alavi et al., 1998; Burch et al., 2002; Li & Gewirth, 2003; Tang et al., 2004; Kitchin et al., 2004) The adsorption geometry of NO and the positions of the atoms in all but the bottom Pt layer in the slab model were relaxed during the optimization, the bottom Pt layer being fixed at the calculated bulk lattice constant, 4.00 Å. A vacuum of ~ 10 Å was used to separate the slabs. Between these slabs, a point dipole was included in the Z direction (the direction perpendicular to the slabs) in order to eliminate the interactions among periodic images. The ionic cores are described by ultrasoft pseudopotentials, (Vanderbilt, 1990; Laasonen et al., 1993) allowing the plane wave basis set to have an kinetic energy cut off of 25 Ry (340 eV). The gradient-corrected exchange-correlation functional PW91-GGA (Perdew et al., 1992) was applied self-consistently. All the surface Brillouin zones were sampled at 4x4x1 Monkhorst-Pack k-point mesh. (Monkhorst & Pack, 1976) Although a gas phase NO molecule is spin polarized, previous studies of NO on transition metal surfaces indicate that chemisorbed NO is not spin polarized due to a strong interaction between the adsorbate and the substrate. (Tsai & Hass, 1995; Hass et al., 1996; Hammer & Nørskov, 1997a; Hammer, 1999) Therefore, all the calculations were nonmagnetic in this study.
Figure 5-1: Schematic of NO adsorbed at various sites on clean Pt (111) surfaces: (a) top view of NO at fcc sites; (a’) side view of NO at fcc sites; (b) top view of NO at hcp sites; (a’) side view of NO at hcp sites; (c) top view of NO at top sites; (a’) side view of NO at top sites.
To be consistent with our previous chapter, the surface alloys and overlayers are designated as \( nM^x/Pt(111) \), modeled by replacing \( n \) Pt atoms in the top Pt layer with other metal atoms (M) such as Rh, and Pd. \( n=1, 2 \) or \( 3 \) are surface alloys with different local concentrations of M, such that \( n=4 \) is an overlayer; \( x \) represents the sites replaced, as marked in Fig. 5-1(a). The initial geometries of NO on all the alloy surfaces and overlayers were taken from the most stable adsorbed configuration of NO on the clean Pt(111) surfaces, as illustrated in Fig. 5-1(a) and (a’).

5.3 Results and discussions

5.3.1 Adsorption of NO on Clean Pt(111)Surfaces

Table 5.1 lists the adsorption energies and the main geometric parameters for NO adsorption at various sites on clean Pt(111) surfaces. The bridge site was found to be an unstable site. It does not correspond to an energy local minimum, and NO goes to the fcc site during the geometry optimization. This phenomenon was also observed by Aizawa et al. (Aizawa et al., 2002) As shown in Table 5.1, the chemisorption of NO on Pt(111) follows the stability order of fcc > hcp > top. The most stable adsorption site of NO on Pt(111) is the fcc hollow site, while the top site has a much lower adsorption energy as compared to those of the threefold hollow sites. This is in agreement with previous theoretical studies. (Aizawa et al., 2002; Burch et al., 2002) Near-edge X-ray absorption fine structure spectroscopy (NEXAFS), (Esch et al., 1996) dynamic low-energy electron diffraction (LEED), (Materer et al., 1994; Matsumoto et al., 2002) and high-resolution X-ray photoelectron spectroscopy (XPS) (Zhu et al., 2003) all found that NO is adsorbed in a threefold fcc site with a \( p(2 \times 2) \) structure at low coverages (\( \theta \leq 0.25 \) ML).

Geometry optimizations for NO at the fcc and hcp sites resulted in the molecule being perpendicular to the surface with the N-end down (refer to Fig. 5-1(a), (a’), (b), (b’)). On the other hand, adsorption of NO at the top site resulted in a tilted geometry (refer to Fig. 5-1(c) and (c’)), with N-O not perpendicular to the surface but
Table 5.1: Adsorption energies (AE) and geometric parameters for NO chemisorption at various sites on clean Pt(111) surfaces.

<table>
<thead>
<tr>
<th>Site</th>
<th>( \text{AE (eV)}^a )</th>
<th>( \text{AE (eV)}^b )</th>
<th>( d_{N-O} (\text{Å})^a )</th>
<th>( d_{N-O} (\text{Å})^c )</th>
<th>( d_{N-Pt} (\text{Å})^a )</th>
<th>( d_{N-Pt} (\text{Å})^c )</th>
</tr>
</thead>
<tbody>
<tr>
<td>fcc</td>
<td>2.10</td>
<td>2.09/2.05</td>
<td>1.219</td>
<td>1.224</td>
<td>2.107</td>
<td>2.094</td>
</tr>
<tr>
<td>hcp</td>
<td>1.97</td>
<td>1.92</td>
<td>1.214</td>
<td>1.221</td>
<td>2.113</td>
<td>2.089</td>
</tr>
<tr>
<td>top</td>
<td>1.69</td>
<td>1.61</td>
<td>1.193</td>
<td>1.199</td>
<td>1.967</td>
<td>1.956</td>
</tr>
</tbody>
</table>

\( ^a \)This work \\
\( ^b \)Reference (Aizawa et al., 2002) \\
\( ^c \)Reference (Burch et al., 2002)

with an angle of 54.7°, predicted to be 54.4° in Burch et al.’s calculations. (Burch et al., 2002) This bent structure has also been reported for NO chemisorption on Pd(111). (Hansen et al., 2002) This upright adsorption geometry at a threefold hollow site and tilted orientation at a on-top site has also been found in NEXAFS (Esch et al., 1996) and LEED studies (Matsumoto et al., 2002). The last four columns in Table 5.1 indicate that the geometry parameters that we obtained are in accordance with previous calculations. (Burch et al., 2002) At an fcc site, the chemisorbed NO bond distance is about 1.22 Å and the N-Pt bond distance is about 2.11 Å in our calculations, in agreement with both NEXAFS \( (d_{N-O} = 1.24 \pm 0.05 \text{Å}) \) (Esch et al., 1996) and LEED measurements \( (d_{N-O} = 1.18 \pm 0.04 \text{Å} \) and \( d_{N-Pt} = 2.07 \text{Å}) \) (Materer et al., 1994).

Since the most stable adsorption site of NO on clean Pt(111) is the fcc site, the initial geometries of NO on all the alloy surfaces and overlayers were chosen to be at the fcc sites formed by a, b, and d surface atoms, as shown in Fig. 5-1(a). Our assumption that the fcc site is the most preferred NO adsorption site on alloys has been tested and confirmed.

5.3.2 NO Chemisorption at fcc Site on Alloy Surfaces and Overlayers

NO Chemisorption at the fcc Site on Rh/Pt(111)

The adsorption energy of NO on various Rh alloyed Pt(111) surfaces are summarized in part (a) of Table 5.2. Noticing that among the single substitution series
Table 5.2: Adsorption energies (AE) of NO chemisorption on: (a) Rh/Pt(111) surfaces and (b) Pd/Pt(111) surfaces.

<table>
<thead>
<tr>
<th>System</th>
<th>Rh/Pt(111) AE (kJ/mol)</th>
<th>Pd/Pt(111) AE (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>clean Pt(111)</td>
<td>-202.6</td>
<td>-202.6</td>
</tr>
<tr>
<td>1Rh\textsuperscript{\textalpha}/Pt(111)</td>
<td>-240.2</td>
<td>-211.5</td>
</tr>
<tr>
<td>1Rh\textsuperscript{\textbeta}/Pt(111)</td>
<td>-240.7</td>
<td>-211.9</td>
</tr>
<tr>
<td>1Rh\textsuperscript{\textgamma}/Pt(111)</td>
<td>-201.9</td>
<td>-215.9</td>
</tr>
<tr>
<td>1Rh\textsuperscript{\textdelta}/Pt(111)</td>
<td>-240.2</td>
<td>-211.3</td>
</tr>
<tr>
<td>2Rh\textsuperscript{\textalpha}/Pt(111)</td>
<td>-273.8</td>
<td>-216.1</td>
</tr>
<tr>
<td>2Rh\textsuperscript{\textbeta}/Pt(111)</td>
<td>-239.8</td>
<td>-224.8</td>
</tr>
<tr>
<td>2Rh\textsuperscript{\textgamma}/Pt(111)</td>
<td>-240.8</td>
<td>-225.5</td>
</tr>
<tr>
<td>2Rh\textsuperscript{\textdelta}/Pt(111)</td>
<td>-273.2</td>
<td>-216.6</td>
</tr>
<tr>
<td>2Rh\textsuperscript{\textalpha\beta}/Pt(111)</td>
<td>-274.0</td>
<td>-216.1</td>
</tr>
<tr>
<td>2Rh\textsuperscript{\textalpha\gamma}/Pt(111)</td>
<td>-239.8</td>
<td>-224.8</td>
</tr>
<tr>
<td>2Rh\textsuperscript{\textalpha\delta}/Pt(111)</td>
<td>-275.1</td>
<td>-230.3</td>
</tr>
<tr>
<td>2Rh\textsuperscript{\textbeta\gamma}/Pt(111)</td>
<td>-300.5</td>
<td>-218.4</td>
</tr>
<tr>
<td>2Rh\textsuperscript{\textbeta\delta}/Pt(111)</td>
<td>-275.1</td>
<td>-230.2</td>
</tr>
<tr>
<td>2Rh\textsuperscript{\textalpha\beta\gamma}/Pt(111)</td>
<td>-301.4</td>
<td>-232.9</td>
</tr>
</tbody>
</table>

(1Rh\textsuperscript{x}/Pt(111), x=a, b, c, or d), the substitution of site c does not affect the adsorption energy of NO. On the other hand, the substitution of the other sites (a, b, or d) which form the fcc site increases the binding strength of NO by about 38 kJ/mol. Similarly, double substitution in which site c is one of those substituted has the similar binding strength as the single substitution without replacing site c, which is about -240 kJ/mol. Triple substitution with site c replaced has a similar adsorption energy to that of the double substitution without a substitution of the c site, which is about -274 kJ/mol. Also, NO adsorbed to the overlayer of Rh on a Pt(111) substrate has an adsorption strength similar to that on the triple substituted 3Rh\textsuperscript{\textalpha\beta\gamma}/Pt(111) substrate.

Therefore, the effect of substituting site c is negligible in nRh\textsuperscript{x}/Pt(111) systems. This is easy to understand from intuition. For the Rh/Pt(111) alloy surfaces, the geometry optimizations show that, when adsorbed upright to the fcc site on the surface, molecular NO bonds almost equally close to the three surface metal atoms (a, b, and d) which form the fcc site, and it is further from site c than to sites a, b, and d as illustrated in Fig. 5-1(a) and (a').
This is similar to the case of adsorption of atomic hydrogen at the hollow site on Pd-Re alloy surfaces. (Pallassana et al., 2000) Therefore, the relatively simple weighted d-band center model proposed by Pallassana et al. (Pallassana et al., 2000) is expected to be applicable in this system. Fig. 5-2 shows the adsorption energy of NO on Rh/Pt(111) surface as a function of the weighted d-band center energy calculated by Pallassana et al.’s weighted d-band center model (Pallassana et al., 2000) as expressed in Eq. (5.1):

\[
E_{d-weighted}^{Pallassana} = \frac{\sum_M V_M^2 E_d^M N^M}{\sum_M V_M^2 N^M}
\]  

(5.1)

where \( V_M^2 \) is the d-band coupling matrix for the surface metal atom M, which has been tabulated as a database by Ruban et al. (Ruban et al., 1997) \( E_d^M \) is the d-band center of the surface metal atom M calculated by taking the first moment of the normalized d-projected density of states (pDOS) about the Fermi level. \( N^M \) is the number of bonds between the surface metal atom M and molecule NO. Fig. 5-2 shows that the adsorption energy of NO on Rh alloyed Pt surfaces has a very strong linear correlation with the weighted d-band center model of Pallassana et al.’s, the \( R^2 \), being 0.98. The closer the weighted d-band center shifts to the Fermi energy level, the stronger the adsorption of NO will be.

**NO Chemisorption at the fcc Site on Pd/Pt(111)**

Pt, Rh, together with Pd are the major active components of the three-way automotive catalyst (TWC). Having studied the NO chemisorption on Rh/Pt(111) in the last subsection, we look at the NO chemisorption on Pd/Pt(111) in this subsection. Part (b) of Table 5.2 lists the adsorption energies of NO on various Pd alloyed Pt(111) surfaces. All the adsorption energies of NO on Pd alloyed Pt(111) surfaces are between 210 KJ/mol and 230 KJ/mol. Although the experimental data does not exist for these alloy systems so far, experimental value for NO adsorption on pure Pd(111) surface has been obtained as 221.65 KJ/mol (about 2.3 eV) with temperature programmed desorption (TPD), high resolution electron energy loss spectroscopy (HREELS), and
Figure 5-2: Adsorption energies of NO on Rh alloyed Pt (111) surfaces and overlayers vs. weighted d-band center of the surfaces calculated by Pallassana et al.'s model (Pallassana et al., 2000).

electron stimulated desorption ion angular distribution (ESDIAD) techniques. (Ramsier et al., 1994) Here, a very different phenomenon from NO chemisorption on Rh/Pt(111) is found in the adsorption of NO on Pd/Pt(111). Among the single substitution series (1Pd^x/Pt(111), x=a, b, c, or d), substitution of site c results in a stronger effect on the adsorption energy of NO than substitutions of each of the other sites, a, b, or d. Also, double substitutions which include site c result in a larger binding strength of NO than those which do not include the substitution of site c. Similarly, among the triple substitution series (3Pd^2/Pt(111)), that 3Pd^abc/Pt(111) has the lowest adsorption energy of NO, because all the other triple substitutions include the substitution of site c. In contrast to nRh^x/Pt(111) systems, the effect of substitution of site c is found to be stronger than that of the other sites (a, b, or d) in nPd^x/Pt(111) systems. This is in contradiction to our intuition. The reason for the difference between Rh/Pt and Pd/Pt will be explained in detail in the next subsection.

Since site c has a strong effect on the adsorption of NO on Pd/Pt(111) surfaces, NO must bind unequally to multiple surface atoms. (Site c is unequal to sites a, b,
and d.) Considering this, a more complicated way for weighting the d-band center of various alloyed surfaces or overlayers proposed by us in the previous study of SO\textsubscript{2} in Chapter 4 should be used for NO chemisorption on Pd/Pt(111). This more complex weighting model is expressed in Eq. (5.2) and Eq. (5.3):

\[ E_{d\text{-weighted}}^{Tang} = \sum_{M} \frac{V_{M}^{2}E_{d}^{M}}{\sum_{M} V_{M}^{2}} \frac{\left(\sum_{i} N_{M-i}^{M-i}S_{M-i}^{SM-i}\right)}{\left(\sum_{i} N_{M-i}^{M-i}\right)} \] (5.2)

where, \( V_{M}^{2} \) and \( E_{d}^{M} \) are the same as those in Eq. (5.1). Similar to \( N_{M}^{i} \) in Eq. (5.1), \( N_{M-i}^{M-i} \) is the number of bonds between the surface metal atom M and the atom i in the adsorbate molecule. Different from Eq. (5.1), \( S_{M-i}^{SM-i} \) is introduced in Eq. (5.2). It represents the bond strength between the surface metal atom M and the atom i in the adsorbate. Inclusion of \( S_{M-i}^{SM-i} \) is important, as will be seen in the comparison in Fig. 5-3. It is added to account for the inequality in the interaction of atoms in the adsorbate and the metal surface atoms (x). The form of \( S_{M-i}^{SM-i} \) is chosen to be electrostatic: (Tang & Trout, 2005a)

\[ S_{M-i}^{SM-i} = \frac{C_{M}C_{i}}{d_{M-i}} \] (5.3)

where, \( C_{M} \) and \( C_{i} \) are the Pauling electronegativities of the metal atom (M) and the atom (i) in the adsorbate, (Allred, 1961) and \( d_{M-i} \) is the distance between these two atoms. More computational details about using this d-band center weighting model can be found in the last Chapter. In the case of NO adsorption on Rh/Pt(111) alloy surfaces, because the effect of substituting site c is negligible and NO bonds almost equally to the three surface metal atoms (a, b, and d in Fig. 5-1(a)) which make up the fcc site, \( S_{M-i}^{SM-i} \) terms in the denominator of Eq. (5.2) and those in the numerator of Eq. (5.2) will cancel out. The complex d-band center weighting model in Eq. (5.2) is therefore reduced to the same model as expressed in Eq. (5.1).

In Fig. 5-3, the behavior of applying the weighted d-band center model from Pallassana \textit{et al.} (Pallassana \textit{et al.}, 2000) to NO adsorption on Pd/Pt(111) (refer to Fig. 5-3(a)) is plotted and compared to that of applying our more complex weighted d-band center model (Tang & Trout, 2005a) to the same system (refer to Fig. 5-3(b)).
Figure 5-3: Adsorption energies of NO on Pd alloyed Pt (111) surfaces and overlayers vs. weighted d-band center of the surfaces: (a) By Pallassana et al.’s model (Pallassana et al., 2000); (b) By our model (Tang & Trout, 2005a).
As shown in Fig. 5-3(a), the linearity of the correlation between the adsorption energy of NO on Pd/Pt(111) and the simple weighted d-band center (Pallassana et al., 2000) is very poor ($R^2=0.61$). The general trend of the NO adsorption strength vs. simple weighted d-band center (Pallassana et al., 2000) still corresponds to that in Fig. 5-2: the closer the d-band center is shifted to the Fermi energy level, the stronger is the adsorption of NO. However, in each series, such as single substitution series, the adsorption energy of NO vs. the simple weighted d-band center has an opposite trend to the general one. The poor linearity in Fig. 5-3(a) can be dramatically improved upon by applying our more complex weighted d-band center model as shown in Fig. 5-3(b). $R^2$ can be enhanced to 0.93. In addition, the trend of NO adsorption strength vs. weighted d-band center (by Eq. (5.2)) in each series now also follows the general trend.

**Explanation for the Different Behavior between Rh/Pt(111) and Pd/Pt(111)**

The different behavior of NO chemisorption on Rh/Pt(111) versus that on Pd/Pt(111) can be explained by the Bond Order Conservation (BOC) concept: In a many-body system, the total bond order of all interacting two-center bonds is conserved. The 'body' means an atom or group of atoms that may be treated as a single entity. (Shustorovich & Sellers, 1998) By applying the BOC concept to the systems of NO adsorption on surfaces as illustrated in Fig. 5-1(a), the summation of bond order for sites a, b, and d with site c (a,b,d-c) and that for sites a, b, d and NO (a,b,d-NO) is conserved. Here we treat the group of atoms (a, b, and d in Fig. 5-1(a)) as a single entity. The gas phase pair-wise bond strength and bond length between different alloyed species and platinum atoms, which are calculated by the Gaussian 03 programs with DFT/B3-LYP method, are summarized in Table 5.3. As listed in Table 5.3, for Rh/Pt systems, the bond strength of Pt-Rh (-68.4 kcal/mol) is not very different from that of Pt-Pt (-64.6 kcal/mol), which means that the bond order of a,b,d-c is similar to that of clean Pt(111) surfaces. Therefore, according to the BOC concept, the bond order of a,b,d-NO is expected not to change very much from that on clean Pt(111) surfaces. This is in agreement with our calculations. The adsorption
energy of NO at the fcc site on 1Rh/\text{Pt}(111) is -201.9 kJ/mol, which is only about 0.7 kJ/mol higher than that on the clean Pt(111) surfaces. (Refer to the last column in Table 5.3.) NO adsorption energy on the other single-site (site a, b, or d) substituted surface is dramatically different from that on clean Pt(111) surfaces. This is due to the change of the electronic structure of the surface, as measured by the change of the d-band center. As can be seen in Fig. 5-2, this can be captured by the d-band center weighting model. In Pd/Pt systems, the bond strength of Pt-Pd (-39.0 kcal/mol) is much smaller than that of Pt-Pt. In another words, the bond order a,b,d-c is much weaker than that of clean Pt(111) surfaces. The BOC concept predicts the bond order of sites a, b, d and NO for NO-Pd/Pt to be much stronger than that for NO-clean Pt(111) systems. Our calculated results show that the adsorption energy of NO at the fcc site on Pt(111) surface with site c substituted by Pd is -215.9 kJ/mol is about 13.3 kJ/mol stronger than that on the pure Pt(111) surfaces. Since Koper et al.’s study found that the Pt-Ru bond was stronger than the Pt-Pt bond, (Koper et al., 2002), the Ru/Pt system is therefore calculated to test the generality of our explanation. As listed in the last row of Table 5.3, the bond strength of Pt-Ru is about 15.3 kcal/mol stronger than that of Pt-Pt, which suggests the bond order of a, b, d and NO to be smaller from the BOC’s point of view. This is also true in our calculations: the adsorption of NO at the fcc site on 1Ru/\text{Pt}(111) is about 10.9 kJ/mol less stable than that on the clean Pt(111) surface. From Table 5.3, we can also see that the bond strength is consistent with the bond length. The longer the Pt-M bond length is, the weaker the Pt-M bond strength and vice versa. Therefore, a simple measure of the change of the adsorption strength of NO on alloyed surfaces is the change of the bond length between the alloyed species and platinum atoms.

5.4 Conclusions

We conclude that a recently proposed d-band center weighting model (Pallassana et al., 2000) describes well some simple systems, such as the adsorption of molecular NO at the fcc site on Rh alloyed Pt(111) surfaces, but has limitations for other simple
Table 5.3: Bond strength and bond length between alloyed species and platinum atoms. Adsorption energy (AE) of NO at an fcc site on 1M°/Pt(111) is also listed for reference.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Bond strength (kcal/mol)</th>
<th>Bond length (Å)</th>
<th>AE° on 1M°/Pt(111) (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt-Pt</td>
<td>-64.6</td>
<td>2.378</td>
<td>-202.6</td>
</tr>
<tr>
<td>Pt-Rh</td>
<td>-68.4</td>
<td>2.377</td>
<td>-201.9</td>
</tr>
<tr>
<td>Pt-Pd</td>
<td>-39.0</td>
<td>2.380</td>
<td>-215.9</td>
</tr>
<tr>
<td>Pt-Ru</td>
<td>-79.9</td>
<td>2.361</td>
<td>-191.7</td>
</tr>
</tbody>
</table>

°Adsorption energy of NO at an fcc site (formed by sites a, b, and d) on 1M°/Pt(111) systems, for example, the adsorption of molecular NO at the fcc site on Pd alloyed Pt(111) surfaces. Actually, NO adsorption on Pd/Pt(111) is not as simple as one might intuit: NO does bind equally to the three metal surface atoms (a, b, and d) which make up the fcc site, but NO binding is affected by site c, which is not part of the fcc site (refer to Fig. 5-1(a)). This is because the bond strength between surface metal atoms can affect adsorption energies, in agreement with the BOC concept, and this additional effect should be considered while considering the binding of adsorbates to the surfaces. The limitation of Pallassana et al.'s model (Pallassana et al., 2000) can be improved by the approach proposed by us for more complicated systems, in which the adsorbates bind unequally to multiple metal surface atoms (Tang & Trout, 2005a). In each surface alloy system, molecular NO adsorption strength depends linearly on the weighted position of the d states of the surface relative to the Fermi level. The closer the weighted d-band center is to the Fermi level, the stronger the adsorption is. These correlations should be useful in selecting which type and local concentration of surface atoms to choose for optimal alloy catalysts.
Chapter 6

Rational Design of Selective, Sulfur-Resistant, Oxidation Emissions Catalysts

A new catalyst design strategy based on optimizing electronic structure has been proposed and then applied to a very important environmental application, the design of selective, sulfur-resistant, oxidation emissions catalysts. The modified d-band center model developed by us in a previous study, together with an energy decomposition scheme, is used to correlate measures of reactivity with reaction barriers of $\text{SO}_2 + \text{O} \rightarrow \text{SO}_3$ and $\text{NO} + \text{O} \rightarrow \text{NO}_2$ on surfaces. Our objective is to find a catalyst which is active in oxidizing NO to NO$_2$, but relatively inactive in oxidizing SO$_2$ to SO$_3$. Ir alloyed Pt(111) surface is found to have the highest selectivity for oxidation of NO over SO$_2$ at 700 K. Unfortunately, there is a slope change in the correlation of the weighted d-band center with the adsorption of NO at the transition state, which narrows down the range of the theoretical selectivity. Our ongoing study aims at understanding the reason for this. The general importance of this study for surface catalysis is also discussed.
6.1 Motivation

Three-way catalysts (TWC), consisting of platinum, palladium, rhodium and other components, are widely used for exhaust aftertreatment in automobiles. They operate by simultaneously reducing nitrogen oxides (NO$_x$) and oxidizing the partial combustion product (CO) and the residual uncombusted hydrocarbons (HC). In order to both reduce and oxidize effectively, they can operate only within a very narrow window around the stoichiometric value of the air-fuel ratio ($\sim 14.7$). (Gross et al., n.d.) However, it is highly desirable to have emissions catalysts that operate under lean (oxygen rich) conditions. Such catalysts could be used for emissions control of diesel engines and of gasoline engines that burn under lean conditions, the latter being useful for increased fuel economy and control range. Thus, the main challenge for controlling emissions under lean conditions is to remove adequately the oxides of nitrogen from exhaust streams that contain a large excess of oxygen, because under these conditions, the conversion efficiency for the reduction reaction of NO$_x$ is low. Possible ways to overcome this difficulty include: selective catalytic reduction (SCR), in which a reductant such as urea or ammonia is added to react preferentially with the oxygen from the NO$_x$; (Shelef, 1995) and lean NO$_x$ trapping, in which NO$_x$ is stored on a trap (such as BaO or CaO) for a period of lean operation, followed by a short period of rich operation, in which stored NO$_x$ is converted to N$_2$ and purged. (Takahashi, 1995) Both of these, especially the latter one, are poisoned by sulfur compounds from the fuel. In the case of the NO$_x$ trap, the oxidizing component (typically Pt) also promotes the oxidation of SO$_2$ to SO$_3$ under lean conditions. SO$_3$ then adsorbs strongly on the NO$_x$ trap and forms thermodynamically stable sulfates, such as BaSO$_4$, which are very hard to purge and which thus deactivate the trap. Solutions for this problem include reducing the amount of sulfur in the fuel or designing new sulfur-resistant catalysts which are selective in the oxidation of NO over SO$_2$. In this paper, we will focus on the latter one: design of selective, sulfur-resistant catalysts.

Alloying metals has long been exploited as an effective way to enhance the reactivities of surfaces via either the electronic effect or the ensemble effect or both.
The electronic effect is due to a change in electronic structure, leading to a change in rate constants of elementary steps, while the ensemble effect is due to a change in distribution and availability of surface reaction sites. So far, most heterogeneous catalysts are developed using heuristics and trial and error methods via continual incremental improvements of existing catalysts or via a combinatorial approach. Incremental improvements are made by modifying existing catalysts and then testing them empirically until better catalysts are found. The TWC’s discussed in the last paragraph are one of the great successes of this kind of catalyst development. They have been continuously improved since the 1970’s. In the combinational approach, a large number of catalyst formulations are synthesized and tested rapidly, for example, via high-throughput screening, in order to optimize catalyst properties. Both approaches are limited by the efficiency of exploring the huge possible parameter space. It would be desirable to be able to propose a priori more limited ranges of compositions to explore.

We use a different approach, called rational catalyst design, based on the relationships between the intrinsic properties of materials and their catalytic activities, the latter being obtained via electronic structure theories of chemical binding and reactivity. A very successful example of this approach is the design of a non-coking steam reforming catalyst by Besenbacher et al. (Besenbacher et al., 1998) This catalyst design was based on the ensemble effect—adding a dopant to the surface to prevent nucleation of carbon material without affecting the activity for steam reforming. Obviously, this approach can save significant cost and time in finding new catalysts.

In this paper, we propose and apply a selective catalyst design strategy based on the electronic effect for oxidation catalysts, with a view to the reduction of emissions from automobile sources. The d-band center weighting model by Tang et al., proven to be suitable for the binding of chemisorbed molecules which bind unequally to multiple types of surface atoms (Tang & Trout, 2005a; Tang & Trout, 2005b), is used together with a scheme for decomposing energies of adsorption and reaction barriers on surfaces (Hammer, 1999; Burch et al., 2002) in order to predict the reactivity of SO₂ and NO oxidation on different surfaces. The objective is to develop
a catalyst which is selective for the oxidation of NO over SO₂. Nudged Elastic Band (NEB) calculations are then performed to validate our assumptions. This study should aid in the development of more effective catalysts for an extremely important environmental application. It addresses exactly the selectivity issue for the future of catalytic research in this area summarized in the review by Shelef et al. (Shelef & McCabe, 2000), of maximum importance is "a search for catalysts active in the oxidation of NO to NO₂ and relatively inactive in the oxidation of SO₂ to SO₃”.

6.2 Details of calculations

All the adsorption energies and reaction barriers on various surfaces were calculated by first principles density functional theory (DFT) methods, implemented in the GNU publicly licensed software DACAPO. (http://www.fysik.dtu.dk/CAMP/dacapo.html, n.d.) The gradient-corrected exchange-correlation functional PW91-GGA (Perdew et al., 1992) was used for all the calculations. The ionic cores were described by ultrasoft pseudopotentials, (Vanderbilt, 1990; Laasonen et al., 1993) allowing the plane wave basis set a cut off kinetic energy of 25 Ry (340 eV). A Monkhorst-Pack mesh with a 4x4x1 k-grid was applied to sample the surface Brillouin zones. (Monkhorst & Pack, 1976) All of the surfaces were modeled by a (2x2) unit cell and periodic three-layer slabs separated by a vacuum region of ~ 10 Å. A point dipole was included between those slabs in the z direction (the direction perpendicular to the slabs) in order to diminish interactions among periodic images. The feasibility of applying this slab model to describe accurately the adsorption properties has been tested thoroughly by previous studies in our group and others. (Tang & Trout, 2005a; Tang & Trout, 2005b; Burch et al., 2002; Mavrikakis et al., 1998; Pallassana et al., 2000; Aizawa et al., 2002; Lin et al., 2004a; Lin et al., 2002; Alavi et al., 1998; Li & Gewirth, 2003; Tang et al., 2004; Kitchin et al., 2004) The adsorbates and the first two-layer metal surface atoms in the slab were allowed to relax during the calculations, the bottom Pt layer being fixed at the calculated bulk lattice constant, 4.00 Å. Taking into account explicitly electron spin was found not to change the adsorption energies.
of either SO$_x$ or NO$_x$ significantly. (Tang & Trout, 2005a; Hammer, 1999; Lin et al., 2004a; Lin et al., 2002; Tsai & Hass, 1995; Hass et al., 1996; Hammer & Nørskov, 1997a) Therefore, all the calculations were nonmagnetic in this study.

Consistent with our previous two papers, (Tang & Trout, 2005a, ?) $nM^x$/Pt(111) is used to designate the surface alloys and overlayers, meaning to replace n Pt atoms in the top Pt layer with other metal atoms (M). $n=1$, 2 or 3 are surface alloys with different local concentrations of M, such that $n=4$ is an overlayer; $x$ represents the sites replaced among those four consisting of the p(2x2) unit cell.

The Nudged Elastic Band (NEB) method (Jónsson et al., 1998; Ulisky & Elber, 1990) was used to determine the Minimum Energy Path (MEP) connecting the initial and final states. The transition state of the reaction corresponds to the saddle point along this path. The NEB method determines the MEP by creating intermediate images along the path that represent replicas of the original system, and then simultaneously relaxing them. Spring constants between the adjacent images are added to insure the continuity of the path. Because the NEB method does not require second or higher order derivatives of the Kohn-Sham energy functional with respect to the atomic coordinates, it is particularly useful when combined with the planewave DFT computations. To save computational cost, we start the minimization process from the previous MEPs of reactions on clean Pt(111) surfaces, (Burch et al., 2002; Lin et al., 2004b) and terminate it when the nudged forces on all images of the chain becomes small ($\sim 0.07$ eV/Å).

6.3 Results and Discussions

6.3.1 Strategy for Selective Catalyst Design

Overall Design Strategy

We design the selective, sulfur-resistant catalysts based on the difference of the energy barriers of SO$_2$+O→SO$_3$ and NO+O→NO$_2$. In order to predict which materials will be most selective, we need a composition-activity relationship, correlating energy
barriers to the intrinsic properties of the electronic structures of surfaces, such as, the
d-band center of metal surfaces. Energy barriers of different reactions as functions of
d-band centers that illustrate possible cases which might occur are plotted in Fig. 6-1.
Dashed lines are for the oxidation of NO, and solid lines are for the oxidation of SO$_2$.
The plot in Fig. 6-1(a) shows that when the d-band center shifts toward the Fermi
energy, the energy barrier for the oxidation of NO decreases much faster than that
of SO$_2$. Since our objective is to activate NO oxidation, but not SO$_2$ oxidation, we
can try to modify the surface so that the d-band center of the surface is as close to
the Fermi level as possible. The energy barrier for the oxidation of NO will therefore
decrease more than that of SO$_2$, and the selectivity will then be enhanced. The
same strategy can be applied to the case illustrated in Fig. 6-1(b). Fig. 6-1(c) gives
an opposite case to that in Fig. 6-1(a): with the increase of the d-band center, the
energy barrier for NO oxidation decreases much slower than that for SO$_2$ oxidation.
Therefore, we need to modify the surface such that the d-band center is as far away
from the Fermi level as possible. In Fig. 6-1(d), the energy barrier of NO+O→NO$_2$
has a similar sensitivity to the d-band center of surfaces as that of SO$_2$+O→SO$_3$.
Thus, another approach, such as exploiting the ensemble effect would need to be
used. Of course, the cases in Fig. 6-1 are merely possibilities, and the real situation
may be more complicated.

Approach to Carry out the Strategy

The adsorption energy of a co-adsorbed system, $E_{co-ads}$, can be decomposed as (Refer
to Fig. 6-2.): (Hammer, 1999; Burch et al., 2002)

$$E_{co-ads} = E_{rebond} + E_{int}$$

(6.1)

where $E_{rebond}$ is called the rebonding potential energy, defined as the sum of the
individual energies of chemisorption of each species in the co-adsorbed system, and
$E_{int}$ is the intermolecular interaction energy between the individual species in the
coa-adsorbed system. Correspondingly, the energy barrier of a reaction, $E_a$, can also
Figure 6-1: Illustration of possible cases of the energy barrier vs. d-band center ($E_d$) for NO oxidation (dashed line) and SO$_2$ oxidation (solid line).

Figure 6-2: Energy decomposition scheme for a co-adsorbed system on surface. All the terms are defined in the text.
be broken down into two contributions: (Hammer, 1999; Burch et al., 2002)

\[ E_a = \Delta E_{\text{rebond}} + \Delta E_{\text{int}} \]  

(6.2)

where \( \Delta E_{\text{rebond}} = E^{TS}_{\text{rebond}} - E^{IS}_{\text{rebond}} \) is the energy change in the rebonding potential energy of non-interacting species between the transition state geometry (TS) and the initial geometry (IS), and \( \Delta E_{\text{int}} = E^{TS}_{\text{int}} - E^{IS}_{\text{int}} \) is the interaction energy change from the initial state to the transition state. Usually, for association reactions, the reactants are well separated. Therefore, it is reasonable to neglect \( E^{IS}_{\text{int}} \).

For the oxidation reactions: \( \text{SO}_2 + \text{O} \rightarrow \text{SO}_3 \) and \( \text{NO} + \text{O} \rightarrow \text{NO}_2 \), previous studies have reported that the rate-limiting steps in both reactions are surface reactions. (Burch et al., 2002; Lin et al., 2004a) At low coverage, the Langmuir-Hinshelwood mechanism is reasonable for both reactions, in which both reactants pre-adsorb to surfaces before the reactions take place. Of course, if other steps are rate limiting, our catalyst design approach could be modified easily to address those steps.

When we apply the above barrier decomposition scheme to these two oxidation reactions, we can decompose the energy barriers of those two oxidation reactions as below:

\[ E_{\text{oxi-SO}_2} = (E^{TS}_{\text{SO}_2} - E^{IS}_{\text{SO}_2}) + (E^{TS}_{\text{O}} - E^{IS}_{\text{O}}) + E^{TS}_{\text{int,SO}_2} \]  

(6.3)

\[ E_{\text{oxi-NO}} = (E^{TS}_{\text{NO}} - E^{IS}_{\text{NO}}) + (E^{TS}_{\text{O}} - E^{IS}_{\text{O}}) + E^{TS}_{\text{int,NO}} \]  

(6.4)

Fig. 6-3 illustrates the Minimum Energy Paths of both oxidation reactions on a clean Pt(111) surface, calculated by the NEB method. Those images with the \( p(2x2) \) unit cell marked as a, b, c, and d are at the initial state (first image of each row in Fig. 6-3) or the transition state (fourth image of each row in Fig. 6-3). For the surface reaction of \( \text{SO}_2(\text{ads}) + \text{O}(\text{ads}) \rightarrow \text{SO}_3(\text{ads}) \), as shown in Fig. 6-3(a), both \( \text{SO}_2 \) and \( \text{O} \) start initially at fcc sites on the surface, in the transition state, \( \text{SO}_2 \) moves to a tilted top position (site a in TS of Fig. 6-3(a)) and the pre-adsorbed oxygen atom moves to a bridge site (between sites c and d in TS of Fig. 6-3(a)) against the \( \text{SO}_2 \) molecule. This is also what our previous study found. (Lin et al., 2004b) Similarly,
in the reaction of NO(ads) + O(ads) → NO₂(ads), (Refer to Fig. 6-3(b).) both NO and O start from the fcc threefold hollow sites and reach a transition state which involves NO positioned just off an atop site (site d in TS of Fig. 6-3(b)) with the pre-adsorbed oxygen atom situated on a bridge site (between sites a and c in Fig. 6-3(b)). This is in agreement with Burch et al.’s study, (Burch et al., 2002), in which two structures with similar energy barriers were located at transition states in which bond formation occurs across an hcp or fcc hollow site. Here, we consider only the one over the hcp site. However, this will still allow us to study the trend of energy barrier change versus the electronic structure of surfaces.

Since in both reaction paths, the pre-adsorbed oxygen atom moves from an fcc site in the initial state to a bridge site in the transition state, it is reasonable to assume that the rebonding energy change due to this pre-adsorbed oxygen atom in Eq. (6.3) and Eq. (6.4) \((E_{TS}^{TS} - E_{TS}^{FS})\) is similar. The interaction energy \((E_{int,SO_2/NO}^{TS})\) usually has two origins: the bonding competition effect and direct Pauli repulsion. (Liu et al., 2003)

The bonding competition effect is strong when two species share bonds with the same surface atoms. In the transition states for both SO₂(ads) + O(ads) → SO₃(ads) and NO(ads) + O(ads) → NO₂(ads), the pre-adsorbed oxygen atom does not share bonds with either SO₂ or NO. Therefore, the contribution of bonding competition to the systems studied here is assumed to be small. The Pauli repulsion effect is short ranged
and is significant only when two species are very close. The distance between SO₂ and pre-adsorbed oxygen in the transition state geometry of SO₂(ads)+O(ads)→SO₃(ads) is about 2.6 Å, (Lin et al., 2004b) where the Pauli repulsion is considered to be small. Although the distance between NO and pre-adsorbed O in the transition state of NO(ads)+O(ads)→NO₂(ads) is about 1.6 Å, $E_{\text{int,NO}}^T$ is found to contribute only a small part (0.2 eV) to the energy barrier (1.52 eV). (Burch et al., 2002) Similar phenomena are also observed in the reaction of NH₂+H→NH₃ on Rh(111). (Liu et al., 2003) This is because in the NH₂+H reaction, NH₂ is activated from the bridge site to just off the atop site, which costs a significant amount of energy. Also, the low coordination of NH₂ in the transition state can change the electronic distribution of NH₂. As a result, the incurred Pauli repulsion between NH₂ and H is reduced. Since the reaction of SO₂(ads)+O(ads)→SO₃(ads) is similar to the reaction of NO+O and NH₂+H, its $E_{\text{int,SO₂}}^T$ should not play an important role in the energy barrier. Thus, to describe the barriers in Eq. (6.3) and Eq. (6.4), we can focus only on the rebonding energy changes for SO₂ and NO.

We are assuming that the geometries of transition states on different surface alloys do not vary dramatically from one to another. This should be valid based on studies in the literature on similar reactions. In the study of carbon monoxide oxidation on the Cu₃Pt(111) alloy surface by Zhang et al., the transition state remains similar to that on clean Pt(111) and Cu(111) surfaces. (Zhang et al., 2001) The variation in the distance between the carbon atom and a surface metal atom is within 0.05 Å. More importantly, we verified this assumption via the NEB calculations in our study, to be discussed later.

Unfortunately, we can not use a simple d-band center to describe the electronic structure of the surface for reasons described in previous studies. (Tang & Trout, 2005a; Tang & Trout, 2005b) We can, however, use the electronic composition-property relationship developed in a previous study, which has been successfully applied to SO₂ (Tang & Trout, 2005a) and NO (Tang & Trout, 2005b) chemisorption on Pt(111) surfaces, alloys, and overlayers. It is used here to correlate the adsorption energies of species in the initial state and the transition state to the weighted d-band
centers of the surfaces. The remaining terms in Eq. (6.3) and Eq. (6.4) can then be easily estimated by only a few calculations. Finally, by examining the sensitivity difference of the energy barriers of \( \text{SO}_2 + O \rightarrow \text{SO}_3 \) and \( \text{NO} + O \rightarrow \text{NO}_2 \) to the weighted d-band center of surfaces, we should be able to predict which alloy surfaces will have better selectivities, as described in the previous section.

### 6.3.2 Estimation of \( E_{X}^{TS} - E_{X}^{IS} \) in \( X + O \rightarrow XO \) (\( X = \text{SO}_2 \) and \( \text{NO} \))

\( E_{\text{SO}_2}^{IS} \) and \( E_{\text{NO}}^{IS} \)

For the reaction of \( \text{SO}_2 + O \rightarrow \text{SO}_3 \), the geometries of \( \text{SO}_2 \) at the initial state on different surfaces were chosen from the most stable adsorbed configuration (fcc \( \eta^2 - S_b, O_a \)) on the clean Pt(111) surface, determined in our previous studies. (Lin et al., 2004a; Lin et al., 2004b) As discussed in our previous paper, (Tang & Trout, 2005a) the adsorption energies of the most stable configurations of \( \text{SO}_2 \) on various surface alloys were found to depend linearly on the weighted d-band centers of the surfaces. Here, the most stable configurations are defined as those for which the adsorption energy decreases as sites are substituted one at a time. This observation is used here to estimate the adsorption strength of \( \text{SO}_2 \) on surfaces with widely varying compositions. The adsorption energies of the most stable configuration of \( \text{SO}_2 \) on various surfaces (summarized in Table 6.1) are plotted as a function of the weighted d-band centers in Fig. 6-4. The equation of the least-squares fitted line is:

\[
y = -124.27x - 440.87 \quad (6.5)
\]

where \( y \) (unit: KJ/mol) represents the adsorption energy of \( \text{SO}_2 \) at the initial state, and \( x \) (unit: eV) represents the weighted d-band center. The \( R^2 \) of this fitted line is 0.86.

For the reaction of \( \text{NO} + O \rightarrow \text{NO}_2 \), previous studies show the most stable adsorption site of \( \text{NO} \) on Pt(111) is the fcc hollow site. (Tang & Trout, 2005b; Burch et al.)
Table 6.1: Adsorption energies (AE) of the most stable configurations of SO$_2$ with initial geometries on various surface alloys nM$^x$/Pt(111) and the weighted d-band center ($E_d$) of each surface.

<table>
<thead>
<tr>
<th>nM$^x$/Pt(111)</th>
<th>AE (KJ/mol)</th>
<th>$E_d$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>clean Pt(111)</td>
<td>-115.73</td>
<td>-2.55</td>
</tr>
<tr>
<td>1Pd$^b$/Pt(111)</td>
<td>-131.07</td>
<td>-2.39</td>
</tr>
<tr>
<td>1Pd$^c$/Pt(111)</td>
<td>-124.22</td>
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<tr>
<td>2Pd$^{bc}$/Pt(111)</td>
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<td>1Cu$^a$/Pt(111)</td>
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<td>1Cu$^b$/Pt(111)</td>
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<td>2Cu$^{bc}$/Pt(111)</td>
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<td>-2.02</td>
</tr>
<tr>
<td>3Ni$^{abc}$/Pt(111)</td>
<td>-217.23</td>
<td>-1.71</td>
</tr>
<tr>
<td>1Ru$^a$/Pt(111)</td>
<td>-141.84</td>
<td>-2.46</td>
</tr>
<tr>
<td>1Ru$^b$/Pt(111)</td>
<td>-115.42</td>
<td>-2.60</td>
</tr>
<tr>
<td>2Ru$^{ab}$/Pt(111)</td>
<td>-145.59</td>
<td>-2.38</td>
</tr>
<tr>
<td>2Ru$^{bc}$/Pt(111)</td>
<td>-173.96</td>
<td>-2.29</td>
</tr>
<tr>
<td>2Ru$^{ad}$/Pt(111)</td>
<td>-158.29</td>
<td>-2.34</td>
</tr>
<tr>
<td>3Ru$^{bed}$/Pt(111)</td>
<td>-202.22</td>
<td>-2.05</td>
</tr>
<tr>
<td>3Ru$^{abd}$/Pt(111)</td>
<td>-163.76</td>
<td>-2.15</td>
</tr>
<tr>
<td>4Ru$^{abcd}$/Pt(111)</td>
<td>-222.13</td>
<td>-1.79</td>
</tr>
</tbody>
</table>
Figure 6-4: Linear relationship between adsorption of SO$_2$ in its most stable configuration at the initial state (fcc site) on various alloyed Pt(111) surfaces and overlayers vs. the weighted d-band center of the surfaces.

The fcc site was therefore chosen here to be the initial position of the reactant NO on each surface. It has been shown in a previous paper of ours (Tang & Trout, 2005b) that the adsorption energy of NO at an fcc site on Rh/Pt(111) and Pd/Pt(111) alloy surfaces has a strong linear correlation with the weighted d-band centers of surfaces calculated by our method. (Tang & Trout, 2005a) In Fig. 6-5, those adsorption energies on different surfaces (summarized in Table 6.2) are plotted vs. the weighted d-band centers in the same figure. Some vacant square points marked as 1M$^d$/Pt(111) are added to test the generality of the linear relationship and were not used in obtaining the relationship. They will also be used to estimate the values of $E_{NO}^{TS}-E_{NO}^{TS}$ on different surfaces later. The $R^2$ of the least-squares fitted line in Fig. 6-5 is 0.90 with the correlation equation:

$$y = -159.42x - 599.34$$  \hspace{1cm} (6.6)

where $y$ (unit: KJ/mol) represents the adsorption energy of NO at an fcc site, and $x$ (unit: eV) represents the weighted d-band center.
Table 6.2: Adsorption energies (AE) (units of KJ/mol) of NO chemisorbed on (a) Rh/Pt(111) surfaces and (b) Pd/Pt(111) surfaces and the weighted d-band center of each surface (Ed) (units of eV).

<table>
<thead>
<tr>
<th>(a) System</th>
<th>AE</th>
<th>Ed</th>
<th>(b) System</th>
<th>AE</th>
<th>Ed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rh/Pt(111) clean Pt(111)</td>
<td>-202.6</td>
<td>-2.55</td>
<td>Rh/Pt(111) clean Pt(111)</td>
<td>-202.6</td>
<td>-2.55</td>
</tr>
<tr>
<td>1Rh\textsuperscript{a}/Pt(111)</td>
<td>-240.2</td>
<td>-2.32</td>
<td>1Pd\textsuperscript{a}/Pt(111)</td>
<td>-211.5</td>
<td>-2.44</td>
</tr>
<tr>
<td>1Rh\textsuperscript{b}/Pt(111)</td>
<td>-240.7</td>
<td>-2.32</td>
<td>1Pd\textsuperscript{b}/Pt(111)</td>
<td>-211.9</td>
<td>-2.44</td>
</tr>
<tr>
<td>1Rh\textsuperscript{c}/Pt(111)</td>
<td>-201.9</td>
<td>-2.55</td>
<td>1Pd\textsuperscript{c}/Pt(111)</td>
<td>-215.9</td>
<td>-2.40</td>
</tr>
<tr>
<td>1Rh\textsuperscript{d}/Pt(111)</td>
<td>-240.2</td>
<td>-2.32</td>
<td>1Pd\textsuperscript{d}/Pt(111)</td>
<td>-211.3</td>
<td>-2.44</td>
</tr>
<tr>
<td>2Rh\textsuperscript{ab}/Pt(111)</td>
<td>-273.8</td>
<td>-2.07</td>
<td>2Pd\textsuperscript{ab}/Pt(111)</td>
<td>-216.1</td>
<td>-2.34</td>
</tr>
<tr>
<td>2Rh\textsuperscript{ac}/Pt(111)</td>
<td>-239.8</td>
<td>-2.32</td>
<td>2Pd\textsuperscript{ac}/Pt(111)</td>
<td>-224.8</td>
<td>-2.29</td>
</tr>
<tr>
<td>2Rh\textsuperscript{bc}/Pt(111)</td>
<td>-240.8</td>
<td>-2.32</td>
<td>2Pd\textsuperscript{bc}/Pt(111)</td>
<td>-225.5</td>
<td>-2.29</td>
</tr>
<tr>
<td>2Rh\textsuperscript{ad}/Pt(111)</td>
<td>-273.2</td>
<td>-2.07</td>
<td>2Pd\textsuperscript{ad}/Pt(111)</td>
<td>-216.6</td>
<td>-2.34</td>
</tr>
<tr>
<td>2Rh\textsuperscript{bd}/Pt(111)</td>
<td>-274.0</td>
<td>-2.07</td>
<td>2Pd\textsuperscript{bd}/Pt(111)</td>
<td>-216.1</td>
<td>-2.34</td>
</tr>
<tr>
<td>2Rh\textsuperscript{cd}/Pt(111)</td>
<td>-239.8</td>
<td>-2.32</td>
<td>2Pd\textsuperscript{cd}/Pt(111)</td>
<td>-224.8</td>
<td>-2.29</td>
</tr>
<tr>
<td>3Rh\textsuperscript{bcd}/Pt(111)</td>
<td>-275.1</td>
<td>-2.07</td>
<td>3Pd\textsuperscript{bcd}/Pt(111)</td>
<td>-230.3</td>
<td>-2.18</td>
</tr>
<tr>
<td>3Rh\textsuperscript{acd}/Pt(111)</td>
<td>-273.8</td>
<td>-2.07</td>
<td>3Pd\textsuperscript{acd}/Pt(111)</td>
<td>-230.5</td>
<td>-2.18</td>
</tr>
<tr>
<td>3Rh\textsuperscript{abd}/Pt(111)</td>
<td>-300.5</td>
<td>-1.80</td>
<td>3Pd\textsuperscript{abd}/Pt(111)</td>
<td>-218.4</td>
<td>-2.32</td>
</tr>
<tr>
<td>3Rh\textsuperscript{abc}/Pt(111)</td>
<td>-275.1</td>
<td>-2.07</td>
<td>3Pd\textsuperscript{abc}/Pt(111)</td>
<td>-230.2</td>
<td>-2.19</td>
</tr>
<tr>
<td>4Rh\textsuperscript{abcd}/Pt(111)</td>
<td>-301.4</td>
<td>-1.80</td>
<td>4Pd\textsuperscript{abcd}/Pt(111)</td>
<td>-232.9</td>
<td>-2.05</td>
</tr>
</tbody>
</table>

Figure 6-5: Linear relationship between NO adsorption at the initial state (fcc site) on various alloyed Pt(111) surfaces and overlayers vs. the weighted d-band center of the surfaces. The vacant square points marked as 1M\textsuperscript{d}/Pt(111) are added to test the generality of the linear relationship.
Figure 6-6: Linear relationship between SO$_2$ adsorption at the transition state on various alloyed Pt(111) surfaces and overlayers vs. the weighted d-band center of the surfaces.

$E^{TS}_{SO_2}$ and $E^{TS}_{NO}$

The geometries of SO$_2$ and NO at transition states are taken and fixed from the NEB chain images at the transition states on pure Pt(111) by removing the pre-adsorbed oxygen atom (refer to Fig. 6-3). At the transition state, the correlations of the adsorption energies of SO$_2$ and NO on different surfaces with the weighted d-band center are plotted in Fig. 6-6 and Fig. 6-7. For SO$_2$ at the TS, surfaces with different types and different local concentrations of alloyed species have been examined. Fig. 6-6 shows that the adsorption strength of SO$_2$ at the transition state has a strong linear correlation with the weighted d-band center of each surface ($R^2=0.94$). The least-squares fitted line has the equation format as given in Fig. 6-6:

\[
y = -100.48x - 331.15 \quad (6.7)
\]

where $y$ (unit: KJ/mol) represents the adsorption energy of SO$_2$ at the transition state, and $x$ (unit: eV) represents the weighted d-band center. For NO at the TS, only surfaces with single substitutions are examined. The single substitution site is chosen to be the tilted top site where NO adsorbs at the transition state. (Refer to site d in TS of Fig. 6-3 (b).) This is because that is the substitution of the site where NO
interacts directly, thus affecting the NO adsorption strength the most. Different from the trend observed in the other systems such as, SO$_2$ at the IS and at the TS and NO at the IS, Fig. 6-7 shows that the adsorption energy of NO at the TS has a minimum as a function of the weighted d-band center. At lower values of the weighted d-band center (lower than -2.22 eV such as 1Au$^d$/Pt(111), clean Pt(111), and 1Ir$^d$/Pt(111)), the NO adsorption energy at the TS becomes stronger as the weighted d-band center shifts closer to the Fermi energy level. At a higher value of the weighted d-band center (higher than -2.22 eV such as 1Ru$^d$/Pt(111), 1Rh$^d$/Pt(111), 1Ni$^d$/Pt(111), and 1Tiy$^d$/Pt(111)), the NO adsorption energy at the TS decreases as the weighted d-band center shifts closer to the Fermi energy level. The correlation of NO adsorption energy vs. weighted d-band center can be represented in the equations below:

\[ y = -130.18x - 498.16 \quad (x \leq -2.22eV) \quad (6.8) \]
\[ y = 70.55x - 56.65 \quad (x > -2.22eV) \quad (6.9) \]

Figure 6-7: Linear relationship between NO adsorption at the transition state on various alloyed Pt(111) surfaces and overlayers vs. the weighted d-band center of the surfaces.
where \( y \) (unit: KJ/mol) represents the adsorption energy of NO at the transition state, and \( x \) (unit: eV) represents the weighted d-band center.

The slope change in Fig. 6-7 is associated with the difference in the d states of surface alloy atoms. Loffreda et al. found that the gas phase NO molecule has the electronic configuration: \([1\sigma]^2[2\sigma]^2[3\sigma]^2[4\sigma]^2[1\pi]^4[5\pi]^2[2\pi^*]^1\), where the \([2\pi^*]\) orbital is an N-O antibonding orbital, containing one electron, and all the others are fully occupied bonding orbitals. (Loffreda et al., 1998) The density of state (DOS) projected on the d orbitals of the surface alloy atoms and the \( p_x \) orbitals of N in NO adsorption at TS (top) on surface alloys are given in Fig. 6-8 (a) and (b) respectively. The zero on the energy axis corresponds to the Fermi level. According to Loffreda et al.’s study, (Loffreda et al., 1998) the peaks at a lower energy level in Fig. 6-8 (b) represent the mixing of \( 5\sigma \) and \( 1\pi \) orbitals, while those at a higher energy level represent \( 2\pi^* \) orbitals. In the gas phase molecule, the occupancy of the anti-bonding states depends on the number of electrons in the system. However, at a metal surface, there is an infinite sea of metallic electrons and the occupancy of the anti-bonding states depends only on the energy of these states relative to the Fermi level. Because the energies of the d states relative to the Fermi level vary substantially from one metal to another, (Refer to Fig. 6-8 (a).) the number of anti-bonding states that are above the Fermi level, and thus empty, will depend on the metal itself. When bonding and anti-bonding states are formed, the strength of the bond will depend on the relative occupancy of these states. If only the bonding states are filled, there will be a strong bond, whereas if the anti-bonding states are also filled, the bond will become considerably weaker. (Nilsson et al., 2005)

For example, as illustrated in Fig. 6-8 (a), Au has d bands well below the Fermi level, and the anti-bonding states at the top of the d bands will end up below the Fermi level and are filled. (Refer to Fig. 6-8 (b).) The d-contribution to the bond is therefore not attractive. This is similar to the case of N adsorbed on Cu(100) in Nilsson et al.’s work. (Nilsson et al., 2005) On the other hand, Pt, Ir, and Rh behave the similarly to the case of Ni in Nilsson et al.’s work. (Nilsson et al., 2005) They have d bands partly above the Fermi level, (see Fig. 6-8 (a)) therefore, the
anti-bonding states at the top of the d bands are partly above the Fermi level and thus the interactions will be much more attractive. (see Fig. 6-8 (b)) The relative strength depend on the relative occupancy of the bonding and anti-bonding states. The Ir alloyed system has the lowest occupation of anti-bonding states, since its peak that is above Fermi level in Fig. 6-8 (b) has the highest energy. Correspondingly, it also has the strongest adsorption energy of NO. Although Ti has most of its d bands above the Fermi level as shown in Fig. 6-8 (a), it still has the anti-bonding states at the top of the d bands which are below the Fermi level and filled, (Refer to Fig. 6-8 (b).) the strength of the interaction is therefore reduced dramatically. This explains the slope change in Fig. 6-7. Interestingly, this phenomenon does not happen when NO adsorbs at IS (fcc). (Refer to Fig. 6-5 and Fig. 6-8 (c).)

**Estimation of** $E_{SO_2}^{TS} - E_{SO_2}^{IS}$ **and** $E_{NO}^{TS} - E_{NO}^{IS}$

Based on the electronic composition-property relationships for SO$_2$ and NO at both initial states and transition states in the previous two subsections, the $E_{SO_2}^{TS} - E_{SO_2}^{IS}$ and $E_{NO}^{TS} - E_{NO}^{IS}$ on different surfaces can be calculated. Fig. 6-9 shows $E_x^{TS} - E_x^{IS}$ (x=SO$_2$ and NO) as functions of the weighted d-band center of surfaces. Note that the weighted d-band center model used in the previous two subsections incorporates the binding strength of atoms in adsorbates and metal surface atoms. It is therefore adsorbate dependent. Thus, we cannot simply subtract equations (6.5) and (6.6) from equations (6.7) and (6.9) in order to compare the barrier between the oxidation of NO and that of SO$_2$ on a given surface. Instead, the surface d-band center is used in Fig. 6-9 which is calculated as $\frac{\sum_{x=a,b,c,d} E^z_d}{4}$, where $E^z_d$ represents the d-band center of surface atom x. (x=a,b,c,or d as marked in Fig. 6-3.) As can be seen in Fig. 6-9, $E_{SO_2}^{TS} - E_{SO_2}^{IS}$ (dashed line) increases as the surface d-band center increases. $E_{NO}^{TS} - E_{NO}^{IS}$ (solid line) slightly decreases with an increase in the surface d-band center until it reaches $\sim$ -2.22 eV. Once it reaches -2.22 eV, the slope of $E_{NO}^{TS} - E_{NO}^{IS}$ vs. surface d-band center changes dramatically. $E_{NO}^{TS} - E_{NO}^{IS}$ increases significantly as the surface d-band center shifts toward the Fermi energy level. Although the plot in Fig. 6-9 is based on the single substitution of a surface Pt atom, double substitution has been
Figure 6-8: Local projected density of state (pDOS) of (a) d orbitals of M in 1M^d/Pt(111), (b) \( p_x \) orbitals of N for NO adsorption at TS (top) on 1M^d/Pt(111), (c) \( p_x \) orbitals of N for NO adsorption at IS (fcc) on 1M^d/Pt(111), where M=Au, Pt, Ir, Rh, and Ti.
tested and found to follow the same trend. As explained in section 6.3.1, the difference in energy barriers of NO oxidation and SO$_2$ oxidation mainly comes from the difference in $E^{TS}_{SO_2} - E^{IS}_{SO_2}$ and $E^{TS}_{NO} - E^{IS}_{NO}$. Therefore, the different sensitivities between $E^{TS}_{SO_2} - E^{IS}_{SO_2}$ and $E^{TS}_{NO} - E^{IS}_{NO}$ to the weighted d-band center of alloy surfaces can be used to guide us to the design of the new selective, sulfur-resistant, oxidation automotive catalysts by applying the design strategy introduced in section 6.3.1.

Using $E^{TS}_{SO_2} - E^{IS}_{SO_2}$ and $E^{TS}_{NO} - E^{IS}_{NO}$ on various surfaces, we can estimate the selectivity of those surfaces for the oxidation of NO. Fig. 6-10 illustrates the selectivity for the oxidation of NO at 700 K as a function of the surface d-band center (same as those in Fig. 6-9). 700 K is chosen, because it is about the operating temperature of lean NO$_x$ traps. The selectivity is defined as the ratio of reaction rate for the oxidation of NO to the sum of the rate for both reactions, oxidation of NO and SO$_2$. The reaction rate is estimated as:

$$rate = A \times exp\left(-\frac{E_a}{RT}\right)$$  \hspace{1cm} (6.10)

where, $A$ is a constant prefactor, $E_a$ is energy barrier of the reaction, $R$ is ideal
Figure 6-10: Plot of selectivity of the oxidation of NO at 700 K vs. the surface d-band center of the surfaces (1Mx/Pt(111), with x=a for SO\textsubscript{2} and x=d for NO). M of each point is marked in the plot. The solid line is for the selectivity calculated by Eq. (6.12), and the dashed line is for the effective selectivity which includes the reactants chemisorption and products desorption steps.

gas constant, and \( T \) is temperature of the system. Therefore, the selectivity can be calculated by:

\[
\text{selectivity} = \frac{A_{oxi-NO} \times \exp\left(\frac{-E_{oxi-NO}}{RT}\right)}{A_{oxi-NO} \times \exp\left(\frac{-E_{oxi-NO}}{RT}\right) + A_{oxi-SO_2} \times \exp\left(\frac{-E_{oxi-SO_2}}{RT}\right)}
\]  
(6.11)

Assuming that \( A_{oxi-NO} \) and \( A_{oxi-SO_2} \) are similar, and applying the energy barrier decomposition schemes in Eq. (6.3) and Eq. (6.4) to Eq. (6.11), the selectivity in Eq. (6.11) can therefore be estimated as:

\[
\text{selectivity} = \frac{\exp\left(\frac{-E_{TS-NO} - E_{TS-NO}}{RT}\right)}{\exp\left(\frac{-E_{TS-NO} - E_{TS-NO}}{RT}\right) + \exp\left(\frac{-E_{TS-SO_2} - E_{TS-SO_2}}{RT}\right)}
\]  
(6.12)

It is also easy to include the reactants chemisorption and products desorption steps in the selectivity calculation by using the effective activation energy in Eq. (6.12).

As shown in Fig. 6-10, the overall selectivity is generally higher than the selectivity calculated by Eq. (6.12). The highest selectivity (about 90\%) occurs at a surface d-band center value of -2.22 eV, which is very close to that of Ir alloyed Pt(111) surfaces.
The selectivity for the oxidation of NO on a clean Pt(111) surface is about 68%. All the other surfaces (such as Au, Rh, Ru, Ni, or Ti alloyed surfaces) have a much lower selectivity (less than 20%). Note that Mitsubishi Heavy Ind. in Japan has found that Ir/Metallosilicate catalyst works for the selective reduction of NOx in lean burning gasoline engines. (Nojima et al., n.d.) The selectivity for the oxidation of NO over SO2 also depends on the temperature. It is found to increase about 20% when the temperature is decreased from 1000 K to 300 K.

6.3.3 Validation of the Design Strategy by NEB Calculations

NEB calculations are carried out to validate the design strategy proposed in this paper and also to confirm the conclusions obtained from the composition-activity relationship illustrated in Fig. 6-9. Au, Ir, and Rh alloyed surfaces are chosen as test systems, and their performance is compared to that of the clean Pt(111) surface. Double substitution for each alloy surface is used here. The Minimum Energy Paths for the oxidation of SO2 and NO on each surface are plotted in Fig. 6-11 (a) and (b) respectively. The geometry of images at each point along the MEP on alloy surfaces is found not to vary much from those on clean Pt(111) surface. This is in agreement with the phenomena in Zhang et al.'s study of the oxidation of CO on Cu3Pt(111) alloy surfaces (Zhang et al., 2001) and validates our assumption in section 6.3.1. The energy barriers of different reactions on each surface are compiled in Table 6.3. As shown in Table 6.3, from 2Au^{bc}/Pt(111), to clean Pt(111), to 2Ir^{bc}/Pt(111), and to 2Rh^{bc}/Pt(111), the energy barrier of SO2+O→SO3 increases slowly but steadily; however, the energy barrier of NO+O→NO2 remains more or less flat from 2Au^{bc}/Pt(111), to clean Pt(111), to 2Ir^{bc}/Pt(111), and increases significantly on 2Rh^{bc}/Pt(111). The values of the barriers in Table 6.3 show that the trend agrees with what we obtained from the composition-activity plot in Fig. 6-9. The selectivity of NO oxidation is also calculated and given in the last column of Table 6.3. The alloy surface 2Ir^{bc}/Pt(111) has the highest selectivity among those four tested surfaces, followed by the clean Pt(111) surface, which has a selectivity of around 60%, in reasonable agreement with the selectivity curve in Fig. 6-10, which is based on the composition-activity plot in
Table 6.3: Energy barriers (E_a) via NEB for the oxidation of (a) SO_2 and (b) NO on various surface alloys nMx/Pt(111) and the selectivity for oxidation of NO at 700 K.

<table>
<thead>
<tr>
<th>nMx/Pt(111)</th>
<th>E_a for (a) (KJ/mol)</th>
<th>E_a for (b) (KJ/mol)</th>
<th>selectivity for (b) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2Au/Pt(111)</td>
<td>39.69</td>
<td>41.01</td>
<td>38</td>
</tr>
<tr>
<td>clean Pt(111)</td>
<td>45.66</td>
<td>43.52</td>
<td>60</td>
</tr>
<tr>
<td>2Ir/Pt(111)</td>
<td>48.56</td>
<td>44.61</td>
<td>72</td>
</tr>
<tr>
<td>2Rh/Pt(111)</td>
<td>51.32</td>
<td>83.34</td>
<td>0</td>
</tr>
</tbody>
</table>

Fig. 6-9. Therefore, our selective, sulfur-resistant catalyst design strategy based on the composition-activity relationship is reliable.

6.4 Conclusions

We have proposed a new design strategy for catalysts based on correlating our recently developed modified d-band center model with reaction barriers on surfaces. (Tang & Trout, 2005a; Tang & Trout, 2005b) We have applied our approach to an important environmental application, the design of sulfur-resistant, lean NO_2 catalysts for emissions reduction from mobile sources. Specifically, we have aimed our design at finding a catalyst with maximum selectivity for oxidizing NO over SO_2. We found that an alloy surface with a surface d-band center around -2.22 eV (such as Ir alloyed Pt(111) surface) has the highest selectivity for oxidation of NO (around 90%). It was unfortunate, however, that the correlation of our modified d-band center with the transition state of NO + O had a change of slope, limiting the theoretical selectivity. On going work aims at understanding the reasons for this. The design strategy proposed in this work is general and could be applied to other catalytic systems.
Figure 6-11: Minimum energy paths of the oxidation of (a) SO$_2$ (b) NO on various alloyed Pt(111) surfaces found via NEB calculations.
Chapter 7

Conclusions and Recommended

Future Work

The overall goals of this thesis were to develop a design strategy that can be applied to sulfur resistant lean NOx automotive catalysts and to design a selective catalyst which is active in oxidizing NO to NO2, but relatively inactive in oxidizing SO2 to SO3. In order to realize our goals, we have focussed on the various aspects described below by using first principles computations.

7.1 Surface phase diagram of O/Pt(111)

As a first step, a complete phase diagram of oxygen atoms adsorbed on a Pt(111) surface with oxygen coverages below half a monolayer has been computed for the first time, Chapter 3, and compared with the surface phase diagrams of related systems. The formation of p(2×2) oxygen islands at low coverages and low temperatures is observed (in agreement with STM experiment) and found to be a consequence of attractive third nearest neighbors interactions, despite strong repulsion between the first and second nearest neighbors. By using a simple statistical mechanics model, oxygen atoms are found to be in the p(2×2) phase under conditions of interest to automotive catalysis, at 0.1 atm and 700 K.
7.2 Development of an electronic composition-property relationship and its application to SO$_2$ and NO chemisorption

In order to relate the surface reactivity to the intrinsic properties of metal surfaces, a new electronic composition-property relationship has been developed that can be applied to the adsorption energy of molecules binding unequally to multiple atoms on metal surfaces. These are related to the electronic properties of the surface, Chapter 4. The new physics of this model involves the incorporation of a simple and general approach to including interactions between various adsorbate atoms and substrate atoms. This has never been done before, yet it is necessary for predicting accurately the adsorption strength of complex molecules on surfaces. This relationship allows the estimation of the relative stability of adsorbates on various surfaces, assuming that the adsorbate adopts the same local configuration on each surface, and therefore also allows the estimation of the adsorption energy of molecules through large regions of parameter space in alloy systems with data from only a few explicit calculations.

This relationship has been applied to both the adsorption of SO$_2$ on Pt surfaces alloyed with Pd, Cu, Ru, and Ni, Chapter 4, and the chemisorption of NO on clean Pt(111), Rh/Pt(111) alloy and Pd/Pt(111) alloy surfaces, Chapter 5. Using our new formula for weighting the metal d-band center, a strong linear relationship was obtained between the weighted d-band centers of surfaces and the most stable molecular adsorption energies. In the study of NO chemisorption, it was also found that the surface compositions of the surface alloys have very different effects on the adsorption of NO on Rh/Pt(111) versus that on Pd/Pt(111). This is due to the different bond strength between the two metals in each alloy system. Our weighted d-band center model can also catch this feature. Therefore, the weighted d-band center model developed in this part of study will be used to optimize the design of the three-way automotive catalysts (TWC) in the next part.

Although our model works fairly well in the systems we study here, there are still
ways in which it needs to be improved. For example, in Chapter 4, the degree of repulsion between the surface and the sulfur atom (positive charge) changes when certain atoms are substituted, and this electrostatic effect is not included in our composition-activity relationship. Also, our choice of the electrostatic form \( S^M_{i} = \frac{C^M C^i}{d_{M-1}} \) in Chapter 4), is, at the end of the day, semi-empirical, and that there could be many possible alternate forms of the weighting term, such as, \( S^M_{i} = \frac{(C^M - C^i)^2}{4d_{M-1}} = \frac{(C^M)^2 + (C^i)^2 - 2C^MC^i}{4d_{M-1}} \), etc.

7.3 Design of selective, sulfur-resistant, oxidation emissions catalysts

Finally, in Chapter 6, a selective catalyst design strategy based on optimizing electronic structure has been proposed and validated with NEB calculations. The weighted d-band center model developed in Chapter 4, proven to be suitable for the binding of chemisorbed molecules which bind unequally to multiple types of surface atoms, is used both for the reactant state and the transition state of \( \text{SO}_2 + \text{O} \rightarrow \text{SO}_3 \) and \( \text{NO} + \text{O} \rightarrow \text{NO}_2 \). The energy barrier, \( E^{TS}_x - E^{IS}_x \) with \( x = \text{SO}_2 \) for \( \text{SO}_2 + \text{O} \rightarrow \text{SO}_3 \) and \( x = \text{NO} \) for \( \text{NO} + \text{O} \rightarrow \text{NO}_2 \), is then obtained and plotted as a function of our weighted d-band center. The \( E^{TS}_x - E^{IS}_x \) (\( x = \text{SO}_2 \) and \( \text{NO} \)) vs. weighted d-band center plot shows that, when the weighted d-band center increases, \( E^{TS}_{\text{SO}_2} - E^{IS}_{\text{SO}_2} \) also increases slowly but steadily, while that \( E^{TS}_{\text{NO}} - E^{IS}_{\text{NO}} \) remains more or less flat at lower weighted d-band center values, but increases significantly after the weighted d-band center reaches the value of around -2.22 eV. Ir alloyed Pt(111) surface with a weighted d-band center of around the value of -2.22 eV is then found to have the highest selectivity for oxidation of \( \text{NO} \) over \( \text{SO}_2 \) at 700 K. This selectivity also depends on the temperature. It can be increased by about 20% when the the temperature is decreased from 1000 K to 300 K. Our calculations suggest that Ir alloyed Pt(111) surface would be a potentially good candidate for a selective, sulfur-resistant, oxidation automotive catalyst, which will be active for the oxidation of \( \text{NO} \) to \( \text{NO}_2 \), but relatively inactive for the oxidation
of SO$_2$ to SO$_3$. This strategy is not restricted to lean-NO$_x$ catalysts system. It could also be applied to other surface catalyst systems, such as fuel cells.

Other catalysts could be designed based on the strategy proposed and validated in Chapter 6. Of course, the ultimate test would be experimental validation.
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