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Oxidation and reduction of carbon monoxide and methane CH
bond activation: Molecular orbital theory

Jen, Shu-Fen, Ph.D.
Case Western Reserve University, 1991
OXIDATION AND REDUCTION OF CO AND METHANE CH BOND ACTIVATION.
MOLECULAR ORBITAL THEORY

by
SHU-FEN JEN

Submitted in partial fulfillment of the requirements
for the degree of Doctor of Philosophy

Thesis Advisor: Alfred B. Anderson

Department of Chemistry
CASE WESTERN RESERVE UNIVERSITY
August, 1991
CASE WESTERN RESERVE UNIVERSITY

GRADUATE STUDIES

We hereby approve the thesis of

Shu-Fen Jen

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OXIDATION AND REDUCTION OF CO AND METHANE CH BOND ACTIVATION.
MOLECULAR ORBITAL THEORY

Abstract
by
SHU-FEN JEN

Calculations with the atom superposition and electron delocalization molecular orbital (ASED-MO) theory show that CO reacts readily with surface O on ZnO to form CO$_2$ which can immediately bind to O$^{2-}$ to form surface carbonate. The reaction with isolated O$^-$ has a higher barrier because O$^-$-CO bond formation promotes the electron to the surface conduction band. In this case CO$_2$ is ejected from the surface, which stabilizes the promoted electron. This explains the experimental results of Kobayashi and coworkers who observed CO$_2$ formation on ZnO surfaces by two reaction paths. We also find that CO$_2$ can bind strongly to Zn$^+$ defect sites as bent CO$_2^-$.

We find CO is attracted to a coadsorbed Al atom on Ni(111) surfaces, forming a non-linear Al-OC-Ni complex with low vibrational frequency. The bonding is characterized by 5$\sigma$ and $\pi$ donation to empty 3p orbitals which allows increased $\pi^*$ back-donation. This gives an electronic explanation for the activation of CO on Ni-Al alloy surfaces observed by Rao et al. and Yates and coworkers. When
trapped in Ni matrices CO again exhibits a large decrease in vibrational frequency. Our calculations show this is due to an interstitial defect structure where Ni atoms contact both C and O ends and back-donate to the empty π* orbitals.

Theoretical evidence is given that OCH$_3$, which is known to spill over from supported Ni and Pt to the alumina support, moves as an anion, OCH$_3^-$, from one Al$^{3+}$ site to another, paired with a proton which moves from one O$^{2-}$ site to another. The reaction of this heterolytically adsorbed pair to form CH$_4$(g) is calculated to be more stabilizing than CH$_3$OH(g) formation. Our findings provide a possible explanation for recent experimental observations of others regarding CO methanation over Ni/Al$_2$O$_3$ and Pt/Al$_2$O$_3$.

O$^-$ hole centers produced by charge transfer photoexcitation in W$_{10}$O$_{32}^{4-}$ abstract H from alkanes as do O$^-$ in numerous solid state and molecular analogs. Upon protonation, forming H$_2$W$_{10}$O$_{32}^{3-}$, this activity increases and this has been modeled with atom superposition and electron delocalization molecular orbital (ASED-MO) calculations by shifting the polyoxometalate valence bands by an amount suggested by the observed decrease in first reduction potential. This strengthens the OH bond that forms at the anion surface when an alkane H is abstracted, and lowers the activation energy for the process. The calculations show that in the absence of acid the resulting alkyl radicals bind weakly to the polyanions because the binding is reductive, promoting an electron to the empty W 5d band, but electron transfer to this band is possible for secondary and tertiary carbon radicals over W$_{10}$O$_{32}^{4-}$, yielding carbocations. In acidic media, the stronger oxidant H$_2$W$_{10}$O$_{32}^{2-}$ is likely to be capable of oxidizing primary carbon radicals and methyl radicals.

Experiments have shown that the addition of CO to a Rh dimer complex with an acyl ligand (bound to a silica support) causes decarbonylation accom-
panied by Rh–Rh bond breaking. This is in opposition to known homogeneous reactions. Based on ASED-MO calculations, we find that the driving force for decarbonylation is the stability of the nearly square planar d$^8$ Rh that is formed:

$$\text{C}_5\text{Me}_5\text{Rh} - \text{RhCOC}_2\text{H}_5 + \text{CO} \rightarrow \text{C}_5\text{Me}_5\text{Rh} \cdots \text{OC} - \text{Rh} - \text{C}_2\text{H}_5$$

Here the Rh–Rh bond has been cleaved and a CO of the complex on the right forms a weak σ-donation bond with the Rh on the left.
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Chapter 1

Introduction

The most important catalytic reactions with the participation of carbon monoxide are reactions involving its reduction, leading to a system of hydrocarbons and oxygen-containing products. Even with modern high vacuum surface spectroscopies, the details of the reaction mechanisms are only now beginning to be charted. Quantum theory calculations and predictions are playing a substantial role in developing the understanding of these reactions. In this dissertation, the atom superposition and electron delocalization molecular orbital (ASEM-MO) theory has been used to study the electronic and structural factors responsible for CO oxidation over ZnO, CO activation on Al-Ni alloys, CO methanation on the alumina support, methane activation by decatungstate anion, and CO insertion to form acyl on a Rh-dimer complex.

CO reacts readily with surface O on ZnO to form CO$_2$ which can immediately bind to O$^{2-}$ to form surface carbonate. The reaction with isolated O$^-$ has a higher barrier because O$^-$-CO bond formation promotes the electron to the surface conduction band. In this case there is a strong driving force for CO$_2$ desorption. CO$_2$ can rebind to the surface. The results are explored in Chapter 3. CO adsorbs on Al-Ni alloys, forming a non-linear Al-OC-Ni complex with low vibrational frequency. When trapped in Ni matrices CO again exhibits a large decrease in vibrational frequency. A molecular orbital discussion of these is given in Chapter 4. The mobility of OCH$_3$ and H and their reaction to form CH$_4$ on Al$_2$O$_3$ are analyzed in Chapter 5. O$^-$ hole centers created by charge
transfer photoexcitation in $\text{W}_{10}\text{O}_{32}^4^-$ abstract H from alkanes. Upon protonation this activity increases, strengthening the OH bond and lowering the activation energy for the process. The alkane oxidation products are affected in the presence of acid. This is explained in Chapter 6. CO inserts into the metal-alkyl bond to form acyl groups in a Rh-dimer complex bound to silica. The decarbonylation reaction occurs on addition of CO, accompanied by the cleavage of Rh–Rh bond. A theoretical examination of the electronic structure of these complexes and some potential reaction intermediates to understand the Rh–Rh bond cleavage is given in Chapter 7.
Chapter 2

Theory

The atom superposition and electron delocalization molecular orbital (ASED-MO) theory\(^1\) is based on the Hellmann-Feynmann force theorem.\(^2\) This theorem states that the quantum mechanical force acting on a nucleus in a molecule is equal to the electrostatic forces due to the presence of all the other nuclei and the electronic charge density distribution in a molecule. Thus for a diatomic molecule \(a-b\), the force acting on nucleus \(b\) is given by\(^3\)

\[
F(R_b) = -\nabla_{R_b} \frac{Z_a Z_b}{|R_b|} + \int \frac{Z_b \rho_{ab}(r, R_b) \nabla_{R_b} \frac{1}{|R_b - r|}}{|R_b - r|} \, dr, \quad (2.1)
\]

where the origin of the coordinate system is on nucleus \(a\) and \(R_b\) is the positional vector of nucleus \(b\), \(\nabla_{R_b}\) is the gradient operator for the position of nucleus \(b\), \(Z_a\) and \(Z_b\) are nuclear charges of the atoms, \(\rho_{ab}\) is the electronic charge density distribution function of the molecule, and \(r\) is the electronic coordinate. The basis of the ASED-MO theory lies in separating the electronic charge density function of a molecule into a sum of rigid free-atom parts and a delocalized bond charge component. In a diatomic system, the molecular charge density is given thusly by

\[
\rho_{ab}(r, R_b) = \rho_a(r) + \rho_b(R_b - r) + \rho_d(r, R_b). \quad (2.2)
\]

where the \(\rho_a(r)\) and \(\rho_b(R_b - r)\) are atomic charge densities centered on nucleus \(a\) and nucleus \(b\) respectively, and integration of each of them over the whole space yields nuclear charge of each neutral atom. \(\rho_d(r, R_b)\) is an electron delocalization or charge density for bond formation and its integration over the space becomes
zero. Equation (2.2) is schematically illustrated in Fig. 2.1. Substituting Eq. (2.2) into Eq. (2.1), yields

\[
F(R_b) = -\nabla_{R_b}\frac{Z_a Z_b}{|R_b|} + \int Z_b \rho_a(r) \nabla_{R_b} \frac{1}{|R_b - r|} \, dr \\
+ \int Z_b \rho_b(R_b - r) \nabla_{R_b} \frac{1}{|R_b - r|} \, dr \\
+ \int Z_b \rho_d(r, R_b) \nabla_{R_b} \frac{1}{|R_b - r|} \, dr.
\] (2.3)

The sum of the first and second terms on the right-hand side of Eq. (2.3) produces a net repulsive force symbolized by \( F_R \) because the nuclear repulsion component of this force increases more rapidly than the attractive force of \( \rho_a \) due to penetration of the \( \rho_b \) charge cloud. The third term becomes zero since the average force acting on the nucleus \( b \) due to \( \rho_b \) is zero. The fourth term is attractive due to the bond formation between \( a \) and \( b \) and is symbolized by \( F_D \). Consequently Eq. (2.3) simplifies to

\[
F(R_b) = F_R + F_D.
\] (2.4)

where

\[
F_R = -\nabla_{R_b}\frac{Z_a Z_b}{|R_b|} + \int Z_b \rho_a(r) \nabla_{R_b} \frac{1}{|R_b - r|} \, dr
\] (2.5)

\[
F_D = \int Z_b \rho_d(r, R_b) \nabla_{R_b} \frac{1}{|R_b - r|} \, dr.
\] (2.6)

As the atoms bond together forming a molecule, the electrostatic forces on nucleus \( b \) are integrated to yield a superposition repulsion energy \( E_R \) caused by atom \( a \) and an attractive energy \( E_D \) due to electron delocalization. The molecular binding energy curve, \( E \), is then the sum of the two nonzero components:

\[
E(R_b) = E_R(R_b) + E_D(R_b)
\] (2.7)
Figure 2.1: Schematic of electronic charge density components for a diatomic molecule.
where the individual energy terms $E_R$ and $E_D$ have the following forms

$$E_R(R_b) = Z_b \left( \frac{Z_a}{|R_b|} - \int \frac{\rho_a(r)}{|R_b - r|} dr \right)$$

(2.8)

$$E_D(R_b) = -Z_b \int_{\infty}^{R_b} \int \rho_d(r, R_{b'}) \nabla_{R_{b'}} \frac{1}{|R_{b'} - r|} dr dR_{b'}.$$  

(2.9)

A potential energy curve of $E$, $E_R$, and $E_D$ as functions of $R_b$ for a diatomic molecule is shown in Fig. 2.2. $E_R$ is easily calculated using available atomic orbitals to generate $\rho_a$, but $E_D$ cannot be obtained from Eq. (2.9) since $\rho_d$ is unknown. Nevertheless, the electron delocalization energy has been found to be well approximated by the change in one-electron extended Hückel molecular orbital energy, $\Delta E_{MO}$, that occurs with bond formation:

$$E_D \approx \Delta E_{MO} = \sum_i n_i \epsilon_i^a - \sum_i n_i \epsilon_i^b - \sum_i n_i \epsilon_i^b$$

(2.10)

where $\epsilon_i^{ab}$ are the valence molecular orbital energies, $\epsilon^a$ and $\epsilon^b$ are the valence atomic orbital energies, and $n_i$ are the orbital occupation numbers (0, 1 or 2), $i$ sums over all atomic and molecular orbitals. This intuitively reasonable discovery yields ASED-MO theory.

The energy of a polyatomic molecule can be derived by the same procedure, in which case we have

$$E = E_R + \Delta E_{MO}$$

(2.11)

where

$$E_R = \sum_{i < b} E_{R}^{ab}(R_{ab})$$

(2.12)

$$E_{R}^{ab}(R_{ab}) = Z_b \left( \frac{Z_a}{|R_a - R_b|} - \int \frac{\rho_a(r)}{|R_b - r|} dr \right)$$

(2.13)
Figure 2.2: Diatomic potential energy curve and energy components as functions of internuclear distance $R$. 
\[ \Delta E_{MO} = \sum_i n_i \varepsilon_i^{MO} - \sum_a n_a \varepsilon_a, \] (2.14)

We set the \( \varepsilon^a \) equal to the negative of the valence state ionization potentials, \( IP^a \). The \( \varepsilon^{MO} \) are calculated by diagonalizing a modified extended Hückel Hamiltonian with matrix elements

\[ H_{ii}^{aa} = \varepsilon_i^a = -IP_i^a \] (2.15)

\[ H_{ij}^{aa} = 0 \] (2.16)

\[ H_{ij}^{ab} = 1.125(H_{ii}^{aa} + H_{jj}^{bb})S_{ij}^{ab} e^{-0.13R} \] (2.17)

where \( S_{ij}^{ab} \) is the overlap integral between orbital \( i \) on center \( a \) and orbital \( j \) on center \( b \), \( \langle \psi_i^a | \psi_j^b \rangle \), and \( R \) is the internuclear distance. The \( IP \)'s are experimentally based,\(^7\) and the valence orbitals are of the Slater form with exponents based on SCF calculations.\(^7\)

In Eq. (2.11) the two-body repulsion energy component of \( E_R \) depends on atomic orbital exponents which determine the radial extensions. \( \Delta E_{MO} \) depends on the atomic orbital ionization potentials and also on the orbital exponents. For homonuclear diatomic molecules, the Slater orbital exponents are adjusted to produce suitable bond lengths. In ionic heteronuclear diatomic molecules, charge transfer takes place and consequently the \( IP \)'s and orbital exponent parameters are systematically adjusted until the charge transfers are close to the ones predicted from Pauling's electronegativity differences and the bond lengths are close to estimated values. Usually such adjustments are made for diatomic fragments and the resulting parameters are then used for studying the larger systems.

For heteronuclear bonds, there are two equivalent ways of evaluating \( E \) by using Eq. (2.7), either by integrating the force on nucleus \( a \) or by integrating
the force on nucleus \( b \): the \( E_R \) and \( E_D \) components are different, but their sum is the same. When the \( E_{MO} \) approximation to \( E_D \) is used, it is usually preferable to evaluate \( E_R \) by integrating the force on the nucleus of the less electronegative atom of each pair that is due to the density distribution, including the nuclear charge, of the more electronegative atom.

The extended Hückel method relates to Hartree-Fock framework. To understand the \( \Delta E_{MO} \) approximation to \( E_D \), the one-electron Fock operator, \( \hat{F}(1) \), for a closed-shell molecule is applied. Let us assume the potential energy of an electron on atom \( a \) in one molecule can be partitioned into intraatomic parts, \( \hat{V}_a \), which include interactions only with electrons and nucleus on atom \( a \), and interatomic parts, \( \hat{V}_{ab} \), which are the potentials due to atom \( b \):

\[
\hat{F}(1) = -\frac{1}{2} \nabla_i^2 + \sum_a \hat{V}_a + \sum_{b\neq a} \hat{V}_{ab}
\]  

(2.18)

then diagonal elements \( F_{ii}^{aa} \) are valence state ionization energies for atomic orbitals when the \( \hat{V}_{ab} \) is neglected.

\[
F_{ii}^{aa} \cong < \psi_i^a | -\frac{1}{2} \nabla^2 + \hat{V}_a | \psi_i^a > \cong E_i^a \cong -IP_i^a
\]  

(2.19)

where \( \psi_i^a \) is an eigenfunction and \( E_i^a \) its eigenvalue. \( IP_i^a \) is the ionization potential for \( \psi_i^a \). It may be noted that the neglected summation may be introduced parametrically if desired. Off-diagonal \( F_{ij}^{aa} \) must be zero due to orthogonality and the remaining off-diagonal elements are approximated as follows:

\[
F_{ij}^{ab} = < \psi_i^a | -\frac{1}{2} \nabla^2 + \sum_c \hat{V}_c | \psi_j^b >
\]

\[= \frac{1}{2} < \psi_i^a | -\frac{1}{2} \nabla^2 + \hat{V}_a + \sum_{c\neq a} \hat{V}_c | \psi_j^b > + \frac{1}{2} < \psi_i^a | -\frac{1}{2} \nabla^2 + \hat{V}_a + \sum_{c\neq b} \hat{V}_c | \psi_j^b >
\]  

(2.20)
The neglect of $\hat{V}_{c}$ leads to

$$ F_{ij}^{ab} \equiv \frac{1}{2} (E_i^a + E_j^b) S_{ij}^{ab} $$

(2.21)

Eqns. (2.19) and (2.21) are the extended Hückel Hamiltonian, wherein $1.75/2$ is used in place of $1/2$ in Eq. (2.21). Eq. (2.17) is a modified form of Eq. (2.21). It may be noted that many other forms for the off-diagonal Hamiltonian have been suggested.\(^8\) Molecular orbital energies, $\epsilon_i^{ab}$, are the solutions of the Fock Hamiltonian and the total electronic energy is

$$ E_{MO} = \sum_i n_i \epsilon_i^{ab} - V_{ee} $$

(2.22)

where $V_{ee}$ is the total electronic repulsion energy. All off-center interatomic contributions to $V_{ee}$ are neglected, but on-center intraatomic contributions are included because experimental values for the $E_i$ are employed. Therefore the total molecular orbital energy must be written as

$$ E_{MO} = \sum_i n_i \epsilon_i^{ab} - \sum_a V_{ee}^a $$

(2.23)

Since $\Delta E_{MO}$ is the difference between atomic and molecular electronic energies

$$ \Delta E_{MO} = \sum_i n_i \epsilon_i^{ab} - \sum_a V_{ee}^a - \sum_a \sum_i n_i \epsilon_i^a + \sum_a V_{ee}^a $$

(2.24)

The cancellation of the intraatomic electron repulsions reduces this to the form of Eq. (2.14). Although all off-center nucleus-electron attractions terms are removed from the Fock Hamiltonian, they are present in the electrostatic determination of $E_R$ in Eq. (2.11). Now the ASED-MO method contains all the interactions except off-center electronic repulsive interactions.

The ASED-MO theory described above has been used to predict molecular structures, stabilities, electronic properties and reaction mechanisms. It
is possible to obtain vibrational force constants if $\rho_d$ behaves like rigid point charges during vibrations. The harmonic force constant can be found by taking the divergence of the force according to Hooke’s law. The divergence of the Hellmann-Feynman force on a nucleus in a molecule produces the Laplacian of the total electronic energy, $E$, as given in Eq. (2.7). Therefore, starting with Eq. (2.7), the Laplacian yields

$$\nabla^2_{R_b} E(R_b) = \nabla^2_{R_b} E_R(R_b) + \nabla^2_{R_b} E_D(R_b)$$

$$= \nabla^2_{R_b} \frac{Z_b Z_a}{|R_b|} - Z_b \int \rho_d(r) \nabla^2_{R_b} \frac{1}{|R_b - r|} dr$$

$$- Z_b \int \nabla_{R_b} \rho_d(r, R_b) \nabla_{R_b} \frac{1}{|R_b - r|} dr$$

$$- Z_b \int \rho_d(r, R_b) \nabla^2_{R_b} \frac{1}{|R_b - r|} dr$$

(2.26)

Since $\rho_d$ is assumed to be a point charge, the last two terms on the right-hand side of Eq. (2.26) are zero. The first term is also dropped by introducing the Dirac delta function $\delta(R)$. $\nabla^2_{R_b} 1/R = -4\pi \delta(R)$, since $\delta(R)$ is zero here. The second term becomes $4\pi Z_b \rho_a(R_b)$ at $R_b = r$. Then, the classical Poisson equation for nuclear motions is obtained.

$$\nabla^2_{R_b} E(R_b) = 4\pi Z_b \rho_a(R_b)$$

(2.27)

For a stretching vibrational mode, eq.(2.27) can be written as

$$\nabla^2_{R_b} E(R_b) = \frac{\partial^2 E(R_b)}{\partial R_b^2} + \frac{2}{R_b} \frac{\partial E(R_b)}{\partial R_b}$$

(2.28)

This equation, when evaluated at the equilibrium internuclear distance, yields the quadratic force constant, $k_e$, since the second term on right-hand side becomes zero. Then $k_e$ is given as

$$k_e = 4\pi Z_b \rho_a(R_e)$$

(2.29)
where $R_e$ is the equilibrium internuclear distance. Higher derivatives of eq. (2.28) yield higher order force constants.$^9$
Chapter 3

CO Oxidation Mechanisms over ZnO.
Molecular Orbital Theory

3.1 Introduction

The reactions of CO and CO$_2$ on ZnO-based catalysts under reducing conditions leading to methanol synthesis have been studied extensively during the past decade.$^{1-13}$ The catalytic oxidation of CO over ZnO has also been known for a long time.$^{14}$ Two recent reports have given new insight into the CO oxidation reaction.$^{15,16}$ A kinetic study by Kobayashi et al.$^{15}$ of CO oxidation to CO$_2$ over partially reduced ZnO showed that there are two reaction paths ($I$ and $II$). For path $I$, the proposed model is the surface reaction of gaseous CO with O$^-$, followed by the rapid desorption of CO$_2$ formed. Path $II$ is controlled by both the surface reaction of gaseous CO with neutral atomic oxygen species and the desorption of CO$_2$ formed. This is summarized as follows:

Path $I$

$$
\text{CO} + \text{O}^- (\text{ads}) \xrightarrow{k_I} \text{CO}_2(\text{ads}) + e^- \xrightarrow{\text{fast}} \text{CO}_2(\text{g}) + e^-
$$

$$E_I^* = 1.11\text{eV}$$

Path $II$

$$
\text{CO} + \text{O}(\text{ads}) \xrightarrow{k_{II}} \text{CO}_2(\text{ads}) \xrightarrow{\text{slow}} \text{CO}_2(\text{g}) \xrightarrow{\Delta H_{II}}
$$

$$E_{II}^* = 0.31\text{eV}$$

$$\Delta H_{II} = 1.30\text{eV}$$
The surface $O^-$ and $O$ species were created by partially reducing ZnO powders by heating, followed by cooling and introducing $O_2$ which, according to ESR, adsorbed as $O_2^-$ at low temperature and, on warming to 190 °C was gone, having evidently dissociated to $O$(ads) and $O^-$(ads). The kinetic studies were carried out over a 190-250 °C range.

Low temperature adsorption of CO and $CO_2$ on $O_2$-annealed and defect $O^{2-}$-covered polar ZnO(0001) basal $\rho$ plane surfaces was studied by Au et al.\textsuperscript{16} using photoelectron spectroscopy (XPS and UPS). The same carbonate-like intermediate formed when CO was adsorbed on ZnO(0001) annealed in oxygen and when $CO_2$ was adsorbed on ZnO(0001) that had been ion-bombarded to create oxygen vacancy defects. Little $CO_3^{2-}$ formed when the annealed surface was exposed to $CO_2$.

Thermal desorption studies have shown a variety of states for adsorbed $CO_2$ on various ZnO surfaces. Physisorbed $CO_2$ desorbed between −173 and −128 °C and chemisorbed $CO_2$ in the form of surface carbonate was completely desorbed at about 127 °C from the defect (0001) surface studies by Au et al.\textsuperscript{16} Cheng and Kung found the corresponding TDS peak for the chemisorbed form created by low temperature exposure appeared at 125 °C on (0001), (5051), (4041), and (1010) surfaces.\textsuperscript{17} A second chemisorbed form has been seen on partially reduced defect surfaces with a TDS peak at 190 °C.\textsuperscript{17} This has been suggested to be $CO_2^-(ads)$ and has been ascribed importance as an intermediate during catalytic CO oxidation on ZnO.\textsuperscript{18} Another high temperature form, with a TDS peak at 400 °C, is characteristic of $CO_2$ adsorbed on the Zn-covered (0001) basal plane of the partially reduced oxide.\textsuperscript{17} The form of the adsorbed $CO_2$ has not been established in this case. In another study\textsuperscript{19} new $CO_2$ desorption temperatures were observed when $CO_2$ was adsorbed on ZnO heated above room
temperature. These states were attributed to adsorption at surface defects which migrate from the bulk at elevated temperatures.

The structural, electronic, and CO adsorption properties of (0001) and (10\(\bar{1}\)0) ZnO surfaces were characterized in recent molecular orbital studies employing cluster models.\textsuperscript{20,21} Relaxations of Zn\(^{2+}\) toward the bulk of 0.35 Å and 0.40 Å on the (0001) and (10\(\bar{1}\)0) surfaces were in close agreement with experimental LEED determinations.\textsuperscript{22} An O\(^{2-}\) relaxation of 0.15 Å toward the bulk also agreed well with experiment. CO adsorption caused Zn\(^{2+}\) to shift 0.1 Å above the bulk-like position and the calculated adsorption energy of 12 Kcal/mol matched experiment.\textsuperscript{22} Dangling s-p surface state orbitals with energies in the O 2p–Zn 4s, 4p band gap were available for the weak CO 5\(\sigma\) donation chemisorption bonding to 3-coordinate surface Zn\(^{2+}\). This increased the CO vibrational force constant, as seen experimentally.\textsuperscript{23} On clusters with 2-fold coordinated Zn\(^{2+}\) new band gap states above and below formed due to orbitals centered on these cations.

It is to be expected that Zn\(^{2+}\) surface dangling orbitals will be important to CO oxidation by O\(^{-}\) because an electron is released by the reaction

\[
\text{CO}(g) + \text{O}^-(\text{ads}) \longrightarrow \text{CO}_2(g) + e^- 
\]

This electron will be most stable in a dangling surface band gap orbital:

\[
\text{Zn}^{2+} + e^- \longrightarrow \text{Zn}^+ 
\]

In this chapter we present results of a molecular orbital study of CO oxidation by O\(^{-}\) and O at the surface of ZnO and we examine the binding of CO\(_2\) to the ZnO surface in the form of CO\(_3^2-\) and CO\(_2^-\). The method, along with cluster models similar to those of the above CO adsorption work are used.
3.2 Models

The atom superposition and electron delocalization molecular orbital (ASEDMO) theory\textsuperscript{24} is in conjunction with surface cluster models. Atomic parameters used in these calculations given in Table 3.1 are from Ref. (21).

3.3 CO oxidation by O\textsuperscript{-} on ZnO

Since the kinetic measurements of Ref.(15) were done over ZnO powder, no surface structure information is available for assigning coordinations for the O and O\textsuperscript{-} which are responsible for CO oxidation by paths I and II. Consequently, we have begun by choosing bulk superimposable cluster models of the (10\overline{1}0) surface with exposed Zn\textsuperscript{2+} and O\textsuperscript{2-}. Figure 3.1 shows a Zn\textsubscript{11}O\textsubscript{11} cluster which has some surface Zn\textsuperscript{2+} in 3-fold and some in 2-fold coordination. The central surface O pointed out by the arrow was chosen for reacting with CO to make CO\textsubscript{2}. If this were initially an O vacancy site for the partially reduced defect surface, then O\textsubscript{2} could bind to the vacancy and dissociate, placing O\textsuperscript{-} at the site and O somewhere on the surface. The presence of 2-fold coordinated Zn\textsuperscript{2+} may be characteristic of the defect surface and, as shown in Fig. 3.2, band gap states due to both 2- and 3-coordinate Zn\textsuperscript{2+} are separated, with a lower gap to the 2-coordinate Zn\textsuperscript{2+} dangling orbitals.

With the valence bands of the Zn\textsubscript{11}O\textsubscript{11} cluster occupied with electrons so that there is one hole at the top of the O 2p band, an activation energy of 1.36 eV is calculated for binding CO to the surface O\textsuperscript{-}. At the transition state the CO axis is in the tetrahedral orientation and the CO bond actually shrinks by 0.02 Å from the calculated free molecule value of 1.11 Å (experiment gives 1.13 Å). This bond length decrease is caused by 5σ donation (Fig. 3.2); the delocalization
Table 3.1: Atomic parameters used in the calculations: principal quantum numbers, $n$, ionization potentials, $IP$ (eV), Slater orbital exponents, $\zeta$ (a.u.), linear coefficients for double-zeta d orbitals, $c$.

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Figure 3.1: Bulk superimposable Zn$_{11}$O$_{11}$ cluster model. The top plane of the model lies in the (1010) surface. Arrow indicates O to which CO bonding is studied.
Figure 3.2: Electronic structures of CO and Zn$_{11}$O$_{11}$ and the transition state for CO binding to O$^-$ at the site indicated by the arrow in Fig. 3.1.
of electrons in the weakly antibonding $5\sigma$ orbital strengthens the bond. The adsorbate C–surface O distance is 2.02 Å in the transition state. As is evident in Fig. 3.2, the formation of the new $\sigma$ bonding orbital from overlap of the CO $5\sigma$ and surface O 2p orbitals leads to promotion of an electron and the hole in the antibonding $\sigma^-$ counterpart orbital. This promotion gives the reaction its barrier.

When the 2-coordinate Zn$^{2+}$ of the Zn$_{11}$O$_{11}$ cluster are capped with O$^{2-}$ so that all surface Zn$^{2+}$ are 3-coordinate, band gap states due to 2-coordinate Zn$^{2+}$ disappear from Fig. 3.2. Now when CO binds to the O$^-$ the electron must be promoted to the higher 3-coordinate Zn$^{2+}$ surface band, resulting in a higher activation energy, calculated to be 1.98 eV.

The 1.36 eV activation energy for forming CO$_2$ adjacent to 2-coordinate Zn$^{2+}$ is closer to the experimental 1.11 eV activation energy than the value calculated for the adjacent 3-coordinate Zn$^{2+}$. However, in the 3-coordinate Zn$^{2+}$ case there is a strong driving force for CO$_2$ desorption, namely the stability the 3-coordinate Zn$^+$ achieves when it becomes 2-coordinate upon CO$_2$ desorption so that the promoted electron drops into the lower band gap state. Since there is uncertainty in the energies of the surface states the activation energy for CO oxidation by O$^-$ adjacent to 3-coordinate Zn$^{2+}$ could be less than calculated. As shown in Fig. 3.3, ASED-band calculations with the same parameters set yield a bulk band gap about double the 3.4 eV experimental optical value. Also shown in this figure are electronic structures for 4- and 6-layer slab band calculations for slabs terminating in (0001) O$^{2-}$ and (0001) Zn$^{2+}$ basal planes. The surface Zn$^{2+}$ dangling orbitals form a narrow band 2.8 eV above the top of the filled O 2p band. These levels are in the same position as for the clusters but the top of the O 2p band is 0.5 eV higher. This means the promotion energy of the electron
Figure 3.3: Electronic structures calculated using the ASED-band theory for bulk ZnO and 4-layer and 6-layer slabs terminating in (0001) Zn$^{2+}$ covered and (0001) O$^{2-}$ covered basal planes.
would be about 0.5 eV less and the activation energy for the CO + O\(^{-}\) would decrease about 0.5 eV to \(\sim\)1.5 eV on the extended (10\(\bar{1}\)0) surface. The activation energy in the presence of 2-coordinate Zn\(^{2+}\) would also decrease. Not only this, but since the bulk band gap is overestimated, the Zn\(^{2+}\) dangling surface orbital band positions are uncertain and might be lower, and if they are lower the calculated activation energy would decrease.

Reaction energies and structures are given in Fig. 3.4. The transition state for CO + O\(^{-}\) in the presence of 3-coordinate Zn\(^{2+}\) shows a CO bond stretch of 0.06 Å because this allows the CO \(\pi^{*}\) orbitals to become stable and accept the electron that is promoted in the O\(^{-}\)-CO \(\sigma^{*}\) orbital. When bonding is complete there is a net stabilization prior to CO\(_{2}\) desorption of 0.96 eV in the presence of 3-coordinate Zn\(^{2+}\) and 2.19 eV in the presence of 2-coordinate Zn\(^{2+}\). The structures of CO\(_{2}\) in both cases are essentially the same. The difference in stabilities reflects the difference in band gap surface dangling orbital to which the electron is promoted. To calculate an approximate value for the CO\(_{2}\) desorption energy a parameter change is necessary. When the parameters of the surface O to which the CO is bound are set equal to the free atom values the upper CO bond length becomes 1.13 Å and the lower one becomes 1.14 Å and it costs 0.15 eV to desorb CO\(_{2}\) from the site adjacent to 2-coordinate Zn\(^{+}\). Desorption from the site adjacent to 3-coordinate Zn\(^{+}\) is exothermic by 1.11 eV. In the latter case CO\(_{2}\) desorption is stabilizing, so if CO\(_{2}\) forms by this higher activation pathway it will desorb very rapidly.
Figure 3.4: Reaction energies and structures. a. CO oxidation by O$^-$ adjacent to 2-coordinate Zn$^{2+}$. b. CO oxidation by O$^-$ adjacent to 3-coordinate Zn$^{2+}$. c. CO oxidation by O.
3.4 CO oxidation by O on ZnO

According to Ref. (15), surface O is formed from the adsorption of O$_2$ at a reduced defect site, forming O$^-$ which dissociates below 190 °C. Where O sits in or on the surface is not known, so the same structure model as for O$^-$ was used, but with 2 holes in the top of the O 2p band. Results for the CO + O reaction using this model are in Fig. 3.4. The activation energy is only 0.25 eV, close to the experimental value of 0.31 eV for path II. The barrier is low because there is no electron promotion to surface dangling orbitals in the band gap. CO binds to the surface O with considerable stability. When the O to which CO binds is given free atom parameters, the above-mentioned relaxations occur and the CO$_2$ desorbs with a stability gain of 0.09 eV. The overall calculated gas phase CO + O $\rightarrow$ CO$_2$ reaction energy in 7.45 eV, compared to 5.46 eV from standard enthalpies. Calculated CO bond lengths are 1.13 Å compared to the experimental 1.16 Å.

There is experimental evidence\textsuperscript{25} for the presence of substantial amounts of O$^-$ on the (000$\overline{1}$) surface after exposure to O$_2$. This suggests the possibility of 2 nearby O$^-$ being involved in CO oxidation. The net reaction in this case would be CO + 2O$^-$($s$) $\rightarrow$ CO$_2$(ads) + O$_2^-$(s) and this would proceed with a low barrier because the electron is promoted to a hole level at the top of the O 2p band, just as when CO binds to surface O, instead of to the higher-lying surface conduction band. This is a likely ancillary or alternative reactin to the reaction of CO with surface O.

3.5 Binding of CO$_2$ to Zn$^+$

Because an empty $2\pi_u$ orbital of CO$_2$ becomes stable when the molecule is bent and is able to take an electron from the dangling orbital of Zn$^+$. CO$_2$ binds to Zn$^+$
in the surface. Orbital interactions are shown in Fig. 3.5 for CO$_2$ binding to Zn$^+$ in a Zn$_{13}$O$_{13}$ model of the cation terminated (0001) surface and the structure is in Fig. 3.6. The calculated adsorption energy to the 3-coordinate Zn$^+$ is 1.89 eV. The CO$_2$ rotational energy barrier is $< 0.01$ eV. From the electronic structure in Fig. 3.5 it can be seen that if the Zn$^+$ were 2-coordinate, the CO$_2$ binding energy would be reduced to about 0.5 eV since the bottom of the 2-coordinate Zn surface band is 1.4 eV lower. The more tightly bound form appears to correspond to the 190°C thermal desorption peak in the literature.$^{17,18}$ If CO$_2$ formed from the O$^- +$ CO reaction were to rebind through C to 2-coordinate Zn$^+$, forming Zn$^{2+}$-CO$_7^-$, it would be expected to desorb at the temperatures of the kinetic study of Ref. (15). CO$_2$ will not adsorb to Zn$^{2+}$ through C according to the calculations. This is because the half-filled Zn–C $\sigma$ bonding orbital of Fig. 3.5. is empty in the case of Zn$^{2+}$.

3.6 Binding of CO$_2$ to ZnO

It is postulated in Ref. (15) that the CO$_2$ formed by path II can become adsorbed on the surface and within this kinetic model the desorption energy is 1.30 eV. This is larger than the ZnCO$_3$(s) $\rightarrow$ ZnO(s) + CO$_2$(g) standard reaction enthalpy of 0.74 eV, but the two processes are not exactly comparable. The adsorption of CO$_2$ to surface O$^{2-}$ is modeled the same way as was done for its adsorption to Zn$^+$: gas phase CO$_2$ parameters are used at first and an adsorption energy on the anion covered (000\overline{1}) surface modeled by Zn$_{13}$O$_{13}$ of 1.07 eV is obtained with the optimized structure shown in Fig. 3.7. The calculated activation energy is only 0.08 eV. The CO bond lengths are close to the experimental value of 1.30 Å, typical for a carbonate anion. The formation of the O–CO$_2$ bond is shown in
Figure 3.5: Orbital correlations for CO₂ binding to Zn⁺ on Zn₁₃O₁₃ representing the cation covered (0001) surface.
Figure 3.6: Structure of CO$_2$ adsorbed to surface Zn$^+$ to form CO$_2^-$ on the Zn$_{13}$O$_{13}$(0001) surface cluster model.
Figure 3.7: Structure of CO$_2$ adsorbed to surface O$^{2-}$ on a Zn$_{13}$O$_{13}$ cluster model of the anion covered (0001) surface.
Fig. 3.8. Since the anion bears a negative charge, a calculation was made with the O\(^{2-}\) parameters on all O atoms and the C 2s and C 2p ionization potentials were also decreased 2.5 eV, just as for O\(^{2-}\). This 2.5 eV shift is the order of magnitude of the O 1s and C 1s core ionization potential decrease on going from CO\(_2\) to CO\(_3^{2-}\) on ZnO as measured by XPS.\(^{10}\) The resulting CO bond lengths increase to values 0.12 Å greater than experiment, largely because of the increased size of O\(^{2-}\). It is evident that a smaller decrease in O 2s and O 2p Slater orbital exponents is appropriate for CO\(_3^{2-}\) than for O\(^{2-}\), which is reasonable since the negative charge is delocalized over 3 O in the carbonate anion.

Bidentate binding of CO\(_3^{2-}\) over the O\(^{2-}\) vacancy site of the (10\(\bar{1}\)0) surface was explored using shifted O and C parameters. A small additional stability was obtained for CO\(_3^{2-}\) bridging two Zn\(^{2+}\). Our calculations apparently underestimate the observed 1.30 eV CO\(_2\) desorption energy from surface CO\(_3^{2-}\), by \(\sim\)0.2 eV.

Whereas CO\(_2\) does not bind to Zn\(^{2+}\) through C, it does through O by \(\sigma\) donation. The adsorption energy is calculated to be 0.35 eV on the 3-coordinate Zn\(^{2+}\) of a Zn\(_{11}\)O\(_{11}\) model of the (10\(\bar{1}\)0) surface: the structure is in Fig. 3.9. The \(\sigma\) donation interactions are visible in Fig. 3.10.

3.7 Conclusions

Our calculations support the two path mechanism for CO oxidation to CO\(_2\) in the presence of O\(_2\) over defective (partially reduced) ZnO. O\(^-\) formed from the adsorption of O\(_2\) to form the superoxide anion O\(_2^-\) which dissociates and reacts with CO impinging from the gas phase to form CO\(_2\) plus an electron promoted to the surface conduction band. The activation energy for this process over the (10\(\bar{1}\)0) surface is \(\sim\)1.5 eV, comparable to the experimental value of 1.11 eV.\(^{15}\) The
Figure 3.8: Orbital correlations for CO$_2$ binding to O$^{2-}$ on the Zn$_{13}$O$_{13}$(0001) surface cluster model.
Figure 3.9: Structure of CO$_2$ $\sigma$-bonded to a 3-coordinate Zn$^{2+}$ on a Zn$_{11}$O$_{11}$ model of the (10\overline{1}0) surface.
Figure 3.10: Orbital correlations for CO$_2$ $\sigma$-bonded to Zn$^{2+}$ as in Fig. 3.9.
desorption of CO₂ creates a lower-lying 2-coordinate Zn²⁺ dangling surface orbital which stabilizes the promoted conduction band electron. This stabilization should cause rapid dissociation of the CO₂ from the surface. The promoted electron contributes to the rise in surface conductivity that is observed in Ref. (15). This rise is limited by the rate by which these electrons are oxidized by O₂ to reform O⁻ which removes the conduction electrons and the rate by which O⁻ reacts with CO. CO₂ can rebind to the surface, either on O²⁻ to form surface coordinated monodentate CO₂⁻ on the (0001) basal plane, or with slight additional stability, as bidentate CO₃²⁻ on the (1010) prism surface. CO₂ can also bind strongly to 3-coordinate surface Zn⁺ to form coordinated CO₇⁻ and this may also play a role in fixing the surface conductivity during the oxidation reaction by removing electrons from the conduction band.

Surface O atoms, formed by dissociation of O₂⁻, react much more readily with CO, forming CO₂, with a low activation energy as observed for Path II in Ref. (15). This CO₂ is likely to form CO₃²⁻ immediately since there is no surface state electron stabilization accompanying dissociation from the surface. The same energetics are obtained when 2O⁻ are involved in place of O, a possible alternative to the O mechanism.

From these results it is expected that there should be a rapid build-up of CO₂(g) and surface carbonate. This makes the observed instantaneous development of a CO₂ pressure understandable. The subsequent slow increase to a final CO₂ pressure over many minutes, while the surface conductivity remains constant, suggest to us that a surface restructuring involving carbonate is taking place. It would certainly be interesting to explore this chemistry and the surface structure using single crystal faces and surface spectroscopies.

These results also help explain the reactivities of O₂-annealed as well as
defective ZnO(0001) toward CO₂ and CO given in Ref. (16). Given the presence of O⁻ on this surface,²⁵ and the low temperature at which CO₂ and surface carbonate form, it is likely that O or 2O⁻ are involved in the CO oxidation since the activation barriers are low. CO₂, on the other hand, will not bind to O or O⁻ which appears to explain why little CO₃²⁻ formed from CO₂ over the annealed surface. On the defect surface CO₂ can react with O²⁻ to form CO₃²⁻ which is likely to have a bidentate coordination if two Zn²⁺ are available or a monodentate coordination if only one is available. CO can only bind weakly to Zn²⁺ sites and does not form CO₂ or CO₃²⁻ since O⁻ or O are not present.
Chapter 4

Activation of CO on Ni–Al Alloy Surfaces and by Interstitial Trapping in a Ni Matrix. Structure and Electronic Factors from MO Theory

4.1 Introduction

It has recently been found that on aluminum-promoted nickel, adsorbed CO has a greatly weakened stretching frequency compared to CO adsorbed on clean nickel surfaces.\(^1,^2\) The complex structure \(\text{Al}_x-\text{OC}-\text{Ni}_y\) was proposed\(^2\) based on the facts that CO binds perpendicular to clean Ni surfaces through the C atom and that Al is oxophilic. However, CO interacts only by weak physisorption bonding to (100)\(^3\) and (111)\(^4\) Al surfaces. The explanation for this weak absorption lies in the closed-shell repulsive interaction between the occupied CO \(5\sigma\) orbital and occupied Al \(\sigma\) orbitals, which counteracts the effect of Al back-donation bonding to the empty CO \(\pi^*\) orbitals.\(^5\) When Al atoms are bound to Ni, there is evidently a significant bonding interaction between Al and O that is created or amplified by the interaction of the C end of CO with Ni or the interaction of Al with Ni or both.

In the work of Rao et al.\(^1\) the CO vibration, determined by electron energy loss spectroscopy (EELS), on polycrystalline Ni with adsorbed Al was found at 1300 cm\(^{-1}\) and a weak broad signal centered near 2000 cm\(^{-1}\) was also seen at 80 K. The 1300 cm\(^{-1}\) signal was gone on warming to 300 K. The 1300 cm\(^{-1}\) vibration was associated with the activated CO, which dissociated when the surface was warmed. The alloy surface structure was unknown. Yates and
coworkers deposited Ni on Al(111) to prepare surfaces of unknown structure and observed activated CO vibrations over the range of 1370 to 1420 cm⁻¹ depending on Ni coverage, CO exposure, method of deposition, and the temperature of their EELS measurements. They also observed vibrations of CO bound to 1-fold and bridging Ni sites. At low Ni ad-atom coverage and saturation CO coverage only 1-fold CO on Ni was observed at 2050 cm⁻¹. With higher Ni coverages adsorbed CO showed a signal at 1930 cm⁻¹ associated with bridging two Ni atoms and a signal due to activated CO at 1385 cm⁻¹. These did not change position with increasing Ni coverage, but the signal from 1-fold bonded CO increased finally to 2090 cm⁻¹. Less than saturation CO coverages showed some variations in these vibrational signals. Deposition of Ni on the Al(111) surface in the presence of excess CO resulted in 1-fold CO/Ni vibrations from 2055 to 2095 cm⁻¹ and activated CO at 1420 cm⁻¹. Heating resulted in shifts of the activated and unactivated CO peaks and dissociation, but a mixture of 1-fold and bridging forms of unactivated CO was not observed. From this it seems that when Ni is deposited on Al(111) in the presence of excess CO, the surface structure of CO and Ni on Al is different from when Ni is introduced before the CO. The possibility of trapping of CO in a Ni matrix was mentioned by Yates and coworkers. In such cases CO vibrations at ~1500⁹ and ~1610 cm⁻¹⁷-⁸ have been observed and attributed to Ni₂-CO-Ni₃ interaction. Whether this happens for deposition on the Al(111) surface is not known.

The activation of CO on transition metals in the presence of early transition metal oxides has been observed in many Fischer-Tropsch catalyst systems and Burch and Flambard⁹ and Sachtlere¹⁰ have proposed a M'-OC-M structure to account for it. Here M' is a cation from the early transition metal oxide and M is a metal catalyst particle surface atom. Support for this structure and an
explanation for the activation of the CO bond were given in the theoretical study of Anderson and Dowd,\textsuperscript{11} who calculated structures and frequencies for CO adsorbed on a two-layer thick Pt\textsubscript{22} cluster model of the Pt(111) surface with co-adsorbed TiO, FeO, Fe, Pt, and ZnO. The adsorbed CO molecule was attracted to the Fe ad-atom and the cation ends of the TiO and FeO ad-molecules, and it tilted toward them at an angle of 55–65 deg from normal, and stretched 0.02–0.03 Å. Vibrational shifts down to \( \sim 1650 \text{ cm}^{-1} \) were calculated, which were comparable to experimental measurements. On the other hand, the adsorbed Pt atom and ZnO molecule repelled the adsorbed CO molecule: there was no tilting and no bond weakening. The ability of the early transition metal atoms to attract the O end of CO adsorbed on the platinum surface was traced to a CO \( \pi \) donation interaction. Such \( \pi \) donation was predicted to be possible when the O end of CO approaches the early transition metal atom because of d orbital holes which allow a net M'–O bond order to exist. Since this orientation becomes allowed, CO 5\( \sigma \) and 4\( \sigma \) donation stabilization is also increased and so is the back donation from the metal atoms to the CO \( \pi^* \) orbital. Consequently the CO bond order decreases, the bond stretches, and the vibrational frequency decreases. The same theoretical effects were found to explain CO bond weakening when adsorbed on Pt\textsubscript{3}Ti,\textsuperscript{12} Cr(110),\textsuperscript{13} and (111) and (100) Fe\textsuperscript{14} surfaces. Fe marked a borderline region of the transition metal series where CO orientation depended on surface structure: on the closest packed (110) surface CO was most stable on a high-coordinate site in the upright position. In the case of coadsorbed ZnO and Pt on the Pt(111) surface mentioned earlier, the absence of d holes made the CO \( \pi + \) M' d interaction become a substantial closed-shell repulsion when CO approached M' and tilted, so it assumed the usual upright orientation and was not activated by these species. As discussed in Refs.(11–14) these theoretical findings are in
accord with experimental observations.

When strongly electropositive alkali metal atoms are adsorbed on Pt at low coverages, there is another effect that explains observations of changes in binding sites and vibrational frequencies of coadsorbed CO. Garfunkel et al.\textsuperscript{15} found that with increasing coverage by potassium, some CO molecules adsorbed at high coordinate sites in addition to the usual 1-fold coordination that dominates for the clean (111) surface. Moreover, the vibrational frequencies of the adsorbed CO molecules in all sites decreased with increasing K coverage. This suggested to Ray and Anderson\textsuperscript{16} that the Pt surface was becoming increasingly cathodically charged with increased K coverage, and they modeled this by shifting the Pt valence band up in energy. They found the CO adsorption energy at the 1-fold site decreased while the adsorption energy at the high coordinate sites increased and surpassed the 1-fold site value. Furthermore, the CO vibrational frequency decreased for all sites, a result seen recently for CO adsorbed on Ni(111) with various K coverages.\textsuperscript{17} The band shift model has also been used to explain a number of electrochemical phenomena, including the potential dependencies of AgC and CN frequencies for CN\textsuperscript{-} adsorbed on an Ag electrode\textsuperscript{18} and CO frequencies on a Pt electrode,\textsuperscript{19} as well as shifts in binding sites on Pt(100) and Pd electrodes.\textsuperscript{20}

With this background in mind, the nature of the hypothesized Al–OC–Ni interaction observed by Rao et al. and Yates and coworkers can be addressed. Al has no d orbitals to stabilize an Al–O interaction by means of CO π donation. Also, Al is not very electropositive like K, in fact its electronegativity is only 0.3 less than Ni, so little charge transfer from Al to Ni is expected. This expectation is supported by the observation by Yates and coworkers that CO vibrations when adsorption is on Ni sites of the Ni/Al surfaces are generally slightly higher than
those observed on clean Ni surfaces, rather than lower. Evidently the Ni–Al bonding is not very ionic. The purpose of this chapter is to address theoretically the cause of the activation of some CO molecules when adsorbed on Ni/Al alloy surfaces at the same time taking into account the absence of activation of those CO molecules bound to Ni centers alone. The ASED-MO method of earlier CO activation studies and similar cluster surface models are employed.

4.2 Models

The atom superposition and electron delocalization molecular orbital (ASED-MO) theory is a semiempirical method for predicting molecular properties from atomic data. It is based on a physical model of partitioning molecular electronic charge density functions into rigid atomic parts that are central on the nuclei and the non-rigid bond charge redistribution part. From integration of the forces on the nuclei as isolated atoms are superimposed into a molecular configuration, pairwise atom-atom interaction energies are defined. These are repulsive and symbolized by $E_r$. Forces on the nuclei from the bond charge delocalization are attractive and symbolized by $E_d$ so that the molecular binding energy $E$ is the sum:

$$E = E_r + E_d \quad (4.1)$$

It has been found in many studies (e.g. Refs.(11–14), (16), and (18–20)) that when the components of $E_r$ are calculated by integrating the force on the nucleus of the less electronegative atom of each pair that is due to the density distribution, including the nuclear charge, of the more electronegative atom. $E_d$
is well approximated by a change in electron orbital energy $\Delta E_{MO}$ given by

$$\Delta E_{MO} = \sum_i n_i \epsilon_{i}^{MO} - \sum_a \sum_i n_i \epsilon_{i}^{a}$$  (4.2)

in Eq.(4.2) $n_i$ is the orbital occupation number, 0, 1, or 2, $\epsilon^{MO}$ is the valence molecular orbital energy, $\epsilon^{a}$ is the valence atomic orbital energy, and the sums are over all orbitals $i$ and all atoms $a$. The $\epsilon^{a}$ are the negative of the valence state ionization potentials, V'SIP. The $\epsilon^{MO}$ are calculated by using a modified extended Hückel Hamiltonian:

$$H_{ii}^{aa} = -V'SIP_i$$  (4.3)

$$H_{ij}^{aa} = 0$$  (4.4)

$$H_{ij}^{ab} = 1.125(H_{ii}^{aa} + H_{jj}^{bb})S_{ij}^{ab}exp(-0.13R_{ij}^{ab})$$  (4.5)

In Eq.(4.5) $S_{ij}$ is the overlap integral between atomic orbitals $i$ on atom $a$ and $j$ on atom $b$ and $R_{ij}^{ab}$ is the distance between the nuclei of atoms $a$ and $b$.

In our modeling of CO adsorption on cluster models of Ni(111), 1 eV increases in Ni VSIP parameters and 1 eV decreases for C and O resulted in a good overall description of CO/Ni bonding. Slightly larger shifts were used in past studies involving surfaces of other metals. For modeling the Al–OC–Ni interaction it was taken into account that the alloy surface structures were unknown in the experimental work, so we decided to use a model consisting of a two-layer thick 19 Ni atom cluster of the (111) surface with an Al ad-atom with its VSIP values increased by 2.6 eV to reduce charge transfer to Ni. A similar model was used in studying the effect of adsorbed transition metal cations and atoms on CO adsorption on Pt(111). To model the effects of trapping the CO molecule in a Ni matrix, a linear Ni–CO–Ni complex, (111) and (100) surface
models with a surface atom vacancy, and a square Ni$_4$ cluster with CO in the center and perpendicular to the metal atom plane were used.

Theoretical parameters are given in Table 4.1. Step sizes of 0.001 Å were used for CO bond length determinations, and step sizes of 10 deg were used for angle determinations. Stretching force constants for CO were found numerically by using the definition formula for second derivative. The Ni$_{19}$ cluster is high-spin, with six unpaired electrons so that each d band level is occupied. The Al/Ni$_{19}$ cluster spin is 5.

4.3 CO binding to Ni(111)

A single CO molecule was found to bind to the Ni$_{19}$ cluster surface in the perpendicular orientation with the site preference order 3-fold > 2-fold > 1-fold. The cluster and site designations are shown in Fig. 4.1. This is consistent with vibrational analysis of Campuzano and Greenler$^{21}$ who found 3-fold site occupation at low 0.05 monolayer coverage, with a shift 2-fold site occupation at 0.30 monolayer coverage, which persisted up to the c(4 × 2) overlayer at 0.50 monolayer coverage. At 0.57 monolayer coverage an ordered ($\sqrt{7}/2 \times \sqrt{7}/2$)R19.1º pattern was observed with 1/4 of the CO molecules on 1-fold and the remaining ones on 2-fold sites. Though we have not studied the coverage dependence, CO interactions through the Ni surface atoms and through space are evidently favoring lower coordination at higher coverages. Our calculated CO adsorption bond energies, given in Table 4.2, appear as is often the case, to be systematically over-estimating the experimentally determined adsorption energies.$^{22}$ Experimental estimates are 26.5 Kcal/mole at low coverage and 23 Kcal/mole at higher coverages where CO resides in 2-fold sites. The difference, 3.5 Kcal/mole, is somewhat
<table>
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<th>$\zeta$</th>
<th>$n$</th>
<th>VSIP</th>
<th>$\zeta$</th>
<th>$c_1$</th>
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<tr>
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<td>12.62</td>
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</table>

Table 4.1: Parameters used in the calculations: principal quantum numbers, $n$, VSIP (eV), orbital exponents, $\zeta$ (a.u.), and linear coefficients, $c$, for double-$\zeta$ orbitals.
Figure 4.1: CO adsorption sites on Ni$_{19}$ model of the Ni(111) surface.
Table 4.2: Calculated CO adsorption energies, E(eV), vibrational excitation energies $\omega_e$ (cm$^{-1}$) with experimental results from Ref.(21) in parenthesis, bond lengths $R_{CO}$ (Å) and C heights $h$ (Å) above the surface for 3-, 2-, and 1-fold sites on Ni$_{19}$ – see Fig. 4.1.

<table>
<thead>
<tr>
<th>property</th>
<th>3-fold</th>
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<th>1-fold</th>
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<td>$\omega_e$</td>
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<td>1921(1910)</td>
<td>2050(2045)</td>
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<tr>
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<td>1.119</td>
<td>1.110</td>
</tr>
<tr>
<td>h</td>
<td>1.46</td>
<td>1.55</td>
<td>1.87</td>
</tr>
</tbody>
</table>
fortuitously closely matched by the 3.2 Kcal/mole calculated difference for 1-fold
and 2-fold adsorption of an isolated CO molecule. A more recent study of Surnev
et al. finds a smaller difference.23

The calculated \( \omega_c \) values in Table 4.2 agree well with those obtained by
Campuzano and Greenler. No coupling to the surface was included in the fre-
quency calculations. The CO bond lengths may be seen in Table 4.2 to relate
inversely to the frequencies, as expected from empirical bond length-force con-
stant and frequency relationships. The CO height above the surface decreases
with increasing Ni coordination. Figure 4.2 shows how the 5\( \sigma \) stabilization in-
creases with coordination and since this would increase \( \omega_c \), the \( \pi^* \) mixing with
filled Ni orbitals, though very weak, is increasing with increased coordination and
causing the CO frequency to decrease.

4.4 Al binding to Ni(111) and coadsorbed CO

Even with the 2.6 eV increase in Al VSIP, the Al 3p orbital levels lie well above
the top of the Ni d band, so Al formally becomes Al\( ^+ \) and its 3p electron is
assumed to pair with a Ni d band electron, reducing the spin of the Ni\(_{19}\) cluster
from 6 to 5. The Al atom favors the 3-fold site with a binding energy of 4.29 eV
and sits at a height of 1.52 Å bearing a small positive charge of 0.07.

The coadsorbed Al atom is calculated to attract the adsorbed CO to a
3-fold site 1 Ni atom away. The O end tilts toward Al, making an angle of 70
deg to the surface normal as shown in Fig. 4.3. The Al and C rise 0.11 Å and
0.04 Å, respectively, and the CO bond stretches 0.027 Å to give a calculated
\( \omega_c \) of 1680 cm\(^{-1}\), omitting vibrational coupling to the surface. This complex is
0.33 eV more stable than an isolated CO molecule in the 3-fold site. As Fig. 4.4
Figure 4.2: CO orbital stabilizations at the sites shown in Fig. 4.1
Figure 4.3: Al-OC-Ni$_x$ at the calculated equilibrium structure.
shows, this activation is made possible by mixing of the empty Al 3p orbitals with the filled CO 5σ and π orbitals. The empty CO π* orbitals are now able to mix in sufficiently with the π to stabilize them and weaken the CO bond. Thus the empty Al 3p orbitals are playing the same role as the empty d orbitals of transition metal atoms in the previous theoretical studies. The Al 3s mixes quite strongly with the CO 4σ and 3σ orbitals as well. The broadening of the CO 5σ and π set and relative shift down of the 4σ orbital was evident in the UPS work of Rao et al. Though the calculated CO ωz shift is less than that seen in the experiments of Rao et al. and Yates and coworkers, these results support the hypothesis that an Alx–OC–Niy complex forms on the alloy surfaces. Calculations with an Al–CO–Ni structure showed it to be about 0.5 eV less stable.

4.5 Interstitial CO

CO trapped in Ni matrices shows different activations, with ωz values of ~1500 cm⁻¹⁶ and ~1610 cm⁻¹⁷,⁸ This suggests there is a structure effect, and since structures are unknown, we set out to explore the structure and electronic properties that would lead to such frequency shifts by using primitive models. Simple linear Ni–CO–Ni complexes were found to not decrease the CO frequency because of the σ nature of the Ni–CO interaction. Binding parallel over 1 atom vacancy substitutional sites on (111) and (100) surface cluster models produced slight shifts in the CO vibrational frequency, which never became less than when adsorbed at the 2-fold site in the upright position. A structure that would force the mixing of CO π* orbitals with Ni orbitals was clearly needed. This was achieved with a model with CO placed symmetrically in the center of square spin zero Ni₄ cluster with its axis perpendicular to the plane. The Ni atom spacing was
Figure 4.4: CO orbital stabilizations for the Al-OC-Ni₉ complex of Fig. 4.3.
varied in 0.1 Å steps, and the CO bond length and frequency were calculated. As shown in Fig. 4.5, with an increase in Ni spacing of 0.2 Å the CO frequency was in the range of 1600 cm\(^{-1}\). There is a strong mixing of CO π* orbitals with Ni d orbitals for this interstitial structure, while the occupied CO orbitals are shifted by approximately the same amounts as when CO is chemisorbed on Ni (Fig. 4.6). Such trapping structures are expected to be metastable because CO is repelled from this site in Ni\(_{4}\) by 1.78 eV when bulk Ni–Ni distances are used and it is attracted by only 0.77 eV when the Ni spacing is increased 0.2 Å, giving rise to the \(\sim 1600\) cm\(^{-1}\) \(\omega_\nu\). The rapid variation of the CO \(\omega_\nu\) as a function of Ni spacing indicates strong sensitivity to defect site structure for interstitial CO, which could account for the variations in measured frequencies. The 1420 cm\(^{-1}\) vibration seen by Yates and coworkers for Ni deposition on Al in the presence of excess CO might be due to interstitial CO in Ni, wherein the Ni cluster structure is perturbed by the Al surface or there is an electronic effect between the CO Ni interstitial complex and the surface.

4.6 Conclusions

Three different topics have been treated in this chapter. Firstly, the binding of an isolated CO molecule on the Ni(111) surface has the stability ordering 3-fold > 2-fold > 1-fold. According to Campuzano and Greenler the 3-fold site is indeed favored at low coverages and at higher coverages 2-fold site adsorption takes over and at maximum coverage there is a mixture of 2-fold and 1-fold coordination. These facts can be rationalized on the basis of our results by assuming that when CO binds in a 3-fold site, three Ni atoms are blocked, so as coverage is allowed to increase to 1/3 monolayer and greater, the CO molecules must bind to 2-
Figure 4.5: Changes of CO bond properties when trapped interstitially in a square Ni$_4$ cluster as a function of changes in Ni atom spacing, $\Delta_{NiNi}$. 
Figure 4.6: CO orbital stabilizations in the square substitutional site with $\Delta_{NiNi} = 0.2 \text{ Å}$. 
fold sites, blocking only two Ni atoms. (The actual changeover occurs over the 0.20–0.25 monolayer coverage range.) At greater than 1/2 monolayer coverage, restructuring occurs to accommodate CO in 2-fold and 1-fold sites. The proper theoretical treatment of coverage dependence would require modeling various coverages, but it seems the isolated ad-molecule energies establish the trend. There is good agreement between the calculated CO vibrational frequencies for the three sites and the Campuzano-Greenler measurements at various coverages and site occupations. From these results it is concluded that the theoretical description of the CO adsorption bond on Ni is satisfactory for treating the other two topics of this study.

To examine CO activation on the Ni–Al alloy surface, use was made of the fact that the electronegativity difference between Al and Ni is small, meaning there is little charge transfer from Al to Ni, an expectation that is confirmed by CO vibrational frequencies measured by Yates and coworkers for non-activated CO on the alloy surfaces. With this in mind, the Ni VSIP were not decreased as for the earlier study of K on Pt, which led to cathodic surface charging, but the Al VSIP were increased to eliminate most of the charge transfer. The Al 3p orbitals nevertheless formed an empty band well above the Fermi level and CO formed σ and π donation bonds into these empty orbitals, resulting in the CO axis tilting with O close to Al. This structure allowed sufficient mixing of the empty CO π* orbitals to significantly lengthen the bond and lower the vibrational frequency. This finding fleshes out the structure suggestion of past workers. The simplicity of the structure model and the approximate nature of the ASED-MO theory in all likelihood account for the theoretical underestimate of the observed CO frequency shift.

In the third study the electronic factors leading to CO activation when
trapped in a Ni matrix were uncovered. While the detailed structures of defect sites were not derived, it at least became evident that interstitial and not substitutional binding is needed for CO activation. Such sites force CO to have strong interactions of the $\pi$ complex type with the matrix atoms, with strong back-donation to the CO $\pi^*$ orbitals and bond weakening.

The general conclusion of this and the previous theoretical studies is that CO bond weakening as observed by vibrational measurements is expected to have associated with it strong CO $\pi^*$ mixing with occupied metal orbitals. This is accomplished when CO is bound to two (or more) metal atoms and one (as in an alloy) or both of them is deficient in electrons so that $\pi$ donation interactions are no longer closed-shell repulsions. The electron deficiency can be in d orbitals, as for the early transition metals, or in p orbitals, at least in the case of the non-transition metal Al. This allows mixing of the CO $\pi^*$ orbitals with the metal orbitals and, consequently, activation. Alternatively, a metastable structure can force CO to have strong $\pi^*$ mixing despite the $\pi$ closed-shell repulsions, as for CO trapped in interstitial sites of Ni, a late transition metal with a nearly filled d band.
Chapter 5

Methoxy Mobility and Methane Formation on the Alumina Support.
Molecular Orbital Theory

5.1 Introduction

At some stage, the CO bond is broken during methanation over metal catalysts, but it is not known when. There is convincing experimental\textsuperscript{1−3} and theoretical\textsuperscript{4} evidence that CO dissociates at low temperature on some early transition metal surfaces, while on late transition metals, including Ni and Pt surfaces, adsorbed CO, which binds upright through C, desorbs on heating.\textsuperscript{5−9} Late transition metals are effective methanation catalysts when they are prepared on titania and other early transition metal oxide supports. In these cases suboxide species migrate over the metal during reduction, blocking many metal sites to CO adsorption and, at the same time, increasing methanation activity.\textsuperscript{10−13} This is called the strong metal-support interaction (SMSI) effect. Low vibrational frequencies are observed for CO adsorbed on SMSI catalysts, and the decrease has been interpreted as catalytic activation of CO. It has been proposed that, since early transition metals are very oxophilic, the adsorbed CO binds to the metal through C and the O end bonds to a nearby cation of the suboxide.\textsuperscript{14,15} Molecular orbital calculations substantiated this hypothesis and characterized the bonding to the cation as π donation from CO to empty d orbitals.\textsuperscript{16} This interaction was also shown to be responsible for the lying-down structure of CO on Cr(110)\textsuperscript{4a} and Fe(100) and (111)\textsuperscript{4b} surfaces which is stable to dissociation at low temperatures.
Not only does $\pi$ donation weaken the CO bonds, but the structure causes increased back-donation to the CO $\pi^*$ orbitals so that the total result is a decrease of CO vibrational frequency by several hundred wavenumbers and a weakening of the CO bond dissociation energy by an order of magnitude. For these reasons it is generally believed that dissociation of adsorbed CO is the first step in CO methanation over SMSI catalysts. A kinetic model based on this hypothesis has been developed for CO methanation over alumina supported metals.\textsuperscript{17} The alternative, that CO is hydrogenated to an intermediate prior to CO bond cleavage, cannot be completely excluded. Calculations\textsuperscript{18} have suggested that the formation of formyl, HCO(a), from CO and H chemisorbed on an iron surface will have a low activation energy and the reaction is close to energy neutral, so it might occur. It can be argued that the same interactions that weaken the CO bond toward dissociation on metal surfaces would also stabilize the formation of a tilted HCO(a) intermediate during methanation.

Recent work has demonstrated an ability of nickel\textsuperscript{19} and platinum\textsuperscript{20} supported on alumina to methanate CO and, at the same time, generate methoxy, CH$_3$O, bound to the alumina. Isotope labeling and vibrational analysis performed over Pt have shown that the CO bond has not broken: the labeled O in CO was found in the methoxy. The methane evolution properties of these two catalytic systems hold special interest. Two methane temperature programmed reaction (TPR) peaks were seen over these catalysts. On Ni/Al$_2$O$_3$ they were around 443 K and 520 K and on Pt/Al$_2$O$_3$ they were around 493–533 K and 613 K. Careful experimental analysis indicated that over Ni/Al$_2$O$_3$ the lower temperature (443 K) methane formation peak came from the hydrogenation of CO adsorbed on the metal, and during desorption of CH$_4$ at the higher temperature (540 K) peak, the support was covered by methoxy. In the absence of
H₂ pressure, the methoxy transferred back to Ni and decomposed to CO. On Pt/Al₂O₃ the lower temperature (493–533 K) TPR peak coincided with methoxy on the support, and its temperature was close to the higher temperature peak for Ni/Al₂O₃, which was also associated with methoxy on the support. The higher temperature (613 K) TPR peak was due to methanation of CO on Pt.

It was concluded by the authors of both of these studies that CO, probably in a hydrogenated form, spilled over from the metal to the Al₂O₃ support. Methoxy is not stable on either clean metal surface at these temperatures.²¹⁻²³ Formate has also been observed on the support, but seems to be independent of the methoxy.²⁰

As part of the supported Pt study water was introduced to the system and it was found to block the formation of methoxy.²⁰ This suggested that dehydroxylation of the alumina surface is a necessary condition for its formation and that CH₃O is probably bound to coordinatively unsaturated (cus) surface Al³⁺, for it is these sites that are blocked when the surface is hydroxylated by water. There are some other pieces to the mechanistic puzzle which may fit in but by no means complete the picture. These are discussed next.

When adsorbed on Ni–Al alloy surfaces, CO shows a vibrational frequency decrease²⁴ which we have explained occurs by a mechanism similar to that in SMISI systems: CO bridges Ni and Al centers with π donation through O to empty valence p orbitals on Al.²⁵ This leads to bond stretching and weakening.

A recent study of CO methanation on supported Al₂O₃ has found that whether or not activity enhancement occurred in reduction experiments at 498 K depended on how the metal support system was prepared.²⁶ It was pointed out that Al₂O₃ can dissolve in acidic solution and preparation of supported Pt from H₂PtCl₆ resulted in an acidic solution which probably dissolved some of the
support and deposited it in some form on the metal and back on the support. This system gave enhanced activity but preparation using [Pt(NH$_3$)$_4$]Cl$_2$ did not, apparently because none of the support dissolved in the non-acidic solution. Reduction of Fe(NO$_3$)$_3$ over Al$_2$O$_3$ also deposited support material on the metal.\textsuperscript{27} Interestingly, in the studies discussed above, where methoxy was produced on the support, the preparations involved H$_2$PtCl$_6$ and Ni(NO$_3$)$_3$, so in both cases activity may have been influenced by support material dispersed on the Pt and Ni. It was proposed that the support material may be reduced to AlO$_x$ during the reducing conditions (high temperature and H$_2$ pressure) used during CO methanation.\textsuperscript{29} Thus, it might be activating CO by the mechanism mentioned above, involving π donation to Al.

The question now arises concerning whether the observed CH$_3$O sites are on the support or on the AlO$_x$ that is dispersed over the metal. Since the amount of adsorbed CO is hardly decreased when AlO$_x$ is present (unlike SMSE catalysts involving early transition metal oxides\textsuperscript{10a,10b,16}), the large observed quantities of CH$_3$O must be bound to the support. The role (if any) of AlO$_x$ on the metals in causing CH$_3$O to form on the support is unknown, but it seems almost certainly responsible for increased methanation activity. The temperature chosen for the reduction experiments in Ref.(26) must also be considered in this regard. Its value, 498 K, is in the Al$_2$O$_3$ TPR peak and in the low temperature tail of the Pt TPR peak shown in Ref.(20). The rate constant for CCl$_4$ formation from CO pulses in H$_2$ at 498 K was seen to increase as a function of increased catalyst reduction temperature and O$_2$ treatment reduced the rate. This is consistent with reduced AlO$_x$ species on the Pt activating the CO for methanation over the Pt surface. It was noted that on earlier transition metals, which already have good CO methanation activity, Rh and Ru, AlO$_x$ did not provide further
From the above, it may be concluded that at least some catalysts active for CO methanation have CO initially activated by π donation bonding of the type M–C–O–M or M–C–O–Mn+. Whether the first step is CO dissociation or hydrogenation to formyl, –CHO, or other intermediates, followed by CO dissociation is not known. Infrared studies have shown no HCO on the surface of Ni/Al2O3 during CO methanation but such an intermediate would be undetectable if it dissociated immediately to adsorbed CH and O. The fragments C, CH, CH2 and CH3 have been detected by static secondary ion mass spectroscopy (SIMS) following CO methanation over Ni(111) but in this case no Al2O3 was present. Hydrogenation of formyl to formaldehyde appears unlikely over the clean unsupported catalysts because at methanation temperatures formaldehyde decomposes to adsorbed CO and H. Methoxy also decomposes to adsorbed CO and H on these metals. However, over saturated surfaces and over surfaces with preadsorbed oxygen methoxy can be stabilized and formyl and formaldehyde have been observed spectroscopically at low temperatures. Therefore one cannot completely exclude mechanisms involving those intermediates.

Methoxy is intriguing. The supported nickel results show its methanation at a higher temperature than CO methanation over the Ni surface. It might be supposed that at the higher temperature the CH3O spills back to Ni, decomposes, and hydrogenates. Yet on supported Pt the lower temperature TPR methane peak corresponds to the consumption of CH3O, and methane is evolved from CO on the Pt at ~100 K higher temperature. Therefore, it appears that in both cases, since the TPR peak occurs in the same temperature range for the CH3O associated CH4 evolution, CH3O hydrogenation must be taking place on the Al2O3 or at its interface with the supported metal particles. We note that
CH₃O forms on the support at \( \leq 385 \) K on both the Ni/Al₂O₃ and Pt/Al₂O₃ systems, well below the temperature of the TPR CH₄ peaks.

What is one of the most important still missing pieces of the mechanistic puzzle is an experimental investigation of whether CH₃O forms on Al₂O₃ in the absence of AlO₂⁻ on the metal particles. It then would form if either CO can be hydrogenated by H that is spilled over onto the Al₂O₃, and such spillover is known for this oxide,¹⁹,²⁰ or if CH₃O formation and its spillover can be activated at the metal-support interface.

We have undertaken a theoretical study of methoxy stability and its mobility and reactivity over Al₂O₃ in order to gain further understanding of the support effect. The atom superposition and electron delocalization molecular orbital (ASED-MO) theory is used in conjunction with cluster models.

5.2 Models

The semiempirical ASED-MO theory employs atomic parameters for predicting properties of molecules.³⁴ It is based on the physical model of partitioning molecular charge density distribution functions into free atom components and the charge redistribution component due to bonding in the molecule. The integral of the Hellmann–Feynman electrostatic force on a nucleus as its corresponding atom is brought from a non-interacting distance into a molecular conformation yields two energy components with this charge density partitioning. One, due to atom superposition, is repulsive and is denoted by \( E_R \), and the other, due to the electron delocalization redistribution density, is attractive and is denoted by \( E_D \):

\[
E = E_R + E_D
\]
In a polyatomic molecule $E_R$ is a sum of pairwise repulsion energies and $E_D$ is a sum over half the nuclei. Only $E_R$ is easily calculated. To find $E_D$ by use of the Hellmann–Feynman force theorem as described above would require the solution of the Schrödinger equation to find the charge density redistribution function, a difficult task which, could be accomplished, would make this model superfluous. The electron delocalization energy calculated using a modified extended Hückel Hamiltonian has been found to approximate $E_D$ quite well for many molecules:

$$E = E_R + \Delta E_{MO}$$

(5.2)

where

$$\Delta E_{MO} = \sum_i n_i \varepsilon_i^{MO} - \sum_n \sum_i n_i \varepsilon_i^n$$

(5.3)

In Eq.(5.3) the $n_i$ are molecular orbital or atomic orbital occupation numbers, $\varepsilon_i^{MO}$ is the energy of molecular orbital $i$, $a$ is the atom index, and $\varepsilon_i^n$ is the energy of atomic orbital $i$ for atom $a$. With the approximations of Eqns.(5.2) and (5.3), better results are usually obtained when each contribution to $E_R$ is calculated using the charge density function of the more electronegative atom and the coulombic interaction of other nucleus in the pair with it. This is done here. Slater-type atomic orbitals are used and the modified extended Hückel Hamiltonian depends on measured valence orbital ionization potentials. In molecules where the initial charge transfer is excessive and bonds are too short with these parameters, self-consistency is emulated by decreasing the anion orbital exponents and ionization potentials and increasing them for the cation. Rules for this and a discussion have been published.$^{35}$

Parameters used for this study are given in Table 5.1. For Al and O, parameters are those used in a past study of the bonding at interfaces between alumina and nickel surfaces.$^{36}$ The C and O parameters are taken from the
Table 5.1: Atomic parameters used in the calculations: principal quantum numbers, n, ionization potentials, IP (eV), Slater orbital exponents, ζ (a.u.).

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<td>IP</td>
<td>ζ</td>
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</table>
previous study of CO adsorption on Ni(111) and its interaction with an adsorbed Al atom. The H ionization potential is treated in the same way as those for C and O.

The alumina support is generally considered to be γ-Al₂O₃ in the experimental studies. The detailed atomic structure of γ-Al₂O₃ has not yet been satisfactorily established. Fourier-transform infrared (FTIR), thermogravimetric analysis (TGA) and x-ray photoelectron spectroscopic (XPS) studies have indicated that aluminas prepared under different conditions will have different types of cus Al³⁺ surface sites after dehydrogenation at various temperature.

In the absence of detailed surface structure information we have chosen a small cluster model based on the known structure of α-Al₂O₃ and have focused on its cus Al³⁺ cation sites. Fig. 5.1 shows an Al₂O₆⁻ cluster which has a surface Al³⁺ in 3-fold coordination (and also one in 4-fold coordination). A second cluster model Al₂O₈⁶⁻ is also shown. It has a surface cus Al³⁺ in 5-fold coordination and the other one is in full (6-fold) coordination. Atom parameters for α-Al₂O₃ are taken from the literature with Al-O bond lengths of 1.8881 and 1.9275 Å.

5.3 Mobility of methoxy on Al₂O₃

Surface defect sites are likely to have surface Al³⁺ in low coordination, and binding at such a site is discussed first. The binding of OCH₃ on the 3-fold cus Al³⁺ site is calculated to be strong, 3.7 eV. The structure is in Fig. 5.2. Two components contribute to this strength, the covalent stabilization of the σ lone-pair orbital by the higher-lying band gap dangling Al³⁺ orbital and the electron transfer from a neighboring surface O²⁻ to the π-type radical orbital, formally generating a methoxy anion. As shown in Fig. 5.3, the electron transfer oxidizes
Figure 5.1: $\text{Al}_2\text{O}_8$ cluster model of 1-fold coordinatively unsaturated surface $\text{Al}^{3+}$ cation and $\text{Al}_2\text{O}_3$ model of a 3-fold coordinatively unsaturated surface cation.
Figure 5.2: Calculated structure for OCH$_3$ bound to the 3-fold coordinatively unsaturated cation of Fig. 5.1.
Figure 5.3: Molecular orbital correlation diagram for -OCH$_3$ binding to a 3-fold cus Al$^{3+}$ on the Al$_2$O$_6$ cluster model.
a neighboring O\textsuperscript{2-} to O\textsuperscript{-}. Methoxy radicals when isolated on the alumina surface might be expected to be immobile, because of the strong bonding to cation sites isolated from one another by anions, and unable to by themselves to migrate beyond the interface region. In fact, the calculations predict a weak repulsion for OCH\textsubscript{3} adsorption on a surface O\textsuperscript{2-} despite the formation of an occupied O–O σ bonding orbital. The repulsion is caused by the promotion of an electron into the O–O σ\textsuperscript{*} antibonding counterpart orbital. The calculations indicate weaker binding of OCH\textsubscript{3}\textsuperscript{-} to the cation site, 2.0 eV. Might it be that the methoxy anion can migrate across the surface while experiencing electrostatic stabilization from the diffuse positive hole charge it created on the oxygen anions? Our calculations cannot answer this question, but it seems unlikely.

The O\textsuperscript{-} that the calculations predict is formed when OCH\textsubscript{3} is bound to a cation on the surface will attract H atoms spilling over from the metal. The calculated OH bond strength in this case is 4.1 eV, which is considerably stronger than the binding energy of a hydrogen atom to a Ni or Pt surface (which is about 2.7 eV\textsuperscript{39,40}). From this it can be concluded that H\textsuperscript{+}–O\textsuperscript{2-} and CH\textsubscript{3}O\textsuperscript{-}–Al\textsuperscript{3+} ion pairs will be stable on the alumina surface and a mechanism for their migration over the surface can be considered. It is probable that the ion pair would migrate from site to site more easily than OCH\textsubscript{3} by itself if the proton mobility is high for them it might be able to provide a stabilizing interaction for the methoxy anion as it moves.

It therefore seems likely that the heterolytic pair migrates over the surface. H\textsuperscript{+} from O\textsuperscript{2-} to O\textsuperscript{2-}, and CH\textsubscript{3}O\textsuperscript{-} from Al\textsuperscript{3+} to Al\textsuperscript{3+}. The mobility of spilled-over hydrogen has been demonstrated by its rapid rate of exchange with surface hydroxyl hydrogen on alumina supports\textsuperscript{41} and its measured activation energy for surface diffusion of 28.5 Kcal/mol.\textsuperscript{42} However, whether the mechanism involves
a coordinated motion of heterolytic $\text{H}^+\cdot\cdot\cdot\text{O}^{2-}$. $\text{H}^-\cdot\cdot\cdot\text{Al}^{3+}$ pairs is not established experimentally. The pairs would have to remain in close association, though their ions could exchange with other nearby pairs, so that the $\text{H}^+\cdot\cdot\cdot\text{OCH}_3$ or $\text{H}^+\cdot\cdot\cdot\text{H}^-$ through-space coulombic interaction keeps them stable.

We note that migration barriers between the surface cations which have higher than 3-fold coordination should be relatively small. This is because the adsorption energies calculated for $\text{OCH}_3$ and $\text{OCH}_3^-$ are weaker, 1.7 eV and 0.07 eV respectively, for 5-fold coordinate $\text{Al}^{3+}$. These ideas also apply to H migration across $\text{Al}_2\text{O}_3$ surfaces. The surface capacity of alumina for hydrogen is about $10^{-3}$ times the number of possible OH groups,\textsuperscript{42} which suggests that most of the chemisorbed hydrogen occupies defect sites and will diffuse rapidly until finding such sites, which is also what our calculated chemisorption energies would indicate.

5.4 Decomposition of the heterolytic pair: methane vs methanol formation

Since the heterolytic pair is so stable, methanol generation from it would be a high temperature process and indeed none has been observed experimentally. Related to this is the strongly held dissociative chemisorption phase of methanol which has been observed on activated (partially dehydroxylated) $\delta$-$\text{Al}_2\text{O}_3$.\textsuperscript{43} From microcalorimetry, the heat of adsorption was estimated to be $-2.3$ eV/CH$_3$OH in the low-coverage limit. The adsorption was thought to be heterolytic, with CH$_3$O$^-$ bound to Al$^{3+}$ of low coordination. The reverse reaction, which corresponds to the recombination of the heterolytic pairs and the desorption of CH$_3$OH, would then be endothermic by 2.3 eV. Our calculations yield 2.12 eV for this process when CH$_3$O$^-$ is bound to 3-fold coordinated Al$^{3+}$. Recombina-
tion to form CH$_4$ and an O atom on the Al$^{3+}$ is endothermic by only 0.65 eV according to our calculations, making this a likely process. The O atom + O$^{2-}$ or the 2 O$^{-}$ which are formed by the elimination of methane would react quickly with gas phase or spilled-over hydrogen to form surface OH or water. If H$_2$ migrates over the surface by a heterolytic H$^+$-O$^{2-}$ + H$^-$.Al$^{3+}$ pair mechanism, the reaction with O would yield 2 OH$^-$ and a cus Al$^{3+}$. These different types of OH, those associated with H$^-$ and those not, should be distinguishable by vibrational measurements. Such measurements might be helpful in determining whether the hydrogen that spills over diffuses over the Al$_2$O$_3$ surface in the heterolytic form.

The energy barrier for CH$_4$ formation cannot be calculated with the present Al$_2$O$_3$ cluster model. The reaction might be expected to be of the SN2 type, with H$^-$ from OH$^-$ on the surface displacing O$^{2-}$ from the adsorbed methoxy anion. The activation energy for OH$^-$ displacement from ROH by H$^-$ in the gas phase has been calculated to be about 21 kcal/mol.$^{44}$ To model this process would require a large cluster with a “catalytic pocket” where OH would be directed toward CH$_3$O$^-$ in such a way that the four-centered O-H-CH$_3$-O transition state could form. Such sites would not be characteristic of a smooth surface but would be associated with steps and defects.

A mechanism wherein -CH$_3$ is released, subsequently capturing H to form CH$_4$, would require weakening of the methoxy C-O bond. This would happen if the surface of the alumina is reduced by, say, reductively homolytically adsorbed hydrogen so that electrons occupy Al band gap surface dangling orbitals. The reasons were given in a recent publication.$^{45}$ and also account for the weakness of the O$^{2-}$-methoxy bond discussed above: when a radical binds to O$^{2-}$, the electron promotion energy in the $\sigma^*$ orbital renders the bond weak.
Chapter 6

Alkane Reactions with Photoactivated Decatungstate in Neutral and Acid Solution.
Molecular Orbital theory

6.1 Introduction

In this chapter we develop a theoretical framework for understanding the effects of protonation of the polyoxotungstate anion, $W_{10}O_{32}^{4-}$ (Fig. 6.1), on photoactivated hydrogen atom abstraction from alkanes. This anion has an optical absorption peak at 3.80 eV which is caused by charge transfer excitation between the filled O 2p and empty W 5d bands. The band edge in the spectrum is about 3.1 eV, which represents the band gap. The reaction

\[ R - H + W_{10}O_{32}^{4-} \rightarrow R^* + HW_{10}O_{32}^{4-} \]  \hspace{1cm} (6.1)

can therefore be viewed as proton transfer to an O$^{2-}$ and electron promotion to the W 5d band. Since the R–H and O–H bond strengths are within a few tenths of an electron-volt of one another and an electron must be promoted over a large band gap, reaction (6.1) does not go spontaneously. If the polyxoanion is prep- prepared by charge transfer photoexcitation, creating a hole at the top of the O 2p band and an electron in the W 5d band, denoted as $W_{10}O_{32}^{4-\cdot}$. the reaction can be spontaneous. In this case one is swapping an O–H bond for an R–H bond which is several tenths of an electron-volt weaker:

\[ W_{10}O_{32}^{4-} + h\nu \rightarrow W_{10}O_{32}^{4-\cdot} \] \hspace{1cm} (6.2)
Figure 6.1: Structure of $W_{10}O_{32}^{4-}$ based on data of Y. Sasaki, T. Yamase, Y. Chashi, Y. Sasada, Bull Chem. Soc. Jpn. 60, 4235 (1987).
\[ W_{10}O_{32}^{4-} + R - H \rightarrow R^* + HW_{10}O_{32}^{4-} \] (6.3)

In reaction (6.3) the electron that comes to the polyanion with the proton is not promoted over the 3.1 eV band gap, but instead reduces the relatively low-lying hole on \( O^- \). The hole is, of course, in a molecular orbital that is delocalized over the \( O^{2-} \) that make up the surface of the polyanion, and a stable localized \( \sigma \) OH orbital forms when \( H \) binds to one of the surface oxygen sites. This process was discussed in a recent theoretical study,\(^2\) where it was shown that the R–H \( \sigma \) orbital energy level indeed lies beneath the hole level at the top of the O 2p band. One can anticipate that if the O 2p band could be made more stable the stability of the \( R^* + HW_{10}O_{32}^{4-} \) products would increase and the activation energy calculated in Ref.(2) might decrease, speeding up the reaction and increasing the quantum yield.

The O 2p band \( W_{10}O_{32}^{4-} \) would be stabilized if positive charge could be added. This might be achieved electrochemically by oxidizing the polyanion over an anode surface, but we are unaware of this being attempted. A second approach would be binding a positively charged species to the polyanion. This has been achieved recently\(^1\) through the addition of acid. Reduction potential decreases of 0.65 and 1.1 V were observed, corresponding to mono- and di-protonation. For H abstraction, one is interested in reducing O 2p holes, not the empty W 5d band, so changes in the reduction potential of \( O^- \) will need to be related to the observed changes in the reduction potential of \( W^{6+} \). Evidence that both shift was provided by measurements of the O 2p – W 5d band gap by optical spectroscopy. Upon diprotonation the peak in the charge transfer optical absorption spectrum is increased by 0.09 eV from 3.80 eV to 3.89 eV. Thus the filled O 2p and empty W 5d bands appear to be shifting rather uniformly and in the same direction on
the energy scale when positive charge is added to the surface of the polyanion.

A 25-fold increase in quantum yield was found for H abstraction from several alkanes when $W_{10}O_{32}^{4-}$ was diprotonated.$^{1}$ While the protonated polyanion was a better oxidant for this reaction, it was not strong enough to perform H abstraction in the absence of holes created by optical charge transfer excitation. The lowering of the W 5d band was insufficient to activate proton transfer to $O^{2-}$ with electron promotion to $W^{6+}$. However, upon monoprotonation the W 5d band stabilization changes the olefin product distribution for 2,3-dimethylpentane and diprotonation leads to sufficient band stabilization that the reaction

$$R^- + H_2W_{10}O_{32}^{5-} \rightarrow R^+ + H_2W_{10}O_{32}^{3-} \quad (6.4)$$

dominates for cyclohexane and cyclooctane, resulting exclusively in olefin products in place of mixtures of coupled rings and olefins obtained for $W_{10}O_{32}^{4-}$ and $HW_{10}O_{32}^{3-}$. This was detected from product distributions: in the presence of acid, dimer coupling to R–R ceased and the amounts of other products formed, typically olefins, increased. This means the radical orbital energy levels in R lie near the W 5d LUMO in the unprotonated polyanion and above it in the protonated version.

Reoxidation of the reduced decatungstate anions is catalyzed by hydrogen evolution catalysts such as Pt and RuO$_2$ added to the solution. For the acidified systems the reoxidation was very slow, compared to 200 turnovers for 4 hours of irradiation for $W_{10}O_{32}^{5-}$. This probably reflects stronger OH bond strengths due to the stabilization of the W 5d band for $H_2W_{10}O_{32}^{2-}$, to which an electron is promoted by OH bond formation.

The binding of the alkyl radicals that are generated by H abstraction to the decatungstate anions will also be sensitive to protonation, for the same reasons
as for H binding to them. A theoretical discussion of C–O bond weakening for methoxy adsorbed on a molybdenum surface has appeared\(^3\) : the bond strength between \(\text{O}^{2-}\) and \(\text{CH}_3\) correlates inversely with the electron promotion energy for the reaction

\[
\text{O}^{2-} + \text{CH}_3 \rightarrow \text{OCH}_3^- + e^- \tag{6.5}
\]

Since C–O single bonds are about 2 eV weaker than O–H bonds, alkoxide formation on the polyanion surfaces may be infrequent, though this might be considered on account of the second EPR signal obtained for the one-electron reduced acidified systems in Ref.(1).

We have carried out an ASED-MO study of alkane dehydrogenation by \(\text{W}_{10}\text{O}_{32}^-\) in its unprotonated and protonated forms. It is a semiempirical study which incorporates the effects of protonation by increasing the O and W valence orbital ionization potentials, which are input data for the ASED-MO theory, by 1 eV, with the result that all of the valence molecular orbital energies of the polyoxyanion increase in stability by about 1 eV. Thus, both the lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) are stabilized by about 1 eV. It will be interesting to see if the O 2p to W 5d charge transfer band gap will increase 0.09 eV as observed for the diprotonated anion, since this is a good test of the ASED-MO theory for its ability to predict perturbations of optical spectra due to electrochemical effects. Rough evidence for such a capability was seen in an earlier discussion of oxygen on an iron electrode.\(^4\)

This molecular orbital band shift approach has already found success in providing qualitative predictions and interpretations of the oxidation and reduction of \(\text{H}_2\text{O}\) on an iron electrode,\(^4\) anodic dissolution of an iron electrode,\(^5\) and the potential dependencies of vibrational frequencies of CN adsorbed on an Ag electrode\(^8\) and
CO on Pt electrodes. In the last study the CO surface structure was found to depend on potential. The essence of the calculated results and this interpretation has been that the electrode valence band shifts, induced by surface charging by the applied potentials, change the electron donor-acceptor interaction between the electrodes and adsorbed molecules, and that this responsible for the observations.

In earlier work are demonstrated the importance of O centers to H abstraction from alkanes at oxide surfaces. Such hole centers can be present as a result of non-stoichiometry, doping with cations of lower valence than the host oxide, or they can be created by optical charge transfer excitation. A study has also been made of H abstraction from methane by charge transfer excited \( W_{10}O_{32}^{4-} \) to explain experimental observations for cyclohexene, alcohols, and other molecules. The present work improves on the last study and extends it to consider protonated \( W_{10}O_{32}^{4-} \).

\[ 6.2 \text{ Modeis} \]

This theory uses atomic parameters, valence Slater orbital exponents and ionization potentials, as input data and yields electronic structures and molecular binding energies. Parameters from Ref.(2). are in Table 6.1. The theory is based on integrating the electrostatic forces on nuclei as atoms bind together, yielding an atom superposition energy, \( E_R \), which is repulsive, and an electron delocalization energy, \( E_D \), which, when added to \( E_R \), yields the Born-Oppenheimer energy surface

\[ E = E_R + E_D \] (6.6)
Table 6.1: Parameters used in the calculations: principal quantum numbers, \( n \), valence state ionization potentials, \( IP \) (eV), orbital exponents, \( \zeta \) (a.u.), and linear coefficients, \( c \), for double-\( \zeta \) d orbitals. From Ref.(2)

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</table>
$E_R$ is calculated directly from the atomic charge density distribution function and $E_D$ is approximated as the molecular orbital electron delocalization energy from diagonalizing of a modified extended Hückel Hamiltonian:

$$H_{ii}^{aa} = -(V S I P)_{ii}^a \quad (6.7)$$

$$H_{ij}^{aa} = 0 \quad (6.8)$$

$$H_{ij}^{ab} = 1.125(H_{ii}^{aa} + H_{jj}^{bb})S_{ij}^{ab} \exp(-0.13R_{ab}) \quad (6.9)$$

where $a$ and $b$ are atom centers. $S$ is an orbital overlap integral, and $R$ is the internuclear distance. The molecular orbital component to this total energy is then

$$\Delta E_{MO} = \sum_i n_{occ}^i \epsilon_i - \sum_{ai} n_{occ}^a H_{ii}^{aa} \quad (6.10)$$

where $n_{occ}$ is the orbital occupation number (0,1 or 2) and $\epsilon_i$ is the energy of molecular orbital $i$. Using this approximation to $E_D$, we have the ASED-MO formula for the Born-Oppenheimer energy surface:

$$E = E_R + \Delta E_{MO} \quad (6.11)$$

In this approximation $E$ is generally more accurate when the pairwise atom-atom contributions to $E_R$ are calculated by integrating the force on the nucleus of the less electronegative atom that comes from the nucleus and electron charge cloud of the more electronegative atom of each pair.

6.3 Effects of protonation on the $W_{10}O_{32}^{4-}$ band gap

In our model we assume the structure of $W_{10}O_{32}^{4-}$ is unchanged by protonation. We simply increase all W and O VSIP by 0.65 and 1 eV, representing the effects
of monoprotonation and diprotonation respectively, and recalculate the molecular orbital energy levels. Resulting bands before and after the VSIP shifts are shown in Fig. 6.2. In modeling the shift due to diprotonation, the HOMO drops from $-11.546$ eV to $-12.501$ eV, not quite 1 eV, and the LUMO drops from $-9.424$ eV to $-10.296$ eV also a bit less than 1 eV. Thus, the VSIP shift does not translate to exactly the same shift in the bands. For a qualitative study of this type there is no need to stabilize the LUMO by exactly 1 eV. The optical absorption spectra due to W 5d $\rightarrow$ O 2p excitations had a peak at 3.80 eV when the polyanion was unprotonated, and it shifted to 3.89 eV as a result of diprotonation. To reproduce absorption spectral shapes theoretically one would have to calculate the electric dipole transition probabilities for all possible transitions and fit to a smoothing fraction. Instead, we will focus on the band gap. From the optical absorption band edge, the band gap is deduced to be about 3.1 eV. Our calculated band gaps are about 0.9 eV less. Modeling the unprotonated polyanion it is 2.122 eV and for the diprotonated anion it is 2.205 eV, so the band gap increase is 0.08 eV, essentially the same as the observed 0.09 eV peak shift when the reduction potential decreased about 1.1 V because of diprotonation. Our calculated band gap increase for the monoprotonated anion is 0.05 eV. The ASED-MO Hamiltonian appears to be doing a good job of predicting perturbations of optical spectra due to surface charging in the instance. More tests are needed to verify this as a general capability. As discussed above, the band shifting techniques of representing the effects of electrode surface charge in the ASED-MO theory has been found in more than one instance to give adsorbate vibrational and structural information in agreement with experiment. In those cases changes in donor-acceptor characteristics of the surface were responsible for the calculated results, and therefore potential induced changes in donor-acceptor
Figure 6.2: Electronic structures of $P^{4-}$, $HP^{3-}$, $H_2P^{2-}$, where $P$ stands for $W_{10}O_{32}$. 
characteristics provided the interpretation for the analyzed experimental findings. While it is true that the donor-acceptor characteristics of the $W_{10}O_{32}^{4-}$ polyanion change upon diprotonation, the change in band gap is a subtle result. It means that, given constant atomic orbital exponents, the electronic structure of a molecule depends on where the orbital energies are on the energy scale. Bands do not shift rigidly up and down in response to electric perturbations.

### 6.4 Methane activation by $W_{10}O_{32}^{4-}$ and $H_2W_{10}O_{32}^{2-}$

In an earlier study\(^2\) some mechanistic and energy properties were calculated for the photoactivated hydrogen abstraction from methane and cyclohexene according to equation (6.3). Cyclohexene was known to dimerize to 3,3'-dicyclohexene\(^9\) and ASED-MO calculations\(^2\) showed the product selectivity was a result of the weak $\alpha$-H bonds allowing small activation energy barriers for H removal. This weakness stemmed from the unusual stability of the radical, caused by participation of the radical orbital in $\pi$-allylic bonding. The $\beta$ hydrogen had a higher barrier and methane a higher one still. In the current work we use methane as a model for studying the abstraction of H from alkanes by $H_2W_{10}O_{32}^{2-}$. The calculations were performed using the $W_3O_{16}^{2-}$ half-cluster after it was found to have practically the same band structure as the full cluster.

In the earlier theoretical study we examined H bonding to the four different types of surface oxygen on $W_{10}O_{32}^{4-}$. Calculated H abstraction activation energies correlated with these OH bond strengths. The calculated OH bond strengths were within 7% of one-another and terminal OH bonds were calculated to be stronger than bridging ones, though the experimental indications and that both protons and H atoms are more stable on bridging oxygen atoms.\(^{11}\)
In our earlier study of methane H abstraction by $W_{10}O_{32}^{4-}$ we determined fewer energy points around the transition state saddle points than now. Consequently, the transition state bond energies and structures are slightly different from those found in this study, which are based on 0.01 Å OH and CH distance increments, 1 deg H–C–H angle increments, and 10 deg increments for orientation of the H⋯CH$_3$ axis to the anion. The activation energies calculated for bridging and terminal oxygen sites were misassigned in Ref. (2). The bridging oxygen abstracted H from methane with the lower, not the higher barrier.

The present calculations show a significant lowering of the activation barrier for H abstraction from CH$_4$ over the 1-fold and bridging oxygen sites of the photoactivated polyanion when the parameters corresponding to $H_2W_{10}O_{32}^{2-}$ are used in place of those for $W_{10}O_{32}^{4-}$. The decrease in both barriers is about 0.28 eV and the bridging oxygen is more active. Product (R· + hydrogenated polyanion) stabilities increase 0.47 eV and 0.57 eV for the bridging and 1-fold oxygen sites as a result of the proton induced valence band shifts in the polyanion. These energy results are summarized in Fig. 6.3, which also illustrates the calculated transition state structures. From the structure parameters it is seen that on $H_2W_{10}O_{32}^{2-}$ the reaction occurs sooner, with longer O⋯H distances and shorter C⋯H distances at the transition state structures. This can be understood by recalling that the overall reaction requires the promotion of an electron from a CH σ orbital to the O 2p hole level. As the oxygen band comes down in energy closer to the lower-lying CH σ energy level, this process requires less energy, which is why products are more stable for $H_2W_{10}O_{32}^{2-}$. In $H_2W_{10}O_{32}^{2-}$, the O 2p hole energy level is about 1 eV more stable than it is in $W_{10}O_{32}^{4-}$, but the products of H abstraction are calculated to be only ~0.5 eV more stable. The OH σ orbital shifts down rigidly with the O 2p band in $H_2W_{10}O_{32}^{3-}$, becoming
Figure 6.3: Energetics and transition state structures for H abstraction from methane over $W_{10}O_{32}^4-$ and $H_2W_{10}O_{32}^2-$. 
1.02 eV more stable (Fig. 6.4). Based simply on this and the change in O 2p hole energy, the OH bond should be 1 eV stronger for $\text{H}_2\text{W}_{10}\text{O}_{32}^{2-}$, and since it is only 0.57 eV stronger, other orbitals are destabilized by H. The lower hydrogen transfer activation energies for the protonated polyanion are a consequence of bonding in the transition state. A stabilized 3-center C–H···O σ bond forms and its antibonding counterpart pushes up in energy, being of the σ* form between C–H and O. These are shown in Fig. 6.5. The antibonding counterpart orbital experiences some stabilization through mixing of the high-lying CH σ* orbital, and this is manifested in a decreased orbital amplitude on H which reduces the antibonding destabilization of the C–H···O σ* orbital. It is clear from Fig. 6.5 that the C–H···O σ* orbital is the vehicle which transports an electron to the O 2p hole, and when the hole level is stabilized, this antibonding orbital loses an electron sooner, so the transition states should come sooner, and with a lower barrier. This is what happens in the calculations.

6.5 Binding of alkyl radicals to $\text{W}_{10}\text{O}_{32}^{4-}$ and $\text{H}_2\text{W}_{10}\text{O}_{32}^{2-}$.

The methyl radical is our prototype for this section just as for H binding to $\text{O}^{2-}$ on these anions. CH$_3$ should bind more strongly to the protonated polyanion because its LUMO, which takes the promoted electron accompanying σ bond formation, is more stable. This is what happens, with bond strengths between CH$_3$ and the terminal capping O$^{2-}$ calculated to be 0.84 eV for $\text{W}_{10}\text{O}_{32}^{4-}$ and 1.37 eV for $\text{H}_2\text{W}_{10}\text{O}_{32}^{2-}$. These are 2.1 eV weaker than the OH bond strengths which are calculated to be 2.93 eV for $\text{W}_{10}\text{O}_{32}^{4-}$ and 3.43 eV for $\text{H}_2\text{W}_{10}\text{O}_{32}^{2-}$. Bond strengths to charge transfer photoexcited anions are calculated to be higher by 2.20 eV for $\text{W}_{10}\text{O}_{32}^{4-}$ and 2.26 eV for $\text{H}_2\text{W}_{10}\text{O}_{32}^{2-}$. The weakness of the CH$_3$-
Figure 6.4: Formation of $\sigma$ bonds between H and terminal O in $W_{10}O_{32}^{4-}$ and $H_2W_{10}O_{32}^{2-}$. 
Figure 6.5: Transition state electronic structures for H abstraction from CH₄ by W₁₀O₄³⁻ and H₂W₁₀O₃₂⁻.
bonds to the two complexes suggests that they do not form, and the second EPR peak observed for one-electron reduced \( H_2W_{10}O_{32}^- \) is probably a result of a second hydrogenation state, as suggested in Ref. (1).

The \( CH_3^- \) radical orbital energy lies in the upper part of the \( W_{10}O_{32}^4^- \) band gap, and now one must consider the possibility that alkyl radicals in general might be oxidized by it or especially by \( H_2W_{10}O_{32}^- \), which has a more stable empty W 5d band. This is done in the next section.

### 6.6 Formation of alkyl cations

We have optimized the structures of \( CH_3^- \), the primary carbon radical \( CH_2CH_2^- \), the secondary carbon radical \( (CH_3)_2CH^- \) and chair form cyclohexyl \( C_6H_{11}^- \), and the tertiary carbon radical \( (CH_3)_3C^- \). The radical energy levels vary respectively as follows: methyl \(-9.76\ eV\), primary \(-9.60\ eV\), secondary \(-9.42\ eV\) and \(-9.33\ eV\), and tertiary \(-9.25\ eV\). These may be related in a qualitative way to observed1 product distributions as follows. In \( W_{10}O_{32}^4^- \) the bottom of the W 5d band is at \(-9.42\ eV\), so the lack of dimerization of 2,3-dimethylpentane is understandable, for tertiary radicals will dominate upon H abstraction and these will be oxidized by \( W_{10}O_{32}^4^- \). Cyclohexane and cyclooctane will form secondary radicals and their radical electron energies are about the same as the \( W_{10}O_{32}^4^- \) LUMO energies, so a mixture of dimer and olefin products is obtained. Mono-protonation lowers the LUMO to \(-9.99\ eV\) and does affect this distribution but di-protonation, which lowers it to \(-10.30\ eV\), gives entirely alkene products. The lack of agreement of the simple energy level picture in predicting product distributions precisely, for based on it \( HW_{10}O_{32}^3^- \) should lead exclusively to olefins for the secondary radicals, is due to errors in the calculated energy levels and
structural and kinetic details of electron transfer. However, the trend toward decreasing CH bond strengths and decreasing radical electron stabilities for the series t < s < p agrees with the observations of Ref. (1).

6.7 Concluding comments

This has essentially been a study of the interaction of radicals (H· and CH₃·) with a closed-shell anion (O²⁻) and an open shell anion (O⁻). Radical bonds are always strong with the open shell anion and these are weak with the closed-shell one because the R···O²⁻ bond order is 1/2. due to 2 electrons in the σ orbital and one in the σ* orbital. When acceptor orbitals are around, such as the 5d orbitals on W⁶⁺, they remove the electron from the σ* orbital, thereby stabilizing the R–O bond. More stable acceptor orbitals stabilize the R–O bond more, and when the R· radical orbital is relatively unstable, as for alkyl radicals compared to H atoms, oxidation to R⁺ must be considered. We have given form to these concepts through ASED-MO calculations on W₁₀O₅⁻ and the stronger oxidant H₂W₁₀O₃₂⁻, explaining their ability to abstract H from alkyl molecules when photoactivated, creating O⁻, and their ability to oxidize the resulting alkyl radicals.
Chapter 7

Why the Addition of CO Leads to Acyl Decarbonylation in a Supported Rh Dimer Complex.
Molecular Orbital Theory

7.1 Introduction

It has been known that rhodium-monomer complexes have good effectiveness for the hydroformylation reaction in homogeneous systems.\textsuperscript{1} The CO insertion reaction is the first step:

\[
\begin{align*}
M^{n+} - R + CO & \quad \xrightarrow{\text{O}} \quad M^{n+} - \overset{\text{O}}{\text{C}} - R \quad \overset{\text{H}_2}{\xrightarrow{\text{H}_2}} \quad \text{HC} - R \\
\end{align*}
\]

(7.1)

In general, the CO insertion proceeds under high pressure and the reverse reaction of decarbonylation of the acyl group takes place under vacuum.\textsuperscript{1}

Recently, Asakura et al. reported a new aspect of reversible CO insertion on an SiO\textsubscript{2}-attached Rh-dimer catalyst which showed good catalytic activity for ethene hydroformylation.\textsuperscript{2,3} Such heterogeneous catalysts were prepared by the reaction of trans-[Rh(C\textsubscript{5}Me\textsubscript{3})(CH\textsubscript{3})\textsubscript{2}(\mu-CH\textsubscript{2})\textsubscript{2}] with surface OH groups of SiO\textsubscript{2} with C\textsubscript{1} elimination as methane. FTIR showed that the CO insertion into an alkyl group to form acyl proceeds by heating to 423–473 K under vacuum. While the decarbonylation of the acyl group to form a dicarbonyl and an alkyl occurs under CO pressure at room temperature. Based on these findings and EXAFS bond length estimates, the following scheme was proposed:
In it, the dotted line represents Rh–Rh bond cleavage. The CO pressure dependence observed for this reaction is opposite to that observed for Rh monomer catalysts, for which CO insertion into the metal-alkyl is brought about by CO pressure. For the Rh-dimer on silica, CO pressure decarbonylates the acyl. The fact that acyl formation was accompanied by Rh–Rh bond formation (2.70 Å bond length) led the authors of Ref.(2) to suggest that the insertion was in fact being promoted by the metal bond formation. There is little literature precedence for this idea. A homogeneous CO insertion involving Fe–Fe bond formation has been observed, but it is, unlike the above scheme, irreversible.\(^4,5\)

The purpose of this chapter is to undertake a theoretical examination of the electronic structure of species I and II and some potential reaction intermediates to understand the Rh–Rh bond cleavage in the above scheme. The proposed promotion effect of the metal bond formation on the acylation will be investigated.
7.2 Models

We have substituted the silica support by hydroxyl groups and also substituted the C₅Me₅ ligand in Rh complexes by C₅H₅ (Cp) to simplify the calculations. The choice of hydroxyl groups to represent the silica is a simplifying approximation since the actual surface structures are not yet established. We have optimized the hydroxyl groups in our calculations because no surface structure information of SiO₂ is available for assigning surface oxygen spacing. We tried fixing the oxygen spacing to be 2.64 Å and 3.60 Å respectively based on spacings in (0001) planes of α-quartz. We found that the calculated structures experienced readjustments in bond angles and lengths and the energies became less stable by up to 1/2 eV, when the fixed oxygen spacings were used. Since we do not know what the oxygen spacing we should use, we have begun by choosing the optimized ones.

The atom superposition and electron delocalization molecular orbital (ASED-MO) theory is used for this study. The details of method are reviewed in Ref.(6). Parameters used in these calculations are given in Table 7.1. They are based on standard valence orbital exponents⁷,⁸ (ζ) and measured valence state ionization potentials⁹ (VSIP) with some adjustments. For rhodium–carbon bonds these were made by studying diatomic RhC: the Rh VSIP was increased and the C VSIP simultaneously decreased in 0.5-eV steps until the calculated charge on C, based on the Mulliken partitioning, approached −0.02. the value estimated from the Pauling electronegativity difference. The final shift was 1.5 eV for the ionization potentials and no exponent changes were used. This yielded a charge transfer of 0.11 and RhC bond length and strength of 1.88 Å (1.61) and 6.4 eV (6.0) where experimental determinations¹⁰ are in parenthesis. The H and O VSIP were assigned the same shifts as C and the hydroxyl oxygen exponents
Table 7.1: Parameters used in the calculations: principal quantum numbers, n, valence state ionization potentials, VSIP (eV), orbital exponents, \( \zeta \) (a.u.), and linear coefficients, c, for double-\( \zeta \) d orbitals.

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<th>Atom</th>
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<th>( \zeta )</th>
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<th>c2</th>
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<td>2.221</td>
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<td></td>
</tr>
<tr>
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<td>2.241</td>
<td>2.221</td>
<td></td>
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<td>2.096</td>
<td>0.6349</td>
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were decreased by 0.2 a.u., as we do for oxides. Other aspects of the model are as follows. The metal–ligand bond lengths are uncertain by \(\sim 0.1 \text{ Å}\). CH bond lengths were overestimated by 0.1 Å, and were optimized to be 1.20 Å for Cp and 1.22 Å for the ethyl group. Cyclopentadienyl was constrained to pentagonal with optimized CC bond lengths which were 1.61 Å for all structures, overestimating actual distance by \(\sim 0.15 \text{ Å}\). Since the RhC bond length was overestimated, it may be anticipated that the calculations will also overestimate the equilibrium distance from Rh to carbonyl ligands.

7.3 Results and discussion

The fully optimized structure of the Rh-dimer containing an acyl group is shown in Fig. 7.1. The calculated Rh–Rh bond strength is 2.86 eV for dissociation to unrelaxed fragments; relaxation would lower this bond strength. The correlation of the d⁷ Rh fragment orbitals with dimer orbitals is given in Fig. 7.2. The left-hand fragment has a wider dispersion because the \(e\) set of orbitals on the cyclopentadienyl group is close in energy to the Rh 4d orbital energies. This leads to its being a donor of one electron to the right-hand Rh fragment and the resulting electron charge transfer stabilization contributions to the Rh–Rh bond strength, making it stronger than experimental for bond order 1. Fragment relaxations would have stabilized the donor orbital, weakening the charge transfer stabilization. The calculated Rh–Rh distance of 2.60 Å, on the other hand, is reasonable for this bond order and is close to the 2.70 Å EXAFS result from Ref.(2). The high-lying empty d orbital on the right-hand-side Rh has 5s and 5p atomic orbitals mixed in. The low-lying occupied orbital of the right-hand fragment is strongly d-like, but has bonding overlap with the ligands. On the left,
Figure 7.1: Calculated structure for the surface Rh-dimer acyl complex bound to OH groups representing the silica surface, CpRh–RhCOC\(_2\)H\(_5\). The Rh atoms are shaded gray and O atoms bound to C are hatched. OH groups representing bonding to Si hang down.
Figure 7.2: Correlation diagram for metal fragments binding in the acylated Rh dimer complex in the structure of Fig. 7.1.
two nearly degenerate orbitals, for which energy levels but not orbital pictures are
given, are bonding between Rh d orbitals and this degenerate Cp ε set of orbitals
and the top two levels are for the antibonding counterparts. The low-lying filled
Cp a orbital and high-lying empty ε orbitals are just outside the energy range of
the figure.

To go from left to right in the reaction scheme, CO attacks the surface
dimer complex, and ultimately the Rh-Rh bond is broken. We have studied the
bonding of CO to the acylated Rh on the right. We find CO binds strongly, 1.66
eV, and the Rh-Rh bond stretches to 5.66 Å. This breaking of the bond is a
result of the electronic structure of the complex and the σ-donation capability
of CO, which pushes the empty orbital on the right-hand fragment up in energy
and rehybridizes some of the occupied orbitals so that the interaction between the
positive fragment on the left and negative fragment on the right becomes a closed-
shell repulsion, as may be seen in Fig. 7.3. Some additional stability, 0.92 eV, is
calculated by placing the CO colinear with the Rh-Rh axis and reoptimizing the
structure, which results in a Rh-Rh distance of 4.82 Å, indicating a σ bonding
stabilization is formed between the O end of the CO ligand and the Rh on the
left.

The CpRhOCHRhCOC$_2$H$_5$ intermediate is calculated to become 0.23 eV
more stable when rearranged to the dicarbonyl shown in Fig. 7.4. A planar
arrangement of ligand bonds is assumed about the right-hand-side d$^8$ Rh. The
4-center Rh—OC—Rh σ bond is due to a net stabilization involving 4σ and 5σ
CO-based orbitals in the right-hand fragment by the LUMO of the left-hand
fragment. Figure 7.3 focuses on these interactions. The calculated strength for
the Rh—O σ bond is 1.56 eV, based on dissociating into unrelaxed Rh monomer
fragments and eliminating the charge transfer stabilization resulting from the
Figure 7.3: Effects of CO coordination to CpRh–RhCOC₂H₅ at the right-hand Rh. See caption to Fig. 7.2.
Figure 7.4: Calculated structure for CpRhOCRh(CO)C₂H₅. See caption to Fig. 7.1.
Figure 7.5: The $\sigma$ interaction between the bridging CO bound to the right-hand Rh fragment and d orbitals on the left-hand fragment.
half-filled HOMO on the left to the half-filled HOMO on the right. The distance between Rh nuclei is 4.87 Å, which is consistent with the EXAFS result showing no Rh–Rh bonding for this species.

We optimized the \ce{CpRh-Rh(CO)2C2H2} complex in structure II of the reaction scheme (see Fig. 7.6), obtaining a local minimum in the energy, i.e. a metastable structure 2.23 eV less stable than with a bridging CO. As may be seen in Fig. 7.7, there is a single bond between the Rh atoms. Given the above results, the electronic structures preference for having the square-planar \(d^8\) complex on the right is 0.67 eV.

7.4 Conclusions

The driving force for acylation by this Rh dimer system is not Rh–Rh bond formation according to Scheme 1 because species II would, according to our calculations, also have a Rh–Rh single bond and, again from our rough energy calculations, would be 0.57 eV more stable than the acyl complex with a free CO molecule. Rather than this, species II takes a more stable structure that is consistent with \(d^6\) Rh on the right, which is square planar with a bridging CO engaged in donation bonding to the left-hand \(d^6\) Rh. This makes species II 2.8 eV more stable than the acyl complex plus a free CO molecule. This is a rather large stability and could be overestimated. The largest contribution is for the initial bonding of CO to the acyl complex, 1.66 eV.

In place of Scheme 1 we propose Scheme 2.
Figure 7.6: Calculated structure for CpRh–Rh(CO)$_2$C$_2$H$_5$. See caption to Fig. 7.1.
Figure 7.7: Correlation diagram for metal fragments binding to form $\text{CpRh}_{1-}\text{Rh(CO)}_2 \text{C}_2 \text{H}_5$ in the structure of Fig. 7.6.
Here CO binds to the acylated Rh fragment on the right to form III. However the Rh–Rh bond in III is broken so it rearranges to IV with CO nearly colinear with the Rh–Rh axis. Species IV rearranges to V which, like II that was proposed in Ref.(2) for Scheme 1, has two CO bound to the right-hand Rh, but one of them binds weakly through O to the left-hand Rh. The Rh–Rh distance in II is large, which is consistent with the EXAFS result and the CO IR spectrum will show splitting as seen in Ref.(3). The activation energy for the CO insertion reaction, going from V to IV, and its reverse, has not been calculated but, based on a theoretical study involving another low-coordinate transition metal cation$^{11}$ it should be small.
References

Chapter 2


Chapter 3


Chapter 4


Chapter 5


Chapter 6


Chapter 7


