

# Adsorption and Dissociation of Methanol on Aluminum (100): Theoretical Analysis of Reaction Mechanism

Lawrence T. Sein, Jr.\* and Susan A. Jansen

Department of Chemistry, Temple University, Philadelphia, Pennsylvania 19122

Received: November 11, 1997; In Final Form: January 27, 1998

The adsorption of methanol on aluminum (100) surface is modeled by quantum mechanical calculations on a small cluster, using hybrid Hartree–Fock/density functional theory. The enthalpy of adsorption at low coverage is calculated for the high-symmetry sites. The relevance of tipping of the prevalent methoxy species before C–O bond scission is examined. A new mechanism for dissociation is proposed, which is in excellent agreement with experimental determinations of the energy of activation for dissociation. Principles of transition-state theory are correlated to theoretical calculation of vibrational frequencies. Current assumptions from molecular orbital theory, as applied to surface reaction energetics, are called into question.

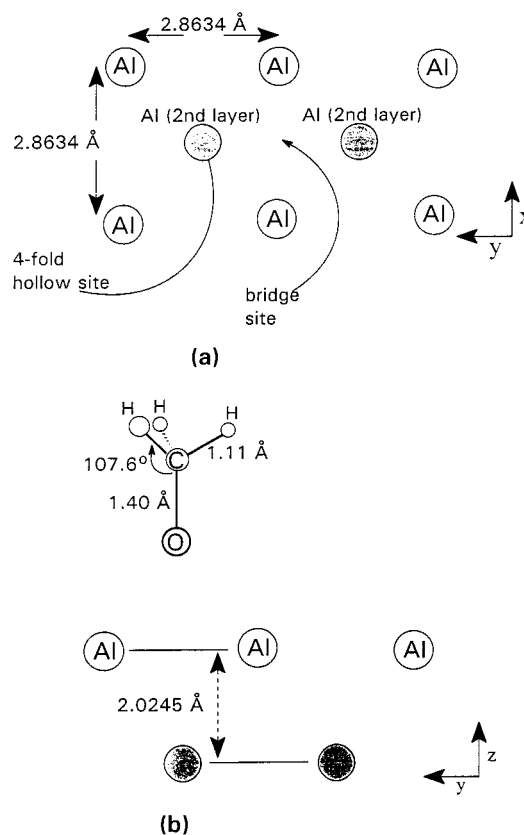
## Introduction

The reactions of alkanes, alcohols, and alkyl derivatives on metal surfaces have been widely studied.<sup>1–14</sup> These reactions are of considerable economic importance, in both industrial manufacturing and synthetic fuels production, as they relate to the production of synthesis gas and Fischer–Tropsch chemistry. Methanol is useful as a product (in oxygenated fuels) and as a reactant. Studies of methanol surface chemistry are critical in understanding the mechanistic details of a variety of important reactions. The typical products of methanol reaction include methane from reduction, formaldehyde, formic acid, and methyl formate from oxidation, and H<sub>2</sub>(g) from decomposition. Rates of conversion of methanol into product and the nature of the products themselves are strongly dependent on both the chemical composition of the surface and, in cases where the surface is a well-defined crystal face, the structure of that face.

Novel binary transition metal/aluminum alloys, such as TiAl, NiAl, and FeAl, are being investigated for their catalytic properties.<sup>15–20</sup> These bimetallic catalysts show hybrid reactivities. The (110) surface contains both transition metal and aluminum species, whereas the (100) surface is composed of a single metal. The most easily manufactured (100) surface is the one that is aluminum terminated. It is to be expected that this terminal aluminum layer would have a decisive effect upon the reactivity of the surface. Aluminum surfaces are easily oxidized and extremely reactive. Titanium, iron, and nickel show markedly different catalytic properties due to differences in their intrinsic chemistry and structure. A clear understanding of the role of the transition metal in such alloys requires the most complete knowledge of the intrinsic properties of pure aluminum surfaces themselves as a prerequisite.<sup>21–26</sup> This work describes a series of *ab initio* calculations that probe the catalytic nature of aluminum (100) and the associated structure sensitivity for methanol adsorption and decomposition.

## Methods

Since experiments strongly confirm that, at elevated temperatures, the prevalent methanol species on the surface is actually

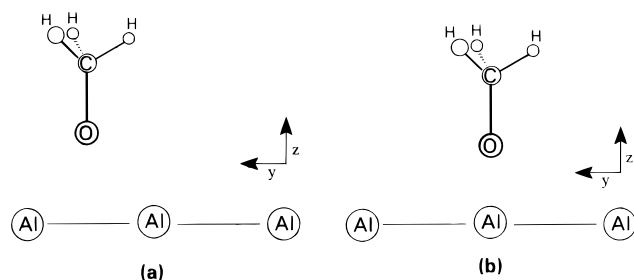


**Figure 1.** Aluminum (100) cluster model used for calculations: top view (a) and side view (b), showing methoxy at the 4-fold hollow.

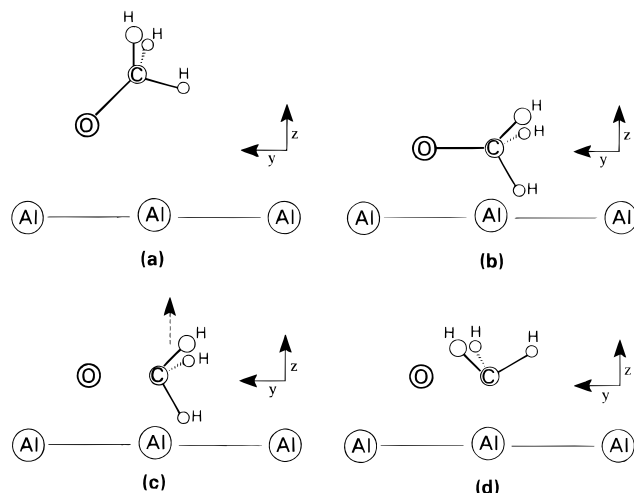
methoxy radical, all calculations were done using this radical.<sup>27</sup> Theoretical discussions of the deprotonation of methanol at the hydroxyl are numerous.<sup>10–12,27,37</sup> The use of the radical MeO<sup>•</sup>, as opposed to the anion, is done largely for computational convenience.<sup>28</sup> The (100) surface (Figure 1) was simulated by a cluster of eight aluminum atoms, six on the surface and two below the hollows, as the second layer. The Al–Al nearest neighbor distance (fcc) is 2.8634 Å. The geometry of the methoxy radical was optimized using the B3LYP functional and the 6-311++G(2d,p) basis set within the Gaussian 94<sup>29</sup> suite

\* Author to whom correspondence is to be sent. E-mail: lsein@thunder.ocis.temple.edu.

## SCHEME 1



## SCHEME 2

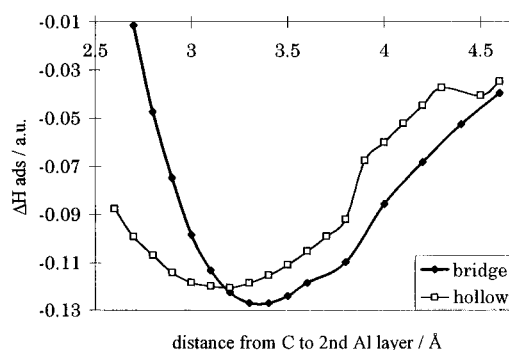


of programs. A series of trial calculations were performed using clusters either enlarged by additional aluminum atoms or else terminated along all nonsurface planes by hydrogen atoms. This was done to address the concern that unsaturation of the aluminum valences would degrade the accuracy of the calculation. In each case, the results were entirely consistent with those from the eight atom cluster.

Single-point energies were computed using the B3LYP/6-311G(d,p) basis set. The B3LYP density functional keyword corrects the Hartree–Fock energy, to account for the effects of electron–electron repulsion. Density functional theory provides high accuracy at minimal cost.<sup>30</sup> In contrast to the effective core potential (ECP) methods,<sup>31</sup> which lump the contributions of the inner electrons into a single electrostatic term, the calculations described in this work explicitly account for all electrons.

Single-point energy calculations were performed for the methoxy radical at steps of 0.1 Å during its trajectory toward the surface during adsorption. Both the trajectory and the radical itself were kept normal to the surface. Trajectories toward both the 4-fold hollow (Scheme 1a) and 2-fold bridge sites (Scheme 1b) were calculated. Calculations of “tipping” were done by tilting the C–O bond axis relative to the plane of the surface, from 0° (normal) to 90° (Scheme 2a,b). Two tipping trajectories were calculated, one with the O in the hollow site and the other with the O in the bridge site. During the tipping, the oxygen atom itself was not moved, and all bond angles (except that of the C–O bond to the surface) and bond lengths were unchanged.

To simulate the dissociated products, energy calculations were performed with the oxygen atom in either the hollow or the bridge site and the methyl group free to move, normal to the surface, directly off the surface (Scheme 2c) from either the bridge site (when the O was in the hollow) or from the hollow (when the O was in the bridge). In these calculations, the methyl group was oriented with the plane of the hydrogens *normal* to



**Figure 2.** Enthalpy of adsorption of methoxy at hollow and bridge sites of Al(100).

**TABLE 1: C–O Vibrations of Methoxy on Al(100) at Hollow Sites, Tipped**

	$\nu_{CO}$ (cm <sup>-1</sup> ) <sup>a</sup>	O charge <sup>b</sup>	C charge <sup>b</sup>	Al charge <sup>b</sup>
free methoxy	994	-0.313	-0.190	
at hollow	1172	-0.755	-0.135	-0.020
tipped at 30°	1123	-0.697	-0.109	-0.031
tipped at 50°	1111	-0.680	-0.133	-0.012
tipped at 60°	1068	-0.657	-0.130	-0.040
tipped at 70°	N/A	-0.636	-0.069	-0.105
tipped at 80°	N/A	-0.610	0.033	-0.112
tipped at 85°	N/A	-0.598	0.364	-0.144

<sup>a</sup> As calculated with B3LYP/6-31 G, using analytical gradients.

<sup>b</sup> Partial charges computed by Mulliken population analysis, using B3LYP/6-311 G(d,p). N/A, not available.

**TABLE 2: C–O Vibrations of Methoxy on Al(100) at Bridge Sites, Tipped**

	$\nu_{CO}$ (cm <sup>-1</sup> ) <sup>a</sup>	O charge <sup>b</sup>	C charge <sup>b</sup>	Al charge <sup>b</sup>
free methoxy	994	-0.313	-0.190	N/A
at bridge	1197	-0.694	-0.073	0.225
tipped at 30°	1166	-0.671	-0.083	0.210
tipped at 50°	1134	-0.636	-0.092	0.191
tipped at 60°	N/A	-0.609	-0.131	0.201
tipped at 70°	1128	-0.586	-0.170	0.194
tipped at 80°	N/A	-0.565	-0.197	0.206
tipped at 85°	1076	-0.549	-0.222	0.168

<sup>a</sup> As calculated with B3LYP/6-31G, using analytical gradients.

<sup>b</sup> Partial charges computed by Mulliken population analysis, using B3LYP/6-311G(d,p). N/A, not available.

the surface. Other calculations, not shown, for the plane of the hydrogens of the methyl group parallel to the surface (Scheme 3d) are invariably much higher in energy.

The calculation of vibrational frequencies was done using the modest B3LYP/6-31G basis set. A larger set was not used, for computational economy. Atomic charges on atoms were computed using the Mulliken scheme, during the single-point calculations at the B3LYP/6-311G(d,p) level.

## Results

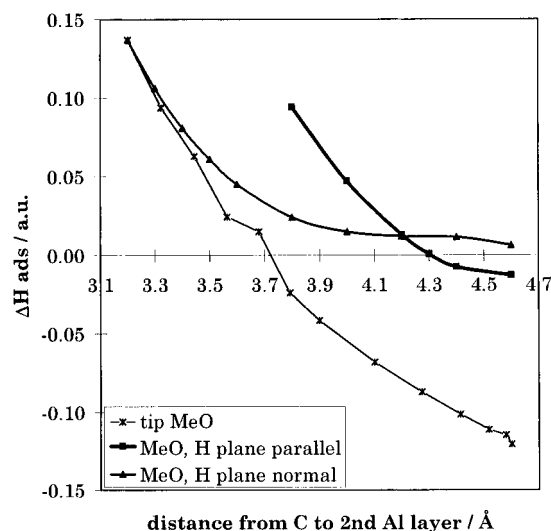
Potential energy curves for the trajectory of the methoxy radical normal to the surface are shown in Figure 2. Contrary to expectation, the lowest energy site is the bridge site. Since the difference in energy between the two sites is ~4 kcal/mol, we can assume that, at low coverage, the barrier to diffusion is also 4 kcal/mol.<sup>27</sup> Other calculations, not shown, have demonstrated that the on-top adsorption site is even higher in energy than either the hollow or bridge. This is inconsistent with experimental determinations of MeO–Al bond strength (in the gas phase) of >38 kcal/mol.<sup>32</sup>

The calculated frequencies of both untipped and tipped methoxy species are shown in Table 1. In Table 2 are the partial

**TABLE 3: Overlap Populations of Methoxy on Al(100) at Bridge Sites, Untipped and Tipped<sup>a</sup>**

	C–O	O–Al (bridge)	C–Al (hollow)
free methoxy	0.3123	N/A	N/A
at bridge, 3.8 Å	0.269g	0.0929	0.0004
at bridge, 3.6 Å	0.2702	0.0642	0.0008
at bridge, 3.4 Å	0.2579	0.0401	0.0012
at bridge, 3.2 Å	0.2456	−0.0056	−0.0234
at bridge, 3.0 Å	0.2229	−0.0088	−0.0194
at bridge, 2.7 Å	0.2580	−0.0343	0.0010
tipped at 30°	0.2532	−0.0318	−0.0159
tipped at 50°	0.2396	0.0715	0.0050
tipped at 60°	0.2036	0.0858	0.0003
tipped at 70°	0.1705	0.0889	−0.0255
tipped at 80°	0.1354	0.0971	−0.0819
tipped at 85°	0.1534	0.0933	−0.0696

<sup>a</sup> Overlap populations computed by Mulliken analysis, using B3LYP/6-311G(d,p). N/A, not available.

**Figure 3.** Enthalpy of adsorption of methoxy, tipped at hollow, parallel Me\*, and normal Me\*.

atomic charges on the carbon, oxygen, and aluminum atoms at the bridge adsorption site, as determined by Mulliken population analysis.

The overlap populations for the C–O, O–Al (bridge), and C–Al (hollow) bonds are listed in Table 3. For both the hollow and the bridge methoxy, initial chemisorption increases the frequency of the C–O over the gas-phase results. This is would be expected for bonding to a group 13 (electron-deficient)

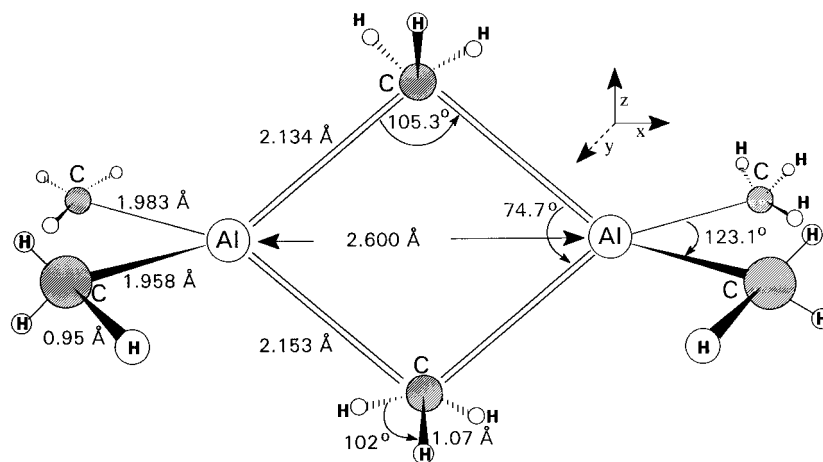
atom.<sup>33</sup> As the radical tips, the frequencies decrease monotonically. While the changes are not tremendously large, they are consistent with the picture of C–O bond-breaking as viewed by conventional transition-state theory. In this theory, at the point of dissociation, a vibrational degree of freedom of the molecule becomes so loose (i.e., has minimal restoring force) that it can be treated as a translation.

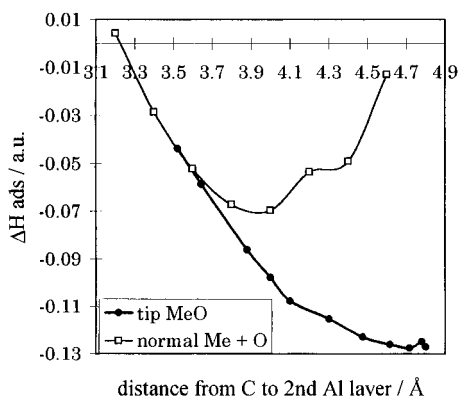
## Discussion

It has been suggested that the C–O bond becomes so weakened upon adsorption that the methyl group ejects upward upon heating. Three reasons have been advanced to justify this hypothesis: first, that there is donation from the Fermi level of the Al metal to an antibonding ( $\sigma^*$ ) MO of the methoxy, thus promoting dissociation;<sup>34</sup> second, that the enthalpy of bond formation between the oxygen and the metal is strong enough to overcome the bond strength of the C–O;<sup>35</sup> and third, that the weakness of alkyl oxygen bonds has been demonstrated by the abstraction of hydrogen from methane by metal oxides in the gas phase.<sup>36</sup> None of these arguments seem convincing.

The  $\sigma^*$  orbital of methanol (or methoxy) is much too high in energy to interact with the Fermi level of the metal.<sup>37</sup> Also, no matter how strong the bond might be between the methoxy oxygen and a metal atom, the orbitals (and electrons) on the oxygen atom are *nonbonding*, so their use elsewhere has virtually no effect on the methyl–oxygen bonding. It is true that metal oxides (including alumina) can abstract hydrogen from methane, but it is not exactly clear how this reflects upon the strength of C–O bonds, as there are no obvious C–O bonds in the gas-phase reaction of metal oxides and methane. The abstraction of hydrogen from methane by aluminum atoms *at 10 K* has been reported.<sup>32</sup>

It initially appeared that the mechanism of dissociation required adsorption at the hollow site, then tipping toward the bridge to form a quasi-methyl-bridged aluminum compound, followed by desorption of the methyl group (Figure 3). Although it is often assumed that molecules chemisorb normal to the surface, this is not necessarily the case.<sup>28</sup> It has been convincingly demonstrated that the predominate source of methane from the reaction of methanol on the surface of aluminide surfaces is methyl radical, which subsequently abstracts a hydrogen from the reaction vessel before detection. This is evident from isotopic labeling experiments.<sup>18</sup> Earlier isotope studies of methanol on pure aluminum were incomplete. The existence of methyl-bridged aluminum compounds, similar to the transition state, is well documented.<sup>38</sup> In  $\text{Al}_2(\text{CH}_3)_6$  (Figure 4) the aluminum–aluminum distance is 2.6 Å, in

**Figure 4.** Molecular structure of  $\text{Al}_2(\text{CH}_3)_6$ .



**Figure 5.** Enthalpy of adsorption of methoxy, tipped at bridge, and dissociation products.

favorable comparison to 2.86 Å on Al(100). There is also experimental evidence for the existence of Al–C bonds during the dissociation.<sup>1,2</sup>

Nevertheless, further analysis of the computations casts doubt on this conclusion. Early TPD experiments on polycrystalline Al determined the energy of activation for the dissociation of methanol to be approximately 29 kcal/mol.<sup>8</sup> Although the cluster used for our calculation is not sufficiently large enough for us to explicitly include adsorbate–adsorbate interactions, the energy of activation necessary to tip the methoxy at the hollow site seemed much too large (>150 kcal/mol).

We therefore calculated the energetics of tipping at the bridge site toward a hollow, and these results are much closer to the experimental results (Figure 5). The steady decrease in both the C–O vibrational frequency and overlap population is consistent with bond weakening. The depolarization of the C–O bond, with the increase of negative charge on the oxygen and decrease of negative charge on the carbon and aluminum, confirms that tipping is sufficient to dissociate the C–O bond. The energy of activation for dissociation is estimated at 36 kcal/mol.

The position of the methyl group in this situation is different from that in the hollow-tipped case. For the hollow-tipped methoxy, the methyl becomes bridged between two aluminum atoms. In the case of the bridged-adsorbed methoxy, the methyl radical, just before desorption from the surface, is in a 4-fold hollow site, for which examples from organometallic chemistry are less forthcoming.<sup>39,40</sup>

## Conclusion

It is possible to determine the site preference of chemisorption of methoxy on the aluminum (100) surface, along with a quantitatively accurate enthalpy of adsorption. Methanol, surprisingly, prefers the 2-fold bridge site to the 4-fold hollow site, although the barrier to diffusion between sites is very low. While tipping from either adsorption site seems to weaken the C–O bond (by forming two bonds: an O–Al one and a H<sub>3</sub>C–Al one), the energy of activation for tipping is much smaller for the bridge-adsorbed methoxy. This energy, as calculated, is in good agreement with the experimentally determined energy of activation for the dissociation reaction of methanol on polycrystalline aluminum. This suggests that the tipping of the C–O axis is the rate-determining step in the dissociation of methanol on aluminum (100).

**Acknowledgment** is made to Mark Kemmerer, for setting up Gaussian 94 to run on the University DEC Alpha-4019. We

also gratefully acknowledge Daniel R. Strongin for his insights with regard to transition metal/aluminum alloys.

## References and Notes

- (1) Chen, J. G.; Beebe, T. P., Jr.; Crowell, J. E.; Yates, J. T., Jr. *J. Am. Chem. Soc.* **1987**, *109*, 1726.
- (2) Basu, P.; Chen, G. Ng, L.; Colaianni, M. L.; Yates, J. T., Jr. *J. Chem. Phys.* **1988**, *89*, (4), 2406.
- (3) Dabrowski, A.; Bogillo, V. I.; Shkilev, V. P. *Langmuir*, **1996**, *12*, 936.
- (4) Kovacs, I.; Solymosi, F. *J. Phys. Chem. B* **1997**, *101*, 5397.
- (5) Legarski, B. R.; Dubois, L. H. *Surf. Sci.* **1992**, *262*, L129.
- (6) Ma, M. C.; Brown, T. C.; Hatnes, B. S. *Surf. Sci.* **1993**, *297*, 312.
- (7) Paul, A.; Yang, M. X.; Bent, B. E. *Surf. Sci.* **1993**, *297*, 327.
- (8) Rogers, J. W., Jr.; Hance, R. L.; White, J. M. *Surf. Sci.* **1980**, *100*, 388.
- (9) Shen, J.; Spiekwak, B. E.; Dumesic, J. A. *Langmuir* **1997**, *13*, 2735.
- (10) Shustorovich, E.; Bell, A. T. *Surf. Sci.* **1992**, *268*, 397.
- (11) Tatibouet, J. M. *Appl. Catal. A* **1997**, *148*, 213.
- (12) Tindall, I. F.; Vickerman, J. C. *Surf. Sci.* **1985**, *149*, 597.
- (13) Weigel, J.; Koeppl, R. A.; Baiker, A.; Wokaun, A. *Langmuir* **1996**, *12*, 5319.
- (14) Whitten, J. E.; Young, C. E.; Pellin, M. J.; Green, D. M.; Jones, P. L. *Surf. Sci.* **1991**, *241*, 73.
- (15) Chaturvedi, S.; Shongin, D. R. *Langmuir* **1997**, *13*, 3162.
- (16) Zhang, Y.; Wang, Y.; Chu, W.; Hsiao, C.; Thompson, A. W. *Scr. Metall. Mater.* **1992**, *26* (6), 925.
- (17) Sheu, B.-R.; Shongin, D. R. *Langmuir* **1994**, *10*, 1801.
- (18) Sheu, B. R.; Strongin, D. R. *J. Catal.* **1995**, *154*, 379.
- (19) Grillo, M. E. *J. Chem. Phys.* **1992**, *97*, 7786.
- (20) Jaeger, R. M.; Kuhlennleck, H.; Freund, H. J.; Wittis, M.; Hoffman, W.; Frandy, R.; Ibach, H. *Surf. Sci.* **1991**, *251*, 866.
- (21) Barger, C. B.; Hall, B. H.; Jette, A. N. *Surf. Sci.* **1982**, *120*, L487.
- (22) Brune, H. *J. Chem. Phys.* **1993**, *99*, 2128.
- (23) Kondoh, H.; Hara, M.; Domen, K.; Nozoye, H. *Surf. Sci.* **1992**, *208*, L287.
- (24) Lauderback, L. L.; Lynn, A. J.; Waltman, C. J.; Larsen, S. A. *Surf. Sci.* **1991**, *243*, 323.
- (25) Schoeichling, J.; Buhnan, K. P.; Hon, K. M. *Surf. Sci.* **1995**, *324*, 113.
- (26) Winkler, A.; Pozgainer, G.; Rendulic, K. D. *Surf. Sci.* **1991**, *251*, 886.
- (27) Benziger, J. B. Thermochemical Methods for Reaction Energetics on Metal Surfaces. In *Metal-Surface Reaction Energetics: Theory and Applications to Heterogeneous Catalysis, Chemisorption, and Surface Diffusion*; Shustorovich, E., Ed.; VCH Publishers, Inc.: New York, 1991; p 92.
- (28) See Zeroka, D.; Hoffmann, R. *Langmuir* **1986**, *3*, 553, for a more theoretical justification.
- (29) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Lahan, M. A.; Zakrewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 94*, Revision D.1; Gaussian Inc.: Pittsburgh, PA, 1995.
- (30) Foresman, J. B.; Frisch, A. *Exploring Chemistry with Electronic Structure Methods*; Gaussian, Inc.: Pittsburgh, 1995, p 6.
- (31) Siegbahn, E. M.; Wahlgen, U. Cluster Modeling of Chemisorption Energetics. In *Metal-Surface Reaction Energetics: Theory and Applications to Heterogeneous Catalysis, Chemisorption, and Surface Diffusion*; E., Ed.; VCH Publishers, Inc.: New York, 1991; p 1.
- (32) Jeong, G.; Klabunde, K. J. *J. Am. Chem. Soc.* **1986**, *108*, 7103.
- (33) Douglas, B.; McDaniel, D.; Alexander, J. *Concepts and Models in Inorganic Chemistry*; John Wiley & Sons: New York, 1994, p 598.
- (34) Sheu, B. R. Doctoral Dissertation, State University of New York at Stonybrook 1994.
- (35) Chen, D. A.; Friend, C. M. *J. Phys. Chem. B* **1997**, *101*, 5712.
- (36) Shiller, P.; Anderson, A. B. *J. Phys. Chem.* **1991**, *95*, 1396.
- (37) Jansen, S. A.; Hoffmann, R. *Surf. Sci.* **1988**, *197*, 474.
- (38) Mak, T. C. W.; Zhou, G.-D. *Crystallography in Modern Chemistry: A Resource of Crystal Structures*; J. C. Wiley and Sons: New York, 1992, p 1024.
- (39) Damrauer, R.; Krempp, M.; Schmidt, M. W.; Gordon, M. S. *J. Am. Chem. Soc.* **1991**, *113*, 2393.
- (40) Uppal, J. S.; Staley, R. H. *J. Am. Chem. Soc.* **1982**, *104*, 1235.