

A Periodic Density Functional Theory Study of the Dehydrogenation of Methanol over Pt(111)

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Nonlocal gradient-corrected periodic density functional theory calculations were used to examine the dehydrogenation of methanol to CO over the Pt(111) surface. Two decomposition routes were examined—one involving the activation of the O–H bond of methanol to form the methoxide intermediate and the other involving C–H bond activation to form the hydroxymethyl intermediate. These intermediates can subsequently react to form formaldehyde, formyl, and finally CO on the surface. Although these pathways are interesting because of their potential relevance for methanol fuel cells, under UHV conditions, we find that methanol will more likely desorb than react on Pt(111). The barriers for C–H and O–H bond activation were found to be much higher than the measured heat of desorption. This is consistent with experimental evidence. Our results indicate that methanol adsorbs weakly at the atop site on Pt. At 25% surface coverage, the hydroxymethyl (CH_2OH), methoxide (CH_3O), formaldehyde (HCHO), and formyl (HCO) species that can form adsorb at the atop, hollow, di- σ , and hollow ($\eta^2-\eta^1\text{-C,O}$) sites, respectively. CO and atomic hydrogen adsorb in the three-fold-hollow sites. The chemisorption energies of CH_3OH , CH_2OH , CH_3O , HCHO , HCO , CO, and H in their most favorable adsorption sites on the Pt surface were predicted to be -43 , -209 , -161 , -49 , -237 , -168 , and -269 kJ/mol, respectively. The computed adsorption energies were used to calculate the overall reaction energies for the proposed series of elementary steps in the metal-catalyzed dehydrogenation of methanol. The C–H bond activation of methanol to form the hydroxymethyl intermediate was calculated to be exothermic by -16 kJ/mol. This path is thermodynamically favored over the competing path involving the activation of the O–H bond of methanol to form methoxide, which was found to be endothermic by $+65$ kJ/mol. The activation barrier for the dehydrogenation of methanol to form the hydroxymethyl intermediate was found to be 50 kJ/mol lower than the barrier to form methoxide. Both barriers are nevertheless too high, and therefore, methanol desorbs rather than reacts over ideal Pt(111) in a vacuum. The dehydrogenation of the hydroxymethyl intermediate to formaldehyde is endothermic by $+37$ kJ/mol, whereas the dehydrogenations of formaldehyde to formyl and of formyl to CO were both found to be exothermic at -63 and -80 kJ/mol, respectively. CO was found to be strongly bound on the metal surface ($\Delta E_{\text{ads}} = -168$ kJ/mol) and is, therefore, likely to be a poison during the dehydrogenation of methanol.

1. Introduction

The electrooxidation of methanol over Pt is at the heart of the direct methanol fuel cell. The catalytic chemistry that occurs at the Pt (or more typically PtRu) anode, however, is quite complex because of the complicated reaction environment present at the electrode. The Pt surface structure; its interaction with the support, solution, and electric field; and the presence of a second metal such as Ru can all impact the surface chemistry. A fundamental understanding of how each of these components contributes to the surface chemistry could offer insight into the design of new materials with improved catalytic performance. At the most basic level, methanol chemisorbs and reacts over Pt to form CO, which is then oxidized to CO_2 . Methanol decomposition over well-defined crystal surfaces of Pt has, therefore, been studied in detail to elucidate the possible reaction pathways. The relevance of experimental and theoretical single-crystal studies, typically performed in the vapor phase under ultrahigh-vacuum (UHV) conditions, to the actual catalytic chemistry that occurs at the anode of a working cell can be

brought into question. Despite various experimental efforts, the adsorption of methanol with water under ultrahigh-vacuum conditions does not lead to an electrocatalytic response.

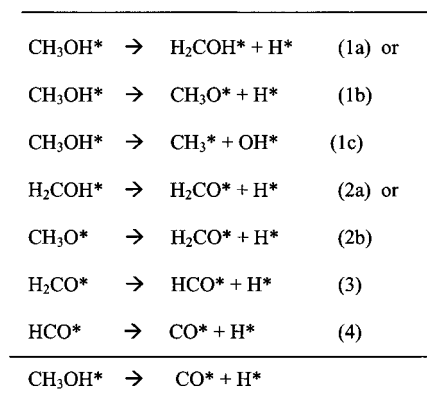
Stuve et al., however, provide an elegant review of methanol decomposition under UHV conditions and discuss its relevance to electrocatalysis.¹ The decomposition of methanol to different CH_xO ($x = 0-4$) intermediates might be of direct importance to the chemistry that occurs at the anode. On the basis of the recent surface-science results and actual electrocatalytic experiments, Stuve et al. proposed the mechanism highlighted in Scheme 1 for the electrooxidation of methanol to form CO. Methanol reacts to form either a hydroxymethyl (CH_2OH) or methoxide (CH_3O) intermediate on Pt, which can subsequently react to form various other intermediates before finally going on to form CO. Little, however, is known about these intermediates or the reaction mechanism.

Our goal in this paper, therefore, is simply to understand Pt-catalyzed decomposition of methanol in the vapor phase. In a subsequent paper, we will outline the effect of the solution and its changes to the surface chemistry. We use gradient-corrected periodic density functional theory to investigate the chemisorption energies, adsorption geometries, overall reaction energies,

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SCHEME 1



and relevant activation barriers for the decomposition of methanol over Pt(111). We also briefly compare these results with those calculated earlier for methanol dehydrogenation over Pd(111).

2. Background

The chemisorption and decomposition of methanol over various transition metals have been widely studied. Methanol typically adsorbs at low temperatures to form either isolated methanol intermediates or multilayers of hydrogen-bonded methanol molecules.² At higher temperatures, methanol can desorb or react to form $\text{C}_x\text{H}_y\text{O}$ intermediates. On most late-transition metals, methanol dissociates into CO and hydrogen at temperatures of about 200–300 K under ultrahigh-vacuum conditions.^{1,3} The reaction proceeds via the activation of the O–H bond in methanol to form a surface methoxide (CH_3O) species and atomic hydrogen. The methoxide species can then undergo successive C–H bond-activation steps to ultimately form CO on the metal surface. On copper and silver surfaces, a stable methoxide species has been identified that decomposes to gaseous formaldehyde and hydrogen at higher temperatures.^{4,5} Masel et al.^{6a} examined the decomposition of methanol over Pt(110) under ultrahigh-vacuum conditions. Using isotope substitution, they showed that the decomposition reaction proceeds via O–H bond scission to yield a methoxide intermediate, which then decomposes to CO. Similar results were found over supported Pt particles.^{6b} The methoxide intermediate is also thought to form on oxygen-precovered Pt(111) and Pt(100) surfaces.³ In the absence of coadsorbed oxygen, however, a stable surface methoxide intermediate has only been identified on the Pt(110)-(1 × 2) surface.^{7,8} Whereas methanol interacts with Pt(100) via its methyl as well as hydroxyl hydrogens, the decomposition is again thought to occur via the methoxide intermediate. Defect-free Pt(111) has been shown to be unreactive toward methanol decomposition.⁹ On a rough Pt(111) surface, ultrahigh-vacuum experiments indicate that methanol decomposes into CO and H_2 predominantly over defect sites without any evidence for the formation of other stable intermediates.¹⁰ In this paper, we examine the chemistry over ideal Pt(111) simply to provide insights into the electrooxidation of methanol.

Over the past few years, it has been demonstrated that theoretical techniques can serve as useful tools for obtaining a fundamental understanding of elementary reaction chemistry. Shustorovich and Bell¹¹ used the bond-order-conservation approach to resolve the reaction energies and activation barriers for the various elementary steps for the reverse reaction involving the hydrogenation of CO to methanol over Pt(111).

More recently, Kua et al.¹² and Ishikawa et al.¹³ independently presented first-principles theoretical studies on the oxidation of methanol over platinum and other transition metal clusters. These studies provide an excellent starting point for understanding the dehydrogenation mechanism. We advance their ideas here by performing calculations using periodic density functional theory (DFT). The previous studies used clusters containing 8–10 metal atoms, which can lead to spurious artifacts due to cluster size effects and the use of frozen unoptimized clusters. To eliminate these effects, we performed fully periodic DFT calculations, which allow for a more complete description of the electronic structure of the metal. In addition, we calculated the activation barriers for the relevant elementary steps.

3. Computational Details

Nonlocal gradient-corrected periodic density functional theory (DFT) calculations were performed using the Vienna ab Initio Simulation Package (VASP).¹⁴ The Kohn–Sham equations¹⁵ were solved self-consistently by using a plane-wave basis set. A cutoff kinetic energy of 330 eV was used to make the plane-wave basis set finite. We performed a series of calculations to verify the convergence of the computed electronic energies at the chosen cutoff energy. The nuclei and core electrons of the atoms were described using ultra-soft scalar relativistic pseudo-potentials.¹⁶ The Perdew Wang 91 GGA¹⁷ exchange correlation functional was used for all electronic structure calculations. A $5 \times 5 \times 1$ *k*-point grid was used to describe the first Brillouin zone. We carried out calculations at various grid sizes to ensure that the $5 \times 5 \times 1$ *k*-point mesh was sufficient to provide accurate energetic and structural information. Increasing the number of *k* points in the first Brillouin zone to $7 \times 7 \times 1$ was found to produce only slight changes in the adsorption geometries and less than 0.03-eV changes in the adsorption energies. For better convergence of the self-consistent field, an electronic temperature of $k_{\text{B}}T = 0.1$ was chosen for the Fermi distribution. All final energies were subsequently extrapolated back to 0 K.

A 2×2 unit cell was chosen to perform all calculations. The 2×2 unit cell consisted of four metal atoms on the surface layer on which a single CH_3O species such as methanol was allowed to adsorb. The model therefore corresponds to an adsorbate surface coverage of 25%. We are aware that the adsorption energies and geometries of the organic intermediates might be coverage-dependent. It is computationally very demanding, however, to examine the energetics and the most-favored structural conformation for all of the intermediates involved in the catalytic dehydrogenation of methanol at various coverages. For the present study, we chose a consistent coverage of one-quarter monolayer for all adsorbates to make a direct comparison of the computed chemisorption energies and structural conformations.

The metal surface is described here by three layers of hexagonally close-packed Pt atoms that make up the (111) surface. We examined the chemisorption of hydrogen over three-, four-, and five-layer Pt(111) slabs. The binding energies for atomic hydrogen over these three slabs were calculated to be less than 5 kJ/mol apart. This difference is within the present accuracy of the density functional theory methodology. Hence, a three-layer Pt(111) slab is sufficiently accurate to model the energetics over a Pt(111) surface. We also reconfirmed that the computed chemisorption energies were accurately converged with respect to the thickness of the platinum slab for the more strongly bound intermediates such as CO and formyl.

To obtain the theoretical lattice constant of bulk platinum, a series of single-point calculations was performed to map the

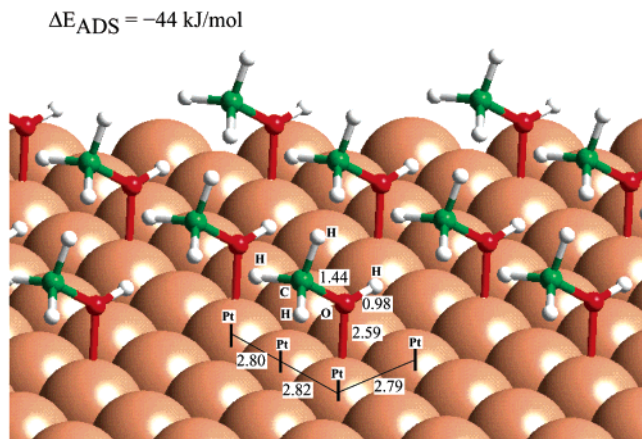


Figure 1. DFT-optimized structure of methanol adsorbed in a 2×2 overlayer at the atop site on Pt(111). The adsorption energy of methanol was calculated to be -44 kJ/mol .

electronic energy of platinum as a function of the lattice constant. The total energy of bulk platinum was found to be at a minimum for a lattice constant of 2.81 \AA . This is close to the experimental lattice constant of bulk platinum metal (2.78 \AA).¹⁸ The calculated lattice constant (2.81 \AA) was subsequently used for all calculations reported herein to maintain a true energy minimum with respect to the bulk Pt reference state. However, to allow for likely changes in the surface structure upon adsorption of the organic intermediates, the first two layers of the Pt(111) slab were fully relaxed during every geometry optimization. The metal atoms in the third layer of the Pt(111) surface were not directly involved in interactions with the adsorbate and were therefore held fixed at their bulk positions. All atomic coordinates of the adsorbates and metal atoms (except for the metal atoms in the third layer of the slab) were optimized to a force of less than 0.08 eV/\AA on each atom.

In periodic slab calculations, a unit cell consisting of a finite number of metal atoms and adsorbates is repeated in space along the crystal lattice vectors (a_1 , a_2 , and a_3 in Figure 1). This creates a truly two-dimensional Pt(111) surface that fully takes into account the metallic nature of platinum. A vacuum region is used to separate the surface from its periodic image in the direction normal to the surface (a_3 vector). We used a vacuum region of 11-\AA thickness in the third dimension. We also verified that the chosen vacuum region was sufficiently large to eliminate any unphysical interactions between the Pt(111) slab and its periodic image along the a_3 vector.

All of the chemisorption energies reported herein were calculated using the equation

$$\Delta E_{\text{ads}} = E_{\text{adsorbate/Pt(111)}} - E_{\text{adsorbate}} - E_{\text{Pt(111)}} \quad (1)$$

where ΔE_{ads} is the adsorption energy of the adsorbate on Pt(111), $E_{\text{adsorbate/Pt(111)}}$ is the total electronic energy of the optimized adsorbate on Pt(111), $E_{\text{adsorbate}}$ is the total electronic energy of the adsorbate, and $E_{\text{Pt(111)}}$ is the total electronic energy of the clean Pt(111) slab. The convention used here is that $\Delta E_{\text{ads}} < 0$ refers to a favorable heat of adsorption as it indicates a release of energy.

The reaction energies were calculated using the equation

$$\Delta E_{\text{reaction}} = -\sum(\Delta E_{\text{ads}})_{\text{reactants}} + (\Delta E_{\text{reaction}})_{\text{gas phase}} + \sum(\Delta E_{\text{ads}})_{\text{products}} \quad (2)$$

where $\Delta E_{\text{reaction}}$ is the energy change associated with the

elementary reaction over the metal surface; $\sum(\Delta E_{\text{ads}})_{\text{reactants}}$ and $\sum(\Delta E_{\text{ads}})_{\text{products}}$ represent the sum of the adsorption energies of all of the reactants and products, respectively; and $(\Delta E_{\text{reaction}})_{\text{gas phase}}$ is the energy change associated with the elementary reaction step in the gas phase. The ΔE_{ads} term for all of the reactants and products is calculated using eq 1. The $(\Delta E_{\text{reaction}})_{\text{gas phase}}$ term on the RHS of eq 2 was calculated as the difference between the total electronic energy of the products in the gas phase and the total electronic energy of the reactants in the gas phase. In our convention, a negative value of $\Delta E_{\text{reaction}}$ indicates that the reaction is exothermic, and a positive value of $\Delta E_{\text{reaction}}$ indicates that the reaction is endothermic.

Equation 2 refers to idealized reactant and product states. There is no change in the surface coverage, and the reactant and product states are typically calculated at relatively lower coverages so that lateral interactions are small. To begin to calculate the first-order effects of coverage, we also computed all surface reaction energies using the equation

$$\Delta E_{\text{reaction}} = (E_{\text{products}}) - (E_{\text{reactants}}) \quad (3)$$

where $\Delta E_{\text{reaction}}$ is the energy change due to the surface reaction. E_{products} and $E_{\text{reactants}}$ refer to the total electronic energies of the adsorbed products and adsorbed reactants, respectively. The surface coverage increases for a bond-breaking step and decreases for a bond-making step. For bond-breaking steps, such as in the case of the dehydrogenation of methanol, the lateral interactions between the reaction products are typically found to be repulsive. This leads to reaction energies that are about 10 kJ/mol more endothermic (less exothermic) than those computed using eq 2. Nevertheless, the reaction energies associated with the elementary steps in the dehydrogenation of methanol follow exactly the same trend when either eq 2 or eq 3 is used. For a consistent analysis of our results, we chose to describe in detail only the values of reaction energies computed using eq 2.

Transition states for the key reaction steps were all isolated using the nudged elastic band approach.¹⁹ We initiated the transition state search by interpolating a series of images of the system between the reactant and product states. Each image was then optimized in parallel to map the minimum-energy reaction path. For each image and every iteration, the forces acting on the nuclei were decomposed into components parallel and perpendicular to the reaction path. To prevent the images from rolling over to either the reactant or the product states (local minima on the potential energy surface) during optimization, the component of the force parallel to the reaction path was set to zero. The nuclear positions, however, were fully optimized along the normal to the reaction path. This approach helped converge the images to the minimum-energy path. A spring interaction between the images was added to maintain the spacing between adjacent images to a constant. The highest point along the minimum-energy path is the transition state along the chosen reaction path. The energy of the highest point relative to that of the reactant state gives the activation barrier for the reaction.

4. Results and Discussion

The dehydrogenation of methanol begins with the adsorption of methanol from the gas phase onto Pt(111). The adsorbed methanol can then either desorb or decompose via a series of sequential steps to produce various CH_xO intermediates and surface-bound hydrogen atoms (Scheme 1).²⁰

The first decomposition step involves the activation of the C–H, O–H, or C–O bonds of methanol to initiate the catalytic

cycle. The resulting intermediates for C–H, O–H, and C–O activation are CH_2OH^* , $\text{CH}_3^*/\text{OH}^*$, and $\text{CH}_3^*/\text{OH}^*$, respectively. C–O activation is much less favorable than the C–H or O–H activation routes and is therefore not considered here.²¹

The hydroxymethyl and methoxide intermediates that form can dehydrogenate to form formaldehyde (H_2CO^*) and hydrogen on the surface. Formaldehyde can, in turn, dehydrogenate to produce the formyl intermediates (HCO^*) and hydrogen, and the formyl intermediates can dehydrogenate further to produce carbon monoxide and surface hydrogen.

We have broken down our results for the Pt-catalyzed dehydrogenation of methanol into four sections. In section 4.1, we examine the chemisorption of the various surface species produced during the dehydrogenation of methanol to CO. The adsorption energies and geometric structures of the intermediates that form are compared with known theoretical and experimental observations. In sections 4.2 and 4.3, we examine the overall reaction energies and activation barriers for some of the elementary surface reaction steps in the catalytic dehydrogenation of methanol. Finally, in section 4.4, we discuss the relevance of our results to electrocatalytic chemistry.

4.1. Chemisorption Energies. (a) *Methanol.* At 25% surface coverage, methanol binds to the atop site of Pt(111), forming a weak van der Waals-type interaction with the surface through its oxygen atom (Figure 1). The adsorption energy of methanol over the surface was found to be -43.2 kJ/mol. That the interaction of methanol with the surface is weak is indicated by the rather long Pt–O bond distance (2.59 Å) in the optimized structure.

High-resolution electron energy-loss spectroscopy,^{3,6,20} ultraviolet photoelectron spectroscopy,¹⁰ and infrared spectroscopy¹⁰ experiments also suggest that methanol binds to the metal surface via the oxygen. At low coverages, methanol adsorbs as a monomer, whereas at higher coverages, it forms clusters that are stabilized by hydrogen bonding. Temperature-programmed desorption studies by Villegas and Weaver² indicate that methanol desorbs at two temperatures (140 and 180 K) over Pt(111). The low-temperature peak (140 K) was attributed to desorption from the condensed, physisorbed methanol layer, whereas the peak at 180 K was due to desorption of methanol in direct contact with Pt. Assuming first-order kinetics for the desorption of methanol and a preexponential factor of $10^{13}/\text{s}$, the adsorption energy of methanol over Pt was estimated to be -46 kJ/mol. Our value for the adsorption energy is in very good agreement with the experimental result.

(b) *Methoxide Intermediate.* At low coverages ($\sim 10\%$), the methoxide intermediate favorably adsorbs at the three-fold fcc hollow site on Pt. At 25% surface coverage, however, the methoxide intermediate prefers to adsorb at the Pt–Pt bridge site rather than the three-fold-hollow site. The chemisorption energy for methoxide (at 25% coverage) adsorbed at the Pt–Pt bridge was found to be -161 kJ/mol, which is 14 kJ/mol stronger than methoxide bound to the hollow site. Chemisorption of methoxide at the atop sites was the least favorable. During a full geometry optimization, the methoxide intermediates that were bound to the atop sites on Pt were found to readily migrate to the bridge sites, indicating that there is only a small barrier (if any) for the diffusion of the methoxide intermediates from the atop to the Pt–Pt bridge sites.

The bridge-bound methoxide intermediate interacts with the surface through oxygen (Figure 2a), forming two Pt–O bonds that are 2.51 Å long. The internal C–O bond in the bridge-bound methoxide is tilted at an angle of 65° with respect to the surface plane. In contrast, for methoxide chemisorbed at the

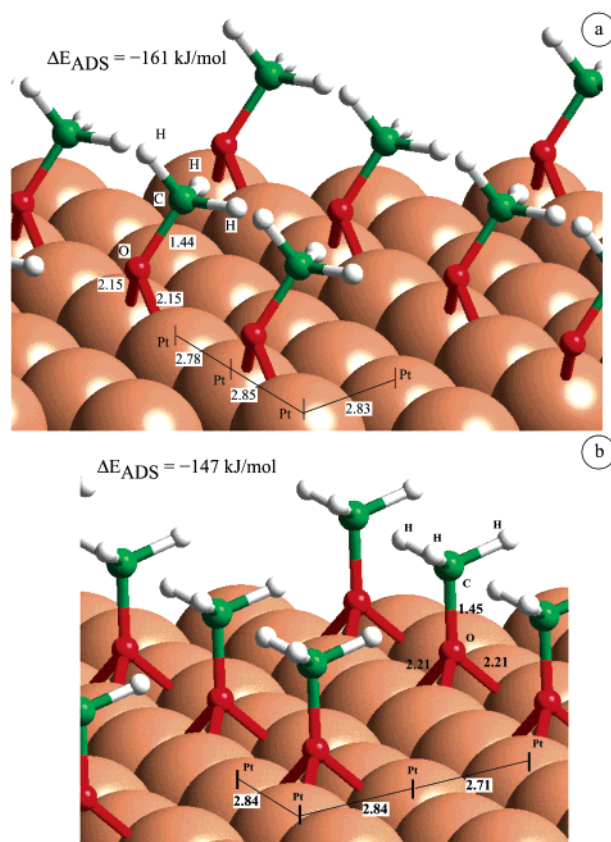


Figure 2. DFT-optimized structures for the methoxide intermediate adsorbed in a 2×2 overlayer (a) at the bridge site ($\Delta E_{\text{ads}} = -161$ kJ/mol) of Pt and (b) at the three-fold fcc hollow site on Pt(111) ($\Delta E_{\text{ads}} = -147$ kJ/mol)

three-fold-hollow site, the C–O bond tends to orient perpendicular to the metal surface, with the methyl group directed away from the surface (Figure 2b). For both the bridge-bound methoxide and the methoxide adsorbed at the hollow site, the direct interaction of the methyl group with the Pt(111) surface was found to be weak.

(c) *Hydroxymethyl Intermediate.* The hydroxymethyl intermediate prefers to adsorb at the atop site on Pt(111) through the carbon atom (Figure 3). The chemisorption energy of the hydroxymethyl intermediate on the Pt surface was calculated to be -209 kJ/mol. This is slightly lower than the value of -240 kJ/mol reported over Pt clusters.¹³ The C–O bond in adsorbed hydroxymethyl is tilted at an angle of 63° with respect to the surface plane, such that the oxygen atom is directed away from the metal surface. This results in a relatively weak interaction between the terminal hydroxyl functional group of hydroxymethyl and the metal. The hydroxymethyl intermediate can therefore freely rotate about the Pt–C bond with less than 1 kJ/mol change in the value of its chemisorption energy.

(d) *Formaldehyde.* Formaldehyde prefers to bind in the di- σ mode on Pt(111) (Figure 4). In the optimized structure, the carbonyl group of formaldehyde is oriented parallel to the metal such that the Pt–C and Pt–O bonds that form are of nearly the same lengths (2.12 and 2.06 Å, respectively), while the hydrogen atoms are directed away from the surface. Delbecq and Sauter²² examined the adsorption of formaldehyde at various sites on Pt(111) using extended Huckel theory. Their analysis also suggests that formaldehyde prefers adsorption in the di- σ mode.

The adsorption energy of formaldehyde over the Pt(111) surface was calculated to be -49 kJ/mol. Formaldehyde is a closed-shell, stable species in the gas phase and hence interacts

$$\Delta E_{\text{ADS}} = -209 \text{ kJ/mol}$$

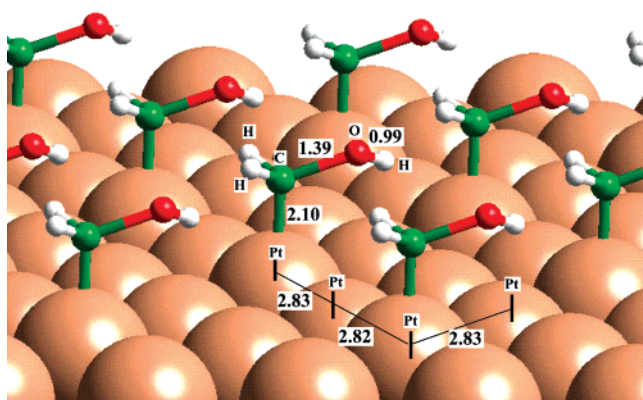


Figure 3. DFT-optimized structure for the adsorption of the hydroxymethyl intermediate in a 2×2 overlayer at the atop site of the Pt(111) surface ($\Delta E_{\text{ads}} = -209$ kJ/mol).

$$\Delta E_{\text{ADS}} = -49 \text{ kJ/mol}$$

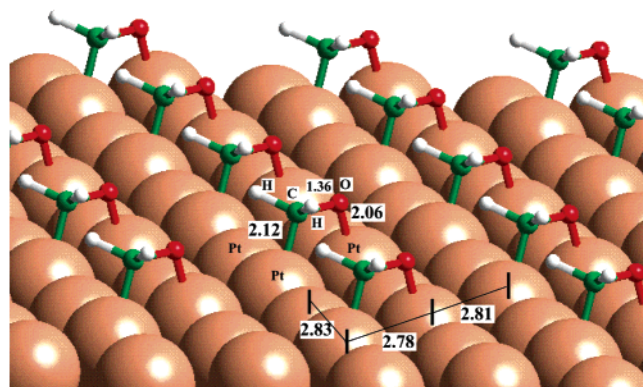


Figure 4. DFT-optimized structure of formaldehyde adsorbed at the di- σ site in a 2×2 overlayer on Pt(111). The adsorption energy of formaldehyde was estimated to be -49 kJ/mol.

weakly with platinum. Using temperature-programmed desorption studies, Abbas et al.²³ estimated the adsorption energy of formaldehyde on Pt(111) to be about -52 kJ/mol. Our calculated value for the heat of adsorption of formaldehyde is in very good agreement with their estimate.

(e) *Formyl Intermediate.* The optimized structure of the formyl intermediate adsorbed on Pt is shown in Figure 5. Formyl prefers to adsorb in the $\eta^2-\eta^1$ -C,O configuration. In this configuration, the carbon atom of formyl is oriented over a Pt-Pt bridge site, and the oxygen atom is oriented on top of an adjacent Pt atom. The carbon atom, which is sp -hybridized in the gas-phase formyl species, partially rehybridizes to sp^3 upon interaction with the metal, resulting in an elongation of the C-O bond from 1.22 Å in gas-phase formyl to 1.29 Å in the chemisorbed intermediate.

The chemisorption energy of the formyl species over the Pt(111) surface was calculated to be -236.6 kJ/mol. Gomes et al.²⁴ reported a slightly higher value of -252 kJ/mol for the heat of adsorption of the formyl intermediate over Pt using density functional theory. The difference in the two values is likely an effect of the finite size of the Pt cluster used in their model. Cluster calculations typically predict stronger binding energies than periodic slab models.

$$\Delta E_{\text{ADS}} = -237 \text{ kJ/mol}$$

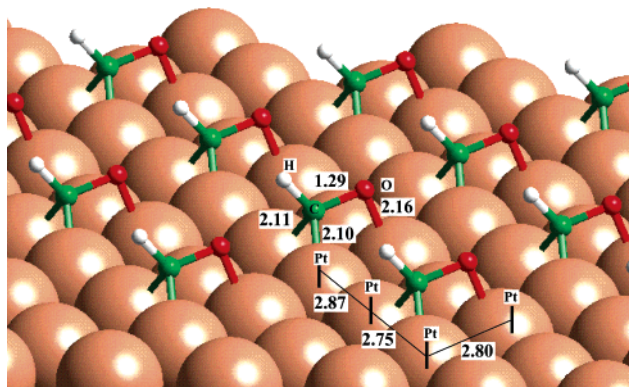


Figure 5. DFT-optimized structure for the formyl intermediate chemisorbed in the $\eta^2-\eta^1$ mode in a 2×2 overlayer on the Pt(111) surface. The chemisorption energy of the formyl intermediate was estimated to be -237 kJ/mol.

(f) *Carbon Monoxide.* The adsorption of carbon monoxide over the Pt(111) surface has been extensively investigated using both theory and experiment. We calculated it here only to provide a consistent set of values necessary for the overall reaction path analysis. It is widely accepted that CO binds to metal surfaces via the Blyholder mechanism,²⁵ in which there is donation of electron density from the 5σ orbital of CO molecule to the metal surface and back-donation of electron density from the surface into the $2\pi^*$ orbital of CO. We examined the adsorption of CO at the atop, bridge, and three-fold hollow sites on Pt(111). At 25% surface coverage, CO prefers to bind in the three-fold hcp hollow site on Pt(111), with a chemisorption energy of -168 kJ/mol. In this adsorption mode, CO interacts with the metal surface through the carbon atom, forming three Pt-C bonds of about 2.11 Å each. The adsorption energies of CO at the atop, bridge, and three-fold fcc hollow sites on the Pt(111) surface were found to be -147 , -161 , and -163 kJ/mol, respectively. Experimental studies using diffraction, vibration spectroscopy, and scanning probe microscopy have shown that the adsorption mode of CO over the Pt(111) surface depends on the surface coverage of CO. Low-energy electron diffraction (LEED) and electron energy loss spectroscopy (EELS)^{26,27} indicate that, at low coverages, the CO adlayer on Pt(111) forms a $(\sqrt{3} \times \sqrt{3})\text{-R}30^\circ$ structure with a preference for chemisorption at the atop sites on the surface layer. At higher coverages, the surface structure of CO converts to $c(4 \times 2)$, with an almost equal preference for both the atop and bridge sites. Density functional theory calculations, however, have consistently predicted that CO prefers to chemisorb on Pt(111) at the three-fold-hollow site rather than at the atop or bridge sites. This is a known issue that was recently addressed by Feibelman et al.²⁸ The discrepancy is likely an artifact of the generalized gradient approximation (GGA) used in DFT calculations, which favors chemisorption at higher-coordination sites.

(g) *Hydrogen.* An excellent theoretical analysis of the adsorption of hydrogen over Pt(111) is provided by Hoffmann et al.²⁹ Their findings show that, at quarter-monolayer surface coverage, the chemisorption strengths of a hydrogen atom are nearly the same at the atop, bridge, and three-fold-hollow sites. A hydrogen atom can therefore move freely on the surface. We examined the adsorption of hydrogen in the three-fold fcc hollow site on Pt(111). The binding energy of a H atom (with respect to gas-phase atomic hydrogen) was found to be -269 kJ/mol.

TABLE 1: Adsorption Energies (kJ/mol) and Most Favorable Adsorption Sites of Reaction Intermediates over Pd(111) and Pt(111)

intermediate	Pd(111)		Pt(111)	
	ΔE_{ads}	adsorption site	ΔE_{ads}	adsorption site
CH ₃ OH	-29.5	atop	-43	atop
CH ₃ O	-171	three-fold hollow	-161	bridge
CH ₂ OH	-179	atop	-209	atop
HCHO	-54	di- σ	-49	di- σ
HCO	-237	$\eta^2-\eta^1\text{-C,O}$	-237	$\eta^2-\eta^1\text{-C,O}$
CO	-191	three-fold hollow	-168	three-fold hollow
H	-267	three-fold hollow	-269	three-fold hollow

This corresponds to an adsorption energy of -86 kJ/mol, which is exothermic with respect to a gaseous dihydrogen molecule. Our result is in very good agreement with the value of -83 kJ/mol reported by Hoffmann et al. Thermal desorption spectroscopy studies show that the heat of dissociative adsorption of H₂ over Pt(111) is about -83 kJ/mol.^{30–32}

Comparisons with Pd(111). The adsorption energies for all of the intermediates discussed thus far for methanol decomposition over Pt are given in Table 1. We carried out the same calculations for these intermediates on Pd(111) and list the results in Table 1 for comparison with the values over Pt. With the exception of the methoxide species, all other dehydrogenation intermediates favor the same adsorption sites on Pt and Pd. The methoxide intermediate prefers to adsorb over the bridge site on Pt(111) but favors the three-fold-hollow site on Pd(111).

The binding energy of methanol over Pd(111) was calculated to be -29.5 kJ/mol, which is slightly lower than its value over the Pt surface. The hydroxymethyl intermediate also binds about 30 kJ/mol more weakly to Pd than to Pt. The methoxide intermediate, on the other hand, binds slightly more strongly on Pd than on Pt. The adsorption energy of methoxide over Pd(111) was predicted to be -171 kJ/mol, which is about 10 kJ/mol higher than the result over Pt(111). The binding energy of formaldehyde over Pd(111) was calculated to be -54 kJ/mol, which is nearly the same as the value over Pt(111). The calculated binding energy of formaldehyde on Pd(111) is in excellent agreement with the experimental value of -51 kJ/mol estimated by Davis and Barteau³³ from temperature-programmed desorption data.

We note that the values reported herein over Pd(111) are all within 5 kcal/mol of the values that we reported earlier from cluster calculations, except the result for the formyl intermediate. Cluster calculations indicate that this energy is on the order of 340 kJ/mol, which is higher than the value determined here. The differences might be due to cluster-size effects.

Adsorption-Induced Surface Corrugation. Bulk platinum metal has a face-centered-cubic crystal structure. Each atom in the bulk is therefore surrounded by 12 neighboring atoms. When a (111) surface is cut from the bulk metal, the coordination number of the atoms forming the surface layer is reduced to 9. The surface atoms therefore have unsaturated bonds, and the surface layer tends to relax inward for the clean Pt(111) slab. The formation of adsorbate–metal bonds through chemisorption can cause the surface atoms directly involved in the adsorption to be pulled outward. This gives rise to a selective degree of corrugation in the surface metal layer. In Table 2, we list the surface corrugation caused by the adsorbates involved in the dehydrogenation of methanol to CO. The surface corrugation was calculated here as the difference in the z coordinates of the highest-lying and lowest-lying metal atoms in the surface layer of the Pt(111) slab. The surface corrugation induced by an adsorbate was found to be directly related to its heat of

TABLE 2: Adsorbate-Induced Corrugation on the Pt(111) Surface Layer

adsorbate	ΔE_{ads} (kJ/mol)	surface corrugation (\AA)
CO	-168	0.214
HCO	-237	0.219
H ₂ CO	-49	0.11
CH ₂ OH	-209	0.27
CH ₃ O	-161	0.147
CH ₃ OH	-43	0.091

adsorption. Methanol and formaldehyde are weakly bound to platinum. They therefore lead to very small changes in the geometry of the surface layer. The surface corrugation is more pronounced for stronger adsorbates such as HCO, CO, and CH₂OH. These values are likely overestimates of surface relaxation because of the gradient corrections from the functionals,³⁴ as well as the limited unit cell size that was employed here. We have reported these relaxations only to relate them qualitatively to the adsorbate–metal bond strength. Calculations with larger unit cells might be necessary to quantify the relaxations.

4.2. Reaction Energies. According to Scheme 1, methanol can dehydrogenate either via the activation of its C–H bond to produce the hydroxymethyl and hydrogen intermediates or via the activation of its O–H bond to produce the methoxide intermediates and surface hydrogen. To understand the surface-catalyzed activation of methanol, we first examine the simple thermal free-radical chemistry that occurs in the gas phase at high temperatures. In the gas phase, the C–H bond-breaking reaction of methanol is calculated to be endothermic by $+419$ kJ/mol, whereas the O–H bond-breaking reaction is endothermic by $+451$ kJ/mol. The reactions are both highly endothermic as the hydroxymethyl, methoxide, and hydrogen that are produced are all in the form of unstable free radicals. The C–H bond-breaking reaction, however, is found to be relatively less endothermic, and hence more favorable, than the O–H bond-activation reaction.

The activation of methanol over Pt is more facile and occurs at much lower temperatures than in the gas phase, as the methoxide, hydroxymethyl, and hydrogen that form as products can all be stabilized by the metal. Over Pt(111), the C–H bond-breaking reaction to form the hydroxymethyl and hydrogen intermediates was found to be exothermic by -16 kJ/mol, whereas the O–H bond-breaking reaction to form the methoxide and hydrogen intermediates was found to be endothermic by $+64$ kJ/mol. As in the gas phase, the C–H bond-breaking reaction of methanol over the surface was found to be thermodynamically more favorable than the O–H bond-breaking reaction.

The C–H bond of methanol is activated in preference to the O–H bond for two reasons. First, as seen from the gas-phase energetics, the C–H bond of methanol is 30 kJ/mol weaker than the O–H bond. Second, and more importantly, when the C–H bond of methanol is activated, the hydroxymethyl intermediate ($\Delta E_{\text{ads}} = -209$ kJ/mol) is produced, which is 50 kJ/mol more strongly bound to the Pt surface than the methoxide intermediate ($\Delta E_{\text{ads}} = -161$ kJ/mol). The reaction leading to the hydroxymethyl intermediate is therefore favored over that leading to the methoxide intermediate by 80 kJ/mol. Quantum chemical calculations performed over platinum clusters also suggest that methanol prefers to dehydrogenate by the activation of its C–H rather than O–H bond.^{12,13}

The hydroxymethyl intermediate that forms can further dehydrogenate to produce formaldehyde and hydrogen. The reaction involves the activation of the O–H bond of hydroxymethyl. Formaldehyde can be also produced by the activation

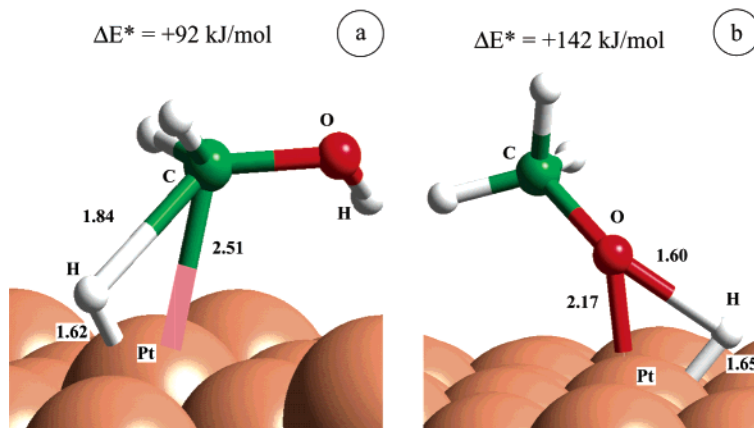


Figure 6. DFT-resolved transition states structures for (a) the C–H bond activation of methanol to form the hydroxymethyl and hydrogen intermediates over Pt(111) and (b) the O–H bond activation of methanol over Pt(111) to form surface methoxide and atomic hydrogen.

of a C–H bond of the methoxide intermediate. We again analyze the surface chemistry by first exploring the thermal free-radical chemistry that can occur in the gas phase at higher temperatures. The reactions of methoxide and hydroxymethyl radicals to form formaldehyde and atomic hydrogen are both endothermic in the gas phase—the former by +113.1 kJ/mol and the latter, which involves O–H bond activation, slightly more endothermic by +145.2 kJ/mol. Recall that the gas-phase reactions to form the methoxide and hydroxymethyl free radicals from methanol were endothermic by over +400 kJ/mol. The lower endothermicity of the reactions leading to formaldehyde as compared to those leading to methoxide and hydroxymethyl is expected as formaldehyde is significantly more stable than methoxide or hydroxymethyl free radicals in the gas phase. Over Pt(111), the dehydrogenation of the methoxide intermediate to form formaldehyde and hydrogen was found to be exothermic by –44 kJ/mol, whereas the dehydrogenation of the hydroxymethyl intermediate to form formaldehyde and hydrogen was still endothermic, but less so, at +37 kJ/mol. Once again, the reaction involving the activation of the C–H bond over the surface was found to be exothermic, whereas the reaction involving the O–H bond activation was endothermic, the former being 80 kJ/mol more favorable than the latter. Earlier, we indicated that methanol prefers to dehydrogenate over the Pt surface via the activation of the C–H bond, forming the hydroxymethyl rather than the methoxide intermediate. The subsequent dehydrogenation of the hydroxymethyl intermediate into formaldehyde and hydrogen, however, was found to be thermodynamically less favored than the dehydrogenation of the methoxide intermediate to produce formaldehyde.

Formaldehyde can undergo C–H bond activation to produce formyl intermediates and atomic hydrogen. Whereas formaldehyde is weakly adsorbed on Pt ($\Delta E_{\text{ads}} = -49$ kJ/mol), both the formyl and the hydrogen intermediates interact very strongly with the surface ($\Delta E_{\text{ads}} = -236.6$ and -269 kJ/mol, respectively). This favorably affects the energetics of dehydrogenation and drives the reaction in the forward direction. The C–H bond activation of formaldehyde to form the formyl and hydrogen intermediates over Pt was found to be exothermic by –62.6 kJ/mol. The subsequent decomposition of the formyl intermediate into CO and atomic hydrogen over Pt(111) was even more exothermic at –79.9 kJ/mol.

In general, it appears that all C–H bond-activation steps that occur during the dehydrogenation of methanol over Pt are exothermic whereas all O–H bond-activation steps are endothermic. The C–H bond-activation steps were found to become

increasingly more exothermic as the remaining number of hydrogen atoms within the CH_xO intermediate becomes reduced. The C–H bond activation of the formyl intermediate over the surface was found to be more exothermic than the C–H bond activation of formaldehyde, which, in turn, was even more exothermic than the C–H bond activation of methoxide.

The formyl intermediate is very strongly bound to Pt. One would therefore expect it to poison the surface toward further dehydrogenation of methanol. However, the C–H bond activation of formyl to produce CO and hydrogen on the surface is a highly exothermic reaction ($\Delta E_{\text{rxn}} = -79.9$ kJ/mol). The formyl intermediate, therefore, though strongly bound to the surface, is likely to decompose readily into CO and hydrogen. Like formyl, CO is very strongly bound to the platinum surface. The desorption of CO from Pt(111) is endothermic by +168 kJ/mol. Unlike for the formyl intermediates, however, no alternative viable route for the decomposition of CO on the surface is available. CO remains adsorbed and can be a poison for the further dehydrogenation of methanol.

4.3. Activation Barriers. In our discussion so far, we have focused on the thermodynamics associated with the elementary reaction steps that can occur during the dehydrogenation of methanol over Pt(111). To gain insights into the kinetics of dehydrogenation, we examined the activation barriers associated with some of the key elementary steps. The calculated overall reaction energies indicate that C–H bond activation should be significantly easier than O–H bond activation. The transition states associated with the C–H and O–H bond-activation steps of methanol over the Pt surface are shown in Figure 6a and b, respectively, and are described here.

In the C–H-activated route, methanol adsorbs on Pt through oxygen, with the carbon atom directed away from the surface (Figure 1). The carbon atom tilts toward the surface where a Pt atom inserts into the C–H bond. As the C–H bond is activated, the oxygen atom begins to move away from the surface. At the transition state, both the C and H atoms of methanol interact with Pt, forming Pt–C and Pt–H bonds that are 2.51 and 1.62 Å long, respectively. This interaction weakens the C–H bond of methanol, which is stretched to 1.84 from 1.09 Å. The transition state reported here for the C–H bond activation of methanol is structurally very similar to results reported previously for the C–H bond activation of other hydrocarbons.³⁵

The O–H bond of methanol is activated by the insertion of a surface Pt atom into the O–H bond. The activated complex for the O–H bond-breaking reaction involves a three-center intermediate comprising O, H, and a surface Pt atom. This is

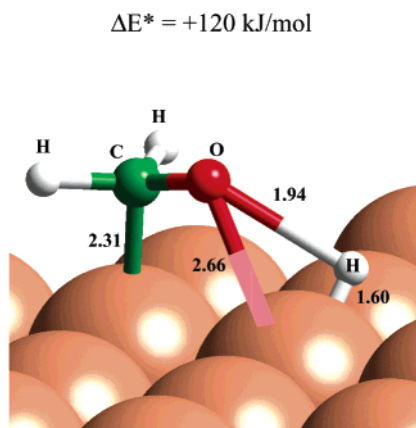


Figure 7. DFT-resolved transition state structure for the C-H bond activation of hydroxymethyl to form formaldehyde and atomic hydrogen over Pt(111).

very similar to the three-center complex for C-H activation. At the transition state, the O-H bond is elongated to 1.60 from 0.98 Å in methanol. As the O-H bond dissociates, the departing hydrogen atom begins to coordinate with a surface Pt atom. The Pt-H bond is only 1.65 Å long at the transition state.

The activation barrier for the O-H bond-breaking reaction of methanol to form methoxide and hydrogen intermediates was calculated to be +142 kJ/mol. The barrier for C-H bond activation was found to be 50 kJ/mol lower (+92 kJ/mol) than that for O-H bond activation. Using the analytic unity bond index-quadratic exponential potential (UBI-QEP) method of Shustorovich and Sellers,³⁶ Ishikawa et al. also predicted that the activation barrier for the C-H bond-breaking reaction of methanol to form the hydroxymethyl and hydrogen intermediates is lower (by about 35 kJ/mol) than that for the O-H bond-breaking reaction.¹³ The calculated activation barriers and overall reaction energies indicate that the formation of the hydroxymethyl intermediate is favored over formation of the methoxide intermediate.

In contrast, the methoxide intermediate is seen on Pt(111) in the presence of preadsorbed oxygen atoms.^{37,38} This is likely because the mechanism for decomposition over oxygen-precovered Pt(111) is different from that over clean Pt(111). The surface oxygen can act as a Brønsted base that facilitates the breaking of the hydroxyl hydrogen of methanol to form the methoxide intermediate because it is more acidic than the methyl hydrogen. Stuve has shown that oxygen acts as a promoter for the activation of the O-H bond,³ which would otherwise break at higher temperatures.

We can obtain additional information on the energetics of methanol dehydrogenation over Pt by invoking the Evans-Polanyi relationship. The Evans-Polanyi relation enables us to draw qualitative relationships between the activation barriers for the elementary reaction steps and the corresponding overall reaction energies. The thermodynamically least-favored step in the pathway examined here for the decomposition of methanol over Pt (via the hydroxymethyl intermediate) is the dehydrogenation of the hydroxymethyl intermediate into formaldehyde and surface hydrogen ($\Delta E_{\text{rxn}} = +37 \text{ kJ/mol}$). According to the Evans-Polanyi relationship, this step should also have the highest activation barrier of all of the proposed steps. Nudged elastic band calculations indicate that the barrier for dehydrogenation of the hydroxymethyl species to formaldehyde is +120 kJ/mol on Pt(111). The transition state for this step involves a three-center structure in which a surface Pt atom inserts into the O-H bond of hydroxymethyl (Figure 7). All other elemen-

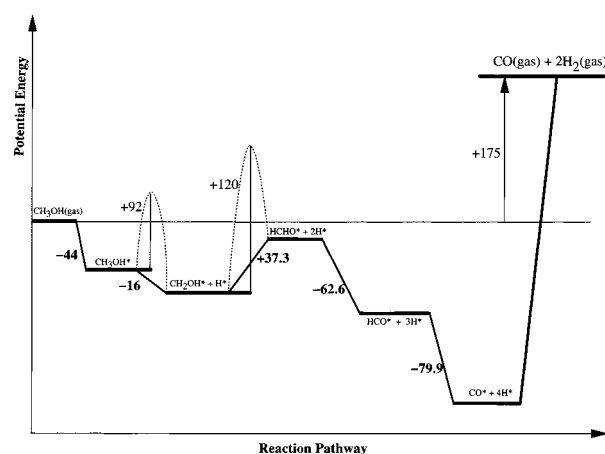


Figure 8. Overall energy cycle for the Pt-catalyzed dehydrogenation of methanol into gaseous CO and H₂. Only the path via the hydroxymethyl intermediate is shown. The dotted lines represent the activation barriers.

tary reactions in the proposed mechanism for the dehydrogenation of methanol over Pt (via the hydroxymethyl intermediate) are exothermic. Judging from the Evans-Polanyi relationship, these reactions are all likely to have lower activation barriers. This, however, is only an approximation. A rigorous search for the transition states for all elementary steps in methanol decomposition would be necessary to quantify the activation barriers accurately.

The overall energy cycle for the dehydrogenation of methanol over Pt(111) is summarized in Figure 8. We find that the formation of the hydroxymethyl intermediate is thermodynamically more favorable and has a lower activation barrier than the formation of the methoxide intermediate. Furthermore, the decomposition of the hydroxymethyl intermediate into formaldehyde was found to be more difficult than its formation. Experimentally, however, a stable hydroxymethyl intermediate has not been identified on Pt(111). Instead, methanol is found to decompose at about 200 K into CO and hydrogen without any evidence for the formation of other stable intermediates. Gibson and Dubois have shown that the decomposition occurs predominantly over defect sites on the surface,⁹ whereas ideal Pt(111) is unreactive.

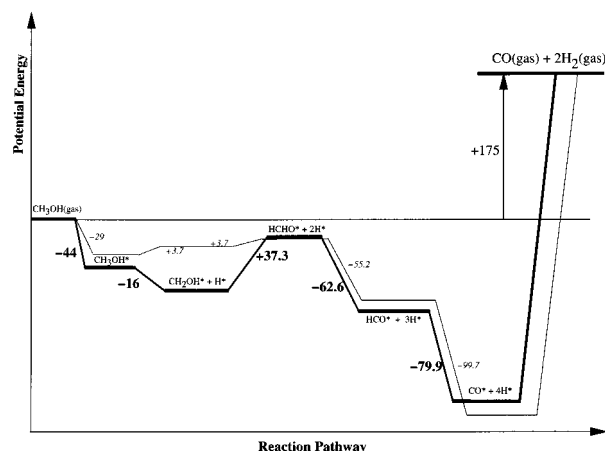
Our results also indicate that defect-free Pt(111) is unreactive. Figure 8, for example, indicates that, at moderate surface coverages, methanol activation is measured from its adsorbed surface state. As such, the activation barriers to form hydroxymethyl (+92 kJ/mol) and methoxy (+120 kJ/mol) are at least 2 times greater than the barrier for molecular desorption (+44 kJ/mol). At surface coverages greater than 25%, the barrier for desorption should decrease as a result of repulsive interactions, whereas the barriers for both C-H and O-H bond activation will increase, thus making Pt(111) unreactive.

We have nevertheless examined the decomposition over the ideal surface simply to provide some insights into the electrooxidation of methanol. Admittedly, the energetics and mechanism over a real Pt(111) surface might be different from those reported here for a defect-free surface. We also note that we have examined only one possible route for the decomposition of hydroxymethyl, which then leads to formaldehyde; we are currently examining alternative pathways and will report these in a future communication.

The chemistry over the Pt and Pd surfaces appears to be very similar. The small differences in the reaction energies (Table 3) are due to differences in the interaction energies of the

TABLE 3: DFT-Computed Reaction Energies for the Dehydrogenation of Methanol to CO over Pt(111) and Pd(111) Surfaces^a

	elementary reaction step	Pt(111)	Pd(111)
1a	$\text{CH}_3\text{OH}^* \rightarrow \text{H}_2\text{COH}^* + \text{H}^*$	-16.0	+3.7
1b	$\text{CH}_3\text{OH}^* \rightarrow \text{CH}_3\text{O}^* + \text{H}^*$	+64.8	+44.0
2a	$\text{H}_2\text{COH}^* \rightarrow \text{H}_2\text{CO}^* + \text{H}^*$	+37.3	+3.7
2b	$\text{CH}_3\text{O}^* \rightarrow \text{H}_2\text{CO}^* + \text{H}^*$	-43.6	-36.7
3	$\text{H}_2\text{CO}^* \rightarrow \text{HCO}^* + \text{H}^*$	-62.6	-55.2
4	$\text{HCO}^* \rightarrow \text{CO}^* + \text{H}^*$	-79.9	-99.7

^a All values are reported in kJ/mol.**Figure 9.** Overall energy cycles for the dehydrogenation of methanol over Pt(111) (black) and Pd(111) (gray).

intermediates over the Pd and Pt surfaces. The methanol and hydroxymethyl intermediates are both more weakly bound over the Pd surface than over Pt. As a result, the energy diagram over the Pd surface is not as deep as that over the Pt surface (see Figure 9), particularly during the initial steps of the dehydrogenation process. For the subsequent dehydrogenation reactions, we find that the differences in the reaction energies over the Pd and Pt surfaces are less than 20 kJ/mol.

4.4. Relevance to Direct Methanol Fuel Cell Chemistry.

Herein, we have modeled the dehydrogenation of methanol over Pt(111) in the vapor phase, which is quite different from the reaction environment that exists at the anode of a direct methanol fuel cell. We can, however, glean some basic information from the vapor-phase study that should also apply in the more complex electrochemical environment.

We have seen that the C–H bond of methanol breaks in preference to the O–H bond, leading to the formation of the hydroxymethyl rather than the methoxide intermediate. This should also hold, and perhaps more so, in the presence of solvent. Franaszczuk et al.^{6a} showed that, even when methanol dehydrogenates in a vacuum via the activation of the O–H bond to form the methoxide intermediate, as is the case over Pt(110), the chemistry in the electrochemical environment occurs by the activation of the C–H bond and involves the formation the hydroxymethyl intermediate. This is because the O–H bond of methanol is more polar and hence more strongly solvated by water molecules than the C–H bond. The energy cost associated with the activation of the O–H bond in solution is therefore high. Unlike the methoxide intermediates, the hydroxymethyl that forms on the activation of the C–H bond has an intact hydroxyl group that is exposed to the solvent and is amenable to solvation.

The vapor-phase study can also be used to elicit qualitative information on the stability of the dehydrogenation intermediates

over the Pt surface in the presence of solution. We find that the formyl and CO intermediates are both very strongly bound to Pt and can potentially poison the surface. Formyl intermediates^{39,40} and CO^{41,42} have both been speculated to be poisons during the dehydrogenation of methanol in the electrochemical environment. Vapor-phase calculations, however, indicate that formyl readily decomposes over Pt to form CO, which then is the more likely poison. This could perhaps explain why most electrochemical studies find that CO is the dominant poison. Formaldehyde that forms during dehydrogenation adsorbs weakly over the surface and likely readily desorbs into solution.

5. Summary and Conclusions

We have used periodic density functional theory to examine the energetics for the Pt-catalyzed dehydrogenation of methanol to form CO and hydrogen. Methanol adsorbs weakly over the Pt surface. The binding energies of the hydroxymethyl, methoxide, formaldehyde, formyl, CO, and hydrogen intermediates that can form during its dehydrogenation over Pt(111) were found to be -209, -161, -49, -237, -168, and -269 kJ/mol, respectively.

The calculations show that methanol is more likely to desorb than decompose over ideal Pt(111) under vacuum conditions. If it decomposes under different conditions perhaps closer to those of the methanol fuel cell, our results suggest that the activation of the C–H bond is easier than the activation of the O–H bond, thus leading to the formation of the hydroxymethyl and hydrogen intermediates. The C–H bond-breaking reaction ($\Delta E_{\text{rxn}} = -16$ kJ/mol) was found to be 80 kJ/mol more favorable than the O–H bond-breaking reaction ($\Delta E_{\text{rxn}} = +64$ kJ/mol), partly because the C–H bond is intrinsically weaker than the O–H bond and partly because the product of C–H bond activation, the hydroxymethyl intermediate, is more strongly bound to the Pt surface ($\Delta E_{\text{ads}} = -209$ kJ/mol) than the product of O–H bond activation, the methoxide intermediate ($\Delta E_{\text{ads}} = -161$ kJ/mol). The activation barrier to the formation of the hydroxymethyl intermediate ($\Delta E_{\text{act}} = +92$ kJ/mol) was found to be 50 kJ/mol lower than the barrier to the formation of the methoxide intermediate ($\Delta E_{\text{act}} = +142$ kJ/mol). The dehydrogenation of the hydroxymethyl intermediate to form formaldehyde and surface hydrogen was the thermodynamically least-favored step in the proposed sequence ($\Delta E_{\text{rxn}} = +37$ kJ/mol), with an activation barrier of +120 kJ/mol. Experimentally, however, there is no evidence for the formation of a stable hydroxymethyl intermediate. Instead, methanol decomposes predominantly over the surface defect sites into CO and hydrogen without forming any stable intermediates.

All C–H bond-breaking reactions that were examined were found to be exothermic, whereas all O–H bond-breaking reactions were found to be endothermic. The exothermicity of the C–H bond-activation reactions was found to increase progressively for each subsequent elementary step during the dehydrogenation of methanol to CO.

The formyl intermediates that form are strongly bound on Pt ($\Delta E_{\text{ads}} = -237$ kJ/mol) but can also favorably dehydrogenate on the surface into CO and hydrogen ($\Delta E_{\text{rxn}} = -79.9$ kJ/mol). CO is also strongly bound to the surface ($\Delta E_{\text{rxn}} = -168$ kJ/mol), but unlike the formyl intermediates, it does not decompose favorably over Pt. CO remains adsorbed on the surface and can poison the catalyst toward further dehydrogenation.

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