

## A First-Principles Study of Methanol Decomposition on Pt(111)

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**Abstract:** A periodic, self-consistent, Density Functional Theory study of methanol decomposition on Pt(111) is presented. The thermochemistry and activation energy barriers for all the elementary steps, starting with O–H scission and proceeding via sequential hydrogen abstraction from the resulting methoxy intermediate, are presented here. The minimum energy path is represented by a one-dimensional potential energy surface connecting methanol with its final decomposition products, CO and hydrogen gas. It is found that the rate-limiting step for this decomposition pathway is the abstraction of hydroxyl hydrogen from methanol. CO is clearly identified as a strong thermodynamic sink in the reaction pathway while the methoxy, formaldehyde, and formyl intermediates are found to have low barriers to decomposition, leading to very short lifetimes for these intermediates. Stable intermediates and transition states are found to obey gas-phase coordination and bond order rules on the Pt(111) surface.

### Introduction

The reaction of methanol on platinum has attracted great interest in recent years as the principal chemistry occurring on the anodes of direct methanol fuel cells (DMFC's). Publications on this subject are too numerous to describe in detail, but excellent reviews describing the behavior of liquid-phase DMFC's exist.<sup>1–3</sup> Briefly, DMFC's offer the prospect of direct conversion of methanol to electricity with efficiencies substantially larger than those obtained with conventional, combustion-based power generation systems. The performance of DMFC's, however, is limited, among other factors, by CO poisoning of the anode surface. This poisoning is acute for pure platinum anodes.

Two general approaches have been followed to solve the problems associated with DMFC's. First, a large effort has been made to identify anode catalysts superior to pure platinum. Among the most notable successes of this effort has been the discovery of Pt–Ru alloy catalysts that show substantially improved CO tolerance. Second, fundamental efforts have been made to understand methanol chemistry on Pt and Pt alloys; it is hoped that insights gained from such investigations will eventually lead to the development of improved DMFC anode catalysts. Many such investigations have focused on liquid-phase DMFC chemistry, but a number of analyses have also dealt with vapor-phase chemistry in both high-pressure and ultra-high-vacuum (UHV) conditions; these vapor-phase conditions are more amenable to highly controlled studies, and they may also

be quite relevant to industrial DMFC use since vapor-phase DMFC's permit easier access of fuel to the anode.<sup>1</sup>

The present study is directly relevant to methanol decomposition on platinum under UHV conditions. A number of experimental studies of this system have been performed. On Pt(111), several authors have studied the decomposition of methanol and of likely reaction intermediates with an array of experimental methods, including TPD, EELS, IRS, UPS, AES, and molecular beam techniques.<sup>4–9</sup> Major conclusions from these studies are that defects can significantly modify methanol chemistry on Pt(111) surfaces and that reaction intermediates between methanol and CO and H<sub>2</sub> are difficult, if not impossible, to observe directly. Thus, these studies have not conclusively determined the mechanism and energetics of methanol decomposition on Pt(111). Theoretical studies of the thermochemistry of this reaction<sup>10,11</sup> have concluded that methanol decomposition to CO and H<sub>2</sub> proceeds through an initial C–H bond scission to produce hydroxymethyl. However, the lack of any kinetic analysis in the calculations leaves open the possibility that other mechanisms, such as an initial O–H scission, may be responsible for the decomposition. The adsorption of certain intermediates (formaldehyde<sup>12</sup> and formyl<sup>13</sup>) in the pathway beginning with O–H scission has been studied individually with

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**Table 1.** Selected Geometric and Energetic Parameters for Methanol Decomposition Intermediates on Pt(111)

species	binding energy (eV)	binding configuration	C–O bond length (Å)	O–C angle (wrt surf. normal) (deg)	O–Pt bond length (Å)	C–Pt bond length (Å)	$\Delta\varphi$ upon ads <sup>a</sup> (eV)
methanol	−0.33	top: bound through oxygen	1.44	63	2.43		−1.08
methoxy	−1.54	top: bound through oxygen	1.40	59	2.03		−0.44
formaldehyde	−0.50	top-bridge-top: bound through oxygen and carbon	1.34	88	2.10	2.17	−0.21
formyl	−2.36	top: bound through carbon	1.21	144		2.02	−0.05
carbon monoxide	−1.82	fcc: bound through carbon	1.20	180		2.13	0.43

<sup>a</sup>  $\varphi$  = work function.

extended Hückel and DFT calculations, but no study of their decomposition barriers exists.

The decomposition of methanol and of possible methanol decomposition intermediates has also been analyzed with TPD, IR, EELS, XPS, and LEED on polycrystalline platinum,<sup>14</sup> Pt(100),<sup>15</sup> and Pt(110).<sup>16–20</sup> In these investigations, O–H scission was seen on (2 × 1)Pt(110)<sup>18,19</sup> while C–O scission was observed on (1 × 1)Pt(110).<sup>20</sup> The results suggest that these pathways, in addition to the pathway beginning with C–H scission in methanol (described above), might deserve a thorough study on Pt(111).

In this article, we present a systematic periodic density functional theory study of the methanol decomposition pathway on Pt(111) starting with O–H scission. We address both the thermochemistry and reaction barriers of all the elementary reaction steps in this pathway, and we present a detailed potential energy surface showing the interconversions of the various intermediates in the pathway.

## Methods

DACAPO, the total energy calculation code developed by Nørskov and co-workers,<sup>21</sup> is used for all calculations in this study. A three-layer slab of Pt, periodically repeated in a super cell geometry with five equivalent layers of vacuum between any two successive metal slabs, is used. A 3 × 3 unit cell (surface coverage of 1/9 ML) is employed. Adsorption is allowed on only one of the two surfaces exposed, and the electrostatic potential is adjusted accordingly.<sup>22</sup> As previous calculations have shown that surface relaxation has very small effects for similar systems,<sup>23,24</sup> and in order to limit the size of the calculations, all of the platinum atoms were kept fixed in their bulk-truncated positions. Ionic cores are described by ultrasoft pseudo-potentials,<sup>25</sup> and the Kohn–Sham one-electron valence states are expanded in a basis of plane waves with kinetic energy below 25 Ry. This kinetic energy cutoff has been shown to be adequate for both thermochemical and kinetic calculations involving ultrasoft pseudo-potentials on transition metals.<sup>24,26</sup> The surface Brillouin zone is sampled at six special **k** points. In all cases, convergence of the total energy with respect to the **k** point set and with respect to the number of metal

layers included is confirmed. The exchange-correlation energy and potential are described by the generalized gradient approximation (GGA-PW91).<sup>27,28</sup> The self-consistent PW91 density is determined by iterative diagonalization of the Kohn–Sham Hamiltonian, Fermi population of the Kohn–Sham states ( $k_B T = 0.1$  eV), and Pulay mixing of the resulting electronic density.<sup>29</sup> All total energies have been extrapolated to  $k_B T = 0$  eV. No zero-point energy corrections are included in the reported results.

The calculated PW91 bond energy for H<sub>2</sub>(g) is 4.57 eV, in reasonable agreement with the experimental value of 4.52 eV at 298 K.<sup>30</sup> The lattice constant for bulk Pt is found to be 4.00 Å, in good agreement with the experimental value of 3.912 Å.<sup>30</sup>

The reaction paths of sequential hydrogen abstraction steps are studied by using the Nudged Elastic Band (NEB) method.<sup>31–33</sup> Linear interpolations between the reactant and product states of each elementary step (using between four and six images) are used as initial guesses for the reaction coordinates, and the coordinates are then optimized with the NEB algorithm (a constrained molecular dynamics algorithm). The transition state of the optimized reaction coordinate is approximated by the image of highest energy; the actual reaction barrier, however, is calculated from a third-order polynomial fit (using both total energies and forces tangent to the reaction coordinate) to the two images nearest the maximum energy point. Although this approach does not employ frequency analyses (see, for example, the ACS Symposium Series<sup>34</sup> for a detailed description of these analyses), the mathematics of the technique are well-defined,<sup>35,36</sup> and it has been shown to give excellent convergence to saddle points on analytical potential energy surfaces.

## Results

**Structure and Adsorption Thermochemistry of Reaction Intermediates.** Schematics of all reaction intermediates, together with a definition of appropriate bond angles, can be found in Figure 1. *Methanol* (CH<sub>3</sub>OH) binds through its oxygen atom in an atop configuration. The O–Pt distance is 2.43 Å (see Table 1 for a summary of geometrical and energetic information), the O–C axis is tilted at 63° from the surface normal, and the binding energy (B.E.) is −0.33 eV. *Methoxy* (CH<sub>3</sub>O) also binds through oxygen in an atop configuration. The O–Pt distance is 2.03 Å, and the O–C axis is inclined by 59° from the surface normal. The binding energy is −1.54 eV with respect to a gas-

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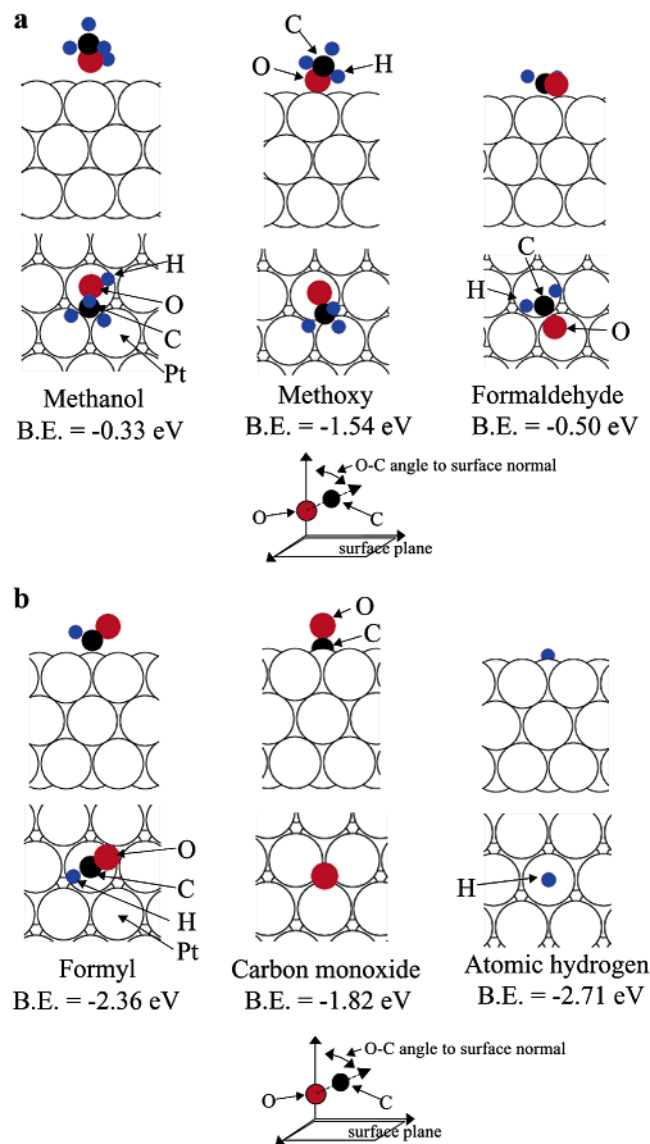
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**Figure 1.** Cross-section and top view of (a) most stable binding configurations for methanol, methoxy, and formaldehyde on Pt(111) and (b) most stable binding configurations for formyl, carbon monoxide, and hydrogen on Pt(111). Zero-point energies are not included.

phase methoxy radical.<sup>37</sup> *Formaldehyde* (HCHO) prefers a top-bridge-top (disigma) configuration. The O–Pt and C–Pt distances are 2.10 and 2.17 Å, respectively, and the O–C axis is inclined by 88° from the normal. The binding energy for HCHO is –0.50 eV. *Formyl* (HCO) does not exhibit strong site preferences on Pt(111). Three configurations with binding energies differing by at most 0.12 eV are found; an atop state has a B.E. of –2.36 eV (see Figure 1), a top-bridge-top state has a B.E. of –2.28 eV, and a state perpendicular to the bridge site (denoted “HhCbOf”) binds with an energy of –2.24 eV, all with respect to a gas-phase formyl radical. In all cases, the formyl radical binds through carbon. The C–Pt distance for the atop configuration is 2.02 Å, and the O–C axis is inclined at 144° to the surface normal. *Carbon monoxide* (CO) also binds through carbon; the preferred site is fcc, the carbon–surface distance is ~1.37 Å (C–Pt distance of 2.13 Å), and the O–C angle with respect to the normal is 180°. The binding energy is

–1.82 eV with respect to gas-phase CO. Finally, *atomic hydrogen* shows a nearly flat potential energy surface on Pt(111). Binding of gas-phase atomic H at atop (B.E. = –2.71 eV), fcc (B.E. = –2.69), and hcp (B.E. = –2.65) sites is quasidegenerate. The bridge site binding energy of –2.67 eV indicates that the hydrogen diffusion barrier is of the order of tens of meV, suggesting that hydrogen is highly mobile on the Pt(111) surface, in agreement with a recent DFT study by Papoian et al.<sup>38</sup>

Finally, as shown in the last column of Table 1, all reaction intermediates, with the exception of CO, decrease the work function of the clean platinum surface, suggesting that there exists a charge transfer from the adsorbate to the surface. The decrease in work function progressively decreases as one proceeds from the adsorption of methanol to the adsorption of methoxy, formaldehyde, and formyl. The latter leaves the work function of Pt(111) almost unchanged, whereas CO increases the work function of Pt(111) by a considerable amount.

**Activation Energy Barriers.** The reaction coordinate for the abstraction of the hydroxyl hydrogen from adsorbed methanol on Pt(111) is presented in Figure 2. The initial and final states of this elementary reaction step are taken to be the most stable states of the adsorbed methanol and methoxy (CH<sub>3</sub>O) species, respectively. The CH<sub>3</sub>O group of CH<sub>3</sub>OH moves relatively little during the hydrogen abstraction process, and the hydroxyl hydrogen moves directly from its initial position on the methanol molecule to an atop position on an adjacent Pt atom. In fact, the only significant change in the CH<sub>3</sub>O group is the O–Pt bond length. Therefore, we tentatively suggest that the O–Pt bond length is most likely to provide a good estimate of the earliness or lateness of the transition state for this particular elementary reaction step. A plot of the O–Pt bond length against the reaction coordinate (well approximated by the O–H bond length in this case) shows that the O–Pt length of the transition state is very similar to that of the final state, suggesting that the transition state for this reaction is more product-like than reactant-like. The energetics of the reaction are consistent with this statement; the overall reaction barrier is 0.81 eV, while the thermochemical barrier (endothermic reaction step) is ca. 0.62 eV.

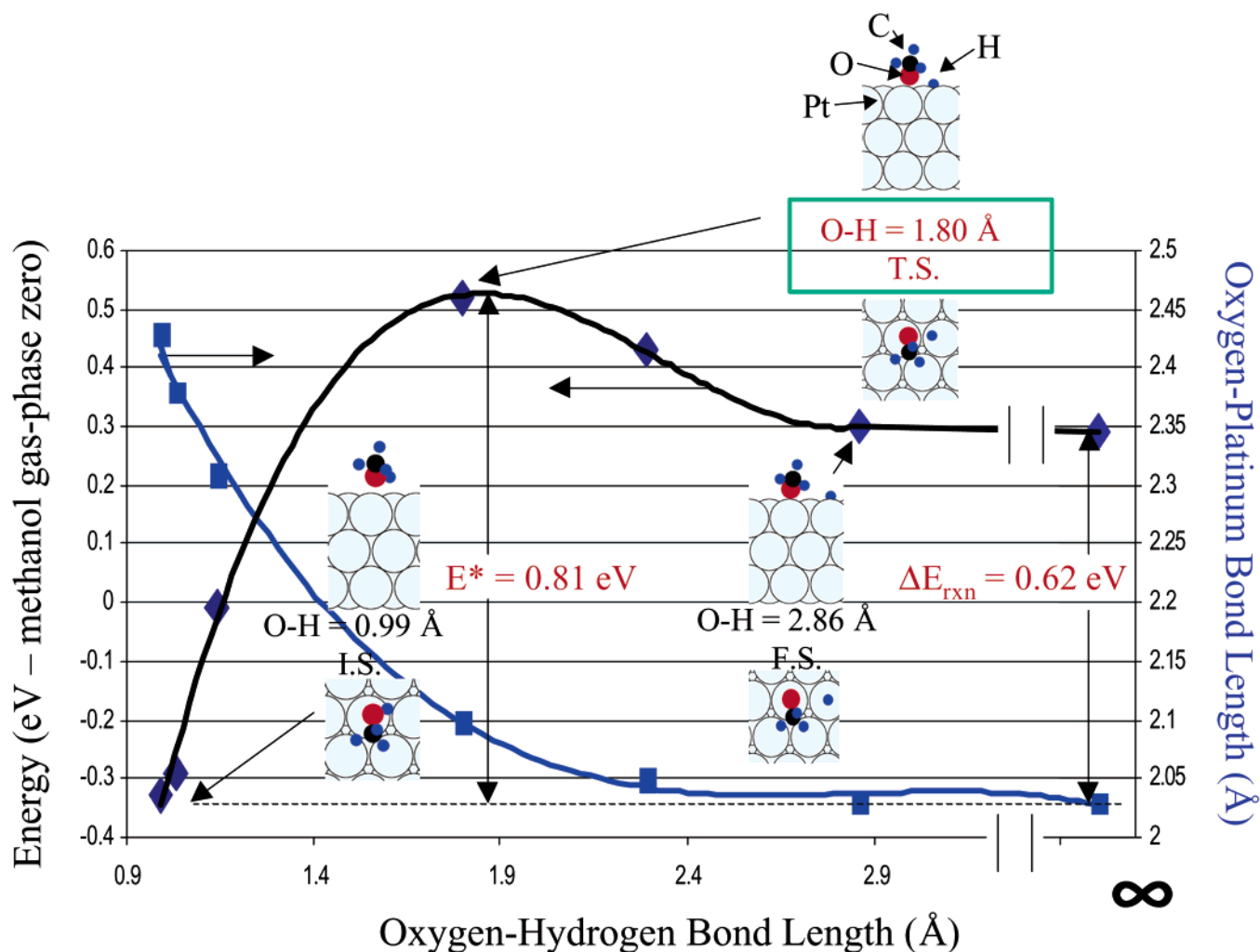
The reaction pathway for the abstraction of a methylic hydrogen from the adsorbed methoxy, leading to adsorbed formaldehyde and hydrogen, is shown in Figure 3. As a hydrogen atom is abstracted from the initial, tilted methoxy state, the CH<sub>2</sub>O group tilts toward the surface and ends in a top-bridge-top configuration. The C–O bond length of the transition state (T.S.), 1.27 Å, is quite close to our calculated gas-phase C–O bond length of formaldehyde, 1.22 Å (experimental value = 1.21 Å<sup>30</sup>), suggesting that the T.S. is more product-like than reactant-like. The C–O bond length progressively increases after the T.S. to reach a value of 1.34 Å for the adsorbed formaldehyde, demonstrating a strong interaction between formaldehyde and platinum. The reaction barrier for this reaction step is 0.25 eV, and the corresponding energy change is –0.36 eV (exothermic reaction step).

The abstraction of hydrogen from adsorbed formaldehyde, yielding an adsorbed formyl radical and adsorbed hydrogen, is a nearly spontaneous process, with an estimated activation

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**Figure 2.** Reaction coordinate for the abstraction of hydroxyl hydrogen from *methanol* on Pt(111). Inserts provide cross-section and top views of I.S. (initial state), T.S. (transition state), and F.S. (final state). Oxygen, carbon, hydrogen, and platinum atoms are as indicated in the transition state insert. Zero-point energies are not included. Lines denoting the total energy of the system and the O–Pt bond length are only guides to the eye.

energy barrier of less than 0.10 eV. The initial state is taken to be the most stable formaldehyde configuration (top-bridge-top). Carbon–hydrogen bond scission is accompanied by a rotation of the C–O axis to a configuration almost perpendicular to the bridge site (carbon end down). The energy change for this elementary reaction step is  $-0.61$  eV (exothermic).

C–H scission from the HhCbOft configuration of adsorbed formyl, leading to adsorbed CO and hydrogen, has a reaction barrier of 0.23 eV (Figure 4). The reaction coordinate is composed of a rotation of the C–O bond toward the surface normal (very little change in the C–O bond length is observed) followed by an extension of the C–H bond; the fact that the C–H bond is not elongated until late in the reaction coordinate suggests that the transition state is reactant-like. The overall energy change for this reaction step is  $-0.97$  eV (exothermic).

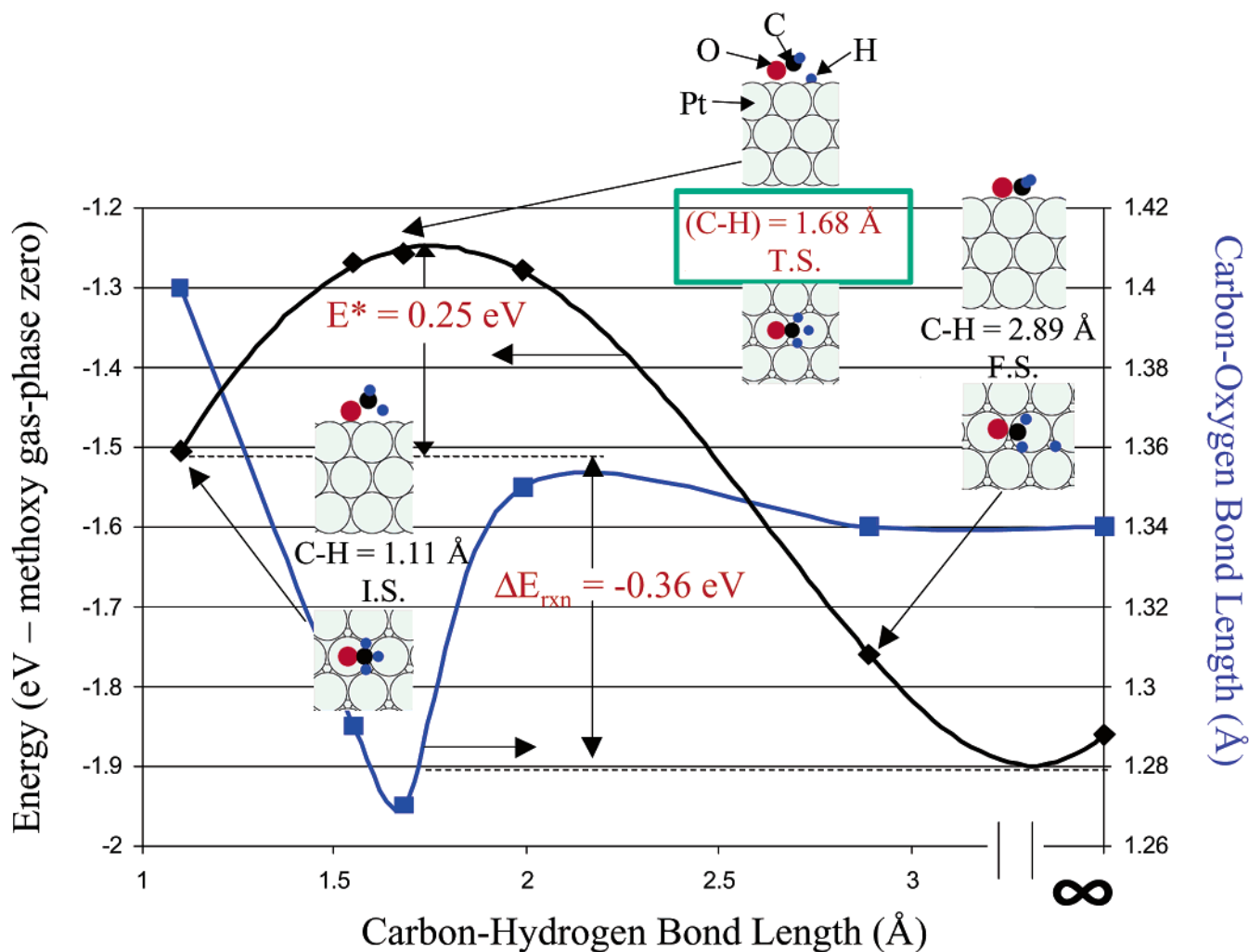
#### Complete Methanol Decomposition Pathway on Pt(111).

A detailed one-dimensional potential energy surface for the decomposition of methanol on Pt(111) is presented in Figure 5. Gas-phase methanol is located on the left side of the figure. The thermochemistry and the activation energy barriers of subsequent hydrogen abstraction steps follow to the right, and gas-phase CO and H<sub>2</sub> are depicted on the extreme right of the figure.

#### Discussion

The adsorption of *methanol* on Pt(111) has been well-studied experimentally. In many Pt(111) single-crystal studies, the decomposition of methanol was shown to be dominated by defects.<sup>6</sup> However, the adsorption characteristics of methanol determined in these studies are likely to be representative of MeOH behavior on (111) terraces at high coverages. The studies were performed such that only saturated methanol monolayers were analyzed, and the low defect concentration on (111) single crystals indicates that these monolayers will be composed primarily of terrace-bonded methanol.

EELS and UPS<sup>4,5,14</sup> have shown unambiguously that methanol adsorbs through oxygen on Pt(111). This result extends to IRAS studies of polycrystalline platinum samples in UHV environments<sup>14</sup> where it was additionally found that the methyl group is oriented at an angle midway between parallel and perpendicular to the surface. Our results, showing that methanol bonds to a top site through oxygen with the methyl group inclined at an angle to the surface normal (Figure 1), are in excellent agreement with these investigations of the structure of adsorbed methanol. Further, we find reasonable agreement between our calculations of the binding energy of methanol and the results of previous experimental and theoretical studies. TPD spectra



**Figure 3.** Reaction coordinate for the abstraction of hydrogen from *methoxy* on Pt(111). Inserts provide cross-section and top views of I.S. (initial state), T.S. (transition state), and F. S. (final state). Oxygen, carbon, hydrogen, and platinum atoms are as indicated in the transition state insert. Zero-point energies are not included. Lines denoting the total energy of the system and the O–C bond length are only guides to the eye. For comparison, the calculated O–C bond length (B.L.) in gas-phase  $\text{H}_2\text{CO}$  is 1.22 Å.

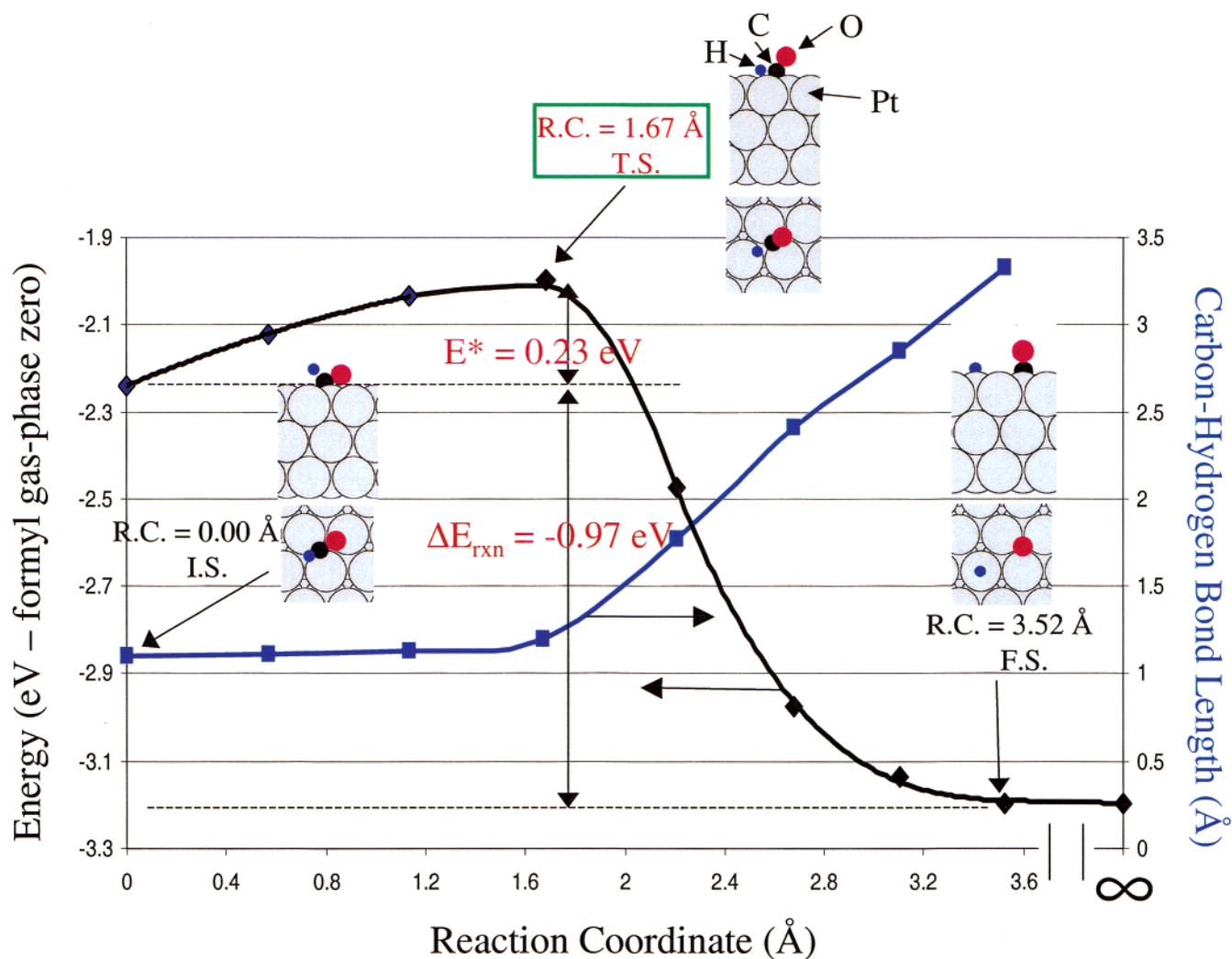
taken at near-saturation coverages on Pt(111)<sup>4,8</sup> and polycrystalline platinum samples<sup>14</sup> indicate that methanol monolayers leave the surface in desorption-limited peaks at 170–190 K. A Redhead analysis of these data gives an estimated MeOH binding energy of  $\sim -0.40$  to  $-0.50$  eV. Previous DFT cluster calculations, using clusters of 8 and 10 Pt atoms, give estimated binding energies of  $-0.65$  and  $-0.66$  eV, respectively.<sup>10,11</sup> The above experimental and theoretical values are larger than our calculated binding energy of  $-0.33$  eV, but these discrepancies can be explained. In the experimental studies, hydrogen bonding in methanol monolayers near saturation could easily have led to estimation of increased binding energies. In our studies on a  $3 \times 3$  unit cell,  $\theta/\theta_{\text{sat}} \approx 0.31$  (based on an estimated saturation coverage of 0.36 ML<sup>39</sup>). This low coverage could lead to a decrease in hydrogen bonding and a concomitant decrease in the binding energy. In the theoretical studies, the fundamental differences between cluster and periodic calculations may explain the discrepancies with our results.

A final comparison of our methanol thermochemistry results with experimental data can be made with work function

information. Our calculated decrease in work function between clean Pt(111) and methanol-covered Pt(111) (1.08 eV at  $\theta = 1/9$  ML, Table 1) is in reasonable agreement with an experimental value for this decrease at saturation coverage of methanol (1.4 eV).<sup>5</sup> With respect to the kinetics (overall reaction barrier) of methanol decomposition on Pt(111), few data exist. A molecular beam study<sup>7</sup> (discussed below) gives good agreement with our calculated O–H bond scission reaction barrier of 0.81 eV (Figure 2).

*Methoxy* is extremely unstable on single-crystal platinum surfaces. In fact, no direct spectroscopic observations of this species exist on clean Pt(111), and therefore no structural information is available about its adsorption configuration on this surface. Peck et al.<sup>8</sup> were able to produce methoxy on clean Pt(111) by using a methyl nitrite precursor. Although they were able to estimate a reaction barrier for methoxy decomposition of *less than* 0.48 eV (in good agreement with our calculated value of 0.25 eV), they were unable to spectroscopically analyze the methoxy species on the surface. Sexton<sup>4</sup> found that methoxy can be isolated on an oxygen pre-covered (but not an oxygen-free) Pt(111) surface; he determined that the vibrational peaks

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**Figure 4.** Reaction coordinate for the abstraction of hydrogen from *formyl* on Pt(111). Inserts provide cross-section and top views of I.S. (initial state), T.S. (transition state), and F.S. (final state). Oxygen, carbon, hydrogen, and platinum atoms are as indicated in the transition state insert. Zero-point energies are not included. Lines denoting the total energy of the system and the C–H bond length are only guides to the eye.

of the identified intermediate are similar to those for methoxy on Cu(100)<sup>40</sup> and Ni(111).<sup>41</sup> Unfortunately, the comparison of the methoxy/O–Pt(111) spectra to the methoxy spectra on Cu(100) and Ni(111) could not provide detailed structural information for methoxy on O–Pt(111); the orientation of the C–O bond with respect to the surface normal, for example, was not conclusively established. Finally, Wang et al.<sup>19</sup> isolated methoxy on a (2 × 1)Pt(110) surface; their EELS spectra for methoxy agree well with those of Sexton on Pt(111).

Fortunately, although no direct experimental spectroscopic signatures for methoxy on clean Pt(111) exist, theoretical techniques have provided some information about the structure and energetics of methoxy on this surface. Kua et al.<sup>10</sup> used cluster DFT methods to calculate a binding energy of –1.09 eV for methoxy on a top site (C–O axis inclined with respect to the surface normal). Ishikawa et al.<sup>11</sup> used similar methods and found a B.E. of –2.07 eV for methoxy adsorbed in a 3-fold hollow site (C–O axis parallel to the surface normal). Our results for methoxy adsorption agree qualitatively with those of Kua et al.;<sup>10</sup> we find that methoxy prefers to bind at a top site with the C–O axis inclined with respect to the surface

normal. Our calculated B.E. of –1.54 eV does not agree well with the B.E. found by Kua et al., but this discrepancy may again be explained by the finite clusters used in their analysis. With respect to the kinetic (overall reaction) barrier for methoxy decomposition to formaldehyde, no calculations exist to compare with our result of 0.25 eV (Figure 3).

Experimental studies of *formaldehyde* interaction with single-crystal platinum surfaces are somewhat more common than are studies of methoxy behavior, but there is still no reliable structural information available. On Pt(111), a submonolayer dose of formaldehyde was found to dissociate instantly at 105 K; at higher coverages, polymerization occurred.<sup>9</sup> The submonolayer result (that formaldehyde decomposes before desorbing) is completely consistent with our finding that the B.E. of formaldehyde (–0.50 eV) is much greater than the decomposition barrier of this species (<0.10 eV). On (2 × 1)Pt(110), a stable monolayer phase of molecular formaldehyde was isolated during a TPD ramp between 112 and 134 K.<sup>16</sup> Redhead analysis of the monolayer desorption peak gives a B.E. of ca. –0.35 eV. Interestingly, formaldehyde polymerization did not occur on this surface. This may have been caused by the open, stepped nature of the (2 × 1)–(110) surface.<sup>16</sup> In addition to the experimental studies of formaldehyde on Pt(111), several

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avored site is again top. With the loss of a coordinated hydrogen atom, the methoxy C–O bond length shrinks to 1.40 Å from the corresponding length in adsorbed methanol (1.44 Å), and the Pt–O distance is reduced from 2.43 Å in methanol to 2.03 Å in methoxy. These changes in bond lengths maintain the oxygen bond order at close to its gas-phase value. For *formaldehyde*, both carbon and oxygen bind to Pt atoms in a top-bridge-top configuration. The C–O bond length of 1.34 Å is substantially larger than the gas-phase value of 1.22 Å, suggesting that this bond is close to a single bond. Thus, the carbon and oxygen atoms are tetravalently and divalently coordinated, respectively, in agreement with gas-phase bonding trends for these atoms. *Formyl* (Figure 1b) binds most favorably through carbon at top sites. The C–O bond length for this configuration is 1.21 Å, nearly identical with its value of 1.22 Å for gas-phase formyl. The C–O bond is thus a double bond when formyl adsorbs on top sites, again showing consistency with gas-phase bond order trends for carbon and oxygen. Finally, *CO* is found to adsorb in an fcc site with a C–O bond length of 1.20 Å. This configuration, suggesting a C–O double bond, seems to give an overcoordinated carbon atom. This counterintuitive result is not surprising, however, given that the DFT calculations seem to miss the experimentally observed C–O preference for top or bridge sites.<sup>42</sup>

These bond order trends appear to extend to the transition states in the methanol decomposition pathway. The transition state (T.S.) for methanol conversion to methoxy shows a divalent oxygen atom (Figure 2). For the T.S. of methoxy conversion to formaldehyde (Figure 3), the carbon atom is approximately tetravalently coordinated, and a roughly divalent oxygen atom is seen. The O–Pt bond at the T.S. is extended by 0.19 Å from the initial state in the reaction pathway (adsorbed methoxy), indicating that this bond contributes only a fraction of a single bond to the valency of oxygen. The O–C bond length is 1.27 Å (a 0.05 Å increase from the double O–C bond in gas-phase formaldehyde), suggesting that this bond contributes a valency of slightly less than 2 to oxygen. Taken together, these results suggest that oxygen has a partial bond to the Pt surface and an O–C bond with bond order slightly less than 2, yielding an approximately divalent oxygen species. The T.S. for an over-bridge dissociation of formyl to yield CO (Figure 4) shows a roughly tetravalent carbon atom. The C–H bond is extended by 0.07 Å from its gas-phase formyl value, suggesting that this bond contributes only a partial bond to the carbon valency. Combined with the bonds contributed by the oxygen and platinum atoms, this fact implies that carbon has a valency of four (or slightly greater than four). While the above arguments are only qualitative, we note that the results are consistent with the findings of Michaelides et al.<sup>23</sup> Those authors determined that transition states for successive hydrogenations of O, C, and N on Pt(111) are always consistent with the gas-phase bonding trends of these atoms.

The potential energy surface for the methanol decomposition reaction is given in Figure 5. We note that the calculated energy change of the overall reaction ( $\text{CH}_3\text{OH}(\text{g}) \rightarrow \text{CO}(\text{g}) + 2\text{H}_2(\text{g})$ ), 2.05 eV (198 kJ/mol), does not agree well with the experimental value of the standard enthalpy of reaction at 300 K, 0.94 eV (91 kJ/mol).<sup>30</sup> This lack of agreement is due, in large part, to the neglect of zero-point energies and finite temperature effects in our calculations. Correction for these

effects by using published vibrational frequencies and thermochemical data<sup>44–46</sup> yields an overall energy change of 1.07 eV,<sup>47</sup> in much better agreement with the experimental value. Remaining errors (ca. 0.15 eV) are likely related to errors in the calculation of gas-phase bond energies. For example, the calculated bond energy of CO is 10.95 eV while the accepted experimental enthalpy value at 300 K is 11.16 eV.<sup>30</sup>

Figure 5 reveals a number of interesting features about the reaction network. First, and most important for applications to direct methanol fuel cell research, CO is seen to be the thermochemical sink for this reaction pathway. The binding is so strong, in fact, that it is likely that CO would poison any methanol decomposition reaction occurring on Pt(111) at low temperatures. In DMFC's with platinum anodes (where temperatures are typically around 100 °C), CO is indeed believed to poison the anode and to cause significant performance losses. This problem has resulted in numerous studies on the interaction of CO with platinum surfaces under both liquid and vacuum experimental conditions.<sup>2,48–52</sup>

Figure 5 demonstrates that the rate-limiting step (RLS) for methanol *decomposition* on Pt(111), through the specific path analyzed, is the loss of the hydroxyl hydrogen of methanol to produce methoxy. In fact, since the barrier for methanol *desorption* is less than the barrier for O–H bond scission, the results imply that methanol desorption (rather than decomposition via O–H scission) will be observed in ultra-high-vacuum (UHV) conditions. This result is consistent with numerous experimental studies of methanol adsorption on Pt(111) in UHV.<sup>4–6,8</sup> In these studies, at least 90% of saturated methanol monolayers desorb without reaction, and only a few percent decompose to CO and H<sub>2</sub>. The small amount of decomposition that is observed is attributed to methanol reaction at defect sites.<sup>6</sup> In addition to the good qualitative agreement of our results with experiment, the reaction barrier that we find for methanol O–H scission (0.81 eV, or 0.48 eV with respect to gas-phase methanol) is in excellent quantitative agreement with a barrier of ~0.5 eV (with respect to gas-phase MeOH) estimated from recent molecular beam experiments.<sup>7</sup>

Although our results for methanol decomposition to methoxy agree well with available experimental evidence on methanol decomposition, it is important to keep in mind that none of the experimental UHV studies of methanol decomposition on Pt(111) have conclusively determined whether the initial decomposition step involves O–H scission or C–H scission. This is directly related to the fact that methanol decomposition intermediates on Pt(111) are extremely short-lived and hence nearly impossible to study. We will address the O–H vs C–H scission question further in a future paper.<sup>53</sup>

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The barriers for hydrogen abstraction from methoxy, formaldehyde, and formyl are quite small (Figure 5), in agreement with the fact that none of these intermediates is observed when methanol is dosed on clean Pt(111) surfaces.<sup>4–6</sup> These experiments show that only CO and H<sub>2</sub> desorb during TPD; the desorption-limited nature of these processes makes estimation of reaction barriers extremely difficult. One experimental estimate for methoxy decomposition to formaldehyde on clean Pt(111) has been obtained, however, using an alternative technique. Peck et al.<sup>8</sup> were able to estimate an *upper bound* of 0.48 eV for this reaction barrier by using CH<sub>3</sub>O–NO as a precursor to prepare methoxy on the Pt(111) surface (although the lifetime of the methoxy species was still too short to permit direct observation). This value is in reasonable agreement with our calculated value of the corresponding reaction barrier of 0.25 eV. To our knowledge, no other experimental or theoretical estimates of methoxy, formaldehyde, or formyl decomposition barriers exist, and our results represent the first estimates of any kind for these barriers.

### Conclusions

First principles periodic DFT calculations have been used to study the thermochemistry and reaction barriers of methanol decomposition on Pt(111). A pathway involving O–H bond scission in methanol, followed by sequential hydrogen abstrac-

tions from the resulting methoxy, formaldehyde, and formyl intermediates, has been analyzed. The rate-limiting step in this pathway is the initial methanol O–H scission reaction, and the end product of the pathway, CO, is shown to be so strongly bound that it could poison the Pt(111) surface. Three intermediates in the pathway (methoxy, formaldehyde, and formyl) have very low barriers to decomposition; this result explains the extreme difficulty in isolating these molecules in experimental studies. Finally, with the exception of CO, stable intermediates and transition states are observed to follow gas-phase bonding and bond order trends on the Pt(111) surface.

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