New Insights into the Pt-Catalyzed CH$_3$OH Oxidation Mechanism: First-Principle Considerations on Thermodynamics, Kinetics, and Reversible Potentials

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**ABSTRACT:** A systematic first-principle study of CH$_3$OH oxidation along indirect and direct pathways on Pt(111) has been carried out, and some new insights into CH$_3$OH oxidation pathways in direct CH$_3$OH fuel cells (DMFCs) are presented. The thermodynamics, kinetics, and reversible potentials for all possible elementary steps, initializing with C−H, O−H, and C−O bond cleavages and proceeding via sequential decomposition and oxidation from the reaction intermediates, are analyzed. Some key reactive intermediates are identified. By comparing the activation energies and reversible potentials of various possible elementary reaction steps, we can speculate that the initial CH$_3$OH oxidation step proceeds by the CH$_3$O intermediate under a nonelectrochemical environment, whereas it prefers to occur by the CH$_3$OH intermediate under electrochemical environment. Furthermore, CHO hydroxylation into HCOOH along a direct pathway is more facile to occur than CHO dehydrogenation into CO along an indirect pathway at the nonelectrochemical interface, whereas the indirect and direct pathways may be parallel pathways on Pt(111) under the present simulated electrochemical environment. Simultaneously, CH$_3$ can be easily formed through C−O bond cleavage in CH$_3$OH, which is a nonelectrochemical step. Thus, the CH$_x$ ($x = 0−3$) species is possibly formed on Pt(111) during CH$_3$OH oxidation regardless of being under an electrochemical or nonelectrochemical environment. The adsorbed CH$_x$ species will result in the blocking of the active sites and the prevention of further CH$_3$OH oxidation. Our present findings on the formation of carbonaceous deposits on Pt(111) are consistent with the experimentally observed C−O bond scission of CH$_3$OH into CH$_x$ species. Thus, we propose that the adsorbed residues that poisoned the Pt surface and impeded the performance of DMFCs may be CH$_x$ species, rather than CO species, since the direct pathway is more favorable on Pt(111) at the nonelectrochemical interface. However, the poisonous species that occupied the active sites of the Pt surface may be CH$_x$ and CO species due to the simultaneous occurrence of oxidation pathways on Pt(111) under the present simulated electrochemical environment. Based on the present study, some new insights into CH$_3$OH oxidation mechanisms and designing strategies of Pt-based alloy catalysts for CH$_3$OH oxidation can be provided.

**INTRODUCTION**

Direct CH$_3$OH fuel cells (DMFCs) are extremely interesting since they can convert CH$_3$OH directly into electricity and efficiencies are significantly higher than conventional power generation systems. In recent years, the CH$_3$OH oxidation that occurred at the anodes of DMFCs has been the subject of numerous studies because of its importance in fuel cell application.$^{1−3}$ So far, the best catalyst for CH$_3$OH oxidation is Pt. However, the performance of DMFCs is impeded because adsorbed residues poison the anode surface. It is now generally accepted that CO is the poisoning species formed during CH$_3$OH oxidation, and the poisoning is acute for the Pt anode. Due to the lack of a detailed oxidation mechanism, the progress in developing improved DMFCs has been hindered. Thus, it is necessary to clarify the CH$_3$OH oxidation mechanisms on the Pt surface to provide some guidelines for effectively designing catalysts used in DMFCs.

So far, experimental and theoretical investigations have made tremendous efforts in order to understand CH$_3$OH oxidation mechanisms on the Pt catalysts; it is hoped that DMFC anode catalysts will be improved eventually based on insights gained from such studies. However, there are still some controversies surrounding the mechanism on Pt despite numerous investigations. The previous experimental investigations focused on CH$_3$OH oxidation mechanisms on Pt were carried out mainly in ultra high vacuum (UHV) with numerous experimental methods, such as temperature-programmed desorption (TPD), low-energy electron loss spectroscopy (LEELS), ultraviolet photoelectron spectroscopy (UPS), auger electron spectroscopy (AES), thermal desorption spectroscopy (TDS), secondary ion mass spectrometry (SIMS),...
infrared reflection adsorption spectroscopy (IRAS), X-ray photoelectron spectroscopy (XPS), temperature-programmed reaction spectroscopy (TPRS), and molecular beam techniques, etc.\textsuperscript{6–21} For example, Sexton,\textsuperscript{6,7} using LEELS and TDS, showed that at temperatures below 140 K CH\textsubscript{3}OH adsorbs molecularly on Pt(111), whereas at higher temperatures it is oxidized into CO. Based on the discussion from Davis and Bertaut,\textsuperscript{22} CH\textsubscript{3}OH oxidation mainly proceeds through methoxy (CH\textsubscript{3}O) on Pt, as a first intermediate, and then forms formaldehyde (CH\textsubscript{2}O), formyl (CHO), and CO by stepwise dehydrogenation. This mechanism is also partly confirmed by another experimental study.\textsuperscript{10,13,14,17–19,23–25} For example, based on the surface science investigations in UHV, Stuve et al.\textsuperscript{24} proposed the CH\textsubscript{2}OH oxidation mechanism into CO, in which CH\textsubscript{3}OH initially oxidizes to form either CH\textsubscript{2}O or hydroxymethyl (CH\textsubscript{2}OH); subsequently, various other intermediates can be formed through further oxidation before finally forming CO. However, little is known about the exact CH\textsubscript{3}OH oxidation mechanisms and the corresponding intermediates. Additionally, some experimental evidence also showed that through initial C–O bond cleavage CH\textsubscript{3}OH can be partially oxidized on Pt to form adsorbed CH\textsubscript{3} (x = 0–3) intermediates. For example, Levis et al.\textsuperscript{20} indicated that adsorbed CH\textsubscript{3}OH can be oxidized to form adsorbed CH\textsubscript{3} species as C–O bond breaking on Pt(111) at 180–220 K by using SMS. The CH\textsubscript{3} can dehydrogenate to form adsorbed C atoms at higher temperatures. Wang and Masel\textsuperscript{11} found that at temperatures above 140 K adsorbed CH\textsubscript{3}OH on Pt(110) can be also oxidized to produce adsorbed CH\textsubscript{2} intermediates through the C–O bond cleavage by using TDS and LEELS. By using in situ ambient-pressure XPS and TPRS, CH\textsubscript{3}OH oxidation has also been examined on Pt(111) between 300 and 650 K, in which CH\textsubscript{3}OH oxidation on Pt proceeds through two competitive routes in the presence of oxygen: One is serial dehydrogenation to CO through the CH\textsubscript{2}O intermediate, and another is oxidation through C–O bond cleavage.\textsuperscript{25} It should be noted that the carbonaceous deposits formed through the methanolic C–O bond cleavage may be able to occupy the active sites of the Pt surface and thereby influence the catalytic activity for CH\textsubscript{3}OH oxidation due to Pt catalyst poisoning and fast deactivation.\textsuperscript{26–30} However, some other experimental studies\textsuperscript{13,31–34} dealing with CH\textsubscript{3}OH on transition metal surfaces ruled out the C–O bond cleavage pathway.

Although some valuable CH\textsubscript{3}OH oxidation mechanism information has been provided by the above experimental investigations, many important questions about the reaction pathways are still ambiguous. Fortunately, the fundamental understanding of elementary reaction pathways can be obtained through theoretical methods. Using the bond-order-conservation approach, Shustorovich et al.\textsuperscript{8} studied the reaction and activation energies for the various possible elementary reaction steps of CO hydrogenation into CH\textsubscript{3}OH on Pt(111). Kua et al.\textsuperscript{36} and Ishikawa et al.\textsuperscript{37} performed density functional theoretical (DFT) studies on CH\textsubscript{3}OH oxidation on Pt, respectively. These studies of the thermochemistry of the reaction\textsuperscript{36,37} have concluded that CH\textsubscript{3}OH oxidation to CO proceeds via initial C–H bond cleavage into the CH\textsubscript{2}OH intermediate. However, the calculations lacked any kinetic analysis, which suggests the possibility of other oxidation pathways, such as initial O–H cleavage, for CH\textsubscript{3}OH oxidation. On the basis of DFT calculations, CH\textsubscript{3}O\textsuperscript{38} and CHO\textsuperscript{39} adsorption in the initial O–H cleavage pathways has been studied, but kinetic barriers for CH\textsubscript{3}OH oxidation were still not considered. Simultaneously, only cluster models containing 8–10 Pt atoms were used in the previous studies, which can make conclusions be not exact because of size effects. Despite all this, an excellent starting point is provided by the above studies in order to systematically understand the CH\textsubscript{3}OH oxidation mechanism on Pt. More recently, for CH\textsubscript{2}OH oxidation on Pt(111), a periodic DFT study was presented. For all the elementary reaction steps, beginning with O–H and C–H bond breaking and proceeding through serial dehydrogenation of the CH\textsubscript{2}O intermediate, the thermodynamic and kinetic analysis are presented.\textsuperscript{23} It is found that the O–H bond cleavage in CH\textsubscript{3}OH is the rate-determining step for the CH\textsubscript{3}OH oxidation mechanism. CO formation is a strong exothermic process, while the further oxidation of CH\textsubscript{2}O, CH\textsubscript{3}O, and CHO intermediates has extremely low activation barriers, which make these intermediates have very short lifetimes. The previous DFT results also suggest that CH\textsubscript{3}OH oxidation to form CH\textsubscript{2}OH through O–H bond cleavage and then further oxidation of CH\textsubscript{3}O into either CH\textsubscript{2}O or CHO intermediates is also an energetically favorable pathway.\textsuperscript{40} However, DFT calculations conducted by Greeley and Mavrikakis\textsuperscript{41} show that the activation energy of C–O bond cleavage is three times larger than that of C–H or O–H bonds on Pt(111), which is disagreeable with some of the above-mentioned previous experimental observations. It seems to mean that the dehydrogenation pathway of CH\textsubscript{2}OH oxidation is more favorable than the initial C–O bond cleavage pathway on Pt(111).

On the basis of the above experimental and theoretical methods, some valuable atomic-level information on the CH\textsubscript{3}OH oxidation mechanism has been obtained. However, CH\textsubscript{3}OH oxidation may follow a dual pathway mechanism that includes both indirect and direct pathways on the Pt surfaces.\textsuperscript{31–43} The indirect pathway proceeds through serial dehydrogenation steps to form CO\textsubscript{2} as demonstrated in the above experimental and theoretical studies. The direct pathway proceeds through the formation of CHO and HCOOH intermediates, which can subsequently be oxidized to form CO\textsubscript{2}. As far as we know, the direct pathway on the Pt surface remains to not be elucidated theoretically at an atomic level, and the corresponding mechanism details of the direct pathway are still unknown. Thus, many key questions about the oxidation pathways are still ambiguous, and controversy exists as to the CH\textsubscript{3}OH oxidation mechanism. For instance, what is the optimal CH\textsubscript{3}OH oxidation pathway, the initial C–H, O–H, or C–O bond cleavage on Pt(111)? Which reaction step is the rate-determining step? Which pathway is responsible for the formation of CH\textsubscript{n} species? Which pathway may more easily occur, the indirect or direct pathway on the Pt catalyst? Additionally, no detailed theoretical investigations focused on the initial C–O bond cleavage mechanism on Pt were found in the literature. Additionally, the design of better catalysts requires a deeper understanding of CH\textsubscript{3}OH oxidation pathways. Thus, CH\textsubscript{3}OH oxidation pathways initiating with C–H, O–H, and C–O bond cleavages of CH\textsubscript{3}OH on Pt catalysts deserve a systematic study. In the present paper, we perform a thorough periodic DFT study on CH\textsubscript{3}OH oxidation on Pt(111) starting with C–H, O–H, and C–O bond cleavages involving indirect and direct pathways. The thermodynamics, kinetics, and reversible potentials for the various possible elementary pathways are addressed, and detailed minimum energy pathways (MEPs) showing the interconversions of the various intermediates are presented.
## RESULTS AND DISCUSSION

### Adsorption Characteristics of Oxidation Intermediates

The possible surface species involved in an indirect pathway on the Pt(111) surface were investigated first. The optimized adsorption configurations of eight species (CH$_3$OH, CH$_2$OH, CH$_3$O, CH$_2$O, CHO, COH, and CO) are given, as shown in Figure 1; the most optimal adsorption sites for the possible intermediates and corresponding adsorption energies are listed in Table 1. The adsorption energies are calculated according to $E_{\text{ads}} = E_{\text{adsorbate/substrate}} - E_{\text{substrate}} - E_{\text{adsorbate}}$. A more negative $E_{\text{ads}}$ value indicates a stronger adsorption.

Experimentally, CH$_3$OH adsorption has been well studied on Pt(111). LEELS and UPS$^{11,13,44}$ have indicated unequivocally that on Pt(111) CH$_3$OH adsorbs via the O atom. The studies from IRAS on Pt under UHV environments$^{45}$ found that the CH$_3$ group in CH$_3$OH is oriented at an angle between perpendicular and parallel to the surface. As shown in Figure 1(a), our present results show that CH$_3$OH weakly adsorbs on Pt(111) through the O atom at the top site with an adsorption energy of $-0.44$ eV, which is consistent with previous experimental investigations on adsorption configuration of CH$_3$OH, showing that the most favorable structure of adsorbed CH$_3$OH that our present studies have described is generally accurate. Further, our calculated adsorption energy of CH$_3$OH is also well consistent with the results of early experimental and theoretical investigations. The previous experimental study on Pt from TPD spectra data$^{6,11,45}$ estimated CH$_3$OH adsorption energy, ca. $-0.45$ eV. Theoretical calculations by the DFT cluster and slab model also gave calculated an adsorption energy of $-0.66$ and $-0.33$ eV, respectively.$^{23,36,37,40}$ The above experimental value is consistent with our present calculated adsorption energy of $-0.44$ eV, whereas the theoretical values using cluster methods are larger than our value. These discrepancies can be explained. In the theoretical studies, the used model differences between periodic and cluster methods may lead to the discrepancies of adsorption energies. In the meantime, the adsorption energy that was previously reported using slab methods is slightly smaller than our adsorption energy. The discrepancies with our results could be explained by coverage, in which the higher coverage was used in previous calculations (1/9 ML), thus leading to the more significant effects of hydrogen bonding.

Methoxy (CH$_3$O) formed via the initial O–H bond cleavage within CH$_3$OH is extremely unstable on Pt, and no direct spectral data of this intermediate exist. Thus, structure information is unavailable about this geometry configuration on Pt. Fortunately, the structure and energetics of CH$_3$O on Pt(111) have been provided by theoretical methods. Using the cluster model, Kua et al.$^{36}$ calculate the adsorption energy of CH$_3$O, ca. $-1.09$ eV, and CH$_3$O adsorbs on a Pt top site through the O atom. Ishikawa et al.$^{37}$ used similar methods to calculate an adsorption energy of $-2.07$ eV for CH$_3$O bound in a 3-fold hollow site. Using periodic DFT methods, Greeley et al.$^{40}$ found an adsorption energy of $-1.54$ eV for CH$_3$O at a top site. Our results showed that CH$_3$O prefers to adsorb at a top site through O atom with the C–O bond inclined on Pt(111), as shown in Figure 1(b), which is consistent with those of Greeley et al. and Kua et al. Our calculated adsorption energy is $-1.74$ eV for CH$_3$O, which is not well consistent with that of Kua et al. The finite cluster model used in previous calculations may again explain this discrepancy. The hydroxymethyl (CH$_2$OH) on Pt(111) is also unstable. To our knowledge, for this intermediate, geometry structural parameters have not been obtained experimentally. However, there exist some DFT

![Figure 1. Optimized geometry configurations of the possible intermediates included in the indirect pathway for CH$_3$OH oxidation on Pt(111): (a) CH$_3$OH, (b) CH$_2$O, (c) CH$_3$OH, (d) CH$_2$O, (e) CHOH, (f) CHO, (g) COH, and (h) CO. Gray, red, brown, and pink spheres represent platinum, oxygen, carbon, and hydrogen atoms, respectively.](image)

| species | sites  | $E_{\text{ads}}$ (eV) |
|---------|-------|----------------------|
| CH$_3$OH | top   | $-0.44$              |
| CH$_2$O | top   | $-1.74$              |
| CH$_3$OH | top   | $-2.10$              |
| CH$_2$O | top   | $-0.57$              |
| CHO    | bridge| $-4.06$              |
| CHO    | fcc   | $-2.41$              |
| COH    | fcc   | $-4.75$              |
| CO     | fcc   | $-1.89$              |

Figure 1. Optimized geometry configurations of the possible intermediates included in the indirect pathway for CH$_3$OH oxidation on Pt(111): (a) CH$_3$OH, (b) CH$_2$O, (c) CH$_3$OH, (d) CH$_2$O, (e) CHOH, (f) CHO, (g) COH, and (h) CO. Gray, red, brown, and pink spheres represent platinum, oxygen, carbon, and hydrogen atoms, respectively.
studies of the CH₂OH intermediate. Using the periodic slab model, Desai et al. and Greeley et al. found that CH₂OH adsors at the Pt top site through the C atom; the corresponding adsorption energies are −2.17 eV and −1.98 eV, respectively. Similar adsorption configurations were also found on Pt(111) by the cluster model with adsorption energies of −2.85 eV and −2.51 eV. As shown in Figure 1(c), the adsorption configuration obtained in our present calculation is in good agreement with the structures observed in previous theoretical investigations. Our calculated adsorption energy of −2.10 eV on Pt(111) for CH₂OH is in agreement with the values obtained from the slab model, whereas it is significantly lower than those calculated from the cluster method. Similarly, the finite cluster sizes may be able to explain this discrepancy. The total energy of CH₂OH on Pt(111) is −0.36 eV lower than that of CH₂O in our present studies, which suggests the CH₂OH formation may be energetically preferred.

By further dehydrogenation of intermediate CH₂O or CH₂OH, formaldehyde (CH₂O) can be formed on Pt(111). Experimental investigations on adsorption of CH₂O on Pt single-crystal surfaces are somewhat more general than CH₂O and CH₂OH. However, the reliable structural parameter for CH₂O is still unavailable. Fortunately, some theoretical investigations on CH₂O adsorption have been performed on Pt(111). Based on Huëckel cluster model calculation, the adsorbed CH₂O with top-bridge-top configuration was found to be energetically more favorable, and the determined adsorption energy was −0.99 eV. Using DFT cluster methods, top-bridge-top configuration was also found to be the best adsorption sites with adsorption energy of −0.42 eV. Periodic DFT slab calculation found that CH₂O adsorbs at top-bridge-top configuration through C and O atoms to an adjacent two Pt top sites; the corresponding adsorption energy is −0.50 eV. As shown in Figure 1(d), our present results also showed that CH₂O weakly adsorbs at the Pt top site through C and O atoms on Pt(111), and the adsorption energy is −0.57 eV, in which the site preference and the value of adsorption energy are in good agreement with the previous theoretical studies. Hydroxymethylene (CHOH) can be formed by further dehydrogenation of intermediate CH₂OH. CHOH species on Pt(111) are also unstable, and experimental structural information and adsorption energy are also not found. A previous DFT cluster study showed that CHOH prefers to adsorb at the top site through the C atom with an adsorption energy of −3.79 eV. The bridge adsorption was found to be a preferable site in another cluster study, and the adsorption energy was determined to be −3.68 eV. The periodic DFT slab study found that CHOH prefers to bind at a bridge site through the C atom with an adsorption energy of −3.24 eV. Our present studies find that CHOH on Pt(111) also prefers to adsorb at the bridge site through the C atom, and the structure is shown in Figure 1(e), which is consistent with the previous reported site preferences. However, our calculated adsorption energies of −4.06 eV are somewhat higher than the previous value.

Formyl (CHO) is formed by dehydrogenation of intermediate CH₂O or CHOH. To our knowledge, no experimental studies of CHO species were found due to its instability on Pt. However, some theoretical investigations on CHO adsorption properties have been carried out. Using the cluster method, CHO was found to adsorb perpendicular to a bridge site through the C atom on Pt(111) with an adsorption energy of −2.61 eV; the adsorptions to top sites through the C atom were also found in other studies, and the adsorption energies were reported to be −2.71 eV and −2.84 eV, respectively. The previous periodic DFT slab methods found that CHO adsorbs at the Pt top site through the C atom; the adsorption energy is −2.36 eV. Our calculated adsorption energy of −2.41 eV for CHO on Pt(111) is lower than those values calculated using the cluster model due to finite size effects of the cluster method. Notably, in our present studies, strong site preferences of CHO were not shown on Pt(111). Four configurations are studied with the difference of adsorption energies of ca. 0.05 eV; the adsorption energies for top, bridge, fcc, and hcp states are −2.36, −2.35, −2.41, and −2.36 eV, respectively, as shown in Figure 1(f). In all configurations, the CHO adsorbs through the C atom. By dehydrogenation of CHOH, the final intermediate hydroxymethylidyne (COH) species may be formed. Using the cluster method, the previous DFT calculations on Pt(111) have obtained adsorption energies of −5.25 eV and −4.86 eV for COH. Our present calculated adsorption energy (−4.75 eV) and the previous value (−4.45 eV) from Greeley et al. are lower than the above value yielded by the cluster model; this difference is also able to be explained by the discrepancies between the cluster and slab method. As shown in Figure 1(g), COH prefers to adsorb at an fcc site through the C atom on Pt(111), which is in good agreement with previous studies. Finally, by dehydrogenation of CHO or COH, carbon monoxide (CO) is generated. As we all know, a poor job of CO chemisorption through DFT methods has been done on transition metal surfaces. For instance, the previous experimental studies showed that top and bridge sites are favored, whereas DFT results indicate that 3-fold hollow sites are the preferred adsorbing sites on Pt(111). Our present DFT studies showed that the 3-fold fcc site of the Pt(111) surface is preferable for CO adsorption, as shown in Figure 1(h). Nonetheless, we note that our calculated adsorption energy of −1.89 eV for CO on Pt(111) is well consistent with the previous experimentally determined value of −1.75 eV using single-crystal adsorption calorimetry methods.

It is well-known that CHO is a generally accepted reactive intermediate in indirect and direct pathways for CH₂OH oxidation. Thus, our present studies for the direct pathway start from CHO hydroxylation, as shown in Scheme 1. The direct pathway on the Pt(111) surface relates to the formation of HCOOH via CHO hydroxylation, and the final production of CO₂ can be produced through the serial dehydrogenation of HCOOH. The possible surface species involved in the direct pathway on Pt(111) are investigated first. The optimized most stable adsorption configurations of four possible intermediates (HCOOH, COOH, HCOO, and CO₂) in the direct pathway are shown in Figure 2, and the most stable adsorption sites and corresponding adsorption energies are listed in Table 2. On Pt(111), HCOOH physically adsorbs in an upright fashion with the CH group pointing down toward the surface and the OH
group pointing up (see Figure 2(a)), and the corresponding adsorption energy is calculated to be −0.13 eV. COOH prefers to adsorb at the Pt top site through the C atom with OH group pointing up and with an adsorption energy of −2.34 eV (see Figure 2(b)). Adsorbed HCOO adsorbs on two neighboring Pt atoms of the Pt(111) surface through two O atoms, which is a bidentate configuration with an adsorption energy of −2.38 eV (see Figure 2(c)). CO2 is nearly parallel to the Pt(111) surface in a linear configuration and weakly physisorbs. and the adsorption energy is extremely small, ca. −0.07 eV, as shown in Figure 2(d). Unfortunately, no experimental or theoretical adsorption energies on Pt(111) exist to compare to our present results in direct pathways of CH3OH oxidation.

**MEP Analysis of Indirect and Initial C–O Bond Scission Pathways.** To understand the surface-catalyzed indirect pathway of CH3OH oxidation on Pt(111), we first studied the thermodynamics and kinetics analysis for the various possible elementary reaction steps that occur in CH3OH oxidation at the nonelectrochemical interface. All possible oxidation steps in the indirect pathway were considered for each reaction, but only the MEP is reported. The reaction pathways on Pt(111) initialized with C–H, O–H, and C–O bond cleavage are discussed in detail, as shown in Figure 3. The most stable adsorbed states of intermediates are used as the initial and final states of the elementary reaction steps. For the C–H bond cleavage of CH3OH to form CH3OH on Pt(111), our calculated activation energy is 1.06 eV; the corresponding reaction energy is −0.24 eV. The present calculated activation energy is 0.84 eV with a reaction energy of 0.60 eV for the initial with O–H bond cleavage of CH3OH into CH2O. For the initial reaction with C–O bond cleavage of CH3OH into CH2O, an activation energy of 0.70 eV is obtained with a reaction energy of 0.28 eV. Almost no experimental data are used to compare our calculated activation energies for initial CH3OH oxidation pathways. Only a molecular beam study gave an estimate of ca. 0.50 eV for the activation energy on Pt(111) in the initial CH3OH oxidation. The lowest value is 0.70 eV among our calculated activation energies, which is approximately consistent with the previous experimental studies. For the initial C–H and O–H cleavage, the previous periodic DFT calculations on a (2 × 2) Pt(111) unit cell have determined activation energies of 0.95 and 1.47 eV, respectively, and the calculated activation energies for CH3OH oxidation on a (3 × 3) Pt(111) unit cell are 0.67, 0.81, and 2.19 eV for C–H, O–H, and C–O bond cleavage, respectively, which are significantly lower or higher than our present calculated values; especially, the activation energy of C–O bond cleavage is considerably larger than our calculated value (2.19 eV vs 0.70 eV). The higher coverage used in the previous study may lead to these significant deviations, in which the higher coverage imposes the increased constraints on the geometry of the transition state. Exceptionally, the previous calculated activation and reaction energies for CH3OH oxidation on the (3 × 3) Pt(111) unit cell are 0.81 and 0.62 eV (endothermic reaction step) for O–H bond cleavage, which are well consistent with our calculated results. According to our DFT calculated activation energies, the formation of intermediates CH3O and CH2O has approximately equal and lower activation energies than that of CH3OH. Thus, the first oxidation on Pt(111) proceeds through two parallel routes: dehydrogenation through O–H bond cleavage into CH2O intermediate and decomposition through C–O bond cleavage into CH3, although the above thermodynamic studies show that CH3OH formation through C–H bond cleavage reactions is found to be relatively more favorable. Actually, some previous experimental evidence also showed that CH3OH on Pt can partially dissociate to form adsorbed CH2 species (x = 0–3).
through the C–O bond breaking, in which the formed carbonaceous deposits can block the Pt surface and prevent further CH₃OH oxidation. Accordingly, our present study shows that the produced CH₂ species through initial C–O bond cleavage can influence catalytic activation of the Pt surface for CH₃OH oxidation. Our present finding of a relatively low activation energy (0.70 eV) for C–O bond cleavage is in good agreement with the experimental observation on Pt(111).

According to DFT calculations, the indirect pathway for CH₃OH oxidation proceeds via CH₂O or CH₃ as a first intermediate on Pt(111). Starting from the CH₄O intermediate, further CH₃O oxidation on Pt(111) through C–H and C–O bond cleavages may be able to produce CH₃O and CH₃ intermediates, respectively. Thereinto, the C–H bond dissociation into CH₂O only requires an activation energy of 0.06 eV with a reaction energy of −0.39 eV, which is a nearly spontaneous process; for the C–O bond cleavage within CH₂O into CH₃, a relatively larger activation energy of 0.39 eV needs to be overcome. However, the activation energy of C–O bond cleavage in CH₃O is also very low, and this reaction is exothermic by about −0.21 eV. Thus, it is obvious that the C–H and C–O bond cleavages in CH₂O individually leading to CH₃O and CH₃ are very possible to occur on Pt(111) due to low activation energy. Thus, the DFT calculated results explained well why CH₂O is very unstable on Pt, and as demonstrated above, geometry configuration of CH₃O is unavailable on Pt(111) experimentally. Although Peck et al. were able to produce CH₃O and estimate an activation energy for CH₃O dissociation of ca. 0.48 eV (well consistent with the present calculated value of 0.39 eV for C–O bond breaking), they were not able to obtain structural parameters of the CH₂O species based on spectral data. Previous periodic DFT calculations on a (3 × 3) Pt(111) unit cell have determined the activation energy of 0.25 eV for CH₂O oxidation to CH₃O, and the corresponding reaction energy is −0.36 eV, which are well consistent with our calculated values. For the dehydrogenation of CH₃ obtained during CH₃OH oxidation via C–O bond scission on Pt(111), CH₃ formation through the C–H bond cleavage requires an activation energy of 1.15 eV with a reaction energy of 0.15 eV (endothermic process). Thus, due to the large activation energy, the C–H bond cleavage into CH₂ is very difficult to occur. The possible intermediate CH₂O may be able to form CHO through the C–H bond cleavage or produce CH on Pt(111) through the C–O bond breaking. The former is exothermic with a reaction energy of −0.62 eV, whereas the latter is endothermic by 0.48 eV. Moreover, the required activation energy for the former is significantly lower than that of the latter (0.13 eV vs. 1.47 eV). Thus, the C–H bond cleavage of CH₂O into CHO is more facile to occur than the C–O bond cleavage on Pt(111) thermodynamically and kinetically. Unfortunately, no experimental results exist to compare to our present calculated reaction and activation energies to CH₂O oxidation. However, previous periodic DFT calculations on a (3 × 3) Pt(111) unit cell also showed that the adsorbed CH₂O dehydrogenation to produce the CHO intermediate is a nonactivated process with an activation energy of less than 0.10 eV, and the corresponding reaction energy for this elementary reaction step is ca. −0.61 eV which are all well consistent with values obtained in our present study. For the dehydrogenation of CH₃ obtained via CH₂ dehydrogenation, the C–H bond breaking into CH requires to overcome an activation energy of 0.69 eV with a reaction energy of −0.55 eV. Starting from CHO oxidation, the C–H bond cleavage occurs to produce CO. This step is highly exothermic by −1.01 eV with an activation energy of 0.54 eV. The C–O bond cleavage is also considered. However, the calculated activation energy is large, 1.89 eV, for this step, and the reaction is endothermic by 0.68 eV, showing that C–O bond breaking is impossible to occur on Pt(111). No experimental results exist to compare to our present calculated reaction and activation energies for further CHO oxidation. The activation energy of 0.23 eV for CHO oxidation into CO has been determined on a (3 × 3) Pt(111) unit cell in previous periodic DFT calculations with a reaction energy of −0.97 eV for this step. Our present calculated values of reaction and activation energies are well consistent with the previous values, although our value of activation energy is slightly higher than the previous value. For the dehydrogenation of CH obtained via CH₂ dehydrogenation, an activation energy of 1.19 eV needs to be overcome for the C–H bond breaks to form C with a reaction energy of 0.56 eV. Simultaneously, we also find that as the residuals of H atoms gradually reduce within CH₂O, the C–H bond cleavage steps are more and more exothermic based on the above MEP analysis; namely, we find that the C–H bond cleavage step within CHO is more exothermic than that within CH₂O, in turn, which is more exothermic than that within the CH₃O intermediate. As demonstrated above, the CHO intermediate adsorbs strongly on Pt(111). Thus, the surface poisoning of CO may be expected to further CH₃OH oxidation. However, we note that on Pt(111) the C–H bond cleavage of CHO into CO is a highly exothermic step. Accordingly, the CHO intermediates are possible to dehydrogenate easily to produce CO though it strongly adsorbs the Pt(111) surface. Similar to CHO, CO binds on the Pt(111) surface very strongly. Furthermore, CO desorption from Pt(111) is strongly endothermic by 1.89 eV, which seems to confirm that adsorbed CO can poison the Pt(111) surface, as speculated in previous experimental studies.

The above thermodynamic and kinetic studies suggest that an indirect pathway for CH₃OH oxidation on Pt(111) can be proposed at the nonelectrochemical interface, namely, CH₃OH* → (CH₂O + H)*, CH₂O* → (CH₃O + H)*, CH₂O* → (CHO + H)*, and CHO* → (CO + H)*. This is the initial O–H bond cleavage pathway despite that the initial C–H bond cleavage within CH₂O is an exothermic step. The rate-determining step of this pathway is CH₂O dehydrogenation through O–H bond cleavage into the CH₃O intermediate since it has relatively higher activation energy and more positive reaction energy. Additionally, an initial C–O bond cleavage pathway is also proposed due to subtle differences of activation energies between the initial O–H and C–O bond breakings within CH₃OH. It mainly proceeds by CH₃OH* → (CH₃ + OH)* or CH₃O* → (CH₂ + O)*, CH₂* → (CH₂ + H)*, CH₁* → (CH + H)*, and CH* → (C + H)*, in which CH₁ species can be formed through CH₃OH and CH₂O oxidation due to relatively lower activation energies; cleavages of the C–H bond in CH₃ and CH to CH₂ and C, respectively, may be the rate-determining step of this pathway since these two steps have approximately equal and relatively higher activation energies than others. Therefore, both of the initial O–H and C–O bond cleavages are all possible to simultaneously occur, which may be parallel on Pt(111) during CH₃OH oxidation. In a recent publication from Kaichev et al., we also noted that the initial C–O bond cleavage pathway was examined experimentally, in which the carbon species can be formed due to
CH$_3$OH oxidation through the C–O bond cleavage. Thus, the recent experimental and our present theoretical results all show that surface poisoning of Pt catalysts and insufficient high activity for CH$_3$OH oxidation may be mainly determined by carbon species that accumulate on Pt.

**MEP Analysis of a Direct Pathway through HCOOH Intermediate.** The direct pathway includes the CHO hydroxylation to produce HCOOH species, which can then form the final product CO$_2$ via serial dehydrogenation (see Scheme 1). The reaction pathways starting from CHO hydroxylation are discussed on Pt(111) at the nonelectrochemical interface, as shown in Figure 4. The formation of HCOOH through CHO hydroxylation requires an activation energy of 0.20 eV with a reaction energy of –0.42 eV (exothermic), which can be overcome at ambient temperature, and is an almost nonactivated process. The results show that CHO hydroxylation on Pt(111) may be facile. Once formed, HCOOH can further oxidize to produce HCOO through O–H bond cleavage or COOH species through C–H bond cleavage. The HCOO formation requires an activation energy of 0.02 eV with a reaction energy of –0.29 eV. For the formation of COOH, the activation energy is 0.19 eV, and this pathway is also exothermic by 0.53 eV. Although the present results show that the activation energy for COOH formation is slightly higher than that of HCOO formation, the formations of both these intermediates have negative reaction energies and very low activation energies, which can be easily overcome by a thermo-activated process. Thus, HCOO and COOH intermediates are all easily formed on Pt(111) during HCOOH oxidation, which may be parallel pathways in the direct pathway for CH$_3$OH oxidation. The adsorbed CHO species can further oxidize into CO through the direct pathway via C–H bond scission into CO$_2$ through the further oxidation of HCOO and COOH intermediates are all easily formed on Pt(111) during the further oxidation of HCOOH, and may be parallel pathways in the direct pathway for CH$_3$OH oxidation, further oxidation of HCOOH via C–H bond scission into CO$_2$ is unfavorable kinetically because of the rigid molecular configuration. The previous studies from Neurock and coauthors also showed that the COOH intermediate could readily decompose to form CO$_2$ on Pt(111) with a low activation energy, and the simultaneous activation of both the C–H bond within HCOO species and the O–H bond within COOH species was not observed.

**Optimal CH$_3$OH Oxidation Pathways at the Non-electrochemical Interface.** By comparing the activation energies of elementary reaction steps, the optimal indirect and direct pathways for CH$_3$OH oxidation have an identical rate-determining step, CH$_3$OH$^*$ → (CH$_3$O + H$^*$), on Pt(111). As shown in Scheme 1, the generally accepted reaction intermediate is CHO during CH$_3$OH oxidation along indirect and direct pathways. Thus, further CHO dehydrogenation into CO and hydroxylation into HCOOH are scrutinized since both of them are competitive pathways on Pt(111). On the basis of the above MEP analysis, the activation energy for CHO dehydrogenation into CO is 0.54 eV, whereas CHO hydroxylation into HCOOH only requires a very low activation energy of 0.20 eV, which can be overcome via a thermo-activated process. Clearly, the activation energy of further CHO oxidation along a direct pathway into HCOOH through hydroxylation is lower by 0.34 eV than CHO dehydrogenation into CO along an indirect pathway. Furthermore, the indirect and direct pathways have an identical rate-determining step. Thus, we can conclude that the direct pathway is more favorable than the indirect pathway on Pt(111).

Simultaneously, it is also noted that the intermediate CH$_x$ formation through C–O bond cleavage of CH$_3$OH and CH$_3$O has slightly lower activation energy than CH$_3$O formation (0.70 eV vs 0.84 eV) based on our DFT calculated activation energy. Thus, CH$_x$ (x = 0–3) species can be formed on Pt(111) during the course of CH$_3$OH oxidation. The adsorbed CH$_x$ species will occupy and block the active sites of the Pt surface, therefore preventing further CH$_3$OH oxidation. Because of the formation of carbonaceous deposits on Pt(111), the catalytic activation of the Pt surface for CH$_3$OH oxidation can be influenced. Our present findings on the formation of carbonaceous deposits due to relatively low activation energy on Pt(111) are consistent with the experimentally observed C–O bond scission of CH$_3$OH into CH$_x$ species, as demonstrated in a previous section. Thus, we can speculate that the adsorbed residues that poisoned the Pt surface and impeded the performance of DMFCs may be CH$_x$ species, rather than CO species since the
Table 3. Activation Energies ($E_{act}$, eV), the Calculated Reaction Gibbs Energies ($\Delta G_{surf}$, eV) for the Adsorbed Species on Pt(111), and the Calculated Reversible Potential ($U_{rev}$, V), and the Values of $U^0$ for the Various Possible Elementary Reaction Steps Involved in the Indirect Pathway for CH$_3$OH Oxidation on Pt(111)

| reaction                           | $E_{act}$ (eV) | $U^0$ (V) | $\Delta G_{surf}$ (eV) | $U_{rev}$ (V) |
|-----------------------------------|----------------|-----------|------------------------|---------------|
| CH$_3$OH$^*$ → CH$_2$OH$^*$ + H + e$^-$ | 1.06           | 1.39      | -0.71                  | -0.71         |
| CH$_3$OH$^*$ → CH$_4$O$^*$ + H + e$^-$ | 0.84           | 1.86      | 0.12                   | 0.12          |
| CH$_2$OH$^*$ → (CH$_2$ + OH)$^*$    | 0.70           | /         | 0.28                   | /             |
| CH$_2$OH$^*$ → CH$_3$O$^*$ + H + e$^-$ | 0.94           | -0.94     | 0.59                   | 0.59          |
| CH$_2$OH$^*$ → CHO$^*$ + H + e$^-$   | 0.74           | 1.06      | -0.90                  | -0.90         |
| CH$_2$O$^*$ → (CHO + OH)$^*$       | 0.06           | -1.42     | -0.25                  | -0.25         |
| CHO$^*$ → HCO$^*$ + H + e$^-$      | 0.47           | 0.66      | -0.03                  | -0.03         |
| COOH$^*$ → CHO$^*$ + H + e$^-$     | 0.26           | -0.84     | 0.81                   | 0.81          |
| COOH$^*$ → CHO$^*$ + H + e$^-$     | 0.13           | 1.16      | -0.68                  | -0.68         |
| COOH$^*$ → CO$^*$ + H + e$^-$      | 0.54           | -1.45     | -0.93                  | -0.93         |
| COOH$^*$ → CO$^*$ + H + e$^-$      | 0.37           | -2.96     | -0.10                  | -0.10         |

Table 4. Activation Energies ($E_{act}$, eV), the Calculated Reaction Gibbs Energies ($\Delta G_{surf}$, eV) for the Adsorbed Species on Pt(111), and the Calculated Reversible Potential ($U_{rev}$, V) for the Various Possible Elementary Reaction Steps Starting from CHO Hydroxylation Involved in the Direct Pathway for CH$_3$OH Oxidation on Pt(111)

| reaction                           | $E_{act}$ (eV) | $U^0$ (V) | $\Delta G_{surf}$ (eV) | $U_{rev}$ (V) |
|-----------------------------------|----------------|-----------|------------------------|---------------|
| (CHO+OH)$^*$ → HCOOH$^*$          | 0.20           | /         | -0.42                  | /             |
| HCOOH$^*$ → CHO$^*$ + H + e$^-$   | 0.19           | 1.52      | -0.69                  | -0.69         |
| HCOOH$^*$ → HCOO$^*$ + H + e$^-$  | 0.02           | 2.04      | -0.21                  | -0.21         |
| HCOOH$^*$ → CO$^*$ + H + e$^-$    | 1.04           | -2.61     | -0.30                  | -0.30         |
| COOH$^*$ → CO$^*$ + H + e$^-$     | 0.42           | -2.09     | 0.18                   | 0.18          |

direct pathway is more favorable on Pt(111) at the nonelectrochemical interface.

Reversible Potentials for CH$_3$OH Oxidation. Due to the complexity of CH$_3$OH–H$_2$O interactions$^{48-50}$ and the difficulty to model a solid/liquid interface theoretically, the present studies do not consider tentatively the modeling of an aqueous electrochemical environment that included solvent effect in the Pt/H$_2$O system. At present, a common challenge in this field is how to treat the H$_2$O environment and determine the electrode potential at the H$_2$O/metal interface. However, based on the linear Gibbs energy relationship (LGER)$^{51,52}$, the reversible potentials for each of the one-electron transfer steps during CH$_3$OH oxidation into CO$_2$ can be calculated. This approach provides a proper way of avoiding the explicit treatment of the solvated protons and modeling qualitatively the electrochemical environment. Furthermore, it is advantageous to use the LGER approach in the present study due to the large number of reactions. The formalism for determining the electrode potentials is as follows. For the reaction

$$\text{Ox} + e^- \rightarrow \text{Red}$$

The reversible potentials for the surface reactions, $U_{surf}^\text{rev}$ versus standard hydrogen electrode (vs SHE), are given to good approximation by$^{51,52}$

$$U_{surf}^\text{rev} = U^0 + \left[ E_{ads}(\text{Ox}) - E_{ads}(\text{Red}) \right] / nF$$

In this equation, $U^0$ (vs SHE) is standard reversible potential during oxidation of CH$_3$OH into CO$_2$, and the values of $U^0$ for each oxidation pathway are from the literature by Anderson et al.$^{51}$ $E_{ads}$ are adsorption energies of various reaction intermediates at the potential of zero charge, as shown in Table 1; $F$ is Faraday’s constant; and $n$ is the number of electrons transferred. Considering the complexity of the electrochemical environment, the present theoretical studies do not include solvent effect. In spite of this, we still expect that the qualitative calculated results can be obtained, and the conclusions in trends are reasonably accurate. For various possible elementary reaction steps involved in the indirect pathway initialized with C–H and O–H bond cleavage into CO and direct pathway starting from CHO hydroxylation into CO$_2$ on Pt(111), the corresponding activation ($E_{act}$), the calculated reaction Gibbs energies ($\Delta G_{surf}$) for the adsorbed species on Pt(111), and the calculated reversible potential ($U_{rev}$) are summarized in Tables 3 and 4, respectively.

The previous theoretical studies form Anderson et al.$^{51,52}$ calculated the reversible potentials for various reaction steps during CH$_3$OH oxidation and predicted that the oxidation pathways with low and negative reversible potentials should have low activation energies. To confirm the previous prediction and compare results with early studies, the reversible potentials are calculated in the present work for each oxidation step involving proton transfer based on the LGER approach. As shown in Table 3, the first oxidation of CH$_3$OH into CH$_3$O has a negative reversible potential, $-0.71$ V, which may make its information more favorable under an electrochemical environment than CH$_3$O formation with the reversible potential of 0.12 V. The fundamentally consistent conclusions were also obtained in a previous theoretical study,$^{7}$ in which the reversible potentials are $-0.74$ and 0.42 V for the first oxidation step into CH$_3$OH and CH$_3$O intermediates on Pt(111), respectively; namely, CH$_3$OH can occupy more spaces on Pt(111) than CH$_3$O. In a previous experimental study, Franaszczuk and coauthors$^{53,54}$ showed that the reaction in the electrochemical aqueous interface occurs by C–H bond activation. However, our present and some previous experimental and theoretical studies on Pt(111) obtained inconsistent conclusions, in which CH$_3$O and CH$_3$ formations have relatively lower activation energies than CH$_3$OH formation, as demonstrated above. This may be able to be attributed to the nonelectrochemical environment that is used.
in the present and previous paper. The difference of first oxidation pathways between the gas-phase and electrochemical aqueous environment may be because the O–H and C–O bonds in CH$_3$OH are more polar and hence more strongly solvated by H$_2$O molecules than the C–H bond, leading to higher energy cost associated with O–H and C–O bond activation in solution. Furthermore, CH$_2$OH that forms on C–H bond activation has an intact OH group that is exposed to the solvent and is amenable to solvation.

Starting from further oxidation of CH$_3$OH, the calculated reversible potentials are 0.59 and −0.90 V for CH$_2$O and CHOH formations, respectively, in reasonable agreement with trends with the previous theoretical study on CH$_3$OH oxidation into CH$_2$O and CHOH intermediates (0.64 and 0.08 V) by Anderson et al.,$^{51}$ suggesting that CHOH formation should have lower activation energy. In fact, the identical conclusions are obtained based on the above MEP analysis (see Table 3); namely, CHOH is easily formed on Pt(111). CH$_2$O may be also formed by CH$_3$OH further oxidation with the calculated reversible potential of −0.25 V, which is well agreeable with that of the corresponding step (−0.52 V) from Anderson et al.$^{51}$ The extremely low activation energy is also obtained for CH$_3$OH oxidation into CH$_2$O in our present study (ca. 0.06 eV). The reversible potentials are calculated as −0.03 and 0.81 V for CHOH further oxidation into COH and CHO, respectively, seeming to show that COH formation is more favorable than CHO. The consistent trends for the corresponding steps are also obtained in a previous theoretical study (−0.56 and −0.13 V). However, our present calculated activation energies are very low for both these steps and can be easily overcome by a thermo-activated process as shown in Table 3. As shown above, it can be observed that our present calculated values of some reversible potential are different from those from a previous study. The difference of adsorption energies among different calculated systems can result in the different reversible potentials. The CHO intermediate may be also able to be easily formed by CH$_3$OH further oxidation with negative reversible potential (−0.68 V) and extremely low activation energy (ca. 0.13 eV), in which the reversible potential is very close to the value of the corresponding process (−0.69 V) from previous work.$^{51}$

After CHO and COH form, the reversible potentials for further oxidation into CO are −0.93 and −0.10 V, respectively, suggesting that CO formation through CHO oxidation may be more favorable due to the significantly negative reversible potential under an electrochemical environment, which is in reasonable agreeable with the previous theoretical study by Anderson et al.$^{51}$ Finally, CO is oxidized into CO$_2$ by hydroxylation with an activation energy of 0.66 eV. Thus, we can propose the possible optimal indirect pathways for CH$_2$OH oxidation under simulated electrochemical environment based on the calculated reversible potentials, CH$_2$OH$^*$ → CH$_2$OH* + H$^+$ + e$^−$, CH$_2$OH$^*$ → CHOH* + H$^+$ + e$^−$, CHOH$^*$ → CHO$^*$ + H$^+$ + e$^−$ or CHOH$^*$ → COH$^*$ + H$^+$ + e$^−$, CHO$^*$ → CO$^*$ + H$^+$ + e$^−$, and (CO$^*$ + OH)$^*$ → CO$_2$* + H$^+$ + e$^−$. The early experimental studies can confirm our present conclusions on the indirect pathways; for example, Xia et al. obtained hydrogenated species such as COH, CHOH, and CH$_2$OH along CO during CH$_3$OH electro-oxidation by using in situ Fourier transform infrared spectroscopy (FTIR) and polycrystalline Pt electrode.$^{55}$ Chen et al. also found the adsorbed intermediate CO on Pt film electrodes by surface-enhanced infrared adsorption spectroscopic (SEIRAS).$^{56}$ The previous theoretical studies from Anderson et al.$^{52}$ also showed that all the CH$_2$OH intermediates with low and negative reversible potentials can form CO and CHO intermediates.

Starting from CHO hydroxylation, HCOOH can be formed with a negative reaction energy of −0.42 eV and low activation energy of ca. 0.20 eV, which make HCOOH formation competitive with CHO further oxidation into CO. In fact, Housmans et al. in a recent study concluded that HCOOH can be formed during CH$_3$OH electro-oxidation in different acid electrolytes on Pt(111) electrodes,$^{57}$ supporting our present conclusions. Subsequently, HCOOH is oxidized to form HCOO and CHOH intermediates, both having negative reversible potentials of −0.21 and −0.69 V, respectively. HCOO and CHOH may be able to be further oxidized to CO$_2$ with the calculated reversible potentials of −0.30 and 0.18 V, respectively. These are referred to as direct pathway. Thereinto, activation of the C–H bond in HCOOH has a relatively more favorable reversible potential of −0.69 V; thus, this is followed by the COOH oxidation into CO$_2$ at low reversible potential. Although further oxidation of HCOO has negative reversible potential compared with COOH, the particularly well-suited structure with two O atoms bonded to the surface leads to our calculated large activation energy, ca. 1.04 eV, and impedes HCOO further oxidation since two O bonds to the surface must be broken. The previous study modeling the aqueous electrochemical interface from Neurock et al. supported our present conclusions,$^{34}$ in which the activation energies of ca. 1.0 eV were also calculated on Pt(111). Our calculated reversible potentials for direct pathway are also accurately consistent with trends with the previous study from Anderson et al.$^{51}$ Therefore, the direct pathway may proceed under the present simulated electrochemical environment by CH$_3$OH$^*$ → CH$_3$OH* + H$^+$ + e$^−$, CH$_3$OH$^*$ → CHOH* + H$^+$ + e$^−$, CHOH$^*$ → CHO$^*$ + H$^+$ + e$^−$, (CHO$^*$ + OH)$^*$ → HCOOH*, HCOOH* → COOH* + H$^+$ + e$^−$, and COOH$^*$ → CO$_2$* + H$^+$ + e$^−$.

By combining the present calculated reversible potentials with activation energies, it can be speculated that the indirect and direct pathways may be able to occur simultaneously on Pt(111) under the electrochemical environment, which may be parallel pathways. Due to lower activation energy of C–O bond activation into CH$_3$ species in CH$_3$OH, which is a non-electrochemical step, CH$_x$ (x = 0–3) species may be able to be formed on Pt(111) during CH$_3$OH oxidation regardless of being in electrochemical or nonelectrochemical environment, which will occupy the surface active sites, thereby preventing further CH$_3$OH oxidation. Thus, our present results show that the adsorbed residues that poisoned the Pt surface and impeded the performance of DMFCs may be CH$_3$ and CO species due to the simultaneous occurrence of oxidation pathways on Pt(111) under the present simulated electrochemical environment. Based on the present study, some new insights into CH$_3$OH oxidation mechanisms and designing strategies of Pt-based alloy catalysts for CH$_3$OH oxidation can be provided. Simultaneously, the present study is also able to partially explain why the first oxidation of CH$_3$OH proceeds through CH$_2$O at the nonelectrochemical interface, whereas it takes place by the CH$_3$OH intermediate under aqueous electrochemical environment on Pt(111) that was observed experimentally.$^{23,24,55}$
CONCLUSIONS

In summary, a systematic first-principle study of CH$_3$OH oxidation along indirect and direct pathways on Pt(111) has been carried out, and some new insights into CH$_3$OH oxidation pathways in DMFCs are presented. The thermodynamics, kinetics, and reversible potentials for all possible elementary steps, starting with C–H, O–H, and C–O bond cleavages and proceeding via sequential decomposition and oxidation from the reaction intermediates are analyzed. Some key reactive intermediates are identified. By comparing the activation energies and reversible potentials of various possible elementary reaction steps, it can be speculated that the initial CH$_3$OH oxidation step proceeds by a CH$_3$O intermediate under a nonelectrochemical environment, whereas it prefers to occur by a CH$_3$OH intermediate under an electrochemical environment.

Furthermore, CHO hydroxylation into HCOOH along the direct pathway is more facile to occur than CHO dehydrogenation into CO along an indirect pathway at a nonelectrochemical interface. By combining the present calculated reversible potentials with activation energies, it can be concluded that the indirect and direct pathways may be parallel pathways on Pt(111) under the present simulated electrochemical environment. Simultaneously, it is observed that CH$_2$ is also easily formed through C–O bond cleavage in CH$_3$OH, which is a nonelectrochemical step. Thus, CH$_x$ (x = 0–3) species are possibly formed on Pt(111) during the course of CH$_3$OH oxidation regardless of being in electrochemical or nonelectrochemical environment. The adsorbed CH$_x$ species will result in the blocking of the active sites and the prevention of further CH$_3$OH oxidation. Our present findings on the formation of carbonaceous deposits on Pt(111) are consistent with the experimentally observed C–O bond scission of CH$_3$OH into CH$_x$ species. Thus, we propose that the adsorbed residues that poisoned the Pt surface and impeded the performance of DMFCs may be CH$_x$ species rather than CO species since the direct pathway is more favorable on Pt(111) at the nonelectrochemical interface. However, the adsorbed species that poisoned the Pt surface may be CH$_x$ and CO species due to the simultaneous occurrence of oxidation pathways on Pt(111) under the present simulated electrochemical environment. Based on the present study, some new insights into CH$_3$OH oxidation mechanisms and designing strategies of Pt-based alloy catalysts for CH$_3$OH oxidation can be provided.

MODELS AND COMPUTATIONAL DETAILS

Using the generalized gradient approximation with the Perdew–Burke–Ernzerhof exchange correlation functional, the periodic DFT slab approach was used to perform all calculations. The nuclei and core electrons were described by ultrasoft pseudopotentials. Using a plane-wave basis set, the Kohn–Sham equations were solved self-consistently. To make the plane-wave basis set finite, a kinetic energy cutoff of 30 Ry and a charge-density cutoff of 300 Ry were used. The smearing technique of Methfessel–Paxton was used to treat the Fermi surface with a parameter of 0.02 Ry. The PWSCF (plane-wave self-consistent field) codes that involved in the Quantum ESPRESSO distribution have been used to implement all calculations in the present study, while the XCrysden (X-Window Crystalline Structures and Densities) graphical package was used to produce the figures of the chemical structures.

In the exposed basal planes of nanoparticles, the (111) facet of Pt is the most stable crystal plane. Therefore, for experimental and theoretical studies, it is generally chosen as the representative surface. Prior to calculations, the thickness of the (111) slab was tested. The total energies of the two-, three-, four-, five-, and six-layer Pt(111) slab with relaxation of top one, two, and three layer Pt atoms were calculated, and the differences of the total energy were obtained between three- and two-layer slab, four- and three-layer slab, five- and four-layer slab, and six- and five-layer slab, in which the differences of the total energy between the four- and three-layer slab, five- and four-layer slab, and six- and five-layer slab are basically constant. In principle, one should use as much as possible slab layers to model the metal surface to achieve high accuracy in calculations. However, increasing the slab layers in supercell systems will decrease the computational efficiency and add computational cost. Thus, a (4 × 4) three-layer fcc(111) slab with theoretical equilibrium lattice constant is used to model the three-dimensionally infinite periodic Pt(111) surface based on the consideration of computational efficiency and cost in the present study. In order to study the adsorption of the CH$_3$OH molecule and their subsequent intermediates, model systems that contained specific intermediates were created. For all the structures explored, the surface metal layers and the adsorbates were optimized. The special-point technique was used to perform Brillouin-zone integrations. For (4 × 4) slabs, (3 × 3) uniformly shifted k-meshes were used, which were tested to converge to a subset of the relative energies. A vacuum layer of 16 Å in thickness was added above the top layer of the slab, which is sufficiently large to ensure that the interactions between repeated slabs are negligible. The top layer Pt atoms on the (4 × 4) three-layer slab and adsorbates are allowed to relax to minimize the total energy of the system, whereas the Pt atoms in the bottom two layers are fixed at the theoretical bulk positions. Structural optimization was performed until the total energy converged to within 10$^{-5}$ Ry and the Cartesian force components acting on each atom were brought below 10$^{-3}$ Ry/Bohr with respect to structural optimization.

The climbing image nudged elastic band (CI-NEB) method was used to locate the saddle points and minimum energy pathways (MEPs). The transition state images from the NEB calculations were optimized by the quasi-Newton method, which made the forces in finding the saddle point be minimized. Structural optimization was also performed for each intermediate point in MEPs. Based on the above analyses, the CH$_3$OH oxidation reaction on the Pt surface may occur via a parallel and dual pathway mechanism. It is well-known that CHO is a generally accepted reactive intermediate in CH$_3$OH oxidation along both indirect and direct pathways. Thus, a simplified schematic of the dual pathways is given in Scheme 1, in which adsorbed HCOOH in direct pathways may result in the formation of adsorbed HCOO or COOH intermediates, and they may be the precursor for the formation of CO$_2$.

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