Selectivity of Direct Ethanol Fuel Cell Dictated by a Unique Partial Oxidation Channel

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Self-consistent periodic slab calculations based on gradient-corrected density functional theory (DFT-GGA) were conducted to investigate the potential energy diagram for ethanol oxidation over Pt(111). Ethanol oxidation on Pt is found to be dominated by an one-step concerted dehydrogenation pathway to produce acetaldehyde, which is about 600 times faster than the traditionally regarded stepwise pathways. The same mechanism is transferable to methanol oxidation but with a minor contribution. The results can help to clarify the long-standing puzzles on the selectivity of direct alcohol fuel cell over Pt.

Compared to traditional fuel cells using hydrogen and methanol, direct ethanol fuel cells (DEFCs) have a theoretically higher mass energy density together with other desired properties, for example, nontoxicity.[1] Experimental studies revealed that DEFCs with Pt-based[1−4] electrodes are, contradictorily, energy inefficient since ethanol is mainly partially oxidized to acetaldehyde and acetic acid (two- and four-electron oxidation, respectively) instead of being fully oxidized (12-electron oxidation).[3,5] This undesired selectivity severely questions the future of DEFCs' applications. It is, therefore, of paramount importance to understand from an atomic level which elementary step controls the selectivity.

Acetaldehyde is the major product of ethanol electro-oxidation on Pt even at oxidative conditions, which is marginally effected by the applied electrical potential.[3,5] The phenomenon, however, is contradictory to newly emerging results from surface science experiments,[6−8] which show that at small coverages, the adsorbed acetaldehyde on Pt(111) can completely decompose (for example, to CH₃CO) without any desorption.

Furthermore, ethanol electro-oxidation on Pt is believed to proceed via stepwise dehydrogenation, that is, $CH_3CH_2OH \rightarrow CH_3CHOH \rightarrow CH_3CHO$ (or CH_3COH) $\rightarrow CH_3CO \rightarrow CH_3COOH$.[3,5] This mechanism is supported by the presence of partially oxidized products (acetaldehyde) and the intermediates (CH_3COH, CH_3CO) based on FTIR experiment.[5,9] If adsorbed acetaldehyde is indeed unstable, the amount of acetaldehyde produced would be always less than that of acetic acid according to the stepwise mechanism. However, this is just opposite to what is observed in ethanol electro-oxidation.[3−5] To date, few theoretical studies have been reported, and only approximate models such as the Bronsted−Evans−Polanyi principle[10] have been applied to estimate the kinetics.[11] Two central questions on selectivity remain elusive. (i) How is CH_3CHO produced from ethanol on Pt, and (ii) is the decomposition of CH_3CHO indeed more favorable than the CH_3CHO desorption?

Here, total energy DFT-slab calculations as implemented in the CASTEP package[12] were used to investigate the catalytic

reactions involved. Our strategy is, first, to divide the whole reaction network into two separate parts, that is, CH_3CH_2OH oxidation to CH_3CHO and CH_3CHO oxidation to CH_3COOH, and then to build the reaction network of each part by iterating the procedures of (i) searching all possible oxidation channels for a given adsorbed species obtained from the previous step (initially, it is CH_3CH_2OH or CH_3CHO) and (ii) only continuing those reaction channels with relatively low reaction barriers (the ones with obviously too-high barriers were discarded). We will demonstrate that such an approach is essential to deconvolute the complex reaction network of ethanol oxidation. Four-layer Pt(111) slabs with the top two layers relaxed were used for all calculations considering that the (111) face is the most stable and thus dominant facet in the Pt electrode. Detailed calculation setups can be found in Supporting Information and previous publications.[13] No attempt was made to simulate the electrochemical conditions since the selectivity is not sensitive to the electrical potential.[3,5]

In constructing the overall reaction profile of ethanol oxidation, the relative energy $E(X)$ of an intermediate X can be determined by referring to the gas-phase ethanol and clean Pt(111), that is

$$E(X) = E^{tot}(X) + mE^{tot}(H) + nE^{tot}(OH) - E^{tot}(e) - (m + n + 1)E^{tot}(sur) \quad (1)$$

where the five terms above are the DFT total energy (E^{tot}) of the adsorbed X, adsorbed H, adsorbed OH, gas-phase ethanol, and clean surface, respectively; m or n is the coefficient to maintain the mass balance whenever a dehydrogenation or a reaction involving OH occurs. For example, for the adsorbed CH_3CHO, $m = 2$ and $n = 0$; for the adsorbed CH_3COOH, $m = 3$ and $n = -1$.

Starting from the adsorbed ethanol, we have identified three distinct pathways that can lead to acetaldehyde (as shown in Figure 1), which are named as the OH path, the CH path, and the concerted path according to the way the first H is detached from ethanol. They are described in the following.

OH Path. This pathway is initiated by the cleavage of the hydroxyl group via TS1 (Figure 1), which produces ethoxyl

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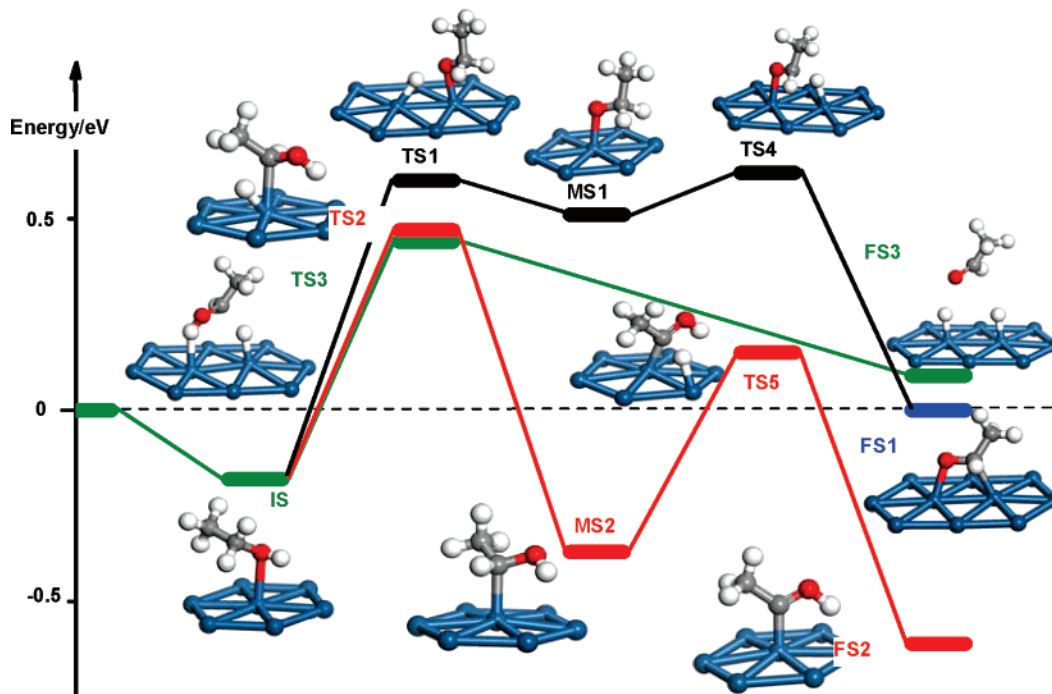
Figure 1. Potential energy diagram for ethanol oxidation leading to acetaldehyde. The meaning of the labeling and their energetics (eV) is as follows. IS: CH_3CH_2OH −0.18; TS1: 0.60; TS2: 0.47; TS3: 0.44; MS1: CH_3CH_2O 0.51; MS2: CH_3CHOH −0.37; TS4: 0.62; TS5: 0.15; FS1: CH_3CHO 0.0; FS2: CH_3COH −0.61; FS3: CH_3CHO^* 0.09.

(CH_3CH_2O, MS1) with a barrier of 0.78 eV. The adsorbed ethoxyl then undergoes a C_α−H breaking ($E_a = 0.11$ eV) to produce adsorbed acetaldehyde (FS1). It is interestingly noticed that the backward and forward reactions of ethoxyl have almost identical reaction barriers, and the product at either side is far more stable. This implies that adsorbed ethoxyl is kinetically unstable, being a transient intermediate.

CH Path. This pathway starts with α-dehydrogenation to produce CH_3CHOH (MS2). The transition state (TS) of this step (TS2) features an sp^3-like α-carbon, which corresponds to an E_a of 0.65 eV. At the TS, the dissociating C−H bond ($d = 1.60$ Å) is over one Pt atom, and the H of OH points to a surface Pt with a H−Pt distance of 2.48 Å, while the C−O bond is closer to a single bond ($d = 1.40$ Å). The produced CH_3CHOH can further degrade via the removal of an α-H to yield CH_3-COH (FS2) (this one shown in Figure 1 is the most favored path for CH_3CHOH degradation, both thermodynamically and kinetically; the other alternative paths are shown in Supporting Information Figure S1).

Concerted Path. This path is the most intriguing, where ethanol undergoes a concerted TS (TS3, $E_a = 0.62$ eV), losing two hydrogens simultaneously ($CH_3CH_2OH \rightarrow CH_3CHO + 2H$). The TS features an sp^2-like α-carbon and a short C−O bond ($d = 1.30$ Å), very close to the features of the gas-phase acetaldehyde. After the TS, both the C_α−H and the O−H bonds break, and a metastable acetaldehyde (CH_3CHO^* FS3) flying over the two adsorbed H's is yielded, which is ready for desorption. Such a concerted dehydrogenation pathway is unusual for reactions on metal surfaces with a two-bond breaking/forming process occurring simultaneously. In contrast to the traditionally regarded stepwise dehydrogenation mechanism, where each fragment after bond breaking immediately adsorbs on the surface to fulfill the otherwise dangling bond, the concerted pathway here tends to evolve an intramolecular C=O double bond, and the product acetaldehyde desorbs as an entity. Below, we will see the profound influence of the concerted TS on ethanol oxidation on Pt.

Next, we investigated the pathways for acetic acid formation from the adsorbed CH_3CHO.[14] The adsorbed CH_3CHO may originate directly from the OH path or indirectly from the concerted path following CH_3CHO readsorption. The overall energy diagram of the process is presented in Figure 2, showing the strong exothermic nature of the oxidation. The lowest energy pathway, we found, starts with the detachment of the aldehydic hydrogen from CH_3CHO ($CH_3CHO \rightarrow CH_3CO + H$), which is very facile with only a 0.10 eV reaction barrier (E_a). This is 0.10 eV lower than that required for CH_3CHO desorption. Then, the produced acetyl (CH_3CO) can react easily with a surface OH group (oxidative conditions) to become CH_3COOH. In addition to hydroxylation, CH_3CO can be reversibly converted to CH_3COH in the presence of H ($CH_3CO + H \rightarrow CH_3COH$, reductive conditions). Since CH_3COH was identified in ethanol electro-oxidation experiments at low electric potentials (0.35 V versus RHE),[9] our results establish an interesting link between CH_3CHO and CH_3COH via CH_3CO, and all of these intermediates can be derived from adsorbed acetaldehyde.

The calculated energy diagram (Figure 1) shows clearly that ethanol oxidation starts to bifurcate at the beginning right. Since three branches have close reaction barriers in the first dehydrogenation step, it is necessary to quantitatively compare the rate constants. The rate constant of reaction (k) can be derived according to classical transition-state theory by computing prefactor A and zero-point-energy (ZPE)-corrected reaction barrier E_a' ($E_a' = E_a + \Delta ZPE^{TS-IS}$). The calculated results are summarized in Table 1. We found that the rate constant is largely dictated by E_a', and the concerted path possesses the largest rate constant. At 300 K, the concerted path could be more than 600 times faster than the CH path and the OH path. The results are consistent with chemical intuition. The concerted reaction, unlike the other two dehydrogenation reactions where only one CH or OH bond breaks, involves the CH and OH bonds (high-frequency modes) breaking in concert with the formation of two soft H−Pt bonds and therefore contributes to a smaller ZPE at the TS and thus a smaller ΔZPE.
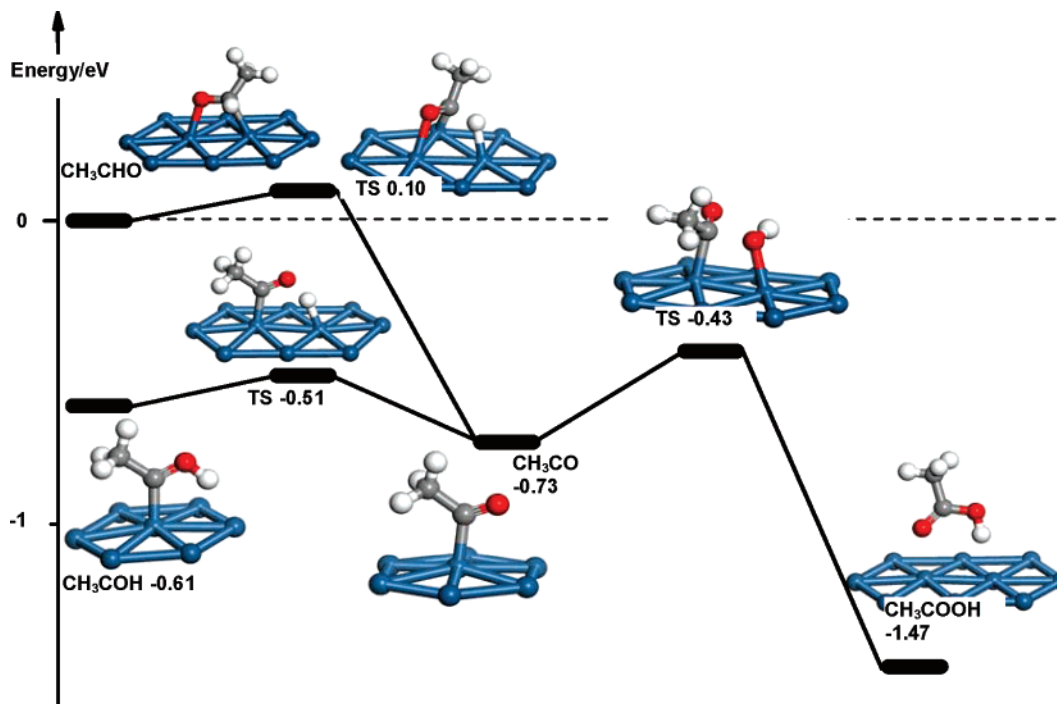
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Figure 2. Potential energy diagram from acetaldehyde to acetic acid.

TABLE 1: Kinetic Parameters (1/4 ML) and the Only Imaginary Mode at the TS (ν^{img}) of the First Dehydrogenation Reaction in the OH Path, the CH Path, and the Concerted Path at 300 K^a

	OH path (TS1)	CH path (TS2)	concerted path (TS3)
E_a (eV)	0.78	0.65	0.62
ΔZPE^{TS-IS} (eV)	−0.17	−0.18	−0.29
E'_a (eV)	0.61	0.47	0.33
A ($\times 10^{12}$ s^{-1})	4.22	4.41	11.76
k (s^{-1})	238	5.60×10^4	3.36×10^7
ν^{img} (cm^{-1})	272i	866i	396i
E_a(+H) (eV)	0.84	0.76	0.74
E_a(+H$_2$O) (eV)	0.84	0.89	0.73

^{a} E_a(+H) and E_a(+H$_2$O) are the reaction barriers in the presence of H and H$_2$O.

As H or H$_2$O species could well be present for ethanol oxidation in DEFC conditions, we also considered their effects on the reactions. The calculated reaction barriers of the coadsorption systems are listed in Table 1. We started by searching for the most stable ISs for the coadsorbed H or H$_2$O with ethanol, respectively, in a $p(2 \times 2)$ unit cell, namely, H + ethanol and H$_2$O + ethanol systems. At the most stable ISs, H is found to be at a neighboring fcc hollow site, while H$_2$O initially can coadsorb with ethanol with its adsorption energy being 0.37 eV and H-bonding clearly present to link the H(water) to the O(ethanol) (optimized structures are shown in Supporting Information Figures S2 and S3). The TSs of the three reactions were then fully optimized in the presence of the H or H$_2$O (Figure S2 and S3). We found that the H atom generally increases the reaction barriers of the three dehydrogenation reactions up to 0.1 eV as the H atom destabilizes the TS more than the IS of the reactions. The concerted path remains to be the one with the lowest reaction barrier in the presence of H (if adding ZPE, the difference will be further increased, as shown above without coadsorbates). By contrast, H$_2$O helps to stabilize ethanol through the H-bonding; however, we found that H$_2$O helps to stabilize the IS more than the TS, and thus, the reaction barriers are also increased. The concerted path is

still the lowest energy pathway. These results appear to be consistent with the experimental fact that the selectivity is not sensitive to electrical potential.[3,5] Because it is known that the surface species on the electrode varies upon electrical potential, that is, from the hydrogen region to the double-layer region (H$_2$O) and to the oxygen region, the high selectivity to acetaldehyde at a wide potential range implies, conversely, that the preference of the dehydrogenation pattern may be insensitive to surface coadsorbates.

With the computed rate constants without coadsorbates and also by ruling out the possible coverage effects due to co-adsorbates, it is clear that ethanol oxidation on Pt initially will be dominated by the direct production of free acetaldehyde (solvated in electrochemical conditions) via the concerted path. The OH path is unlikely to occur because of its too slow rate; the CH path has only a minor contribution, which however, if occurs, will mainly produce CH$_3$COH (not acetaldehyde). Therefore, only the concerted path can explain the observed high selectivity to acetaldehyde. Our results also showed that (i) the decomposition of adsorbed acetaldehyde is indeed more favorable than its desorption, consistent with surface science experiments;[6] (ii) the acetic acid formation from acetaldehyde is very facile under oxidative conditions. Since the acetic acid formation is through the readsorption of acetaldehyde from the concerted path, being a secondary process, it is thus rationalized that the amount of acetic acid is always less than that of acetaldehyde.[3] (iii) CH$_3$COH is mainly derived from CH$_3$CO hydrogenation (Figure 2), which agrees with that proposed by Zhao et al. using FTIR experiment.[6]

While investigating ethanol oxidation, we naturally compared it with methanol oxidation. Experimentally, methanol electro-oxidation on Pt mainly yields CO not HCHO,[16] which differs significantly from ethanol electro-oxidation in selectivity. For comparison, we have searched for the transition states for the reactions CH$_3$OH → CH$_3$O+H, CH$_3$OH → CH$_2$OH+H, and CH$_3$OH → HCHO+2H, which correspond to the OH path, the CH path, and the concerted path, respectively (the concerted path has not been reported). The reaction barriers for them at

1/4 ML were found to be 0.80, 0.49, and 0.79 eV, respectively. The results show that the CH path (α-dehydrogenation to CH_2-OH) is the most favorable channel, in agreement with the literature.[15−17] It should be mentioned that our calculated reaction barrier of the OH path is almost identical to that reported previously,[16] while the reaction barrier of the CH path is about 0.1 eV lower, which is due to the extra energy gain at the TS of the CH bond dissociation if the H of OH group is pointing downward to the surface (the TSs are similar to the analogues in ethanol oxidation shown in Figure 1; also see Supporting Information). Interestingly, we found that the concerted path is comparable to the OH path in reaction barrier and may well contribute to HCHO and HCOOH production[18] in a direct methanol fuel cell.

The sharp contrast in selectivity between methanol and ethanol oxidation implies the critical effect of the methyl ligand. This may not be surprising as the concerted TS involves the formation of the C=O double bond, and thus, the H of the OH group is more proton-like, that is, the TS mimics an adsorbed $[CH_3HC=OH]^{\delta+}$ according to our Mulliken charge analysis. Comparing $[CH_3HC=OH]^{\delta+}$ with $[H_2C=OH]^{\delta+}$, it is expected that the methyl group, which can donate electrons better than H, can help to stabilize the cationic TS and thus to reduce the reaction barrier. Our work shown here implies that by tuning the ligand group of the reactant or varying the metal catalyst composition (this also can be considered as a ligand to TS complex), it is feasible to modify the oxidation selectivity and thus improve the performance of direct alcohol fuel cells.

Supporting Information Available: Calculation details, enlarged view, and structural information of all of the states in Figures 1 and 2, and the IS and TS structures of the coadsorbed systems with H or H_2O. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Lynd, L. R. *Annu. Rev. Energ. Environ.* **1996**, *21*, 403.
(2) Colmenares, L.; Wang, H.; Jusys, Z.; Jiang, L.; Yan, S.; Sun, G. Q.; Behm, R. J. *Electrochim. Acta* **2006**, *52*, 221.
(3) Vigier, F.; Rousseau, S.; Coutanceau, C.; Leger, J. M.; Lamy, C. *Top. Catal.* **2006**, *40*, 111.
(4) Wang, H.; Jusys, Z.; Behm, R. J. *J. Phys. Chem. B* **2004**, *108*, 19413.
(5) Hitmi, H.; Belgsir, E. M.; Leger, J. M.; Lamy, C. R.; Lezna, O. *Electrochim. Acta* **1994**, *39*, 407.
(6) Zhao, H. B.; Kim, J.; Koel, B. E. *Surf. Sci.* **2003**, *538*, 147.
(7) Lee, A. F.; Gawthrope, D. E.; Hart, N. J.; Wilson, K. *Surf. Sci.* **2004**, *548*, 200.
(8) Rajumon, M. K.; Roberts, R. S.; Wang, F.; Wells, P. B. *J. Chem. Soc., Faraday Trans.* **1998**, *94*, 3699.
(9) Iwasita, T.; Pastor, E. *Electrochim. Acta* **1994**, *39*, 531.
(10) Michaelides, A.; Liu, Z. P.; Zhang, C. J.; Alavi, A.; King, D. A.; Hu, P. *J. Am. Chem. Soc.* **2003**, *125*, 3704.
(11) Alcala, R.; Mavrikakis, M.; Dumesic, J. A. *J. Catal.* **2003**, *218*, 178.
(12) Payne, M. C.; Teter, M. P.; Allan, D. C.; Arias, T. A.; Joannopoulos, J. D. *Rev. Mod. Phys.* **1992**, *64*, 1045.
(13) (a) Liu, Z. P.; Hu, P. *J. Am. Chem. Soc.* **2002**, *124*, 5175. (b) Liu, Z. P.; Hu, P. *J. Am. Chem. Soc.* **2003**, *125*, 1958. (c) Wang, C. M.; Fan, K. N.; Liu, Z. P. *J. Am. Chem. Soc.* **2007**, *129*, 2642.
(14) Delbecq, F.; Vigne, F. *J. Phys. Chem. B* **2005**, *109*, 10797.
(15) Hamnett, A. *Catal. Today* **1997**, *38*, 445.
(16) Greeley, J.; Mavrikakis, M. *J. Am. Chem. Soc.* **2004**, *126*, 3910.
(17) Desai, S. K.; Neurock, M.; Kourtakis, K. *J. Phys. Chem. B* **2002**, *106*, 2559.
(18) Chen, Y. X.; Miki, A.; Ye, S.; Sakai, H.; Osawa, M. *J. Am. Chem. Soc.* **2003**, *125*, 3680.