



Short Communication

New insight into the CO formation mechanism during formic acid oxidation on Pt(111)

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ABSTRACT

Density functional theory (DFT) calculations show a new concerted mechanism of formic acid (HCOOH) oxidation on Pt (111), which involves the simultaneous formation of CO₂ and CO via the HCOOH dimer in an elementary step. The newly proposed mechanism rationalizes the easy CO poisoning of Pt-based catalysts and improves our understanding for the mechanism of catalytic HCOOH oxidation.

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1. Introduction

The electro-oxidation of formic acid (HCOOH) catalyzed by Pt-group metals has attracted substantial interest over the past four decades because of its relevance in low-temperature fuel cells [1,2]. It is generally accepted that HCOOH at Pt electrode is oxidized to CO₂ via a dual-pathway mechanism consisting of direct and indirect pathways (Scheme 1). The direct pathway occurs via the dehydrogenation reaction of HCOOH, while the indirect pathway proceeds by the dehydration reaction to form adsorbed CO as an intermediate, which then is oxidized to CO₂ [3,4]. In addition, based on some experimental observations, Behm et al. [2] have also proposed a third pathway of HCOOH oxidation, i.e. the formate pathway, which operates through a HCOO intermediate resulted from the O–H bond scission of HCOOH (Scheme 1). And Samjeske and Osawa [1] have provided experimental support for the formate mechanism.

It is well known that active platinum catalyst sites are easily poisoned by CO-like species [5–8]. Although the most stable Pt (111) surface exhibited the lowest poisoning rate, Herrero et al. [9] confirmed that CO is readily formed at potentials below 0.3 V on Pt (111). Furthermore, through spectral data, Iwasita and co-workers [10] have confirmed the formation of on-top and bridging CO species on Pt (111) in 0.1–0.4 V potential range. To understand the relevant mechanism, several theoretical works based on first-principles have studied HCOOH oxidation on Pt (111) surface [11,12]. In particular, great interest has been focused on the evaluation of the relative feasibility of the indirect and direct pathways of HCOOH oxidation to

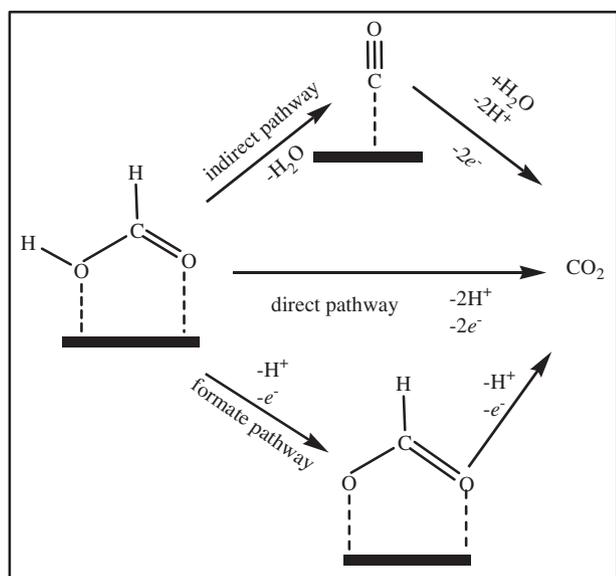
rationalize the experimental observation that Pt-based catalysts are easily poisoned by CO. Unfortunately, all previous calculations give unexpected results that the indirect pathway (the dehydration reaction of HCOOH to form CO intermediate) involves a barrier as high as 32.1–41.5 kcal/mol [11,12], which is also much higher than that (10.4–18.2 kcal/mol [12,13]) involved in the direct pathway (the dehydrogenation reaction of HCOOH). According to such results, HCOOH would be directly oxidized to final product CO₂ rather than to the poisoning intermediate CO. This is clearly inconsistent with the observed easy CO poisoning of Pt-based catalysts. So we conjecture that there must be other mechanisms of HCOOH oxidation, which are not known yet and so greatly attract our interest.

It should be noted that the previous theoretical studies [11–13] set an assumption that HCOOH oxidation proceeds via intramolecular dehydrogenation/dehydration reactions. In fact, HCOOH molecules can form stable dimers through a variety of hydrogen-bonded structures with a formation energy of up to 15 kcal/mol [14–16]. In addition, HCOOH molecules in solution also form hydrogen bonds with surrounding water molecules. These intermolecular hydrogen bonds formed by HCOOH both with each other and with water molecules may play an important role for HCOOH oxidation via the direct or indirect pathway.

2. Model and computational details

In this work, we have conducted a comparative theoretical investigation on the HCOOH oxidation on Pt (111) surface in continuum water solution models via intramolecular and intermolecular dehydrogenation/dehydration reactions. The calculations were based on the plane-wave pseudopotential Density Functional Theory

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Scheme 1. Direct, indirect, and formate pathways of HCOOH oxidation.

(DFT) periodic slab approach [17,18] by using the generalized gradient approximation (GGA) with Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional [19,20], as implemented in the CASTEP code [21]. Calculations were performed using a periodic three-layer slab with a $p(3 \times 3)$ unit cell, where the atoms in the top layer were allowed to be fully relaxed whereas those in the two bottom layers were fixed at their bulk-truncated structure. The vacuum region between slabs is 10 Å. The continuum water solution phase was modeled using 20 explicit water molecules to match the density of water near a metal surface of 0.86 g cm^{-3} at 0 K [22–26]. In view of the fact that a HCOOH molecule matches two water molecules in size and structure, when formic acid molecule is incorporated into the surface, two water molecules in the water solution phase are removed. Integrations in reciprocal space used a 2×2 Monkhorst-Pack k -point grid. The electronic wave functions were expanded in a plane wave basis set with a cutoff kinetic energy of 400 eV, and the ion cores were described by ultrasoft pseudopotentials [27]. The transition states (TSs) were located using the linear and quadratic synchronous transit (LST/QST) algorithm [28], a very promising approach for accurately locating the transition state. This algorithm combines the linear LST or QST method with conjugate gradient refinements. In this algorithm, an LST optimization calculation is first performed to obtain an approximate transition state structure, which is then refined via a QST maximization, followed by an energy minimization in directions conjugate to the reaction pathway. Minimization steps continue until a stationary point is located or the number of allowed QST steps is exhausted.

3. Results and discussion

We here show three optimal pathways of HCOOH oxidation. Pathways I and II are the well-known direct and indirect pathways, involving the dehydrogenation reaction ($\text{HCOOH} \rightarrow \text{CO}_2 + 2\text{H}$) and the dehydration reaction ($\text{HCOOH} \rightarrow \text{COOH} + \text{H} \rightarrow \text{CO} + \text{H}_2\text{O}$) of a isolated HCOOH molecule. Pathway III is the newly proposed one, where a HCOOH dimer is oxidized to CO_2 with the synchronous CO formation via a concerted dehydration–dehydrogenation reaction, i.e. $(\text{HCOOH})_2 \rightarrow \text{CO}_2 + 2\text{H} + \text{CO} + \text{H}_2\text{O}$. We refer to this pathway as the dimer pathway of HCOOH oxidation. The optimized intermediates and transition states involved along these three pathways are gathered in Figs. 1 and 2, and the corresponding energy diagrams are given in Fig. 3.

3.1. Direct pathway of HCOOH oxidation

Pathway I is the most favorable direct pathway located in the present work. It involves the simultaneous C–H and O–H bond scissions from HCOOH to CO_2 ($\text{HCOOH} \rightarrow \text{CO}_2 + 2\text{H}$). This resembles the mechanism proposed by Liu et al. [13]. As shown in Fig. 1, the reaction starts from HCOOH^* , where the HCOOH that will be oxidized to CO_2 via the dehydrogenation reaction initially adsorbs on Pt (111) lying parallel to the surface and is stabilized by four adjacent water molecules via H-bonds. HCOOH^* is converted to $\text{CO}_2^* + 2\text{H}^*$ via transition state TS1, where the dissociating O–H and C–H bonds are stretched to 2.187 and 1.125 Å, respectively. As shown by the geometry of TS1, the forming H atom via the O–H bond scission is solvated by the adjacent water molecule, and at the same time, the forming H atom via the C–H bond scission moves to the adjacent Pt site. In $\text{CO}_2^* + 2\text{H}^*$, the CO_2 has been formed and adsorbs at the Pt (111) surface via the Pt–C and Pt–O bonds. This process is calculated to be exothermic by 18.1 kcal/mol, and needs to overcome a barrier of only 5.8 kcal/mol.

As mentioned in the Introduction, the formate pathway is also an available pathway of HCOOH oxidation [1,2]. Jacob et al. [12] have calculated the mechanism in details along this pathway on Pt (111) and found that the barrier of rate-determining step is 26.7 kcal/mol, which is energetically much less favorable than the direct pathway discussed above.

In addition, in a previous study Neurock et al. [29] proposed another pathway leading to CO_2 from the adsorbed hydroxyl carbonyl by O–H bond breaking with a barrier of ~ 12.0 kcal/mol. We have also performed calculations of the O–H bond breaking of hydroxyl carbonyl. However, using our continuum water solution model, the barrier is found to be 22.1 kcal/mol, which is much higher than that given in the previous study [29]. This fact implies that solvent water plays an intrinsically important role for HCOOH oxidation.

3.2. Indirect pathway of HCOOH oxidation

Pathway II is the most favorable indirect pathway, where the intramolecular dehydration reaction of HCOOH occurs via the successive C–H and C–O scissions ($\text{HCOOH} \rightarrow \text{COOH} + \text{H} \rightarrow \text{CO} + \text{H}_2\text{O}$). The C–H bond scission proceeds through transition state TS2, where the breaking C–H bond is elongated to 1.406 Å from 1.103 Å in IM1. This process is calculated to be exothermic with a reaction energy of 15.0 kcal/mol, and needs to overcome a barrier of 19.3 kcal/mol. As the dissociated H atom moves to an atop position on an adjacent Pt atom, the newly formed COOH binds to the surface through its C atom in an atop configuration, as shown in $\text{COOH}^* + \text{H}^*$. And then the C–O scission occurs via transition state TS3 with a barrier as high as 32.9 kcal/mol and an energy release of 19.5 kcal/mol. As shown by $\text{CO}^* + \text{H}_2\text{O}^*$ in Fig. 1, the C–O bond scission results in the formation of CO which tilts toward the surface to form a bridge-like configuration through its C atom with two adjacent Pt atoms. From the energy diagram shown in Fig. 3a, the C–O bond scission is the rate-determining step along this pathway, which is in good agreement with previous calculations [11,12]. It is noted that the barrier of 32.9 kcal/mol involved in pathway II is much higher than that in pathway I, clearly indicating that the formation of CO cannot compete with that of CO_2 .

3.3. Dimer pathway of HCOOH oxidation

Our attention now focuses on pathway III, $(\text{HCOOH})_2 \rightarrow \text{CO}_2 + 2\text{H} + \text{CO} + \text{H}_2\text{O}$. As shown in Fig. 2, in 2HCOOH^* two HCOOH molecules form a dimer via two intermolecular H-bonds with the C–H···O distance being 2.093 and 2.129 Å, respectively. Previous studies show that in the gas phase HCOOH prefers to bind to the surface vertically [11,30], while in solution its parallel [11,12] and vertical [13,29] adsorption modes are of nearly equivalent. From our present calculation of HCOOH dimer adsorption in solution, it is found that both two HCOOH molecules in the

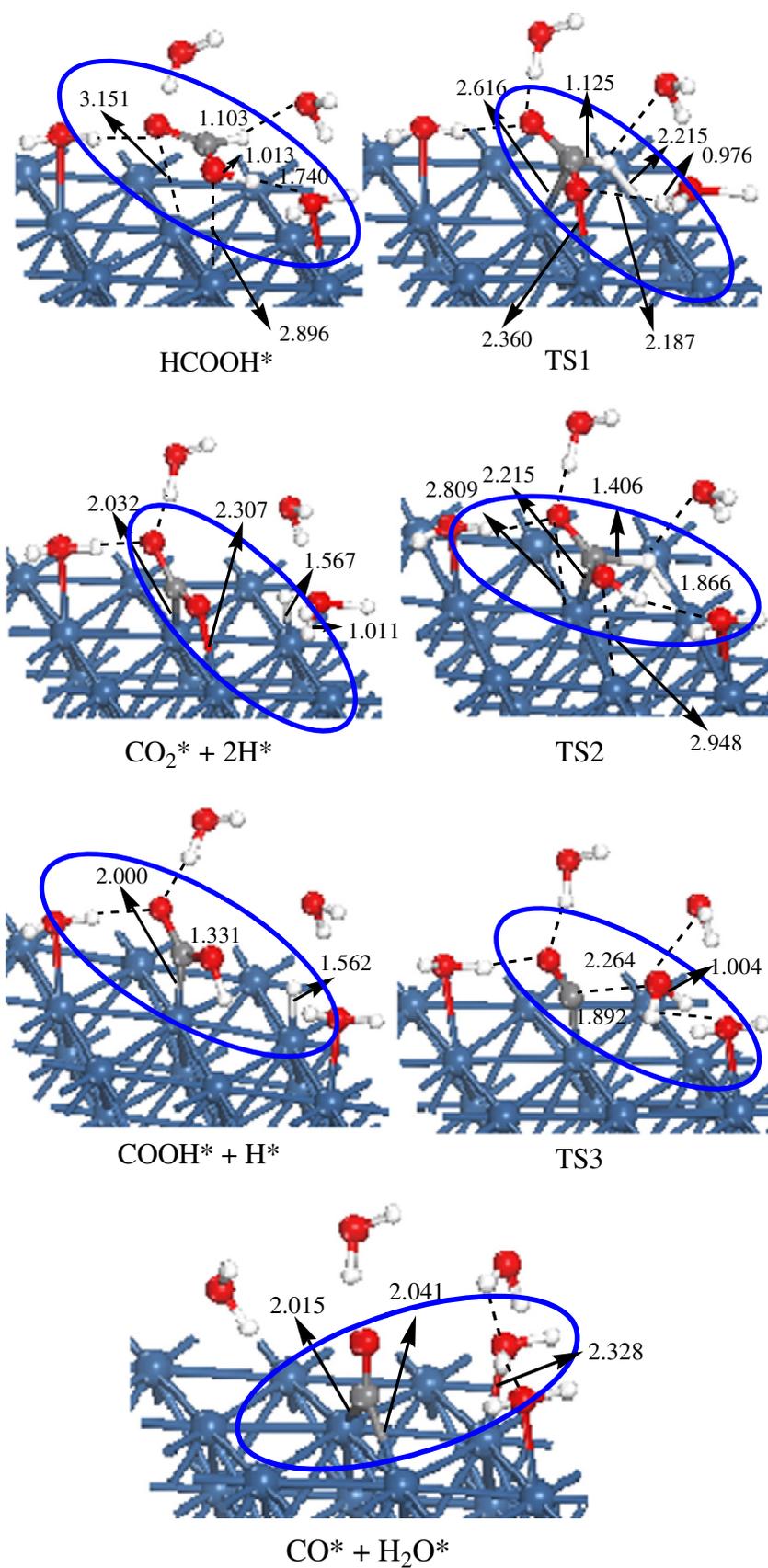


Fig. 1. Optimized geometries of intermediates and transition states involved in the direct and indirect pathways of HCOOH oxidation. The blue, gray, red, and white balls denote Pt, C, O and H atoms, respectively, and same for Fig. 2. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

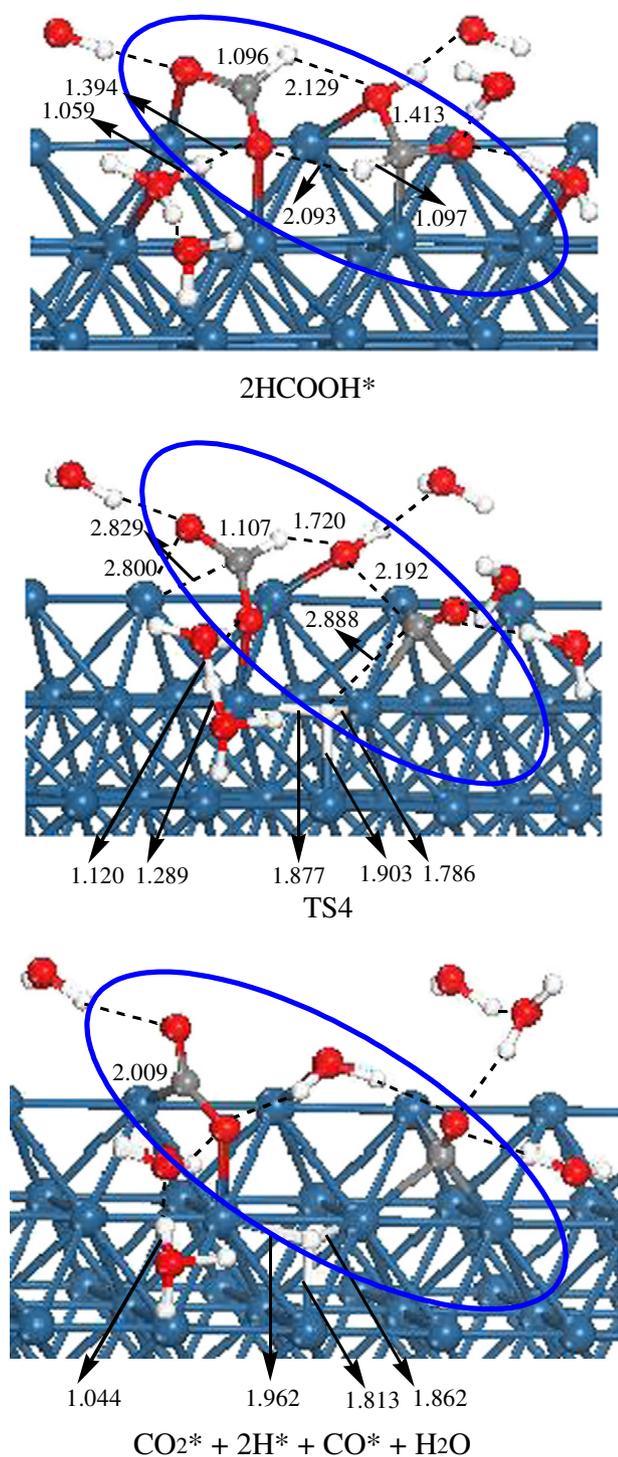


Fig. 2. Optimized geometries of intermediates and the transition state involved in the newly proposed dimer pathway of HCOOH oxidation. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

dimer are almost parallel to the surface. Note that one O–H bond in the dimer has been highly activated, as indicated by the calculated large O–H bond distance (1.394 Å). This situation is in agreement with the recent study by Liu et al. [13]. Meanwhile, one C–O bond distance (1.413 Å) in the dimer is also larger by 0.058 Å than that in the free HCOOH molecule, suggesting that this C–O bond has also been activated along with the formation of the dimer on Pt (111) surface. Our calculations show that 2HCOOH^* can be converted to $\text{CO}_2^* + 2\text{H}^* + \text{CO}^* + \text{H}_2\text{O}^*$ via TS4 with a barrier of 15.1 kcal/mol and an energy release of

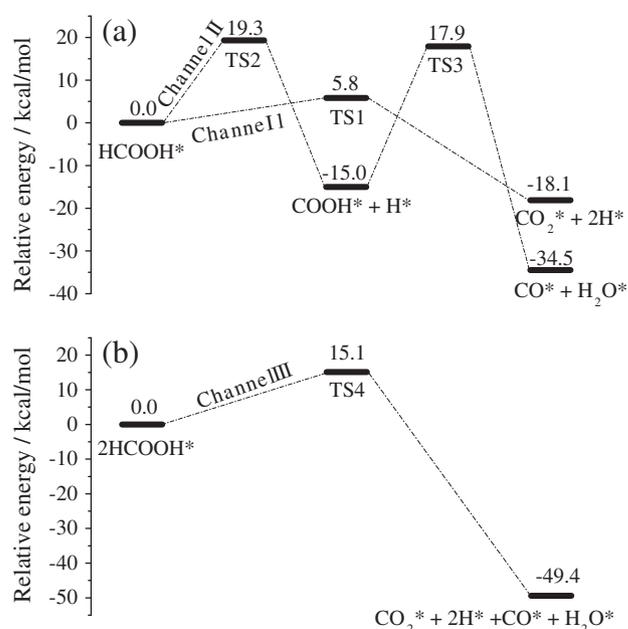


Fig. 3. Calculated potential energy profiles of HCOOH oxidation on the Pt (111) surface along (a) the indirect and direct pathways, and (b) the newly proposed dimer pathway.

49.4 kcal/mol. This process involves the simultaneous scissions of the C–O bond and two C–H bonds as well as the formation of a new O–H bond. The forward product of TS4 is $\text{CO}_2^* + 2\text{H}^* + \text{CO}^* + \text{H}_2\text{O}^*$, where the CO and CO_2 have been formed and adsorb on the Pt (111) surface in an fcc and a bridge site of the surface, respectively. We refer this process as the concerted pathway of HCOOH oxidation because it involves the synchronous formation of CO_2 and CO in one elementary step. Such a concerted mechanism of HCOOH oxidation is intrinsically different from the well-known dual pathway mechanism. In particular, the calculated barrier according to this mechanism is only 15.1 kcal/mol, which is much lower than that (32.9 kcal/mol) in the indirect pathway and hence can compete with the direct pathway. Thus we can easily understand the easy CO poisoning of Pt-based catalysts.

4. Conclusions

Summing up, our DFT calculations have shown a new model of HCOOH oxidation on Pt (111) surface, where CO_2 and CO can be simultaneously formed via the HCOOH dimer in an elementary step. The newly proposed pathway involves a barrier of 15.1 kcal/mol, which is comparable with the barrier of 5.8 kcal/mol involved in the direct pathway but much lower than that (32.1 kcal/mol) involved in the indirect pathway. The present results indicate that during HCOOH oxidation the CO formation is competing with the CO_2 formation, which rationalize the experimental fact that Pt-based catalysts are easily poisoned by CO.

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References

- [1] G. Samjeske, M. Osawa, *Angewandte Chemie International Edition* 44 (2005) 5694–5698.
- [2] Y.X. Chen, M. Heinen, Z. Jusys, R.J. Behm, *Angewandte Chemie International Edition* 45 (2006) 981–985.
- [3] A. Capon, R. Parsons, *Journal of Electroanalytical Chemistry* 45 (1973) 205–231.
- [4] S.G. Sun, J. Clavilier, *Journal of Electroanalytical Chemistry* 240 (1988) 147–159.

- [5] K. Kunimatsu, H. Kita, *Journal of Electroanalytical Chemistry* 218 (1987) 155–172.
- [6] D.S. Corrigan, M.J. Weaver, *Journal of Electroanalytical Chemistry* 241 (1988) 143–162.
- [7] S. Park, Y. Xie, M.J. Weaver, *Langmuir* 18 (2002) 5792–5798.
- [8] A. Miki, S. Ye, M. Osawa, *Chemical Communications* 14 (2002) 1500–1501.
- [9] M.D. Macia, E. Herrero, J.M. Feliu, *Electrochimica Acta* 47 (2002) 3653–3661.
- [10] T. Iwasita, X.H. Xia, E. Herrero, H.D. Liess, *Langmuir* 12 (1996) 4260–4265.
- [11] W. Gao, J.A. Keith, J. Anton, T. Jacob, *Dalton Transactions* 39 (2010) 8450–8456.
- [12] W. Gao, J.A. Keith, J. Anton, T. Jacob, *Journal of the American Chemical Society* 132 (2010) 18377–18385.
- [13] H.F. Wang, Z.P. Liu, *Journal of Physical Chemistry C* 113 (2009) 17502–17508.
- [14] F.A. Gianturco, R.R. Lucchese, J. Langer, I. Martin, M. Stano, G. Karwasz, E. Illenberger, *European Physical Journal D* 35 (2005) 417–428.
- [15] W. Qian, S. Krimm, *Journal of Physical Chemistry A* 106 (2002) 6628–6636.
- [16] C.S. Tautermann, M.J. Loferer, A.F. Voegelé, K.R. Liedl, *Journal of Chemical Physics* 120 (2004) 11650–11657.
- [17] D. Cao, G.Q. Lu, A. Wieckowski, S.A. Wasileski, M. Neurock, *The Journal of Physical Chemistry. B* 109 (2005) 11622–11633.
- [18] M.J. Janik, M. Neurock, *Electrochimica Acta* 52 (2007) 5517–5528.
- [19] M.J. Janik, C.D. Taylor, M. Neurock, *Topics in Catalysis* 46 (2007) 306–319.
- [20] C.D. Taylor, S.A. Wasileski, J.S. Filhol, M. Neurock, *Physical Review B: Condensed Matter Materials in Physics* 73 (2006) 165402–165416.
- [21] J. Rossmeisl, J.K. Nørskov, C.D. Taylor, M.J. Janik, M. Neurock, *The Journal of Physical Chemistry. B* 110 (2006) 21833–21839.
- [22] P. Hu, D.A. King, M.H. Lee, M.C. Payne, *Chemical Physics Letters* 246 (1995) 73–78.
- [23] P. Hu, D.A. King, S. Crampin, M.H. Lee, M.C. Payne, *Chemical Physics Letters* 230 (1994) 501–506.
- [24] J.P. Perdew, J.A. Chevary, S.H. Vosko, K.A. Jackson, M.R. Pederson, D.J. Singh, C. Fiolhais, *Physical Review B* 46 (1992) 6671–6687.
- [25] J.P. Perdew, K. Burke, M. Ernzerhof, *Physical Review Letters* 77 (1996) 3865–3868.
- [26] M.C. Payne, M.P. Teter, D.C. Allen, T.A. Arias, J.D. Joannopoulos, *Reviews of Modern Physics* 64 (1992) 1045–1097.
- [27] D. Vanderbilt, *Physical Review B* 41 (1990) 7892–7895.
- [28] N. Govind, M. Petersen, G. Fitzgerald, S.D. King, J. Andzelm, *Computational Materials Science* 28 (2003) 250–258.
- [29] M. Neurock, M. Janik, A. Wieckowski, *Faraday Discussions* 140 (2008) 363–378.
- [30] Q.Q. Luo, G. Feng, M. Beller, H.J. Jiao, *Journal of Physical Chemistry C* 116 (2012) 4149–4156.