

# Theoretical Study on the Oxidation of HCOOH on Pt Catalyst

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**Abstract:** New pathway for HCOOH decomposition to CO in the gas-phase on Pt(111) surface is proposed. By performing density functional theory calculations, this paper has evaluated the detailed reaction process, including energies and geometric structures of intermediates and transition states. The present theoretical calculation results show that the formation of CO on Pt(111) surface arises from HCOOH dehydration pathway. The present theoretical study rationalizes the early experimental findings well and provides insights into the deactivation problem of Pt catalyst in the process of HCOOH oxidation.

## 1. Introduction

As a promising alternative to H<sub>2</sub> production, the electrocatalytic oxidation of formic acid (HCOOH) on metal surfaces will play a very significant role in energy-efficient green power utilization in the future, especially in driving portable electronic appliances.[1] It is widely accepted that electrochemical oxidation of HCOOH proceeds via dual pathways, namely, dehydrogenation and dehydration.[2] The former pathway starts from the O-H bond dissociation converting to CO<sub>2</sub>. The latter pathway leads to CO via C-H bond first scission. Generally, dehydrogenation or dehydration may predominate, depending on the properties of catalyst used. For HCOOH oxidation on Pt catalyst, the dehydrogenation pathway to yield CO<sub>2</sub> is well-known to be facile.[3] However, Pt catalyst always loses a large amount of its activity during HCOOH oxidation owing to the poisoning adsorption of CO[4], indicating HCOOH dehydration with participation of CO intermediate should be considered as a potential pathway. Nevertheless, recent theoretical investigations for HCOOH decomposition on Pt(111) unanimously reported that the dehydration pathway involves a much higher barrier than the dehydrogenation one (1.39-1.80 eV vs. 0.45-0.79 eV) [5]. Thus HCOOH should be directly oxidized to final product CO<sub>2</sub> rather than to the adsorbed CO intermediate. This is clearly inconsistent with the observed facile CO poisoning of Pt(111). Now, the question is where CO originates mainly from in the process of the HCOOH oxidation on Pt catalyst. Answering this issue would provide insights into the deactivation problem. By performing density functional theory (DFT) calculations, we show the potential energy surface details of CO formation according to the possible mechanism which involving subtly different reaction intermediates and transition states are explicitly obtained. We hope to understand the easy poisoning effects on Pt catalyst.

## 2. Computational Details

DFT periodic slab calculations were performed using the CASTEP package[6] with ultrasoft pseudopotentials and the spin polarized generalized gradient approximation (GGA) exchange–correlation functional proposed by Perdew, Burke, and Ernzerhof (PBE)[7]. The Kohn-Sham one-electron states are expanded in a plane wave basis set up to a cutoff energy of 400 eV. Monkhorst-Pack meshes with  $2 \times 2 \times 1$  k-grid sampling in the surface Brillouin zone are used. The criteria for energy and maximum force convergence used are  $2.0 \times 10^{-5}$  eV/atom and 0.05 eV/Å. With this setting we get the lattice constant of bulk Pt as 3.96 Å, which agrees well with the experimental

finding, 3.92 Å.[8] HCOOH has the trans and the cis forms, depending on the orientation of the hydroxyl group (-OH). Experiment has confirmed that the trans conformer is the dominant in the gas phase, and the energy difference between the two conformers is about 0.17 eV.[9] In this study, the energy of the trans form was calculated to be 0.15 eV lower than that of the cis form, which is in good agreement with the experimental value.

Previous work comparing 3 and 5 layer metal slabs found little change on the structural water.[10] Therefore, Pt(111) surface is modeled by a periodic slab containing three atomic layers with full relaxation of the uppermost layer. A  $p(3 \times 3)$  unit cell with 9 metal atoms per layer is used in this study. The vacuum separation between periodically repeated slabs is 10 Å, which is large enough to avoid interactions between slabs. The transition states (TSs) are searched for with the linear and quadratic synchronous transit (LST/QST) complete search.[11]

The adsorption energies are defined as  $E_{ad} = E_{adsorbate} + E_{surf} - E_{total}$ , where  $E_{adsorbate}$ ,  $E_{surf}$ , and  $E_{total}$  refer to the energies of free adsorbate, the clean surface, and the adsorbed system, respectively. For a CO formation reaction, the activation barrier ( $E_a$ ) is calculated by  $E_a = E_{TS} - E_{total}$ , respectively, where  $E_{TS}$  and  $E_{total}$  are the transition state and adsorbed system, respectively.

### 3. Result and Discussion

Initially, it should be emphasized that most settings and parameters described in the model and method section, including the  $p(3 \times 3)$  supercell, three-layer slab,  $2 \times 2 \times 1$  k-point, 10 Å vacuum zone, and the energy cutoff of 400 eV, have been extensively confirmed in literature to be accurate enough for the periodic slab calculations on noble metal surfaces[12]. To further calibrate the selected method, we here compare several calculated results with available experimental values. (i) The O-H, C-H, C=O, and C-O bond distances in a free HCOOH are calculated to be 0.986, 1.105, 1.218, and 1.354 Å, while the corresponding experimental values[13] are 0.972, 1.097, 1.202, and 1.343 Å, respectively. (ii) The calculated largest adsorption energy of HCOOH on Pt(111) surface is 0.41 eV, while previous theoretical result is 0.43 eV[14]. These data show good agreements with the calculated results and available reference values, indicating sufficiency of the model and method used. In addition, in the present work our main concern is the accuracy of the relative energies for several adsorption and decomposition processes considered. Energy errors for the initial state and the final state of a chemical process are almost the same and can counteract each other. It should be mentioned that GGA DFT is not accurate enough to describe long-range attractive contribution to van der Waals interactions although it can handle the dispersion force near the van der Waals minimum.[15] However, it is expected that systematic errors resulting from long-range van der Waals interactions are mostly counteracted in our relative energy calculations. Therefore the deficiency of GGA DFT in describing van der Waals interactions may not change the present conclusions, which are drawn out from calculated relative energy differences of intermediates and transition states involved during the HCOOH decomposition. Thus, we consider that the conclusion to be drawn in the present work based on calculated relative energies is reliable.

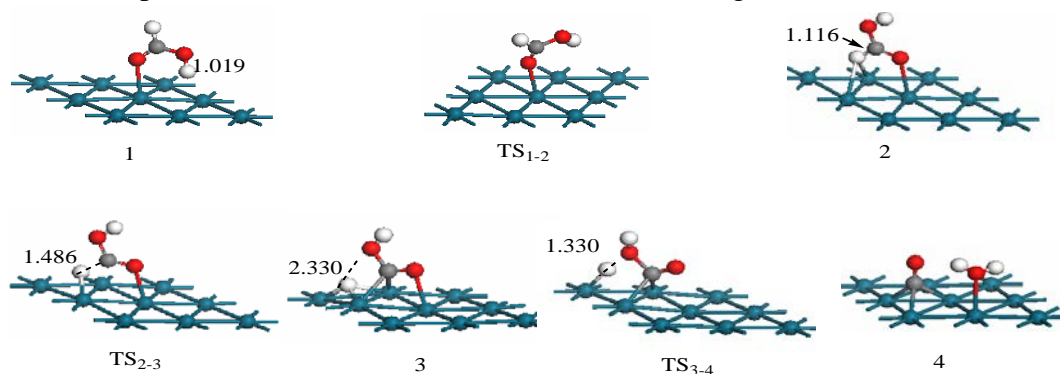


Figure 1. Optimized geometries for the intermediates and the transition states involved during CO formation along the path for HCOOH oxidation. For clarity, only one layer is illustrated. Distances are in angstroms.

We then perform calculations of the possible decomposition route, and locate various intermediates and TSs along the pathway. Their structures with the key geometrical parameters are shown in Figure 1. The relevant potential energy surface (PES) profile along the reaction coordinate in Figure 2, where the sum of the energy of the isolated reactants (HCOOH and the clean Pt surface) is taken as zero energy.

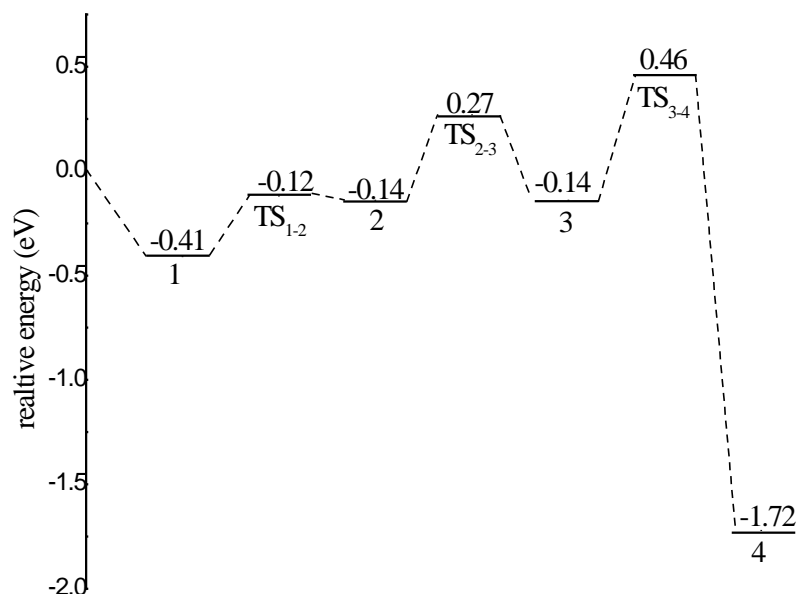


Figure 2. Calculated potential energy surface profile for forming CO along the reaction paths

From our calculations, the path involves two elementary steps: the breaking of C-H bond and the formation of CO and H<sub>2</sub>O molecules. We first obtained the possible molecular adsorbed form of formic acid (labeled structure 1 in Figure 1), which is the starting point for the subsequent mechanism. In structure 1, the carbonyl oxygen is bonded on top of one Pt atom and the OH points asymmetrically to two neighboring Pt atoms. This structure is analogous to the bidentate structures, which were observed for formate on the Pt(111) surface.[16] Our result is consistent with other theoretical studies reported in literature.[14] The most evident change in structure 1 is the O-H bond length (1.019 Å), which is longer than that of an isolated HCOOH (0.986 Å). The computed adsorption energy for 1a is 0.41 eV, which is agreement with the result obtained in the other theoretical studies.[17] The C-H bond is difficult to be activated in structure 1 since it points away from the Pt surface. In order to dissociate this bond, HCOOH must be clockwise rotated about the axis of the C=O bond, making the carbonyl hydrogen atom point to the surface (structure 2), which requires 0.29 eV. Configuration 2 shows an adsorption geometry in which the carbonyl oxygen interacts strongly and the carbon H weakly with the surface with  $E_{ad} = 0.14$  eV. The C-H bond length is slightly increased to 1.116 Å from a gas phase value of 1.105 Å, while no similar increase is observed in structure 1. If the C-H bond of formic acid in structure 2 is activated, COOH forms in structure 3. Structures 2 and 3 are connected by transition state TS<sub>2-3</sub>, where the C-H bond stretches to 1.486 Å. The reaction barrier of the C-H bond breaking is 0.41 eV. After the O-H bond scission, breaking the C-OH bond via the transition state TS<sub>3-4</sub> can generate the product 4, CO and H<sub>2</sub>O. The distance between H atom and O atom of OH group are shorted to 1.330 Å in TS<sub>3-4</sub> from 2.330 Å in structure 3. The activation barrier for this elementary reaction is 0.60 eV. From Figure 2, we can see that this step is the rate-determining step in this path. This barrier is lower than the 0.88 eV required to dissociate the C-OH bond when HCOOH is absorbed as an unstable cis-HCOOH species.[17] Not surprisingly, the difference between these two barriers is due to the different adsorption structures of HCOOH.

Comparing with the previous studies,[14] it should be noted that O-H or C-H bond breaking is

dependent on adsorbed HCOOH orientation, meaning each orientation will have different possible intermediates and pathways. From the potential energy surface of pathway shown in Figure 2, the rate-determining step in this path is 0.60 eV, which is lower than those reported in the literature,[14] indicating that CO formation in the gas phase from the decomposition of formic acid on Pt(111) is energetically favorable, which agrees well with experimental findings.[4]

#### 4. Conclusion

The formation of CO on Pt(111) surface during HCOOH decomposition under gas-phase conditions has been studied in detail with DFT. Our aim is to hunt a new possible pathway that lead to the formation of CO to rationalize the poisoning of Pt-based catalysts. The proposed pathway for CO formation involves the rate-determining step barrier of 0.60 eV. The present result imply that the reaction of HCOOH decomposition to CO becomes favorable thermodynamically, which rationalize the experimental fact well.

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