An insight into methanol oxidation mechanisms on RuO$_2$(100) under an aqueous environment by DFT calculations†

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In this work, we have studied methanol oxidation mechanisms on RuO$_2$(100) by using density functional theory (DFT) calculations and ab initio molecular dynamics (MD) simulations with some explicit interfacial water molecules. The overall mechanisms are identified as: CH$_3$OH$^*$ → CH$_2$O$^*$ → HCHO$^*$ → HCH(OH)$_2$$^*$ → HCOOH$^*$ → mono-HCOO$^*$ → CO$_2$$^*$, without CO formation. This study provides a theoretical insight into C$_1$ molecule oxidation mechanisms at atomic levels on metal oxide surfaces under an aqueous environment.

The electrooxidation of alcohol has been the subject of numerous studies for its potential application in fuel cells over the past decades. Liquid methanol has many advantages in safety and transportation and a high energy density as fuels in direct methanol fuel cells (DMFCs). The equilibrium potential in methanol oxidation and a lot of surfaces have been studied by first principles calculations. Some studies have been carried out theoretically towards the establishment of reaction mechanisms for methanol oxidation, we have investigated the reaction mechanisms in the presence of explicit interfacial water molecules, we may learn a great deal about electrocatalysis at the atomic scale than without them. Some results have shown that the presence of aqueous solution has a great impact on mechanisms and energetics of surface reactions.

Herein, in order to reveal the inherent catalytic activity of the RuO$_2$(100) surface for methanol oxidation, we have investigated the reaction mechanisms in the presence of explicit interfacial water molecules within a DFT framework. An indirect C–H bond breaking mechanism is revealed in which the C–H bond breaking takes place after the O–H bond is broken. A series of reactive intermediates are identified and the presence of water molecules is found to have an important role in formic acid oxidation to CO$_2$. We anticipate that this work would be of benefit for the further study of small organic molecules reactions in Ru/RuO$_2$ systems and on other metal oxide surfaces.

The electronic structure calculations were performed using Perdew–Burke–Ernzerh (PBE) generalized gradient approximation

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(GGA) exchange–correlation functional in Vienna Ab-initio Simulation Package (VASP). The core electron interaction was described by projector-augmented-wave (PAW) pseudopotentials.34–38 The RuO$_2$(100) surface was modelled by the $p(1 \times 3)$ unit cell in a seven-layered slab with 21 Ru atoms and 42 O atoms with a height of 30 Å and the cut-off energy was set to 450 eV. The bottom 9 Ru atoms and 18 O atoms were fixed during geometry optimization processes. A $4 \times 2 \times 1$ Monkhorst–Pack $\bar{k}$-point sampling was used. The surface models of RuO$_2$(100) are displayed in Fig. 1 from top and side views. The transition states were localized using a constrained minimization approach with the convergence of forces being 0.05 eV Å$^{-1}$. For modelling the aqueous RuO$_2$(100) interface, 12 explicit interfacial water molecules were set as shown in Fig. 1c. According to the previous work about influence from the number of water layers, the first solvation shell plays the most important role for calculating the reaction energy.31,32 Here, in our model, 12 explicit water molecules could already form three water layers above the surface that can describe the energy appropriately.

In all the MD simulations, the RuO$_2$(100) surface and adsorbed species were fixed. In the simulation of the initial water layer structure, the running time of MD simulations was extended to 20 ps until the water structure was relatively stable. Since the water interfacial structures for the initial, transition and final states may be different, the water molecules were running ab initio molecular dynamics (MD) for 6 ps (0.5 fs per step, 300 K) for each initial, transition and final state, respectively. The MD simulations were performed at 300 K, and 6 ps time was thus necessary for reaching equilibrium. Using a higher temperature, the simulation time could be reduced. For each state in MD simulations, at least five samples were optimized and the most stable one was chosen. Since the water structure was relatively stable, the running time of MD simulations was extended to 20 ps until the water structure was relatively stable. Since the water interfacial structures for the initial, transition and final states may be different, the water molecules were running ab initio molecular dynamics (MD) for 6 ps (0.5 fs per step, 300 K) for each initial, transition and final state, respectively. The MD simulations were performed at 300 K, and 6 ps time was thus necessary for reaching equilibrium. Using a higher temperature, the simulation time could be reduced. For each state in MD simulations, at least five samples were optimized and the most stable one was chosen. This method has been reported and its accuracy has been tested in the previous work.32 In the calculation of adsorption energy at the aqueous interface, the adsorption energy was defined as: $E_{\text{ad,aq}} = E(\text{ad/surf, aq}) - E(\text{ad}) - E(\text{surf, aq})$, in which the water competitive adsorption was taken into account.

The RuO$_2$(100) surface exposes three kinds of surface atoms as illustrated in Fig. 1a: the bridging oxygen (O$_{br}$) atoms coordinated to two Ru atoms with the Ru–O bond length of 1.94 Å, the one-fold under-coordinated Ru (Ru$_{1f-cus}$) atoms bonded to five O atoms, and the three-fold coordinated oxygen (O$_{3f}$) atoms bonded to three Ru atoms. At the aqueous RuO$_2$(100) interface, CH$_3$OH* has an adsorption energy of $-0.33$ eV via the O-Ru bond with a distance of 2.13 Å. Since CH$_3$OH* could be activated via C–H bond or O–H bond pathways with the formation of CH$_2$OH* or CH$_3$O*,20 we have examined the two pathways respectively. In the C–H bond dissociation pathway, CH$_3$OH* $\rightarrow$ CH$_2$OH* + H*, the barrier is as high as 1.40 eV. The C–H bond length is 1.60 Å at the transition state, as shown in Fig. 2a. Such a large barrier suggests that there is little possibility for direct C–H bond activation in CH$_2$OH* to take place at room temperature. On the other hand, CH$_3$OH* activation via the O–H bond as reaction (1) is found to be favourable with the reaction energy of 0 eV and a tiny barrier of 0.09 eV (TS1) for transferring the hydroxyl H to one near an O$_{br}$ atom. The C–H bond breaking in CH$_3$O* is easier than that in CH$_2$OH*. The barrier is reduced to 0.57 eV with the C–H bond length being 1.33 Å at the TS2 and the formation of formaldehyde (HCHO*) is exothermic by $-0.57$ eV in reaction (2). These findings indicate that the O–H bond breaking in CH$_2$OH* could activate the C–H bond effectively. The energy profile and the structures of intermediates and transition states in HCHO* formation are presented in Fig. 3. All the calculated data can be found in Table S1 (ESI†).

$$\text{CH}_3\text{OH}^* \rightarrow \text{CH}_2\text{O}^* + \text{H}^* \quad (1)$$

$$\text{CH}_3\text{O}^* \rightarrow \text{HCHO}^* + \text{H}^* \quad (2)$$

It is noteworthy that the C–H bond breaking barrier is calculated on the clean surface without H* from O–H bond cleavage. However, we find that in the presence of H*, the barrier associated with C–H bond breaking in reaction (1) was increased from 0.57 eV to 0.82 eV. This indicates that, the produced H* from methanol should be removed from surface as soon as possible; otherwise it will give rise to a low activity for dehydrogenation. We thus further calculated the H desorption potential, according to the reaction, H* $\rightarrow$ H$^*$ + e$^-$, where the free energy of H$^*$ can be replaced by that of 1/2 H$_2$, under SHE conditions.31 The results show that H* will desorb into solution at 0.84 V (vs. SHE), suggestive of a clean RuO$_2$(100) surface. Since the experimental working potential of methanol electrooxidation is about 1 V, H* produced from methanol dissociation under this condition can be readily transferred into solution as a complete catalytic reaction cycle.
Formaldehyde (HCHO*) has a weak adsorption energy of $-0.20 \text{ eV}$ at the interface and the O–Ru bond is 2.16 Å, indicating that HCHO* prefers to move away from surface. We find that it is difficult for HCHO* to decompose directly via the C–H bond due to the high barrier being 1.73 eV. The C–H bond is 1.31 Å at the transition state as shown in Fig. 2b. The previous experiments and DFT modelling on RuO$_2$(110) also have shown that further oxidation of formaldehyde is unlikely and HCHO* would desorb into the gas phase,$^{19}$ which is in agreement with our results that direct HCHO* decomposition is difficult. However, we note that, since the reactions occur under an aqueous environment, the abundance of interfacial water molecules may open a possible pathway to activate HCHO*. Because of the weak adsorption of HCHO*, a sufficient amount of HCHO* in aqueous solution would be hydrated. HCHO* is found to be active and is easily hydrated to form HCH(OH)$_2$* as reaction (3) with a large equilibrium constant in aqueous solution. We have calculated this step in aqueous solution including 32 water molecules. The computational details can be seen in the ESI. The hydration of HCHO is highly exothermic by $-0.94 \text{ eV}$ with a slight barrier of 0.1 eV, indicative of a very easy step. Previous calculations have confirmed this path in acetaldehyde electrooxidation.$^{13}$ The calculated results reveal that the reactive intermediate for following reactions is indeed HCHO(OH)$_2$* instead of HCHO*.

$$\text{HCHO}^* + \text{H}_2\text{O} \rightarrow \text{HCHO(OH)}_2^*$$

The adsorption energy of HCHO(OH)$_2$* is $-0.41 \text{ eV}$. The optimized configuration is one OH group bonded to the Ru site and the other OH group points upwards being stabilized by the water molecules. Since the molecular geometry of HCHO(OH)$_2$* is similar to CH$_2$OH* with one OH group replacing one H, the oxidation mechanism of HCHO(OH)$_2$* is similar to that of CH$_2$OH*.

The energy profile and the structures of intermediates and transition states in HCHO(OH)$_2$* oxidation to HCOOH* are presented in Fig. 4. Specifically, the dissociation of OH group firstly occurs forming HCHOOH* with a tiny barrier of 0.06 eV for transferring H to O$_\text{OH}$ as reaction (4). The O–H bond distance is elongated to 1.20 Å at the TS3 from the initial 0.99 Å. Then, HCHOOH* easily breaks the C–H bond forming HCOOH* with the barrier of 0.47 eV.

The C–H bond length is 1.31 Å at the TS4. The reaction (5) is highly exothermic with a barrier of $-1.37 \text{ eV}$. The direct C–H bond activation of HCHO(OH)$_2$* hardly takes place due to the barrier being as high as 1.16 eV in the reaction, HCHO(OH)$_2$* $\rightarrow$ HC(OH)$_2$* + H*, and the transition state is shown in Fig. 2c.

$$\text{HCHO(OH)}_2^* \rightarrow \text{HCOOH}^* + \text{H}^*$$

HCOOH* at the water/RuO$_2$(100) interface prefers to dissociatively adsorb on the Ru site without a distinct barrier in reaction (6). Two possible configurations of the adsorbed formate (HCOO*) are compared, i.e., mono-dentate (mono-HCOO*) and bi-dentate (bi-HCOO*). In mono-HCOO*, one O atom is bonded to the Ru site and the other O atom points upwards while in bi-HCOO*, two O atoms are both bonded to two neighbouring Ru sites, as shown in Fig. 5b. Mono-HCOO* is more stable than bi-HCOO* by 0.32 eV; the bare O atom forms several hydrogen bonds with water molecules for stabilizing mono-HCOO*. Not only the higher stability, but also the higher activity of mono-HCOO* than bi-HCOO* for CO$_2$ formation, indicating that mono-HCOO* is the reactive intermediate. The C–H bond breaking barrier is calculated to be 0.54 eV, which is close to those in CH$_2$O* (0.57 eV) and HCHOO* (0.47 eV), but the C–H bond breaking barrier in bi-HCOO* is 1.10 eV. The C–H bond length is 1.38 Å at the TS5 and 1.29 Å at the TS6. Once the C–H bond is broken as reaction (7), the newly formed linear CO$_2$* would desorb into solution immediately because of a very weak adsorption energy being only $-0.14 \text{ eV}$. The energy profile for HCOOH* oxidation to CO$_2$* and the structures of intermediates and transition states are presented in Fig. 5.

$$\text{HCOOH}^* \rightarrow \text{mono-HCOO}^* + \text{H}^*$$

$$\text{mono-HCOO}^* \rightarrow \text{CO}_2^* + \text{H}^*$$

The dehydrogenation mechanism on RuO$_2$(100) differs from that on metal surfaces following a step-wise dehydrogenation mechanism resulting in inevitable CO formation.$^{18,20-24}$ On the RuO$_2$ surface, an indirect C–H bond breaking mechanism is suggested that the O–H bond breaking can effectively lower the C–H bond breaking barriers. On the OH* covered palladium
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Fig. 5 (a) Energy profile and (b) optimized structures of intermediates and transition states for HCOOH* oxidation to CO2*. TS5: bi-HCOO* → CO2*; TS6: mono-HCOO* → CO2*.

In summary, some insights into the methanol oxidation at the aqueous RuO2(100) interface have been gained by combining first principles calculations and ab initio MD simulations. The methanol oxidation mechanisms have been identified as: CH3OH* → CH2O* → HCHO* → HCHO(H2)O* → HCHO* → HCOOH* → mono-HCOO* → CO2*, which is very different from that on metal surfaces where CO formation is inevitable. The coupling between HCHO* and one water molecular forming HCH(OH)2O* is the key step for the following reactions. Aqueous environment is found to stabilize mono-HCOO* effectively via hydrogen bonding between the dangling O atom and water molecules, making the higher stability and activity of mono-HCOO* than bi-HCOO* for CO2 formation. This theoretical study of C1 small organic molecules would help understand the catalytic process of other metal oxide surfaces.

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Notes and references