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Article

Unveiling the decomposition mechanism of formic acid on Pd/WC(0001) surface by using density function theory

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ABSTRACT

In pursuit of low-cost direct formic acid fuel cells, tungsten carbide (WC) supported Pd catalyst is considered as an ideal candidate for efficient decomposition of formic acid due to low Pd utilization and excellent performance. Herein, different adsorption configurations and active sites of the intermediates, involved in the HCOOH decomposition, on WC(0001)-supported Pd monolayer (Pd/WC(0001)) surface investigated by using density functional theory. The results reveal that trans-HCOOH, HCOO, cis-COOH, trans-COOH, HCO, CO, H₂O, OH and H exhibit chemisorption on Pd/WC(0001) surface, whereas cis-HCOOH and CO₂ exhibit weak interactions with Pd/WC(0001) surface. In addition, the minimum energy pathways of HCOOH decomposition are analyzed to generate CO and CO₂ due to the fracture of C–H, H–O and C–O bonds. The adsorbed HCOOH, HCOO, mHCOO, cis-COOH and trans-COOH configurations exhibit dissociation rather than desorption. CO formation occurs through the decomposition of cis-COOH, trans-COOH and HCO, whereas the CO₂ formation happens due to the decomposition of HCOO. It is found that the most favorable pathway for HCOOH decomposition on Pd/WC(0001) surface is HCOOH→HCOO→CO₂, where the formation of CO₂ from HCOO dehydrogenation determines the reaction rate. Overall, CO₂ is the most dominant product of HCOOH decomposition on Pd/WC(0001) surface. The presence of WC, as monolayer Pd carrier, does not alter the catalytic behavior of Pd and significantly reduces the Pd utilization.

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1. Introduction

As an alternative power source for portable electronic devices, direct formic acid fuel cell (DFAFC) has garnered significant interest due to its distinct advantages, such as limited fuel crossover, high electromotive force, non-toxicity of formic acid, and high practical power density at low temperature [1,2]. Furthermore, an increasing number of theoretical and experimental studies has focused on the decomposition of HCOOH to probe catalyst activity, intermediates, and possible reaction

mechanism [3–23].

For instance, platinum (Pt), palladium (Pd) are widely studied electrocatalysts for HCOOH oxidation. Hence, these metals are utilized as the anode material in DFAFCs, where the decomposition of HCOOH [17–26] produces CO or CO₂. Both Pd and Pt belong to the same group of the periodic table and possess similar electronic structure, leading to similar electrocatalytic behavior. However, the lower-price and excellent anti-poisoning performance of Pd make it a promising anode candidate in DFAFCs. Moreover, recent studies have demonstrated

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that the electrocatalytic performance of Pd for HCOOH oxidation is superior to Pt [27–30]. Therefore, Pd-based catalytic electrodes are considered as ideal substitutes for Pt-based catalytic materials.

However, the limited reserves of Pd in earth crust hinders the widespread utilization of Pd as an electrocatalyst for formic acid oxidation in DFAFCs. The large-scale commercial utilization of Pd-based catalysts can be realized by reducing the amount of precious metals and increasing the catalytic activity of Pd-based nanocomposite.

In general, the catalytic performance is influenced by the composition, structure and carrier of the catalyst material. The most commonly used carriers are activated carbon (AC), graphite, and carbon nanotubes (CNTs), however, these materials exhibit poor stability due to low pH, high humidity, high oxygen concentration, and high potential. On the other hand, the transition metal tungsten carbide renders excellent electrical conductivity and electrochemical stability. In 1973, Levy et al. [31] had reported that the surface electronic properties carbon-modified WC resemble Pt. Therefore, WC exhibits Pt-like catalysis behavior, which makes it an interesting catalyst carrier for fuel cell applications [32–35].

Since the catalytic reaction mainly occurs on the catalyst surface, gold (Au), Pt and Pd monolayer catalysts have attracted extensive attention. Furthermore, WC-supported monolayer Au [36], Pt [37] and Pd [38,39] are usually used as low-cost electrocatalysts for electrode reactions. For instance, Zhang et al. [40] have investigated the kinetics of oxygen reduction reaction (ORR) on the WC(0001) supported monolayer Au, Pd, and Pt catalysts, where WC supported Pd nanoparticles have rendered superior stability and high activity in alkaline electrolytes, which are comparable to Pt-based catalysts [39].

The close attachment of the WC nanocrystal with the Pd nanoparticles suggests a strong interaction between the WC and Pd by the elemental mapping analysis, the HRTEM and HAADF-STEM analysis, which is expected to produce synergistic effects between WC and Pd for enhanced catalytic activity [41].

Xin's group [42] reported that the $3d_{5/2}$ binding energies of Pd species showed a shift from 336.0 eV for Pd/C to 336.13 eV for Pd/WC-C as a result of modification by WC by X-ray photoelectron spectroscopy (XPS), which exhibited the metal-support interactions between Pd and WC. The better catalytic activity for the FAEO was observed on the Pd/WC-C catalyst, which was 2.5 times higher than that of the Pd/C catalyst on the basis of the specific surface area of the catalysts. A slower current decay was observed on the WC supported catalysts, compared with that on the carbon supported catalysts. This result revealed the synergistic interactions of Pd and WC catalysts, leading to both stabilization and promotion of the catalytic activity for the FAEO.

The oxidation of formic acid generally follows a dual path mechanism, which can be divided into a direct path and an indirect path. In the direct path, CO_2 is generated by fracturing the O–H and C–H bonds, whereas, in the indirect path, CO is generated by breaking the C–O and C–H bonds. Then, the resulting CO is further oxidized to CO_2 . Tao et al. [41] have in-

vested that the chronopotentiometric curves of formic acid oxidation on Pd-WC_r/Graphene is smooth, confirming formic acid oxidation on Pd-WC_r/Graphene with no obvious poisonous species CO on the surface. Guo et al. [43] have experimentally studied that the catalytic influence of WC-supported Pd catalyst on formic acid oxidation and demonstrated the direct dehydrogenation path of formic acid oxidation. However, the detailed reaction mechanism is still unclear. Herein, we aimed to explore the detailed reaction of direct and indirect pathways of formic acid oxidation on Pd/WC(0001) surface by using the first principle calculations. The adsorption of different intermediate species and the decomposition mechanism of HCOOH have been investigated on Pd/WC(0001) surface and results are compared with Pd(111) surface. The decomposition mechanism of formic acid on Pd/WC(0001) is consistent with that on Pd clusters. Formic acid prefers to decompose through dehydrogenation rather than dehydrate on both Pd/WC(0001) surface and Pd₇ cluster, and CO_2 would be the main product [44].

2. Experimental

2.1. Computational methods

In this paper, program package DMol3 [45] of Materials Studio was utilized to perform the spin-unrestricted density functional theory (DFT) calculations. The generalized gradient approximation, with Perdew-Burke-Ernzerhof functional (GGA-PBE) [46], was used to describe the electron exchange and correlation. GGA-PBE method is widely used in DFT calculations of catalytic materials and their adsorbates [47–50]. A double-numerical basis with polarization functions (DNP) is utilized to expand the valence electron functions into a set of numerical atomic orbitals. The core treatment is set with density functional semicore pseudopotential (DSPP) and the real-space global orbital cutoff radius was set at 4.9 Å to improve the accuracy and efficiency of DFT calculations. The convergence standard for geometric optimizations and energy calculations was set to the tolerance for SCF, energy, maximum force, and maximum displacement of 1.0×10^{-6} Ha, 1.0×10^{-5} Ha, 0.002 Ha/Å, and 0.005 Å, respectively.

The transition states (TS) were identified by using the complete LST/QST method of the elementary reactions [51]. The frequency analysis of the transition states was carried out, and only one imaginary frequency is validated by using eigenvalue, which followed the optimization method and assured the transition state.

2.2. Surface models

W-terminated WC(0001) exhibits excellent stability and activity, importantly, the presence of Pd monolayer on W-terminated WC(0001) demonstrates better energy efficient than the C-terminated WC(0001) surface [52]. Therefore, W-terminated WC(0001) is chosen as the carrier of monolayer Pd. Pd atoms were sequentially deposited on W-terminated WC(0001) to obtain a single layer structure, which simulates

the surface of Pd/WC(0001). The same method has been adopted in the previously published reported[40]. The Pd atoms firmly adhered to the hcp position of WC(0001) to the hcp position of WC (0001) on the top of C atoms.

Starting from the bulk WC structure, a (3×3) supercell model, with 9 atoms in each layer, was established to simulate the surface of Pd/WC(0001). The supercell was modeled by arranging periodically repeated slabs with 7 atomic layers, consisting of three WC bilayers and one Pd monolayer, and providing a vacuum region of 15 Å, which separated the periodically arranged slabs. Brillouin zone integration was performed on a $5 \times 5 \times 1$ grid, by using the Monkhorst-Pack k points. DFT-D correction has been carried out for all calculations, and long-range Vander interactions has been considered. During the optimization process, the bottom four atomic layers were constrained to simulate bulk characteristics, whereas the remaining layers, including the subsequently deposited Pd monolayer and adsorbates, were allowed to relax freely.

3. Results and discussion

The surface energy ($E_{\text{Pd,surf}}$), adsorption energy (E_{ads}), total enthalpy change (ΔH), activation energy (E_{b}), electron density difference ($\Delta\rho$) and co-adsorption energy (E_{coads}) were calculated by using the following mathematical formula:

$$E_{\text{Pd,surf}} = 1/n(E_{\text{Pd/WC(0001)}} - E_{\text{WC(0001)}} - nE_{\text{Pd,bulk}}) \quad (1)$$

where $E_{\text{Pd/WC(0001)}}$ is the total energy of the slab, $E_{\text{WC(0001)}}$ is the total energy of the substrate, n is the number of Pd atoms, and $E_{\text{Pd,bulk}}$ is the bulk energy per Pd atom obtained from an independent bulk calculation. If the surface energy is lower than zero, the dispersed Pd atoms on WC(0001) surface would be favoured. Conversely, if the surface energy is higher than 0, the dispersed Pd atoms would prefer to accumulate to form clusters or particles.

$$E_{\text{ads}} = E_{\text{adsorbate/Pd/WC(0001)}} - E_{\text{Pd/WC(0001)}} - E_{\text{adsorbate}} \quad (2)$$

where $E_{\text{adsorbate/Pd/WC(0001)}}$ refers to the total energy of adsorbate and Pd/WC(0001) system in the equilibrium state, $E_{\text{Pd/WC(0001)}}$ represents the total energy of an adsorbate-free Pd/WC(0001) surface, and $E_{\text{adsorbate}}$ corresponds to the total energy of free adsorbates. Based on this definition, the negative values of adsorption energy correspond to the favorable and stable adsorption of Pd/WC(0001).

$$\Delta H = E_{\text{FS}} - E_{\text{IS}} \quad (3)$$

where E_{FS} and E_{IS} represent the energies of final state (FS) and initial state (IS), respectively.

$$E_{\text{b}} = E_{\text{TS}} - E_{\text{IS}} \quad (4)$$

where E_{TS} and E_{IS} represent the energies of the transition state (TS) and initial state (IS), respectively.

$$\Delta\rho = \Delta\rho_{\text{adsorbate/Pd/WC(0001)}} - \Delta\rho_{\text{Pd/WC(0001)}} - \Delta\rho_{\text{adsorbate}} \quad (5)$$

where $\Delta\rho$ represents the electron density difference, $\Delta\rho_{\text{adsorbate/Pd/WC(0001)}}$ refers to the total electron density of adsorbate and Pd/WC(0001) system in the equilibrium state, $\Delta\rho_{\text{Pd/WC(0001)}}$ denotes the total electron density of a clean Pd/WC(0001) surface, and $\Delta\rho_{\text{adsorbate}}$ corresponds to the total electron density of the free adsorbate.

$$E_{\text{coads}} = E_{\text{(A+B)/Pd/WC(0001)}} - E_{\text{Pd/WC(0001)}} - E_{\text{A}} - E_{\text{B}} \quad (6)$$

where E_{A} , E_{B} , $E_{\text{Pd/WC(0001)}}$ and $E_{\text{(A+B)/Pd/WC(0001)}}$ are represent the

total energy for the correlative free molecule of A and B, the Pd/WC(0001) slab with a (3×3) supercell and the co-adsorbed (A+B) and Pd/WC(0001) slab systems, respectively.

3.1. Evaluation of calculation method and model

In the case of bulk WC, the calculated lattice parameters, $a = b = 2.906$ Å, and $c = 2.838$ Å are consistent with the experimental data ($a = b = 2.91$ Å and $c = 2.83$ Å) [53].

The free formic acid in gaseous phase exhibits, both cis and trans configurations. The calculated energy of trans conformation is 0.142 eV lower than the cis-HCOOH, which is consistent with the experimental value of 0.17 eV [54]. The calculated C–H, C=O, C–OH and O–H bond lengths in the trans-HCOOH configuration are 1.105 (1.097) Å, 1.215 (1.202) Å, 1.358 (1.343) Å and 0.983 (0.972) Å, respectively. One should note that the as-calculated values are consistent with the previously reported experimental values, as displayed in the parentheses.

The calculated surface energy is -1.06 eV per atom, indicating that Pd atoms are favoured to be dispersed over W-terminated WC(0001) surface since the chemical bonds between the W atoms and Pd atoms are considerably strong. According to the calculated result, it can conclude that in reality WC(0001) supported monolayer Pd surfaces should commonly exist, which is in agreement with the result of Zhang's report [40].

3.2. Intermediates adsorption on Pd/WC(0001) surface

The adsorption energies were calculated for intermediates and the results are summarized in Table 1. Moreover, the most stable adsorption configuration and the corresponding key structural parameters of all intermediates at their favorable positions are also listed in Table 1. The most stable structures of all intermediates, involving HCOOH adsorbed on Pd/WC(0001) surface, are presented in Fig. 1. The electron density difference map exhibits the charge transfer between the intermediate, including formic acid and the Pd/WC(0001) surface(Fig. 1). The blue-colored portion indicates the gained

Table 1

Adsorption sites, adsorption energies and key structural parameters of different intermediates on Pd/WC(0001) surface.

Species	Adsorption sites	Configurations	Bond length/Å	E_{ads}/eV
HCOOH	top	O-bound	2.30(O-Pd)	-0.87
cis-HCOOH	—	above surface	—	-0.42
HCOO	bridge	O-bound	2.18(O-Pd)	-3.51
mHCOO	bridge	O-bound	2.16(O-Pd)	-2.56
cis-COOH	top	C-bound	2.05(O-Pd)	-2.68
trans-COOH	top	C-bound	2.09(O-Pd)	-2.57
HCO	bridge	C-bound	2.04(C-Pd)	-2.26
CO	fcc	C-bound	2.21(C-Pd)	-1.51
H ₂ O	top	O-bound	2.36(O-Pd)	-0.60
OH	fcc	O-bound	2.29(O-Pd)	-3.15
CO ₂	—	above surface	—	-0.29
H	fcc	H-bound	1.92(H-Pd)	-2.67

Fig. 1. The upper panels of each represent top-views of the most stable adsorption configurations of different reaction intermediates (built-in side-views in top right upper corner), involved in HCOOH decomposition, on Pd/WC(0001). The bottom-panels of each represent side-views of electron density difference of corresponding intermediates, respectively. Red, orange, blue, gray and white balls represent O atoms, Pd atoms, W atoms, C atoms and H atoms, respectively.

charge region, whereas the red-colored portion indicates the lost charge region.

Among two isomers of formic acid, the trans-HCOOH configuration is more stable than the cis-HCOOH configuration in the gaseous phase. Moreover, there are several adsorption configurations of formic acid on Pd/WC(0001) surface. For instance, the formic acid molecular plane can be parallel or perpendicular to the catalyst surface. In addition, there are different adsorption sites in the vertical configuration. Fig. 1(a) presents the most stable adsorption configuration for HCOOH, where carbonyl oxygen is combined with the top site of the Pd atom and the O–Pd distance is 2.30 Å. Moreover, the OH group points asymmetrically to two the adjacent Pd atoms and the distance between adjacent H and Pd atoms is 2.46 and 2.47 Å, respectively. Also, the O–H bond lengthened from 0.98 to 1.11 Å with increasing 0.13 Å. The calculated adsorption energy of HCOOH is –0.87 eV, which indicates that the process is energetically favorable.

HCOO also exhibited two different adsorption configura-

tions: bidentate (Fig. 1(b)) and monodentate (Fig. 2(i)), where bidentate configuration is more stable than monodentate configuration due to total energy. In monodentate adsorption, only one O atom is bound to the Pd atom on the surface and the C–H bond obliquely points to the adjacent Pd atom with the adsorption energy of –2.56 eV. In the bidentate model, there is only one type of bidentate adsorption configuration, where two O atoms are combined with two adjacent Pd atoms, respectively, and the C–H bond is vertically upward. Herein, the whole HCOO molecule is located on the bridge site of two Pd atoms. The two oxygen atoms of HCOO strongly interact with Pd/WC(0001) surface and form two O–Pd bonds with a bond length of 2.18 Å. Moreover, the C=O bond is elongated from 1.268 to 1.273 Å in the gaseous phase. In general, the adsorption process is exothermic (3.51 eV), which indicates strong chemical adsorption. It can be seen from the electron density difference of HCOO (Fig. 1(b)) that more charge transferred between the surface Pd atoms and HCOO, resulting in a stronger O–Pd bond.

In the case of COOH, four adsorption sites and two isomers

Fig. 2. The upper panels of each represent top-views of the optimized co-adsorption structures of different products (built-in side-views in top right upper corner), involved in HCOOH decomposition, on Pd/WC(0001). The bottom-panels of each represent side-views of electron density difference of corresponding co-adsorption products, respectively.

(cis-COOH and trans-COOH) are considered. Cis-COOH configuration is less stable than the trans-COOH configuration in the gaseous phase due to total energy. It has been observed that cis-COOH and trans-COOH configurations, adsorbed on the top site of Pd/WC(0001) surface, are the most stable structures (Fig. 1(c) and 1(d)) with the adsorption energies of -2.68 and -2.57 eV, respectively. Both C atoms are bonded to Pd atom with the C–Pd bond length of 2.05 and 2.09 Å, respectively. Moreover, the C=O bond is almost parallel to the Pd/WC(0001) surface.

In the case of free HCO in the gaseous phase, the C=O bond length is 1.19 Å and H–C=O bond angle is 123.1° , which are consistent with the experimental values of 1.17 Å and 127° [56]. On the Pd/WC(0001) surface, HCO tends to adsorb at the bridge site of Pd/WC(0001) surface (Fig. 1(e)), where the C atom is bonded to the Pd atom on the top site, C=O bond occupies the bridge site and becomes parallel to the surface. The H–C=O bond angle was found to be 115.7° . The bond length of C–Pd, O–Pd and C=O bonds is 2.04 , 2.31 and 1.25 Å, respectively. Moreover, the exothermic energy of 2.26 eV indicates a strong chemical adsorption.

Furthermore, CO stably adsorbed on four high symmetry sites of Pd/WC(0001). The preferential adsorption of CO occurred at the FCC site of Pd/WC(0001) surface with an adsorption energy of -1.51 eV (Fig. 1(f)). In addition, the C–O bond axis is perpendicular to the Pd/WC(0001) surface with a C–O bond length of 1.18 Å. The distance between C atom and the nearest Pd atom is 2.21 Å. The previous studies reported that CO preferentially adsorbs on the hollow sites of Pt(111) [56] and Pd(111) [17] surfaces.

Moreover, we have investigated all adsorption sites for H₂O. The results reveal that H₂O is only adsorbed on the top site of Pd/WC(0001) surface (Fig. 1(g)), where the oxygen atom is directly above the bound Pd atom with the O–Pd distance of 2.36 Å and H₂O molecule is almost parallel to the Pd/WC(0001) surface. The H–O bond length and H–O–H bond angle are 0.978 Å and 104.3° , respectively, which are close to the values of H₂O molecules in the gaseous phase (0.98 Å and 103.68°). In addition, the corresponding adsorption energy of -0.60 eV indicates weak adsorption of water molecules on Pd/WC(0001) surface.

In the case of OH, it has been observed that OH cannot be stably adsorbed on the top site, whereas it can be stably adsorbed at the FCC site. OH is connected to the surrounding three Pd atoms through the oxygen atom (Fig. 1(h)), where O–H bond is perpendicular to the surface. At the FCC site, the adsorption energy of -3.51 eV is slightly higher than the HCP site, which exhibits the strong chemical adsorption. The closest distance between the oxygen atom and three Pd atoms is 2.29 Å, whereas the length of O–H bond is slightly reduced from 0.99 to 0.973 Å in vacuum.

In the case of CO₂, it has been reported that CO₂ prefers to remain as a free specie rather than adsorbed on the metal surfaces [58]. CO₂ is far from the Pd/WC(0001) surface, where O=C=O bond angle and C=O bond length are close to the CO₂ molecule in the gas phase (Fig. 1(i)). It is found that the interaction between CO₂ and Pd/WC(0001) surface is weak and the

adsorption energy is -0.29 eV, which is consistent with the experimental results. This can be seen from the top- and side-views of electron density difference of CO₂ with little charge transfer between the CO₂ and the surface (Fig. 1(i)).

Four stable adsorption sites have been observed for H, which preferentially adsorbs on the FCC site on the Pd/WC(0001) surface with an adsorption energy of -2.67 eV (Fig. 1(j)). The H atom is closer to the surface and the minimum distance between H and three nearby Pd atoms is 1.92 Å.

In summary, the adsorption of HCOOH, HCOO, trans-COOH, cis-COOH, HCO, CO, H₂O, OH and H on Pd/WC(0001) surface followed the chemisorption process. However, cis-HCOOH and CO₂ can be considered as physisorption due to their weak interaction with Pd/WC(0001) surface.

It has been observed that HCOOH, trans-COOH, cis-COOH and H₂O preferentially adsorb on the top sites; HCOO, mHCOO and HCO occupy the bridge sites; and CO, H and OH adsorb on FCC sites. There is charge transfer from Pd to the carrier, with an average of 0.13 electron per Pd atom. Compared with Pd(111) surface [17], the corresponding adsorption energies of all species are distinctly different in the case of Pd/WC(0001) surface, which can be ascribed to the different arrangement of Pd atoms and synergy between WC carrier and monolayer Pd.

3.3. Co-adsorption on Pd/WC(0001) surface

In order to investigate the decomposition mechanism of HCOOH on Pd/WC(0001) surface, the most stable co-adsorption configurations of (a) HCOO + H, (b) cis-COOH + H, (c) trans-COOH + H, (d) CO + H₂O, (e) HCO + OH, (f) CO₂ + H and (g) CO + OH have been studied. The combined configurations are selected based on the final product of HCOOH decomposition. The optimized co-adsorption configurations are shown in Fig. 2, whereas the corresponding adsorption sites and co-adsorption energies are summarized in Table 2.

In all calculations, for the initial co-adsorption configuration on the Pd/WC(0001) surface, the corresponding intermediates are located at the adjacent and the most stable adsorption sites. For example, for the co-adsorption of HCOO+H on Pd/WC(0001) surface, the initial structure is that H atom is located on fcc sites and HCOO is on the adjacent bridge sites. After geometric optimization, it is found that most of the optimized co-adsorption configurations maintain their initial state. The co-adsorption energies of HCOO + H, cis-COOH + H, trans-COOH + H, CO + H₂O, HCO + OH, CO₂ + H and CO + OH are

Table 2

The most stable co-adsorption structures on Pd/WC(0001) surface and corresponding co-adsorption energies.

Species	Corresponding adsorption sites	E_{coads} /eV
HCOO + H	bridge + fcc	-6.17
cis-COOH + H	top + fcc	-5.14
trans-COOH + H	top + fcc	-5.21
CO + H ₂ O	fcc+ top	-2.19
HCO + OH	bridge + fcc	-5.34
CO ₂ + H	--- + fcc	-2.98
CO + OH	fcc + fcc	-4.54

Table 3

Energy barrier (E_b) and reaction energy (ΔH) of the HCOOH decomposition reactions on Pd/WC(0001) surface.

Reaction	TS	Reaction	E_b /eV	ΔH /eV
HCOOH $\rightarrow$ HCOO + H	TS1	R1	0.61	-0.60
HCOOH $\rightarrow$ cis-COOH+H	TS2	R2	0.77	0.19
HCOOH $\rightarrow$ CO + H ₂ O	TS3	R3	0.93	-0.37
HCOOH $\rightarrow$ HCO + OH	TS4	R4	1.05	0.67
HCOOH $\rightarrow$ cis-HCOOH	TS5	R5	0.62	0.58
cis-HCOOH $\rightarrow$ HCO+OH	TS6	R6	0.46	0.09
cis-HCOOH $\rightarrow$ trans-COOH+H	TS7	R7	0.12	-0.53
HCO+OH $\rightarrow$ CO + H ₂ O	TS8	R8	0.23	-1.05
HCOO $\rightarrow$ CO ₂ + H	TS9	R9	1.09	0.53
HCOO $\rightarrow$ mHCOO	TS10	R10	1.05	0.95
HCOO $\rightarrow$ cis-COOH	TS11	R11	2.91	0.59
mHCOO $\rightarrow$ CO ₂ + H	TS12	R12	0.21	-0.37
trans-COOH $\rightarrow$ cis-COOH	TS13	R13	0.52	-0.03
trans-COOH $\rightarrow$ CO + OH	TS14	R14	0.16	-0.05
trans-COOH $\rightarrow$ CO ₂ + H	TS15	R15	1.37	-0.09
cis-COOH $\rightarrow$ CO + OH	TS16	R16	0.47	-0.01
cis-COOH $\rightarrow$ CO ₂ + H	TS17	R17	1.27	0.28

-6.17, -5.14, -5.21, -2.19, -5.34, -2.98 and -4.54 eV, respectively.

3.4. Decomposition of adsorbed intermediates on Pd/WC(0001) surface

Furthermore, the possible reaction pathways of HCOOH decomposition on Pd/WC(0001) surface are systematically studied. Initially, the trans-HCOOH configuration is used based on the HCOOH bond cleavage and configuration flipping pathway (Fig. 1(a)). In the bond cleavage, the decomposition starts from the formation of (I) HCOO by O-H bond cleavage, (II) cis-COOH by C-H bond cleavage, (III) CO and H₂O by simultaneous bond

Fig. 4. The network of reaction steps for HCOOH decomposition on Pd/WC(0001) surface.

cleavage of C-H and O-H bond and (IV) HCO and OH by C-O bond cleavage. In the configuration flipping, C=O and C-H bonds in trans-HCOOH configuration (Fig. 1(a)) are rotated at 180° along the C-O bond, resulting in cis-HCOOH configuration (Fig. 2(h)). Moreover, the configurational transitions and dissociation pathways between HCOO, mHCOO, cis-COOH and trans-COOH have been investigated by using DFT. The reaction energy barriers (E_b) and reaction energies (ΔH) of each reaction are calculated and results are summarized in Table 3.

The relevant transition states (TS) of the elementary reactions are shown in Fig. 3 and the reaction network of HCOOH decomposition is presented in Fig. 4. Among all the possible routes, the most stable adsorption structure of the intermediates on Pd/WC(0001) surface is selected as the initial reactant. Moreover, the final reaction products are considered as the

Fig. 3. The upper panels of each represent top-views of the TS (built-in side-views in top right upper corner) on Pd/WC(0001). The bottom-panels of each represent side-views of electron density difference of corresponding TS, respectively.

corresponding co-adsorption configurations of the most stable monomer adsorption sites.

3.4.1. The scission of O–H, C–H and C–O bonds of HCOOH on Pd/WC(0001) surface

Four bond cleavage pathways are considered to investigate the decomposition of HCOOH on Pd/WC (0001) surface.

(I) $\text{HCOOH} \rightarrow \text{HCOO} + \text{H}$: Once the O–H bond is broken, the adsorbed HCOOH (Fig. 1(a)) is decomposed into HCOO and H in TS1 (Fig. 3). The dissociated H atom migrates to the vicinity of FCC site and the O atom of C–O bond moves to the top site of the adjacent Pd atom. The distance between the dissociated H and O atoms increases to 1.56 Å, which is an increase of 0.54 Å from the initial bond length of 1.02 Å. After TS1, the dissociated H atom is located at the FCC site and the bidentate HCOO is adsorbed on two adjacent Pd atoms by forming O–Pd bonds. The activation and exothermic energies of the elementary reaction are 0.61 and 0.60 eV, respectively. In terms of adsorption energy, HCOOH is more prone to dissociation on Pd/WC(0001) surface than desorption.

(II) $\text{HCOOH} \rightarrow \text{cis-COOH} + \text{H}$: With the cleavage of C–H bond, HCOOH (Fig. 1(a)) is decomposed into cis-COOH and H in the vicinity of top and FCC sites in TS2, respectively (Fig. 3). The C–H bond length is extended to 1.51 Å and the reaction overcomes the energy barrier of 0.77 eV, whereas the endothermic energy is 0.19 eV. In terms of adsorption energy, HCOOH is more prone to dissociation on Pd/WC(0001) surface than desorption.

(III) $\text{HCOOH} \rightarrow \text{CO} + \text{H}_2\text{O}$: With the simultaneous cleavage of C–H and C–O bonds, HCOOH (Fig. 1(a)) is decomposed into H, CO and OH on top sites in TS3 (Fig. 3). After TS3, CO moves to the nearby FCC site and the dissociated H atom combines with OH and forms H_2O to remain on the top site. The reaction overcomes an energy barrier of 0.93 eV and exhibits exothermic energy of 0.37 eV.

(IV) $\text{HCOOH} \rightarrow \text{HCO} + \text{OH}$: With the cleavage of C–O bond, HCOOH is decomposed into co-adsorbed HCO and OH, occupying the vicinity of two adjacent top sites. In TS4, the distance between the oxygen atom of OH and C atom is 2.15 Å (Fig. 3). After TS4, HCO remains on the top site and OH moves to the nearby FCC site. The activation energy and endothermic energy of the elementary reaction are 1.05 and 0.67 eV, respectively.

(V) $\text{HCOOH} \rightarrow \text{cis-HCOOH}$: cis-HCOOH (Fig. 2(h)) is the adsorption configuration after HCOOH conversion. Even though it is not as stable as the initial reaction of HCOOH (Fig. 1(a)), it is beneficial to subsequent decomposition. Two H atoms of cis-HCOOH configuration lie on the same side and point towards Pd/WC(0001) surface. HCOOH to cis-HCOOH transformation occurs by simultaneous reorientation of C–H and C=O bonds around 180° along the C–O bond. One should note that C=O and C–H bond lengths in TS5 are still 1.22 and 1.10 Å, respectively. However, the position of C=O and C–H bonds deviated from the original vertical position. This process overcomes an energy barrier of 0.62 eV and exhibits an endothermic energy of 0.58 eV.

(VI) $\text{cis-HCOOH} \rightarrow \text{HCO} + \text{OH}$: Once C–O bond is broken,

cis-HCOOH configuration decomposes into co-adsorbed HCO and OH, occupying the vicinity of two adjacent top sites on Pd/WC(0001) surface, respectively. In TS6 (Fig. 3), the distance between the oxygen atom of OH and C atom is 2.15 Å. After TS6, the HCO remains on the top site and OH moves to the nearby FCC site. The activation energy and endothermic energy of the elementary reaction are 0.46 and 0.09 eV, respectively. It is worth mentioning that this reaction is more favorable than R4 due to its lower activation energy.

(VII) $\text{cis-HCOOH} \rightarrow \text{trans-COOH} + \text{H}$: In TS7 (Fig. 3), C–H bond is elongated to 1.49 Å, trans-COOH configuration occupies the top site and H moves to the vicinity of FCC site, which later occupies the FCC site. The reaction overcomes an energy barrier of 0.12 eV and exhibits exothermic energy of 0.53 eV.

(VIII) $\text{HCO} + \text{OH} \rightarrow \text{CO} + \text{H}_2\text{O}$: The HCO and OH, obtained from R4 and R6, further changed to CO and H_2O through TS8 (Fig. 3). The lengths of C–H and O–H bonds are 1.21 and 1.48 Å, respectively. After the transition state, the CO moves to the nearby FCC site and H_2O occupies the top site. The activation energy and exothermic energy of the reaction are 0.23 and 1.05 eV, respectively.

3.4.2. The Decomposition of HCOO on Pd/WC(0001) surface

(I) $\text{HCOO} \rightarrow \text{CO}_2 + \text{H}$: The fracture of C–H bond in bidentate HCOO is selected (Fig. 1(b)) as an initial state, which is directly dissociated into CO_2 and H by TS9. In TS9, the distance between the dissociated H and C atoms extends from 1.11 to 1.52 Å and H atom occupies the top site. In the co-adsorbed state, CO_2 molecule is far from the surface and H atom is on the FCC site. The activation energy and endothermic energy of the elemental reaction are 1.09 and 0.53 eV, respectively.

(II) $\text{HCOO} \rightarrow \text{mHCOO}$: Herein, the reaction occurs by the inversion of adsorption configuration. The bidentate HCOO, adsorbed on the Pd/WC(0001) surface, becomes monodentate HCOO (Fig. 2(i)), where an O–Pd bond breaks and only one O atom combines with adjacent Pd atom to form an O–Pd bond. As a result, C–H bond is obliquely directed to adjacent Pd atom. As shown in Fig. 3 (TS10), the bond length C–H (1.13 Å) did not exhibit any significant change. The reaction energy barrier and endothermic energy are 1.05 and 0.95 eV, respectively.

(III) $\text{HCOO} \rightarrow \text{cis-COOH}$: The C–H bond in HCOO breaks and H atom moves to the adjacent O atom to form cis-COOH. In TS11 (Fig. 3), the bond lengths of C–H and O–H bonds become 1.35 and 1.19 Å, respectively. The activation energy and endothermic energy of the elementary reaction are 2.91 and 0.59 eV, respectively.

(IV) $\text{mHCOO} \rightarrow \text{CO}_2 + \text{H}$: The C–H bond of the monodentate HCOO breaks to form CO_2 and H. In TS12 (Fig. 3), the C–H bond is elongated to 1.71 Å. The activation energy and exothermic energy of the reaction are 0.21 and 0.37 eV, respectively.

3.4.3. Decomposition of COOH on Pd/WC(0001) surface

In the case of COOH, the total energy of trans-COOH and cis-COOH configurations on Pd/WC(0001) surface is not much different. Hence, the configuration conversion and decomposi-

tion between the two are studied, which resulted in five different reaction pathways.

(I) Trans-COOH $\rightarrow$ cis-COOH: During cis-COOH to trans-COOH transition (TS13), C atom exists in the vicinity of the original top site, where O-H bond is reversed and changes from original oblique downward to the oblique side and attains a final oblique upward position (Fig. 3). However, the bond length of O-H bond is still 0.98 Å. This energy barrier and exothermic energy of the given reaction are 0.52 and 0.03 eV, respectively.

(II) Tans-COOH $\rightarrow$ CO + OH: During the cleavage of C-O bond of trans-COOH configuration on Pd/WC (0001) surface, the initial state is trans-COOH adsorbed on the top site (Fig. 1(d)). In TS14 (Fig. 3), the C atom is located near the original Pd atom and O-H bond is flipped and moved to the adjacent bridge site. After TS14, CO and OH are located on the FCC sites. The reaction exhibits an energy barrier and exothermic energy of 0.16 and 0.05 eV, respectively.

(III) Trans-COOH $\rightarrow$ CO₂ + H: Trans-COOH configuration results in CO₂ and H via TS15, as shown in Fig. 3. The distance between dissociated H and O atom increased from 0.98 to 1.53 Å. After TS15, the dissociated H atom moves to the adjacent FCC site and the CO₂ molecule moves away from the surface. The reaction needs to overcome the energy barrier of 1.37 eV and exhibits exothermic energy of 0.09 eV.

(IV) Cis-COOH $\rightarrow$ CO + OH: During the cleavage of C-O bond of cis-COOH configuration on Pd/WC (0001) surface, the initial state is the cis-COOH configuration, as shown in Fig. 1(c). Herein, OH dissociates from the adsorbed cis-COOH configuration and co-adsorbs with remaining CO. In TS16 (Fig. 3), the distance between the oxygen atom, dissociated from OH, and C atom increased to 1.88 Å. After TS16, both CO and OH occupied the adjacent FCC sites. The reaction exhibited an energy barrier of 0.47 eV and exothermic energy of 0.01 eV.

(V) Cis-COOH $\rightarrow$ CO₂ + H: During the cleavage of O-H bond of cis-COOH configuration, CO₂ and H are generated according to TS17, as shown in Fig. 3. In TS17, the distance between dissociated H and O atoms increased from 0.99 to 1.42 Å and O-H bond points towards Pd/WC(0001) surface. After TS17, CO₂ molecule moves away from the surface and dissociated H atom moves to the adjacent FCC site. The reaction needs to overcome

an energy barrier of 1.27 eV and exhibits endothermic energy of 0.28 eV.

3.4.4. The brief summary

The potential energy surface for HCOOH decomposition through HCOO, mHCOO, cis-HCOOH, cis-COOH, trans-COOH and HCO intermediates on Pd/WC(0001) surface is shown in Figs. 5 and 6, which includes the following pathways (Fig. 4):

- (1) HCOOH $\rightarrow$ HCOO $\rightarrow$ CO₂;
- (2) HCOOH $\rightarrow$ HCOO $\rightarrow$ mHCOO $\rightarrow$ CO₂;
- (3) HCOOH $\rightarrow$ cis-HCOOH $\rightarrow$ HCO $\rightarrow$ CO;
- (4) HCOOH $\rightarrow$ cis-HCOOH $\rightarrow$ trans-COOH $\rightarrow$ CO;
- (5) HCOOH $\rightarrow$ cis-HCOOH $\rightarrow$ trans-COOH $\rightarrow$ CO₂;
- (6) HCOOH $\rightarrow$ cis-HCOOH $\rightarrow$ trans-COOH $\rightarrow$ cis-COOH $\rightarrow$ CO;
- (7) HCOOH $\rightarrow$ cis-HCOOH $\rightarrow$ trans-COOH $\rightarrow$ cis-COOH $\rightarrow$ CO₂;
- (8) HCOOH $\rightarrow$ cis-COOH $\rightarrow$ CO;
- (9) HCOOH $\rightarrow$ cis-COOH $\rightarrow$ CO₂;
- (10) HCOOH $\rightarrow$ HCOO $\rightarrow$ cis-COOH $\rightarrow$ CO;
- (11) HCOOH $\rightarrow$ HCOO $\rightarrow$ cis-COOH $\rightarrow$ CO₂;
- (12) HCOOH $\rightarrow$ HCO $\rightarrow$ CO;
- (13) HCOOH $\rightarrow$ CO.

By comparing the adsorption energy and dissociation energy barrier of the intermediates, it is demonstrated that the dissociation of adsorbed HCOOH, HCOO, mHCOO, cis-COOH and trans-COOH is more favorable on Pd/WC(0001) surface than desorption. According to the corresponding activation energy, HCOO is the main dissociation intermediate of HCOOH on Pd/WC(0001) surface. One should note that the generation of CO₂ is more difficult from HCOO than the formation of CO from trans-COOH and cis-COOH configurations, which is similar to the decomposition of HCOOH on the Pd(111) surface [57] and indicates that HCOO may accumulate on Pd/WC(0001) surface. HCOOH is converted into cis-HCOOH and, then, the trans-COOH configuration is generated. Overall, CO is the main dissociation intermediate of trans-COOH configuration on Pd/WC(0001) surface.

Furthermore, the cleavage of C-O bond in both cis- and trans-COOH configuration is easier than O-H bond cleavage, which indicates that CO is formed before CO₂. In addition, CO is directly produced from decomposition of HCOOH or HCO,

Fig. 5. Potential energy profiles of HCOOH decomposition on Pd/WC(0001) surface.

Fig. 6. Potential energy profiles of HCOO, mHCOO, trans-COOH and cis-COOH decomposition on Pd/WC(0001) surface.

however, the probability is extremely low due to the corresponding high energy barrier, as discussed in the case of TS3 and TS4 in Fig. 3. As long as a small part of HCOOH is converted into cis-HCOOH through TS5, prior to its decomposition into HCOO, cis-HCOOH is easily decomposed into HCO and OH by TS6, which are rapidly decomposed into CO after TS8. Overall, $\text{HCOOH} \rightarrow \text{HCOO} \rightarrow \text{CO}_2$ (Path 1) is the most probable pathway of HCOOH decomposition on Pd/WC(0001) surface, where the decomposition of HCOO into CO_2 is the rate-determining step.

4. Conclusions

In summary, periodic DFT is utilized to investigate the possible pathways of HCOOH decomposition on Pd/WC(0001) surface, where the decomposition of HCOOH is initiated by the activation of C–H, O–H, and C–O bonds. The most stable adsorption configuration of the reaction intermediates is determined by using DFT. It has been demonstrated that HCOOH, HCOO, mHCOO, cis-COOH, trans-COOH, CO, H_2O , OH and H exhibit chemical adsorption, whereas cis-HCOOH and CO_2 exhibit weak interactions with Pd/WC(0001) surface. Furthermore, different reaction pathways of HCOOH decomposition are proposed to unveil the decomposition mechanism. The results reveal that O–H bond cleavage exhibits the minimum energy barrier, whereas the bidentate HCOO is the main intermediate of HCOOH decomposition, which can be further converted into monodentate HCOO. The energy barrier of CO_2 generation from monodentate HCOO is 0.04 eV lower than bidentate HCOO. In the case of HCOO, CO_2 is the main dissociation product, which determines the reaction rate. On the other hand, CO is the major dissociation product of cis-COOH and trans-COOH configurations. In addition, the direct generation of CO from HCOOH exhibits a relatively higher energy barrier. Furthermore, it has been demonstrated that the most favorable HCOOH decomposition route on Pd/WC(0001) surface is $\text{HCOOH} \rightarrow \text{HCOO} \rightarrow \text{CO}_2$, where the dehydrogenation of HCOO determines the rate of CO_2 production.

The present study provides a detailed overview of the kinetics and mechanism of active intermediates and HCOOH decomposition on Pd/WC (0001) surface. Overall, CO formation

occurs through the decomposition of cis-COOH, trans-COOH and HCO, whereas the CO_2 formation happens due to the decomposition of HCOO. In general, CO_2 is the main product of formic acid decomposition on the surface of the catalyst. These observations are consistent with the previously published reports about formic acid decomposition on Pd(111) surface [58], implying that the presence of WC, as monolayer Pd carrier, does not alter the catalytic behavior of Pd and significantly reduces the Pd utilization.

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Graphical Abstract

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Unveiling the decomposition mechanism of formic acid on Pd/WC(0001) surface by using density function theory

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The network of reaction steps for HCOOH decomposition on Pd/WC(0001) surface are presented. Red, orange, blue, gray and white balls represent O atoms, Pd atoms, W atoms, C atoms and H atoms, respectively.

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DFT法研究HCOOH在Pd/WC(0001)上的分解机理

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摘要: 作为便携式电子设备的动力源, 直接甲酸燃料电池(DFAFC)具有燃料跨界范围小、电动势大、甲酸无毒、低温下功率密度大等优点, 因而引起了人们的极大兴趣. DFAFC商业化的主要挑战之一是阳极电催化剂材料的高成本和低CO耐受性. 阳极通常需要高负载的贵金属电催化剂(Pt或Pd)氧化甲酸(HCOOH)以获得所需的电能. 完全电氧化甲酸在Pt和Pd表面上会产生强吸附的CO, 从而降低了Pt或Pd催化剂的活性. Pt和Pd储量少且价格昂贵, 减少Pt和Pd含量且保持催化性能的燃料电池催化剂一直是研究者的奋斗目标.

本文用周期性密度泛函理论(DFT)系统地研究了WC负载的单分子层Pd (Pd/WC(0001))催化剂对甲酸的分解机理, 这可为所需的反应路径设计、筛选催化剂提供指导.

Trans-HCOOH通过C–H, O–H, C–O键的活化发生分解. 关于吸附, 确定了可能反应中间体的最稳定吸附构型. trans-HCOOH, HCOO, mHCOO, cis-COOH, trans-COOH, CO, H₂O, OH和H的吸附过程是化学吸附, 而cis-HCOOH和CO₂与Pd/WC(0001)表面的相互作用较弱, 是物理吸附. 此外, 提出了trans-HCOOH分解的不同途径来探索分解机理. trans-HCOOH中O–H, C–H和C–O键的活化能垒分别为0.61, 0.77和1.05 eV, O–H键断裂的能垒最小, 则trans-HCOOH优先通过O–H键断裂生成HCOO. 双齿HCOO是HCOOH分解的主要中间体, 它可以转变为单齿HCOO, 这条路线生成CO₂的能垒比双齿HCOO的低0.04 eV. CO₂是HCOO主要解离产物, 这一步是总反应的决速步骤. 对于cis-COOH和trans-COOH, CO是其主要解离产物. 此外, trans-HCOOH也能直接生成CO, 但克服的能垒较大. 在Pd/WC(0001)表面上分解trans-HCOOH的最有利途径是HCOOH→HCOO→CO₂, 其中HCOO脱氢形成CO₂的步骤是速率决定步骤.

本文提供了HCOOH在Pd/WC(0001)表面上分解的活性中间体、能垒和机理的推测, CO形成主要是通过cis-COOH、trans-COOH及HCO的分解, CO₂的形成主要是通过HCOO的分解, CO₂占主导. 该结论与Pd(111)面上甲酸分解结果一致, 说明WC作为Pd载体没有改变Pd对甲酸的催化性能, 但降低了Pd的使用量.

综上, 本文阐明了WC负载单分子层Pd催化剂上甲酸催化分解机理, 得出甲酸分解的最佳反应路径, 为直接甲酸燃料电池设计低贵金属含量、高活性的负载型Pd催化剂提供了理论指导; 可用于预测不同载体负载Pd催化剂的性能, 大大减少实验成本, 以验证提出的实验假设.

关键词: 密度泛函理论; 甲酸; 直接甲酸燃料电池; WC(0001)负载单分子层Pd; 分解机理

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