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Article

Density functional theory calculations on single atomic catalysis: Ti-decorated $\text{Ti}_3\text{C}_2\text{O}_2$ monolayer (MXene) for HCHO oxidation

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ABSTRACT

Formaldehyde (HCHO) is a common indoor pollutant, long-term exposure to HCHO may harm human health. Its efficient removal at mild conditions is still challenging. The catalytic oxidation of HCHO molecules on a single atomic catalyst, Ti-decorated $\text{Ti}_3\text{C}_2\text{O}_2$ (Ti/ $\text{Ti}_3\text{C}_2\text{O}_2$) monolayer, is investigated by performing the first principles calculations in this work. It demonstrates that Ti atoms can be easily well dispersed at the form of single atom on $\text{Ti}_3\text{C}_2\text{O}_2$ monolayer without aggregation. For HCHO catalytic oxidation, both Langmuir-Hinshelwood (LH) and Eley-Rideal (ER) mechanisms are considered. The results show that the step of HCHO dissociative adsorption on Ti/ $\text{Ti}_3\text{C}_2\text{O}_2$ with activated O_2 can release high energy of 4.05 eV based on the ER mechanism, which can help to overcome the energy barrier (1.04 eV) of the subsequent reaction steps. The charge transfer from *OH group to CO molecule (dissociated from HCHO) not only promotes *OH group activation but also plays an important role in the H_2O generation along the ER mechanism. Therefore, HCHO can be oxidized easily on Ti/ $\text{Ti}_3\text{C}_2\text{O}_2$ monolayer, this work could provide significant guidance to develop effective non-noble metal catalysts for HCHO oxidation and broaden the applications of MXene-based materials.

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1. Introduction

Formaldehyde (HCHO) as a common aldehyde, frequently found in households, offices, building materials and manufacturing industries, has been attracting immense concerns as one of the most toxic indoor air pollutants [1]. Long-term exposure to HCHO may cause chest congestion, skin allergies, mucus membrane irritation of lung, nasal and eyes and even cancer [1,2]. Thus, considerable works for removing HCHO have aroused extensive attention from both experimentalists and

theoreticians.

Generally, there are two methods to eliminate HCHO: adsorption and catalytic oxidation. It has been known that adsorption is one of the most popular and efficient procedures. Different adsorbents, such as MOF [3], α -zirconium phosphate [4], Al/ C_2N [5,6], Al/graphene [7] and Ti/graphene [8], have been reported to be able to adsorb HCHO effectively. However, the removal efficiency was not satisfying as expected owing to their limited capacity, and the removal efficiency decreases gradually after a period of time because of the deactivation of

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active adsorption sites in adsorbents. Catalytic oxidation, which includes photo-catalytic and direct oxidation, is recognized as a more efficient technology for HCHO treatment, especially for the treatment of low concentration HCHO. For the direct oxidation, different catalytic systems, such as Au/CeO₂ [9], Pt/TiO₂(101) [10] and Au/FeO_x [11], have been found to have a good degradation efficiency on HCHO direct oxidation. On the other hand, photo-catalytic oxidation (PCO) systems have also attracted great attention due to its mild reaction condition and non-selectivity [12], such as TiO₂ [13], g-C₃N₄/TiO₂ [14], F/CN [15] and Fe/WO₃ [16] have been reported to be able to generate highly active species (*e.g.* ·OH, ·O₂⁻, *etc.*) by illuminating UV or visible light to degrade HCHO at ambient temperature. Therefore, PCO is considered as a promising method for HCHO elimination. PCO can eliminate VOCs with simple requirement on reaction conditions, but it requires photo irradiation to generate electron-hole pairs [12]. Different from the photo-catalysis, direct oxidation without photo irradiation normally eliminates VOCs at higher temperature, mostly ranging from 100 to 400 °C [17]. In this work, we focus on direct oxidation of HCHO, and aim to reduce the oxidation temperature as low as possible.

Recently, explosive growth in research on the oxidation of HCHO by exploiting single metal atom supported on different substrates have raised intensive attention due to their high activity, selectivity and stability. Noble metal catalysts, such as Au [18,19], Pt [1,20–23], Ag [24] and Pd [25], have been proven to have a high efficiency for HCHO oxidation. However, the high cost of noble metals limits their wide spread applications. Therefore, we focus on developing catalysts for HCHO oxidation with high efficiency at low temperature as well as low cost, *i.e.* high efficient non-precious metals catalysts are preferred, *e.g.* Cu [26] and Mo [27] systems. Besides, the amount of the metal elements in single metal atom catalytic systems (SACs) used can be reduced remarkably, the cost can be further reduced, and the catalytic efficiency might be improved further based on the fact that reducing the size of metals to a single atom can enhance the activities significantly, such as in Pd/Mo₂CO₂ [28], Ti/FeO_x [29], Ti/Graphdiyne [30], Al/graphene [31], Pt₁/FeO_x [32], Ir₁/FeO_x [33,34] and Pt/graphene [35,36].

The activity and stability of SACs not only depend on the species of single atom, but also depend on the supported materials. Two-dimensional (2D) materials are known as great platforms for chemical reactions due to their high specific surface area. Many 2D materials, such as graphene [37], MOFs [38], hexagonal BN [39] and g-C₃N₄ [40], have been investigated as promising materials for methanol electro-oxidation, methane storage, benzyl alcohol oxidation and benzene oxidation, respectively. Very recently, a new class of 2D materials, MXene, which was first proposed in 2011 [41–43], has attracted worldwide attention due to their unique morphologic, outstanding electrical, thermoelectric, superconductive, optical and catalytic properties [44,45]. MXene thus has wide applications as sensors [46,47], catalysts [28,48,49], energy storage materials [50,51] and capacitors [52].

Generally, MXene phases could be successfully obtained by

etching MAX phases. MAX phases are described by a general formula of M_{n+1}AX_n (*n* = 1, 2, or 3), where “M” denotes early *d* transition metal, “X” represents C and/or N, and “A” mainly represents an A-group (mostly IIIA and IVA) element. Because the bonds between M and A are weaker than the M-X bonds, it is easy to separate MXene from MAX after etching A layers from MAX phase by immersing MAX to HF solution [41]. But free-standing surfaces of MXene monolayer are always inevitably terminated by functional groups (OH, F and O, *etc.*). It has been reported that the energies of M₂CT₂ (M = Ti, Zr and Hf, T = O, OH or F) with presence of F or OH group were obviously weaker than those of M₂CT₂ with -O termination, which demonstrates that the -O terminated MXenes are more stable than those decorated by the F or OH [53]. In addition, MXene saturated with O, and/or OH groups was considered to be more stable, because -F termination on MXene would be replaced by OH groups when they are washing and/or storing in water [41]. Moreover, Zhang et al. [48] proposed that -OH terminated Ti₃C₂ would transfer into -O terminated structure after high temperature treatment. Thus, MXene with O termination is preferred in experimental synthesis.

As a representative MXene, Ti₃C₂O₂, not only possesses high-surface-area and unique morphologies but also exhibits strong stability and excellent surface properties [54]. The outer surface of Ti₃C₂O₂ is fully terminated by O functional groups, indicating that Ti₃C₂O₂ would have potential to build strong interaction with various metals [55]. Moreover, SACs could not only maximize the efficiency of metal utilization but also offer a considerable method to modulate the stability, selectivity and activity of SACs [36]. When a single atom is strongly anchored onto high specific surface supports, SACs would provide a great potential to significantly tune the catalytic performances, which is critical to improve efficiency during the catalytic reactions, such as Ti/CeO₂ [56] and Pt₁/FeO_x [32] for CO oxidation, Mn/CeO₂ [57] for HCHO oxidation. Considering the above outstanding properties of Ti₃C₂O₂, it is anticipated that it should be a promising candidate as the substrate in SACs for HCHO oxidation.

In this work, we will perform first-principles calculations to elucidate the reaction mechanism of HCHO oxidation on a new SACs catalyst, single metal atom decorated on Ti₃C₂O₂ monolayer. The charge transfer of adsorbates and the energy barriers of the reaction are analyzed, and the corresponding mechanisms are systematically investigated. This study would provide theoretical guidance for designing effective non-noble metal nano-catalysts for HCHO oxidation and shed light on prospects for MXene applications in the area of pollutants catalytic degradation.

2. Computational details

The spin-unrestricted density functional theory (DFT) calculations are performed using Dmol³ module in Materials Studio software [58]. The generalized gradient approximation (GGA) with Perdew-Burke-Ernzerhof (PBE) is used as the exchange-correlation functional [59]. The method proposed by Tkatchenko and Scheffler (TS method) for DFT-D correction is

chosen to involve the weak van der Waals interaction [60]. DFT Semi-core Pseudopotentials (DSPPs) [61] core treatment is used for relativistic effects and double numerical plus polarization (DNP) [62] is adopted as the basis set. We take an energy of 10^{-5} Hartree (1 Hartree = 27.21 eV) as the convergence tolerance [31], and the maximum allowed force and displacement are 0.002 Ha/Å and 0.005 Å, respectively. A smearing parameter of 0.005 Ha is applied to accelerate structure convergence.

For the phonon calculation, the first-principles investigations of the phonon dispersion are performed by using the linear response [63,64] method in CASTEP module [65,66]. The interactions between the electrons and core ions are adopted by utilizing norm-conserving pseudopotentials [67].

To investigate the minimum energy pathway for HCHO oxidation on Ti/Ti₃C₂O₂, linear synchronous transit/quadratic synchronous transit (LST/QST) [68] and nudged elastic band (NEB) [69] tools in Dmol³ module are used. In the simulation, a slab model of $3 \times 3 \times 1$ supercell is used to represent a single layer Ti₃C₂O₂, and a 25 Å [70] vacuum above the layer is taken to minimize the interlayer interaction. The Brillouin zone (BZ) is sampled by using $5 \times 5 \times 1$ k-point grid for geometry relaxation or density of states (DOS) calculations. To obtain more accurate calculation result, all atoms are allowed to relax until atomic forces were less than 0.002 Ha/Å. To calculate the Mulliken charge, population analysis was used. GGA-PBE is used in CASTEP module to calculate the electron orbitals of Ti atom, the free/adsorbed HCHO and O₂ molecules. For the calculations of DOS and electron orbitals, the energy cut-off is set as 340 eV.

The binding energy (E_b) and the adsorption/desorption energy ($E_{\text{ads/des}}$) of metal atoms or adsorbents are calculated by the following equations:

$$E_b = E_{\text{metal/MXene}} - E_{\text{MXene}} - E_{\text{metal}} \quad (1)$$

$$E_{\text{ads/des}} = E_{\text{total}} - E_{\text{substrate}} - E_{\text{adsorbate}} \quad (2)$$

where $E_{\text{metal/MXene}}$, E_{MXene} , E_{metal} , E_{total} , $E_{\text{substrate}}$ and $E_{\text{adsorbate}}$ represent the total energies of metal/Ti₃C₂O₂, the Ti₃C₂O₂ monolayer, the isolate atom in the same slab, the substrate and adsorbate system, the isolate substrate and the free molecule in the same slab, respectively. The reaction energy barrier (E_{bar}) and reaction energy (ΔE) are defined by the following equations:

$$E_{\text{bar}} = E_{\text{TS}} - E_{\text{IS}} \quad (3)$$

$$\Delta E = E_{\text{FS}} - E_{\text{IS}} \quad (4)$$

where E_{IS} , E_{TS} and E_{FS} are the energy of the initial, transition and final states, respectively. According to this definition, the negative and positive ΔE values represent exothermic and endothermic reactions, respectively.

The energetic span (δE) model was employed to elucidate the efficiency of the catalytic cycles. According to the literature [71], there were only two states can determine δE , i.e., determining transition state (DTS) and determining intermediate state (DIS), respectively. Furthermore, the smaller the energetic span is, the faster the reaction would be. δE is shown as:

$$\delta E = \begin{cases} T_{\text{DTS}} - T_{\text{DIS}} & \text{if DTS after DIS} \\ T_{\text{DTS}} - T_{\text{DIS}} + \Delta G_r & \text{if DTS after DIS} \end{cases} \quad (5a)$$

$$\delta E = \begin{cases} T_{\text{DTS}} - T_{\text{DIS}} & \text{if DTS after DIS} \\ T_{\text{DTS}} - T_{\text{DIS}} + \Delta G_r & \text{if DTS after DIS} \end{cases} \quad (5b)$$

where T_{DTS} , T_{DIS} and ΔG_r in Eq. (5) represent the total energy of determining transition state, determining intermediate state

and the energy of the reaction, respectively.

3. Results and discussion

3.1. Geometry and stability of single Ti on Ti₃C₂O₂ monolayer

First, the geometries of Ti₃C₂ monolayer and its oxygenated counterpart (Ti₃C₂O₂) are relaxed. As shown in Fig. 1(a), all atoms in Ti₃C₂ monolayer are located between the Ti-(1)-C-Ti-(2)-C-Ti-(1) quintuple layers forming an edge-shared Ti₆C octahedral. Besides, there are three different possible types of O-terminated Ti₃C₂ due to different O sites, as shown in the Fig. 1(b)–1(d). For type I, O atoms are located on the hollow sites between three neighbouring C atoms and point directly toward the Ti-(2) atom layer on the both sides of the Ti₃C₂ layer. For type II, O atoms are located above the top of C atoms. In the case of type III, the configuration can be regarded as a combination of the previous two structures and forming an asymmetric arrangement, where the O atoms are placed at the top of C atoms on the top side and at the hollow site of C atoms on the bottom side. As shown in Fig. S1, the band structure of three different types of Ti₃C₂O₂ monolayer were also calculated, and the result demonstrated that all three types are metallic, and the calculated metallic behaviours for these 3 different Ti₃C₂O₂ monolayer are in good agreement with reported results [47]. To investigate the stability of the Ti₃C₂O₂ monolayer, the total energies of the three different types of O-terminated Ti₃C₂ were calculated (Table S1). The results confirm that the most stable type is type I-Ti₃C₂O₂, which has the lowest total energy and is consistent with reported results [50]. Therefore, our calculations are focused on type I-Ti₃C₂O₂ in the following.

For single atom catalysis system, it is challenging to obtain well dispersed single atoms on substrate due to the surface atom aggregation into cluster. Therefore, to investigate which metal is suitable for SAC on the Ti₃C₂O₂ surface, a series of no-

Fig. 1. (a) Top and side views of the geometry of Ti₃C₂ monolayer; Top and side views of the optimized configurations of type I-Ti₃C₂O₂ (b), II-Ti₃C₂O₂ (c), and III-Ti₃C₂O₂ (d). The letters a, b and c in the top view of type I-Ti₃C₂O₂ represent the representative anchoring sites of Ti atom. The sliver, gray and red balls are Ti, C and O atoms, respectively.

ble and non-noble metals anchored on the $\text{Ti}_3\text{C}_2\text{O}_2$ surface were calculated. The corresponding binding energy E_b and charge transfer by Mulliken analysis are shown in Table 1. The results show that Ti, V, Cr, Ni and Hg have higher binding energy compared with their corresponding cohesive energy, while Ti has the strongest binding energy and also presents obvious electrons transfer between the Ti atom and the $\text{Ti}_3\text{C}_2\text{O}_2$ surface. This indicates that the Ti atom can be best dispersed on the $\text{Ti}_3\text{C}_2\text{O}_2$ surface due to the highest binding energy with modest cohesive energy. Therefore, Ti atoms can be easily anchored on the $\text{Ti}_3\text{C}_2\text{O}_2$ surface without aggregation. It is worthy to note that different adsorption sites on the $\text{Ti}_3\text{C}_2\text{O}_2$ surface (the top of C atom (Site *a*), the top position of Ti (1) atom (Site *b*) or the top site of O atom (Site *c*) as shown in Fig. 1b) have been considered for the different metal atoms adsorption, and the results for the most favourite adsorption configurations are shown in Table 1. On the other side, the electronegativity of the Ti atom is 3.46 eV [72], which is the lowest among the single-metal (as shown in Table S2). This suggests more electrons loss from Ti atoms to $\text{Ti}_3\text{C}_2\text{O}_2$, which is also confirmed by the most positive atomic charges of Ti atom as list in Table 1. This may explain why the Ti atoms can be anchored on the $\text{Ti}_3\text{C}_2\text{O}_2$ surface easily. Moreover, Ti element already exists in the $\text{Ti}_3\text{C}_2\text{O}_2$ substrate, it may be easy to be decorated on $\text{Ti}_3\text{C}_2\text{O}_2$ surface during the preparation of $\text{Ti}_3\text{C}_2\text{O}_2$ in experiment. Furthermore, Ti element is an environmentally friend non-noble metal, which satisfies the requirements of green, efficient and sustainable development catalysts. Therefore, Ti atom is selected as the dispersed single atom on $\text{Ti}_3\text{C}_2\text{O}_2$ surface as the catalyst in the following calculations.

Then the structural and electronic properties of single Ti atom decorated on $\text{Ti}_3\text{C}_2\text{O}_2$ were discussed. 3 representative anchoring positions located above 3 neighboring oxygen atoms are considered. As indicated in Fig. 1(b), the Ti atom was located at three different typical sites, sites *a*–*c*. After geometry optimization, the binding energies and Mulliken charge of the deposited Ti atom at 3 different positions of $\text{Ti}_3\text{C}_2\text{O}_2$ were calculated (as shown in Table 1). The results demonstrate that the

most stable site is Site *a* with the strongest binding energy of -8.36 eV, and 1.12 |e| is transferred from the Ti atom to the $\text{Ti}_3\text{C}_2\text{O}_2$ surface.

To further confirm the stability of Ti atoms on the $\text{Ti}_3\text{C}_2\text{O}_2$ surface, the diffusion behavior of the anchored Ti atom on Site *a* to its nearest Site *a* on $\text{Ti}_3\text{C}_2\text{O}_2$ monolayer was examined. The corresponding diffusion pathway of the Ti atom was shown in Fig. S2, and the result demonstrated that the barriers for the rate-limiting step in the diffusion is as high as 1.66 eV, which demonstrates that the Ti atom is stable and the surface diffusion is difficult to happen, thus avoiding the aggregation of Ti atoms. Moreover, a second Ti atom was added on top of the first anchored Ti to further study the possibility of aggregation, and the corresponding binding energy and Mulliken charge were investigated (Fig. S3 and Table S3). The result indicated that the binding energy of the second Ti is only -1.40 eV, which is much lower than that of the first Ti atom (-8.36 eV). In addition, the binding energy of the first Ti atom at Site *a* is obviously much stronger than the cohesive energy of Ti element of -4.85 eV/atom [73]. Therefore, Ti atoms can be easily well dispersed at the form of single atom on $\text{Ti}_3\text{C}_2\text{O}_2$ monolayer without aggregation.

To understand the strong binding of the Ti atom on $\text{Ti}_3\text{C}_2\text{O}_2$ monolayer, the projected density of states (PDOS) were calculated, and the result are shown in Fig. 2. It can be distinctly observed from the PDOS that there is an intense hybridization above the Fermi level at the energy ~ 1 eV and below the Fermi level -6 eV between the 3*d*-orbital of the anchored Ti atom and the 2*p*-orbital of O atoms (top O). Furthermore, the Mulliken analysis (which is shown in Table S4) demonstrates that there would be charge transfer from the 3*d*-orbital of the anchored Ti atoms to the 2*p*-orbital of the O atoms, indicating that the interaction between the Ti atoms with the $\text{Ti}_3\text{C}_2\text{O}_2$ monolayer is quite strong.

3.2. HCHO and O_2 adsorption on Ti/ $\text{Ti}_3\text{C}_2\text{O}_2$

As mentioned in the introduction, direct oxidation is a

Table 1

The binding energies E_b , Mulliken charge (|e|) and cohesive energy of single-metal atom at different adsorption sites on the $\text{Ti}_3\text{C}_2\text{O}_2$ surface.

Metal	E_b (eV)			Charge (e)			Cohesive energy (eV/atom)
	Site <i>a</i>	Site <i>b</i>	Site <i>c</i>	Site <i>a</i>	Site <i>b</i>	Site <i>c</i>	
Au	-0.98	-0.45	-1.24	+0.34	+0.32	+0.31	-3.81
Ag	-2.03	-1.97	-1.76	+0.47	+0.45	+0.46	-2.95
Ru	-3.72	-3.81	-3.43	+0.69	+0.70	+0.69	-6.74
Rh	-3.73	-3.03	-2.86	+0.50	+0.48	+0.48	-5.75
Pt	-1.93	-1.03	-2.42	+0.47	+0.40	+0.47	-5.84
Pd	-2.00	-1.76	-1.44	+1.04	+1.03	+1.00	-3.89
Ti	-8.36	-7.70	-7.70	+1.12	+1.14	+1.14	-4.85
V	-6.11	-5.76	-5.60	+0.90	+0.89	+0.87	-5.31
Cr	-4.11	-4.03	-3.81	+0.66	+0.61	+0.64	-4.10
Co	-4.26	-4.11	-3.86	+0.71	+0.72	+0.70	-4.39
Ni	-4.72	-4.56	-3.89	+0.55	+0.55	+0.56	-4.44
Cu	-2.77	-2.07	-1.04	+0.52	+0.50	+0.47	-3.49
Zn	-1.11	-0.52	-0.34	+0.73	+0.71	+0.74	-1.35
Cd	-0.89	-0.31	-0.57	+0.60	+0.58	+0.54	-1.16
Hg	-0.49	-0.78	-0.34	+0.10	+0.12	+0.09	-0.67

Fig. 2. PDOS of 3d-orbital of the anchored Ti atom and the 2p-orbital of top O atoms on the Ti/Ti₃C₂O₂ surface. The pink dashed line indicates the Fermi level.

promising way for the treatment of low concentration HCHO. Therefore, it is important to understand the adsorption behaviors of the reaction species (O₂ and HCHO molecules) and the corresponding oxidation pathway on the surface of Ti/Ti₃C₂O₂.

3.2.1. HCHO adsorption on Ti/Ti₃C₂O₂

After considering all possible adsorption configurations of O₂ or HCHO molecule on the Ti/Ti₃C₂O₂ surface, Figs. 3(a) and 3(b) show the favorable configurations of HCHO and O₂ adsorption on Ti/Ti₃C₂O₂. Fig. 3(a) shows that the HCHO molecule is chemically adsorbed and parallel to the Ti/Ti₃C₂O₂ surface, and the O atom is placed on the top site of the anchored Ti atom. The corresponding adsorption energies and Mulliken charge of HCHO adsorption on the Ti/Ti₃C₂O₂ surface are provided in Table S5. From the table, it is known that ~ 0.18 |e| is transferred from the Ti/Ti₃C₂O₂ surface to the HCHO molecule, and the adsorption energy of HCHO is quite strong (-2.03 eV), which matches the configuration in Fig. 3(a) with chemical bonds formation between the HCHO molecule and the Ti/Ti₃C₂O₂ surface. The PDOS and orbitals for the absorbed HCHO as well as the corresponding free isolated HCHO molecule are exhibited in Fig. 3(c), showing full occupation of the 4 orbitals after adsorption. According to Fig. 3(c), it is found that the 5 δ orbital is mainly contributed by the C–O bond. This suggests that the HCHO molecule takes the role as an electron acceptor since the C–O bond is pointed to the anchored Ti atom (transfer electrons to the HCHO molecule), which is consistent with the above Mulliken charge transfer analysis. In addition, compared with the free HCHO, the intensity of 5 δ peak is reduced obviously and it shifts 1.04 eV to the left in the absorbed system, which shows that the C–O bond donates its 5 δ electrons to the Ti-3d states and shows the back-donation of Ti-3d electrons to HCHO-2 π^* states (the electrons of the 2 π^* orbital increase from half-full state to almost full state). This is also in agreement with Mulliken analysis results of the absorbed molecule accepting 0.18 |e| electrons from the deposited Ti atom. From the PDOS, we can also see the strong hybridization of the decorated Ti atom with the orbitals of 1 π and 5 δ for the absorbed HCHO.

Fig. 3. A schematic illustration of top and side views of the optimized configurations of one HCHO (a) and one O₂ molecule (b) adsorbed on the Ti/Ti₃C₂O₂ surface; PDOS and orbitals of one HCHO (c) and one O₂ (d) adsorbed on the Ti/Ti₃C₂O₂ surface and the corresponding free HCHO and O₂ molecules, where 4 different electrons orbitals are exhibited by arrows. The Fermi level is shown by the pink dashed lines, which is set to be zero.

3.2.2. O₂ adsorption on Ti/Ti₃C₂O₂

After considering all the representative adsorption configurations, the O₂ molecule prefers to be absorbed on the Ti/Ti₃C₂O₂ surface with a slightly tilted angle, as shown in Fig. 3(b), the O=O bond length is 1.45 Å and the adsorption energy is -3.48 eV. To understand the stability and chemical activity as well, the dissociative adsorption of an O₂ on the Ti/Ti₃C₂O₂ surface was investigated, and the dissociation pathway is shown in Fig. S4. It is found that the dissociated two O atoms attached on the anchored Ti atom with slightly shortened Ti–O bond length from 1.82 to 1.70 Å. Meanwhile, the distance between the two O atoms is enlarged from 1.45 to 2.74 Å. The results indicate the preference of the dissociative adsorption of O₂ molecules on the Ti/Ti₃C₂O₂ surface as well as relatively low dissociative energy barrier (0.78 eV) is found, which means that the dissociation of O₂ can occur spontaneously on the Ti/Ti₃C₂O₂ surface at room temperature.

As shown in Fig. 3(d), 3 orbitals (4 δ , 5 δ and 1 π) of free O₂

are fully occupied, while $2\pi^*$ anti-bond orbital is half filled due to its beta orbital being located on the right of Fermi level, which agrees with the reported results that O_2 molecule has spin [28,31]. According to Mulliken analysis, $\sim 0.53 |e|$ was transferred from the anchored Ti atom to the O_2 molecule. Hence, the $2\pi^*$ orbital of adsorbed O_2 was almost full near Fermi level. This result is in concordance with a lower peaks presence for $2\pi^*$ orbital of adsorbed O_2 , the electron transform from the $5d$ to $Ti-3d$ orbital then to the $2\pi^*$ orbital of O_2 , which elongates the length of $O=O$ bond length from $1.23 \text{ \AA}$ in free O_2 molecule to $1.45 \text{ \AA}$ in the O_2 molecule adsorbed on $Ti/Ti_3C_2O_2$. Therefore, both O_2 and HCHO molecules can be chemically adsorbed on the anchored Ti atom on $Ti_3C_2O_2$ surface, which provides perfect precondition for the further oxidation of HCHO on the $Ti/Ti_3C_2O_2$ surface.

3.3. Mechanisms of HCHO oxidation on $Ti/Ti_3C_2O_2$

It is well known that there are two possible pathways for CO oxidation: Langmuir-Hinshelwood (LH) and Eley-Rideal (ER) mechanisms [74,75], which both strongly depend on the adsorption energy of O_2 and CO molecules on the catalyst surface. In this work, the both mechanisms were systematically investigated and discussed. In the LH mechanism, HCHO and O_2 molecules are co-adsorbed onto the $Ti/Ti_3C_2O_2$ surface before the reaction starts. For the ER mechanism, an O_2 molecule is first adsorbed and activated, a free HCHO molecule approaches the activated O_2 molecule adsorbed on the $Ti/Ti_3C_2O_2$ surface, then forms an intermediate state product.

3.3.1. LH mechanism

The LH mechanism of HCHO oxidation was firstly considered. To explore the most energetically favorable configuration, all the representative co-adsorption structures of O_2 and HCHO on the $Ti/Ti_3C_2O_2$ surface were considered, and the most stable co-adsorption configuration is shown in Fig. 4 as initial state (IS), where the O_2 molecule approaches the HCHO molecule to form an intermediate $*CH_2O_3$ group, and both the HCHO and O_2 molecules present a slight tilt angle to the $Ti/Ti_3C_2O_2$ surface. In addition, the co-adsorption configuration has stronger adsorption energy (-4.36 eV) than that of individual O_2 (-3.48 eV) or HCHO (-2.03 eV) on the surface, indicating that there is a strong interaction between the anchored Ti atom and the intermediate group. It is understandable that co-adsorption would induce structure deformation of adsorbed molecules as well as the adsorbent, which requires energy consumption. Thus, the co-adsorption energy is smaller than the sum of the individual adsorption energy of O_2 and HCHO. Similar result that the co-adsorption energy is smaller than the sum of adsorption energy of adsorbates was also reported in other systems [28]. Considering the fact that the O_2 molecule has higher adsorption energy than that of the HCHO molecule, we performed a new calculation that a second O_2 molecule replaced the HCHO molecule in the co-adsorption configuration to see which system has stronger adsorption energy. The results indicated that the co-adsorption energy of two O_2 molecules is -3.04 eV , lower than the co-adsorption structure of HCHO and O_2 molecules (-4.36 eV), which means that the HCHO molecule prefers to combine with the O_2 molecule to form the co-adsorption configuration rather than the two O_2 molecules

Fig. 4. The reaction pathway of HCHO oxidation on the $Ti/Ti_3C_2O_2$ surface along the LH mechanism.

co-adsorption. Therefore, we believe that the co-adsorption of HCHO and O₂ molecules on the Ti/Ti₃C₂O₂ surface is preferred.

The O=O bond length of the adsorbed O₂ molecule in IS is also elongated to 1.48 Å, longer than that in free O₂ (1.23 Å) and individual adsorbed O₂ (1.45 Å). Based on the Mulliken analysis, the O atoms in the intermediate group have similar atomic charges to the individual adsorbed O₂ molecule, which confirms the strong chemical adsorption remained. In addition, the double bond in the *O=O group breaks into single O–O bond first and one of O atoms in the adsorbed O₂ molecule forms an O–C bond with the C atom in HCHO molecule, generating a *CH₂O₂ group. Then, intermediate product (MS1) was formed with the single *O–O bond broken and *CH₂O₂ rotating almost 90 degrees. As shown in the reaction pathway cycle in the center of Fig. 4, there is an energy barrier of 0.45 eV from IS to MS1, and this step is an exothermic process, releasing energy of 0.59 eV. The low energy barrier and exothermic process indicate that this step is not only thermodynamically but also kinetically favored. The energy barriers (reaction energy) of each reaction step (TS) are listed in Table S6 and the corresponding configurations of each transition states are shown in Fig. S5, respectively. At the next step, one of the C–H bonds in the *CH₂O₂ group is broken as shown in TS2 in Fig. S5, and the dissociated H atom binds with the remained O atoms and forms an O–H bond, as shown in the intermediate product 2 (MS2). For this step, there is a high energy barrier (1.40 eV) by passing TS2, but releases energy of 2.88 eV from MS1 to MS2. Therefore, this step is not kinetically favored at room temperature due to the high energy barrier but thermodynamically preferable with high energy releasing. Then, via TS3, the second C–H bond is broken and cleaved from the COOH* group, generating a *OCO group (Fig. S5). Then the CO₂ molecule is released from the surface, and the dissociated H atom binds with the O–H bond on the surface, resulting in the generation of a *H₂O group binding with the anchored Ti atom (MS3). For this step, low energy barrier of 0.87 eV is present from MS2 to MS3 as well as an endothermic process by absorbing 0.50 eV. Subsequently, the CO₂ molecule is desorbed from the surface, and the *H₂O group has a tendency of getting close to the desorbed CO₂ molecule, as shown in the MS4. Finally, the formed *H₂O is desorbed and forms a H₂O molecule (FS) is an endothermic process by absorbing 0.63 eV energy. Note that the desorption energy of CO₂ and H₂O are 0.61 and 0.76 eV, respectively.

To better understand the desorption behavior of the obtained CO₂ and H₂O molecules at ambient conditions, the desorption time (τ) is implemented [31], expressed as:

$$\tau = \frac{1}{Ae^{\left(\frac{E_{\text{des}}}{k_B T}\right)}} \quad (6)$$

where A is bond vibration frequency in the range of 10^{12} Hz, k_B is the Boltzmann constant (8.63×10^{-5} eV/K) and T is room temperature 300 K. The calculated desorption time for CO₂ and H₂O molecules in the LH mechanism at ambient temperature are respectively 1.14×10^{-3} and 1.76 s, which indicates that the CO₂ and H₂O molecules are physical adsorption, would desorb easily and facilitate the reaction along the pathway in Fig. 4.

Therefore, from IS to final state (FS), the whole process has

an energy barrier of 1.40 eV and releases energy (ΔG_r) 1.77 eV. Obviously, the DIS of LH mechanism is MS2 (the lowest intermediate state on the Fig. 4), and the DTS is TS2 (the highest energy state). As the TDTS comes after the TDI for this reaction, Eq. 5(a) should be applied. Hence, the δE for LH mechanism is 2.51 eV, which means that the efficiency of catalytic cycles of LH mechanism is unsatisfactory. On the other side, due to the high energy barrier and exothermic reaction, HCHO molecules cannot be oxidized smoothly at room temperature if the energy released in the initial step cannot be fully used for subsequent steps. Note that the energy barrier at the second step for the LH mechanism is high, which is the rate limiting step for the whole process. The results agree well with previous report that the higher energy value difference (1.45 eV) between the adsorption energy of individual HCHO and O₂ molecule is, the higher energy barrier for the HCHO oxidation reaction would be [57]. Once the *COOH group is generated, the pathway of catalytic dissociation: *COOH + *OH $\rightarrow$ CO₂(ad) + H₂O(ad) is pretty easy to occur and the reaction pathway can proceed promptly at low temperature. Note that MS2 has the lowest energy, then the system energy increases. As discussed above, the CO₂ and H₂O molecules would prefer to desorb from the surface promptly, which would increase the entropy (S) of the system sharply. Based on the Gibbs free energy function, $G = H - TS$ where G , T , S are Gibbs free energy, system temperature, and entropy of system, the sharp S increase would facilitate the desorption reaction, which would promote the HCHO oxidation reaction irreversibly along the pathway in Fig. 4.

3.3.2. ER mechanism

The ER mechanism of HCHO oxidation process was also investigated. It is known from the above results that the adsorption of the O₂ molecule is stronger than that of the HCHO molecule, i.e., it is considered that the O₂ molecule may be chemically adsorbed and activated into two O atoms by the catalyst first, then the HCHO molecule approaches to the pre-adsorbed O₂ molecule. After LST and NBE calculation on the O₂ molecule activation process from the state of O₂ molecule adsorption in IS to the state of O=O bond broken (MS1) as shown in Fig. 5, it is found that the dissociation energy barrier of O₂ is relatively low as 0.78 eV as with an endothermic process by absorbing 0.28 eV shown in Fig. 5, which means that this process can react easily at room temperature. Therefore, the favorite adsorption configuration of a HCHO molecule adsorbed on Ti/Ti₃C₂O₂ with two dissociated O atoms is selected as MS2 as shown in Fig. 5. As we can see in the state IS from Fig. 5, a free CO molecule is produced automatically by the dissociation of HCHO without any barrier and releasing energy of 4.05 eV, which is considered as the first step- for HCHO oxidation. Then the remaining two H atoms from the HCHO approach to the two dissociated O atoms and form two *OH groups with O–H bond length 0.99 Å. Considering that the large energy release (4.05 eV) of spontaneous transformation of HCHO to CO, the phonon dispersion of the MS3 system is calculated and shown in Fig. S6 to confirm its structural stability. The result indicated that there is no negative frequency of MS3, which means this catalytic system is stable.

Fig. 5. The reaction pathway of HCHO oxidation on the Ti/Ti₃C₂O₂ surface along the ER mechanism.

Subsequently, as depicted in MS3, a H atom from one of the *OH groups moves to the other *OH group and generating a H₂O molecule (MS4 in ER pathway) by crossing TS2 (the structure is shown in Fig. S7) via a reaction barrier of 1.04 eV. This is an exothermic process with a low reaction energy of 0.15 eV. Meanwhile, the CO molecule gets close to the *H₂O group, and the remaining O atom in the *OH group, which lost a H atom, is still on the decorated Ti with the Ti–O bond length reduced from 1.80 to 1.64 Å. The O atom approaches the free CO molecule to produce a CO₂ molecule (MS5) after overcoming an energy barrier (TS3, as shown in Fig. S7) of 0.92 eV with a low endothermic reaction energy of 0.41 eV from Fig. 5. Finally, the H₂O molecule is released from the Ti/Ti₃C₂O₂ surface by desorption from the Ti/Ti₃C₂O₂ surface. The reaction is endothermic by consuming energy of 0.26 eV. Note that the desorption energies of the CO₂ and H₂O molecules are respectively 0.54 and 0.73 eV. While the calculated desorption times are respectively 1.71×10^{-2} and 5.61 s for CO₂ and H₂O molecule in terms of Eq. (6), which means the easy desorption of both the CO₂ and H₂O molecules from the Ti/Ti₃C₂O₂ monolayer.

When the energetic span approximation is applied to the ER mechanism, it is found that the DTS comes at the TS2 state, while the DIS is MS4 (even though it is not the lowest state of the ER pathway). Consequently, eq. 5b defines the energetic span here and leads to $\delta E = 1.04$ eV for ER mechanism. Compared with δE LH mechanism, the energetic span of ER mechanism is much lower than that of LH mechanism, which means that ER mechanism is preferred in the catalytic cycles.

Note that the energy released (4.05 eV) in the step from MS2 to MS3 could promote the subsequent reaction steps. According to Eq. (6), if the reaction time in the range of 1 min, the reaction temperature is 379 K for the corresponding energy barrier of 1.04 eV for ER pathway, while the reaction temperature is 511 K for LH pathway. The reaction temperature along ER mechanism is much lower than the previous reports in other systems such as, Mn_{0.5}Ce_{0.5}O₂ (546 K) [76], CuO/MnO₂ (453 K) [77], nano-Co₃O₄ (503 K) [78], Pt/TiO₂(101) (1.16 eV) [1]. Even if the energy released from the initial step cannot be directly utilized for the subsequent steps, temperature of the reaction system would increase remarkably due to high energy release, which would promote the subsequent reaction steps. In other words, external heating may not be required, the exothermic reaction of the initial step would increase the system temperature remarkably to smooth the subsequent reaction steps. Therefore, HCHO can be oxidized easily on the single-atom catalysis system Ti/Ti₃C₂O₂ without any noble metal. In addition, MS4 has the lowest energy, and energy increases after this state. As discussed above, the CO₂ and H₂O molecules would prefer to desorb from the surface with low desorption energy, which induces the reaction going through irreversibly along the pathway in Fig. 5. Note that the energy barriers and reaction energy of each reaction step (TS) are listed in Table S7 and the corresponding configurations of each transition states are shown in Fig. S7, respectively. In the LH mechanism as discussed above, the calculated reaction barrier of the rate-limiting step is from MS1 to MS2 with an energy barrier of

1.40 eV. In the ER mechanism, the energy barrier of the rate-limiting step is from MS3 to MS4, the barrier is reduced to 1.04 eV. The ER mechanism would be more preferable for HCHO oxidation on the Ti/Ti₃C₂O₂ not only the huge released energy from the step MS2 to MS3 can support the subsequent reaction steps through increasing the system temperature remarkably, but also the excellent catalytic cycles efficiency ($\delta E = 1.04$ eV for ER mechanism).

Since the step from MS3 to MS4 is the key for the ER oxidation pathway, to better understand the strong interaction between the CO molecule (generated from the HCHO molecule) and the H1 atom (which was from *OH group and labelled in Fig. 6(a)), we calculated the Mulliken charge and PDOS of the CO molecule and H1 atom along the ER mechanism (Fig. 6). In view of the Mulliken charge transform, as shown in Fig. 6(a), the CO molecule has a positive charge (0.05 |e|) while that of the H1 atom is positively charged by 0.41 |e| in MS3. However, it is found that in TS2 the CO obtains 0.03 |e| from the surface by its O atom, and H1 atom loses 0.02 |e|. Note that the charge of C in CO of TS is the same as that of MS3. Obviously, the electron is transferred from the H1 atom of *OH group to the CO molecule, leading a weakened O–H bond, which is beneficial for the movement of H1 atom to the neighboring O atom.

It is interesting that CO can promote such H1 movement

during the ER mechanism, which can be confirmed by the PDOS results. As shown in Figs. 6(b) and (c), compared with the TS2 structure, the sum PDOS of H1 atom in MS3 overlaps with that of the CO molecule over the whole energy region, especially around ~ 7 eV, which demonstrates the fact that the *OH group can be activated by the physical adsorption of the CO molecule. Moreover, CO-2 π^* orbitals in both MS3 and TS2 are empty occupied as shown in Fig. 6d, due to little charge of electron transformation during the oxidation.

In addition, compared with the MS3 structure, the CO-5 δ orbital is increased slightly and the sum PDOS of CO molecule shifts 0.48 eV to the right in the TS2 structure, which is in agreement with Mulliken analysis results that the CO molecule loses 0.03 |e|. Moreover, the H1 atom was pulled towards the CO molecule, then the H1 atom relocates to the other *OH group, leading to the formation of a *H₂O group, as we can see in Fig. 6(a), which offers further proof for the strong interaction between the H1 atom and the CO molecule. Simultaneously, it would facilitate the formation of H₂O molecule. Therefore, the charge transformation of the CO molecule and *OH group were regulated by the Ti/Ti₃C₂O₂ surface, where the charge transfer from *OH group to CO molecule not only promotes *OH group activation but also plays a significant role in the generation of H₂O molecules.

Fig. 6. (a) A schematic illustration of views of the optimized configurations of MS3 and TS2 in ER oxidation pathway; PDOS analysis of CO molecule and H1 atom for ER-MS3 (b) and ER-TS2 (c); (d) The PDOS analysis of CO in ER-MS3 and ER-TS2. The Fermi level is shown by the pink dashed lines, which is set to be zero.

4. Conclusions

In conclusion, the stability of a single transition metal atom decorated on $\text{Ti}_3\text{C}_2\text{O}_2$ monolayer (TM/ $\text{Ti}_3\text{C}_2\text{O}_2$, TM=Au, Ag, Ru, Rh, Pt, Pd, Ti, V, Cr, Co, Ni, Cu, Zn, Cd and Hg) was system investigated by performing the first principles calculations for the first time. Among them, Ti/ $\text{Ti}_3\text{C}_2\text{O}_2$ is the most stable system, and the Ti atoms can be easily well dispersed at the form of single atom on $\text{Ti}_3\text{C}_2\text{O}_2$ surface without aggregation. Subsequently, the single-atom catalysis system of Ti/ $\text{Ti}_3\text{C}_2\text{O}_2$ was utilized for the HCHO catalytic oxidation into CO_2 and H_2O molecules. Both LH and ER oxidation mechanisms were investigated in detail, and it is found that the ER pathway is more preferable with a lower energy barrier (1.04 eV) at the rate limiting step and the huge energy release (4.05 eV) of HCHO dissociative adsorption on Ti/ $\text{Ti}_3\text{C}_2\text{O}_2$ with activated O_2 can promote the subsequent reaction steps as well as good catalytic cycles efficiency (low energetic span 1.04 eV). For ER pathway, the key step is the automatic formation of CO from HCHO, releasing energy of 4.05 eV, which supports subsequent reaction steps. In addition, at the next step, the charge transfer from *OH to the CO molecule (dissociated from HCHO) not only promotes *OH group activation but also plays a significant role in the H_2O generation. Our results demonstrate that the single-atom catalysis system Ti/ $\text{Ti}_3\text{C}_2\text{O}_2$ without any noble metal demonstrates excellent activity for HCHO catalytic oxidation, which could provide theoretical guidance for the experimental development of non-noble metal nano-catalysts for HCHO oxidation. Although Ti/ $\text{Ti}_3\text{C}_2\text{O}_2$ has good performance for HCHO oxidation, the degradation performance for other volatile organic compounds (VOCs) is unclear, the degradation of more VOCs on MXene-based catalysts will be the focus of our future research.

References

- [1] S. Li, X. Lu, W. Guo, H. Zhu, M. Li, L. Zhao, Y. Li, H. Shan, *J. Organomet. Chem.*, **2012**, 704, 38–48.
- [2] C. Zhang, H. He, *Catal. Today*, **2007**, 126, 345–350.
- [3] M. Wen, G. Li, H. Liu, J. Chen, T. An, H. Yamashita, *Environ. Sci. Nano*, **2019**, 6, 1006–1025.
- [4] H. Nakayama, A. Hayashi, T. Eguchi, N. Nakamura, M. Tsuchihashi, *Solid State Sci.*, **2002**, 4, 1067–1070.
- [5] Y. Su, Z. Ao, Y. Ji, G. Li, T. An, *Appl. Surf. Sci.*, **2018**, 450, 484–491.
- [6] Y. Su, W. Li, G. Li, Z. Ao, T. An, *Chin. J. Catal.*, **2019**, 40, 664–672.
- [7] B. Liu, W. Zhao, Q. Jiang, Z. Ao, T. An, *Sustain. Mater. Technol.*, **2019**, 21, e00103.
- [8] H. P. Zhang, X. G. Luo, X. G. Lin, X. Lu, Y. Leng, H. T. Song, *Appl. Surf. Sci.*, **2013**, 283, 559–565.
- [9] M. Jing, W. Song, L. Chen, S. Ma, J. Deng, H. Zheng, Y. Li, J. Liu, Z. Zhao, *J. Phys. Chem. C*, **2017**, 122, 438–448.
- [10] C. Zhang, F. Liu, Y. Zhai, H. Ariga, N. Yi, Y. Liu, K. Asakura, M. FlytzaniStephanopoulos, H. He, *Angew. Chem. Int. Ed.*, **2012**, 51, 9628–9632.
- [11] C. Li, Y. Shen, M. Jia, S. Sheng, M. O. Adebajo, H. Zhu, *Catal. Commun.*, **2008**, 9, 355–361.
- [12] Z. Zhang, Z. Jiang, W. Shangguan, *Catal. Today*, **2016**, 264, 270–278.
- [13] T. N. Obee, R. T. Brown, *Environ. Sci. Technol.*, **1995**, 29, 1223–1231.
- [14] J. Yu, S. Wang, J. Low, W. Xiao, *Phys. Chem. Chem. Phys.*, **2013**, 15, 16883–16890.
- [15] J. Li, W. Zhao, J. Wang, S. Song, X. Wu, G. Zhang, *Appl. Surf. Sci.*, **2018**, 458, 59–69.
- [16] C. Sheng, C. Wang, H. Wang, C. Jin, Q. Sun, S. Li, *J. Hazard. Mater.*, **2017**, 328, 127–139.
- [17] M. S. Kamal, S. A. Razzak, M. M. Hossain, *Atmos. Environ.*, **2016**, 140, 117–134.
- [18] Y. Shen, X. Yang, Y. Wang, Y. Zhang, H. Zhu, L. Gao, M. Jia, *Appl. Catal. B*, **2008**, 79, 142–148.
- [19] S. Liu, P. Jin, D. Zhang, C. Hao, X. Yang, *Appl. Surf. Sci.*, **2013**, 265, 443–451.
- [20] Z. Xu, J. Yu, M. Jaroniec, *Appl. Catal. B*, **2015**, 163, 306–312.
- [21] C. Zhang, H. He, K. I. Tanaka, *Appl. Catal. B*, **2006**, 65, 37–43.
- [22] H. Huang, D. Y. C. Leung, *J. Catal.*, **2011**, 280, 60–67.
- [23] F. Liu, J. Shen, D. Xu, W. Zhou, S. Zhang, L. Wan, *Chem. Eng. J.*, **2018**, 334, 2283–2292.
- [24] Z. Huang, X. Gu, Q. Cao, P. Hu, J. Hao, J. Li, X. Tang, *Angew. Chem. Int. Ed.*, **2012**, 51, 4198–4203.
- [25] H. Huang, X. Ye, H. Huang, L. Zhang, D. Y. C. Leung, *Chem. Eng. J.*, **2013**, 230, 73–79.
- [26] J. Y. Bo, S. Zhang, K. H. Lim, *Catal. Lett.*, **2009**, 129, 444–448.
- [27] C. Robert Dennis, I. M. Potgieter, S. S. Basson, *React. Kinet. Mech. Catal.*, **2011**, 104, 1–7.
- [28] C. Cheng, X. Zhang, M. Wang, S. Wang, Z. Yang, *Phys. Chem. Chem. Phys.*, **2018**, 20, 3504–3513.
- [29] F. Li, Y. Li, C. Z. Xiao, Z. Chen, *ACS Catal.*, **2015**, 5, 544–552.
- [30] Z. Z. Lin, *Carbon*, **2016**, 108, 343–350.

Graphical Abstract

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Density functional theory calculations on single atomic catalysis: Ti-decorated $\text{Ti}_3\text{C}_2\text{O}_2$ monolayer (MXene) for HCHO oxidation

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Formaldehyde, a common indoor air pollutant, which can be magically oxidized to H_2O and CO_2 molecules on a single atomic catalyst (SAC), Ti-decorated $\text{Ti}_3\text{C}_2\text{O}_2$ (MXene) monolayer, at low temperature based on density functional theory study.

- [31] Q. G. Jiang, Z. M. Ao, S. Li, Z. Wen, *RSC Adv.*, **2014**, 4, 20290–20296.
- [32] B. Qiao, A. Wang, X. Yang, L.F. Allard, Z. Jiang, Y. Cui, J. Liu, J. Li, T. Zhang, *Nat. Chem.*, **2011**, 3, 634–641.
- [33] J. Lin, A. Wang, B. Qiao, X. Liu, X. Yang, X. Wang, J. Liang, J. Li, J. Liu, T. Zhang, *J. Am. Chem. Soc.*, **2013**, 135, 15314–15317.
- [34] J. X. Liang, J. Lin, X. F. Yang, A. Q. Wang, B. T. Qiao, J. Liu, T. Zhang, J. Li, *J. Phys. Chem. C*, **2014**, 118, 21945–21951.
- [35] H. Yan, Y. Lin, H. Wu, W. Zhang, Z. Sun, H. Cheng, W. Liu, C. Wang, J. Li, X. Huang, T. Yao, J. Yang, S. Wei, J. Lu, *Nat. Commun.*, **2017**, 8, 1070.
- [36] J. Liu, *ACS Catal.*, **2016**, 7, 34–59.
- [37] Y. Li, W. Gao, L. Ci, C. Wang, P. M. Ajayan, *Carbon*, **2010**, 48, 1124–1130.
- [38] M. Eddaoudi, J. Kim, N. Rosi, D. Vodak, J. Wachter, M. O’Keeffe, O. M. Yaghi, *Science*, **2002**, 295, 469–472.
- [39] L. Wang, L. Shen, X. Xu, L. Xu, Y. Qian, *RSC Adv.*, **2012**, 2, 10689–10693.
- [40] X. Chen, J. Zhang, X. Fu, M. Antonietti, X. Wang, *J. Am. Chem. Soc.*, **2009**, 131, 11658–11659.
- [41] M. Naguib, O. Mashtalir, J. Carle, V. Presser, J. Lu, L. Hultman, Y. Gogotsi, M. W. Barsoum, *ACS Nano*, **2012**, 6, 1322–1331.
- [42] M. Naguib, J. Come, B. Dyatkin, V. Presser, P. L. Taberna, P. Simon, M. W. Barsoum, Y. Gogotsi, *Electrochem. Commun.*, **2012**, 16, 61–64.
- [43] M. Naguib, M. Kurtoglu, V. Preeser, J. Lu, J. Niu, M. Heon, L. Hultman, Y. Gogotsi, M. W. Barsoum, *Adv. Mater.*, **2011**, 23, 4248–4253.
- [44] M. Naguib, V. N. Mochalin, M. W. Barsoum, Y. Gogotsi, *Adv. Mater.*, **2014**, 26, 992–1005.
- [45] P. Eklund, J. Rosen, P. O. Å. Persson, *J. Phys. D: Appl. Phys.*, **2017**, 50, 113001.
- [46] X. F. Yu, Y. C. Li, J. B. Cheng, Z. B. Liu, Q. Z. Li, W. Z. Li, X. Yang, B. Xiao, *ACS Appl. Mater. Interfaces*, **2015**, 7, 13707–13713.
- [47] S. J. Kim, H. J. Koh, C. E. Ren, O. Kwon, K. Maleski, S. Y. Cho, B. Anasori, C. K. Kim, Y. K. Choi, J. Kim, Y. Gogotsi, H. T. Jung, *ACS Nano*, **2018**, 12, 986–993.
- [48] X. Zhang, J. Lei, D. Wu, X. Zhao, Y. Jing, Z. Zhou, *J. Mater. Chem. A*, **2016**, 4, 4871–4876.
- [49] X. Zhang, Z. Zhang, J. Li, X. Zhao, D. Wu, Z. Zhou, *J. Mater. Chem. A*, **2017**, 5, 12899–12903.
- [50] Q. Tang, Z. Zhou, P. Shen, *J. Am. Chem. Soc.*, **2012**, 134, 16909–16916.
- [51] M. Okubo, A. Sugahara, S. Kajiya, A. Yamada, *Acc. Chem. Res.*, **2018**, 51, 591–599.
- [52] M. R. Lukatskaya, O. Mashtalir, C. E. Ren, Y. Dall’Agnese, P. L. Taberna, M. Naguib, P. Simon, M. W. Barsoum, Y. Gogotsi, *Science*, **2013**, 341, 1502–1505.
- [53] H. Zhang, G. Yang, X. Zuo, H. Tang, Q. Yang, G. Li, *J. Mater. Chem. A*, **2016**, 4, 12913–12920.
- [54] N. K. Chaudhari, H. Jin, B. Kim, D. San Baek, S. H. Joo, K. Lee, *J. Mater. Chem. A*, **2017**, 5, 24564–24579.
- [55] Y. Gao, H. Zhuo, Y. Cao, X. Sun, G. Zhuang, S. Deng, X. Zhong, Z. Wei, J. Wang, *Chin. J. Catal.*, **2019**, 40, 152–159.
- [56] L. Yi, C. Wen, G. Yun, G. Lu, Y. Wang, *J. Phys. Chem. C*, **2010**, 114, 9889–9897.
- [57] H. Wu, S. Ma, W. Song, E. J. M. Hensen, *J. Phys. Chem. C*, **2016**, 120, 13071–13077.
- [58] B. Delley, *J. Chem. Phys.*, **2000**, 113, 7756–7764.
- [59] J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.*, **1996**, 77, 3865–3868.
- [60] A. Tkatchenko, M. Scheffler, *Phys. Rev. Lett.*, **2009**, 102, 073005/1–073005/4.
- [61] B. Delley, *Phys. Rev. B*, **2002**, 66, 155125/1–155125/9.
- [62] B. Delley, *J. Chem. Phys.*, **1990**, 92, 508–517.
- [63] S. Baroni, S. De Gironcoli, A. Dal Corso, P. Giannozzi, *Rev. Mod. Phys.*, **2001**, 73, 515–562.
- [64] A. Deb, J. M. Ralph, E. J. Cairns, U. Bergmann, *Phys. Rev. B*, **2006**, 73, 115114/1–115114/9.
- [65] W. Frey, J. Y. Lee, V. Jaeger, *Z. Kristallogr. New Cryst. Struct.*, **2005**, 220, 567–568.
- [66] M. D. Segall, P. J. D. Lindan, M. J. Probert, C. J. Pickard, P. J. Hasnip, S. J. Clark, M. C. Payne, *J. Phys.: Condens. Matter*, **2002**, 14, 2717–2744.
- [67] D. R. Hamann, M. Schlüter, C. Chiang, *Phys. Rev. Lett.*, **1979**, 43, 1494–1497.
- [68] T. A. Halgren, W. N. Lipscomb, *Chem. Phys. Lett.*, **1977**, 49, 225–232.
- [69] G. Henkelman, B. P. Uberuaga, H. Jonsson, *J. Chem. Phys.*, **2000**, 113, 9901–9904.
- [70] Y. Zhao, J. Zhao, *Appl. Surf. Sci.*, **2017**, 412, 591–598.
- [71] S. Kozuch, S. Shaik, *Acc. Chem. Res.*, **2011**, 44, 101–110.
- [72] R. G. Parr, L. J. Bartolotti, *J. Am. Chem. Soc.*, **1982**, 104, 3801–3803.
- [73] C. Kittel, *Introduction to solid state physics*, Wiley New York, 1976.
- [74] H. P. Bonzel, R. Ku, *J. Vac. Sci. Technol.*, **1972**, 9, 663–667.
- [75] B. C. Sales, J. E. Turner, M. B. Maple, *Surf. Sci.*, **1982**, 114, 381–394.
- [76] J. W. Li, K. L. Pan, S. J. Yu, S. Y. Yan, M. B. Chang, *J. Environ. Sci.*, **2014**, 26, 2546–2553.
- [77] J. Pei, X. Han, Y. Lu, *Build. Environ.*, **2015**, 84, 134–141.
- [78] B. Bai, H. Arandiyana, J. Li, *Appl. Catal. B*, **2013**, 142, 677–683.

单原子催化剂Ti/Ti₃C₂O₂催化氧化甲醛的密度泛函理论研究

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摘要: 甲醛是一种比较常见的室内污染物, 长期接触甲醛会危害人体健康. 如何在低温条件下有效去除低浓度甲醛仍然是当前具有挑战性的研究课题. 本文采用第一性原理计算方法研究了甲醛分子在单原子催化剂(Ti原子修饰的单层MXene-Ti₃C₂O₂)表面上的吸附和催化氧化性能. 结果表明, Ti原子在Ti₃C₂O₂表面的结合能和扩散能分别为−8.36和1.66 eV, 说明Ti能够以单原子形式稳定分散在Ti₃C₂O₂表面, 而不会产生团簇现象. 为了研究甲醛和氧气分子在Ti/Ti₃C₂O₂上的吸附机理, 我们计算了分波态密度(PDOS), Mulliken电荷分析以及分子轨道. 结果表明, Ti原子修饰改变了Ti₃C₂O₂表面上的电

荷分布, 甲醛分子和氧气分子都能接受自Ti原子处转移而来的电子成为电子受体, 增强了吸附质和Ti/Ti₃C₂O₂之间的相互作用, 从而加强了吸附能力.

此外, 为了研究甲醛分子在Ti/Ti₃C₂O₂上的催化氧化机理, 我们考虑了Langmuir-Hinshelwood (LH)和Eley-Rideal (ER)两种机理. 结果表明, 无论是从动力学还是热力学角度, ER机理是一种更为理想的催化氧化甲醛的方式, 甲醛分子在已经被氧气活化的Ti/Ti₃C₂O₂上能够自动解离成CO分子, 而两个H原子则和活化的O原子形成两个*OH基团, 并且释放4.05 eV的热量, 从而有助于克服后续反应所要跨越的能垒(1.04 eV). 而从*OH基团到CO分子的电荷转移不仅能够促进*OH基团的活化, 而且也为下一步的水分子的形成也提供了重要作用. 综上所述, 甲醛可以很容易地在单原子催化剂Ti/Ti₃C₂O₂上被氧化. 综上, 本文为开发高效去除甲醛的非贵金属催化剂以及扩大MXene材料应用范围提供重要指导.

关键词: 甲醛氧化; MXene; Ti/Ti₃C₂O₂; 单原子催化剂; 非贵金属催化剂

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