Theoretical studies of MXene-supported single-atom catalysts: Os₁/Ti₂CS₂ for low-temperature CO oxidation

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ABSTRACT We report herein a new sulfur-functionalized MXene Ti₂C (Ti₂CS₂)-supported osmium-metal single-atom catalyst (SAC) Os₁/Ti₂CS₂ with high low-temperature catalytic activity for CO oxidation. Using periodic density functional theory calculations, the most stable SAC, Os₁/Ti₂CS₂, has been screened from a series of group 8–11 transition metal SACs M₁/Ti₂CS₂ (M = Fe, Co, Ni, Cu; Ru, Rh, Pd, Ag; Os, Ir, Pt, Au). The calculations show that it is favorable for O₂ and CO to be coadsorbed on the Os₁ single atom (SA) of Os₁/Ti₂CS₂ and the adsorption energy of the first O₂ molecule is slightly higher than that of CO. Moreover, the termolecular co-adsorption of O₂ + 2CO on Os₁ SA is also possible, which is favorable for CO oxidation on Os₁ SA through a novel three-molecule reaction mechanism. Accordingly, four different catalytic mechanisms, the Langmuir–Hinshelwood (L–H), Eley–Rideal (E–R), termolecular Langmuir–Hinshelwood-A (TLH-A) and termolecular Langmuir–Hinshelwood-B (TLH-B), are systematically studied for CO oxidation by O₂ on Os₁/Ti₂CS₂. The theoretical studies indicate that the TLH-B mechanism is the most feasible for CO oxidation with the reaction barrier energy of only 0.74 eV, which is far lower than for L–H, E–R and TLH-A with barrier energies of 1.06, 1.09 and 1.47 eV, respectively. The results provide fundamental understanding to the surface chemistry of MXene and designing new sulfur-functionalized two-dimensional MXene catalytic nanomaterials.

Keywords: single-atom catalyst, MXene, CO oxidation, termolecular Langmuir–Hinshelwood, 2D nanomaterial

INTRODUCTION

Since the concept of single-atom catalysis was firstly proposed by Zhang, Li, Liu *et al.* in 2011 [1], considerable attention has been paid to this area because of its unique homogeneous structural characteristics of a single-atom (SA) active center and the excellent catalytic performance in heterogeneous catalysis [2–10]. Several reviews [11–15] have summarized the development of single-atom catalysts (SACs), the structure–function relationship between SACs and their catalytic performance, and the diverse applications of SACs in heterogeneous catalysis [16–23]. Over the past decade, SAC has expanded rapidly and the concept of SAC has been further developed into dynamic SACs

[24] and single-cluster catalysts (SCCs) [25,26]. Many studies [27–36] have been devoted to obtaining SACs with high stability, high selectivity and high reactivity [37–39] for thermocatalysis, photocatalysis, electrocatalysis, and photoelectrocatalysis reactions [15,40–43], such as CO oxidation, water gas shift reaction, activation of C–H bonds, photo- and electro-catalytic water splitting, and CO₂ reduction reaction, oxygen reduction reaction, hydrogen evolution reaction, oxygen evolution reaction, hydrogenation reactions, and nitrogen reduction reaction [5,15,43–54].

As is well known, two-dimensional (2D) nanomaterials-supported SACs exhibit great application potential in catalysis, optics, and electrochemistry [55–60] owing to their excellent light absorption and conductivity properties [61–67]. Recently, MXenes composed with transition metal carbides, carbonitrides and nitrides [68], as a new type of multilayer 2D nanomaterial, have received a lot of attention both theoretically and experimentally because of their versatile applications in energy storage, catalysis, sensors, flexible functional materials, etc. [32,69–76]. The general formula of MXene is denoted as M_{n+1}X_nT_x (n = 1–4) [68,77–79], where M is an early transition metal (Ti, V, Cr, Nb, Mo, etc.), X is carbon and/or nitrogen, and T is the surface-terminated species (O, S, F, OH, etc.) [80,81]. Among these terminated MXenes, O- and OH-functionalized MXenes are the most stable. Especially at high temperatures, OH groups will be converted into O terminations. MXenes as a family of inorganic 2D materials have unique properties such as thin layers, excellent electronic conductivity, high stability, wide tunability (M/X/T), and strong binding sites for metal atoms on the surface. They are therefore potentially robust support for synthesizing high-performance SACs.

In our previous study, O-terminated MXene-supported SACs were screened and a promising non-noble-metal SAC with high activity for CO oxidation was obtained using theoretical calculations. While sulfur and oxygen are elements of the same main group, sulfur is less electronegative than oxygen, thus offering opportunity for tuning the catalytic properties of SACs with sulfur-terminated MXenes. Investigating the difference in catalytic performance between O- and S-functionalized MXenes-based SACs can help to discover new catalytic materials for key chemical reactions. Herein, we first screened a series of SAC M₁/Ti₂CS₂ (M = Fe, Co, Ni, Cu; Ru, Rh, Pd, Ag; Os, Ir, Pt, Au) supported by the surfaces of sulfur-functionalized Ti₂C (Ti₂CS₂)

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MXenes by optimizing the geometries of these SACs and calculated the binding energies (BEs) of metal SAs [82]. The selection of these metals is based on the common catalytic features of the middle-to-late transition metals in various important catalytic reactions. The calculations show that $\text{Os}_1/\text{Ti}_2\text{CS}_2$ is the most stable SAC. Furthermore, we systematically investigated the catalytic activity of $\text{Os}_1/\text{Ti}_2\text{CS}_2$ for CO oxidation by considering a series of different reaction mechanisms of Eley–Rideal (E–R), Langmuir–Hinshelwood (L–H), termolecular Langmuir–Hinshelwood–A (TLH–A), and termolecular Langmuir–Hinshelwood–B (TLH–B) based on the different adsorption modes of CO or O_2 and their co-adsorption on $\text{Os}_1/\text{Ti}_2\text{CS}_2$. Bader charge analysis, the partial electron density differences (PEDD) and the density of states (DOS) were also calculated to evaluate the performance of the $\text{Os}_1/\text{Ti}_2\text{CS}_2$ for CO oxidation. Based on these theoretical calculations, a possible TLH–B catalytic mechanism has been proposed because the barrier energy of the rate-determining step of this pathway is only 0.74 eV for CO oxidation, indicating $\text{Os}_1/\text{Ti}_2\text{CS}_2$ is a superb low-temperature catalyst for CO oxidation. This work helps in designing a highly active sulfur-functionalized Ti_2C MXene-supported SAC for CO oxidation at ambient condition.

THEORETICAL METHODS

All the calculations for the geometry and electronic properties of the 2D Ti_2C and the adsorbed states of $\text{M}_1/\text{Ti}_2\text{CS}_2$ ($\text{M} = \text{Fe}, \text{Co}, \text{Ni}, \text{Cu}; \text{Ru}, \text{Rh}, \text{Pd}, \text{Ag}; \text{Os}, \text{Ir}, \text{Pt}, \text{Au}$) were carried out using density functional theory (DFT) with the Vienna *ab initio* simulation package [83,84]. The generalized gradient approximation (GGA) with the Perdew–Burke–Ernzerhof (PBE) exchange–correlation functional was adopted to describe the electron–exchange–correction potential [85–88]. The projector augmented wave (PAW) method was used to describe the electron–ion interaction. The planewave cutoff energy was set to 580 eV with a convergence tolerance of 0.02 eV $\text{\AA}^{-1}$ for the force on all atoms. Periodic boundary conditions were considered along with the growth directions of the 2D materials. A vacuum distance of 14 $\text{\AA}$ was used to maintain the negligible interlayer interaction between the adjacent cells of the periodic 2D materials. $5 \times 5 \times 1$ and $11 \times 11 \times 1$ Monkhorst–Pack grids were used for geometry optimization and DOS calculations, respectively.

The geometries of the initial structure (IS), transition state (TS), intermediate state (IM) and final state (FS) were fully optimized without any symmetry constraints. Vibrational frequency calculations were performed at the same level of theory to ascertain the sole imaginary frequency for all TS species. The dimer method [89] was applied to determine the reaction TS geometries. The reaction activation energy (E_a) and the reaction energy were calculated using $E_a = E_{\text{TS}} - E_{\text{IS}}$ and $\Delta E = E_{\text{FS}} - E_{\text{IS}}$, respectively, where the E_{IS} , E_{TS} and E_{FS} are the energies of the TS, IS and FS, respectively. The BE of metal atoms anchored on the Ti_2C MXene is defined by Equation (1) following the thermodynamics convention. The adsorption energy (E_{ads}) of an adsorbate (X) was calculated through Equation (2). Here $E_{\text{M}_1/\text{Ti}_2\text{CS}_2}$, $E_{\text{X}\cdots\text{Os}_1/\text{Ti}_2\text{CS}_2}$, $E_{\text{Os}_1/\text{Ti}_2\text{CS}_2}$, $E_{\text{Ti}_2\text{C}}$, E_{C} , E_{O} , E_{M} , E_{Os} and E_{X} represent the total energy of the $\text{M}_1/\text{Ti}_2\text{CS}_2$, $\text{X}\cdots\text{Os}_1/\text{Ti}_2\text{CS}_2$ adsorption system, and adsorbate, respectively, in Equation (1).

$$\text{BE}_{\text{M}} = E_{\text{M}_1/\text{Ti}_2\text{CS}_2} - E_{\text{Ti}_2\text{CS}_2} - E_{\text{M}} \quad (1)$$

$$E_{\text{ads}} = E_{\text{X}\cdots\text{Os}_1/\text{Ti}_2\text{CS}_2} - E_{\text{Os}_1/\text{Ti}_2\text{CS}_2} - E_{\text{X}} \quad (2)$$

The differential electron densities of $\text{Os}_1/\text{Ti}_2\text{CS}_2$ and $\text{X}\cdots\text{Os}_1/\text{Ti}_2\text{CS}_2$ adsorption systems are defined by Equation (3), where ρ_{AB} are the electron densities of the entire $\text{Os}_1/\text{Ti}_2\text{CS}_2$ and $\text{X}\cdots\text{Os}_1/\text{Ti}_2\text{CS}_2$, ρ_{A} are the electron densities of Os_1 SAs of $\text{Os}_1/\text{Ti}_2\text{CS}_2$, CO, O_2 or co-adsorption adsorbates of $\text{X}\cdots\text{Os}_1/\text{Ti}_2\text{CS}_2$, and ρ_{B} are the electron densities of Ti_2CS_2 or $\text{Os}_1/\text{Ti}_2\text{CS}_2$.

$$\Delta\rho = \rho_{\text{AB}} - \rho_{\text{A}} - \rho_{\text{B}} \quad (3)$$

RESULTS AND DISCUSSION

Geometry and electronic structure of $\text{Os}_1/\text{Ti}_2\text{CS}_2$

Based on previously calculated primitive cell parameters ($a = b = 3.0379 \text{ \AA}$) of 2D Ti_2C [79], the S atom is here used to terminate both the top and bottom surfaces of Ti_2C . There are three different configurations for S atoms, I (TH_a: face-centered cubic (fcc) hollow), II (TH_b: hexagonal close-packed (hcp) hollow) and III (TH_a at top and TH_b at bottom surfaces), as shown in Fig. S1 of the Supplementary information (SI). The optimized configurations with their relative energies are displayed in Fig. 1. It can be seen that configuration I (Fig. 1a) of Ti_2CS_2 is the most stable structure with the lowest energy. Thus, based on the most stable structure of Ti_2CS_2 , a series of transition metal atoms ($\text{M} = \text{Fe}, \text{Co}, \text{Ni}, \text{Cu}; \text{Ru}, \text{Rh}, \text{Pd}, \text{Ag}; \text{Os}, \text{Ir}, \text{Pt}, \text{Au}$) from groups 8–11 of the Periodic Table are anchored on the surface of Ti_2CS_2 to screen for a possible stable and highly active SAC $\text{M}_1/\text{Ti}_2\text{CS}_2$ for CO oxidation. There are three different anchoring sites on the surface of Ti_2CS_2 as shown in Fig. S2, namely, TH_a for the threefold fcc hollow site, TH_b for the threefold hcp hollow site and Bridge_S for the bridge site between two sulfur atoms. The calculated BEs of metal SAs (BE_{M}) of $\text{M}_1/\text{Ti}_2\text{CS}_2$ are collected in Fig. 2 and Table S1. As seen from Fig. 2 and Table S1, almost all the most stable anchoring sites of different metal SAs ($\text{M} = \text{Fe}$,

Figure 1 Optimized structures and calculated total relative energies of sulfur-functionalized Ti_2C MXenes with different arrangements of the surface atoms: top views of (a) I- Ti_2CS_2 , (b) II- Ti_2CS_2 and (c) III- Ti_2CS_2 ; (a1–c1) side views of I- Ti_2CS_2 , II- Ti_2CS_2 and III- Ti_2CS_2 , respectively.

Figure 2 (a) The calculated binding energy (BE_M) of metal (M) single atoms in each of the most stable SACs of M_1/Ti_2CS_2 . (b) Side and top views of the optimized geometry of Os_1/Ti_2CS_2 . (c) The PDOS of Os-5d (black) and S-3p (purple) states. (d) Side and top views of PEDD, where blue and red refer to an increase and decrease of the electron density, respectively. Isovalue = ± 0.002 a.u. The Fermi level is set to zero.

Co, Ni, Cu; Ru, Rh, Pd, Ag; Os, Pt, Au) are the threefold hcp hollow sites (TH_b) except for Ir, which anchors on a fourfold hollow site formed by four atoms at the surface of Ir_1/Ti_2CS_2 (shown in Fig. S3), and the calculated BE_M ($M = Fe, Co, Ni, Cu; Ru, Rh, Pd, Ag; Os, Pt, Au$) in the SACs M_1/Ti_2CS_2 are -4.10, -4.48, -4.29, -2.85; -5.11, -4.76, -2.80, -1.62; -5.38, -3.78, -1.14 eV, respectively, and -5.29 eV for Ir of Ir_1/Ti_2CS_2 . It follows that Os_1/Ti_2CS_2 , in which Os_1 is at the hcp hollow site, is the most stable due to the highest BE_M (-5.38 eV). Additionally, we further calculated the diffusion barrier of single Os_1 atom to examine its stability, and carried out the periodic energy decomposition analysis (PEDA) of interactions (in eV) between Os_1 and the Ti_2CS_2 surface. It is found that the binding of Os_1 atom on the Ti_2CS_2 surface is dominated by Os-5d and S-3p orbital interactions, as shown in Fig. S4 and Table S2 in SI. Moreover, the calculated Bader charge ($|e|$) of Os_1 of Os_1/Ti_2CS_2 is +0.45 $|e|$, which is close to the Bader charge of Os in the Os-OH cluster [90], showing that the valence state of Os is likely close to +I upon adsorption at the MXene surface.

Furthermore, the interaction between Os_1 SA and its three bonded S atoms (S1, S2 and S3, Fig. 2b) in Os_1/Ti_2CS_2 was investigated and expressed by the partial DOS (PDOS) and the PEDD in Fig. 2c and d, respectively. Fig. 2c shows that the interaction between Os_1 SA and the three bonded S atoms is relatively strong, due to the overlap of Os-5d and S-3p near the Fermi level, which can be further understood by the PEDD of

Os_1/Ti_2CS_2 SAC in Fig. 2d. As seen from Fig. 2d, blue color indicates an area where the electron density has increased; conversely, and red color indicates an area where the density has decreased. The larger electron densities on the three Os-S bonds clearly show the formation of a strong covalent interaction between Os_1 SA and the three S atoms in Os_1/Ti_2CS_2 . Furthermore, the calculated Bader charges of the Os_1 SA and the three bonded S atoms (S1, S2 and S3, Fig. 2b) are +0.45, -0.56, -0.55 and -0.55 $|e|$, respectively, showing that charges are transferring from Os to the three S atoms and the formation of a relatively strong covalent bond with significant ionic bonding characteristic of Os-S in Os_1/Ti_2CS_2 SAC.

CO oxidation mechanism on Os_1/Ti_2CS_2 SAC

Different molecular adsorption modes of CO and O_2 on the surface of Os_1/Ti_2CS_2 SAC may lead to different reaction pathways for CO oxidation. The calculated adsorption energy of O_2 (-2.24 eV) is slightly larger than that of CO (-2.16 eV) on the Os_1 SA, indicating that O_2 is preferably adsorbed. Thus, we first considered the L-H mechanism for the co-adsorption of CO and O_2 on the surface of Os_1/Ti_2CS_2 , and the E-R mechanism for CO to be adsorbed on the surface of Os_1 SA while O_2 is in the gas phase. Based on the possibility of multimolecular adsorption on the surface of Os_1/Ti_2CS_2 SAC, we further investigated two types of trimolecular mechanisms for CO oxidation: TLH-A and TLH-B.

L-H mechanism

The predicted reaction pathway of the L-H mechanism for CO oxidation is presented in Fig. 3. It shows that there are three relatively strong chemical bonds between Os₁ SA and its three surrounding S atoms in the original model (i) with a bond length of 2.161 Å, which is close to the Os-S single bond length [91]. In step ii, O₂ is adsorbed on the Os₁ SA of Os₁/Ti₂CS₂ with the adsorption energy of -2.24 eV, and is significantly activated to peroxide (O₂²⁻, 1.447 Å). Based on the stable structure of O₂ adsorption, the first CO is also adsorbed on the Os₁ SA in step iii. Subsequently, reaction of the co-adsorption of O₂ and CO takes place through the superoxide-like OCOO transition state (TS1, 377i cm⁻¹) with a relatively high barrier energy of 1.06 eV. The two bond lengths (2.069 Å) of Os-O in step iii become longer than those (1.961 and 1.960 Å) in step ii because of the weakening of the interaction between adsorbed O₂ and Os₁ SA originating from CO adsorption. Moreover, the adsorbed O₂ is activated to superoxide (O₂⁻, 1.354 Å) after CO adsorption, with the bond length of O-O changing from 1.447 Å in step ii to 1.354 Å in step iii. Then, the first CO₂ is formed, which is still adsorbed on the surface of Os₁/Ti₂CS₂ with the bond length of O-O increasing from 1.381 Å in TS1 to 1.534 Å in step iv. Furthermore, CO₂ desorbs almost without an energy barrier (0.13 eV) from the surface of Os₁/Ti₂CS₂ through TS2

(124i cm⁻¹) with only one O atom remaining adsorbed on Os₁ SA in step v.

Next, the second CO₂ is formed on the surface of Os₁/Ti₂CS₂ originating from the second CO adsorbing on the Os₁ SA in step vi with a strong interaction between co-adsorbed O and CO with the activation energy of 0.69 eV (TS3, 397i cm⁻¹). For step vii, although the formed CO₂ is still adsorbed on the Os₁ SA, it is easily desorbed from the surface of Os₁/Ti₂CS₂ SAC, requiring only a reaction barrier of -0.29 eV (TS4, 48i cm⁻¹). Finally, the Os₁/Ti₂CS₂ SAC is restored to the original structure.

For the analysis of the entire potential energy profile, the rate-determining step for CO oxidation is the formation of the first CO₂ with the activation energy of 1.06 eV, indicating that CO oxidation is difficult on Os₁/Ti₂CS₂ SAC through the L-H mechanism at room temperature.

E-R mechanism

As the adsorption energy of an O₂ molecule on Os₁ SA of Os₁/Ti₂CS₂ is slightly higher than that of a CO molecule by 0.08 eV, the E-R reaction mechanism based on pre-adsorption of an O₂ molecule is considered for the CO oxidation reaction as well. The predicted potential energy profile is shown in Fig. 4. Based on the structure of O₂ adsorption on the Os₁ SA, the first CO is very weakly adsorbed on the surface of Os₁/Ti₂CS₂ SAC (step iii),

Figure 3 Predicted energy profile and optimized structures of the corresponding stationary states for CO oxidation catalyzed by Os₁/Ti₂CS₂ via the L-H mechanism, in which the TS is marked with red boxes and the relative energies and selected bond lengths are in eV and Å, respectively.

and the calculated adsorption energy of CO is as low as -0.02 eV. Then, the CO in the gas phase attacks one atom of the adsorbed O_2 with a small barrier energy of 0.35 eV (TS1, $435i\text{ cm}^{-1}$), in which the O–O bond is remarkably elongated from 1.447 Å to 1.634 Å and the distance between the O from O_2 and the C from C–O is significantly decreased from 3.129 to 1.893 Å . With the first formed CO_2 desorbing from the surface of Os_1/Ti_2CS_2 , the remaining O atom is still adsorbed on the Os_1 SA (step iv). Similarly, the calculated adsorption energy of the second CO in the gas phase is also -0.02 eV, showing that the strength of CO adsorption is rather weak. When the second CO approaches the remaining O atom, the distance of the C atom of CO and the remaining O atom decreases from 3.166 to 1.548 Å ; accordingly, the bond length of Os–O increases from 1.723 to 2.398 Å (TS2, $665i\text{ cm}^{-1}$). Passing over TS2 with the barrier energy of 1.09 eV, the second CO_2 is formed and desorbed from the surface of Os_1/Ti_2CS_2 SAC.

In this process, the second CO_2 is formed with a high barrier energy of 1.09 eV, indicating that it is the rate-determining step for CO oxidation through the E–R mechanism. Therefore, with this E–R mechanism it is also relatively difficult for the CO oxidation reaction at room temperature.

Trimolecular mechanisms

Based on the stable structure of co-adsorption of CO and O_2 on

the Os_1 SA of Os_1/Ti_2CS_2 , the adsorption of a third molecule of CO or O_2 is further considered, and the optimized structures are displayed in Fig. S5. As seen from Fig. S5g and S5f, the adsorption energy of the CO is -1.36 eV, which is much higher than that (-0.39 eV) of the O_2 , indicating that the tri-molecular adsorption of O_2+2CO is favored. Note that, while energetically O_2 adsorption is favored at first, which makes O_2+2CO co-adsorption kinetically preferred, the co-adsorption of three CO molecules is thermodynamically competitive and should be evaluated when considering comprehensive kinetics of this reaction. The predicted energy profiles of two trimolecular L–H (TLH) mechanisms for CO oxidation, named TLH-A and TLH-B, are shown in Figs 5 and 6, respectively. Based on the stable structure of Os_1/Ti_2CS_2 (step i), O_2 molecules are preferentially adsorbed laterally on the Os_1 SA and the calculated adsorption energy of O_2 is -2.24 eV (step ii), and the first CO also tends to be adsorbed on the Os_1 SA, forming the co-adsorbed CO + O_2 (step iii). Successively, the second CO molecule continues to be adsorbed on Os_1 SA and gradually approaches an O atom in the adsorbed O_2 , leading to an Os–O bond cleavage (step iv). This interaction between CO and O atom eventually results in the activation of the adsorbed O_2 and increase of the Os–O bond distance (step v) via the transition state (TS1) with only one imaginary frequency of $261i\text{ cm}^{-1}$. In this reaction step, the bond length of O–O increases from 1.372 to 1.482 Å , whereas the

Figure 4 Predicted energy profile and optimized structures of the corresponding stationary states for CO oxidation catalyzed by Os_1/Ti_2CS_2 via the E–R mechanism, in which the TS is marked with red boxes and the relative energies and selected bond lengths are in eV and Å, respectively.

Figure 5 Predicted energy profile and optimized structures of the corresponding stationary states for CO oxidation catalyzed by $\text{Os}_1/\text{Ti}_2\text{CS}_2$ via the TLH-A mechanism, in which the TS is marked with red boxes and the relative energies and selected bond lengths are given in eV and Å, respectively.

distance between an O atom of O_2 and C atom of CO decreases from 1.866 to 1.394 Å, showing that O_2 is activated from superoxide to peroxide and the anionic CO_2 -like molecule is formed on the surface of $\text{Os}_1/\text{Ti}_2\text{CS}_2$ simultaneously, which is still adsorbed on the Os_1 SA in step v owing to its nonlinear structure.

There are two different pathways for the formation of the second CO_2 , TLH-A and TLH-B, according to the way the activated O–O bond breaks following the structure in step v in Figs 5 and 6, respectively. As shown in Fig. 5, the adsorbed O atom from O_2 leaves Os_1 SA and turns to the C atom from the second adsorbed CO to produce a new intermediate (step vi) CO, which requires a relatively high activation barrier energy of 1.47 eV (TS2, 65i cm^{-1}) and produced a new intermediate (step vi). For the intermediate, the activated peroxide O_2^{2-} acts as a bridge between two CO molecules. Subsequently, the breaking of the O–O bond yields two CO_2 molecules through TS3, requiring only a small activation energy of 0.30 eV with an imaginary frequency of 206i cm^{-1} . Moreover, the two newly formed CO_2 molecules (vii) are desorbed from the surface of $\text{Os}_1/\text{Ti}_2\text{CS}_2$ to restore the SAC for a new catalytic CO oxidation cycle.

Unlike the TLH-A pathway, in the TLH-B pathway, the O–O bond is completely broken, and the first formed CO_2 is desorbed from Os_1 SA through TS2 (361i cm^{-1}), following the structure in step v in Fig. 6 with the activation energy of 0.23 eV, in which

the bond distance of O–O is stretched from peroxide 1.482 Å in step v to 1.832 Å in TS2 and only one O atom remains adsorbed on Os_1 SA in step vi. Obviously, the direct breaking of the peroxide O–O bond with a barrier energy of 0.23 eV in pathway TLH-B is much easier than the transfer of an O atom from Os_1 SA to the C atom of the second adsorbed CO that has a barrier energy of 1.47 eV in pathway TLH-A because the peroxide species has a much longer bond length (1.482 Å) and lower bond energy (19–50 kcal mol^{-1}) than that of the Os–O single bond (2.008 Å) [92]. After the desorption of the first CO_2 molecule, the remaining adsorbed O atom reacts with the second adsorbed CO to form the second CO_2 molecule in step vii via TS3 with the activation energy of 0.70 eV, which is desorbed from Os_1 SA through TS4 with the activation energy of 0.19 eV. From the analysis of the whole potential energy profile, the activation energies in these steps TS2, TS3 and TS4 (0.23, 0.70 and 0.19 eV, respectively) are much smaller than TS1 (0.74 eV) for the formation of the first CO_2 , indicating that the formation of the first CO_2 is the rate-determining step for CO oxidation catalyzed by $\text{Os}_1/\text{Ti}_2\text{CS}_2$. Accordingly, the CO oxidation reaction catalyzed by $\text{Os}_1/\text{Ti}_2\text{CS}_2$ can proceed through the TLH mechanism at low temperature.

In order to explore the role of matrix Ti_2CS_2 for the reaction, the Bader charges of Os_1 SA and the three S atoms bonding with Os_1 in the structures of selected elementary steps were calcu-

Figure 6 Predicted energy profile and optimized structures of the corresponding stationary states for CO oxidation catalyzed by $\text{Os}_1/\text{Ti}_2\text{CS}_2$ via the TLH-B mechanism, in which the TS is marked with red boxes and the relative energies and selected bond lengths are in eV and Å, respectively.

lated. As seen from Fig. 7, the Bader charge of single atom Os_1 of $\text{Os}_1/\text{Ti}_2\text{CS}_2$ changes from 0.448 |e| in step i to 1.0 |e| in step iii, and the Bader charge of the three surrounding S atoms changes from -1.658 |e| in step i to -2.079 |e| in step iii after CO and O_2 adsorption on the single atom Os_1 of $\text{Os}_1/\text{Ti}_2\text{CS}_2$. These data indicate that there are some charge transferring from single atom Os_1 to the S atoms of Ti_2CS_2 when the adsorbates are adsorbed on the single atom Os_1 . As CO oxidation reaction proceeds from the step iii to TS3, the Bader charges of Os_1 and its surrounding three S atoms change little. Until the formation of the second CO_2 molecule in step vii, the Bader charges of single atom Os_1 and the three S atoms gradually return to the initial state from step vii to viii. Thus, Ti_2CS_2 indeed dictates the reaction of CO oxidation through regulating the charge state and d-band energy of single atom Os_1 .

Comparing these reaction mechanisms, the reaction activation energy for CO oxidation in the rate-determining step through the L-H reaction mechanism (1.06 eV) is almost the same as the E-R (1.09 eV). However, the barrier energy of the rate-determining step of the TLH-A mechanism is 1.47 eV, which is far higher than that (0.74 eV) of the TLH-B mechanism. In addition, in order to further investigate the micro-kinetic behavior of the TLH-B mechanism, we calculated the reaction rates of the rate-determining step (iv→TS1), the calculation details of which are given in the SI. And the calculated rate constant is $3.98 \times 10^4/(\text{s mol L}^{-1})$, which further corroborates the feasibility of the

Figure 7 Calculated Bader charges of Os_1 , SAs and the three S atoms bonding with Os_1 in the structures of elementary steps in the TLH-B mechanism.

TLH-B mechanism. Accordingly, $\text{Os}_1/\text{Ti}_2\text{CS}_2$ shows high catalytic activity for CO oxidation through the TLH-B mechanism for CO_2 oxidation at low temperature.

The crystal orbital Hamilton population (COHP) analysis was also performed to evaluate the strength of Os-Ti and Os-S interactions for iv and TS1 in the rate-determining step, as shown in Figs S6 and S7. It is found that the integration of the

COHP up to the Fermi level (ICOHP) of the Os–Ti interaction is less than -0.2 , indicating that it is much weaker than the Os–S interaction (ICOHP = -1.4 (iv), -1.6 (TS1)) due to the long Os–Ti distance. Besides, the Os–Ti interaction changes slightly during the rate-determining step and only a moderate increase in the antibonding interaction below the Fermi level is seen. For the Os–S interaction, one can see that it is mainly dominated by the covalent bonding interaction. As the O atom of O_2 moves toward the CO molecule, the antibonding Os–S interaction below the Fermi level will shift up in energy and the Os–S strength increases as the ICOHP value becomes more negative from iv to TS1, indicating that the formation of the CO_2 -like molecule increases the Os–Ti interaction and decreases the interaction between the adsorbate and the catalyst. Therefore the Ti_2CS_2 support plays a crucial role in controlling the electronic structure and catalytic performance of the SACs.

CONCLUSIONS

Extensive density functional calculations have been carried out on the geometries, stabilities of metal SACs M_1/Ti_2CS_2 ($M = Fe, Co, Ni, Cu; Ru, Rh, Pd, Ag; Os, Ir, Pt, Au$), in which a series of metals anchored on different sites of sulfur-functionalized Ti_2C (Ti_2CS_2) 2D materials are screened for highly stable SACs. The calculations show that the Os_1/Ti_2CS_2 has the highest stability among these metal SACs. We have further analyzed the geometric structure and electronic structure characteristics of the Os_1/Ti_2CS_2 SAC, as well as the single adsorption and co-adsorption properties of O_2 and CO. Furthermore, based on its adsorption properties for O_2 and CO, four possible reaction mechanisms (the L–H, E–R, TLH–A and TLH–B mechanisms) of CO oxidation reactions over Os_1/Ti_2CS_2 are systematically investigated. The results show that the rate-determining step of the L–H and TLH–B reaction mechanisms is the formation of the first CO_2 molecule with reaction activation energies of 1.06 and 0.74 eV, respectively. However, the rate-determining step of E–R and the TLH–A reaction mechanism is the formation of the second CO_2 with reaction activation energies of 1.47 and 1.09 eV, respectively. These results indicate that the novel termolecular Langmuir–Hinshelwood (TLH–B) reaction mechanism is the most feasible for CO oxidation catalyzed by Os_1/Ti_2CS_2 . Of particular interest is the theoretical prediction that this osmium SAC with highly stable Ti_2CS_2 MXene as support can serve as low-temperature catalyst for CO oxidation, which can be potentially applicable in fuel cell applications. These studies will help to expand further the application of MXene for transition metal SACs.

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Author contributions Li J directed the research. Zhu C, Liang JX and Meng Y conducted the DFT calculations. Zhu C, Liang JX, Xu CQ and Meng Y analyzed the data. All the authors discussed the results and co-wrote the manuscript.

Conflict of interest The authors declare that they have no conflict of interest.

Supplementary information See supplementary material for the way of oxygen-terminated Ti₂C, the different adsorption sites of metal single atoms on Os₁/Ti₂CS₂, as well as the optimized geometry of Ir₁/Ti₂CS₂. In addition, the optimized stable structures and the calculated relative energies of

different molecule adsorption on Os₁/Ti₂CS₂ SAC are also available in the online version of the paper.

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MXene负载的钨单原子催化剂Os₁/Ti₂CS₂催化低温CO氧化反应的理论研究

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摘要 本文报道了一种对CO氧化反应具有低温催化活性的新型硫功能化MXene-Ti₂C (Ti₂CS₂)负载的钨金属单原子催化剂Os₁/Ti₂CS₂。通过密度泛函理论计算, 从一系列过渡金属(M = Fe, Co, Ni, Cu; Ru, Rh, Pd, Ag; Os, Ir, Pt, Au)中筛选出最稳定的钨金属单原子催化剂。计算结果表明, Os₁/Ti₂CS₂有利于O₂和CO的共吸附, 且O₂分子的吸附能略高于CO分子。此外, 由于O₂+2CO能稳定地共吸附在Os₁单原子上, CO氧化反应可能通过三分子反应机理进行。因此, 我们研究了CO在Os₁/Ti₂CS₂单原子催化剂上发生氧化反应的四种不同的催化机理: Langmuir-Hinshelwood (L-H)、Eley Rideal (E-R)、termolecular Langmuir-Hinshelwood-A (TLH-A)和termolecular Langmuir-Hinshelwood-B (TLH-B)机理。结果表明TLH-B机理最可能发生, 其反应势垒仅为0.74 eV, 远低于L-H、E-R和TLH-A的反应势垒(分别为1.06, 1.09和1.47 eV)。上述研究结果有助于理解MXene的表面化学并设计稳定的新型二维硫端基MXene催化材料。