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CO₂ reduction on single-atom Ir catalysts with chemical functionalization[†]

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As promising catalytic systems, single-atom catalysts (SACs) demonstrate improved catalytic performance for electrochemical reactions. However, the pinning of metal atoms on surfaces usually depends on the adsorption on defects. In this study, defect-free functionalization by attaching IrX_3 (X = F or Cl) complexes on the MoS₂ monolayer is theoretically demonstrated. The ligand-based method offers a damage-free route for stabilizing SACs on 2D materials. We demonstrate the CO₂ reduction process on MoS₂–IrX₃ with a small change in free energy and a low onset potential. The d⁶ shell of Ir acts as a molecular joint with universal orbital orientations, which benefits the adsorption of different reaction intermediates. This study shows the superiority of defect-free functionalization of 2D materials using SAC–ligand complexes.

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1. Introduction

For promoting modern energy conversion technologies, the exploration of stable and high-efficiency catalysts is extremely important. Usually, for energy conversion, precious metal-based catalysts are confirmed as efficient catalysts. However, their scarcity and high cost limit their large-scale applications.¹⁻³ For promoting clean energy conversion, the development of cost-efficient and highly active catalysts is important.⁴⁻⁶ Single atom catalysts (SACs) with atomically dispersed reactive centers on supports show promising prospects for a wide range of applications for emerging energy sources. Due to their maximum atom utilization for metal species, SACs deliver improved catalytic performance for many catalytic processes.^{7–17} Using SACs, the chemical properties of 2D materials can be tuned by surface functionalization. The surface functionalization of 2D materials mostly depends on the adsorption of atoms or molecules on defects. Since structural defects always lead to limitations on electronic properties, there are limited applications of decorated 2D materials. Many 2D materials have saturated surfaces, which are disadvantageous for the adsorption of SACs. Therefore, it is necessary to examine a method to modify saturated surfaces with SACs.

Among modern energy conversion approaches, CO_2 reduction (CO_2RR) has been confirmed to be an environmentally friendly promising technique.^{18,19} Because CO_2RR comprises multiple elementary steps, the efficiency is limited by the sluggish kinetics of the rate-determining step. Recent studies show that SACs are favorable for improving the catalytic selectivity of CO_2RR .²⁰⁻²⁵

For electrochemical applications, the conductivity of catalyst substrates is necessary. Therefore, to realize favorable electrical properties, defect-free functionalization is required for the anchoring of SACs on 2D materials. Recently, a spontaneous defect-free functionalization method attaching Au on the MoS₂ monolayer *via* a S–Au– Cl coordination complex has been demonstrated.²⁶ On the MoS₂ surface, the Au coordination complex is synthesized without the presence of additional defects by taking advantage of the lone pair electrons of S atoms. Since the coordination number of reactive centers has been considered an important factor in the structureactivity relationship of SACs,²⁷ this coordination-based method offers a damage-free route for functionalizing 2D materials.

A recent theory shows that rather than the d-band center and charge states, the spatial structure and orientation of frontier orbitals closest to the Fermi level play an important role in determining the catalytic activity of SACs.²⁸ For MoS₂- MX_3 (X = halogens) complexes, the coordination of X⁻ and S forms a square coordination field, which leads to the dsp² hybridization of M³⁺ and the split of other d orbitals. For MoS₂- IrX_3 , the unsaturated d⁶ configuration of Ir^{3+} enables the binding of Ir SACs with the reaction intermediates. In this study, we observe the effect of the Ir d⁶ shell with various orbital orientations and symmetries acting as a universal molecular joint. The advantage of IrX₃ SAC in CO₂RR is then demonstrated. With a low onset potential, the reaction $COOH^* + H^+ +$ $e \rightarrow CO^* + H_2O$ on MoS₂-IrX₃ shows activities similar to those on the (111) surfaces of noble metals. Furthermore, the reaction $CO^* + H^+ + e \rightarrow CHO^*$ on MoS_2 -IrX₃ exhibits activities similar to those on the (211) surfaces of noble metals. This work shows the stability and catalytic activity of SAC-ligand complexes on 2D materials and the superiority of defect-free functionalization.

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2. Computational methods

The simulation model is set up using a 4×4 supercell of the 1H MoS₂ monolayer. Density functional theory (DFT) calculations are performed using the Vienna ab initio simulation package (VASP).²⁹⁻³² The projector-augmented wave method^{33,34} is used with a kinetic energy cutoff of 500 eV. The exchange and correlation of electrons are described using the Perdew-Burke-Ernzerhof (PBE) functional.³⁵ The correction of van der Waals interactions is treated using the DFT-D3 method with Becke–Johnson damping.^{36,37} To consider the solvation effect of water at the solvent-catalyst interface, an implicit solvation model is applied in the VASPsol package.^{38,39} The Brillouinzone integration is performed using a 5 \times 5 \times 1 Monkhorst-Pack grid. The convergence of total energy is considered to be achieved when the total energy difference of two iterated steps is $<10^{-5}$ eV. In the direction perpendicular to the MoS₂ surface, the replicas of the simulation system are separated by a vacuum layer of 16 Å. Geometries are completely relaxed without any symmetric constraints until the Hellmann-Feynman forces are <0.005 eV Å⁻¹. All the INCAR files are listed in Supplementary II Section 1 (ESI[†]). The POSCAR of all the relaxed structures are listed in Supplementary II Sections 3 and 4 (ESI[†]).

To improve the description of DFT total energies and barriers to chemical accuracy, r^2 SCAN, the regularized-restored strongly constrained and appropriately normed functional,⁴⁰ is employed to calculate the single-point energies of all the geometries relaxed at the PBE-D3 level. The r^2 SCAN functional at the *meta*-GGA level modifies the regularizations introduced in regularized SCAN⁴¹ to enforce adherence to the exact constraints obeyed by SCAN. Testing has indicated that the r^2 SCAN functional at least matches the accuracy of the parent SCAN functional but with significantly improved numerical efficiency and accuracy under low-cost computational settings. Based on the abovementioned model, the binding energy of IrX₃ (X = F, Cl, and Br) on MoS₂ is defined as

$$E_{\rm b} = E_{\rm DFT}(\rm MoS_2-IrX_3) - E_{\rm DFT}(\rm MoS_2) - E_{\rm DFT}(\rm IrX_3)$$
(1)

As per ref. 42, the binding energies of reaction intermediates COOH*, CO*, and CHO* are defined as

$$E_{b}(\text{COOH}^{*}) = E_{\text{DFT}}(\text{MoS}_{2} - \text{IrX}_{3} - \text{COOH}) - E_{\text{DFT}}(\text{MoS}_{2} - \text{IrX}_{3}) - E_{\text{DFT}}(\text{CO}_{2}) - \frac{1}{2}E_{\text{DFT}}(\text{H}_{2})$$
(2)

$$E_{b}(CO^{*}) = E_{DFT}(MoS_{2}-IrX_{3}-CO) - E_{DFT}(MoS_{2}-IrX_{3}) - E_{DFT}(CO)$$
(3)

$$E_{b}(CHO^{*}) = E_{DFT}(MoS_{2}-IrX_{3}-CHO) - E_{DFT}(MoS_{2}-IrX_{3}) - E_{DFT}(CO) - E_{DFT}(H_{2})$$
(4)

To look for the migration paths and barriers of IrX_3 on MoS_2 , the climbing image nudged elastic band method^{43–45} is used. The reaction paths are relaxed by minimizing residual forces using the quasi-Newton algorithm.

In addition to the calculations of migration barriers, the structural stability of IrX_3 on the MoS_2 surface is confirmed by molecular dynamics (MD) simulations at 300 K. The canonical (*NVT*) ensemble is implemented using the Langevin thermostat

$$m_i \vec{r}_i = \vec{F}_i - \gamma m_i \vec{r}_i + \vec{G}_i \tag{5}$$

applied on the MoS_2 sheet with the friction coefficient $\gamma = 10 \text{ ps}^{-1}$ and the random force \vec{G}_i sampled from a Gaussian distribution. To save computation time, the MD simulations are performed at the PBE-D3 level. The time step is set to 1 fs. After a pre-equilibrium of 1 ps, the simulations last for 7 ps.

To investigate the reaction mechanism of CO_2RR at applied voltage *U*, the constant-potential grand canonical ensemble method⁴⁶ is employed for calculating the electronic free energy. A Legendre transformation

$$G(n, U) = F(n) - n\mu_{\rm SHE} + neU$$
(6)

is used to convert from fixed-charge free energy F(n) of electrons to grand canonical G(n, U), where *n* is the number of electrons in the systems, *e* is the elementary positive charge and μ_{SHE} (-4.44 eV below the vacuum level) is the chemical potential of electrons in the standard hydrogen electrode. In DFT calculations, *n* is increased by 0.5, 1.0, 1.5 and 2.0, and the grandcanonical electron free energy G(n, U) of electrons is fitted by a quartic expansion of *n* (for details on calculation and data processing, see Supplementary Section S6 (ESI†) with an example). Finally, the ground state is obtained by minimizing G(n, U):

$$GCP(U) = \min G(n, U)$$
(7)

On the basis of grand-canonical calculations of electrons, the free energy of each species is calculated using standard statistical thermodynamics. The vibrational modes of each species are used to determine the zero-point energies, entropies, and heat capacities.⁴⁷ At T = 300 K, the free energy is calculated according to

$$G = \text{GCP}(U) + E_{\text{ZPE}} + \int_0^T C_P dT - TS, \qquad (8)$$

where E_{DFT} is the DFT total energy, E_{ZPE} is the zero-point energy, $\int_0^T C_P dT$ is the integrated heat capacity, *T* is the temperature, and *S* is the entropy. Thermodynamics definition establishes $\int_0^T C_P dT - TS = U + PV - TS$ (*U* is the internal energy, *P* is the pressure and *V* is the volume). For solid phases, *PV* is ignored and $U - TS = -kT \ln Q$, where the partition function *Q* is evaluated by the vibrational frequencies (for data processing, see Supplementary II Section S2, ESI†). For gas-phase molecules, $\int_0^T C_P dT - TS = -kT \ln Q$ is obtained using standard ideal gas methods,⁴⁷ in which molecules do not interact with one another and the molecular partition function *Q* is separated into the translational, rotational and vibrational parts. All gaseous species from CO₂RR are assumed to have a fugacity of 101 325 Pa. The free energy of liquid H₂O is calculated as an ideal gas with an adjusted fugacity of 3534 Pa (the vapor pressure of H₂O at 300 K). The free energies of CH₃OH, HCHO, and HCOOH are adjusted to a fugacity of 6080, 14, and 19 Pa (corresponding to an aqueous activity of $0.01^{48,49}$). For the reactions from CO₂ to small molecules CO, HCHO, CH₃OH and CH₄, the experimental values of the change of free energy (Supplementary Section S1, ESI†) are used instead of DFT values.

At any pH value, the reaction $H^+ + e \leftrightarrow \frac{1}{2}H_2(g)$ is equilibrated at 0 V. At an electrode potential *U* relative to the hydrogen electrode, the electron energy is shifted by -eU. Then, the free energy of a proton–electron pair reads $G(H^+) + G(e) = \frac{1}{2}G(H_2) - eU$. Subsequently, the free energy change for a general reaction $CO_2(g) + nH^+$ $+ ne \rightarrow P^*$ is written as

$$\Delta G(\mathbf{P}^*) = G(\mathbf{P}^*) - G(\mathbf{CO}_2) - nG(\mathbf{H}^+) - nG(\mathbf{e})$$

= $G(\mathbf{P}^*) - G(\mathbf{CO}_2) - \frac{1}{2}nG(\mathbf{H}_2) + neU$ (9)

This equation is used to evaluate the free energy changes of elementary steps.

3. Results and discussion

3.1 Structure, thermal stability, and molecular orbitals of IrX_3 on MoS_2

IrX₃ (X = F, Cl, and Br) on MoS₂ is expected to have a square structure with Ir–X bonds and an S → Ir coordinate bond from MoS₂. In the ligand field, the Ir atom forms dsp² hybridization to bond with three X atoms and one S atom in MoS₂. We consider three possible high-symmetry adsorption sites, including the top of the S atom, the top of the Mo atom, and the center of the Mo–S hexagon (hollow site). The results (Table 1) demonstrate that, for IrX₃ adsorption, the top of the S atom (Fig. 1(a)) is the most stable site. The binding energies of IrX₃ molecules on MoS₂ are in the range of -1.73 to -0.38 eV. For IrF₃ and IrCl₃, the binding energies are sufficiently large for them to be stable on MoS₂ at room temperature. But the binding energy of IrBr₃ is too small for it to be stable. Therefore, in the following study on CO₂RR, we only consider IrF₃ and IrCl₃.

In the electrolyte, we focus on the coordination of H_2O on IrX_3 . Therefore, we calculate the binding energy of H_2O on IrX_3 , which is defined as

$$E_{b}(H_{2}O) = E_{DFT}(MoS_{2}-IrX_{3}:2H_{2}O) - E_{DFT}(MoS_{2}-IrX_{3}) - E_{DFT}(H_{2}O)]$$
(10)

For IrF₃ and IrCl₃, the results are $E_b(H_2O) = -0.21$ and -0.35 eV. The $E_b(H_2O)$ values of IrF₃ and IrCl₃ are low for H₂O to be bound.

Table 1 Binding energies and migration barriers of IrX ₃ on MOS ₂					
Molecule	Binding energy (eV)	Relative energy (eV)			Migration
		S-top	Mo-top	Hollow	barrier (eV)
IrF ₃	-1.73	0	1.49	1.44	1.42
IrCl ₃	-0.62	0	0.60	0.55	0.53
IrBr ₃	-0.38	0	0.31	0.25	0.25



Fig. 1 The structures (a) and migration barriers (b) of IrX₃ on MoS₂.

To investigate the thermal motion of IrX₃ on MoS₂, the migration paths and barriers are calculated. In the previous experiment, the motion of bare Au atom on MoS₂ was observed. However, AuCl₃ can be stably anchored.²⁶ The calculated barriers $E_a = 0.13$ eV for bare Au and $E_a = 0.63$ eV for AuCl₃ (Fig. S1, ESI[†]) obviously demonstrate that AuCl₃ on MoS₂ is considerably more stable than bare Au. These barriers can be compared with those of IrX₃. Fig. 1(b) shows the energy changes of IrX₃ along the migration paths. The migration of IrX₃ starts from the top of the S atom and climbs over the Mo-S hexagonal hollow (with barriers $E_a = 0.25-1.42$ eV, Table 1) and reaches the top of another S atom. Because the barriers of IrF₃ and IrCl₃ are close to or larger than that of AuCl₃, we believe that IrF₃ and IrCl₃ could be stably anchored on MoS₂ at room temperature. Nevertheless, the migration barrier of IrBr₃ is too small for it to be anchored. Additionally, the thermal motion of IrCl₃ is then examined via MD simulations at 300 K. The simulation shows the thermal migration of Au on MoS₂ (Fig. S2, ESI[†]). For AuCl₃ (Fig. S3, ESI[†]) and IrCl₃ (Fig. S4, ESI[†]), the systems keep stable without any migration during the simulation time. The calculated barriers are a little different at the PBE-D3/r²SCAN level (Table S3, ESI[†]). For AuCl₃, the barriers under the both functionals are close. For IrF₃ (IrCl₃), the barrier at the r²SCAN level is larger than (close to) the barrier of AuCl₃. It is worth noting that MD simulation cannot be conclusive evidence of stability because of its short time scale. To confirm the stability, we compare the calculated barriers and experiment result. Previous experimental observation²⁶ confirms the stability of AuCl₃ on MoS₂, and the calculated migration barrier of AuCl₃ on MoS₂ is 0.63 eV. In comparison, the migration barrier $E_a = 1.42$ eV of IrF₃ on MoS₂ is much larger, indicating that it is more stable than AuCl₃. For IrCl₃, the barrier $E_a = 0.53$ eV is a little lower than but close to that of AuCl₃. So, IrCl₃ should also be stable.

Fig. 2(a) shows the molecular orbitals of square MoS_2 -IrX₃ (X = F, Cl). A dsp² hybridization occurs in the Ir $5d_{x^2-y^2}$, 6s and 6p orbitals. Then, σ bonding occurs *via* coupling of the Ir dsp²



Fig. 2 The orbitals and bonding in MoS₂-IrX₃. (a) The formation of molecular orbitals in MoS₂-IrF₃. The PDOS of (b) IrF₃ and (c) IrCl₃ on MoS₂.

hybrid orbitals with the p orbitals of X and S atoms. Ir $5d_{xy}$, $5d_{xz}$, and $5d_{yz}$ orbitals are split by the square ligand field and couple with the p orbitals of X *via* π bonding. The d6 configuration of Ir (with a spin $S = 1 \mu_{\rm B}$) does not completely fill the 5d shell and provides a chance for combining CO₂RR intermediates.

3.2 Combination of CO₂RR intermediates on MoS₂-IrX₃

Usually, to analyze the catalytic activity of noble or transition metal surfaces, the d-band center and charge states are considered. However, in a recent theory, the spatial orientation of frontier orbitals close to the Fermi level is suggested as a criterion for the catalytic activity of SACs.²⁸ By coupling with the p orbitals of F or Cl, the energies of $5d_{xy}$ -, $5d_{xz}$ - and $5d_{yz}$ -p anti-bonding π orbitals are pushed up. As per the projected

density of states (PDOS) of MoS_2 -IrF₃ (Fig. 2(b)) and MoS_2 -IrCl₃ (Fig. 2(c)), the orbitals of Ir d⁶ electrons lie close to the Fermi level and leave two empty 5d orbitals for accepting electrons from the reaction intermediates. Because the d orbitals have different special orientations, the Ir 5d shell can adapt to different molecules and combine with them. In CO_2RR , MoS_2 -IrF₃ and MoS_2 -IrCl₃ exhibit good combinations with the key intermediates COOH*, CO*, and CHO*.

To measure the catalytic ability of MoS_2 -IrX₃ in CO₂RR, we turn to the criteria developed by Peterson *et al.*⁵⁰ The key steps of CO₂RR are determined as follows

$$CO_2(g) + H^+ + e \rightarrow COOH^*$$
 (11)

$$COOH^* + H^+ + e \rightarrow CO^* + H_2O(l)$$
(12)

$$CO^* + H^+ + e \rightarrow CHO^*$$
 (13)

The reaction from CO₂ to CO* should be fast if COOH* is moderately bound to the catalyst (*i.e.*, $E_{\rm b}({\rm COOH}^*)$ is comparable to $E_{\rm b}({\rm CO}^*)$). For the further reaction of CO*, moderate bonding to intermediate CHO^{*} (*i.e.* $E_{\rm b}$ (CHO^{*}) is comparable to $E_{\rm b}({\rm CO}^*)$) is necessary. The study of Peterson *et al.*⁵¹ demonstrates that the catalytic activity of usual transition metal surfaces is limited by a linear scaling relationship between $E_{\rm b}({\rm COOH^*})$ and $E_{\rm b}({\rm CO^*})$, in addition to a similar relation between $E_b(CHO^*)$ and $E_b(CO^*)$. The solid lines in Fig. 3(a) and (b) show the scaling lines of (111) and (211) surfaces of transition metals. Any catalyst with a significantly improved activity compared to transition metals must stabilize COOH* and CHO^{*} more than CO^{*} such that their $E_{\rm b}$ (COOH^{*}) and $E_{\rm b}({\rm CHO}^*)$ versus $E_{\rm b}({\rm CO}^*)$ should negatively deviate from the scaling lines. For MoS₂-IrF₃ and MoS₂-IrCl₃, our calculation results show that their $(E_b(CO^*), E_b(COOH^*))$ points locate at the scaling line of the (111) surfaces of transition metals (Fig. 3(a)), and the $(E_b(CO^*), E_b(CHO^*))$ points locate at the scaling line of the (211) surfaces of transition metals. The (211) line denotes a higher catalytic activity than the (111) line. The above results indicate that the catalytic activity of MoS_2 -IrF₃ and MoS_2 -IrCl₃ for $CO_2 \rightarrow CO^*$ is similar to that of metal (111) surfaces. Furthermore, the catalytic activity for $CO^* \rightarrow CHO^*$ is better than that for general transition metals.

To demonstrate the effect of the Ir d⁶ shell as a universal molecular joint with different orbital orientations, the bonding of MoS₂–IrF₃–COOH, MoS₂–IrF₃–CO, and MoS₂–IrF₃–CHO is examined. Their PDOS is shown in Fig. 3(c)–(e). In MoS₂–IrF₃–COOH, both Ir and C atoms contribute one electron for σ bonding in which the Ir 5d_{z²} orbital couples with the C 2p_z orbital. The left Ir d⁵ shell shows a spin $S = \frac{1}{2} \mu_{\rm B}$. In MoS₂–IrF₃–COO $\pi_{\rm 2p} \pi$ bonding strengthen the combination of CO on IrX₃, thus resulting in a spin S = 0 in the Ir atom. In MoS₂–IrF₃–CHO, the Ir 5d_{z²}–C 2p_z σ bonding is similar to that of MoS₂–IrF₃–CHO, the Ir 5d_{z²}–C 2p_z σ bonding is similar to that of MoS₂–IrF₃–COOH,



Fig. 3 The binding of CO_2RR intermediates on MoS_2-IrX_3 . Binding energies (a) $E_b(COOH)$ and (b) $E_b(CHO)$ versus $E_b(CO)$ (with data reported in ref. 42). The black and blue lines are the scaling relations of (111) and (211) transition metal surfaces, respectively. The black and blue points are (111) and (211) surfaces of certain transition metals, respectively. The red points are our calculation results for MoS_2-IrF_3 and MoS_2-IrCl_3 . The PDOS of (c) IrF_3-COOH , (d) IrF_3-CHO on MoS_2 .

3.3 Free energy surface of CO₂RR on MoS₂-IrX₃

To show the details of CO₂RR on MoS₂–IrX₃, the free energy of the reaction intermediate at each step is determined (Fig. 4(a) and (c) for MoS₂–IrF₃/MoS₂–IrCl₃, respectively; for detail data including G(n, U), E_{ZPE} , and $\int_0^T C_P dT - TS$, see Supplementary IV (ESI†), the Excel file). In the first step of CO₂RR, CO₂ can be reduced to COOH* or HCOO*. The possible reaction paths are CO₂ \rightarrow COOH* \rightarrow CO* and CO₂ \rightarrow HCOO* \rightarrow HCOOH. Generally, COOH* has a lower energy than HCOO*. Here, on MoS₂–IrX₃, COOH* forms one C–Ir bond. However, HCOO* requires two O–Ir bonds that are more difficult to form. According to the calculations, the free energy of G(HCOO*) is indeed larger than that of G(COOH*). The favored CO* path is the basis for subsequent reactions.

In an usual CO₂RR process, along the CO₂ \rightarrow COOH^{*} \rightarrow CO^{*} path, *G*(COOH^{*}) is higher than *G*(CO₂) and *G*(CO_{*}). Thus, COOH^{*} is the first high point on the free energy surface. The low free energy of CO^{*} (*G*(CO^{*}) = -0.36 (-0.31) eV) on MoS₂–IrF₃ (MoS₂–IrCl₃) avoids the generation of gas phase CO (*G*(CO(g)) = +0.21 eV). On MoS₂–IrX₃, the free energy of the subsequent process CO^{*} \rightarrow CHO^{*} \rightarrow HCHO goes up. On MoS₂–IrCl₃, HCOH^{*} (*G*(HCOH^{*}) = -0.21 eV) with a lower free energy is an alternative to HCHO (*G*(HCHO) = +0.34 eV). On MoS₂–IrF₃, CHO^{*} \rightarrow HCHO is the only pathway. Such free energy surfaces

lead to the evolution of $CO^* \rightarrow CHO^* \rightarrow HCHO$ to be the rate determining step of CO_2RR . To lower the reaction free energy, a potential *U* is applied on the cathode, and the reaction free energy ΔG of an elementary step (obtaining one electron) becomes $\Delta G + eU$. An onset potential *U*, by which the free energy goes downhill through the entire reaction path, is needed to perform the reaction.

The free energy increases in the following steps $CO^* + H^+ +$ $e \rightarrow CHO^*$ and $CHO^* + H^+ + e \rightarrow HCHO$. For calculating each following step, we test several trial structures of the reactant and identified the rational results that the geometries are able to maintain in the geometry relaxation. For MoS₂–IrF₃, the step $CHO^* \rightarrow HCHO$ is rate determining, and an onset potential $U = (G(CHO^*) - G(HCHO))/e = -0.44$ V is needed to let the reaction free energy go down through the overall CO₂RR process (see the red steps in Fig. 4(a)). For MoS₂-IrCl₃, we find another pathway CHO* + H^+ + $e \rightarrow HCOH^*$ along which the free energy decreases, and thus $CO^* \rightarrow CHO^*$ is rate determining with an onset potential $U = (G(CO^*) - G(CHO^*))/e = -0.40$ V to let the reaction free energy go down through the whole process (see the red steps in Fig. $4(\mathbf{c})$). It is worth noting that the onset potential of hydrogen evolution on MoS₂-IrF₃ (MoS₂-IrCl₃) is -0.59 (-0.71) V (for the evolution of reaction free energy, see Fig. S5, ESI^{\dagger}), which is lower than the onset potential of CO₂RR.



Fig. 4 The reaction free energy G of CO_2RR on (a) MoS_2-IrF_3 and (c) MoS_2-IrCl_3 . (b) and (d) The structures of intermediates on MoS_2-IrF_3 and MoS_2-IrCl_3 , respectively.

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For subsequent processes, MOS_2 -IrF₃ and MOS_2 -IrCl₃ show different reaction paths. For MOS_2 -IrF₃, CHO* can be reduced to HCHO (aq) and then to CH_3O^* or CH_2OH^* , both of which can lead to the final product CH_3OH (aq.). The free energy of CH_2OH^* is lower than that of CH_3O^* . So, the path *via* CH_2OH^* is thermodynamically favorable. For MOS_2 -IrCl₃, CHO* can lead to HCHO (aq) or HCOH*. The latter is more favorable in free energy. On MOS_2 -IrCl₃, HCHO (aq) or HCOH* can only lead to CH_2OH^* , which may lead to the production of CH_3OH (aq) or CH_2^* . The latter is thermodynamically favorable and subsequent process, *i.e.*, $CH_2^* \rightarrow CH_3^* \rightarrow CH_4(g)$, decreases in free energy. Therefore, on MOS_2 -IrCl₃, it strongly tends to produce $CH_4(g)$.

3.4 Carrier concentration in MoS₂-IrX₃

For CO₂RR, the conductivity of the catalyst substrate is important for performing electrochemical reactions. As discussed previously, IrX₃ on MoS₂ forms 5d localized states close to the Fermi level. With certain empty 5d orbitals above the Fermi level, IrX₃ induces p-type doping in MoS₂. Figs. S6(a) and (b) (ESI[†]) show the energy bands of MoS₂–IrF₃ and MoS₂–IrCl₃, respectively. The hole concentration in the MoS₂ sheet can be evaluated as

$$p = \int_{E < \text{VBM}} D(E) \left(1 - \frac{1}{e^{(E - E_{\text{F}})/kT} + 1} \right) dE$$
(14)

with the integral below the valence band maximum (VBM) (for details on the calculation method, see Supplementary Section S5 (ESI†); the FORTRAN code and the VASP input and data files are provided in Supplementary III, ESI†). Note that D(E) is the density of states and E_F is the Fermi energy. Using the model of a 4 × 4 MoS₂ supercell with IrX₃ (a molecular coverage of 6.25%), the calculated hole concentrations are 9 × 10¹² and 6 × 10¹² cm⁻² for IrF₃ and IrCl₃, respectively, at room temperature. We can estimate that hole concentration roughly increases by ~1% for every 1% increase in molecular coverage. Such a carrier concentration is of the same order of magnitude as that of graphene. The electron transfer $Q = p \times S$ (where *S* is the surface area of MoS₂) from MoS₂ to IrF₃ (IrCl₃) is 0.13 (0.09) *e*. The p-type doping of IrX₃ ensures that the MoS₂ sheet is conductive for CO₂RR.

4. Conclusions

MoS₂–IrF₃ and MoS₂–IrCl₃ are proposed to be SACs for CO₂RR. The special reaction path leads to a small change in free energy for the process CO₂ → COOH^{*} → CO^{*}. Note that MoS₂–IrF₃ tends to generate CH₃OH. However, CH₄ production is more favorable on MoS₂–IrCl₃. These two MoS₂–IrX₃ have similar onset potentials. The catalytic activity of MoS₂–IrX₃ at the CO^{*} + H⁺ + e → CHO^{*} step is evaluated to be better than that on the usual transition metal (111) surfaces. Due to dsp² hybridization, MoS₂–IrX₃ holds a square-like structure with three X and S atoms providing a ligand field that splits the 5d_{xy}, 5d_{xz}, 5d_{yz} and 5d_{x²-y²} orbitals of Ir. Due to different special orientations, the Ir 5d orbitals act as universal joints to combine with different types of molecules, thus presenting adaptation to stabilize the CO_2RR intermediates. Moreover, F or Cl ligands play an important role in stabilizing Ir on MOS_2 and preventing its thermal migration. To summarize, IrF_3 and $IrCl_3$ on the surface of the MOS_2 monolayer are presented as a new type of SAC for CO_2RR anchored without defects.

Data availability

All the related data are included in this publication.

Conflicts of interest

The authors declare that they have no conflict of interest.

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