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## Single-atom catalysts on supported silicomolybdic acid for CO<sub>2</sub> electroreduction: a DFT prediction†

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The electrocatalytic CO<sub>2</sub> reduction reaction (CO<sub>2</sub>RR) is an effective way to convert CO<sub>2</sub> into fuels which relies on efficient catalysts due to extreme reaction activation barriers. As a new frontier in the field of catalysis, single-atom catalysts (SACs) play an important role in the CO<sub>2</sub>RR owing to their maximum atomic availability and unique properties. Herein, a new type of electrocatalyst combining transition metal (TM = Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Y, Zr, Nb, Mo, Tc, Ru, Rh, Pd, Ag and Cd) with  $\alpha$ -Keggin type Na<sub>4</sub>[SiMo<sub>12</sub>O<sub>40</sub>] (Na<sub>4</sub>SiMo<sub>12</sub>) was investigated by density functional theory (DFT) calculations. Through comprehensive screening, TM@Na<sub>4</sub>SiMo<sub>12</sub> (TM = Sc, Ti, V, Cr, Mn, Zn, Y, Zr, Nb and Cd) have been found to exhibit robust stability. Among them, TM@Na<sub>4</sub>SiMo<sub>12</sub> (TM = Sc, Cr, Mn, Ti, and V) have excellent catalytic activity for the CO<sub>2</sub>RR; in particular, the limiting potential ( $U_L$ ) for CO<sub>2</sub>RR by Cr@Na<sub>4</sub>SiMo<sub>12</sub> is  $-0.23$  V and the product is HCOOH. Meanwhile, Mn@Na<sub>4</sub>SiMo<sub>12</sub> has high CO<sub>2</sub>RR selectivity and good catalytic performance ( $U_L = -0.48$  V). During the electrochemical CO<sub>2</sub>RR, polyoxometalates (POMs) act as "electron sponges", accepting and donating electrons. It is expected that the present work will spur the development of new SACs for the CO<sub>2</sub>RR.

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## 1. Introduction

The dramatic rise in carbon dioxide (CO<sub>2</sub>) emissions into the atmosphere has caused environmental problems such as the greenhouse effect and ocean acidification.<sup>1–3</sup> Converting CO<sub>2</sub> into renewable chemical fuels is considered to be one of the most efficient solutions.<sup>4–7</sup> The electrocatalytic CO<sub>2</sub> reduction reaction (CO<sub>2</sub>RR) has attracted extensive attention due to its mild reaction conditions, high faradaic efficiency, and environmental driving force caused by the synergistic effect with renewable energy (such as wind energy and solar energy).<sup>8</sup> CO<sub>2</sub> is a chemically inert molecule with linear C=O bond energy up to 803 kJ mol<sup>–1</sup>, meaning that it is difficult to activate. Therefore, the CO<sub>2</sub>RR has to rely on efficient catalysts in multi-electron transfer processes for producing the target products. Many catalysts have been explored to break the strong C=O bonds, such as sulfides,<sup>9,10</sup> phosphates,<sup>11,12</sup> oxides,<sup>13,14</sup> etc. However, the catalytic performance of these catalysts for the CO<sub>2</sub>RR is still unsatisfactory.<sup>15</sup> Therefore, it is of great

significance to develop electrochemical CO<sub>2</sub>RR catalysts with high selectivity and high efficiency.

Since Zhang and co-workers firstly reported a Pt<sub>1</sub>/FeO<sub>x</sub> single atom catalyst (SAC) in 2011,<sup>16</sup> SACs have attracted extensive attention both in experimental and theoretical fields.<sup>6,17–20</sup> Due to the maximum atom utilization and unique performance, SACs show great potential in rational utilization of metal resources and the realization of atom economy.<sup>21–23</sup> Different from nanoparticles and metal clusters, when the dispersion of particles reaches the size of a single atom, SACs might produce many new characteristics, such as the sharp increase of surface free energy, quantum size effect, unsaturated ligand environment and metal–support interaction. Among them, the strong metal–support interaction enables the support to regulate the electronic structure of the metal atom to the greatest extent, thus affecting the adsorption behavior of reaction intermediates at the active center. Therefore, SACs can be ideal candidates for the electrochemical CO<sub>2</sub>RR and are expected to achieve high-efficiency activation and directional CO<sub>2</sub> conversion.<sup>24–27</sup> However, there are many inevitable problems in the preparation of SACs. One of the most challenging problems is the aggregation of single atoms on the surface of the support, resulting in reduced catalyst activity or even deactivation. Therefore, the key to the synthesis of SACs is to explore a suitable support to avoid the aggregation effect of metals.

Polyoxometalates (POMs), a class of nanoscale metal oxide clusters composed of d-block transition metal (M = W, Mo, V, Nb, Ta, etc.) ions, are connected by common edge and common

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angle oxygen junctions.<sup>28,29</sup> POMs are widely investigated in the field of catalysis owing to their well-defined structures, high thermal stability and fascinating physical and chemical properties.<sup>30–32</sup> In the family of POMs, the best known structure of  $\alpha$ -Keggin type has the general formula  $[XM_{12}O_{40}]^{n-}$  (X = P, As, Si, Ge, etc.). As shown in Fig. 1, an  $\alpha$ -Keggin type POM is a  $T_d$  symmetric structure formed by 12  $MO_6$  octahedrons surrounding the central  $XO_4$  tetrahedron. The oxygen atoms of an  $\alpha$ -Keggin type POM can be divided into three categories: oxygen ( $O_a$ ) connected to the central atom; terminal oxygen ( $O_t$ ) connected to a single metal atom; and bridging oxygen ( $O_b$ ) connected to three metal clusters. The exposed O atoms provide a series of coordination sites, including the single corner site, the bridge site ( $O_t$ – $O_b$ –bridge site), the three-fold hollow site (3-H- $O_t$  and 3-H- $O_b$ ), and the four-fold hollow site (4-H),<sup>33</sup> which offer the possibility of anchoring a single atom. Zhang *et al.* synthesis of POM supported single-atom catalysts. Low loading Pt (1 wt%) can be effectively dispersed on Keggin type phosphomolybdic acid (PMA),<sup>34</sup> and a Pt<sub>1</sub>/PMA single-atom catalyst has been proved to have excellent catalytic performance in the hydrogenation of nitrobenzene and cyclohexanone. Notably, Pt atom exhibit strong adsorption at the 4-H site of PMA, showing a twisted square-planar geometry. In addition, Rh was also found to be deposited on the surface of phosphotungstic acid (PTA) by the self-assembly method.<sup>35</sup> When the loading amount of Rh is reduced to 0.9 wt%, Rh is located at the 4-H site of PTA together with the chemically adsorbed  $O_2$ , which can be used for CO oxidation with significantly low activation energy. Recently, Liu *et al.* have prepared SACs for enhancing the diborization activity of alkynes with Pt<sub>1</sub> stably anchored to PMA in the cavities of various metal–organic frameworks (MOFs).<sup>36</sup> These results indicate that the POM-SACs have practical application potential, providing an ideal platform for further research on SACs. However, the catalytic activity and mechanism of POM-SACs in the CO<sub>2</sub>RR need to be clarified.

In this work, by using first principles calculations and a series of filters, we have comprehensively investigated the electrocatalytic CO<sub>2</sub>RR activity of  $\alpha$ -[SiMo<sub>12</sub>O<sub>40</sub>]<sup>4-</sup>-supported single metal catalysts in which the transition metals (Sc to Zn and Y to Cd) are from d-block elements in the periodic table. The geometric structure, stability and CO<sub>2</sub>RR catalytic activity of the studied SACs were systematically explored. Based on the screening results, we observed that TM@Na<sub>4</sub>SiMo<sub>12</sub> (TM = Sc,

Cr, Mn, Ti and V) have high catalytic activity for the CO<sub>2</sub>RR, and the HER is inhibited, which are expected to be potential electrocatalysts for the CO<sub>2</sub>RR. Particularly, the limiting potential ( $U_L$ ) for the CO<sub>2</sub>RR catalyzed by Cr@Na<sub>4</sub>SiMo<sub>12</sub> is only  $-0.23$  V. Under the equilibrium potential of CO<sub>2</sub>/HCOOH, Mn@Na<sub>4</sub>SiMo<sub>12</sub> is not disturbed by H<sub>2</sub>O. At the same time, POMs are found to play the role of electron sponge in the catalytic reaction. The present work is expected to provide valuable information for designing POM-based SACs and deepening the understanding the mechanism of the electrocatalytic CO<sub>2</sub>RR so as to realize the effective utilization of CO<sub>2</sub>.

## 2. Computational details

All geometric optimizations and single point energy calculations were performed using the Vienna *Ab initio* Simulation Package (VASP).<sup>37,38</sup> The generalized gradient approximation (GGA) with the Perdew–Burke–Ernzerhof (PBE)<sup>39</sup> exchange–correlation functional was chosen to describe the exchange–correlation interactions, and the DFT-D3 method was chosen to correctly describe van der Waals (vdW) interactions.<sup>40</sup> A plane wave cutoff energy of 450 eV was used. The geometric structure was optimized by cubic cells with a side length of 30 Å, and the Brillouin zone was sampled using only the  $\Gamma$  point, until the convergence criteria of energy and force were less than  $10^{-4}$  eV and  $0.04$  eV Å<sup>-1</sup>, respectively. The charge transfer was obtained based on the Bader charge analysis. To investigate the chemical bonding between the TM atom and the adsorbate, we performed crystal orbital Hamilton population (COHP) analysis,<sup>41–43</sup> as implemented in the LOBSTER code.<sup>44</sup>

The adsorption energy ( $E_{\text{ads}}$ ) was calculated using the following equation:

$$E_{\text{ads}} = E_{\text{A-S}} - E_{\text{S}} - E_{\text{A}} \quad (1)$$

where  $E_{\text{A-S}}$ ,  $E_{\text{S}}$ , and  $E_{\text{A}}$  are the total energies of the adsorbate–substrate (A–S) complex, the substrate (S), and the adsorbate (A), respectively.

The Gibbs free energy change ( $\Delta G$ ) was calculated using the computational hydrogen electrode (CHE) model developed by Nørskov *et al.*,<sup>45</sup> and is defined as:

$$\Delta G = \Delta E + \Delta E_{\text{ZPE}} - T\Delta S + \Delta G_{\text{pH}} + \Delta G_{\text{U}} \quad (2)$$

where  $\Delta E$  is the difference of reaction energy, which can be directly obtained from DFT calculations.  $\Delta E_{\text{ZPE}}$  and  $\Delta S$  are the change of zero-point energy and entropy, respectively.  $\Delta E_{\text{ZPE}}$  can be calculated by summing vibrational frequencies ( $\Delta E_{\text{ZPE}} = 1/2\sum\hbar\nu$ ). The entropies of gas phase molecules (CO<sub>2</sub>, H<sub>2</sub>, and H<sub>2</sub>O) were obtained from the NIST database.<sup>46</sup>  $T$  is the temperature (298.15 K).  $\Delta G_{\text{pH}}$  is the contribution of free energy due to the change of H concentration;  $\Delta G_{\text{pH}} = k_{\text{B}}T \times \ln 10 \times \text{pH}$ , where  $k_{\text{B}}$  is the Boltzmann constant, and the value of pH was set to be zero in this work.  $\Delta G_{\text{U}} = -neU$ , where  $n$  is the number of transferred electrons and  $U$  is the electrode potential relative to the standard hydrogen electrode (SHE). The  $U_L$  of the reaction is obtained by using the formula  $U_L = -\Delta G_{\text{max}}/e$ . A conductor-like

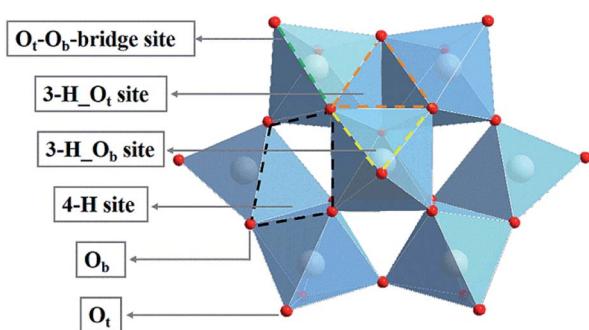


Fig. 1 Structure of an  $\alpha$ -Keggin type polyoxometalate.

screening model (COSMO) was considered to simulate the water solvent environment throughout the whole process.<sup>47</sup> The energy correction of the solvent effect was implemented under an implicit solvation model (named *VASP sol*) developed by Hennig and colleagues.<sup>48,49</sup> In order to evaluate the stability of  $\text{Na}_4\text{SiMo}_{12}$ , an *ab initio* molecular dynamics (AIMD) simulation was performed by using the PBE functional and PAW pseudo-potential. The Nose-Hoover method was used to control the temperature.<sup>50</sup> AIMD simulation in the NVT ensemble was carried out at 500 K with a time step of 1.0 fs for a total of 10 ps.

### 3. Results and discussion

#### 3.1 Calculation model of TM@ $\text{Na}_4\text{SiMo}_{12}$

A previous study has proved that the incorporation of counterions into the computational models is crucial to accurately reproduce the properties of polyoxoanions.<sup>51</sup> In this work, the charge of  $\alpha\text{-}[\text{SiMo}_{12}\text{O}_{40}]^{4-}$  ( $\text{SiMo}_{12}$ ) was compensated by using four sodium ions to ensure the electroneutrality of the system. Based on the experimental result, we constructed a preliminary geometric model of the adsorption of  $\text{Na}_4\text{SiMo}_{12}$  on graphene.<sup>34</sup> After optimization, the average distance between the  $\text{Na}_4\text{SiMo}_{12}$  and graphene is 2.95 Å (Fig. 2a and c). In order to understand the interaction between  $\text{Na}_4\text{SiMo}_{12}$  and graphene, the charge density difference of  $\text{Na}_4\text{SiMo}_{12}$  adsorbed on graphene was analyzed and is shown in Fig. S1 of the ESI.† Herein, yellow represents the electron density accumulation region, and cyan represents the electron density depletion region. We can see the obvious electron transfer from the counterions to  $\text{SiMo}_{12}$ , indicating that the  $\text{SiMo}_{12}$  and counterions have strong interaction, while the charge distribution on graphene is negligible, indicating that the interaction between graphene and  $\text{Na}_4\text{SiMo}_{12}$  is weak, and that graphene plays the role of conductive support in the experiment. Thus, graphene will not be taken into account in the following calculations in order to reduce computational cost (Fig. 2b and d).

Previous studies have shown that Pt atom dispersed on PMA and the most stable adsorption site is 4-H site.<sup>34,36</sup> In addition to the 4-H site, the other sites of the Keggin type anion, such as 3-H<sub>O</sub>, 3-H<sub>O<sub>b</sub></sub>, and O<sub>t</sub>-O<sub>b</sub>-bridge, may also trap metal atoms. Taking Sc and Y as examples, all possible adsorption sites were studied to verify the most stable adsorption site on  $\text{Na}_4\text{SiMo}_{12}$ .

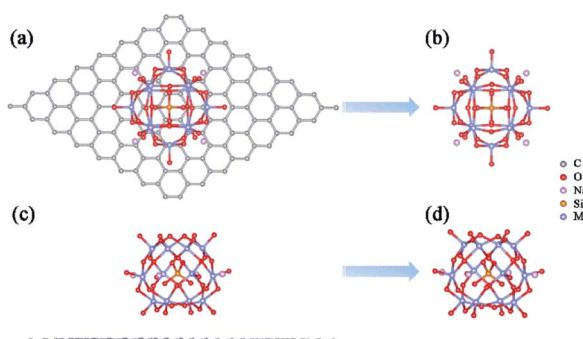


Fig. 2 Top views (a and b) and side views (c and d) of the most stable structures of  $\text{Na}_4\text{SiMo}_{12}$  loaded with or without graphene.

The optimized structures and calculated adsorption energies of the TMs (TMs = Sc and Y) on  $\text{Na}_4\text{SiMo}_{12}$  are shown in Fig. S2 of the ESI.† It is found that the TMs prefer to anchor to the 4-H site of  $\text{Na}_4\text{SiMo}_{12}$ , which is consistent with the previous studies.<sup>34,36,52-55</sup> Based on the above analysis, the calculation model of TM@ $\text{Na}_4\text{SiMo}_{12}$  was confirmed and is shown in Fig. 3a, in which the TMs are anchored on the POM 4-H site.

#### 3.2 Stability of TM@ $\text{Na}_4\text{SiMo}_{12}$

For SACs, due to the high surface energy and small migration barrier of metal atoms, agglomeration can easily occur during preparation and reaction, resulting in deactivation of the catalysts. In order to evaluate the stability of the studied POM-SACs, the  $E_{\text{ads}}$  of single atoms anchored on the 4-H site of  $\text{Na}_4\text{SiMo}_{12}$  was computed and the results are shown in Fig. 3b and Table S1 of the ESI.† The  $E_{\text{ads}}$  was calculated using the equation:<sup>56</sup>

$$E_{\text{ads}} = E_{(\text{TM@Na}_4\text{SiMo}_{12})} - E_{(\text{Na}_4\text{SiMo}_{12})} - \mu_{(\text{TM})} \quad (3)$$

where  $E_{(\text{TM@Na}_4\text{SiMo}_{12})}$ ,  $E_{(\text{Na}_4\text{SiMo}_{12})}$  and  $\mu_{(\text{TM})}$  represent the total energies of the transition metal (TM) atom supported on  $\text{Na}_4\text{SiMo}_{12}$ ,  $\text{Na}_4\text{SiMo}_{12}$  substrates and the chemical potential of the TM atom calculated from the metal bulk, respectively. According to this definition, a negative  $E_{\text{ads}}$  means that a single metal atom is energetically favorable to be anchored on the 4-H site of  $\text{Na}_4\text{SiMo}_{12}$ . As shown in Fig. 3b, the  $E_{\text{ads}}$  values of TM@ $\text{Na}_4\text{SiMo}_{12}$  (TM = Sc, Ti, V, Cr, Mn, Zn, Y, Zr, Nb and Cd) are all negative, indicating that these TMs anchored on  $\text{Na}_4\text{SiMo}_{12}$  have high stability and may hold great promise for synthesis. However, the remaining TM atoms (TM = Fe, Co, Ni, Cu, Mo, Tc, Ru, Rh, Pd and Ag) may exist in the form of nanoparticles or aggregate in the bulk phases. The TM-O bond lengths of TM@ $\text{Na}_4\text{SiMo}_{12}$  (TM = Sc, Ti, V, Cr, Mn, Zn, Y, Zr, Nb and Cd) are summarized in Table S2 of the ESI.† and are similar to those of the synthesized Pt@POMs reported in previous experiments.<sup>34,36,55</sup>

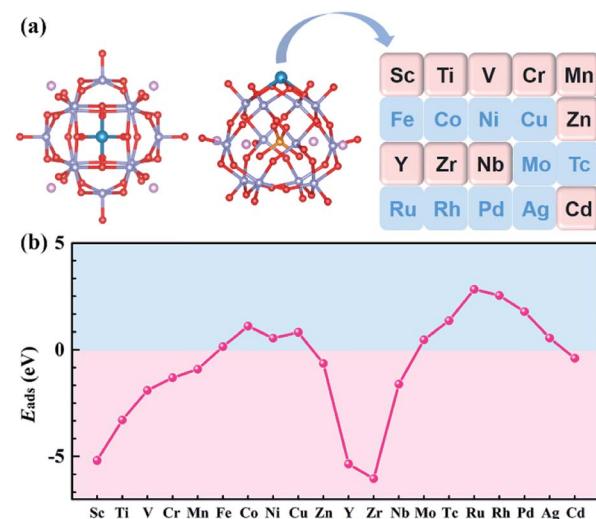
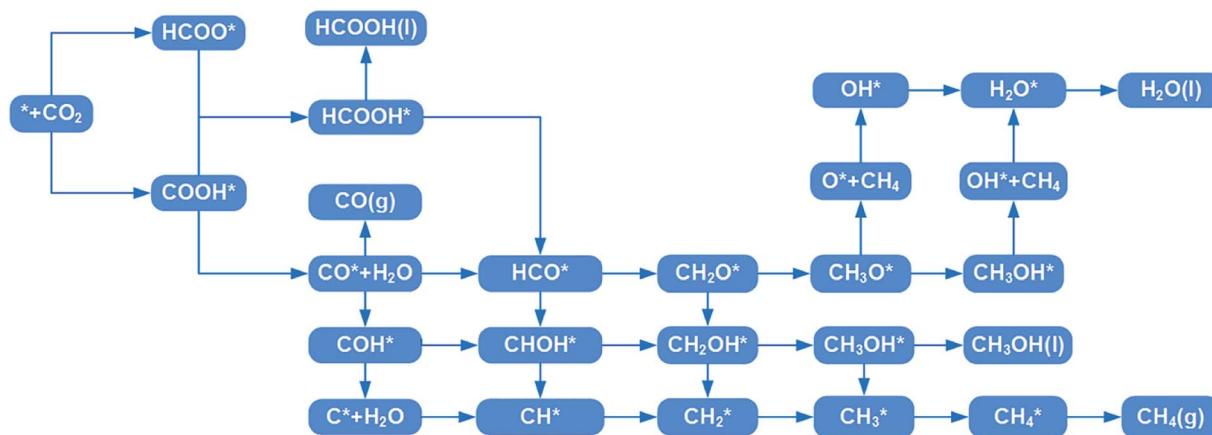


Fig. 3 (a) Schematic illustration of the transition metals anchored on  $\text{Na}_4\text{SiMo}_{12}$ . (b) The adsorption energies of transition metal atoms anchored on  $\text{Na}_4\text{SiMo}_{12}$ .



Scheme 1 All considered reaction pathways for  $\text{CO}_2$  reduction on  $\text{TM}@\text{Na}_4\text{SiMo}_{12}$ .

The stability of  $\text{Na}_4\text{SiMo}_{12}$  was further verified by AIMD simulation. No obvious structural deformation was observed after  $\text{Na}_4\text{SiMo}_{12}$  was simulated at 500 K with a time step of 1.0 fs for a total of 10 ps, indicating its high thermal stability (Fig. S3 of the ESI†).

### 3.3 Electrochemical $\text{CO}_2$ RR on $\text{TM}@\text{Na}_4\text{SiMo}_{12}$

**3.3.1  $\text{CO}_2$  adsorption.** In the following, the study focuses on whether  $\text{TM}@\text{Na}_4\text{SiMo}_{12}$  can efficiently catalyze  $\text{CO}_2$ . The first step to initialize the reduction reaction is the  $\text{CO}_2$  adsorption on  $\text{TM}@\text{Na}_4\text{SiMo}_{12}$ , which is often neglected in many studies. If  $\text{CO}_2$  can be effectively captured and activated, the catalytic performance of the  $\text{CO}_2$ RR can be improved. The charge density difference, adsorption energy and charge transfer amount of  $\text{CO}_2$  adsorption over  $\text{TM}@\text{Na}_4\text{SiMo}_{12}$  ( $\text{TM} = \text{Sc}, \text{Ti}, \text{V}, \text{Cr}, \text{Mn}, \text{Y}, \text{Zr}$  and  $\text{Nb}$ ) were computed and are shown in Fig. S4 of the ESI.† It is observed that these catalysts can effectively capture and activate  $\text{CO}_2$  with the adsorption energy in the range of  $-0.30$  to  $-0.73$  eV. The O atom of  $\text{CO}_2$  prefers to be adsorbed on TM atoms, and  $\text{TM}@\text{Na}_4\text{SiMo}_{12}$  donate electrons to  $\text{CO}_2$  (around 0.02–0.07e).

To further clarify the role of anchored transition metals in the catalytic cycle, the charge density difference of the system doped with transition metals was analyzed by taking  $\text{Cr}@\text{Na}_4\text{SiMo}_{12}$  as an example (Fig. S5a of the ESI†). The charge density difference shows that the electron transfers from the anchored Cr atom to the neighboring oxygen atoms, and the Bader charge analysis (Fig. S8 of the ESI†) suggests that the Cr atom is positively charged due to losing  $1.45e$ , and chemical bonds are formed between the Cr atom and the oxygen atoms of  $\text{Na}_4\text{SiMo}_{12}$ . The partial density of states (PDOS) of  $\text{Cr}@\text{Na}_4\text{SiMo}_{12}$  was further analyzed and is shown in Fig. S5b of the ESI† in which the d orbitals of the Cr atom strongly hybridize with the p orbitals of adjacent O atoms near the Fermi level ( $E_F$ ). The d orbitals of Cr near the Fermi level show high reactivity, which may trigger adsorption in the catalytic cycle.

**3.3.2 Initial protonation steps of the  $\text{CO}_2$ RR vs. HER.** The first protonation step in the electrochemical  $\text{CO}_2$ RR is the formation of carboxyl ( $\text{COOH}^*$ ) or formate ( $\text{HCOO}^*$ )

intermediates, from which various carbon-containing products are subsequently produced (Scheme 1). Under the same reaction conditions,  $\text{H}^*$  can also produce competitive HER by consuming the same proton-electron pair ( $\text{H}^+ + \text{e}^-$ ), which affects the faradaic efficiency of the  $\text{CO}_2$ RR. Therefore, we first evaluated the  $\Delta G$  for  $\text{COOH}^*$ ,  $\text{HCOO}^*$ , and  $\text{H}^*$  to select catalysts that might catalyze the  $\text{CO}_2$ RR with high selectivity. Based on the Brønsted–Evans–Polanyi relation,<sup>57,58</sup> low free energy reactions are more selective. As shown in Fig. 4, except where  $\text{TM} = \text{Cd}$  and  $\text{Zn}$ ,  $\text{TM}@\text{Na}_4\text{SiMo}_{12}$  ( $\text{TM} = \text{Sc}, \text{Ti}, \text{V}, \text{Cr}, \text{Mn}, \text{Y}, \text{Zr}$  and  $\text{Nb}$ ) are below the diagonal, indicating that these catalysts prefer to catalyze the  $\text{CO}_2$ RR rather than the HER. The calculated free energy changes for the  $\text{CO}_2$ RR on  $\text{TM}@\text{Na}_4\text{SiMo}_{12}$  ( $\text{TM} = \text{Sc}, \text{Ti}, \text{V}, \text{Cr}, \text{Mn}, \text{Y}, \text{Zr}$ , and  $\text{Nb}$ ) are presented in Table S3 of the ESI.† The  $\Delta G$  for  $\text{COOH}^*$  formation by candidate catalysts is much larger than those of  $\text{HCOO}^*$  formation, so  $\text{HCOO}^*$  is considered to be the only intermediate for subsequent hydrogenation. For catalysts with a single active site, it is unlikely to generate C2 products through the C–C coupling of C1 intermediates based on the Langmuir–Hinshelwood mechanism,<sup>59,60</sup> so this work only considers the generation of C1 products.

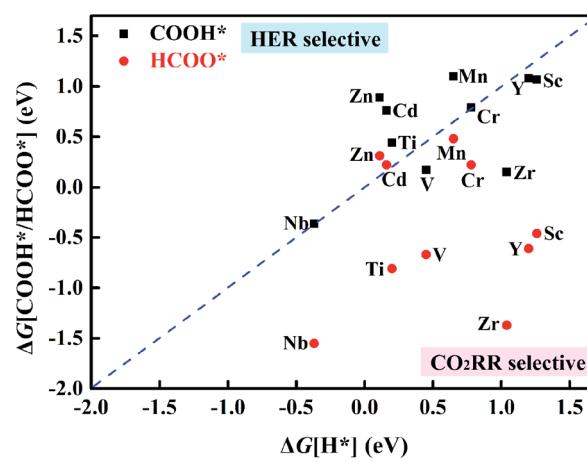


Fig. 4 Free energy change ( $\Delta G$ ) of the first protonation step in the  $\text{CO}_2$ RR and HER on  $\text{TM}@\text{Na}_4\text{SiMo}_{12}$ .

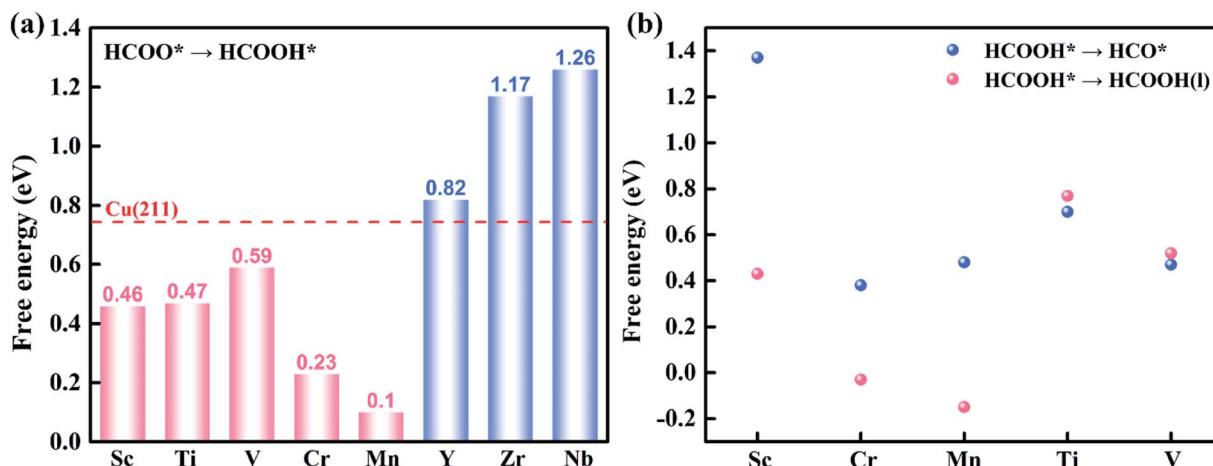


Fig. 5 (a) The  $\Delta G$  of  $\text{HCOO}^* + \text{e}^- + \text{H}^+ \rightarrow \text{HCOOH}^*$  on TM@ $\text{Na}_4\text{SiMo}_{12}$  (TM = Sc, Ti, V, Cr, Mn, Y, Zr and Nb). The screening criterion for catalytic activity is set to  $\Delta G < 0.74$  eV (red dashed line). (b) The  $\Delta G$  for  $\text{HCOOH}^*$  hydrogenation ( $\text{HCOOH}^* + \text{e}^- + \text{H}^+ \rightarrow \text{HCO}^* + \text{H}_2\text{O}$  (l)) and desorption ( $\text{HCOOH}^* \rightarrow \text{HCOOH}$  (l) +  ${}^*$ ) on TM@ $\text{Na}_4\text{SiMo}_{12}$  (TM = Sc, Cr, Mn, Ti and V).

**3.3.3 HCOOH\* hydrogenation vs. desorption.** In order to evaluate the catalytic activity of TM@ $\text{Na}_4\text{SiMo}_{12}$ , the  $\Delta G$  of HCOO\* hydrogenation was computed and the limiting potential ( $-0.74$  V) of CO<sub>2</sub> reduction on the Cu (211) surface is taken as the screening criterion.<sup>61</sup> From Fig. 5a, Y, Zr and

Nb@ $\text{Na}_4\text{SiMo}_{12}$  exhibit weak catalytic activity with high  $\Delta G$  values ( $>0.74$  eV). In contrast, HCOOH\* formation by TM@ $\text{Na}_4\text{SiMo}_{12}$  (TM = Sc, Ti, V, Cr, and Mn) have lower free energies ( $\Delta G < 0.74$  eV), so they are screened as potential catalysts for further investigation.

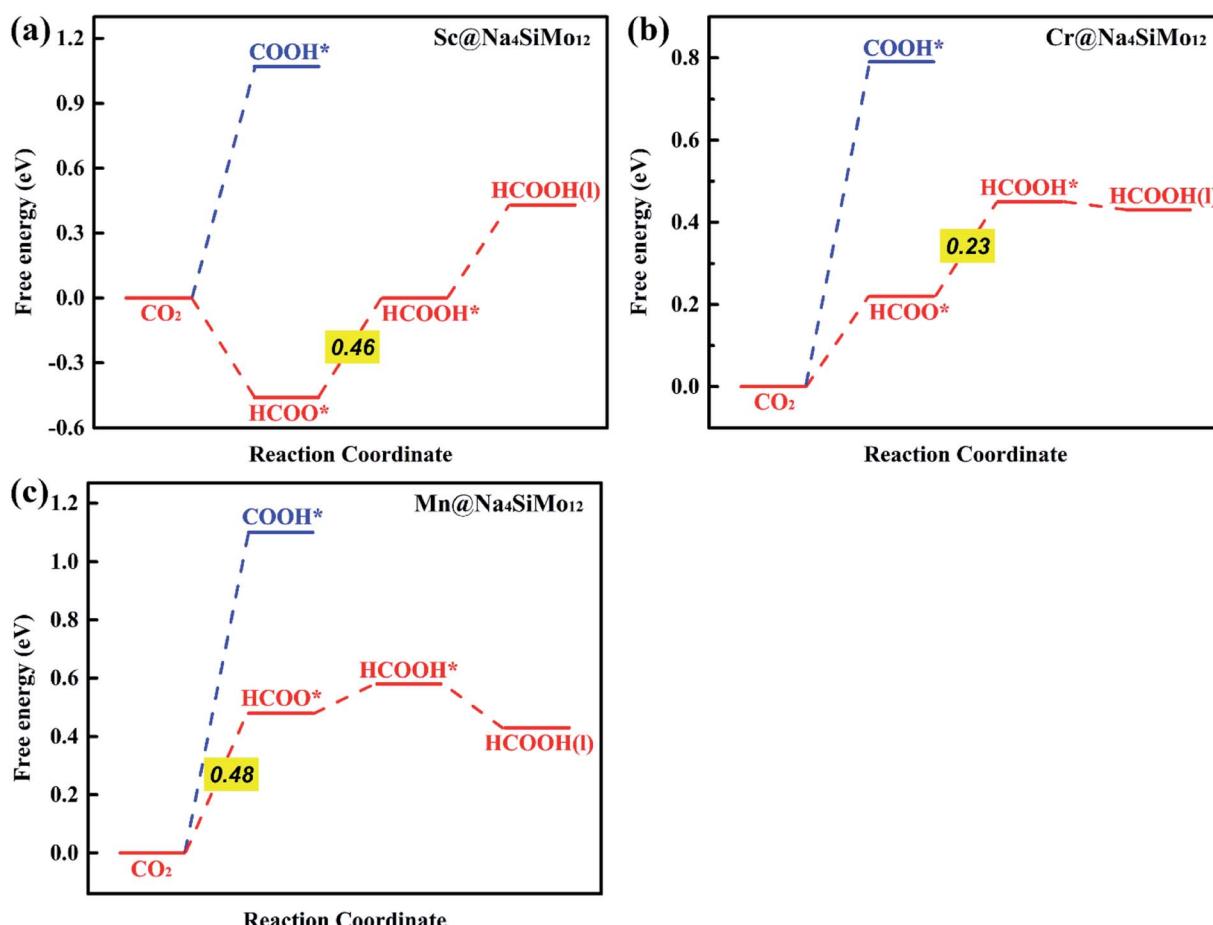


Fig. 6 Calculated free energy diagrams for the electrochemical CO<sub>2</sub>RR on (a) Sc@ $\text{Na}_4\text{SiMo}_{12}$ , (b) Cr@ $\text{Na}_4\text{SiMo}_{12}$  and (c) Mn@ $\text{Na}_4\text{SiMo}_{12}$ .

**Table 1** The calculated potential determining step (PDS) and  $U_L$  (V) for HCOOH and CH<sub>4</sub> formation on TM@Na<sub>4</sub>SiMo<sub>12</sub>

Metal	PDS	$U_L$
Sc <sup>a</sup>	HCOO* + e <sup>-</sup> + H <sup>+</sup> → HCOOH*	-0.46
Cr <sup>a</sup>	HCOO* + e <sup>-</sup> + H <sup>+</sup> → HCOOH*	-0.23
Mn <sup>a</sup>	CO <sub>2</sub> * + e <sup>-</sup> + H <sup>+</sup> → HCOO*	-0.48
Ti <sup>b</sup>	HCOOH* + e <sup>-</sup> + H <sup>+</sup> → HCO* + H <sub>2</sub> O (l)	-0.70
V <sup>b</sup>	OH* + e <sup>-</sup> + H <sup>+</sup> → H <sub>2</sub> O*	-0.74

<sup>a</sup> HCOOH production. <sup>b</sup> CH<sub>4</sub> production.

HCOOH\* can be desorbed (HCOOH\* → HCOOH (l) + \*) from the catalyst or further hydrogenated (HCOOH\* + H<sup>+</sup> + e<sup>-</sup> → HCO\* + H<sub>2</sub>O (l)). As shown in Fig. 5b, the HCOOH\* desorption on TM@Na<sub>4</sub>SiMo<sub>12</sub> (TM = Sc, Cr, and Mn) is easier than further hydrogenation, indicating that these three catalysts tend to produce HCOOH. In contrast, the HCO\* intermediate is formed on Ti and V@Na<sub>4</sub>SiMo<sub>12</sub> with  $\Delta G$  of 0.70 eV and 0.47 eV, which are lower than the  $\Delta G$  of HCOOH\* desorption (0.77 eV and 0.52 eV). Therefore, the subsequent protonation process will be considered for Ti and V@Na<sub>4</sub>SiMo<sub>12</sub>.

**3.3.4 CO<sub>2</sub>RR to HCOOH on TM@Na<sub>4</sub>SiMo<sub>12</sub> (TM = Sc, Cr, and Mn).** Based on the above results, the CO<sub>2</sub>RR on TM@Na<sub>4</sub>SiMo<sub>12</sub> (TM = Sc, Cr, and Mn) is a  $2e^-$  reaction in which the main product is HCOOH, and the calculated free energy diagrams are presented in Fig. 6. The optimal reaction path of these catalysts is CO<sub>2</sub> (g) → HCOO\* → HCOOH\* → HCOOH (l). The  $\Delta G$  of each step and the structures corresponding to the optimal reaction path are shown in Table S3 and Fig. S6 of the ESI.† The potential determination steps (PDS) and  $U_L$  for the most favorable products are summarized in Table 1.

First, the H<sup>+</sup> + e<sup>-</sup> pair attacks the carbon atom of CO<sub>2</sub> to form HCOO\*. It should be noted that the  $\Delta G$  for CO<sub>2</sub> + H<sup>+</sup> + e<sup>-</sup> → HCOO\* on Sc@Na<sub>4</sub>SiMo<sub>12</sub> is -0.46 eV, while for Cr and Mn@Na<sub>4</sub>SiMo<sub>12</sub>, the  $\Delta G$  is 0.22 eV and 0.48 eV, respectively. Afterwards, HCOO\* can be further reduced to form HCOOH\* on TM@Na<sub>4</sub>SiMo<sub>12</sub> (TM = Sc, Cr and Mn) with  $\Delta G$  of 0.46, 0.23, and 0.10 eV, respectively, which are less than the  $\Delta G$  of HCOOH\* hydrogenation to HCO\*. Therefore, for TM@Na<sub>4</sub>SiMo<sub>12</sub> (TM = Sc, Cr and Mn), HCOOH\* will not undergo further hydrogenation and is released in the form of a liquid. For Sc and Cr@Na<sub>4</sub>SiMo<sub>12</sub>, the PDS is the step of HCOO\* → HCOOH\* with  $U_L$  of -0.46 V and -0.23 V, respectively. For Mn@Na<sub>4</sub>SiMo<sub>12</sub>, CO<sub>2</sub> → HCOO\* is the PDS with  $U_L$  of -0.48 V.

**3.3.5 CO<sub>2</sub>RR to CH<sub>4</sub> on TM@Na<sub>4</sub>SiMo<sub>12</sub> (TM = Ti and V).** Different from the above catalysts, HCOOH\* has strong adsorption on the surface of Ti and V@Na<sub>4</sub>SiMo<sub>12</sub>, and can be further hydrogenated with the H<sup>+</sup> + e<sup>-</sup> pair to obtain the HCO\* intermediate. In this process, the  $\Delta G$  for Ti and V@Na<sub>4</sub>SiMo<sub>12</sub> is 0.70 and 0.47 eV, respectively. Subsequently, HCO\* is hydrogenated to produce CHO<sup>+</sup> or CH<sub>2</sub>O\*. As can be seen from Fig. 7, the CH<sub>2</sub>O\* generation on these two catalysts is an exothermic process, which is more favorable than CHO<sup>+</sup> formation. In the next step, CH<sub>2</sub>O\* is further hydrogenated to form a CH<sub>2</sub>OH\* or CH<sub>3</sub>O\* intermediate. For Ti@Na<sub>4</sub>SiMo<sub>12</sub>, the H<sup>+</sup> + e<sup>-</sup> pair attacks the O atom of CH<sub>2</sub>O\* to form CH<sub>2</sub>OH\* with

$\Delta G$  of 0.54 eV, which is much easier than CH<sub>3</sub>O\* formation (1.68 eV). In the following steps, the H<sup>+</sup> + e<sup>-</sup> pairs continuously attack the C atom of the intermediates: CH<sub>2</sub>OH\* → CH<sub>3</sub>OH\* → CH<sub>4</sub> + OH\*, which is a continuous exothermic process with  $\Delta G$  of -0.72 and -1.64 eV. Finally, the CH<sub>4</sub> molecule is desorbed from the catalyst surface due to the weak adsorption energy (-0.65 eV). The remaining OH\* is further hydrogenated to produce an H<sub>2</sub>O molecule with a  $\Delta G$  of 0.69 eV. For the CO<sub>2</sub>RR on Ti@Na<sub>4</sub>SiMo<sub>12</sub>, the most favorable reaction pathway is CO<sub>2</sub> → HCOO\* → HCOOH\* → HCO\* → CH<sub>2</sub>O\* → CH<sub>2</sub>OH\* → CH<sub>3</sub>OH\* → CH<sub>4</sub> + OH\* → CH<sub>4</sub> + H<sub>2</sub>O, and the PDS is the step of HCOOH\* → HCO\* with  $U_L$  of -0.70 V.

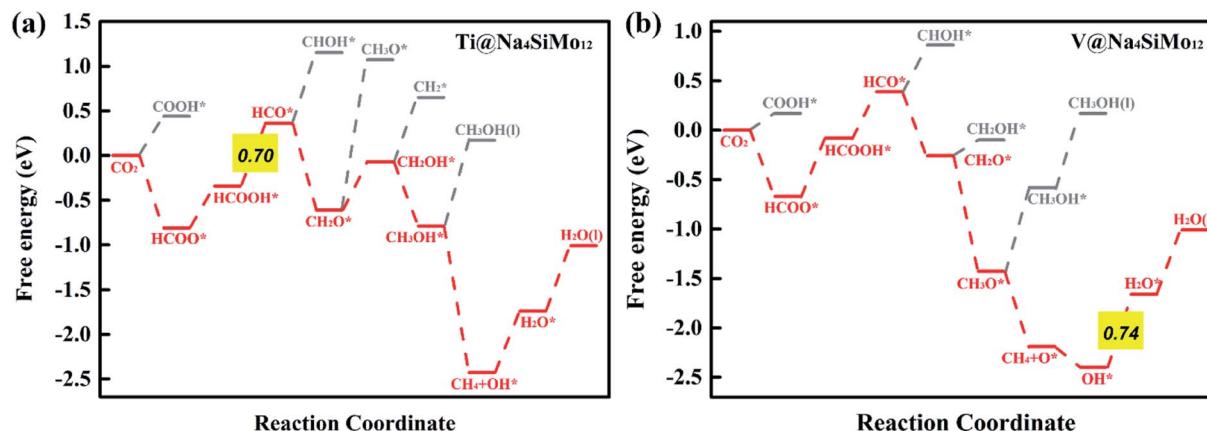
For V@Na<sub>4</sub>SiMo<sub>12</sub>, once the intermediate CH<sub>2</sub>O\* is obtained, subsequent H<sup>+</sup> + e<sup>-</sup> pairs continue to attack the C atom until the C–O bond is broken and the CH<sub>4</sub> molecule is released. Due to the weak adsorption energy of CH<sub>4</sub> (-0.40 eV), it eventually desorbs from the surface as a product. The remaining O\* undergoes two successive hydrogenation steps to produce an H<sub>2</sub>O molecule, and the corresponding free energy changes are -0.21 eV and 0.74 eV, respectively. For V@Na<sub>4</sub>SiMo<sub>12</sub>, the most favorable reaction pathway is CO<sub>2</sub> → HCOO\* → HCOOH\* → HCO\* → CH<sub>2</sub>O\* → CH<sub>3</sub>O\* → CH<sub>4</sub> + O\* → OH\* → H<sub>2</sub>O, and the PDS is the step of OH\* → H<sub>2</sub>O with  $U_L$  of -0.74 V.

In summary, TM@Na<sub>4</sub>SiMo<sub>12</sub> (TM = Sc, Cr, Mn, Ti and V) are promising high efficiency SACs for the electrochemical CO<sub>2</sub>RR with low  $U_L$ , and are superior to the Cu (211) catalyst (-0.74 V).<sup>61</sup> The competition between the H<sub>2</sub>O and CO<sub>2</sub> adsorption also needs to be investigated.<sup>62</sup> To further evaluate the stability of the above TM@Na<sub>4</sub>SiMo<sub>12</sub> (TM = Sc, Cr, Mn, Ti and V) in water, we calculated the surface Pourbaix diagrams as a function of the standard hydrogen electrode ( $U_{SHE}$ ) and pH. As shown in Fig. S9 of the ESI,† when pH = 0, TM@Na<sub>4</sub>SiMo<sub>12</sub> (TM = Sc, Cr, Mn, Ti and V) require voltages of -0.80, -0.60, 0.43, -1.34, and -0.99 V, respectively, to protect the catalyst from being covered by OH\* in water. When the actual potential is higher than the cathodic protection potential, the TM anchored on Na<sub>4</sub>SiMo<sub>12</sub> begins to be covered by OH\* in water. These catalysts are oxidized by O\* when the  $U_{SHE}$  values increase to 0.88, -0.20, 0.66, -0.42, and -0.62 V, respectively. In this work, the equilibrium potential of CO<sub>2</sub>/HCOOH and CO<sub>2</sub>/CH<sub>4</sub> is -0.22 and -0.13 V, respectively. Therefore, the catalyst should possess a high stability in water below the equilibrium potential of CO<sub>2</sub>/HCOOH or CO<sub>2</sub>/CH<sub>4</sub>. The results show that under the conditions of equilibrium potential, Mn@Na<sub>4</sub>SiMo<sub>12</sub> will remain exposed and will not be disturbed by H<sub>2</sub>O. In contrast, TM@Na<sub>4</sub>SiMo<sub>12</sub> (TM = Sc, Cr, Ti and V) will be covered by OH\*, affecting the performance of the CO<sub>2</sub>RR.

It can be seen that Cr@Na<sub>4</sub>SiMo<sub>12</sub> has a high catalytic activity for CO<sub>2</sub> reduction to HCOOH, while the selectivity of the CO<sub>2</sub>RR is not good due to the competition from H<sub>2</sub>O. In comparison, Mn@Na<sub>4</sub>SiMo<sub>12</sub> has high selectivity and relatively good catalytic performance ( $U_L$  = -0.48 V).

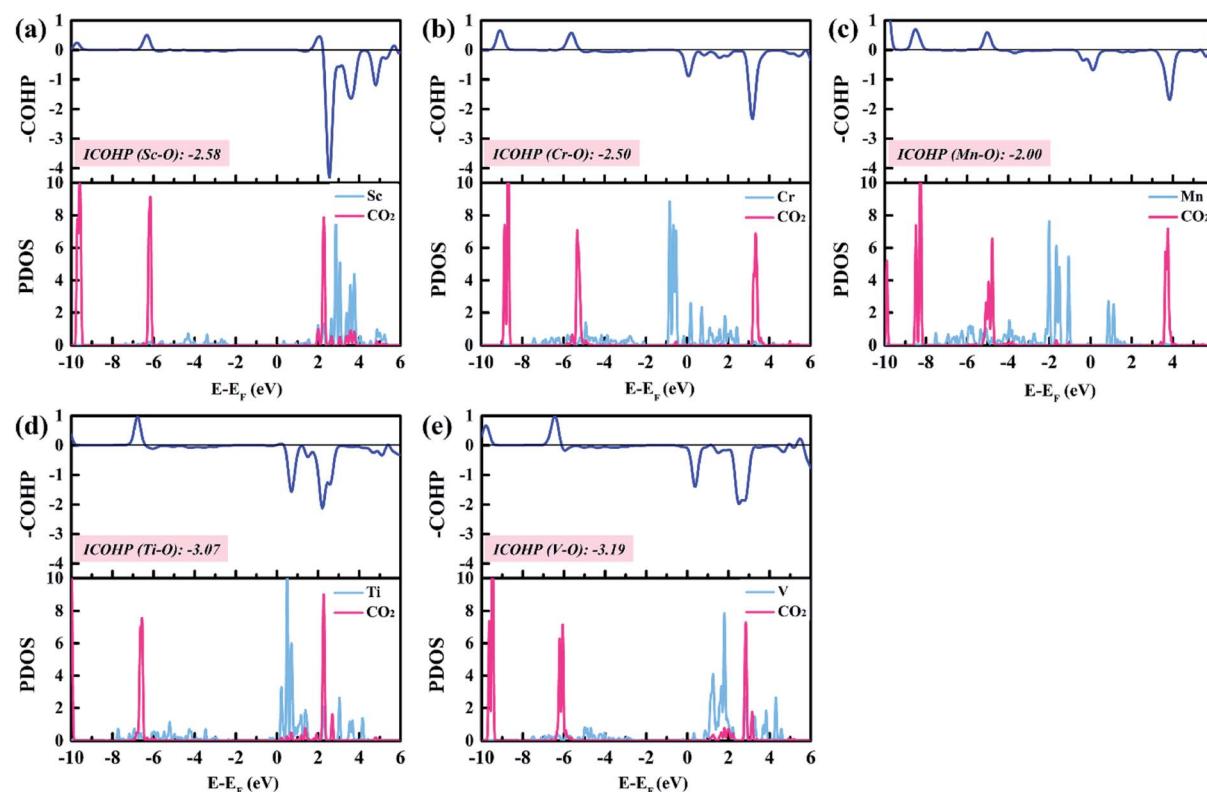
### 3.4 Difference in the catalytic activity of TM@Na<sub>4</sub>SiMo<sub>12</sub>

To gain insight into the catalytic performance of TM@Na<sub>4</sub>SiMo<sub>12</sub> (TM = Sc, Cr, Mn, Ti and V), the PDOS of CO<sub>2</sub> adsorbed

Fig. 7 Calculated free energy diagrams for the electrochemical CO<sub>2</sub>RR on (a) Ti and (b) V@Na<sub>4</sub>SiMo<sub>12</sub>.

on TM@Na<sub>4</sub>SiMo<sub>12</sub> was calculated and is shown in Fig. 8. It can be seen that Sc, Ti and V have obvious hybridization with CO<sub>2</sub>, and the hybridization range is wide, further indicating that TM@Na<sub>4</sub>SiMo<sub>12</sub> (TM = Sc, Cr, Mn, Ti and V) have strong interaction with CO<sub>2</sub>. In order to evaluate the TM–O binding interaction from CO<sub>2</sub> adsorbed on the TM@Na<sub>4</sub>SiMo<sub>12</sub> (TM = Sc, Cr, Mn, Ti and V), integrated-crystal orbital Hamilton population (ICOHP) analysis was performed by integrating the band states up to the highest occupied energy level to measure the bond strength (Fig. 8). Moreover, the more negative the value of ICOHP, the stronger the bonding interaction. The results show that the

ICOHP values change as follows: V (−3.19) < Ti (−3.07) < Sc (−2.58) < Cr (−2.50) < Mn (−2.00), and the bonding strength order is Mn–O < Cr–O < Sc–O < Ti–O < V–O. The relationship between the  $\Delta G$  of CO<sub>2</sub> hydrogenation to HCOO\* and the ICOHP values of the TM–O bond is plotted in Fig. S7 of the ESI.† It is interesting to find an approximately linear correlation with  $R^2$  of 0.75. In other words, the TM–O bond with a smaller ICOHP value is stronger, resulting in a smaller  $\Delta G$  value of CO<sub>2</sub> → HCOO\*, which also explains why the five catalysts have obvious differences in the first step of hydrogenation. In addition, we studied the relationship between the adsorption energies ( $E_{\text{ads}}$ )

Fig. 8 The PDOSs and COHPs of CO<sub>2</sub> on TM@Na<sub>4</sub>SiMo<sub>12</sub> (TM = Sc, Cr, Mn, Ti and V).

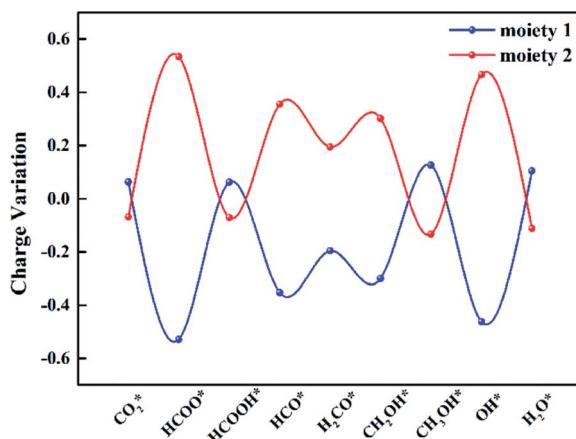


Fig. 9 Charge variation of the two moieties for  $\text{Ti}@\text{Na}_4\text{SiMo}_{12}$  along the optical reaction pathway. Moieties 1 and 2 represent the adsorbed  $\text{C}_x\text{H}_y\text{O}_z$  species and  $\text{Ti}@\text{SiMo}_{12}$ , respectively. Negative and positive values indicate electron gain and loss.

of  $\text{CO}_2$  on the  $\text{TM}@\text{Na}_4\text{SiMo}_{12}$  ( $\text{TM} = \text{Sc, Cr, Mn, Ti and V}$ ) and the Bader charges of TMs (Fig. S8 of the ESI†). As the charge amount of transition metals increases, the  $E_{\text{ads}}$  of  $\text{CO}_2$  increases, which in turn affects the catalytic performance of the  $\text{CO}_2\text{RR}$ .

To explore the role of  $\text{TM}@\text{Na}_4\text{SiMo}_{12}$  in the electrochemical  $\text{CO}_2\text{RR}$ ,  $\text{Ti}@\text{Na}_4\text{SiMo}_{12}$  is taken as an example to analyze the charge transfer between the reaction intermediates and the catalyst through Bader charge analysis along the optimal reaction pathway. As shown in Fig. 9, the studied system was divided into two parts including adsorbed  $\text{C}_x\text{H}_y\text{O}_z$  species (moiety 1) and  $\text{Ti}@\text{SiMo}_{12}$  (moiety 2). Counterions were not included because their charges remain essentially unchanged during the reaction. Firstly,  $\text{CO}_2$  gains  $0.07e$  by adsorption on  $\text{Ti}@\text{SiMo}_{12}$ , and  $\text{Ti}@\text{SiMo}_{12}$  loses the same amount of charge. As the reaction goes on,  $\text{Ti}@\text{SiMo}_{12}$  continuously donates and accepts electrons during the electrochemical  $\text{CO}_2\text{RR}$ , behaving as an “electron sponge”. Therefore,  $\text{Ti}@\text{SiMo}_{12}$  acts as an electron reservoir in the electrochemical  $\text{CO}_2\text{RR}$ .

## 4. Conclusions

In summary, a series of SACs with TMs ( $\text{TM} = \text{Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Y, Zr, Nb, Mo, Tc, Ru, Rh, Pd, Ag, and Cd}$ ) anchored on  $\text{Na}_4\text{SiMo}_{12}$  are proposed. Counterions are introduced into the calculation model, which is crucial to accurately reproduce the properties of polyoxoanions. Based on the DFT calculations,  $\text{TM}@\text{Na}_4\text{SiMo}_{12}$  ( $\text{TM} = \text{Sc, Ti, V, Cr, Mn, Zn, Y, Zr, Nb and Cd}$ ) are found to possess good stability, and might be synthesized in the experiment. Furthermore,  $\text{Sc, Cr, Mn, Ti, and V}@\text{Na}_4\text{SiMo}_{12}$  are predicted to be efficient catalysts for the  $\text{CO}_2\text{RR}$  due to the low  $U_{\text{L}}$ ; in particular,  $\text{CO}_2\text{RR}$  by  $\text{Cr}@\text{Na}_4\text{SiMo}_{12}$  has a very low  $U_{\text{L}}$  of  $-0.23$  V.  $\text{Mn}@\text{Na}_4\text{SiMo}_{12}$  has high selectivity and good catalytic performance for  $\text{CO}_2$  reduction to  $\text{HCOOH}$  with  $U_{\text{L}}$  of  $-0.48$  V. In addition, POMs act as “electron sponges” during the electrochemical  $\text{CO}_2\text{RR}$ , continuously accepting and donating electrons. This work provides valuable

insights into the design of highly selective and efficient SAC electrocatalysts for the  $\text{CO}_2\text{RR}$ .

## Conflicts of interest

There are no conflicts to declare.

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