SUPPORTING INFORMATION

Single–atom catalysts on supported silicomolybdic acid for CO_2 electroreduction: a DFT prediction

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Surface Pourbaix diagrams calculation

The oxidation mechanism of the catalyst by OH* and O* is as follows:

$$H_2O + * \rightarrow OH^* + H^+ + e^- \text{ (S1)}$$

$$OH^* \rightarrow O^* + H^+ + e^- \text{ (S2)}$$

where * represents the catalyst surface. OH* and O* are hydroxide and oxygen adsorbed on catalyst surface, respectively.

According to the computational hydrogen electrode model proposed by Nørskov et al.

$$H^+ + e^- = 1/2H_2\,(g) \text{ (S3)}$$

At given pH and potential, the free energy of reaction (S3) is:

$$\Delta G = eU + k_B T \ln 10\ pH \text{ (S4)}$$

Equation (S1) and (S2), which include the pH and potential, can be written as,

$$\Delta G(OH^*) = G(OH^*) - G(*) - G(H_2O) + 1/2G(H_2) - \Delta G \text{ (S5)}$$

$$\Delta G(O^*) = G(O^*) - G(*) - G(H_2O) + G(H_2) - 2\Delta G \text{ (S6)}$$

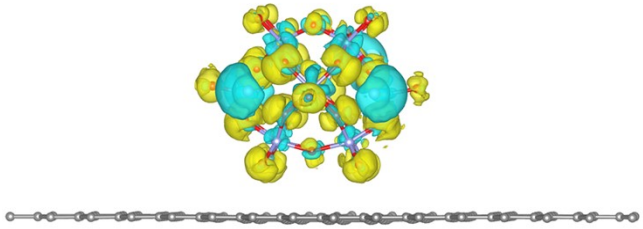

Fig. S1 Charge density difference of Na_4SiMo_{12} adsorbed on graphene, with isosurface level of 0.002 e/Å^3. The cyan and yellow regions represent electron depletion and accumulation, respectively.

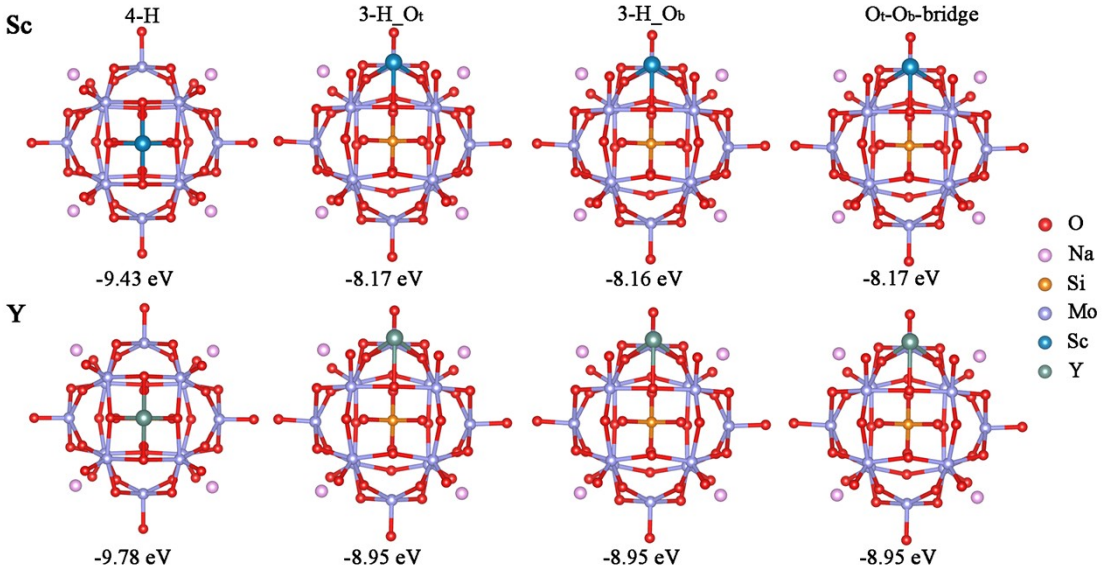

Fig. S2 Optimized configurations of TM (TM = Sc and Y) on Na_4SiMo_{12} with TM initially located in 4–H, 3–H_O_t, 3–H_O_b, and O_c–O_b–bridge, respectively. The values in the figure represent the adsorption energies (E_{ads}) of transition metals anchored at different sites of Na_4SiMo_{12}.

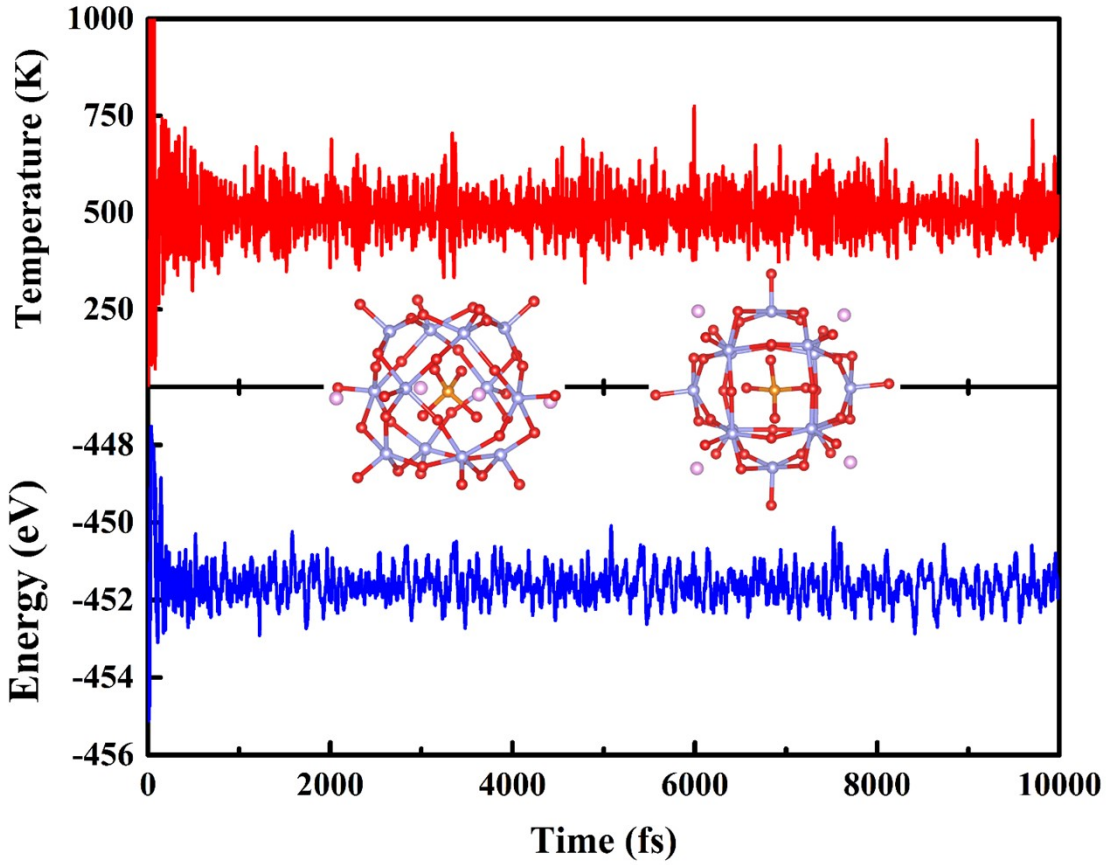

Fig. S3 Variations of temperature and energy against time for AIMD simulation of Na_4SiMo_{12}, and the insets show top and side views of the snapshot of the atomic configuration. The simulation is run at 500 K for 10 ps with a time step of 1 fs.

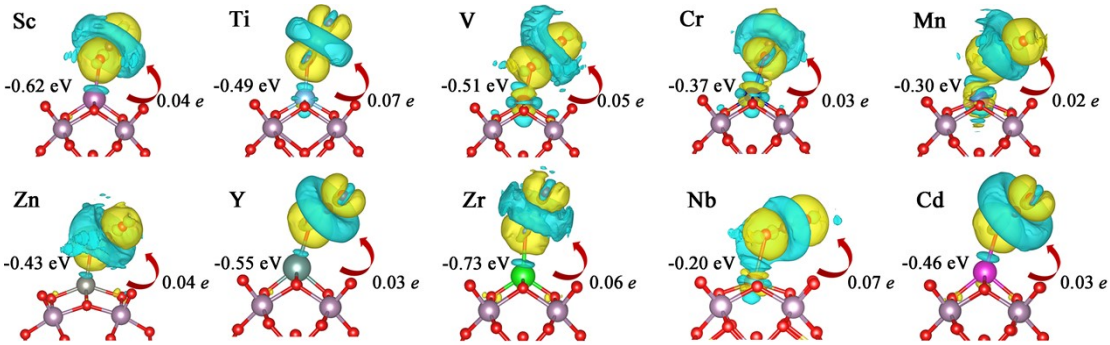

Fig. S4 Charge density difference of CO_2 adsorption over TM@Na_4SiMo_{12} (TM = Sc, Ti, V, Cr, Mn, Zn, Y, Zr, Nb and Cd), with isosurface level of 0.005 e/Å^3. The cyan and yellow regions represent electron depletion and accumulation, respectively. The values in the figure represent the adsorption energies (E_{ads}) of CO_2 anchored at TM@Na_4SiMo_{12} and the amount of charge transferred from the TM@Na_4SiMo_{12} to CO_2.

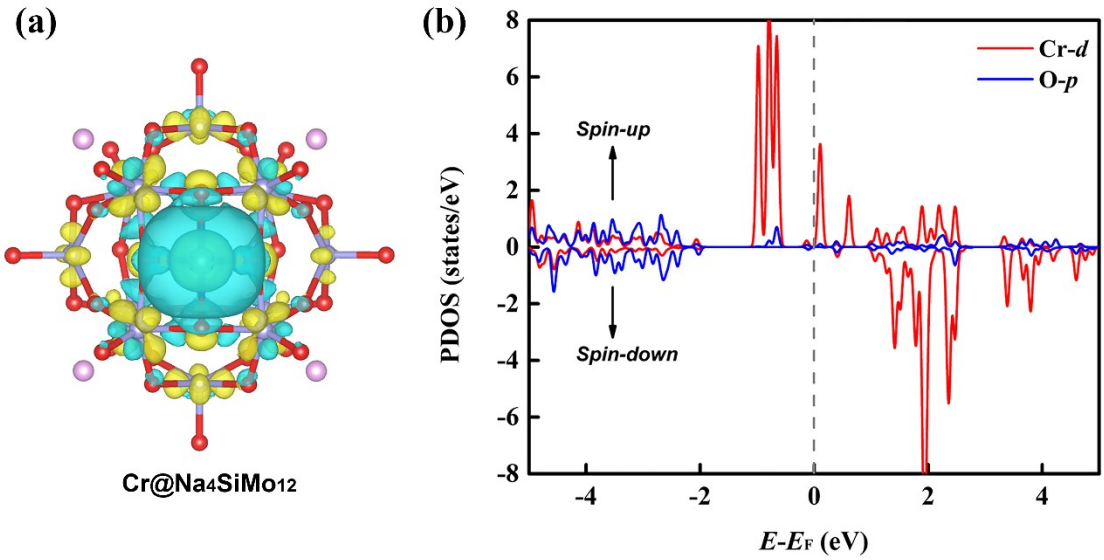

Fig. S5 (a) The charge density difference of Cr anchor on the Na_4SiMo_{12}, with isosurface level of 0.005 e/Å^3. The cyan and yellow regions represent electron depletion and accumulation, respectively. (b) The partial density of states (PDOS) of Cr anchor on the Na_4SiMo_{12}. The Fermi level is zero.

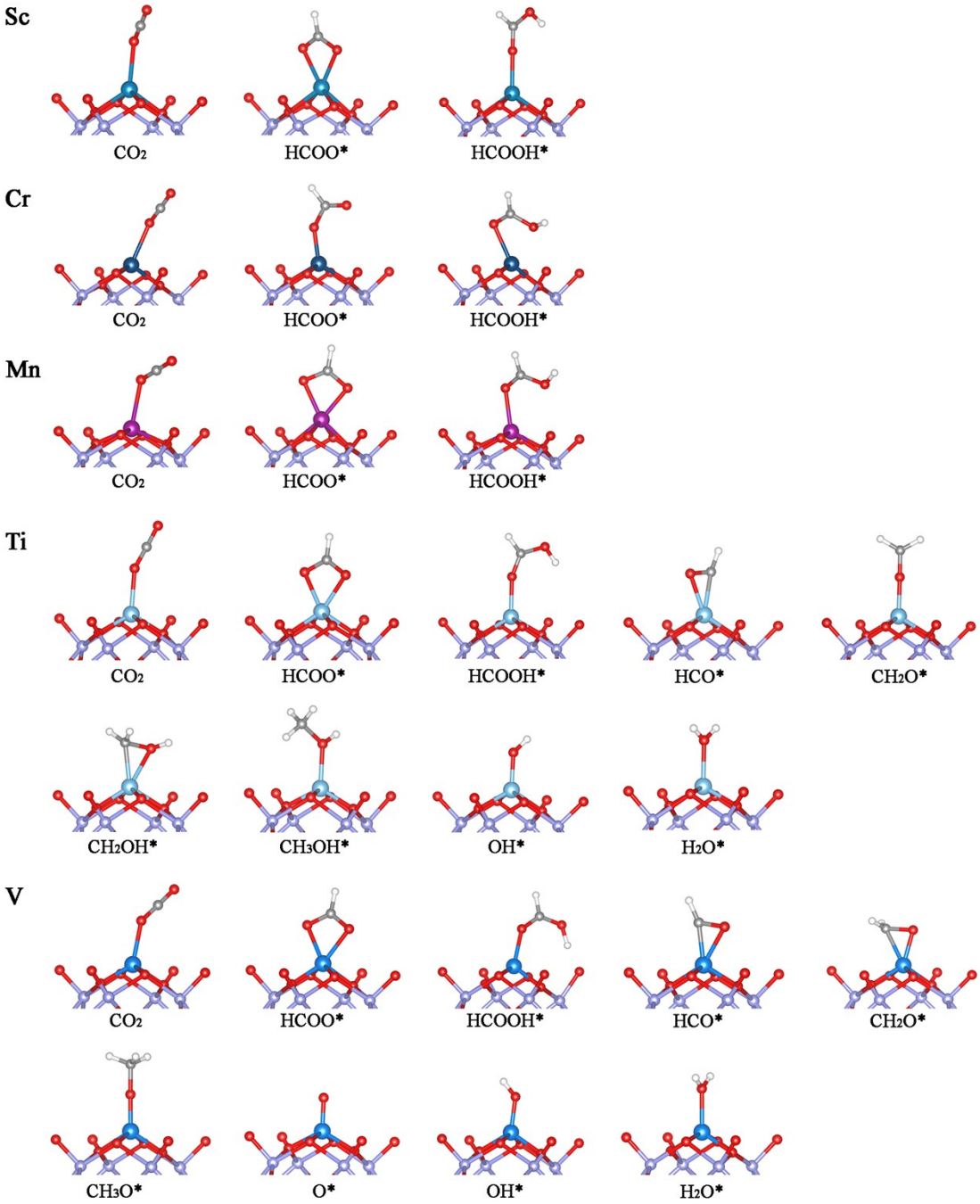

Fig. S6 The optimized CO_2RR intermediates along the most favorable pathway on TM@Na_4SiMo_{12} (TM = Sc, Cr, Mn, Ti and V).

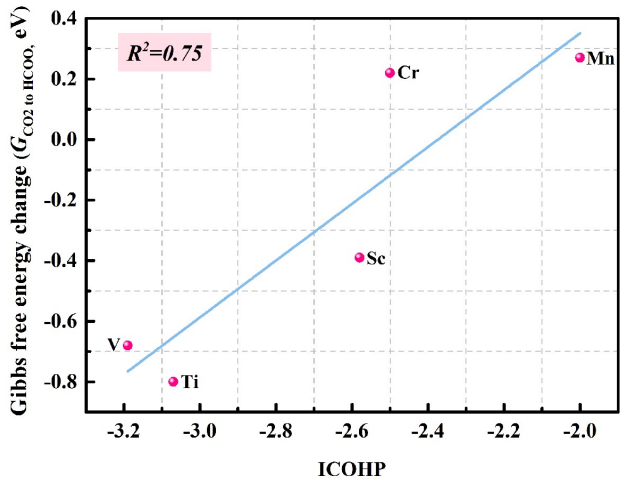

Fig. S7 The relationship of calculated ICOHP values of the TM–O bond and the Δ*G* of CO_2 to HCOO* on TM@Na_4SiMo_{12} (TM = Sc, Cr, Mn, Ti and V).

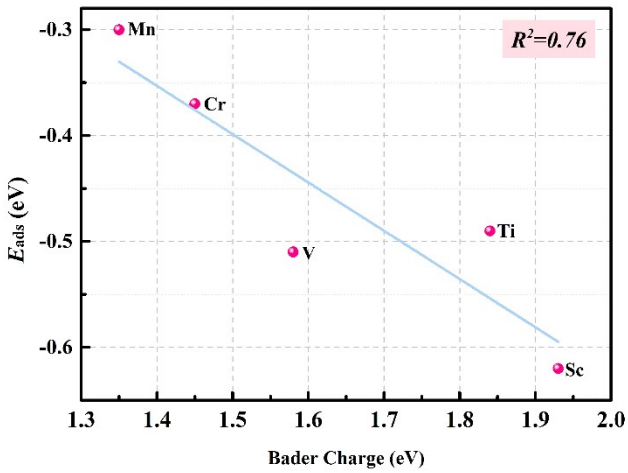

Fig. S8 The relationship between the adsorption energies (E_{ads}) of CO_2 and the Bader charges of TMs anchored on the TM@Na_4SiMo_{12} (TM = Sc, Cr, Mn, Ti and V).

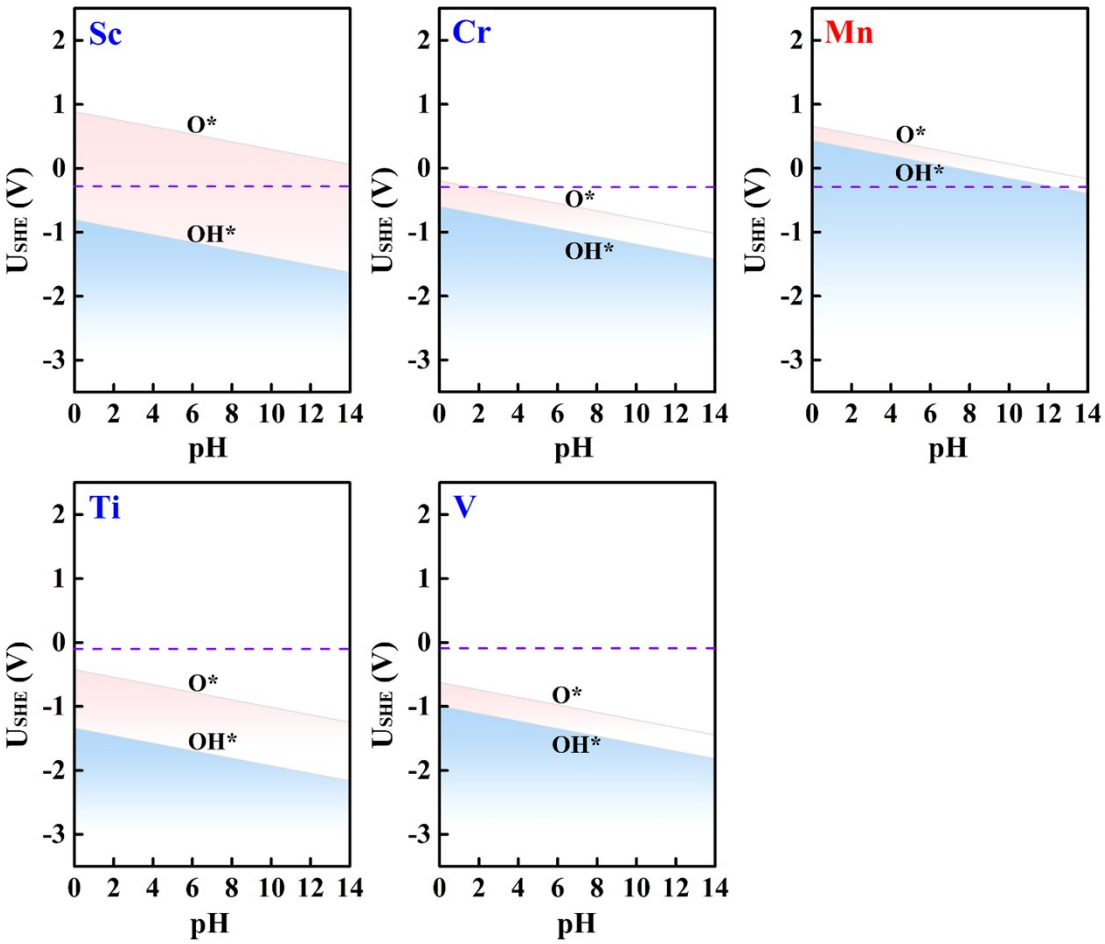

Fig. S9 Surface Pourbaix diagrams of TMs@Na_4SiMo_{12} (TM = Sc, Cr, Mn, Ti and V).

Table S1 The chemical potential of TM atom calculated from the metal bulk, and the corresponding adsorption energy (E_{ads}).

Metal	μ_{TM} (eV)	E_{ads} (eV)
Sc	–6.30	–5.18
Ti	–8.05	–3.29
V	–8.92	–1.90
Cr	–9.46	–1.31
Mn	–9.38	–0.91
Fe	–8.23	0.15
Co	–7.27	1.10
Ni	–5.47	0.55
Cu	–3.73	0.82
Zn	–1.04	–0.64
Y	–6.55	–5.35
Zr	–8.67	–6.03
Nb	–10.09	–1.61
Mo	–10.92	0.47
Tc	–10.41	1.35
Ru	–9.70	2.83
Rh	–7.27	2.53
Pd	–5.21	1.78
Ag	–2.71	0.55
Cd	–0.66	–0.40

Table S2 The Bader charge of TMs and TM–O bond lengths for TM@Na_4SiMo_{12} (TM = Sc, Ti, V, Cr, Mn, Zn, Y, Zr, Nb and Cd).

Metal	Bader charge (eV)	Pt–O bond length (Å)
Sc	1.93	2.05, 1.95, 2.05, 1.95
Ti	1.84	1.93, 1.85, 1.93, 1.86
V	1.58	1.91, 1.86, 1.91, 1.86
Cr	1.45	1.96, 1.82, 1.96, 1.82
Mn	1.35	1.89, 1.85, 1.89, 1.85
Zn	1.21	2.09, 1.98, 2.09, 1.99
Y	2.08	2.07, 1.99, 2.07, 1.98
Zr	2.39	2.03, 1.95, 2.03, 1.94
Nb	2.09	1.98, 1.94, 1.98, 1.93
Cd	1.48	1.96, 1.81, 1.96, 1.82

Table S3 Calculated free energy changes (in eV) for CO_2RR on $TM@Na_4SiMo_{12}$ (TM = Sc, Cr, Mn, Y, Zr, Ti and V)

	Elementary steps	Sc	Cr	Mn	Y	Zr	Nb
$1e^-$	$CO_2 + e^- + H^+ \rightarrow COOH^*$	1.07	0.79	1.10	1.08	0.15	–0.36
	$CO_2 + e^- + H^+ \rightarrow HCOO^*$	–0.46	0.22	0.48	–0.61	–1.37	–1.55
$2e^-$	$HCOO^* + e^- + H^+ \rightarrow HCOOH^*$	0.46	0.23	0.10	0.82	1.17	1.26
	$HCOOH^* \rightarrow HCOOH(l) + *$	0.43	–0.03	–0.15	0.22	0.63	0.72
$3e^-$	$HCOOH^* + e^- + H^+ \rightarrow HCO^* + H_2O$	1.37	0.38	0.48	1.22	0.62	0.15

	Elementary steps	Ti	V
$1e^-$	$CO_2 + e^- + H^+ \rightarrow COOH^*$	0.44	0.17
	$CO_2 + e^- + H^+ \rightarrow HCOO^*$	–0.81	–0.67
$2e^-$	$HCOO^* + e^- + H^+ \rightarrow HCOOH^*$	0.47	0.59
	$HCOOH^* \rightarrow HCOOH(l) + *$	0.77	0.52
$3e^-$	$HCOOH^* + e^- + H^+ \rightarrow HCO^* + H_2O$	0.70	0.47
$4e^-$	$HCO^* + e^- + H^+ \rightarrow CH_2O^*$	–0.97	–0.65
	$HCO^* + e^- + H^+ \rightarrow CHOH^*$	0.79	0.47
$5e^-$	$CH_2O^* + e^- + H^+ \rightarrow CH_3O^*$	1.68	–1.17
	$CH_2O^* + e^- + H^+ \rightarrow CH_2OH^*$	0.54	0.16
$6e^-$	$CH_2OH^* + e^- + H^+ \rightarrow CH_3OH^*$	–0.72	—
	$CH_2OH^* + e^- + H^+ \rightarrow CH_2^* + H_2O$	0.72	—
	$CH_3O^* + e^- + H^+ \rightarrow CH_3OH^*$	—	0.85
	$CH_3OH^* \rightarrow CH_3OH(g) + *$	0.96	0.75
	$CH_3O^* + e^- + H^+ \rightarrow CH_4 + O^*$	—	–0.76
$7e^-$	$CH_3OH^* + e^- + H^+ \rightarrow CH_4 + OH^*$	–1.64	–1.83
	$O^* + e^- + H^+ \rightarrow OH^*$	—	–0.21
$8e^-$	$OH^* + e^- + H^+ \rightarrow H_2O^*$	0.69	0.74
	$H_2O^* \rightarrow H_2O(l) + *$	0.73	0.66