Supplementary Information

Unraveling the Superiority of Ni_1-MoS_2 Single-Atom Catalyst in CO_2 Hydrogenation to Methanol: A DFT Combined Microkinetic Study

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Details of Microkinetic Analysis

The microkinetic analysis was performed by using CATKINAS software package [S1]. The reaction conditions were maintained at T = 483.15 K with partial pressures of CO_2 and H_2 set to 8 bar and 24 bar, respectively, which is consistent with previous study [S2]. The TOF maps and reaction orders of CH_3OH formation on M_1-MoS_2 were maintained at a temperature range 300−600 K and a total pressure of 1−100 bar (P_{CO2}: P_{H2} = 1: 3). The partial pressure of products (CH_3OH, HCOOH, H_2O) were fixed at a very low value. To evaluate the overall catalytic activity of methanol formation on Ni_1(Pt_1, Cu_1, Pd_1, Rh_1, Ni_1)-MoS_2, key steps include the dissociation of H_2 molecule, hydrogen diffusion and the CO_2 hydrogenation. Four active sites were considered, namely, H_2 molecule firstly adsorbed on one α-S (the first active site #1), then dissociated into two $H_{\alpha\text{-}out}$ at two α-S (#1 and the second active site #2), CO_2 as well as C-containing species and inward H_{c_in} adsorbed at another α-S (the third active site #3), the $H_{\alpha\text{-}out}$ diffused to β-S to form H_β (the fourth active site #4), the fifth site (#5) to outward H_{c_out} as shown in Fig.S18. Elementary steps that involved in the microkinetic model as listed in Table S7–12. The reaction rates, activation energy, coverage of surface species were calculated when the catalytic system reaches steady state.

The collision theory was used to treat the kinetic coefficient of molecular H_2 and CO_2 adsorption, the corresponding adsorption rate constant (k_{ads}) can be written according **Eq. S1**:

$$k_{ads} = \frac{S \cdot P \cdot A}{\sqrt{2\pi k_B m T}} \qquad (S1)$$

where k_B, m and T are Boltzmann constant, mass of adsorbed gas, reaction temperature, respectively. S is the sticking coefficient, is seen as 1, P is the partial pressure of adsorbed species. A is the area of active site, which is assumed to be 1 $Å^2$.

The rate constant of desorption (k_{des}) can be calculated as **Eq. S2**:

$$k_{des} = \frac{k_{ads}}{K} \qquad (S2)$$

where K is the adsorption equilibrium constant of the reaction.

While the kinetic coefficients for surface reactions were determined by transition state theory, the reaction rates for the forward reaction i (k_f) were calculated according to **Eq. S3**:

$$k_f = \frac{k_B T}{h} \exp\left(\frac{-E_{a_i}}{k_B T}\right) \quad (S3)$$

where k_B, T, h and E_{ai} are Boltzmann constant, reaction temperature, the Planck constant and the energy barrier for reaction i.

The corresponding reverse reaction rates (k_r) for reaction i were calculated by **Eq**. **S4**.

$$k_r = \frac{k_f}{K_i} \quad (S4)$$

where K_i is the equilibrium constant of reaction i.

The rate constant ($k_{ads/des,f/r}$) of the each elementary step are listed in Table S7-12. Next, the coverage of intermediates (*COOH, *$C(OH)_2$, *$CH(OH)_2$, *CHOH, and *CH_2OH) are listed in Table S15.

S2. Figures and Tables

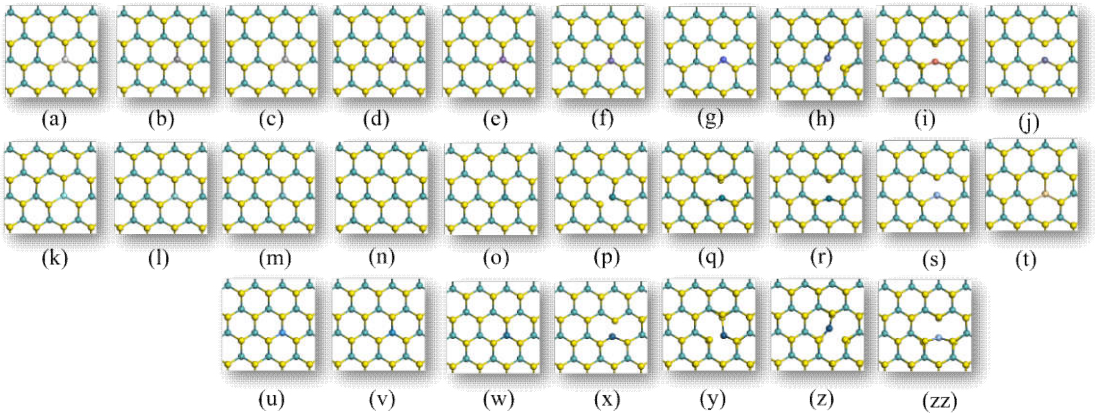

Fig. S1. From (a) to (zz) are the structures of Sc-Zn, Y-Cd and Ta-Au transition metals substituted Mo atoms in plane MoS_2. Sc-Fe, Y-Tc and Ta-Re atoms prefer to form six-coordinated structure, Co-Zn, Ru-Cd and Os-Au tend to from tetra-coordinated structures. The yellow, cyan spheres represent sulfur S and Mo atoms, respectively.

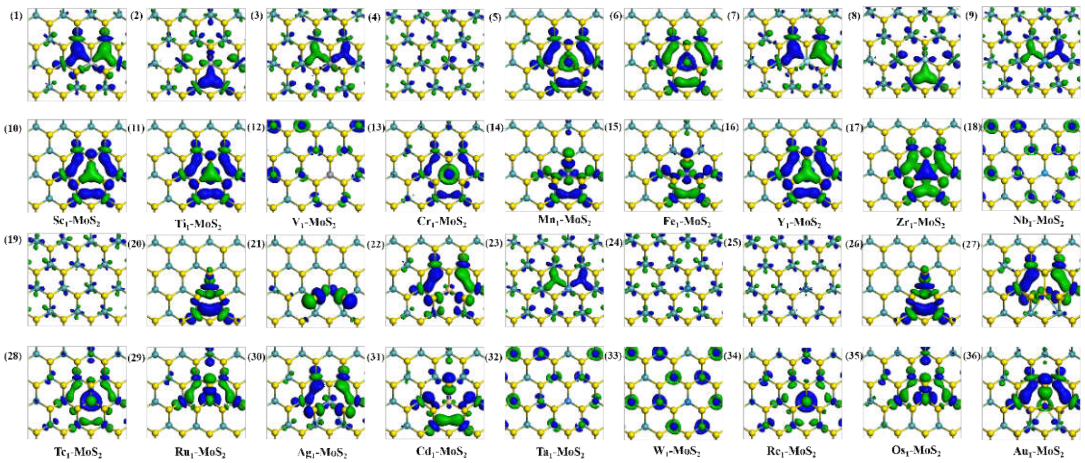

Fig. S2. The profile distributions of the highest occupied molecular orbital (1−9, 19−27) and the lowest unoccupied molecular orbital (10−18, 28−36) of M_1-MoS_2. The isosurface value is 0.03 e/Å^3.

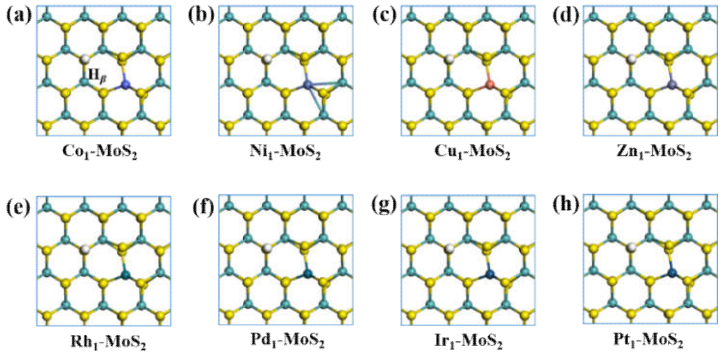

Fig. S3. The structures of one H atoms adsorbed on the β-S atoms (1H-1) on (a–h) Co_1, Ni_1, Cu_1, Zn_1, Rh_1, Pd_1, Ir_1 and Pt_1-MoS_2. The adsorption energies ($E_{1H\text{-}1}$) are 0.94, 1.36, 0.93, 0.52, 1.13, 1.03, 1.50 and 0.43 eV (as listed in **Table S2**), respectively. The H atoms in the β-S are labeled as H_β. The yellow, cyan, white and blue spheres represent S, Mo, H and doped atoms, respectively.

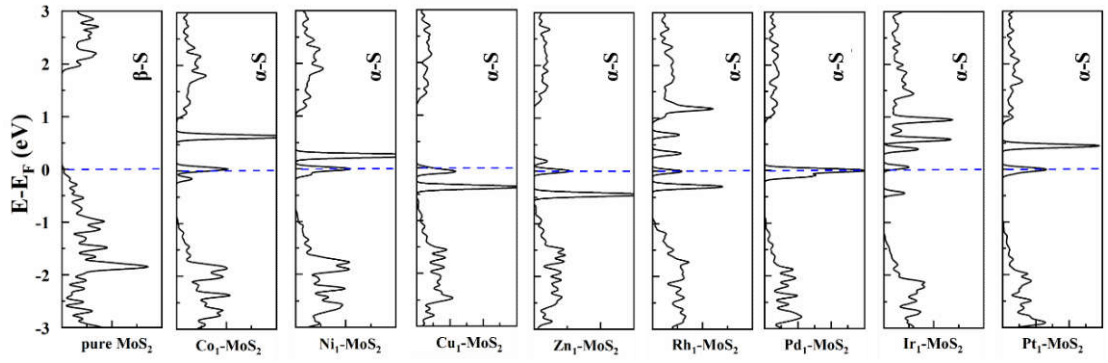

Fig. S4. The projected density of states (PDOS) of in-plane β-S atoms from pure MoS_2, and in-plane α-S atoms on Co_1-MoS_2, Ni_1-MoS_2, Cu_1-MoS_2, Zn_1-MoS_2, Rh_1-MoS_2, Pd_1-MoS_2, Ir_1-MoS_2 and Pt_1-MoS_2, respectively. The position of the Fermi level is shown in blue dashed lines.

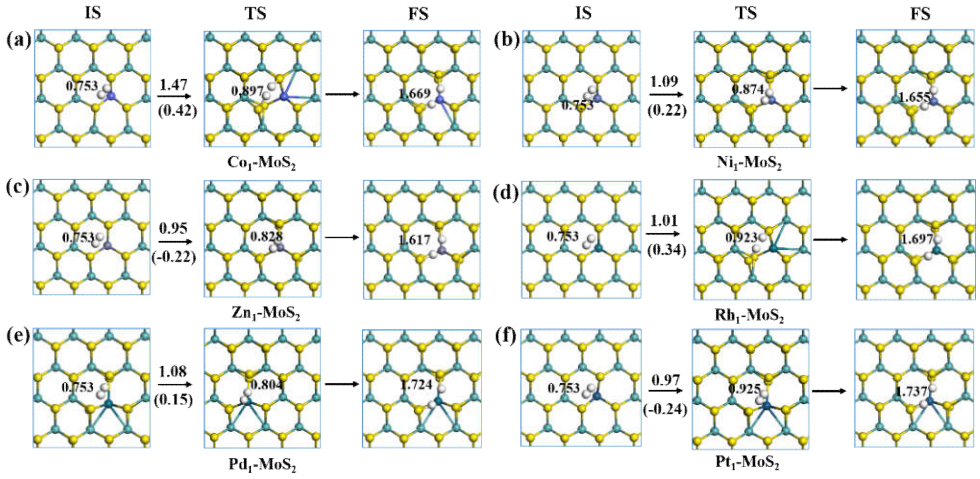

Fig. S5. The energy profile and corresponding geometric structures of H_2 dissociation into 2H-3 over (a−f) Co_1, Ni_1, Zn_1, Rh_1, Pd_1 and Pt_1-MoS_2. The numbers above and below the arrow are energy barriers and reaction energies. The yellow, cyan, white and blue spheres represent S, Mo, H and doped atoms, respectively.

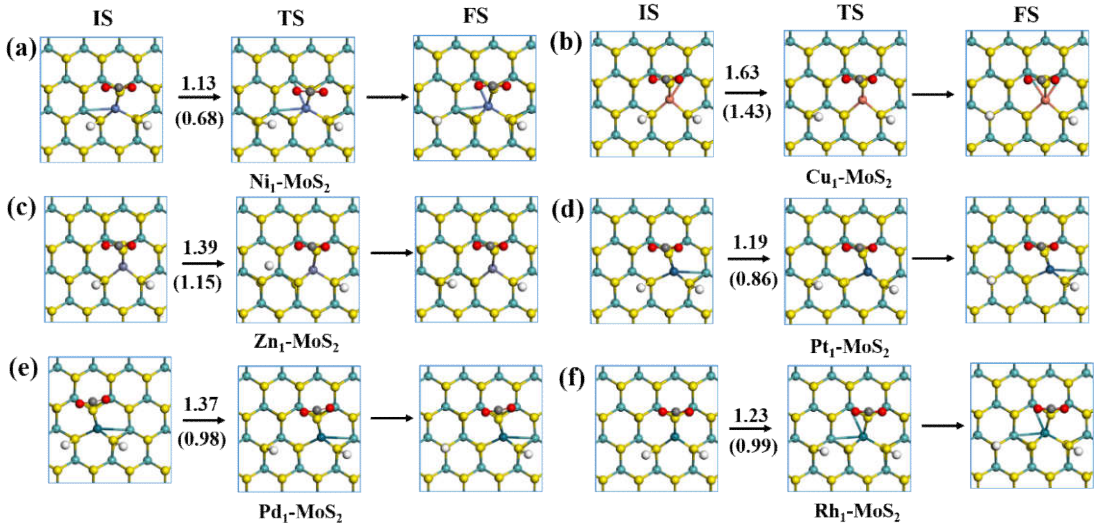

Fig. S6. The geometric structures of initial states (**IS**), transition states (**TS**), final states (**FS**) for the diffusion of $H_{\alpha\text{-out}}$ to H_{β}. The numbers above and below the arrows are the corresponding energy barriers and reaction energies on Ni_1, Cu_1, Zn_1, Pt_1, Pd_1 and Rh_1-MoS_2, respectively. The yellow, cyan, white, red and blue spheres represent S, Mo, H, O and doped atoms, respectively.

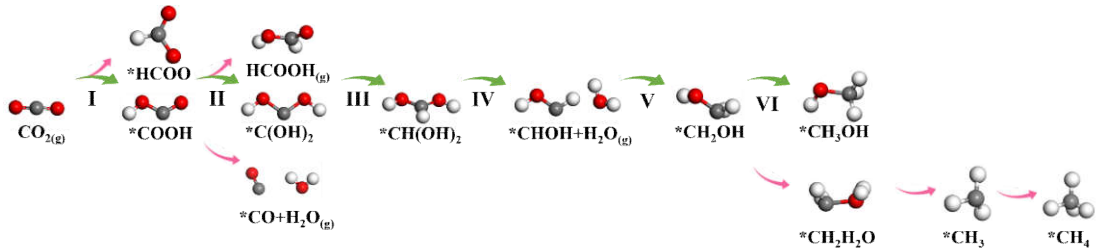

Fig. S7. The considered reaction routes and the corresponding intermediates during methanol synthesis from CO_2 thermo-reduction on M_1-MoS_2. The white, red and gray spheres represent H, O and C atoms, respectively.

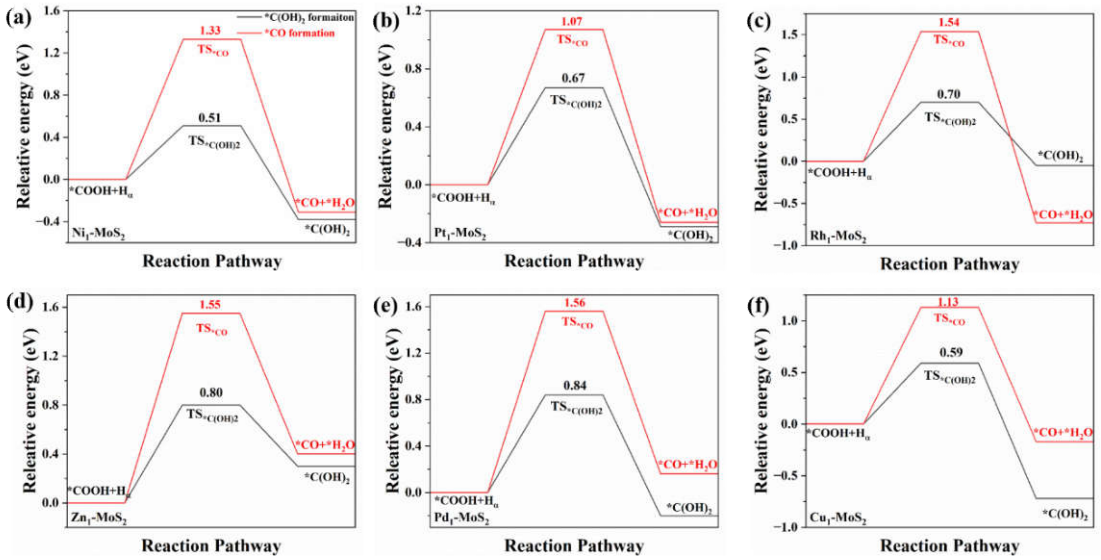

Fig. S8. The energy profile for *COOH reaction into *$C(OH)_2$ and *CO+*H_2O on (a−f) Ni_1, Pt_1, Rh_1, Zn_1, Pd_1 and Cu_1-MoS_2.

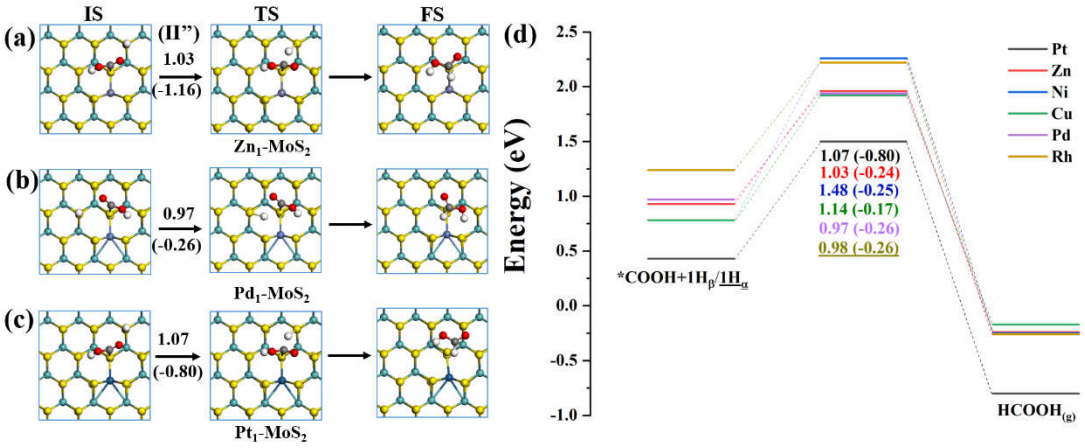

Fig. S9. The energy barriers and reaction energies as well as the involved structures of *COOH hydrogenation into $HCOOH_{(g)}$: (**II"**) *+ COOH + $1H_{\beta}/\underline{1H_{\alpha}}$⇌* +$HCOOH_{(g)}$ on (a) Zn_1, (b) Pd_1, (c) Pt_1-MoS_2, respectively. The numbers above and below the arrows are the energy barriers and reaction energies, and the numbers in (d) are the corresponding reaction barriers (reaction energies), respectively.

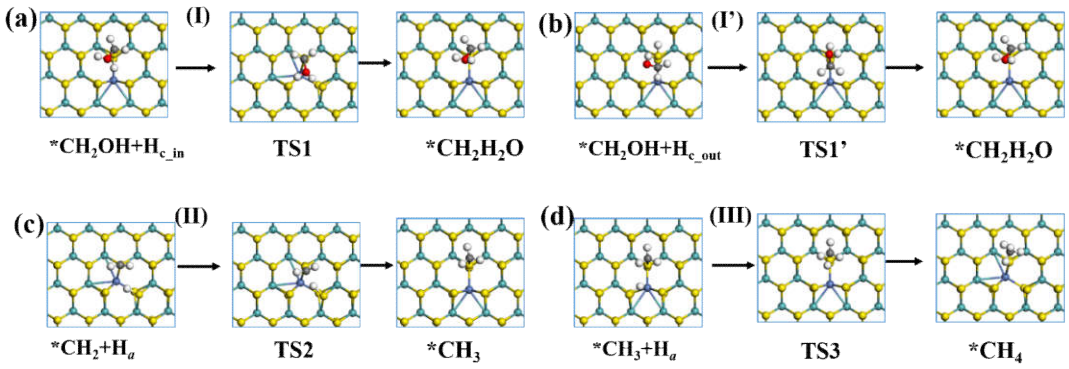

Fig. S10. The energy profile and corresponding geometric structures of (a – b) H_{c_in} and H_{c_out} reacting with *CH_2OH to form *CH_2H_2O, (c–d) *CH_2* and CH_3* reacting with hydrogen to form *CH_3 and *CH_4 on M_1-MoS_2.

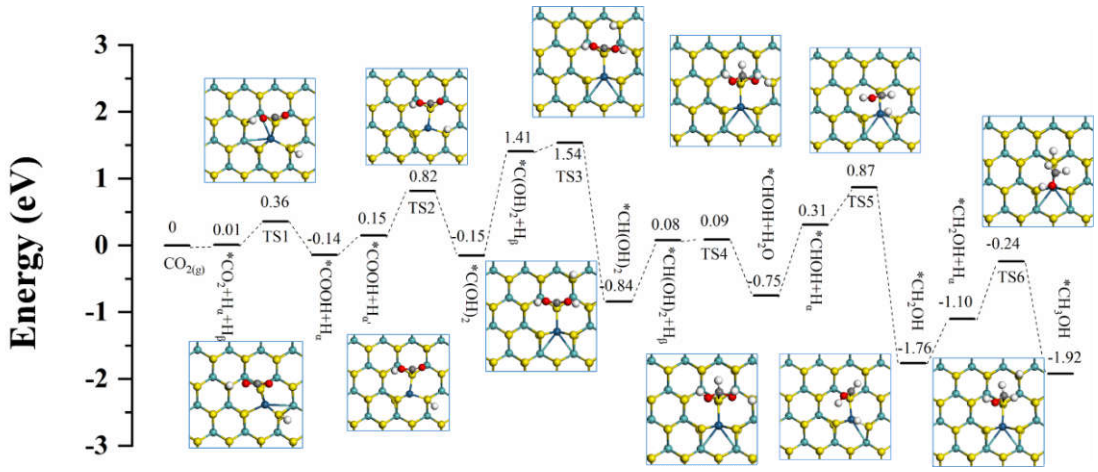

Fig. S11. The geometric structures of initial states (**IS**) and transition states (**TS**) of each elementary step along the optimal CO_2 reduction pathway on Pt_1-MoS_2: **I** (* + *CO_2 + H_α + H_β ⇌ * + *COOH + H_α), **II'** (* + *COOH + H_α ⇌ * + *$C(OH)_2$), **III** (* + *$C(OH)_2$ + H_β ⇌ * + *$CH(OH)_2$), **IV** (* + *$CH(OH)_2$ + H_β ⇌ * + *CHOH + H_2O), **V'** (* + *CHOH + H_α ⇌ * + *CH_2OH), **VI'** (* + *CH_2OH + H_α ⇌ * + *CH_3OH). The yellow, cyan, white, red, gray, blue, spheres represent S, Mo, H, O, C, Pt atoms, respectively.

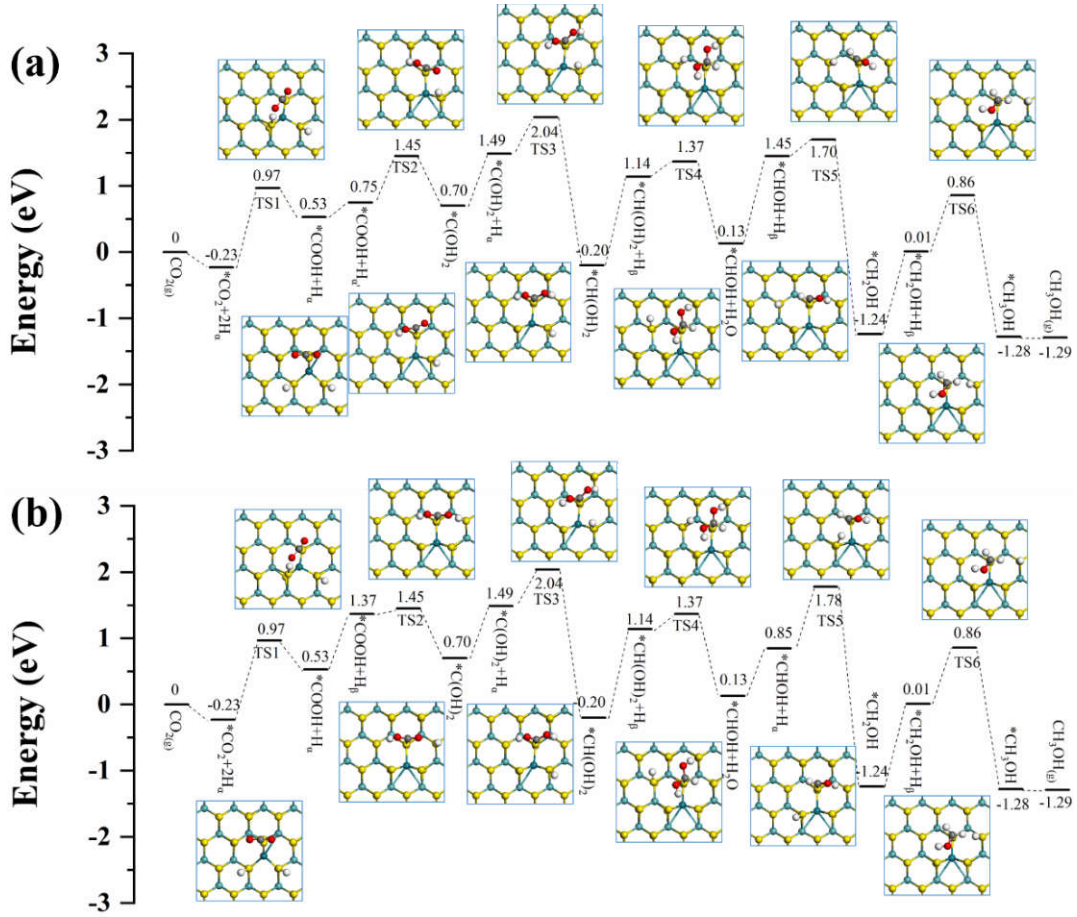

Fig. S12. The geometric structures of initial states (**IS**) and transition states (**TS**) of each elementary step along the comparable CO_2 reduction pathways on Rh_1-MoS_2: (a) **I'** (* + $*CO_2$ + $2H_\alpha$⇌ * + *COOH + H_α), **II'** (* + *COOH + H_α ⇌ * + $*C(OH)_2$), **III'** (* + $*C(OH)_2$ + H_α ⇌ * + $*CH(OH)_2$), **IV** (* + $*CH(OH)_2$ + H_β ⇌ * + *CHOH + H_2O), **V** (* + *CHOH + H_β ⇌ * + $*CH_2OH$), **VI** (* + $*CH_2OH$ + H_β ⇌ * + $*CH_3OH$), (b) **I'** (* + $*CO_2$ + $2H_\alpha$⇌ * + *COOH + H_α), **II** (* + *COOH + H_β ⇌ * + $*C(OH)_2$), **III'** (* + $*C(OH)_2$ + H_α ⇌ * + $*CH(OH)_2$), **IV** (* + $*CH(OH)_2$ + H_β ⇌ * + *CHOH + H_2O), **V'** (* + *CHOH + H_α ⇌ * + $*CH_2OH$), **VI** (* + $*CH_2OH$ + H_β ⇌ * + $*CH_3OH$). The yellow, cyan, white, red, gray, blue, spheres represent S, Mo, H, O, C, Rh atoms, respectively.

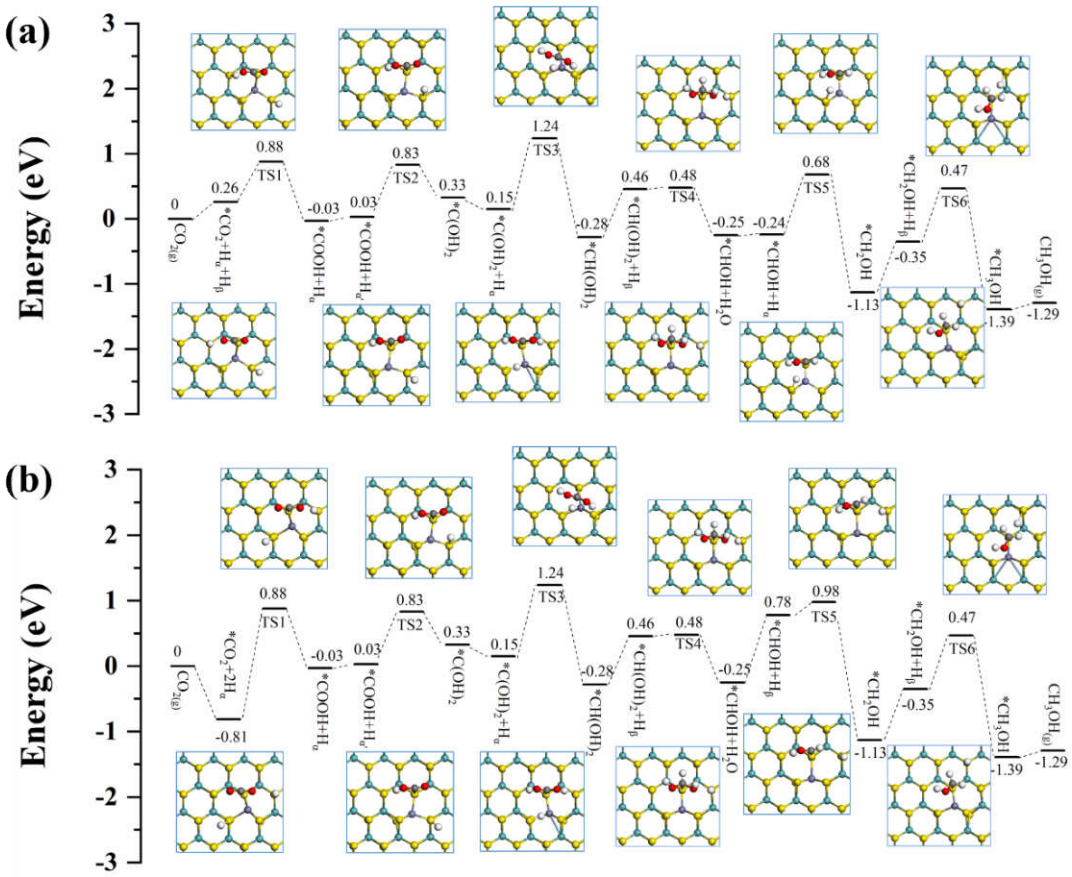

Fig. S13. The geometric structures of initial states (**IS**) and transition states (**TS**) of each elementary step along the comparable CO_2 reduction pathways on Zn_1-MoS_2: (a) **I** (* + *CO_2 + H_α + H_β ⇌ * + *COOH + H_α), **II'** (* + *COOH + H_α ⇌ * + *$C(OH)_2$), **III'** (* + *$C(OH)_2$ + H_α ⇌ * + *$CH(OH)_2$), **IV** (* + *$CH(OH)_2$ + H_β ⇌ * + *CHOH + H_2O), **V'** (* + *CHOH + H_α ⇌ * + *CH_2OH), **VI** (* + *CH_2OH + H_β ⇌ * + *CH_3OH); (b) **I'** (* + *CO_2 + $2H_\alpha$⇌ * + *COOH + H_α), **II'** (* + *COOH+H_α ⇌ * + *$C(OH)_2$), **III'** (* + *$C(OH)_2$ + H_α ⇌ * + *$CH(OH)_2$), **IV** (* + *$CH(OH)_2$+H_β ⇌ * + *CHOH + H_2O), **V** (* + *CHOH + H_β ⇌ * + *CH_2OH), **VI** (* + *CH_2OH +H_β ⇌ * + *CH_3OH). The yellow, cyan, white, red, gray, blue, silver spheres represent S, Mo, H, O, C, Zn atoms, respectively.

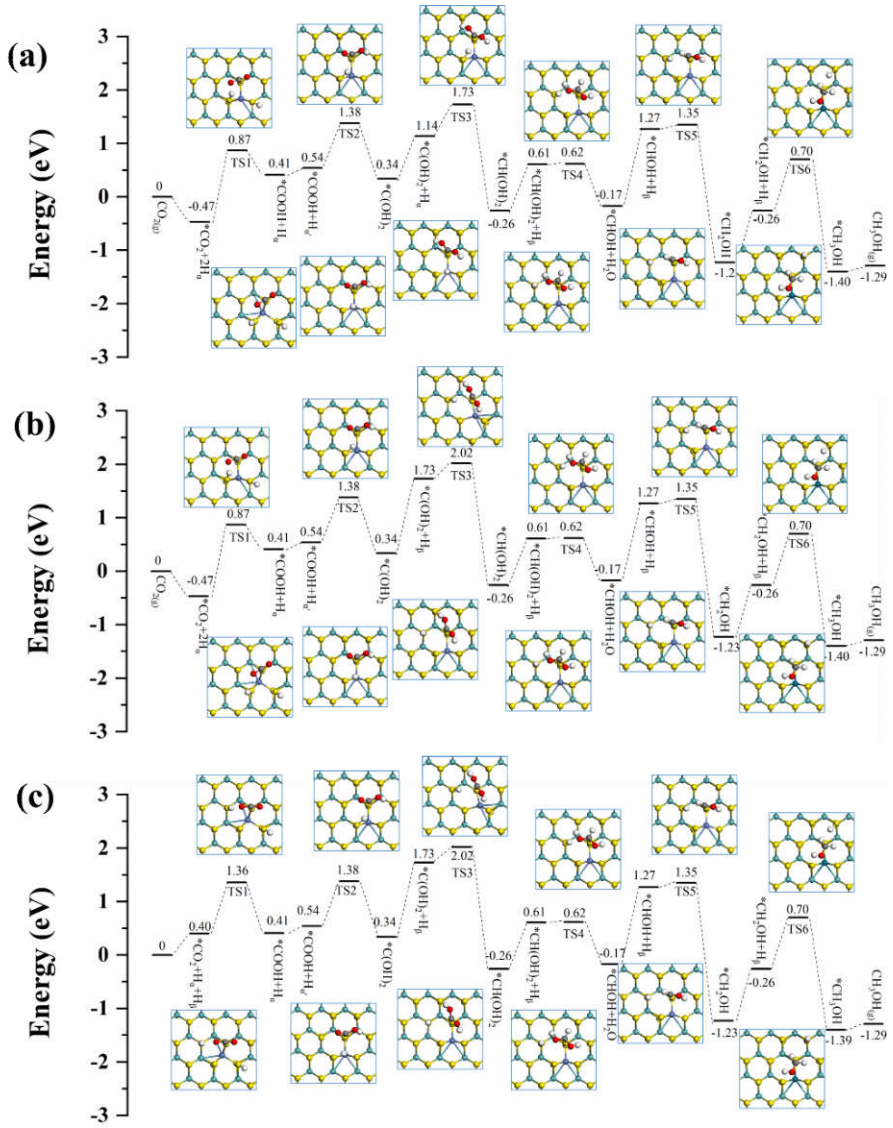

Fig. S14. The geometric structures of initial states (**IS**) and transition states (**TS**) of each elementary step along the comparable CO_2 reduction pathways on Pd_1-MoS_2: (a) **I'** (* + *CO_2 + $2H_\alpha$⇌ * + *COOH + H_α), **II'** (* + *COOH+H_α ⇌ * + *$C(OH)_2$), **III'** (* + *$C(OH)_2$ + H_α ⇌ * + *$CH(OH)_2$), **IV** (* + *$CH(OH)_2$+H_β ⇌ * + *CHOH + H_2O), **V** (* + *CHOH + H_β ⇌ * + *CH_2OH), **VI** (* + *CH_2OH +H_β ⇌ * + *CH_3OH); (b) **I'** (* + *CO_2 + $2H_\alpha$⇌ * + *COOH + H_α), **II'** (* + *COOH+H_α ⇌ * + *$C(OH)_2$), **III** (* + *$C(OH)_2$ + H_β ⇌ * + *$CH(OH)_2$), **IV** (* + *$CH(OH)_2$+H_β ⇌ * + *CHOH + H_2O), **V** (* + *CHOH + H_β ⇌ * + *CH_2OH), **VI** (* + *CH_2OH +H_β ⇌ * + *CH_3OH); (c) **I** (* + *CO_2 + H_α + H_β⇌ * + *COOH + H_α), **II'** (* + *COOH + H_α ⇌ * + *$C(OH)_2$), **III** (* + *$C(OH)_2$ + H_β ⇌ * + *$CH(OH)_2$), **IV** (* + *$CH(OH)_2$+H_β ⇌ * + *CHOH + H_2O), **V** (* + *CHOH + H_β ⇌ * + *CH_2OH), **VI** (* + *CH_2OH +H_β ⇌ * + *CH_3OH). The yellow, cyan, white, red, gray, blue spheres represent S, Mo, H, O, C, Pd atoms, respectively.

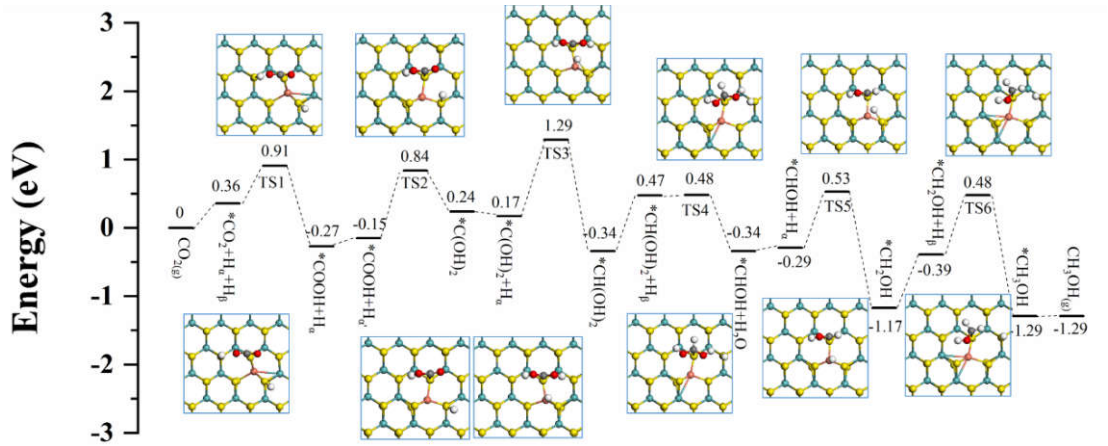

Fig. S15. The geometric structures of initial states (**IS**) and transition states (**TS**) of each elementary step along the optimal CO_2 reduction pathway on Cu_1-MoS_2: **I** (* + *CO_2 + H_α + H_β ⇌ * + *COOH + H_α), **II'** (* + *COOH + H_α ⇌ * + *$C(OH)_2$), **III'** (* + *$C(OH)_2$ + H_α ⇌ * + *$CH(OH)_2$), **IV** (* + *$CH(OH)_2$ + H_β ⇌ * + *CHOH + H_2O), **V'** (* + *CHOH + H_α ⇌ * + *CH_2OH), **VI** (* + *CH_2OH + H_β ⇌ * + *CH_3OH). The yellow, cyan, white, red, gray, blue, brick-red spheres represent S, Mo, H, O, C, Cu atoms, respectively.

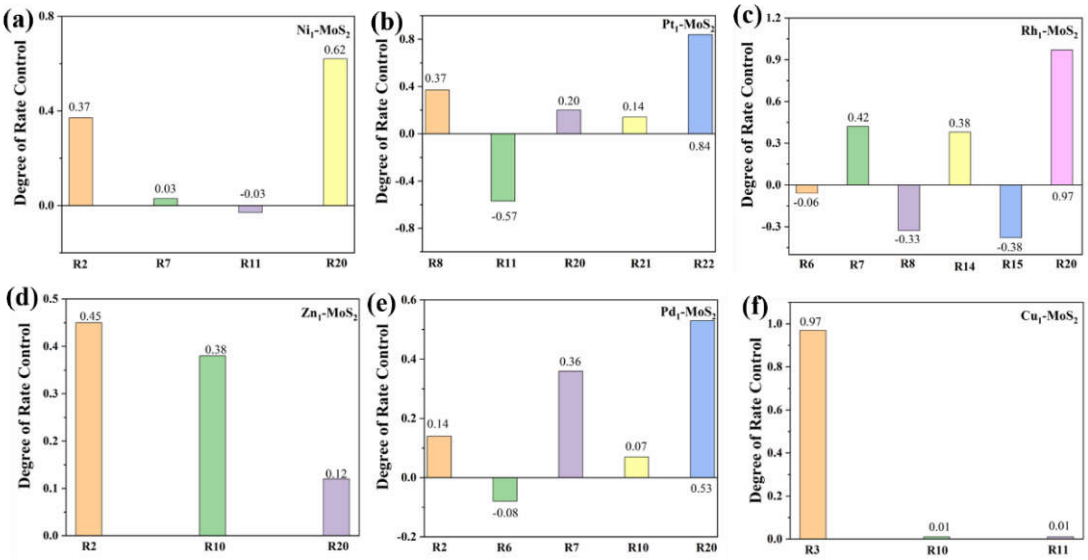

Fig. S16. Degree of rate control (DRC) of elementary steps of the catalytic CO_2 hydrogenation reaction on (a–f) Ni_1, Pt_1, Rh_1, Zn_1, Pd_1, Cu_1-MoS_2.

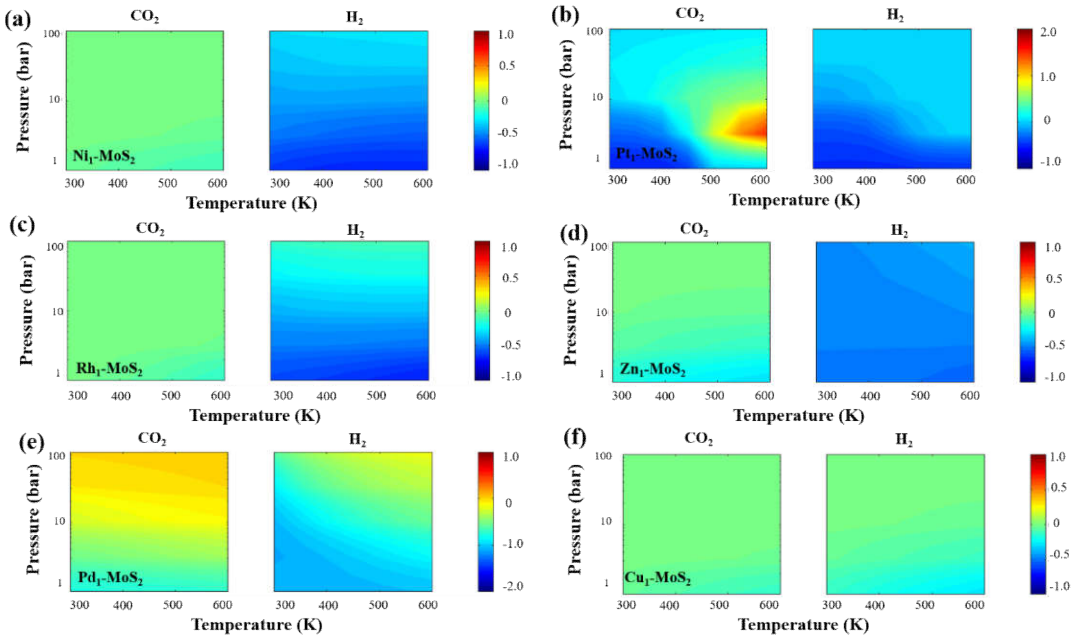

Fig. S17. The calculated reaction order map of CO_2 and H_2 on (a) Ni_1-MoS_2, (b) Rh_1-MoS_2, (c) Rh_1-MoS_2, (d) Zn_1-MoS_2, (e) Pd_1-MoS_2 and (f) Cu_1-MoS_2.

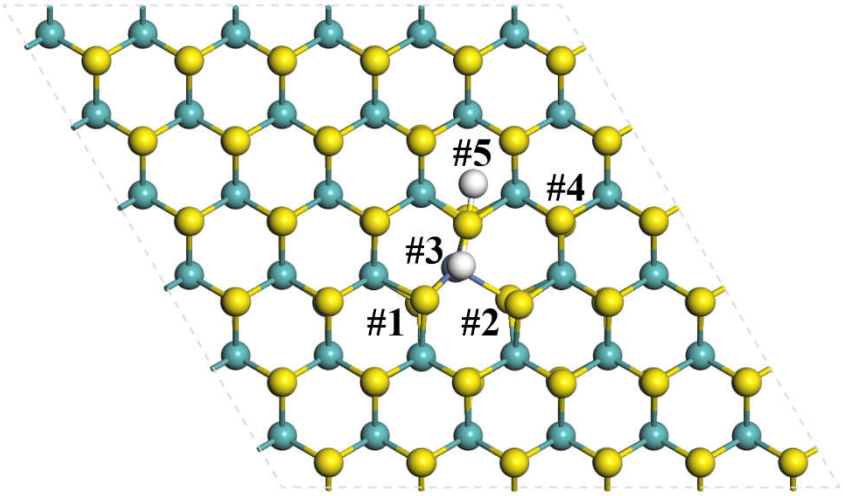

Figure S18. The active sites adopted in microkinetic simulations.

Table S1. The number of transfer electrons (**Q**) and valence electrons (**V**) in doped transition metal atoms of M_1-MoS_2.

	Sc	**Ti**	**V**	**Cr**	**Mn**	**Fe**	**Co**	**Ni**	**Cu**	**Zn**
Q	+0.39	+0.16	−0.10	−0.36	−0.32	−0.16	−0.33	−0.04	−0.12	+0.16
V	2.61	3.84	5.10	6.36	7.32	8.16	9.33	10.04	11.12	11.84
	Y	**Zr**	**Nb**	**Mo**	**Tc**	**Ru**	**Rh**	**Pd**	**Ag**	**Cd**
Q	+1.23	+0.48	+0.23	−0.09	−0.28	−0.31	−0.28	−0.19	+0.06	+0.31
V	1.79	3.52	4.77	6.09	7.28	8.31	9.28	10.19	10.94	11.69
			Ta	**W**	**Re**	**Os**	**Ir**	**Pt**	**Au**	
Q			+0.32	−0.08	−0.32	−0.44	−0.40	−0.04	−0.15	
V			4.68	6.08	7.32	8.44	9.40	10.04	11.25	

* Q represents the number of transferring electrons, + represents losing electrons, – represents getting electrons. V represents the valence electrons in doped metal.

Table S2. The adsorption energies ($E*$) (eV) of different H atom on Co_1, Ni_1, Cu_1, Zn_1, Rh_1, Pd_1, Ir_1 and Pt_1-MoS_2.

	Co_1	**Ni_1**	**Cu_1**	**Zn_1**	**Rh_1**	**Pd_1**	**Ir_1**	**Pt_1**
$E_{H\alpha}$	−0.50	−0.72	−0.52	−0.41	−0.66	−0.52	−0.46	−1.06
$E_{H\beta}$	0.94	1.36	0.93	0.52	1.13	1.03	1.50	0.43
E_{H2}	−0.05	−0.04	0.09	−0.04	0.00	0.00	/	0.00
$E_{2H\text{-}1}$	−0.28	−0.48	−0.96	−0.76	−0.30	−0.44	0.12	−0.84
$E_{2H\text{-}2}$	−0.09	−0.21	−0.81	−0.58	−0.07	−0.16	0.36	−0.57
$E_{2H\text{-}3}$	0.38	0.18	−0.46	−0.16	0.34	0.14	0.78	−0.24
$E_{2H\text{-}4}$	0.22	0.08	−0.06	0.08	0.32	0.12	0.62	−0.44

Table S3. The calculated formation energies of S_v on Ni_1(Pt_1, Pd_1, Cu_1, Zn_1, Rh_1)-MoS_2.

	Ni_1-MoS_2	Pt_1-MoS_2	Pd_1-MoS_2	Cu_1-MoS_2	Zn_1-MoS_2	Rh_1-MoS_2
E_{Sv}	0.37	−0.14	0.40	1.41	0.72	0.27

Table S4. The adsorption energies of $CO_{2(g)}$, *COOH and *HCOO species over Ni_1, Cu_1, Zn_1, Rh_1, Pd_1 and Pt_1-MoS_2.

	Ni_1	Cu_1	Zn_1	Rh_1	Pd_1	Pt_1
$E_{CO2(g)}$ (eV)	−0.05	−0.02	−0.05	−0.11	0.00	−0.01
E_{*HCOO} (eV)	0.68	0.79	1.02	0.70	0.86	0.33
E_{*COOH} (eV)	0.00	0.13	0.27	0.08	0.17	−0.37
$\Delta E_{*HCOO-*COOH}$ (eV)	0.68	0.66	0.75	0.62	0.69	0.70

Table S5. The calculated relative energies of the initial states (IS), transition states (TS) and final states (FS) of each elementary step on Ni_1, Cu_1, Zn_1, Rh_1, Pd_1 and Pt_1-MoS_2.

	IS1'	**TS1'**	**IS1**	**TS1**	**FS1**	**IS2'**	**TS2'**	**IS2**	**TS2**	**FS2**	/	/
Ni_1	−0.41	0.93	0.18	1.04	0.26	0.50	1.01	0.78	0.92	0.12	/	/
Cu_1	−0.99	0.84	0.36	0.91	–0.27	−0.15	0.84	0.78	0.86	0.24	/	/
Zn_1	−0.81	0.88	0.26	0.88	−0.03	0.03	0.83	0.93	0.96	0.33	/	/
Rh_1	−0.23	0.97	0.60	1.44	0.53	0.75	1.45	1.37	1.45	0.70	/	/
Pd_1	−0.47	0.87	0.40	1.36	0.41	0.54	1.38	0.97	1.07	0.34	/	/
Pt_1	−0.85	0.93	0.01	0.36	−0.14	0.15	0.82	0.43	0.56	−0.15	/	/
	IS3'	**TS3'**	**IS3**	**TS3**	**FS3**	**IS4'**	**TS4'**	**IS4**	**TS4**	**FS4**	/	/
Ni_1	1.02	2.14	1.49	2.27	−0.36	−0.16	0.50	0.44	0.51	−0.39	/	/
Cu_1	0.17	1.29	1.25	1.78	−0.34	−0.82	0.13	0.47	0.48	−0.34	/	/
Zn_1	0.15	1.24	1.14	1.74	−0.28	−0.73	0.25	0.46	0.48	−0.25	/	/
Rh_1	1.49	2.04	2.07	2.57	−0.20	−0.28	0.89	1.14	1.37	0.13	/	/
Pd_1	1.14	2.05	1.73	2.02	−0.26	−0.15	0.76	0.61	0.62	−0.17	/	/
Pt_1	0.87	1.73	1.41	1.54	−0.84	−0.72	0.95	0.08	0.09	−0.75	/	/
	IS5'	**TS5'**	**IS5**	**TS5**	**FS5**	**IS6'**	**TS6'**	**IS6"**	**TS6"**	**IS6**	**TS6**	**FS6**
Ni_1	0.46	1.58	1.01	1.52	−1.37	−1.10	0.26	−0.88	−0.43	−0.60	0.53	−1.33
Cu_1	−0.29	0.53	0.92	1.09	−1.16	−1.54	0.27	−0.61	−0.35	−0.39	0.48	−1.29
Zn_1	−0.24	0.68	0.78	0.98	−1.13	−1.32	0.51	−0.63	0.33	−0.35	0.47	−1.39
Rh_1	0.85	1.78	1.45	1.70	−1.24	−0.49	1.06	−0.32	−0.13	0.01	0.86	−1.28
Pd_1	0.69	1.53	1.27	1.35	−1.23	−0.84	0.47	−0.54	−0.25	−0.26	0.70	−1.39
Pt_1	0.31	0.87	0.77	0.85	−1.76	−1.39	−0.07	−1.10	−0.24	−0.83	0.04	−1.93

*The **IS**, **TS** and **FS** marked with a " ' " label represent the reactions in which H_α participates, **IS6'**, **TS6'** represent the reaction in which H_{c_in} participates, **IS6"**, **TS6"** represent the reaction in which H_{c_out} participates, the other numbers indicate the reaction in which H_β participates.

Table S6. The calculated energy barriers and reaction energies for the competition reaction between $*CH_2OH+*H$ to CH_3OH and $*CH_2H_2O$ and the evolution of $*CH_2H_2O$ to $*CH_4$.

	Pt_1-MoS_2		Ni_1-MoS_2		Rh_1-MoS_2	
Reactions	E_a(eV)	ΔE(eV)	E_a(eV)	ΔE(eV)	E_a(eV)	ΔE(eV)
$*CH_2OH+H_{c\_out}\rightleftharpoons *CH_3OH$	0.86	−0.86	0.43	−0.45	0.19	−0.97
$*CH_2OH+H_{c\_out}\rightleftharpoons *CH_2H_2O$	0.96	−0.10	1.03	0.02	0.95	−0.17
$*CH_2OH+H_{c\_in}\rightleftharpoons *CH_3OH$	1.32	−0.53	1.36	−0.23	1.55	−0.79
$*CH_2OH+H_{c\_in}\rightleftharpoons *CH_2H_2O$	0.80	0.18	0.96	0.03	1.12	0.01
$*CH_2H_2O\rightleftharpoons *CH_2+H_2O_{(g)}$	0.04	0.04	0.84	0.84	0.08	0.08
$*CH_2+H_a\rightleftharpoons *CH_3$	0.36	−2.67	0.17	−2.26	0.21	−2.18
$*CH_3+H_a\rightleftharpoons *CH_4$	2.02	−0.82	1.91	−0.61	2.21	−0.96
	Pt_1-MoS_2		Ni_1-MoS_2		Rh_1-MoS_2	
Reactions	E_a(eV)	ΔE(eV)	E_a(eV)	ΔE(eV)	E_a(eV)	ΔE(eV)
$*CH_2OH+H_{c\_out}\rightleftharpoons *CH_3OH$	0.30	−0.76	0.29	−0.86	0.26	−0.68
$*CH_2OH+H_{c\_out}\rightleftharpoons *CH_2H_2O$	0.80	0.65	0.98	−0.13	0.84	−0.21
$*CH_2OH+H_{c\_in}\rightleftharpoons *CH_3OH$	1.83	−0.07	1.31	−0.55	1.81	−0.54
$*CH_2OH+H_{c\_in}\rightleftharpoons *CH_2H_2O$	0.85	−0.18	1.29	0.17	1.40	0.78
$*CH_2H_2O\rightleftharpoons *CH_2+H_2O_{(g)}$	0.22	0.22	0.07	0.07	0.08	0.08
$*CH_2+H_a\rightleftharpoons *CH_3$	0.37	−1.61	0.01	−2.49	0.38	−1.73
$*CH_3+H_a\rightleftharpoons *CH_4$	2.58	−0.16	2.58	−0.16	2.68	0.05

Table S7. The energy barriers (E_a), reaction energies (ΔE), reaction rates for forward (k_f) and reverse reactions (k_r) of the considered elementary steps on Pt_1-MoS_2.

	Reactions	E_a**(eV)**	ΔE**(eV)**	k_f	k_r
R1	H_2+#1⇌H_2#1	0.00	0.00	8.44×10^{7}	8.44×10^{7}
R2	H_2#1+#2⇌H_a#1+H_a#2	0.97	−0.84	7.67×10^{2}	1.33×10^{-6}
R3	H#1+#4⇌#1+H#4	1.19	0.86	3.89×10^{0}	3.64×10^{9}
R4	$CO_{2(g)}$+#3⇌CO_2#3	0.00	−0.01	1.81×10^{7}	1.42×10^{7}
R5(I')	CO_2#3+H#2⇌COOH#3+#2	1.78	0.71	2.73×10^{-6}	6.94×10^{1}
R6(I)	CO_2#3+H#4⇌COOH#3+#4	0.35	−0.14	2.25×10^{9}	7.79×10^{7}
R7(II')	COOH#3+H#2⇌$C(OH)_2$#3+#2	0.67	−0.29	1.03×10^{6}	9.75×10^{2}
R8(II)	COOH#3+H#4⇌$C(OH)_2$#3+#4	0.13	−0.58	4.43×10^{11}	3.95×10^{5}
R9(II'')	COOH#3+H#4⇌HCOOH+#3	1.07	−1.23	6.94×10^{1}	1.03×10^{-11}
R10(III')	$C(OH)_2$#3+H#2⇌$CH(OH)_2$#3+#2	0.86	−1.71	1.08×10^{4}	1.57×10^{-14}
R11(III)	$C(OH)_2$#3+H#4⇌$CH(OH)_2$#3+#4	0.13	−2.25	4.43×10^{11}	1.50×10^{-12}
R12(IV')	$CH(OH)_2$#3+H#2⇌CHOH#3+H_2O+#2	1.67	0.03	3.83×10^{-5}	7.87×10^{-5}
R13(IV)	$CH(OH)_2$#3+H#4⇌CHOH#3+H_2O+#3	0.01	−0.83	7.92×10^{12}	1.74×10^{4}
R14(V')	CHOH#3+H#2⇌CH_2OH#3+#2	0.56	−2.07	1.45×10^{7}	3.71×10^{-15}
R15(V)	CHOH#3+H#4⇌CH_2OH#3+#4	0.08	−2.53	1.47×10^{12}	6.00×10^{-15}
R16	CH_2OH#3+H#2+#5⇌CH_2OH#5+H_{c_in}#3 +#2	0.15	−0.10	2.74×10^{11}	2.48×10^{10}
R17	CH_2OH#3+H#4+#5⇌CH_2OH#3+H_{c_out}#5+#4	0.87	−0.24	8.47×10^{3}	2.66×10^{1}
R18(VI')	CH_2OH#3+H_{c_out}#5⇌CH_3OH#3+#5	0.86	−0.86	1.08×10^{4}	1.15×10^{-5}
R19(VI'')	CH_2OH#5+H_{c_in}#3⇌CH_3OH#5+#3	1.32	−0.53	1.71×10^{-1}	5.07×10^{-7}
R20(VI)	CH_2OH#3+H#4⇌CH_3OH#3+#4	0.87	−0.24	8.47×10^{3}	2.66×10^{1}
R21	CH_3OH#3⇌CH_3OH+#3	0.64	0.64	4.47×10^{0}	2.12×10^{7}
R22	CH_3OH#5⇌CH_3OH+#5	0.64	0.64	4.47×10^{0}	2.12×10^{7}
R23	CH_2OH#3+H_{c_out}#5⇌CH_2H_2O#3 + #5	0.96	−0.10	9.75×10^{2}	8.83×10^{1}
R24	CH_2OH#3+H_{c_in}#3⇌CH_2H_2O#3+#3	0.80	0.18	4.55×10^{4}	3.43×10^{6}
R25	CH_2H_2O#3⇌CH_2#3+H_2O	0.04	0.04	1.08×10^{7}	2.82×10^{7}
R26	CH_2#3+H#2⇌CH_3#3+#2	0.36	−2.67	1.77×10^{9}	2.49×10^{-19}
R27	CH_3#3+H#2⇌CH_4#3+#2	2.02	−0.82	8.55×10^{-9}	2.39×10^{-17}
R28	CH_4#3⇌CH_4+#3	0.52	0.52	1.13×10^{2}	2.99×10^{7}
R29	CH_4#5⇌CH_4+#5	0.52	0.52	1.13×10^{2}	2.99×10^{7}

Table S8. The energy barriers (E_a), reaction energies (ΔE), reaction rates for forward (k_f) and reverse reactions (k_r) of the considered elementary steps on Ni_1-MoS_2.

	Reactions	E_a**(eV)**	ΔE**(eV)**	k_f	k_r
R1	H_2+#1⇌H_2#1	0.00	−0.04	8.44×10^{7}	3.23×10^{7}
R2	H_2#1+#2⇌H_α#1+H_α#2	1.09	−0.98	4.30×10^{1}	2.57×10^{-9}
R3	H#1+#4⇌#1+H#4	1.13	0.68	1.64×10^{1}	2.04×10^{8}
R4	$CO_{2(g)}$+#3⇌CO_2#3	0.00	−0.05	1.81×10^{7}	5.44×10^{6}
R5(I')	CO_2#3+H#2⇌COOH#3+#2	1.34	0.67	1.06×10^{-1}	1.03×10^{6}
R6(I)	CO_2#3+H#4⇌COOH#3+#4	0.86	0.08	1.08×10^{4}	7.36×10^{4}
R7(II')	COOH#3+H#2⇌$C(OH)_2$#3+#2	0.51	−0.38	4.82×10^{7}	5.24×10^{3}
R8(II)	COOH#3+H#4⇌$C(OH)_2$#3+#4	0.14	−0.66	3.49×10^{11}	4.55×10^{4}
R9(II'')	COOH#3+H#4⇌HCOOH+#3	1.48	−0.92	3.67×10^{-3}	9.30×10^{-13}
R10(III')	$C(OH)_2$#3+H#2⇌$CH(OH)_2$#3+#2	1.12	−1.38	2.09×10^{1}	8.42×10^{-14}
R11(III)	$C(OH)_2$#3+H#4⇌$CH(OH)_2$#3+#4	0.78	−1.85	7.36×10^{4}	3.71×10^{-15}
R12(IV')	$CH(OH)_2$#3+H#2⇌CHOH#3+H_2O+#2	0.66	−0.23	1.31×10^{6}	5.24×10^{3}
R13(IV)	$CH(OH)_2$#3+H#4⇌CHOH#3+H_2O+#3	0.07	−0.83	1.87×10^{12}	4.12×10^{3}
R14(V')	CHOH#3+H#2⇌CH_2OH#3+#2	1.12	−1.83	2.09×10^{1}	1.70×10^{-18}
R15(V)	CHOH#3+H#4⇌CH_2OH#3+#4	0.51	−2.38	4.82×10^{7}	7.20×10^{-18}
R16	CH_2OH#3+H#2+#5⇌CH_2OH#5+H_{c_in}#3 +#2	0.10	−0.21	9.12×10^{11}	5.88×10^{9}
R17	CH_2OH#3+H#4+#5⇌CH_2OH#3+H_{c_out}#5+#4	1.13	−0.29	1.64×10^{1}	1.55×10^{-2}
R18(VI')	CH_2OH#3+ H_{c_out}#5⇌CH_3OH#3+#5	0.43	−0.45	3.29×10^{8}	6.66×10^{3}
R19(VI'')	CH_2OH#5+H_{c_in}#3⇌CH_3OH#5+#3	1.36	−0.23	6.56×10^{-2}	2.62×10^{-4}
R20(VI)	CH_2OH#3+H#4⇌CH_3OH#3+#4	1.13	−0.73	1.64×10^{1}	3.99×10^{-7}
R21	CH_3OH#3⇌CH_3OH+#3	0.04	0.04	8.10×10^{6}	2.12×10^{7}
R22	CH_3OH#5⇌CH_3OH+#5	0.04	0.04	8.10×10^{6}	2.12×10^{7}
R23	CH_2OH#3+H_{c_out}#5⇌CH_2H_2O#3 + #5	1.03	0.02	1.82×10^{2}	2.93×10^{2}
R24	CH_2OH#3+H_{c_in}#3⇌CH_2H_2O#3+#3	0.96	0.03	9.75×10^{2}	2.00×10^{3}
R25	CH_2H_2O#3⇌CH_2#3+H_2O	0.84	0.84	4.88×10^{-2}	2.82×10^{7}
R26	CH_2#3+H#2⇌CH_3#3+#2	0.17	−2.26	1.70×10^{11}	4.52×10^{-13}
R27	CH_3#3+H#2⇌CH_4#3+#2	1.91	−0.61	1.20×10^{-7}	5.21×10^{-14}
R28	CH_4#3⇌CH_4+#3	0.02	0.02	1.85×10^{7}	2.99×10^{7}
R29	CH_4#5⇌CH_4+#5	0.02	0.02	1.85×10^{7}	2.99×10^{7}

Table S9. The energy barriers (E_a), reaction energies (ΔE), reaction rates for forward (k_f) and reverse reactions (k_r) of the considered elementary steps on Rh_1-MoS_2.

	Reactions	E_a**(eV)**	ΔE**(eV)**	k_f	k_r
R1	H_2+#1⇌H_2#1	0.00	0.00	8.44×10^{7}	8.44×10^{7}
R2	H_2#1+#2⇌H_a#1+H_a#2	1.01	−0.29	2.93×10^{2}	2.77×10^{-1}
R3	H#1+#4⇌#1+H#4	1.23	0.99	1.49×10^{0}	3.16×10^{10}
R4	$CO_{2(g)}$+#3⇌CO_2#3	0.00	−0.11	1.81×10^{7}	1.29×10^{6}
R5(I')	CO_2#3+H#2⇌COOH#3+#2	1.20	0.76	3.06×10^{0}	2.59×10^{8}
R6(I)	CO_2#3+H#4⇌COOH#3+#4	0.84	−0.07	1.74×10^{4}	3.24×10^{3}
R7(II')	COOH#3+H#2⇌$C(OH)_2$#3+#2	0.70	−0.05	5.03×10^{5}	1.51×10^{5}
R8(II)	COOH#3+H#4⇌$C(OH)_2$#3+#4	0.08	−0.67	1.47×10^{12}	1.51×10^{5}
R9(II'')	COOH#3+H#4⇌HCOOH+#3	0.98	−1.50	6.03×10^{2}	1.36×10^{-13}
R10(III')	$C(OH)_2$#3+H#2⇌$CH(OH)_2$#3+#2	0.55	−1.69	1.84×10^{7}	4.34×10^{-11}
R11(III)	$C(OH)_2$#3+H#4⇌$CH(OH)_2$#3+#4	0.50	−2.27	6.13×10^{7}	1.28×10^{-16}
R12(IV')	$CH(OH)_2$#3+H#2⇌CHOH#3+H_2O+#2	1.17	0.41	6.29×10^{0}	1.19×10^{5}
R13(IV)	$CH(OH)_2$#3+H#4⇌CHOH#3+H_2O+#3	0.23	−1.01	4.02×10^{10}	1.17×10^{0}
R14(V')	CHOH#3+H#2⇌CH_2OH#3+#2	0.93	−2.09	2.00×10^{3}	3.17×10^{-19}
R15(V)	CHOH#3+H#4⇌CH_2OH#3+#4	0.25	−2.69	2.48×10^{10}	2.17×10^{-18}
R16	CH_2OH#3+H#2+#5⇌CH_2OH#5+H_{c_in}#3 +#2	0.26	0.16	1.95×10^{10}	9.12×10^{11}
R17	CH_2OH#3+H#4+#5⇌CH_2OH#3+H_{c_out}#5+#4	0.84	−0.33	1.74×10^{4}	6.29×10^{0}
R18(VI')	CH_2OH#3+ H_{c_out}#5⇌CH_3OH#3+#5	0.19	−0.97	1.05×10^{11}	8.00×10^{0}
R19(VI'')	CH_2OH#5+H_{c_in}#3⇌CH_3OH#5+#3	1.55	−0.79	6.84×10^{-4}	3.93×10^{-12}
R20(VI)	CH_2OH#3+H#4⇌CH_3OH#3+#4	0.85	−1.29	1.37×10^{4}	4.79×10^{-10}
R21	CH_3OH#3⇌CH_3OH+#3	0.00	−0.01	2.12×10^{7}	1.67×10^{7}
R22	CH_3OH#5⇌CH_3OH+#5	0.00	−0.01	2.12×10^{7}	1.67×10^{7}
R23	CH_2OH#3+H_{c_out}#5⇌CH_2H_2O#3 + #5	0.95	−0.17	1.24×10^{3}	2.09×10^{1}
R24	CH_2OH#3+H_{c_in}#3⇌CH_2H_2O#3+#3	1.12	0.01	2.09×10^{1}	2.66×10^{1}
R25	CH_2H_2O#3⇌CH_2#3+H_2O	0.08	0.08	4.13×10^{6}	2.82×10^{7}
R26	CH_2#3+H#2⇌CH_3#3+#2	0.21	−2.18	6.49×10^{10}	1.18×10^{-12}
R27	CH_3#3+H#2⇌CH_4#3+#2	2.21	−0.96	8.92×10^{-11}	8.64×10^{-21}
R28	CH_4#3⇌CH_4+#3	0.15	0.15	8.15×10^{5}	2.99×10^{7}
R29	CH_4#5⇌CH_4+#5	0.15	0.15	8.15×10^{5}	2.99×10^{7}

Table S10. The energy barriers (E_a), reaction energies (ΔE), reaction rates for forward (k_f) and reverse reactions (k_r) of the considered elementary steps on Zn_1-MoS_2.

	Reactions	E_a**(eV)**	ΔE**(eV)**	k_f	k_r
R1	H_2+#1⇌H_2#1	0.00	−0.04	8.44×10^{7}	3.23×10^{7}
R2	H_2#1+#2⇌H_a#1+H_a#2	0.95	−0.71	1.24×10^{3}	4.87×10^{-5}
R3	H#1+#4⇌#1+H#4	1.39	1.15	3.19×10^{-2}	3.16×10^{10}
R4	$CO_{2(g)}$+#3⇌CO_2#3	0.00	−0.05	1.81×10^{7}	5.44×10^{6}
R5(I')	CO_2#3+H#2⇌COOH#3+#2	1.69	0.78	2.37×10^{-5}	3.24×10^{3}
R6(I)	CO_2#3+H#4⇌COOH#3+#4	0.62	−0.29	3.43×10^{6}	3.24×10^{3}
R7(II')	COOH#3+H#2⇌$C(OH)_2$#3+#2	0.80	0.30	4.55×10^{4}	6.13×10^{7}
R8(II)	COOH#3+H#4⇌$C(OH)_2$#3+#4	0.03	−0.60	4.90×10^{12}	2.70×10^{6}
R9(II'')	COOH#3+H#4⇌HCOOH+#3	1.03	−1.16	1.82×10^{2}	1.44×10^{-10}
R10(III')	$C(OH)_2$#3+H#2⇌$CH(OH)_2$#3+#2	1.09	−0.43	4.30×10^{1}	1.41×10^{-3}
R11(III)	$C(OH)_2$#3+H#4⇌$CH(OH)_2$#3+#4	0.60	−1.42	5.55×10^{6}	6.73×10^{-9}
R12(IV')	$CH(OH)_2$#3+H#2⇌CHOH#3+H_2O+#2	0.98	0.48	6.03×10^{2}	6.13×10^{7}
R13(IV)	$CH(OH)_2$#3+H#4⇌CHOH#3+H_2O+#3	0.02	−0.71	6.23×10^{12}	2.44×10^{5}
R14(V')	CHOH#3+H#2⇌CH_2OH#3+#2	0.92	−0.89	2.55×10^{3}	1.33×10^{-6}
R15(V)	CHOH#3+H#4⇌CH_2OH#3+#4	0.20	−1.91	8.25×10^{10}	9.85×10^{-10}
R16	CH_2OH#3+H#2+#5⇌CH_2OH#5+H_{c_in}#3 +#2	0.30	−0.15	7.47×10^{9}	2.04×10^{8}
R17	CH_2OH#3+H#4+#5⇌CH_2OH#3+H_{c_out}#5+#4	0.82	−0.28	2.81×10^{4}	3.38×10^{1}
R18(VI')	CH_2OH#3+ H_{c_out}#5⇌CH_3OH#3+#5	0.30	−0.76	7.47×10^{9}	8.83×10^{1}
R19(VI'')	CH_2OH#5+H_{c_in}#3⇌CH_3OH#5+#3	1.83	−0.07	8.20×10^{-7}	1.53×10^{-7}
R20(VI)	CH_2OH#3+H#4⇌CH_3OH#3+#4	0.82	−1.04	2.81×10^{4}	3.99×10^{-7}
R21	CH_3OH#3⇌CH_3OH+#3	0.10	0.10	1.92×10^{6}	2.12×10^{7}
R22	CH_3OH#5⇌CH_3OH+#5	0.10	0.10	1.92×10^{6}	2.12×10^{7}
R23	CH_2OH#3+H_{c_out}#5⇌CH_2H_2O#3 + #5	0.80	0.65	4.55×10^{4}	2.74×10^{11}
R24	CH_2OH#3+H_{c_in}#3⇌CH_2H_2O#3+#3	0.85	−0.18	1.37×10^{4}	1.82×10^{2}
R25	CH_2H_2O#3⇌CH_2#3+H_2O	0.22	0.22	1.43×10^{5}	2.82×10^{7}
R26	CH_2#3+H#2⇌CH_3#3+#2	0.37	−1.61	1.39×10^{9}	2.24×10^{-8}
R27	CH_3#3+H#2⇌CH_4#3+#2	2.58	−0.16	1.23×10^{-14}	2.64×10^{-16}
R28	CH_4#3⇌CH_4+#3	0.12	0.12	1.68×10^{6}	2.99×10^{7}
R29	CH_4#5⇌CH_4+#5	0.12	0.12	1.68×10^{6}	2.99×10^{7}

Table S11. The energy barriers (E_a), reaction energies (ΔE), reaction rates for forward (k_f) and reverse reactions (k_r) of the considered elementary steps on Pd_1-MoS_2.

	Reactions	E_a**(eV)**	ΔE**(eV)**	k_f	k_r
R1	H_2+#1⇌H_2#1	0.00	0.00	8.44×10^{7}	8.44×10^{7}
R2	H_2#1+#2⇌H_a#1+H_a#2	1.08	−0.44	5.46×10^{1}	1.41×10^{-3}
R3	H#1+#4⇌#1+H#4	1.37	0.98	5.16×10^{-2}	8.61×10^{8}
R4	$CO_{2(g)}$+#3⇌CO_2#3	0.00	0.00	1.81×10^{7}	1.81×10^{7}
R5(I')	CO_2#3+H#2⇌COOH#3+#2	1.34	0.88	1.06×10^{-1}	1.60×10^{8}
R6(I)	CO_2#3+H#4⇌COOH#3+#4	0.96	0.01	9.75×10^{2}	1.24×10^{3}
R7(II')	COOH#3+H#2⇌$C(OH)_2$#3+#2	0.84	−0.20	1.74×10^{4}	1.43×10^{2}
R8(II)	COOH#3+H#4⇌$C(OH)_2$#3+#4	0.10	−0.63	9.12×10^{11}	2.44×10^{5}
R9(II'')	COOH#3+H#4⇌HCOOH+#3	0.97	−1.23	7.67×10^{2}	1.13×10^{-10}
R10(III')	$C(OH)_2$#3+H#2⇌$CH(OH)_2$#3+#2	0.91	−1.40	3.24×10^{3}	8.07×10^{-12}
R11(III)	$C(OH)_2$#3+H#4⇌$CH(OH)_2$#3+#4	0.29	−1.99	9.50×10^{9}	1.66×10^{-11}
R12(IV')	$CH(OH)_2$#3+H#2⇌CHOH#3+H_2O+#2	0.91	−0.02	3.24×10^{3}	2.00×10^{3}
R13(IV)	$CH(OH)_2$#3+H#4⇌CHOH#3+H_2O+#3	0.01	−0.78	7.92×10^{12}	5.79×10^{4}
R14(V')	CHOH#3+H#2⇌CH_2OH#3+#2	0.84	−1.92	1.74×10^{4}	1.63×10^{-16}
R15(V)	CHOH#3+H#4⇌CH_2OH#3+#4	0.08	−2.50	1.47×10^{12}	1.23×10^{-14}
R16	CH_2OH#3+H#2+#5⇌CH_2OH#5+H_{c_in}#3 +#2	0.18	−0.19	1.33×10^{11}	1.39×10^{9}
R17	CH_2OH#3+H#4+#5⇌CH_2OH#3+H_{c_out}#5+#4	0.96	−0.19	9.75×10^{2}	1.02×10^{1}
R18(VI')	CH_2OH#3+ H_{c_out}#5⇌CH_3OH#3+#5	0.29	−0.86	9.50×10^{9}	1.02×10^{1}
R19(VI'')	CH_2OH#5+H_{c_in}#3⇌CH_3OH#5+#3	1.31	−0.55	2.18×10^{-1}	3.99×10^{-7}
R20(VI)	CH_2OH#3+H#4⇌CH_3OH#3+#4	0.96	−1.13	9.75×10^{2}	1.59×10^{-9}
R21	CH_3OH#3⇌CH_3OH+#3	0.10	0.10	1.92×10^{6}	2.12×10^{7}
R22	CH_3OH#5⇌CH_3OH+#5	0.10	0.10	1.92×10^{6}	2.12×10^{7}
R23	CH_2OH#3+H_{c_out}#5⇌CH_2H_2O#3 + #5	0.98	−0.13	6.03×10^{2}	2.66×10^{1}
R24	CH_2OH#3+H_{c_in}#3⇌CH_2H_2O#3+#3	1.29	0.17	3.52×10^{-1}	2.09×10^{1}
R25	CH_2H_2O#3⇌CH_2#3+H_2O	0.07	0.07	5.26×10^{6}	2.82×10^{7}
R26	CH_2#3+H#2⇌CH_3#3+#2	0.01	−2.49	7.92×10^{12}	8.42×10^{-14}
R27	CH_3#3+H#2⇌CH_4#3+#2	2.58	−0.16	1.23×10^{-14}	2.64×10^{-16}
R28	CH_4#3⇌CH_4+#3	0.00	−0.01	2.99×10^{7}	2.35×10^{7}
R29	CH_4#5⇌CH_4+#5	0.00	−0.01	2.99×10^{7}	2.35×10^{7}

Table S12. The energy barriers (E_a), reaction energies (ΔE), reaction rates for forward (k_f) and reverse reactions (k_r) of the considered elementary steps on Cu_1-MoS_2.

	Reactions	E_a**(eV)**	ΔE**(eV)**	k_f	k_r
R1	H_2+#1⇌H_2#1	0.00	0.09	8.44×10^{7}	7.33×10^{8}
R2	H_2#1+#2⇌H_a#1+H_a#2	0.79	−1.05	5.79×10^{4}	6.45×10^{-7}
R3	H#1+#4⇌#1+H#4	1.63	1.43	1.00×10^{-4}	8.25×10^{10}
R4	$CO_{2(g)}$+#3⇌CO_2#3	0.00	−0.02	1.81×10^{7}	1.12×10^{7}
R5(I')	CO_2#3+H#2⇌COOH#3+#2	1.83	0.72	8.20×10^{-7}	2.66×10^{1}
R6(I)	CO_2#3+H#4⇌COOH#3+#4	0.55	−0.63	1.84×10^{7}	4.95×10^{0}
R7(II')	COOH#3+H#2⇌$C(OH)_2$#3+#2	0.99	0.39	4.74×10^{2}	5.55×10^{6}
R8(II)	COOH#3+H#4⇌$C(OH)_2$#3+#4	0.08	−0.54	1.47×10^{12}	3.43×10^{6}
R9(II'')	COOH#3+H#4⇌HCOOH+#3	1.14	−0.17	1.29×10^{1}	2.18×10^{-1}
R10(III')	$C(OH)_2$#3+H#2⇌$CH(OH)_2$#3+#2	1.12	−0.51	2.09×10^{1}	1.00×10^{-4}
R11(III)	$C(OH)_2$#3+H#4⇌$CH(OH)_2$#3+#4	0.53	−1.59	2.98×10^{7}	7.75×10^{-10}
R12(IV')	$CH(OH)_2$#3+H#2⇌CHOH#3+H_2O+#2	0.95	0.48	1.24×10^{3}	1.26×10^{8}
R13(IV)	$CH(OH)_2$#3+H#4⇌CHOH#3+H_2O+#3	0.01	−0.81	7.92×10^{12}	2.81×10^{4}
R14(V')	CHOH#3+H#2⇌CH_2OH#3+#2	0.82	−0.87	2.81×10^{4}	2.37×10^{-5}
R15(V)	CHOH#3+H#4⇌CH_2OH#3+#4	0.17	−2.08	1.70×10^{11}	3.41×10^{-11}
R16	CH_2OH#3+H#2+#5⇌CH_2OH#5+H_{c_in}#3 +#2	0.59	−0.01	7.06×10^{6}	5.55×10^{6}
R17	CH_2OH#3+H#4+#5⇌CH_2OH#3+H_{c_out}#5+#4	0.87	0.22	8.47×10^{3}	1.67×10^{6}
R18(VI')	CH_2OH#3+ H_{c_out}#5⇌CH_3OH#3+#5	0.26	−0.68	1.95×10^{10}	1.58×10^{3}
R19(VI'')	CH_2OH#5+H_{c_in}#3⇌CH_3OH#5+#3	1.81	−0.54	1.33×10^{-6}	3.09×10^{-12}
R20(VI)	CH_2OH#3+H#4⇌CH_3OH#3+#4	0.82	−1.04	2.81×10^{4}	3.99×10^{-7}
R21	CH_3OH#3⇌CH_3OH+#3	0.00	0.00	2.12×10^{7}	2.12×10^{7}
R22	CH_3OH#5⇌CH_3OH+#5	0.00	0.00	2.12×10^{7}	2.12×10^{7}
R23	CH_2OH#3+H_{c_out}#5⇌CH_2H_2O#3 + #5	0.84	−0.21	1.74×10^{4}	1.12×10^{2}
R24	CH_2OH#3+H_{c_in}#3⇌CH_2H_2O#3+#3	1.40	0.78	2.51×10^{-2}	3.43×10^{6}
R25	CH_2H_2O#3⇌CH_2#3+H_2O	0.08	0.08	4.13×10^{6}	2.82×10^{7}
R26	CH_2#3+H#2⇌CH_3#3+#2	0.38	−1.73	1.09×10^{9}	9.85×10^{-10}
R27	CH_3#3+H#2⇌CH_4#3+#2	2.68	0.05	1.12×10^{-15}	3.71×10^{-15}
R28	CH_4#3⇌CH_4+#3	0.01	0.01	2.35×10^{7}	2.99×10^{7}
R29	CH_4#5⇌CH_4+#5	0.01	0.01	2.35×10^{7}	2.99×10^{7}

Table S13. The theoretical TOF (h^{-1}) to produce CH_3OH, HCOOH and CH_4 on each M_1-MoS_2.

TOF	Pt_1-MoS_2	Ni_1-MoS_2	Rh_1-MoS_2	Zn_1-MoS_2	Pd_1-MoS_2	Cu_1-MoS_2
CH_3OH	3.02	80.81	6.67	2.76	0.77	0.12
HCOOH	2.37×10^{-10}	3.41×10^{-10}	8.66×10^{-10}	6.35×10^{-6}	2.35×10^{-8}	1.87×10^{-7}
CH_4	7.29×10^{-9}	1.79×10^{-106}	3.30×10^{-116}	4.56×10^{-103}	1.22×10^{-113}	2.25×10^{-92}

Table S14. The energy barriers (E_a), reaction energies (ΔE) of the hydrogenation of C-containing species along the comparable CO_2 hydrogenation pathway on Ni_1, Pt_1, Rh_1, Zn_1, Pd_1, Cu_1-MoS_2.

M_1-MoS_2	Reaction Step	E_a(eV)	ΔE(eV)
Ni_1-MoS_2	CO_2#3+H#2⇌COOH#3+#2	1.34	0.67
	COOH#3+H#2⇌$C(OH)_2$#3+#2	0.51	−0.38
	$C(OH)_2$#3+H#4⇌$CH(OH)_2$#3+#4	0.78	−1.85
	$CH(OH)_2$#3+H#4⇌CHOH#3+H_2O+#3	0.07	−0.83
	CHOH#3+H#4⇌CH_2OH#3+#2	0.51	−2.38
	CH_2OH#3+H#4⇌CH_3OH#3+#4	1.13	−0.73
	CH_3OH#5⇌CH_3OH+#5	0.04	0.04
Pt_1-MoS_2	CO_2#3+H#4⇌COOH#3+#4	0.35	−0.14
	COOH#3+H#2⇌$C(OH)_2$#3+#2	0.67	−0.29
	$C(OH)_2$#3+H#4⇌$CH(OH)_2$#3+#4	0.13	−2.25
	$CH(OH)_2$#3+H#4⇌CHOH#3+H_2O+#3	0.01	−0.83
	CHOH#3+H#2⇌CH_2OH#3+#2	0.56	−2.07
	CH_2OH#3+H#4⇌CH_3OH#3+#4	0.87	−0.24
	CH_3OH#5⇌CH_3OH+#5	0.64	0.64
Rh_1-MoS_2(a)	CO_2#3+H#2⇌COOH#3+#2	1.20	0.76
	COOH#3+H#4⇌$C(OH)_2$#3+#4	0.08	−0.67
	$C(OH)_2$#3+H#2⇌$CH(OH)_2$#3+#2	0.55	−1.69
	$CH(OH)_2$#3+H#4⇌CHOH#3+H_2O+#3	0.23	−1.01
	CHOH#3+H#2⇌CH_2OH#3+#2	0.93	−2.09
	CH_2OH#3+H#4⇌CH_3OH#3+#4	0.85	−1.29
	CH_3OH#5⇌CH_3OH+#5	0.00	−0.01
Rh_1-MoS_2(b)	CO_2#3+H#2⇌COOH#3+#2	1.20	0.76
	COOH#3+H#2⇌$C(OH)_2$#3+#2	0.70	−0.05
	$C(OH)_2$#3+H#2⇌$CH(OH)_2$#3+#2	0.55	−1.69
	$CH(OH)_2$#3+H#4⇌CHOH#3+H_2O+#3	0.23	−1.01
	CHOH#3+H#4⇌CH_2OH#3+#4	0.25	−2.69
	CH_2OH#3+H#4⇌CH_3OH#3+#4	0.85	−1.29
	CH_3OH#3⇌CH_3OH+#3	0.00	−0.01
Zn_1-MoS_2(a)	CO_2#3+H#2⇌COOH#3+#2	1.69	0.78
	COOH#3+H#2⇌$C(OH)_2$#3+#2	0.80	0.30
	$C(OH)_2$#3+H#2⇌$CH(OH)_2$#3+#2	1.09	−0.43
	$CH(OH)_2$#3+H#4⇌CHOH#3+H_2O+#3	0.02	−0.71
	CH_2OH#3+H#4⇌CH_3OH#3+#4	0.82	−1.04
	CH_3OH#5⇌CH_3OH+#5	0.10	0.10
Zn_1-MoS_2(b)	CO_2#3+H#4⇌COOH#3+#4	0.62	−0.29
	COOH#3+H#2⇌$C(OH)_2$#3+#2	0.80	0.30
	$C(OH)_2$#3+H#2⇌$CH(OH)_2$#3+#2	1.09	−0.43
	$CH(OH)_2$#3+H#4⇌CHOH#3+H_2O+#3	0.02	−0.71
	CHOH#3+H#2⇌CH_2OH#3+#2	0.92	−0.89

	CH_2OH#3+H#4⇌CH_3OH#3+#4	0.82	−1.04
	CH_3OH#5⇌CH_3OH+#5	0.10	0.10
Pd_1-MoS_2(a)	CO_2#3+H#2⇌COOH#3+#2	1.34	0.88
	COOH#3+H#2⇌$C(OH)_2$#3+#2	0.84	−0.20
	$C(OH)_2$#3+H#4⇌$CH(OH)_2$#3+#4	0.29	−1.99
	$CH(OH)_2$#3+H#4⇌$CHOH$#3+H_2O+#3	0.01	−0.78
	$CHOH$#3+H#4⇌CH_2OH#3+#2	0.08	−2.50
	CH_2OH#3+H#4⇌CH_3OH#3+#4	0.96	−1.13
	CH_3OH#5⇌CH_3OH+#5	0.10	0.10
Pd_1-MoS_2(b)	CO_2#3+H#2⇌COOH#3+#2	1.34	0.88
	COOH#3+H#2⇌$C(OH)_2$#3+#2	0.84	−0.20
	$C(OH)_2$#3+H#2⇌$CH(OH)_2$#3+#2	0.91	−1.40
	$CH(OH)_2$#3+H#4⇌$CHOH$#3+H_2O+#3	0.01	−0.78
	$CHOH$#3+H#4⇌CH_2OH#3+#2	0.08	−2.50
	CH_2OH#3+H#4⇌CH_3OH#3+#4	0.96	−1.13
	CH_3OH#5⇌CH_3OH+#5	0.10	0.10
Pd_1-MoS_2(c)	CO_2#3+H#2⇌COOH#3+#2	1.34	0.88
	CO_2#3+H#4⇌COOH#3+#4	0.96	0.01
	$C(OH)_2$#3+H#4⇌$CH(OH)_2$#3+#4	0.29	−1.99
	$CH(OH)_2$#3+H#4⇌$CHOH$#3+H_2O+#3	0.01	−0.78
	$CHOH$#3+H#4⇌CH_2OH#3+#2	0.08	−2.50
	CH_2OH#3+H#4⇌CH_3OH#3+#4	0.96	−1.13
	CH_3OH#5⇌CH_3OH+#5	0.10	0.10
Cu_1-MoS_2	CO_2#3+H#4⇌COOH#3+#4	0.55	−0.63
	COOH#3+H#2⇌$C(OH)_2$#3+#2	0.99	0.39
	$C(OH)_2$#3+H#2⇌$CH(OH)_2$#3+#2	1.12	−0.51
	$CH(OH)_2$#3+H#4⇌$CHOH$#3+H_2O+#3	0.01	−0.81
	$CHOH$#3+H#2⇌CH_2OH#3+#2	0.82	−0.87
	CH_2OH#3+H#4⇌CH_3OH#3+#4	0.82	−1.04
	CH_3OH#5⇌CH_3OH+#5	0.00	0.00

Table S15. The coverage of all carbon-containing intermediates on Ni_1, Pt_1, Rh_1, Zn_1, Pd_1, Cu_1-MoS_2.

	θ_{*COOH}	$\theta_{*C(OH)2}$	$\theta_{*CH(OH)2}$	θ_{*CHOH}	θ_{*CH2OH}
Ni_1-MoS_2	1.88×10^{-8}	1.99×10^{-4}	8.75×10^{-12}	3.40×10^{-7}	9.98×10^{-1}
Pt_1-MoS_2	1.54×10^{-9}	2.96×10^{-9}	1.72×10^{-10}	5.45×10^{-11}	9.74×10^{-1}
Rh_1-MoS_2	2.86×10^{-9}	1.12×10^{-10}	3.30×10^{-7}	3.53×10^{-7}	9.70×10^{-1}
Zn_1-MoS_2	8.65×10^{-5}	1.76×10^{-5}	1.09×10^{-9}	6.48×10^{-8}	2.42×10^{-1}
Pd_1-MoS_2	2.37×10^{-8}	3.25×10^{-8}	7.57×10^{-11}	3.94×10^{-10}	6.15×10^{-1}
Cu_1-MoS_2	1.98×10^{-3}	1.73×10^{-6}	1.92×10^{-9}	1.32×10^{-9}	5.78×10^{-1}

S3. References

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