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Supporting Information

Unveiling Electrochemical Reaction Pathways of CO_2 Reduction to C_N Species at S-Vacancies of MoS_2

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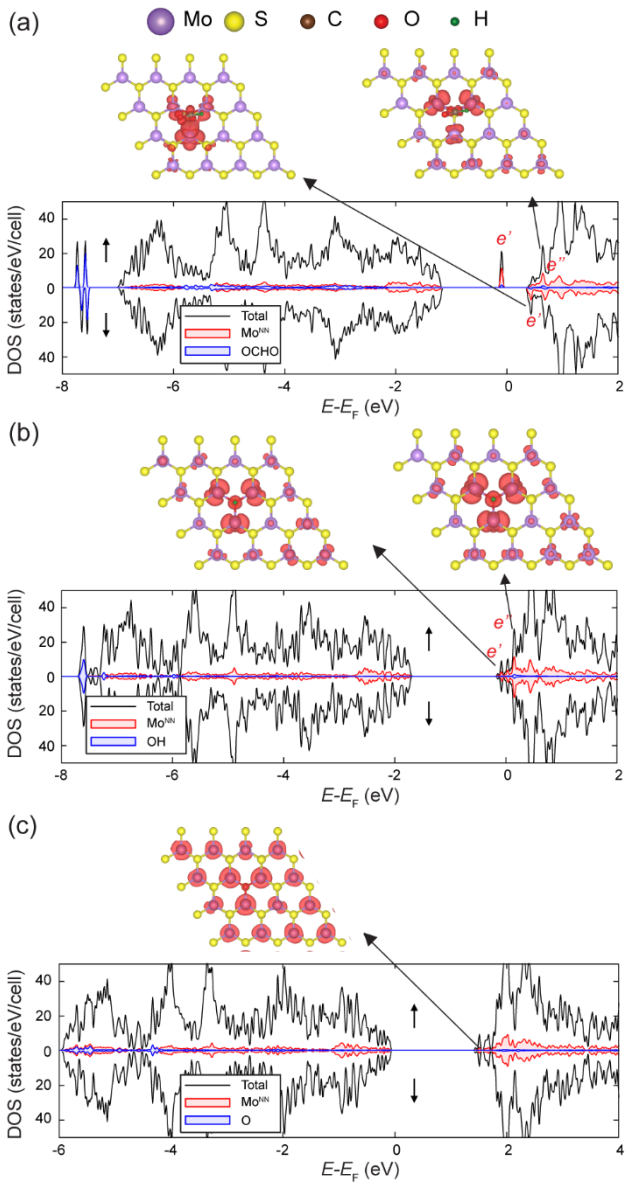

Figure S1. Spin-resolved DOSs and partial charge densities of (a) *OCHO, (b) *OH, and (c) *O. Partial DOSs projected on adsorbates (blue) and three nearest neighbor Mo ions (red) are presented. e′ and e′′ denote the antibonding characters of defect states.

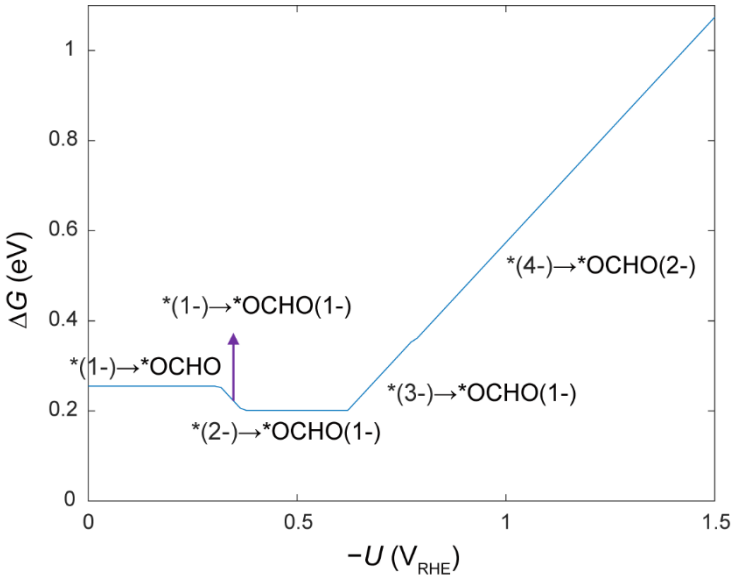

Figure S2. The reaction free energy of the first protonation step of CO_2 depending on potential U.

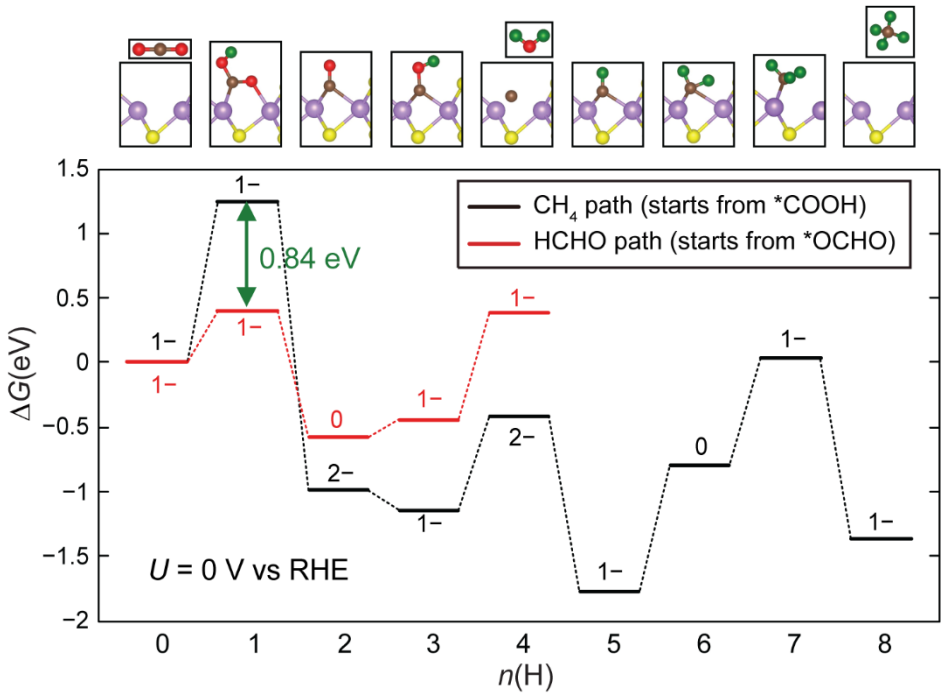

Figure S3. Free energy diagrams for the lowest energy pathways to CH_4 starting with *COOH (black) and to HCHO with *OCHO (red).

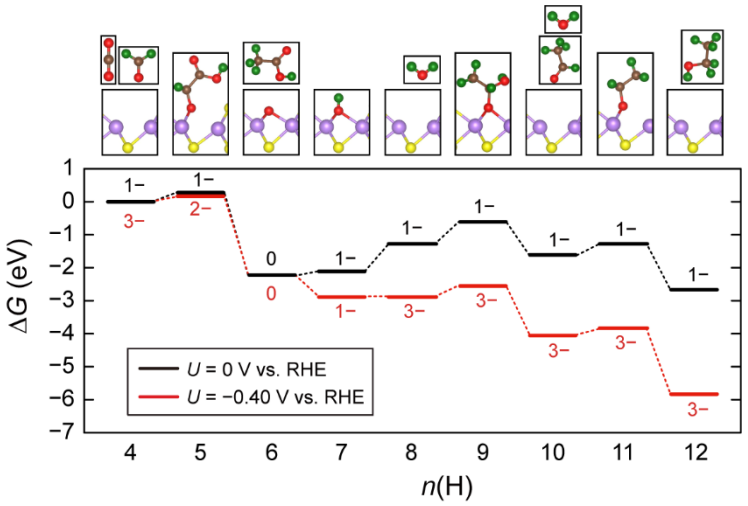

Figure S4. Free energy diagrams for the lowest energy pathways to CH_3CH_2OH led by the adsorption of CO_2 to *HCHO.

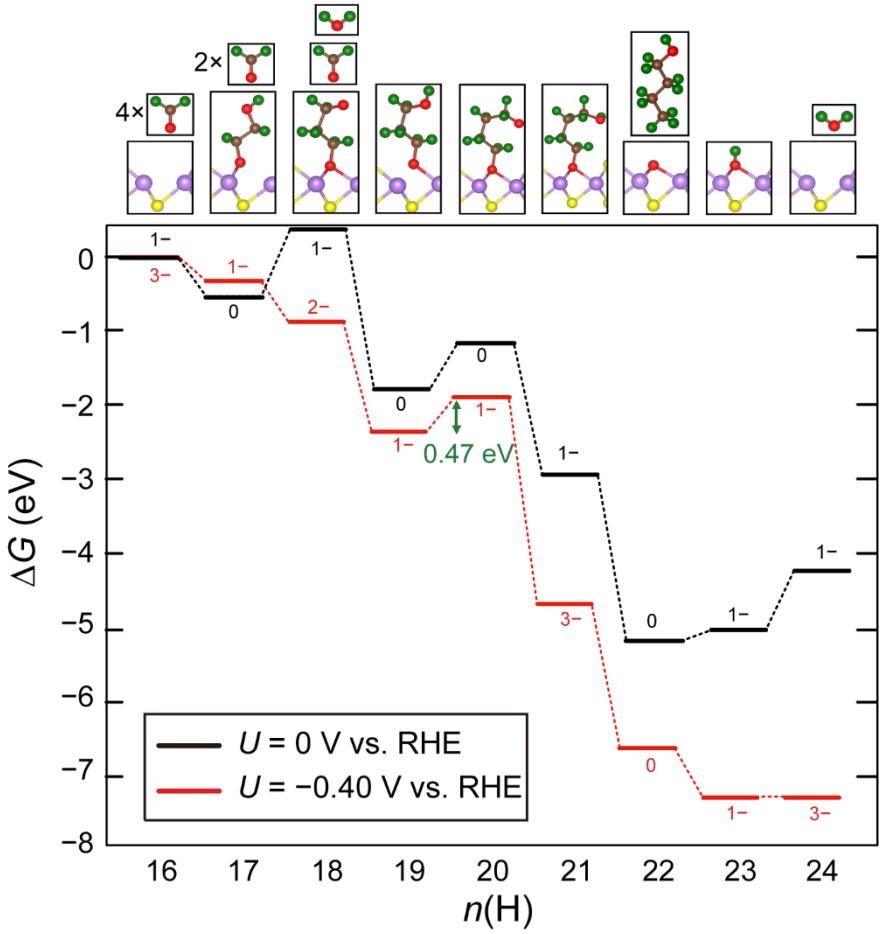

Figure S5. Free energy diagrams for the lowest energy pathways to $CH_3CH_2CH_2CH_2OH$.

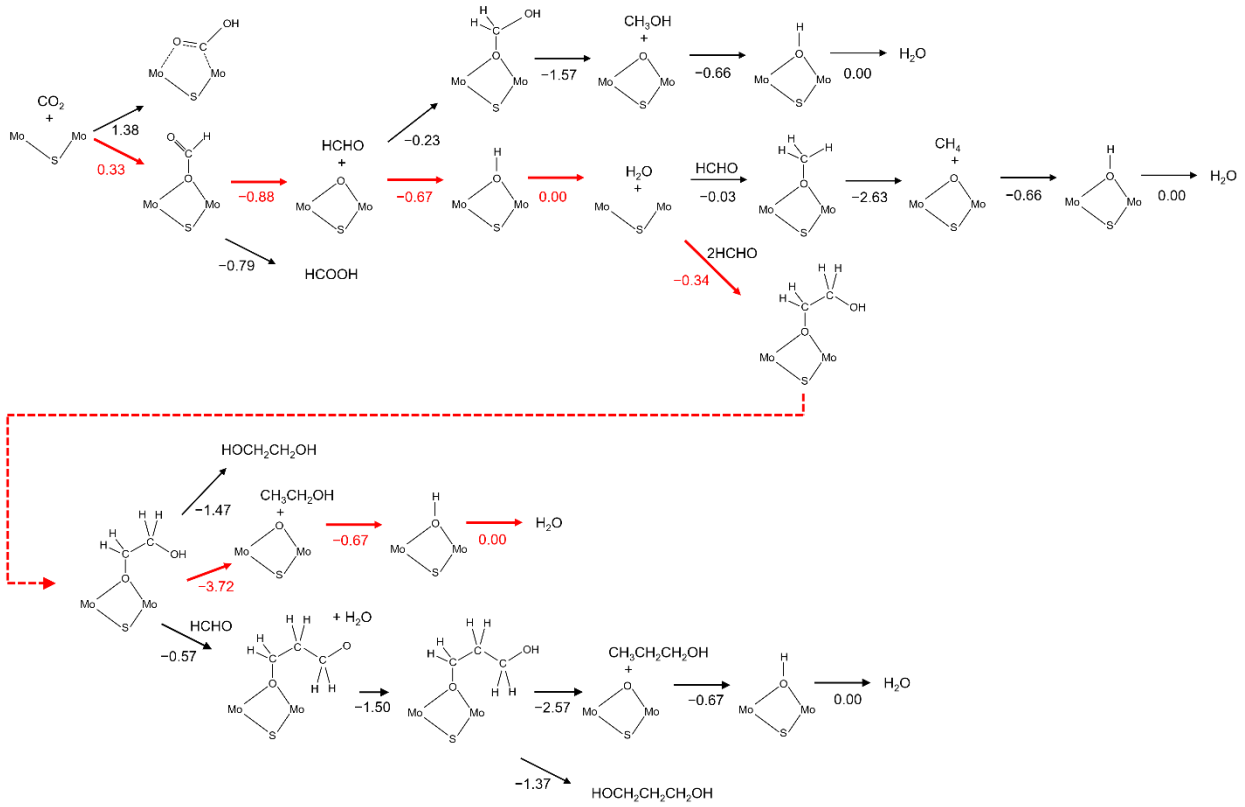

Figure S6. Schematics of every reaction pathway considered in the present study. The number at the bottom of each arrow indicates the reaction free energy in eV unit at −0.4 V vs. RHE. The pathway following red arrows is energetically most favorable.

ΔG (eV)	*H	*O	*OH	*OCHO	*OCH_2OH
PBE	0.06	−0.86	−0.11	0.67	0.65
PBE-D2	−0.04	−1.00	−0.18	0.16	0.10
PBE-D3	0.00	−0.99	−0.10	0.27	0.17
PBE-TS	0.00	−0.99	−0.10	0.24	0.10
PBE-TS+SCS	0.03	−0.83	0.02	0.20	0.03
opt888-DF	0.03	−1.02	−0.09	−0.07	−0.02

Table S1. Impact of a type of van der Waals (vdW) functional on the free energy of several adsorbates with respect to the free energy of V_S-MoS_2 under the RHE condition. Except for the PBE functional, the results are consistent with each other within 0.2 eV.

Intermediate	File	Charge state	DFT energy (eV)
*	CONTCAR_VS_1-	1−	−351.097
*OCHO	CONTCAR_OCHO_1-	1−	−379.113
*O	CONTCAR_O_0	0	−360.060
*OH	CONTCAR_OH_1-	1−	−364.363
*OCH_3	CONTCAR_OCH3_1-	1−	−379.684
*OCH_2OH	CONTCAR_OCH2OH_1-	1−	−386.161
*OCH_2CH_2OH	CONTCAR_OCH2CH2OH_0	0	−401.860
*$OCH_2CH_2CH_2O$	CONTCAR_OCH2CH2CH2O_1-	1−	−414.313
*$OCH_2CH_2CH_2OH$	CONTCAR_OCH2CH2CH2OH_0	0	−418.640

Table S2. DFT energy of CO_2R intermediates of stable charge state at 0 V vs. RHE. The corresponding CONTCAR files, which include geometry information of supercell, are provided.

Intermediate	File	Charge state	DFT energy (eV)
*	CONTCAR_VS_3-	3−	−353.667
*OCHO	CONTCAR_OCHO_2-	2−	−379.535
*O	CONTCAR_O_0	0	−360.060
*OH	CONTCAR_OH_1-	1−	−364.363
*OCH_3	CONTCAR_OCH3_2-	2−	−380.105
*OCH_2OH	CONTCAR_OCH2OH_3-	3−	−386.887
*OCH_2CH_2OH	CONTCAR_OCH2CH2OH_1-	1−	−402.648
*$OCH_2CH_2CH_2O$	CONTCAR_OCH2CH2CH2O_2-	2−	−414.930
*$OCH_2CH_2CH_2OH$	CONTCAR_OCH2CH2CH2OH_1-	1−	−419.312

Table S3. DFT energy of CO_2R intermediates of stable charge state at −0.4 V vs. RHE. The corresponding CONTCAR files, which include geometry information of supercell, are provided.