Supporting Information for

Two-dimensional $Mo_3(C_6O_6)_2$ exhibits high activity and selectivity as a catalyst for CO_2 reduction reactions

Weixiang Geng,[†] Tianchun Li,[†] Xiaorong Zhu,[§] Yu Jing*,[†]

[†]Jiangsu Co-Innovation Centre of Efficient Processing and Utilization of Forest Resources, College of Chemical Engineering, Nanjing Forestry University, Nanjing 210037, China

[§] School of Chemistry and Chemical Engineering, Nantong University, 226019, China

To whom correspondence should be addressed. Email: yujing@njfu.edu.cn(YJ)

The number of pages: 4 (S1-S6)

The number of Figures: 3 (Figures S1-S5)

The number of Tables: 1 (Tables S1)

The chemical reduction of CO_2 is a multi-step reaction process, usually involving 2, 6, 8 or 12 electron reaction pathways. The thermodynamically determined equilibrium potentials (^{U_0}) for CO_2 reduction to several most common products are listed below:

$$CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O \quad (U = -0.11\ V)$$

$$CO_2 + 2H^+ + 2e^- \rightarrow HCOOH_{(aq)} \quad (U = -0.20\ V)$$

$$CO_2 + 6H^+ + 6e^- \rightarrow CH_3OH(aq) + H_2O \quad (U = +0.30\ V)$$

$$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O \quad (U = +0.17\ V)$$

$$2CO_2 + 12H^+ + 12e^- \rightarrow C_2H_4 + 4H_2O \qquad (U = +0.08\ V)$$

Table. S1 DFT total energies (E_{total}), zero-point energies (zpe), entropies (T*S) multiplied by temperature (T = 298.15K), and free energies(G) of gas molecules.

	E_{total} (eV)	zpe (eV)	T*S	G(eV)
H_2	-6.77	0.27	0.41	-6.91
H_2O	-14.22	0.56	0.67	-14.33
CO_2	-22.95	0.31	0.66	-23.30

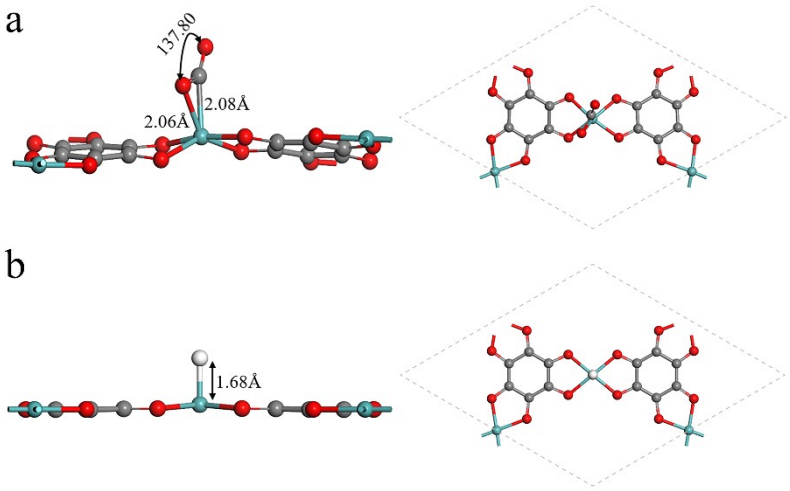

Fig. S1 The side and top views of CO_2 (a) and *H (b) adsorbed on $Mo_3(C_6O_6)_2$. The colors of H, C, and O atoms are white, gray, and red, respectively.

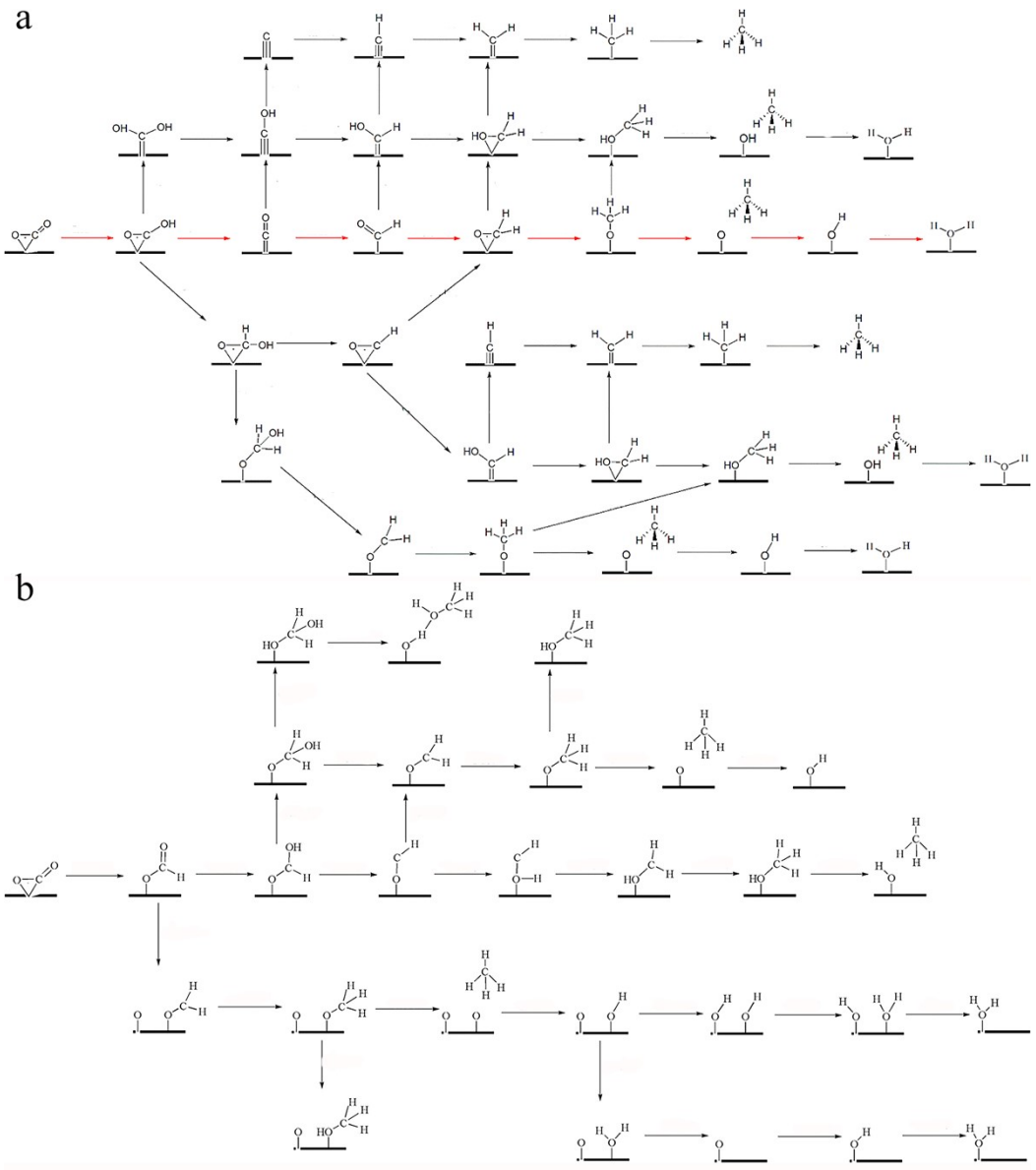

Fig. S2 Reaction pathways in the (a) "COOH" path and (b) the "OCHO" path. The optimal path is indicated in red arrows.

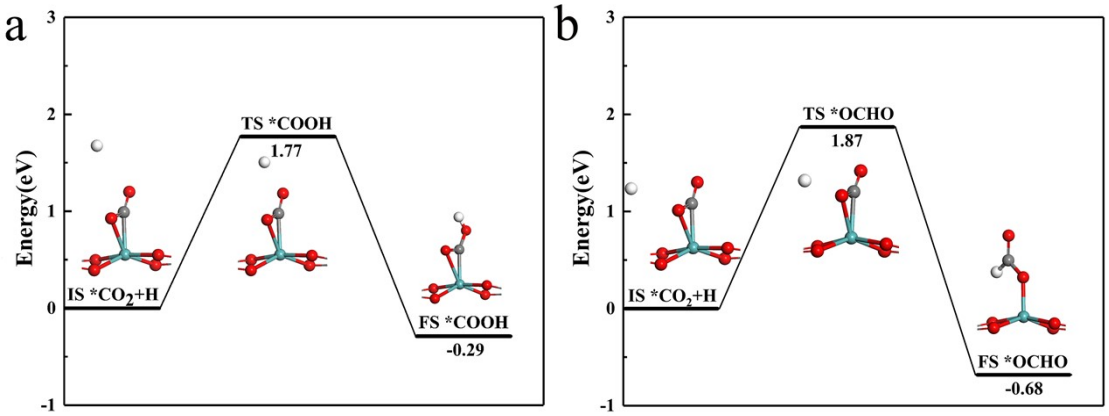

Fig. S3 Energy profiles for the formed *COOH(a) and *OCHO(b) intermediates by the initial hydrogenation of carbon dioxide at $Mo_3(C_6O_6)_2$. The structure of each state is given. The *H and O/C atomic distances in each step are given.

To investigate the most stable surface conformation of $Mo_3(C_6O_6)_2$ under working conditions. We have plotted Pourbaix diagrams based on thermodynamic data. As shown in Fig. S1, the surface of 2D $Mo_3(C_6O_6)_2$ is completely covered by *OH species when the electrode potential is 0 V, independent of the pH value. When an electrode potential of -0.28 V was applied, OH started to be reduced, and the OH coverage on the material surface was 1/3 ML when at the operating potential of CRR. This proves the presence of stable Mo active sites on the MOF surface at the working potential. At an applied potential of -0.90 V, all OH on the $Mo_3(C_6O_6)_2$ surface is hydrogenated.

Since the working potential of $Mo_3(C_6O_6)_2$ monolayer catalyzed CRR is -0.58 V at pH = 0 when less than 1/3 of the active sites on the surface are occupied by *OH, we further considered the effect of axial *OH ligands on $Mo_3(C_6O_6)_2$ monolayer to catalyze CRR. The subsequent calculations showed that $Mo_3(C_6O_6)_2$-OH can catalyze the reduction of CO_2 to CH_4 at a limiting potential of -0.39 V, and according to the Pourbaix diagram there is a large amount of *OH ligands present on the $Mo_3(C_6O_6)_2$ surface at this limiting potential, indicating the good stability of the material during the reaction.

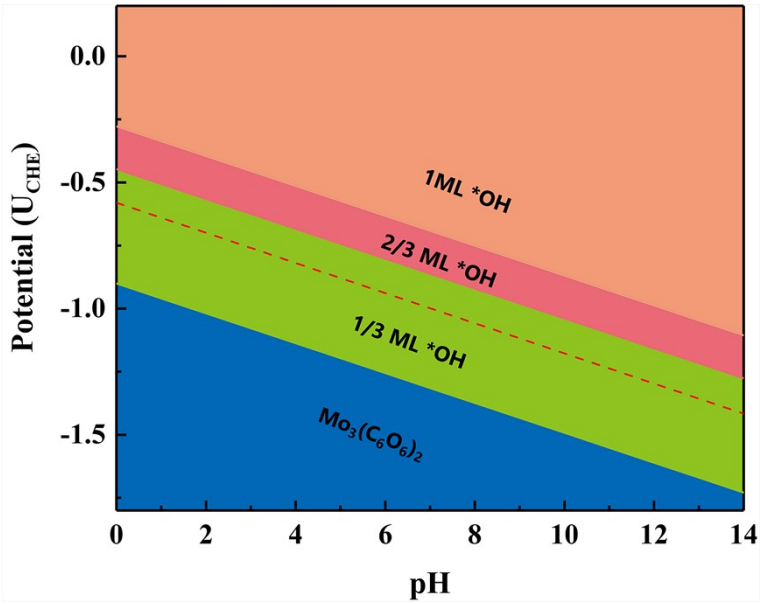

Fig. S4 Pourbaix diagram for the $Mo_3(C_6O_6)_2$ system. The red dashed line represents the limiting potential of CH_4 formation.

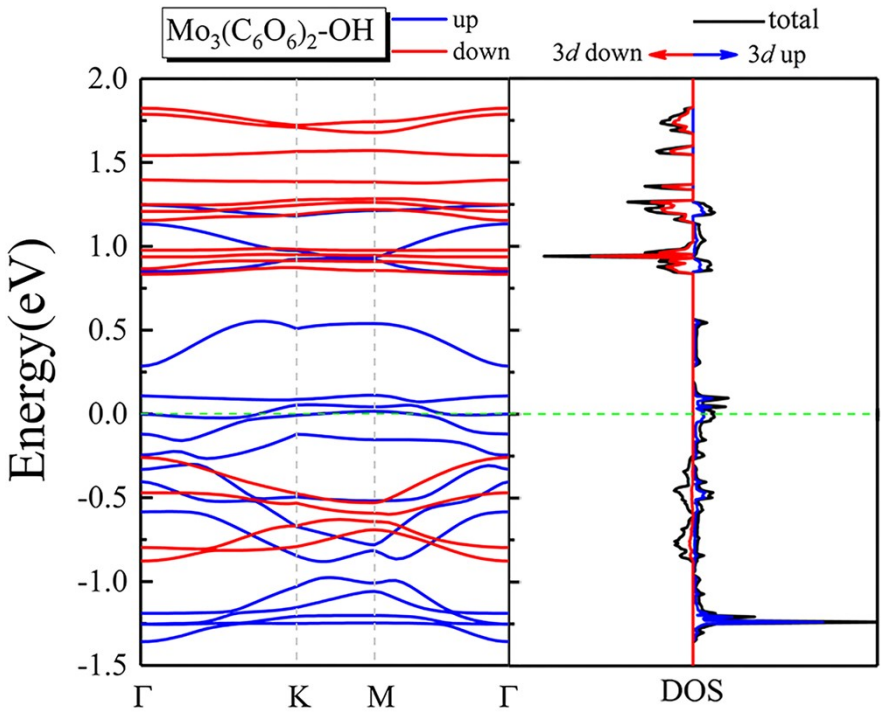

Fig. S5 Spin-polarized band structures and density of state of $Mo_3(C_6O_6)_2$-OH monolayer. The blue solid line and red solid line represent the spin-up and spin-down, respectively, and the green dashed line denotes the Fermi level.