Supporting Information for

Two-dimensional Mo$_3$(C$_6$O$_6$)$_2$ exhibits high activity and selectivity as a catalyst for CO$_2$ reduction reactions

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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:

\[
\begin{align*}
\text{CO}_2 + 2\text{H}^+ + 2\text{e}^- & \rightarrow \text{CO} + \text{H}_2\text{O} \\
(U = - 0.11 \text{ V}) \\
\text{CO}_2 + 2\text{H}^+ + 2\text{e}^- & \rightarrow \text{HCOOH}_{(aq)} \\
(U = - 0.20 \text{ V}) \\
\text{CO}_2 + 6\text{H}^+ + 6\text{e}^- & \rightarrow \text{CH}_3\text{OH}_{(aq)} + \text{H}_2\text{O} \\
(U = + 0.30 \text{ V}) \\
\text{CO}_2 + 8\text{H}^+ + 8\text{e}^- & \rightarrow \text{CH}_4 + 2\text{H}_2\text{O} \\
(U = + 0.17 \text{ V})
\end{align*}
\]
\[2\text{CO}_2 + 12\text{H}^+ + 12\text{e}^- \rightarrow \text{C}_2\text{H}_4 + 4\text{H}_2\text{O}\]  \hspace{1cm} (U = + 0.08 \text{ V})

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

<table>
<thead>
<tr>
<th></th>
<th>(E_{\text{total}}) (eV)</th>
<th>zpe (eV)</th>
<th>T*S</th>
<th>G(eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{H}_2)</td>
<td>-6.77</td>
<td>0.27</td>
<td>0.41</td>
<td>-6.91</td>
</tr>
<tr>
<td>(\text{H}_2\text{O})</td>
<td>-14.22</td>
<td>0.56</td>
<td>0.67</td>
<td>-14.33</td>
</tr>
<tr>
<td>(\text{CO}_2)</td>
<td>-22.95</td>
<td>0.31</td>
<td>0.66</td>
<td>-23.30</td>
</tr>
</tbody>
</table>

**Fig. S1** The side and top views of \(\text{CO}_2\) (a) and \(*\text{H}\) (b) adsorbed on Mo\(_3\)(C\(_6\)O\(_6\))\(_2\). 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$_6$O$_6$)$_2$. 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$_6$O$_6$)$_2$ under working conditions. We have plotted Pourbaix diagrams based on thermodynamic data. As shown in Fig. S1, the surface of 2D Mo$_3$(C$_6$O$_6$)$_2$ 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$_6$O$_6$)$_2$ surface is hydrogenated.

Since the working potential of Mo$_3$(C$_6$O$_6$)$_2$ 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$_6$O$_6$)$_2$ monolayer to catalyze CRR. The subsequent calculations showed that Mo$_3$(C$_6$O$_6$)$_2$-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$_6$O$_6$)$_2$ surface at this limiting potential, indicating the good stability of the material during the reaction.

**Fig. S4** Pourbaix diagram for the Mo$_3$(C$_6$O$_6$)$_2$ 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$_6$O$_6$)$_2$-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.