Catalyzed Activation of CO₂ by a Lewis Base Site in W-Cu-BTC Hybrid Metal Organic Frameworks

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Figure S1. The periodic (a) and cluster (b) models of W-Cu-BTC. The blue, green, red, grey and white balls represent W, Cu, O, C and H atoms, respectively.

Figure S2. (Top) The binding energies/adsorption energies ($E_{ads}$) and the adsorbed geometries of CO$_2$ binding on Mo-Cu-BTC and Cr-Cu-BTC. The abilities of catalyzing CO$_2$ by the three hybrid MOFs are found to be in the order of W-Cu-BTC > Mo-Cu-BTC > Cr-Cu-BTC. Although the coordination complex $\eta_2(CO)$ can be formed on Mo-Cu-BTC, the binding energy of 0.44 eV is much smaller than that of W-Cu-BTC (1.34 eV). In the case of Cr-Cu-BTC, the $\eta_2(CO)$ complex can not be obtained. Instead, the structural optimization shows a favorable angularly-binding structure $(\eta_1^2(O))$ with CO$_2$ remaining the original linear structure ($E_{ads} = 0.33$ eV), which indicates that the Cr-Cu node is unable to activate CO$_2$. Indeed, as mentioned in the introduction, the ability to activate CO$_2$ is related to the ability of losing electrons, which is in the order of Cr < Mo < W. (Bottom) The comparison of HOMO for W-Cu-BTC, Mo-Cu-BTC and Cr-Cu-BTC. The gradually weaker $dz^2$ character is well consistent with the weaker catalyzing ability in the order of W-Cu-BTC > Mo-Cu-BTC > Cr-Cu-BTC.
Figure S3. The vibrational frequency modes of CO$_2$ adsorption on the open metal W sites in various models except $\eta^2$(CO).
$\nu_{\text{asym}} = 1749 \text{ cm}^{-1}$

$\nu_{\text{sym}} = 1200 \text{ cm}^{-1}$

$\nu_{1 \text{ bend}} = 687 \text{ cm}^{-1}$

$\nu_{2 \text{ bend}} = 677 \text{ cm}^{-1}$

$\nu_{\text{sym}} = 1269 \text{ cm}^{-1}$

$\nu_{\text{asym}} = 1568 \text{ cm}^{-1}$

$\nu_{\text{asym}} = 1257 \text{ cm}^{-1}$

$\nu_{1 \text{ bend}} = 673 \text{ cm}^{-1}$

$\nu_{2 \text{ bend}} = 674 \text{ cm}^{-1}$
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Figure S5. The physisorbed structures and binding energies/adsorption energies ($E_{ads}$) of CO$_2$ angularly and linearly binding on W-BTC (top layer) and Cu-BTC (bottom layer).

Table S1. Comparison of the adsorption energy ($E_{ads}$) and geometries of CO$_2$ adsorbed on W-Cu-BTC, Cu-BTC and W-BTC.

<table>
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<tr>
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<th>W-Cu-BTC</th>
<th>Cu-BTC</th>
<th>W-BTC</th>
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<tr>
<td></td>
<td>$E_{ads}$</td>
<td>$\angle$COC</td>
<td>$E_{ads}$</td>
</tr>
<tr>
<td>$\eta_1^1$(O)</td>
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<td>0.10</td>
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<tr>
<td>$\eta_1^2$(O)</td>
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<td>178°</td>
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<td>$\eta_1$(C)</td>
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<td>-</td>
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<tr>
<td>$\eta_2$(CO)</td>
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<td>-</td>
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<tr>
<td>$\eta_2$(OO)</td>
<td>-0.40</td>
<td>108°</td>
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Figure S6. The desorption process of formic acid (HCOOH) from W-Cu-BTC after hydrogenation by two H atoms on the activated CO₂ in η²(CO) complex.

![HCOOH Desorption Process](image)

Figure S7. The desorption process of methylene glycol (H₂C(OH)₂) from W-Cu-BTC after hydrogenation by four H atoms on the activated CO₂ in η²(CO) complex.

![H₂C(OH)₂ Desorption Process](image)