Electronic Supplementary Material (ESI) for Chemical Science

Catalyzed Activation of CO_2 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.

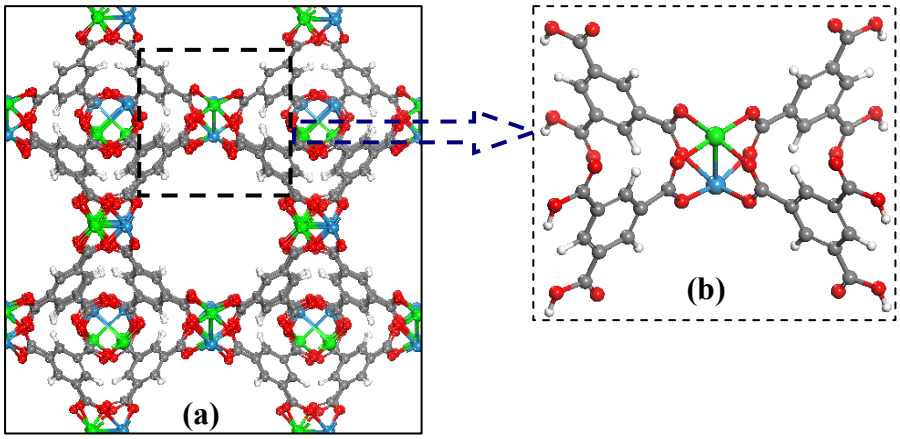


Figure S2. (Top) The binding energies/adsorption energies (E_{ads}) and the adsorbed geometries of CO_2 binding on Mo-Cu-BTC and Cr-Cu-BTC. The abilities of catalyzing CO_2 by the three hybrid MOFs are found to be in the order of W-Cu-BTC > Mo-Cu-BTC > Cr-Cu-BTC. Although the coordination complex η^2(CO) 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 η^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.

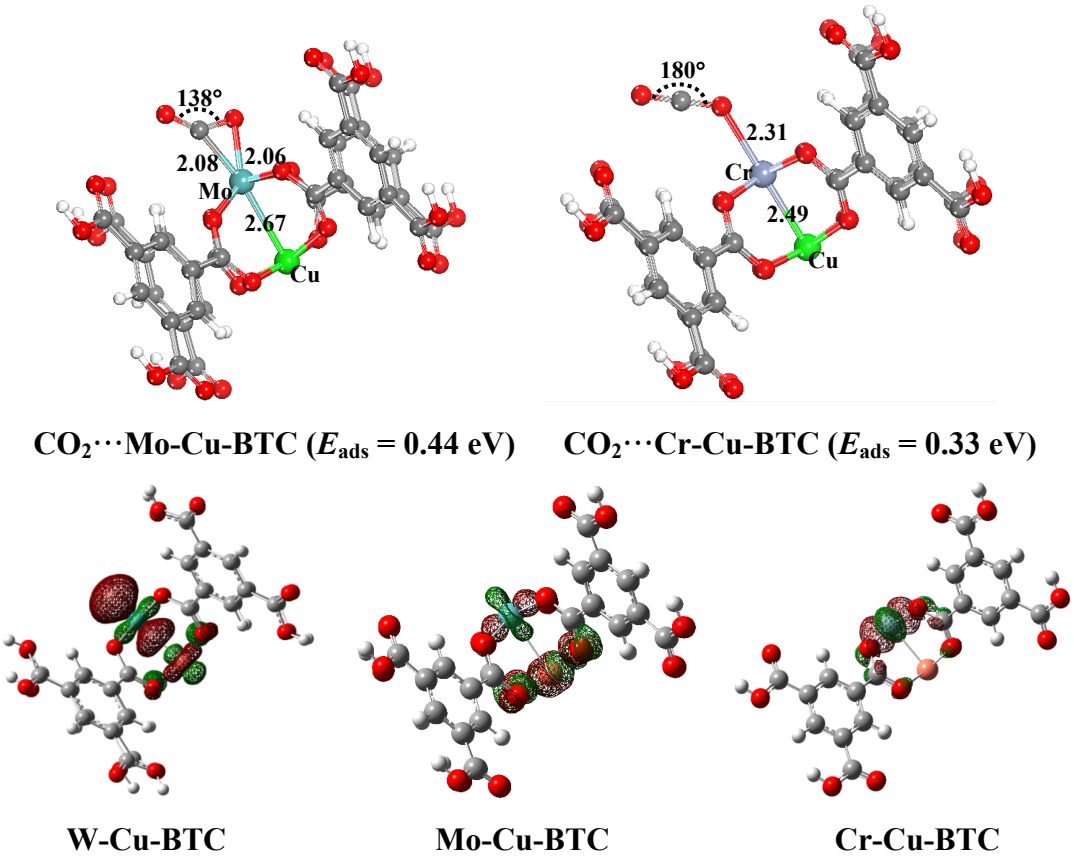
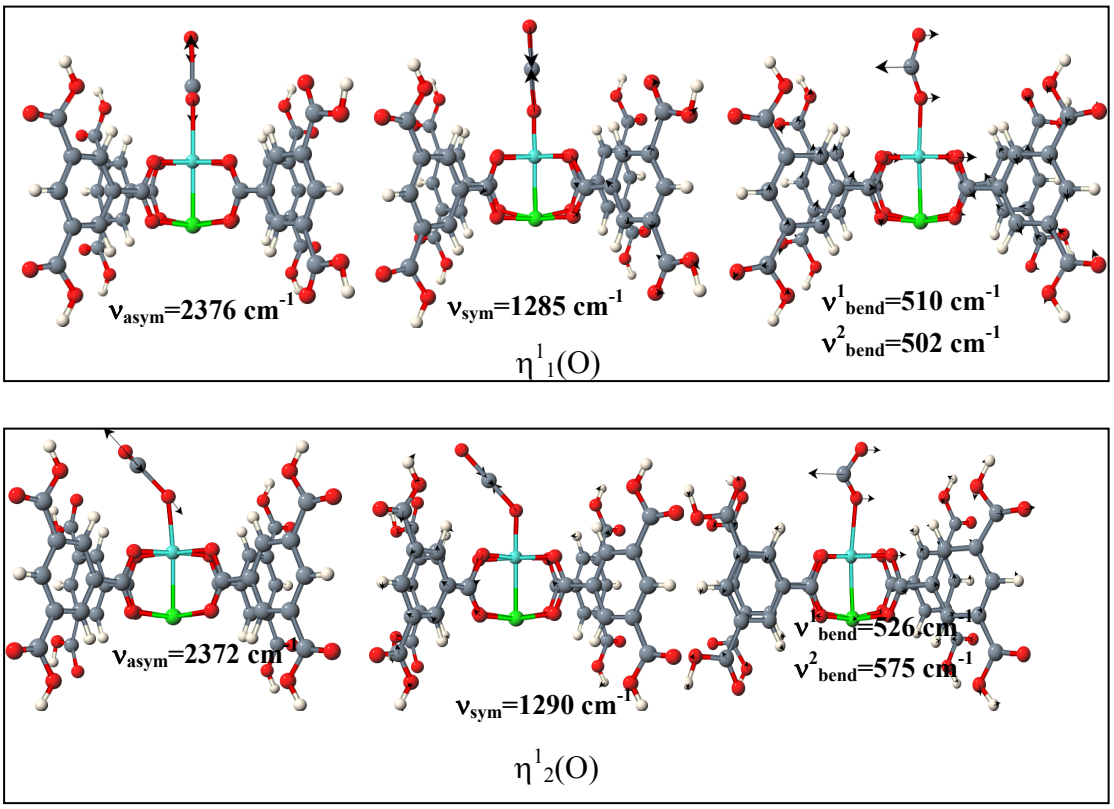
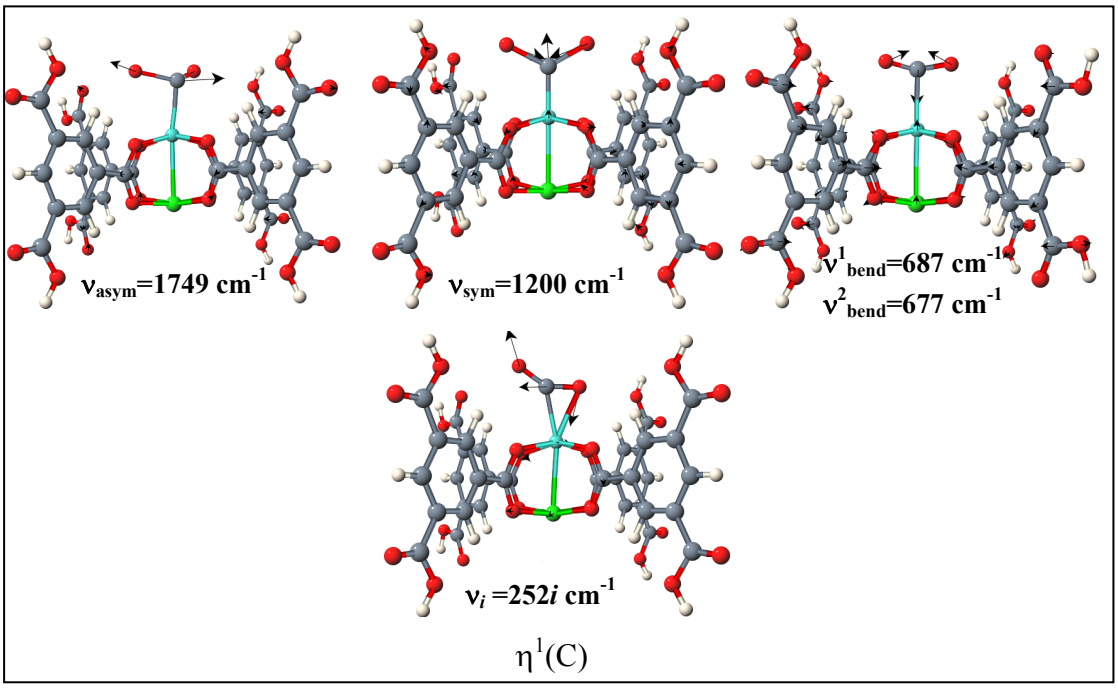


Figure S3. The vibrational frequency modes of CO_2 adsorption on the open metal W sites in various models except η^2(CO).




ν_{asym}=1749 cm^{-1}
ν_{sym}=1200 cm^{-1}
ν^1_{bend}=687 cm^{-1}
ν^2_{bend}=677 cm^{-1}
ν_i =252i cm^{-1}
η^1(C)

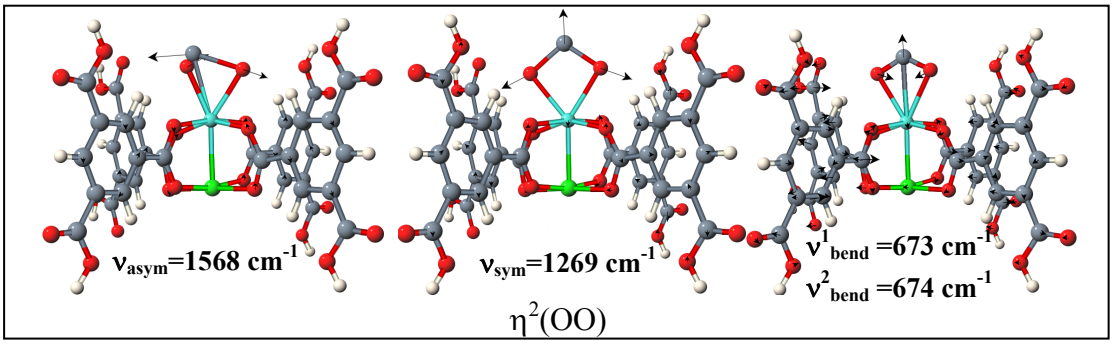

ν_{asym}=1568 cm^{-1}
ν_{sym}=1269 cm^{-1}
ν^1_{bend} =673 cm^{-1}
ν^2_{bend} =674 cm^{-1}
η^2(OO)

Figure S4. LDOS of the open W ion in W-Cu-BTC and η^2(CO) complex of CO_2-W-Cu-BTC including the 6*s*, 5*dz*^{2} and the 5*d* orbitals.

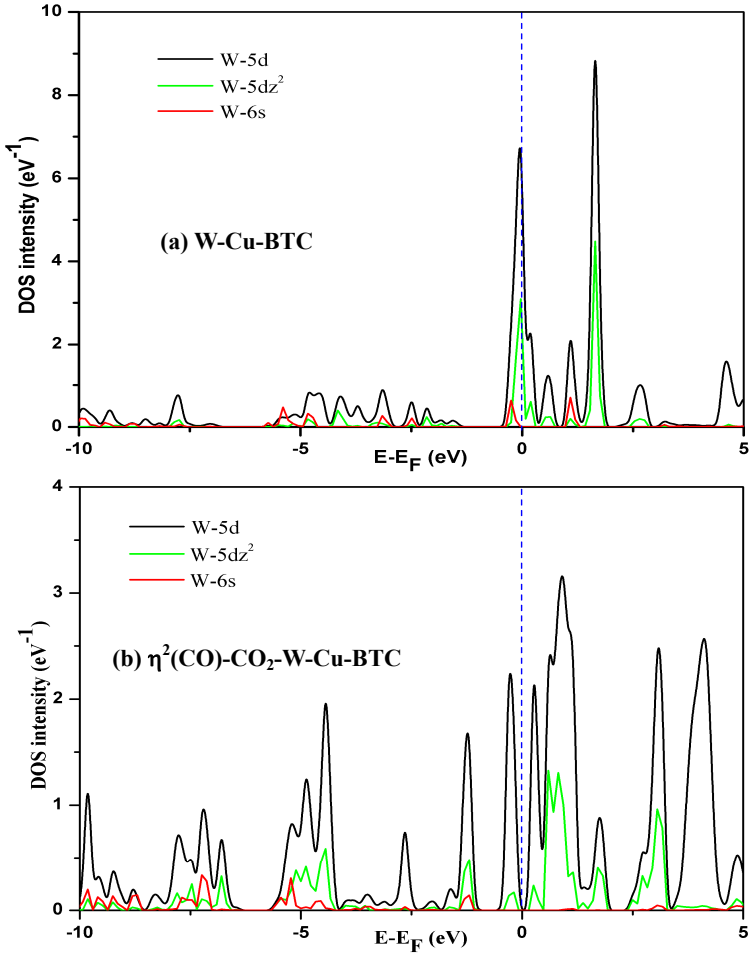
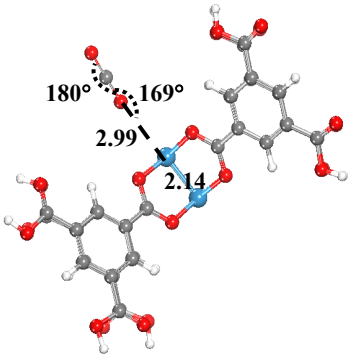
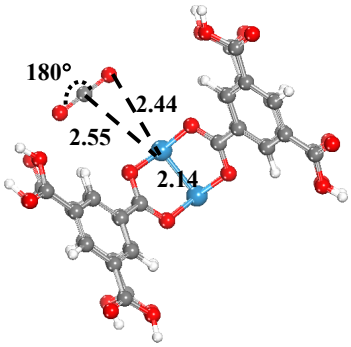


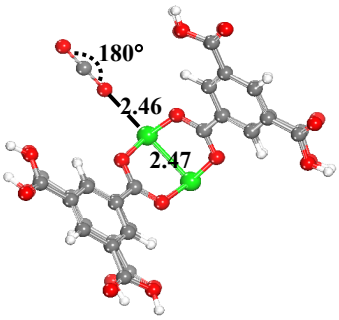
Figure S5. The physisorbed structures and binding energies/adsorption energies (E_{ads}) of CO_2 angularly and linearly binding on W-BTC (top layer) and Cu-BTC (bottom layer).



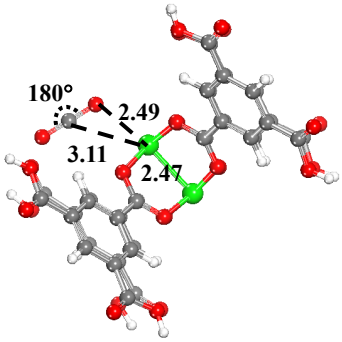
$\eta^1{}_1$(O) (E_{ads}= 0.07 eV)



$\eta^1{}_2$(O) (E_{ads}= 0.06 eV)



$\eta^1{}_1$(O) (E_{ads} = 0.10 eV)



$\eta^1{}_2$(O) (E_{ads} = 0.13 eV)

Table S1. Comparison of the adsorption energy (E_{ads}) and geometries of CO_2 adsorbed on W-Cu-BTC, Cu-BTC and W-BTC.

	W-Cu-BTC		**Cu-BTC**		**W-BTC**	
	E_{ads}	∠COC	E_{ads}	∠COC	E_{ads}	∠COC
$\eta^1{}_1$(O)	0.22	180°	0.10	180°	0.07	180°
$\eta^1{}_2$(O)	0.24	178°	0.13	180°	0.06	180°
η^1(C)	0.25	144°	-	-	-	-
η^2(CO)	1.34	136°	-	-	-	-
η^2(OO)	-0.40	108°	-	-	-	-

Figure S6. The desorption process of formic acid (HCOOH) from W-Cu-BTC after hydrogenation by two H atoms on the activated CO_2 in η^2(CO) complex.

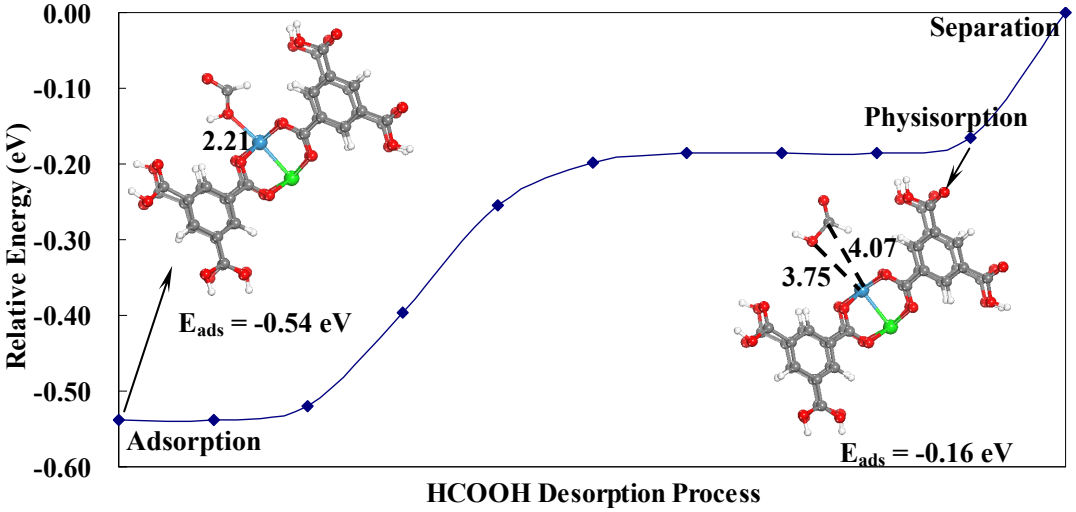


Figure S7. The desorption process of methylene glycol ($H_2C(OH)_2$) from W-Cu-BTC after hydrogenation by four H atoms on the activated CO_2 in η^2(CO) complex.