Structures and Mechanisms of CO_2 cycloaddition with styrene oxide on bimetallic M-Cu-BTC MOFs (M= Mg, Ca, Al, and Ga): A DFT study

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Supporting Information

Table S1. Gibbs free energies (kcal mol^{-1}) for the CO_2 cycloaddition with styrene oxide on the Al site of Al-Cu-BTC paddlewheel using different basis sets for non-metal atoms to calculate the electronic energy of complexes.

Steps	M06-L/BS1	M06-L/BS2	M06-L/BS3	M06-L/BS4	M06-L/BS5
SO_ads	–29.2	–29.0	–28.2	–28.2	–27.9
TS	–0.2 ($\Delta G^{\ddagger}_{298}$= 29.0)	0.9 ($\Delta G^{\ddagger}_{298}$= 29.9)	2.0 ($\Delta G^{\ddagger}_{298}$= 30.2)	2.0 ($\Delta G^{\ddagger}_{298}$= 30.2)	3.5 ($\Delta G^{\ddagger}_{298}$= 31.4)
SC_ads	–15.2	–13.0	–11.2	–11.6	–10.3

BS1 = 6-31G(d,p) + SDD
BS2 = 6-311G(d,p) + SDD
BS3 = 6-311++G(d,p) + SDD
BS4 = 6-311G(2d,2p) + SDD
BS5 = 6-311G(2df,2p) + SDD

Table S2. Gibbs free energies (kcal mol^{-1}) for the CO_2 cycloaddition with styrene oxide on the Al site of Al-Cu-BTC paddlewheel using different DFT functionals with the 6-311G(d,p) + SDD mixed basis set for calculating electronic energy of complexes.

Steps	M06-L[a]	M06-L-D3[a]	M06[a]	B3LYP[a]	B3PW91[a]
SO_ads	–29.0	–31.3	–27.4	–21.1	–17.6
TS	0.9 ($\Delta G^{\ddagger}_{298}$= 29.9)	–2.2 ($\Delta G^{\ddagger}_{298}$= 29.1)	2.9 ($\Delta G^{\ddagger}_{298}$= 30.3)	10.0 ($\Delta G^{\ddagger}_{298}$= 31.1)	15.1 ($\Delta G^{\ddagger}_{298}$= 32.7)
SC_ads	–13.0	–15.7	–16.6	–9.1	–7.4

[a]The free energy corrections were taken from calculations using M06-L/6-31G(d,p) + SDD mixed basis set.

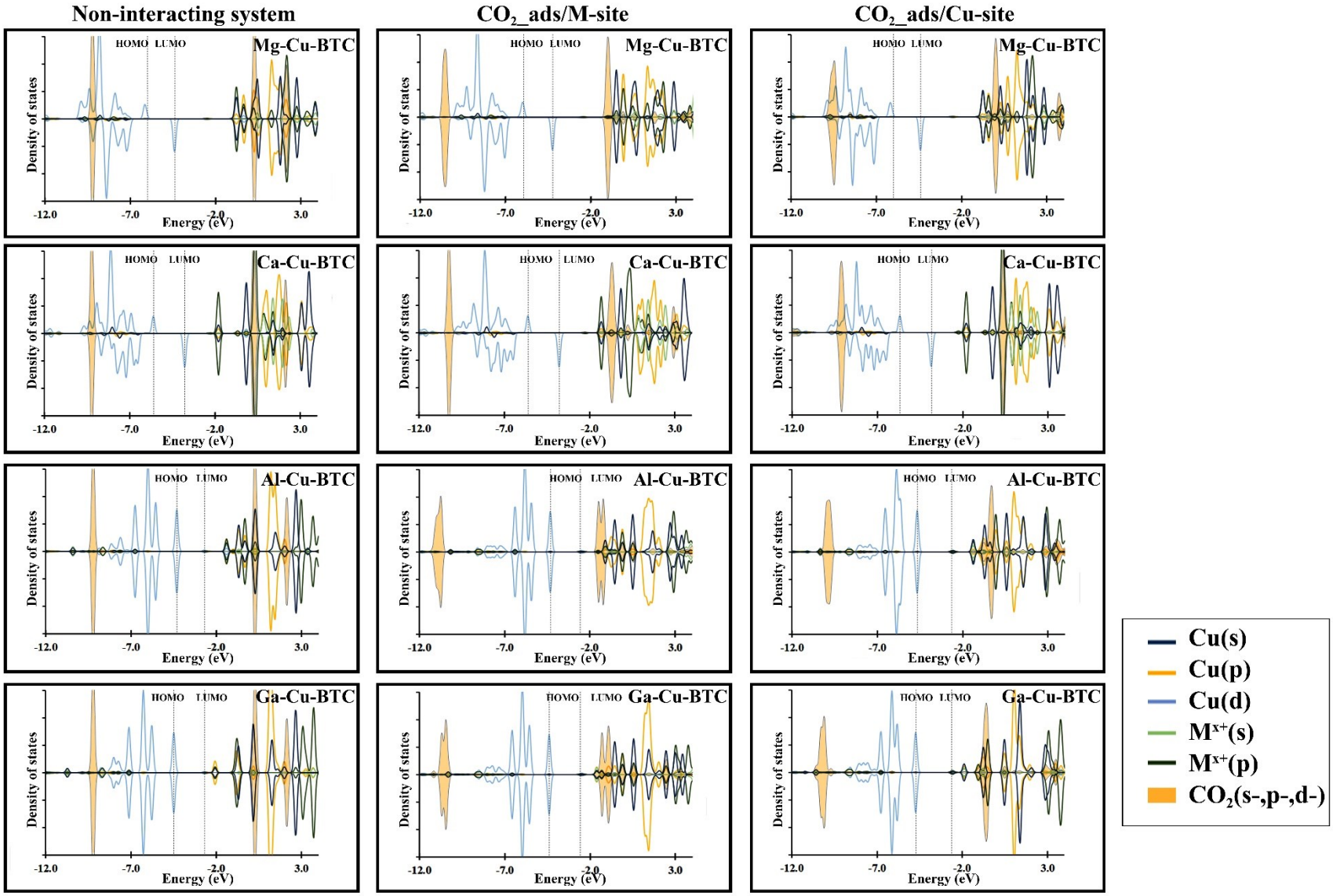

Fig. S1. Plots of density of states projected on atomic orbitals of Cu and substituted metal atoms of bimetallic paddlewheel nodes and the CO_2 molecule in the CO_2 adsorption complexes and the non-interacting systems are compared.

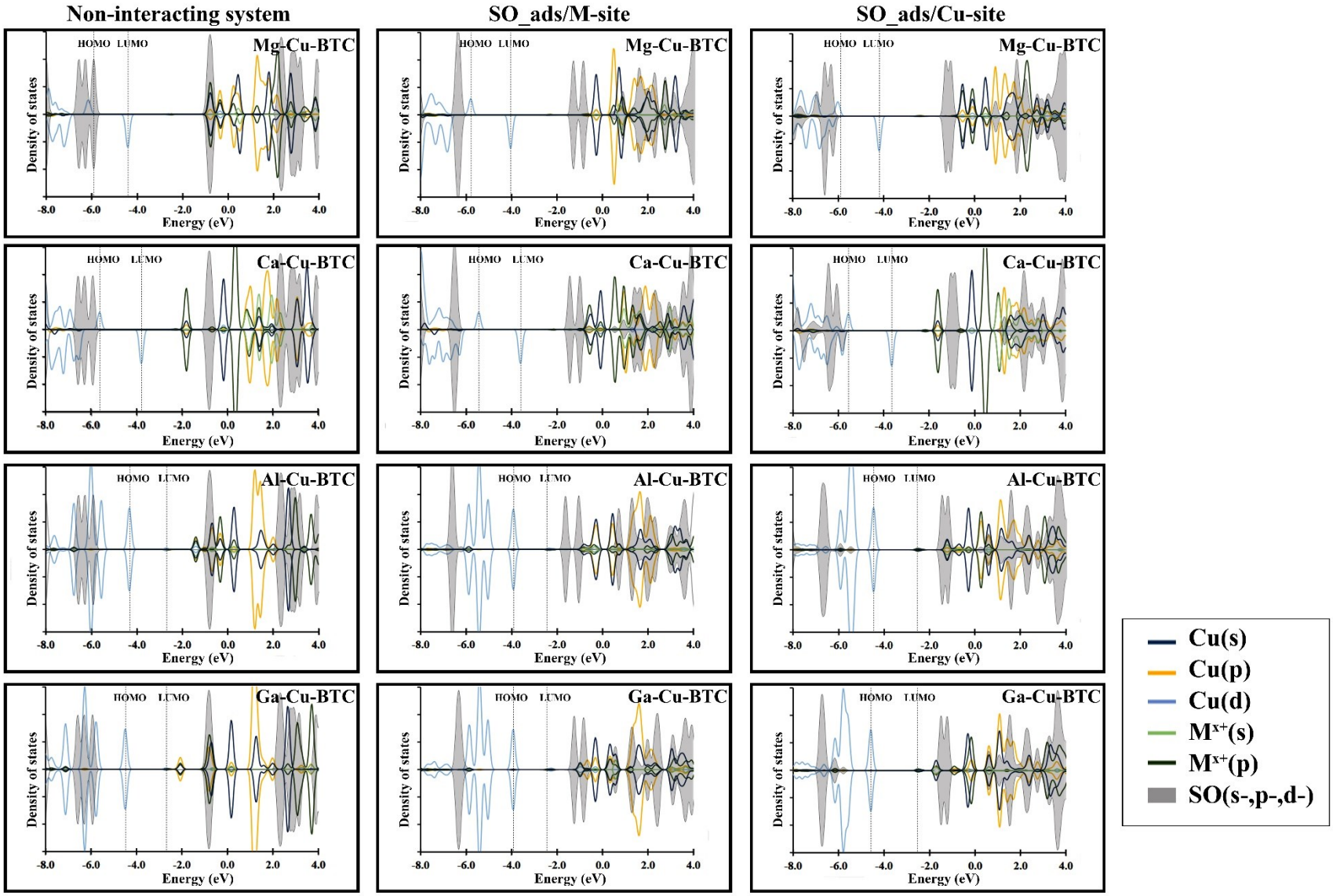

Fig. S2. Plots of density of states projected on atomic orbitals of Cu, substituted metal atoms of bimetallic paddlewheel nodes and the styrene oxide (SO) molecule in the SO adsorption complexes and the non-interacting systems are compared.