Supporting Information

Mechanistic insights into CO_2 cycloaddition of styrene oxide on paddle-wheel metal clusters: a theoretical study

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Table S1. Distortion-interaction free energy analysis of the transition state of the CO_2 cycloaddition with styrene oxide via the α-pathway. The values are in kcal mol^{-1}.

Systems	ΔG_{dist}(SO/M-BTC)[a]	$\Delta G_{dist}(CO_2)$[b]	ΔG_{int}[c]	$\Delta G^{\neq}$
Fe-BTC	14.7	27.1	-11.5	30.3
Co-BTC	30.2	11.7	-7.4	34.5
Ni-BTC	31.1	10.1	-6.1	35.1
Cu-BTC	33.7	10.1	-5.3	38.5
Zn-BTC	28.1	11.2	-6.9	32.4

[a]ΔG_{dist}(SO/**M**-BTC) = $G^{TS1}_{SO/M-BTC} - G_{SO\_ads}$

[b]$\Delta G_{dist}(CO_2)$ = $G^{TS1}_{CO_2} - G^{isolated}_{CO_2}$

[c]ΔG_{int} = $G^{TS1}_{CO_2/SO/M-BTC} - (G^{TS1}_{SO/M-BTC} + G^{TS1}_{CO_2})$

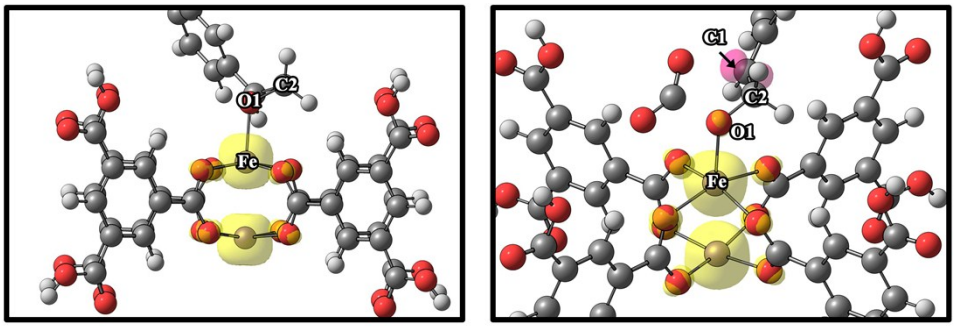

Fig. S1 Spin density distribution of SO adsorption and TS1(α) complexes on the Fe-BTC catalyst. Areas, where spin polarization is larger than 0.01 *e* a.u.$^{-3}$, are shown in yellow and pink for alpha and beta spins, respectively.

ONOM-based calculations for Cu-BTC

To account the confinement effects from the framework of Cu-BTC, the Cu-BTC is modeled by the ONIOM2 model (*cf.* Fig. S2). In the ONIOM2 model, the system is divided into two parts: inner and outer regions. For the ONIOM2 model of Cu-BTC, a paddle-wheel unit of the Cu-BTC was assigned to be the inner layer, whereas the other atoms were assigned as the outer layer of ONIOM2 model. The active center (inner layer) was treated accurately with the M06-L functional, while the rest of the model (outer layer) was approximated by using the UFF force field. This combination was previously used to study the catalytic performance of Cu-MOF-505 for the Mukaiyama aldol reaction[1]. During optimization, only atoms in the inner layer were allowed to relax. Geometry optimizations were carried out by using the (M06-L/6-31G(d,p)+SDD:UFF) scheme. The former and latter basis sets were used for all non-metal atoms and transition metal atoms, respectively. To obtain more reliable energies, single point calculations were carried out at the ONIOM2 (M06-L/6-311G(d,p)+SDD:UFF) level of theory. The electronic energies from single-point calculations were combined with the thermodynamic corrections at ONIOM2(M06-L/the 6-31G(d,p)+SDD:UFF) as similar as done in the cluster-model based calculations to obtain the Gibbs free energies. All calculations were carried out by using the Gaussian 09 program.

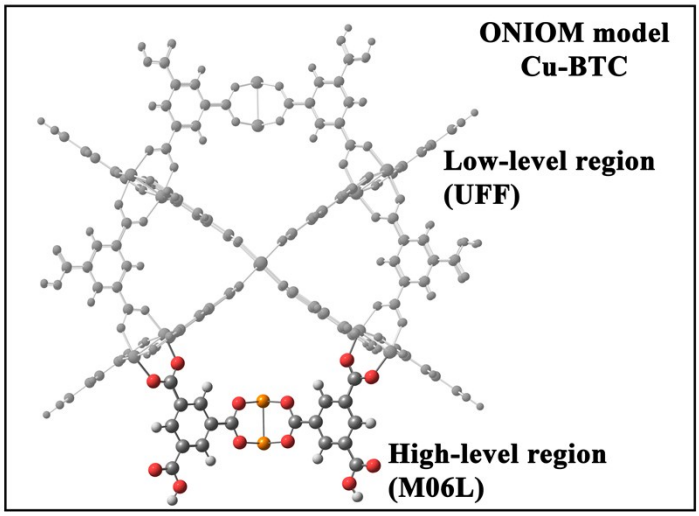

Fig. S2 ONIOM model of Cu-BTC catalyst. The atoms belonging to the high-level and low-level regions are displayed in different modes.

Table S2. Free energy profiles for the CO_2 cycloaddition with styrene oxide on the Cu-BTC quantum cluster model (QM) and on the Cu-BTC ONIOM model (ONOM).

Steps	Free energies (kcal/mol)	
	QM model	ONIOM Model
SO_ads	-3.9	-9.8
α-pathway		
TS1(α)	34.6 **(E_a = 38.5)**	29.2 **(E_a = 39.0)**
SC_ads	4.0	0.2
β-pathway		
TS1(β)	50.3 **(E_a = 54.2)**	42.2 **(E_a = 52.0)**
SC_ads	5.2	0.8

1. S. Yadnum, S. Choomwattana, P. Khongpracha, J. Sirijaraensre and J. Limtrakul, *ChemPhysChem*, 2013, **14**, 923-928.