

Electronic Supplementary Information

A computational study of the catalytic aerobic epoxidation of propylene over the coordinatively unsaturated metal–organic framework Fe₃(btc)₂: formation of propylene oxide and competing reactions

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Table S1 Relative energies, ΔE, ΔE+ZPE and ΔG values for the first cycle of propylene epoxidation on the Fe₃(btc)₂.

Reaction Coordinates	ΔE (kcal/mol)		ΔE+ZPE (kcal/mol)		ΔG (kcal/mol)	
	Spin9	Spin11	Spin9	Spin11	Spin9	Spin11
O2_Ads	-20.1	-25.2	-13.5	-24.6	-1.7	-13.3
co_Ads	-22.4	-29.4	-21.5	-28.6	1.6	-5.8
TS1_a	-11.1	-12.8	-10.6	-12.2	13.6	12.0
Int1_a	-18.3	-18.6	-17.2	-17.7	7.1	7.3
TS2_a1	5.9	2.9	5.8	1.6	30.2	25.8
TS2_a2	-8.9	-10.4	-8.5	-10.0	15.6	14.3
Prod_a1	-78.8	-72.7	-76.1	-71.0	-52.6	-47.3
Prod_a2	-42.3	-40.8	-39.5	-38.3	-15.8	-14.2
TS1_b	-10.1	-12.1	-9.7	-11.4	14.6	14.6
Int1_b	-19.8	-20.0	-18.3	-18.8	5.3	10.6
TS2_b1	-1.5	-6.6	-0.8	-6.8	24.0	17.9
TS2_b2	-4.3	-12.8	-3.4	-12.1	21.5	14.5
Prod_b1	-69.3	-58.7	-66.8	-57.1	-43.5	-33.7

Table S2 Relative energies, ΔE , $\Delta E+ZPE$ and ΔG values for the second cycle of propylene epoxidation on the $\text{Fe}_3(\text{btc})_2$.

Reaction	ΔE (kcal/mol)		$\Delta E+ZPE$ (kcal/mol)		ΔG (kcal/mol)	
Coordinates	Spin9	Spin11	Spin9	Spin11	Spin9	Spin11
Ads_C3	-48.3	-34.7	-44.5	-32.0	-21.5	-9.2
TS3_a	-46.5	-43.3	-43.6	-40.3	-19.9	-16.9
Int2_a	-66.5	-61.8	-62.7	-58.7	-38.6	-34.3
TS4_a1	-54.1	-28.2	-51.7	-28.9	-27.4	-5.1
TS4_a2	-63.0	-43.3	-58.6	-23.6	-34.7	1.1
Prod2_a1	-112.7	-73.4	-106.8	-69.0	-83.3	-45.9
Prod2_a2	-85.5	-37.9	-78.3	-43.2	-54.2	-9.8
TS3_b	-46.8	-41.6	-43.4	-39.5	-20.3	-16.0
Int2_b	-68.6	-67.4	-64.1	-64.1	-40.9	-40.9
TS4_b1	-55.8	-25.1	-55.1	-25.3	-28.6	-1.3
TS4_b2	-64.1	-27.4	-59.5	-25.3	-35.9	-1.7
Prod2_b1	-103.2	-66.5	-96.9	-62.8	-72.8	-38.5

Table S3 Relative energies, ΔE , $\Delta E+ZPE$ and ΔG values for the first cycle of the pi-allyl radical formation on $\text{Fe}_3(\text{btc})_2$.

Reaction	ΔE (kcal/mol)		$\Delta E+ZPE$ (kcal/mol)		ΔG (kcal/mol)	
Coordinates	Spin9	Spin11	Spin9	Spin11	Spin9	Spin11
O2_Ads	-20.1	-25.2	-13.5	-24.6	-1.7	-13.3
co_Ads	-22.4	-29.4	-21.5	-28.6	1.6	-5.8
TS_allyl_1	-5.4	-6.7	-8.0	-9.3	15.7	14.4
Pi_allyl_1	-14.4	-13.2	-14.4	-13.4	8.2	9.0

Table S4 Relative energies, ΔE , $\Delta E+ZPE$ and ΔG values for the second cycle of the pi-allyl radical formation on $\text{Fe}_3(\text{btc})_2$.

Reaction	ΔE (kcal/mol)		$\Delta E+ZPE$ (kcal/mol)		ΔG (kcal/mol)	
Coordinates	Spin9	Spin11	Spin9	Spin11	Spin9	Spin11
Ads_C3	-40.5	-31.1	-44.5	-32.0	-21.5	-9.2
TS_allyl_2	-40.9	-39.4	-39.7	-38.8	-16.6	-14.8
Pi_allyl_2	-63.2	-62.5	-61.5	-61.1	-38.8	-38.7

Table S5. Comparison of the activation barriers for the propylene oxide, carbonylic products and pi-allyl radical formation reactions on $\text{Fe}_3(\text{btc})_2$ MOFs with the ones given in previous studies on metals oxide surfaces.

Reactions	Activation barrier (kcal/mol)					
	$\text{Fe}_3(\text{btc})_2^{\text{a}}$	$\text{Ag}_2\text{O}(001)$	$\text{Ag}(111)$	$\text{Ag}(100)$	$\text{Ag}_3/\text{Al}_2\text{O}_3$	$\text{Cu}(111)$
C1-O formation	16.4 ^{a1} , 1.1 ^{a2}	8 ^b	13.8 ^d	14.1 ^c , 15.3 ^c	-	12.4 ^d
C2-O formation	17.2 ^{a1} , 0.8 ^{a2}	9 ^b	28.0 ^d , 12.4 ^c 6.9 ^c	11.5 ^c , 13.6 ^c	19.4 ^e	-
Propylene oxide formation	7.7 ^{a1} , 3.4 ^{a1} , 4.1 ^{a2} , 4.6 ^{a2}	17 ^b , 20 ^b	18.2 ^c	14.3 ^d , 14.8 ^c 11.5 ^c	18.4 ^e	22.1 ^d
Acetone formation	19.3 ^{a1} , 11.0 ^{a2}	39 ^b	22.7 ^c	16.7 ^c	-	-
Propanal formation	8.7 ^{a1} , 9.0 ^{a2}	42 ^b	12.9 ^d	22.9 ^c	-	25.4 ^d
pi-allyl radical formation	19.3 ^{a1} , 4.8 ^{a2}	9 ^b	7.8 ^c , 6.9 ^d	6.9 ^c	12.2 ^e	13.8 ^d

^aPresent work (a1 and a2 refer to the first and second cycle processes, respectively), ^bM. F. Fellah et al.⁶⁷, ^cA. Pulido et al.⁶⁸, ^dD. Torres et al.⁶⁹, ^eY. Lei et al.⁷⁰

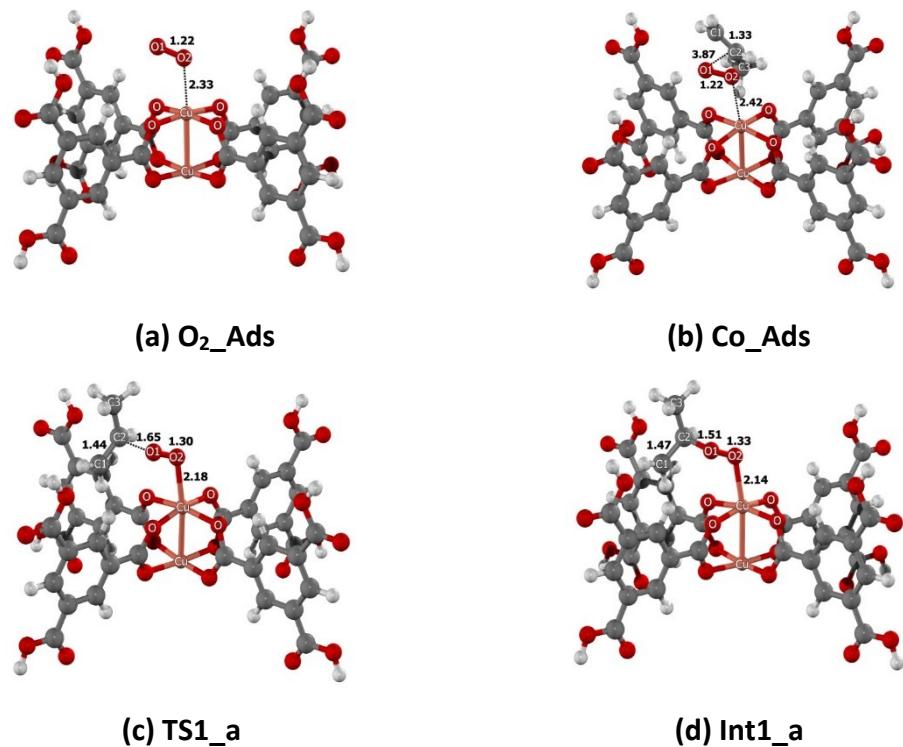


Fig. S1. Optimized structures of the species in the most stable spin state of the rate-determining step of the propylene to propylene oxide epoxidation on the $\text{Cu}_3(\text{btc})_2$ catalyst.

Table S6. Relative energies, ΔE , $\Delta E+ZPE$ and ΔG values for the propyleneoxy intermediate formation on $Cu_3(btc)_2$.

Reaction	ΔE (kcal/mol)		$\Delta E+ZPE$ (kcal/mol)		ΔG (kcal/mol)	
Coordinates	Spin9	Spin11	Spin9	Spin11	Spin9	Spin11
O2_Ads	-6.2	-5.4	-5.5	-5.0	-5.3	-4.2
co_Ads	-13.1	-12.8	-12.2	-11.0	-11.6	-10.1
TS1_a	14.9	12.9	12.2	13.8	12.3	13.9
Int1_a	11.0	12.8	13.0	14.3	13.1	14.6

Table S7. Comparison of the relative energies for the rate-determining step of the propylene epoxidation over $Fe_3(btc)_2$ (solid line) and $Cu_3(btc)_2$.

Reaction	$\Delta E+ZPE$ (kcal/mol)	
Coordinates	$Fe_3(btc)_2$	$Cu_3(btc)_2$
O2_Ads	-24.6	-5.5
co_Ads	-28.6	-12.2
TS1_a	-12.2 (Ea=16.4)	12.2 (Ea=24.4)
Int1_a	-17.7	13.0

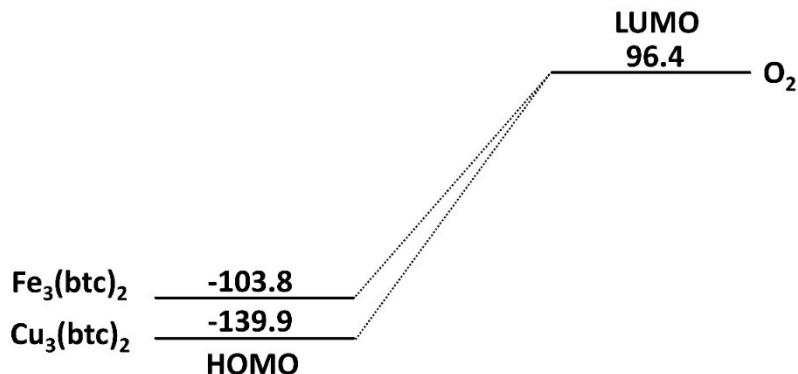


Fig. S2. Energy levels of the frontier molecular orbitals (FMOs) of MOFs and O_2 (energies in kcal/mol).