

Supplementary Information

Ethane C–H Bond Activation on the Fe(IV)-Oxo Species in a Zn-Based Cluster of Metal-Organic Framework: A Density Functional Theory Study

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Table S1 Relative energies ΔE , ΔE_{zero} and ΔH at 298.15 K and 1 atm for the decomposition of N_2O over $\text{Fe-Zn}_3\text{O}(\text{pyrazole})_6$ cluster as calculated at the B3LYP-D3/def2-TZVP level of theory.

Quintet spin state

Reaction coordinate	Relative energy (kcal mol ⁻¹)		
	ΔE	ΔE_{zero}	ΔH_{298}
Adsorption	-3.4	-2.1	-2.3
Transition state	17.8 ($E_{\text{a}}=21.2$)	17.6 ($E_{\text{a}}=19.7$)	17.6 ($E_{\text{a}}=19.9$)
Product	-33.4	-32.3	-31.9
Desorption	-31.4	-30.7	-30.9

Triplet spin state

Reaction coordinate	Relative energy (kcal mol ⁻¹)		
	ΔE	ΔE_{zero}	ΔH_{298}
Adsorption	19.3 ($E_{\text{ads}}=-3.5$)	21.0 ($E_{\text{ads}}=-2.1$)	21.2 ($E_{\text{ads}}=-1.8$)
Transition state	31.7 ($E_{\text{a}}=12.4$)	32.2 ($E_{\text{a}}=11.2$)	31.9 ($E_{\text{a}}=10.7$)
Product	-18.0	-16.6	-17.0
Desorption	-13.5	-12.6	-16.3

The quintet spin state is the most stable one throughout the reaction. E_{ads} and E_{a} refer to the adsorption energy and activation energy, respectively.

Table S2 Relative energies ΔE , ΔE_{zero} and ΔH at 298.15 K and 1 atm for the ethane C–H bond activation over FeO-Zn₃O(pyrazole)₆ cluster as calculated at B3LYP-D3/def2-TZVP level of theory.

Reaction coordinate	Relative energy (kcal mol ⁻¹)		
	ΔE	ΔE_{zero}	ΔH_{298}
ADS ⁵	0.0	0.0	0.0
TS _{σ} ⁵	E _a =22.5	E _a =17.4	E _a =17.7
TS _{π} ⁵	E _a =26.9	E _a =22.4	E _a =22.5
INT _{σ} ⁵	15.4	13.0	13.3
INT _{π} ⁵	17.3	14.7	15.2
ADS ³	17.7	18.1	18.5
TS _{π} ³	42.6 (E _a =24.9)	38.2 (E _a =20.1)	38.1 (E _a =19.6)
TS _{δ} ³	30.3 (E _a =12.6)	25.9 (E _a =7.8)	26.0 (E _a =7.5)
INT _{π} ³	29.0	26.9	27.6
INT _{δ} ³	17.6	15.0	15.5

Table S3 Electronic energies of $\text{Zn}_4\text{O}(\text{benzoate})_6$, $\text{Fe-Zn}_3\text{O}(\text{benzoate})_6$, $\text{FeO-Zn}_3\text{O}(\text{benzoate})_6$, $\text{Fe-Zn}_3\text{O}(\text{pyrazole})_6$ and $\text{FeO-Zn}_3\text{O}(\text{pyrazole})_6$ relative to the species with the lowest energy (B3LYP-D3/def2-TZVP calculations).

System	Spin multiplicity	*Relative energy (kcal mol⁻¹)
$\text{Zn}_4\text{O}(\text{benzoate})_6$	Singlet	0.0
	Triplet	79.4
	Quintet	158.9
	Septet	238.5
	Nonet	318.2
$\text{Fe-Zn}_3\text{O}(\text{benzoate})_6$	Singlet	47.1
	Triplet	26.3
	Quintet	0.0
	Septet	56.0
	Nonet	140.2
$\text{FeO-Zn}_3\text{O}(\text{benzoate})_6$	Singlet	22.9
	Triplet	4.7
	Quintet	0.0
	Septet	6.4
	Nonet	85.7
$\text{Fe-Zn}_3\text{O}(\text{pyrazole})_6$	Singlet	38.7
	Triplet	22.8
	Quintet	0.0
	Septet	94.8
	Nonet	184.8
$\text{FeO-Zn}_3\text{O}(\text{pyrazole})_6$	Singlet	44.8
	Triplet	18.0
	Quintet	0.0
	Septet	26.3
	Nonet	120.9

*Relative energy compared to the most stable spin state in each cluster system

Table S4 Optimized geometric parameters of $\text{Zn}_4\text{O}(\text{benzoate})_6$ in the singlet ground state compared with experimental data from X-ray diffraction and data from a previous calculation.

Parameter	Calculation		Experiment
	This work	Ref. ²⁶	Ref. ²³
Bond distance (Å)			
Zn–O _μ	1.98	1.98	1.93
Zn–O1	1.97	1.98	1.91
Zn–Zn	3.23	-	3.16
C1–O1	1.26	1.28	1.30
C1–C2	1.49	1.50	1.46
Bond angle (°)			
Zn–O1–C1	131.8	130.7	130.3
O1–C–O1	125.4	126.1	125.0
O1–C1–C2	117.3	117.0	117.5
C1–C2–C3	120.2	120.2	120.4
Dihedral angle (°)			
O _μ –Zn–O1–C1	0.6	0.0	0.0
O1–C1–C2–C3	178.2	180.0	180.0

Table S5 Energy barriers from ΔE for the C–H bond activation of ethane over the $\text{FeO-Zn}_3\text{O}(\text{pyrazole})_6$ cluster, as calculated at the DFT-D3/def2-TZVP//B3LYP-D3/def2-TZVP level of theory.

Pathway	Energy barrier (kcal mol ⁻¹)	
	PBE	M06
σ^5	24.8	19.2
π^5	27.1	32.8
π^3	25.2	30.0
δ^3	24.9	9.4

Table S6 Comparison of selected geometrical parameters in the optimized geometries of $\text{Zn}_4\text{O}(\text{benzoate})_6$ in the singlet ground state and of $\text{Fe-Zn}_3\text{O}(\text{benzoate})_6$ in the quintet ground state. B3LYP-D3/def2-TZVP calculations; M is Zn for $\text{Zn}_4\text{O}(\text{benzoate})_6$ and Fe for $\text{Fe-Zn}_3\text{O}(\text{benzoate})_6$.

Parameter	System	
	$\text{Zn}_4\text{O}(\text{benzoate})_6$	$\text{Fe-Zn}_3\text{O}(\text{benzoate})_6$
Bond distance (Å)		
M-O _μ	1.98	2.03
M-O1	1.97	2.00
M-Zn	3.23	3.25
C1-O1	1.26	1.26
C1-C2	1.49	1.49
Bond angle (°)		
M-O1-C1	131.8	132.2
O1-C1-O1	125.4	125.1
O1-C1-C2	117.3	117.7
C1-C2-C3	120.2	120.2
Dihedral angle (°)		
O _μ -M-O1-C1	0.6	2.2
O1-C1-C2-C3	178.2	179.8

Table S7 Geometrical parameters along the pathway of the N₂O decomposition over Fe-Zn₃O(pyrazole)₆ in the quintet ground state. Bond distances are given in Å and bond angles in degrees (°).

Parameter	N ₂ O/Fe-Zn ₃ O(pyrazole) ₆ system				
	Isolated state	Adsorption	Transition state	Product	Desorption
Fe-N	2.06	2.06	2.09	2.04	2.04
Fe-N'	2.07	2.07	2.07	2.04	2.04
Fe-N''	2.07	2.08	2.08	2.04	2.04
Fe-O _μ	2.00	2.01	2.00	1.97	1.97
O-N1	1.18	1.19	1.34	-	-
N1-N2	1.12	1.12	1.14	1.09	-
Fe-O	-	3.17	1.98	1.63	1.63
∠N-N-O	180.0	179.8	138.4	-	-

Table S8 Key geometrical parameters along the pathway of the ethane C–H bond activation over FeO-Zn₃O(pyrazole)₆. Bond distances are given in Å and bond angles in degrees (°). Superscripts 3 and 5 refer to the triplet and quintet spin states, respectively, and subscripts σ , π and δ indicate the respective pathways.

C₂H₆/FeO-Zn₃O(pyrazole)₆ system										
Parameter	Adsorption complex (ADS)		Transition state (TS)				Intermediate (INT)			
	ADS ³	ADS ⁵	TS _{π} ³	TS _{δ} ³	TS _{σ} ⁵	TS _{π} ⁵	INT _{π} ³	INT _{δ} ³	INT _{σ} ⁵	INT _{π} ⁵
Fe–O	1.61	1.63	1.75	1.80	1.78	1.76	1.82	1.82	1.82	1.82
O–H	2.48	2.57	1.18	1.24	1.22	1.24	0.97	0.97	0.97	0.97
C–H	1.09	1.09	1.35	1.30	1.29	1.37	2.73	2.46	2.39	2.68
Fe–N	1.92	2.04	1.96	2.03	2.05	2.03	1.95	2.02	2.02	2.02
Fe–N'	2.00	2.04	2.01	2.05	2.10	2.05	1.98	2.05	2.05	2.01
Fe–N''	2.00	2.04	1.97	2.05	2.10	2.05	2.01	2.05	2.05	2.05
Fe–O _{μ}	1.94	1.97	1.93	1.96	2.03	1.96	1.94	1.95	1.95	1.94
\angle Fe–O–H	139.4	161.5	116.9	109.4	139.5	112.4	110.5	107.8	107.2	107.0
\angle N'–Fe–N''	168.2	120.5	169.2	133.5	129.1	132.6	166.1	130.3	130.9	132.9

Table S9 $\langle S^2 \rangle$ values for the N₂O decomposition over Fe-Zn₃O(pyrazole)₆.

System	Triplet	Quintet
Isolated state	2.474	6.010
Adsorption	2.452	6.009
Transition state	2.504	6.639
Product	2.042	6.051
Desorption	2.023	6.051

The $\langle S^2 \rangle$ value for a pure triplet spin state is 2.0. From the Table S6, it can be seen that the $\langle S^2 \rangle$ values of isolated state, adsorption state and transition state are larger than 2.0 on triplet potential energy surface. An analysis of the natural orbitals and the occupation number shows that an artificial mixing with the quintet ground state occurs, as is indicated by the fractional occupations of d-orbitals of the Fe center. The stationary points on the triplet surface are stabilized by such ‘spin contamination’ and their energies are less reliable. Even though it is artificially stabilized, the energy surface of the triplet spin state is higher than the quintet energy surface throughout the reaction pathway as shown in Fig. S1. Theoretically, the quintet surface is the thermodynamically favorable pathway for the N₂O decomposition over Fe-Zn₃O(pyrazole)₆ cluster.

Table S10 $\langle S^2 \rangle$ values for the ethane C–H bond activation over FeO-Zn₃O(pyrazole)₆ cluster.

System	Triplet	Quintet
ADS	2.023	6.051
TS	2.313 (π^3)/ 3.063 (δ^3)	6.671 (σ^5)/ 6.045 (π^5)
INT	2.388 (π^3)/ 3.045 (δ^3)	6.044 (σ^5)/ 6.044 (π^5)

Fig. S1 Energy profile for the N_2O dissociation over $Fe-Zn_3O(pyrazole)_6$ in the triplet and quintet spin states. The inserted numbers are the relative energies ΔE in $kcal\ mol^{-1}$.

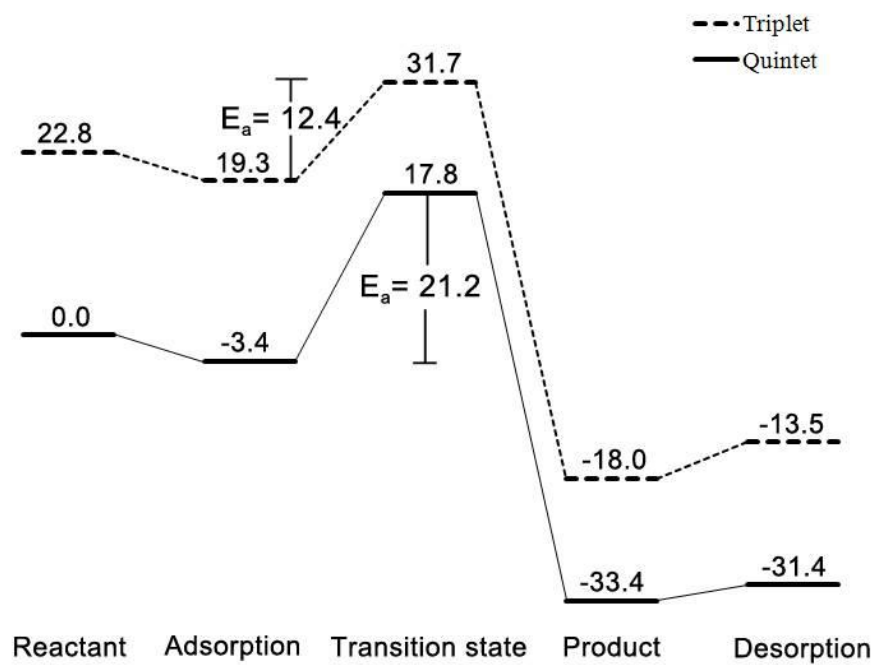


Fig. S2 Optimized geometries of the adsorption complex (ADS) and of the intermediate (INT) for ethane C–H bond activation over FeO-Zn₃O(pyrazole)₆ cluster. Superscript 3 and 5 refer to the triplet and quintet spin states, respectively. Subscript σ , π and δ represent the σ , π and δ mechanistic pathways, respectively.

