Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supplementary Information: Entropic influence on the generation of Fe(IV)O species at mononuclear Fe(II) sites in metal-organic frameworks

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S.1 Validation of CP2k calculations

We justify in Fig. S4 the choice of 500 Ry as the energy cutoff for running our CP2k simulations throughout this work. These energies are computed with the methane molecule placed far away from the Fe(IV)Ooxo active site. These preliminary results show that beyond 500 Ry, the total energy plateaus, making higher cutoff values provide little accuracy at an extra computational cost.

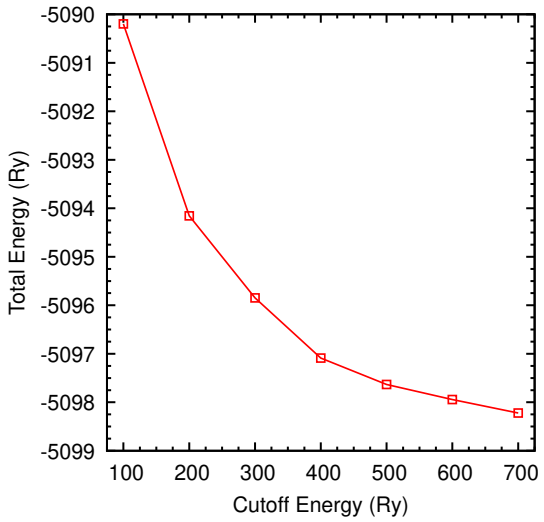

Figure S1: The evolution of system's the total energy vs. energy cutoff in CP2k with CP2k with the functional HSE06.

S.2 NO quartet reorientation during abstraction step

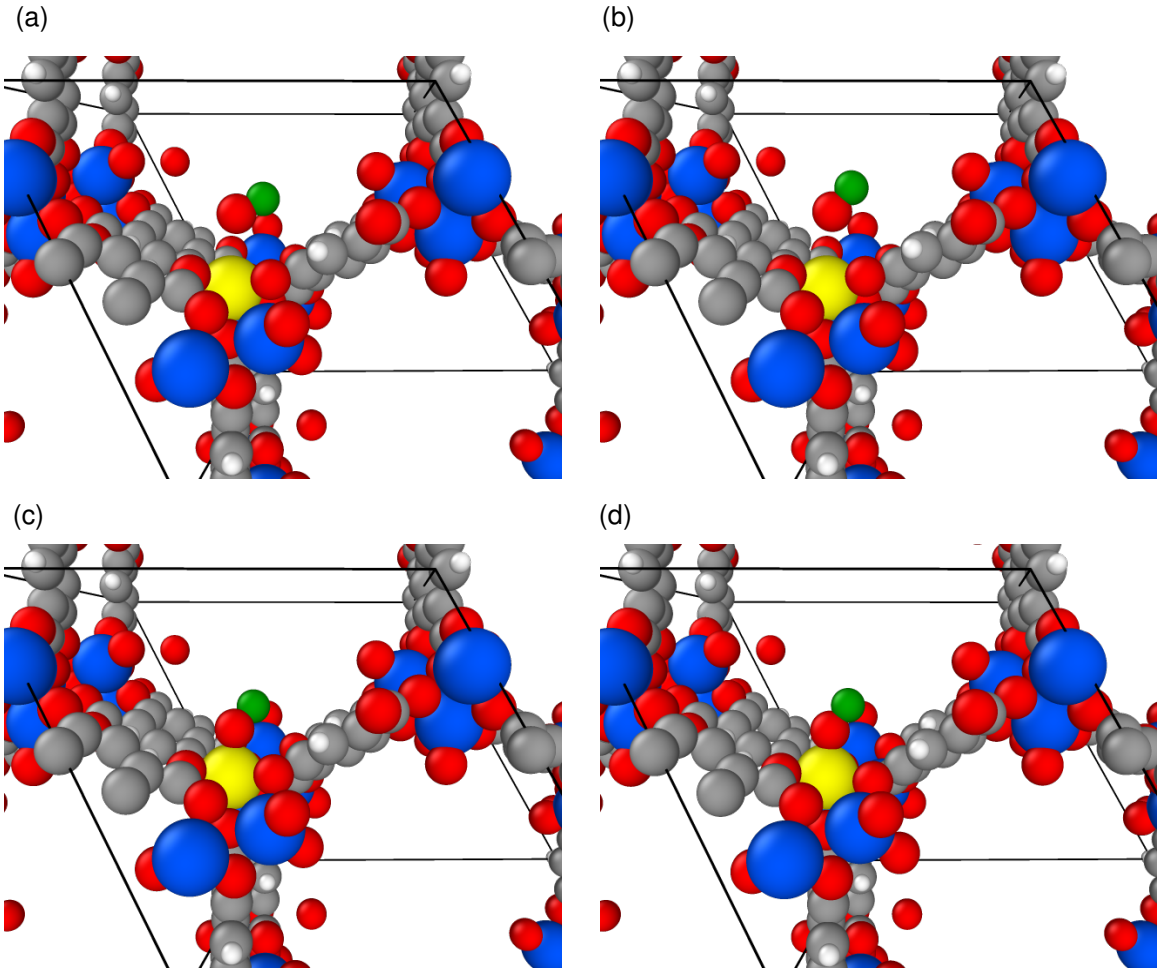

Figure S2: Snapshots of spatial orientation of the incoming quartet NO molecule during its abstraction at Fe(II)-Ooxo distances of Å 2.98 (a), 2.89 Å (b), 1.88 Å (c), and 1.80 Å (d). Fe atoms are blue (with the exception of the active Fe(II) atom, is yellow), N atoms green, O atoms red, C atoms grey, and H atoms in white.

S.3 Evolution of the N-O bond length during the nitric oxide abstraction

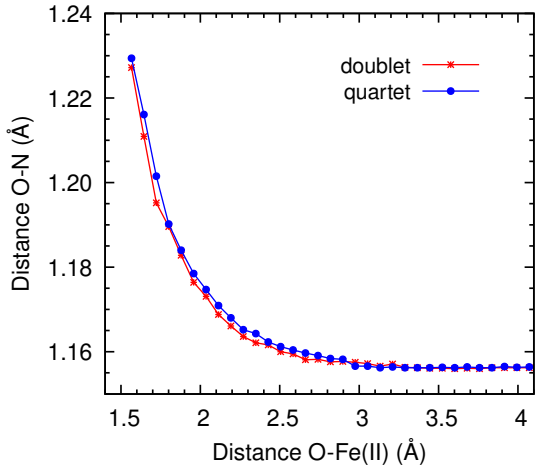

Figure S3: Evolution of the N-O bond length during the nitric oxide abstraction by the Fe(II) atom for the doublet and quartet spin configurations of the latter.

S.4 Charges and spin during NO_2 action by static approach

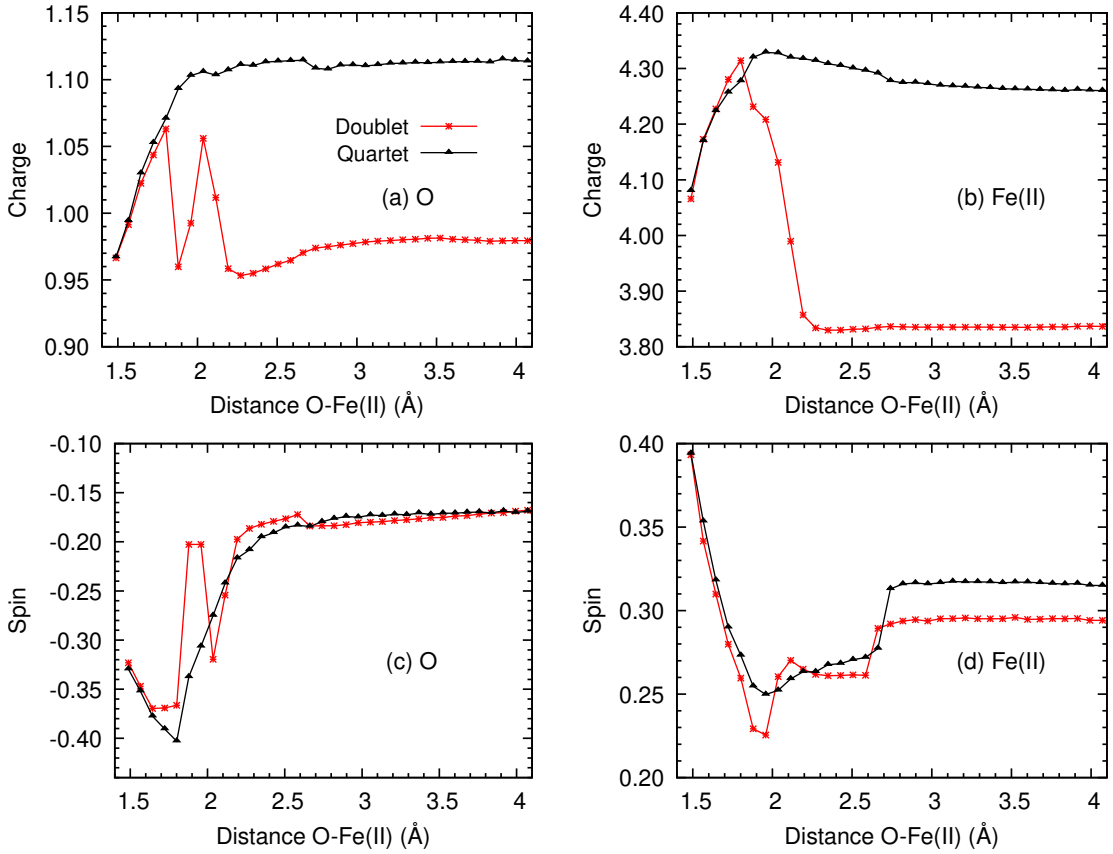

Figure S4: The evolution of charges (panel (a) for oxygen and panel (b) for iron Fe(II) center) and spins (panel (c) for oxygen and panel (d) for iron Fe(II) center) in the doublet and quartet spin states as a function of the separation between these two atoms.

S.5 Rebound step for NO: abstraction of NO and O_2 by complex Fe(III)Ooxo–N

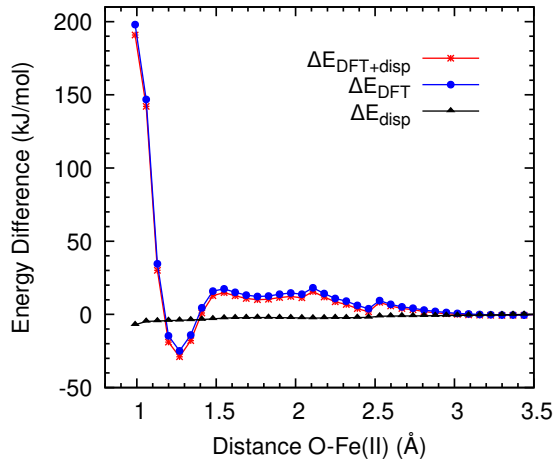

Figure S5: The difference of the total ($\Delta E_{DFT+disp}$), DFT (ΔE_{EDFT}), and long-range dispersion (Δ_{disp}) energies with respect to their values at 3.51 Å *vs.* the distance between two nitrogen atoms, one from the incoming NO molecule and the other already absorbed in the Fe(III)Ooxo–N complex..

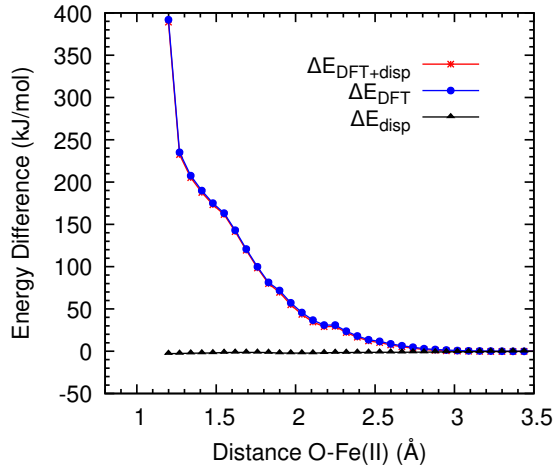

Figure S6: The difference of the total ($\Delta E_{DFT+disp}$), DFT (ΔE_{EDFT}), and long-range dispersion (Δ_{disp}) energies with respect to their values at 3.51 Å *vs.* the distance between the oxygen of the incoming NO molecule and the nitrogen in the Fe(III)Ooxo–N complex.

S.6 NO doublet reorientation during detachment step

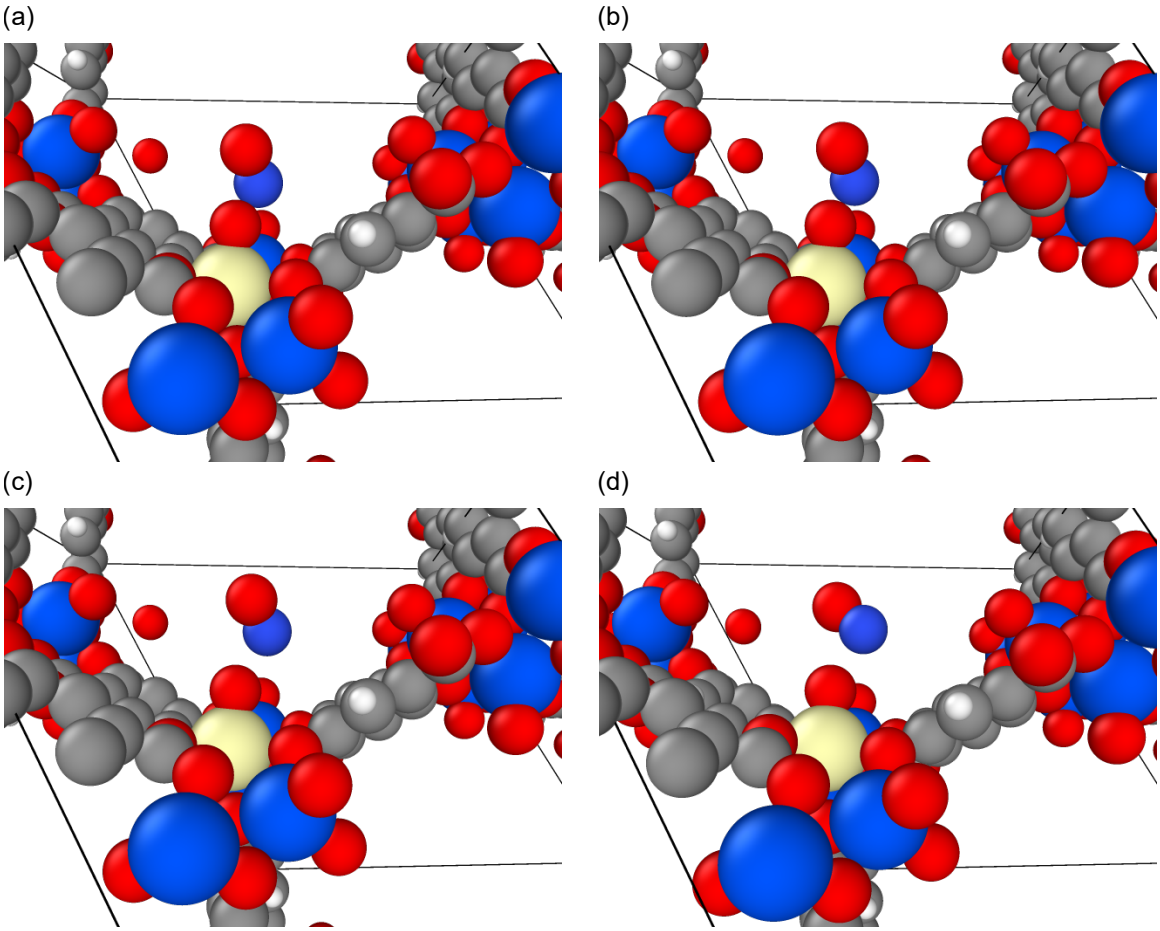

Figure S7: Snapshots of spatial orientation of the departing doublet NO molecule during its detachment at Fe(II)-Ooxo distances of Å 1.58 (a), 1.66 Å (b), 2.19 Å (c), and 2.26 Å (d).

S.7 XYZ coordinates of the initial Fe(IV)O(oxo)-MOF74 structure

We list next the XYZ coordinates of the initial Fe(II)-MOF74 structure for the abstraction step after the geometry is optimised with CP2k.

C -1.6776825 2.4363816 5.2872143
C 2.941902 -1.0587657 5.9381766
C 0.6698782 0.1921026 2.5444112
C 1.7730325 6.0939307 8.2138949
C -2.8706668 9.5272856 7.5927983
C -0.52514 8.3436766 10.8971664
C -0.7533373 3.3510883 6.0230918
C 3.8524912 -2.1751614 6.3239279
C 1.5863966 0.3851233 1.3945097
C 0.8536732 5.2018781 7.4468799
C 3.1532371 10.6298914 7.1898575
C 0.8794696 -6.8200832 12.0580368
C 0.6193787 3.0685761 6.2438178
C 5.2157688 -2.2302866 5.9479852
C 2.962503 0.7027402 1.5481581
C -0.5164998 5.4848485 7.2237697
C 4.1050391 -4.2783413 7.5663538
C -2.8063543 7.8158002 11.916709
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C -0.9630516 -3.3146057 6.3876243
C 3.7259581 0.8304798 0.3850099
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C 1.0600454 0.2120478 0.1119771
Fe 0.2883169 0.1057578 5.5794716
Fe 4.8468844 -0.3255392 3.7086003
Fe 2.5342257 1.7228304 4.326848
Fe -0.1104008 8.3699532 7.7394161
Fe 2.2208121 8.8090229 9.8217974
Fe -2.4198976 6.7929878 9.1624355
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H 2.295902 -3.171505 7.4104047
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Fe 9.1690569 8.8089323 9.8234377
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