

Supplementary Information:
Unveiling the catalytic potential of the Fe(IV)oxo species for the
oxidation of hydrocarbons in the solid state

Fernan Saiz and Leonardo Bernasconi

S.1 Validation of CP2k geometry relaxations in the H-abstraction reaction

We justify in Fig. S1 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.

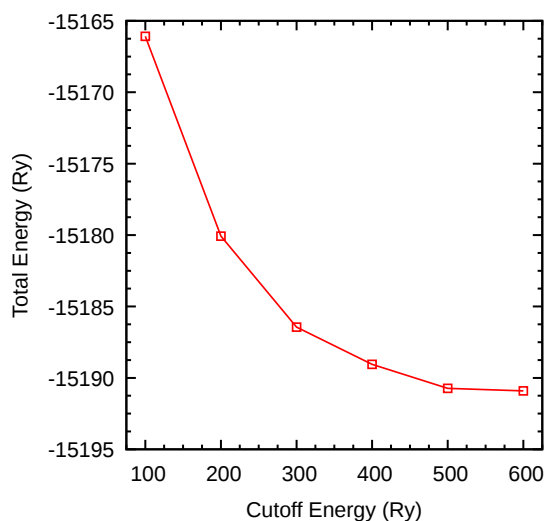


Figure S1: The evolution of system's the total energy vs. energy cutoff in CP2k with CP2k with the functional HSE06.

S.2 Detachment of methanol: role of the temperature

In order to explore the stability of the complex formed by the product CH_3OH molecule and the MOF-Fe site, we run a series of unconstrained AIMD simulations at different temperatures for 2250 AIMD steps (1.125 ps) and monitor the average Fe-O(oxo) distance (Figure S2) for the last 1000 AIMD steps. For consistency of notation we will continue to indicate as O(oxo) the O atom of the product CH_3OH . The Fe-O(oxo) bond exhibits a weak dependence on the temperature (ca. 0.04 \AA) up to about 700 K, whereas a more marked distance is observed at 800 K, which indicates that the release of the product molecule is likely to be more favourable at higher temperature. We also observe that, even at 800 K, the MOF's structure remains virtually unaffected.

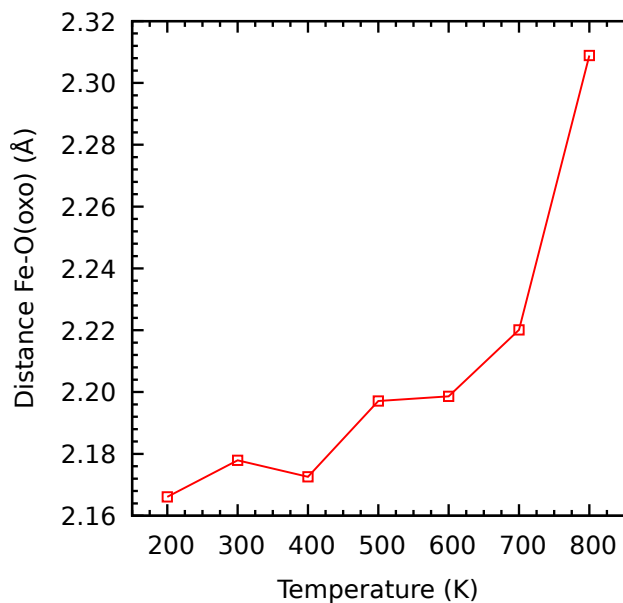


Figure S2: Fe-O(oxo) distance as a function of temperature after the formation of the product CH_3OH molecule.

S.3 Mobilities of the $\text{CH}_3\cdot$ radical and CH_4 molecule with AIMD

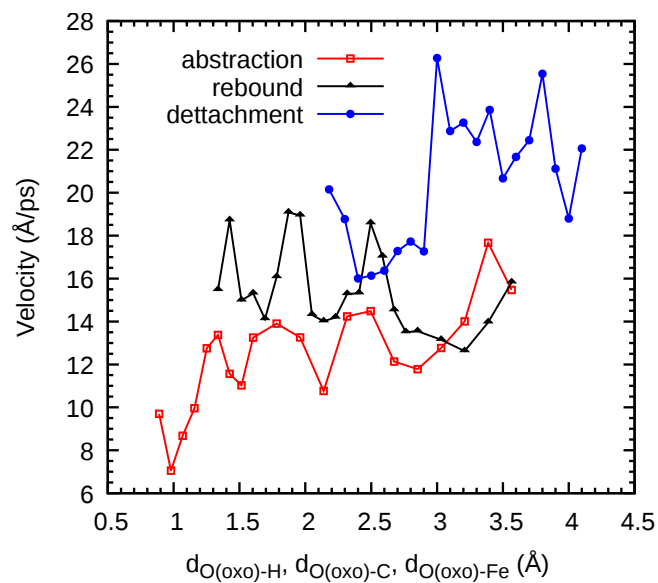


Figure S3: Average velocity of the methane's central carbon and the three unreacted hydrogens *vs.* the separations between the O(oxo) and the reactive hydrogen d_{C-H} for the abstraction, between the O(oxo) and radical's $\text{CH}_3\cdot$ carbon ($d_{\text{O(oxo)-C}}$) for the rebound, and between the methanol's O(oxo) and Fe(IV) for the detachment.

S.4 Mulliken analysis during the rebound step: $\text{CH}_3\cdot$ radical and Fe(IV)OoxoH intermediate

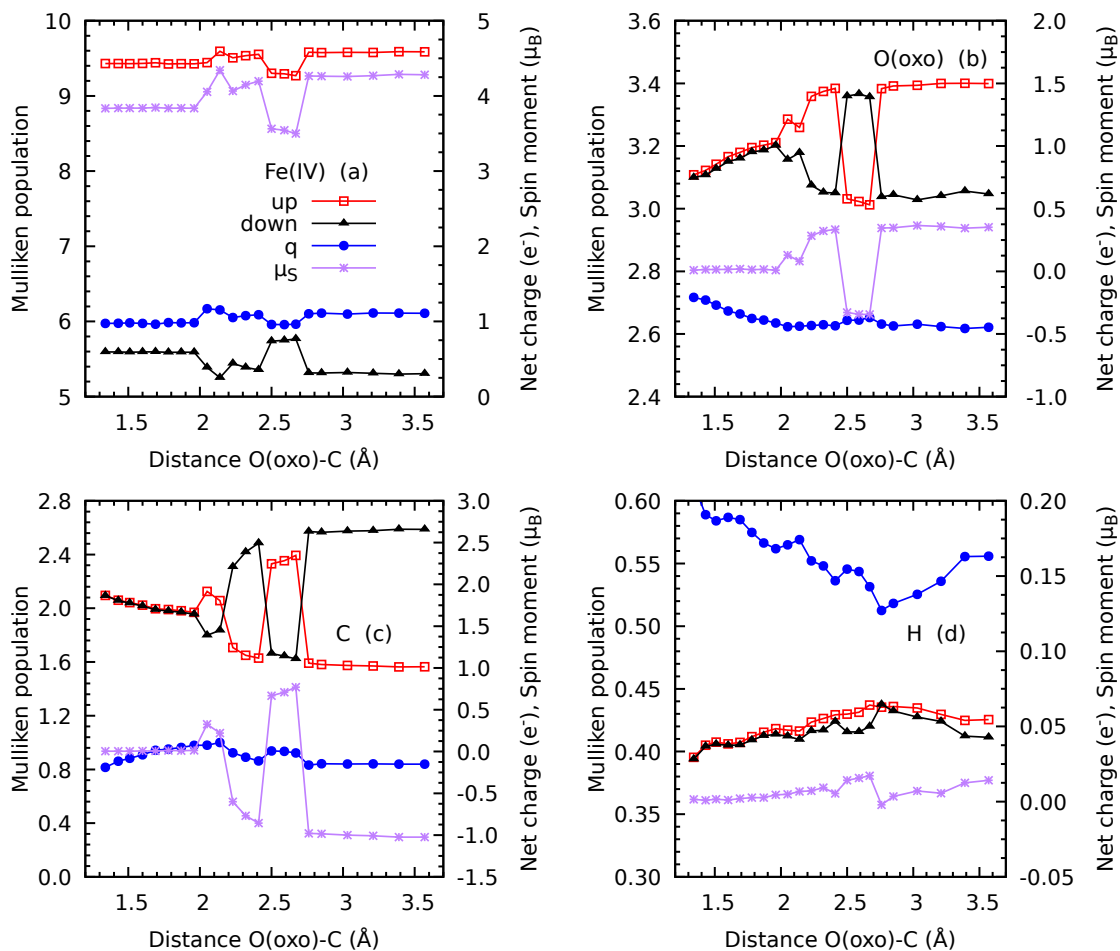


Figure S4: Evolution of the Mulliken's orbital populations with \uparrow (up) and \downarrow (down) spin polarisations, net charge (q in elemental charge e^-), and spin moment (μ_S in Bohr magnetons μ_B) of the atoms Fe(IV) (a), O(oxo) (b), the carbon C in the CH_3 radical (c), and the absorbed hydrogen H by O(oxo) (d) with respect to the distance $d_{\text{O(oxo)-C}}$ during the rebound step.

S.5 XYZ coordinates of the initial Fe(IV)O(oxo)-MOF74 structure

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

Fe 5.4769406126 7.8562497298 0.9706534095
O 4.4678907604 6.6504811742 2.3676937512
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