Structural single Fe(II) sites in MIL-type metal-organic frameworks for oxidation of methane to methanol and ethane to ethanol

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ABSTRACT: Single non-heme Fe(II) ions present as structural metals in several metal organic frameworks (e.g. MIL-100, MIL-101, MIL-808) are identified by Kohn-Sham density functional calculations as promising catalysts for C-H bond activation, with energetic barriers as low as 40 kJ mol\(^{-1}\) for ethane and 60 kJ mol\(^{-1}\) for methane following oxidative activation of iron. Through consideration of the full reaction profile leading to the corresponding alcohols ethanol and methanol, we have identified key changes in the chemical composition of the node that would modulate catalytic activity. The thermal and chemical stability of these MOFs together with the scalability of their syntheses make them attractive catalysts for the selective low temperature conversion of light alkanes to higher-value oxygenates.

KEYWORDS. MOFs, C-H bond activation, catalysis, non-heme iron, density functional theory, multireference methods, MIL-100.

Supporting Information Placeholder

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1. INTRODUCTION

Conversion of gaseous light hydrocarbons like methane and ethane to liquid fuels is a pivotal missing piece for the full economic exploitation of biogas and natural gas.\(^1\) Such conversion would also have important environmental repercussions, as it would reduce gas flaring in oil fields (estimated to exceed 140 billion cubic meters per year),\(^2\) which occurs because transportation of natural gas, in absence of a dedicated pipeline, is not economically viable. Efficient catalysts able to convert methane and ethane (the two major components of natural gas) into liquid, or solid, chemical feedstocks would thus constitute a turning point in the worldwide energetic supply. Given the importance of this goal, many efforts to catalyze such reactions have been undertaken, but no catalyst to date has advanced to the level of having clear potential in an industrial-scale process.\(^2\)

C-H bonds in alkanes are apolar and both heterolytic and homolytic scissions are thus unfeasible. For methane and ethane, the enthalpies associated to the homolytic scission of C-H bond are very high: 439 and 423 kJ mol\(^{-1}\), respectively at room temperature.\(^3\) Their cleavage thus requires highly active oxidation catalysts and in many instances high temperatures and pressures are employed to improve yields. A particular challenge, however, is that the C-H bonds of initially oxidized species, e.g. alcohols are more reactive than those in the starting light alkanes, making it difficult to suppress overoxidation.\(^4\) In the metalloenzyme arena, methane monooxygenases are able to selectively convert methane to methanol at room temperature and atmospheric pressure exploiting one or more copper or two iron atoms in their active sites,\(^5\)\(^6\) but progress has been slow in translating the selectivity of the enzymes into simpler synthetic systems.\(^7\)

From the synthetic point of view, high surface area supports have been extensively studied as matrices for the introduction of biomimetically inspired active sites.\(^8\) Among these species, iron based zeolites are particularly intriguing for being able to catalyze the hydroxylation of methane at room temperature,\(^5\)\(^9\) with activity attributable to single Fe(II) sites (\(\alpha\)-Fe(II) sites) characterized by high-spin ground state, constrained coordination geometries and a minimal number of ligands around Fe.\(^5\)\(^10\)\(^11\) These three characteristics have been determined to be key for activity. However in zeolites, the active ions are hosted as extra-framework species. Thus, although the hosting material is crystalline, the Fe ions are disordered and multiple species are present in the solid.\(^9\) The relative amounts of those species and their nature can be strongly dependent on the synthetic procedure.\(^9\)\(^12\)\(^13\) Besides decreasing the selectivity of the reaction, such disorder makes the isolation and characterization of the reacting species particularly difficult, with inactive spectator ions often the majority of deposited Fe. Indeed, the structure of the \(\alpha\)-Fe(II) species was only recently elucidated after many years of effort.\(^11\)

Metal organic frameworks (MOFs) comprise a relatively new class of materials that has begun to demonstrate its utility for various applications.\(^14\) One of their hallmarks is an intrinsic flexibility in design owing to their construction as sets of inorganic nodes interconnected by organic linkers. Thus, modulation of their chemical and physical properties can be achieved by changing their building units. Moreover, most MOFs are crystalline solids, which is a characteristic of primary importance for materials design and MOFs have been exploited as catalysts for many different reactions.\(^15\) In analogy to the zeolites discussed above, extra-framework iron species in MOFs have been demonstrated to be active for C-H bond cleavage\(^16\)\(^17\) although this extra-framework character poses the same challenges to characterization and optimization that have already been discussed.\(^17\) In other instances, iron species at structural
positions of inorganic MOFs building units have catalysis with good selectivity and cyclability under mild conditions, e.g. ethanol to ethane for Fe$_x$Mg$_{1-x}$($\mu$-O)($\mu$-O)($\mu$-O)$_n$(dobic)$_2$ (also called MOF-74-Fe)\(^{19-20}\) and methanol to methanol for MIL-53-(Al,Fe).\(^{21}\) The iron species in these MOFs have different oxidation states, Fe(II) for MOF-74 and Fe(III) in MIL-53, and consequently their mechanisms may be expected to differ but these catalysts nevertheless share common features: in both cases, the active sites are single, non-heme iron species in an octahedral environment, obtained through high dilution of the iron atoms into the otherwise inert framework established with a different structural metal. While promising, these materials offer room for improvement. Fe$_x$Mg$_{1-x}$($\mu$-O)($\mu$-O)$_n$(dobic)$_2$ is not particularly stable in air.\(^{22-23}\) While MIL-53-(Al,Fe) does not suffer from similar instability,\(^{23}\) it has been synthesized only in low yield using an electrochemical approach.\(^{24}\) Finally, the inorganic components of both MOF-74 and MIL-53 consist of one dimensional chains of coordinated metal sites.\(^{19,21}\) So, in order to better isolate the iron atoms, in both cases the loading in the active Fe has to be kept very low (<5 mol%). This requirement, in addition to complicating the synthesis, decreases the yield of oxygenates per mass of catalyst and has the potential to lead also to heterogeneity in active sites.

Triiron oxo-centered clusters Fe$_x$(III)($\mu$-O)(X)(COOH)$_n$ (with X = OH, F, Cl; see central part of Figure 1) are recurrent in the structure of many MOFs, including MIL-100 and MIL-101, two MOFs characterized by exceptional chemical and thermal stability\(^{25}\) and for which simple, sustainable and high-scalable synthetic protocols have been reported.\(^{26}\) Interestingly, upon thermal activation, one of the three iron atoms in each node can be reduced to Fe(II) with the simultaneous elimination of the –X group and opening of one coordination site. These MOFs have been reported to catalyze several reactions involving C–H bond activation, e.g. benzene to phenol.\(^{26}\) Their activity for the oxidation of light hydrocarbons, however, has not yet been reported, nor have computational predictions been made. The square pyramidal geometry of the active Fe(II) site in the MIL series is very similar to that found in MOF-74. Moreover, the zero-dimensionality of the MIL nodes makes MIL active sites intrinsically monodisperse: no small alkane can coordinate to more than a single iron center. This offers potential advantages with respect to the density of active sites—in principle, one Fe(II) per node i.e. 33 mol%—that the triiron oxo-centered MOFs can present (versus < 5 mol% for MOF-74 and MIL-53). In addition, the incorporation of heteroatoms in the node itself may offer the opportunity to tune Fe site reactivity, in analogy to reports for bulk (doped) metal oxides.\(^{27-28}\) MIL-100 and MIL-101 have also been synthesized using metals other than Fe, in particular, Al and Cr. Mixed-metal forms of these MOFs have been also reported.

In this work, we have used Kohn-Sham density functional theory (DFT) and a MOF cluster model to predict the activity of the Fe(II) species in the Fe$_x$(III)Fe(II)($\mu$-O)(COOH)$_n$ node for the hydroxylation of ethane to ethanol and methane to methanol. Al- or Cr-doped clusters have also been considered in order to assess the effect of Fe dilution on activity, i.e. having general formula of M$_1$(III)M$_2$(II)Fe(II)($\mu$-O)(COOH)$_n$, where M$_1$ and M$_2$ = Al, Cr or Fe (M$_1$M$_2$Fe). We note that the Fe(III) atoms at the "other" positions on the node are similar to those reported to catalyze methane to methanol in MIL-53.\(^{23}\) However, catalysis of alkane hydroxylation by Fe(III) uses H$_2$O as an oxidant and involves different activation and reaction pathways\(^{24}\) than for Fe(II) and we will not investigate them here.

2. METHODS

Kohn-Sham Density Functional Calculations. All the density functional theory (DFT) calculations were performed using the Gaussian 09 program.\(^{29}\) The cluster used to model the triiron metal node is shown in Figure 1. Formate groups were adopted as capping groups. This model has been previously demonstrated to describe the adsorption of small molecules with similar accuracy to the one obtained using larger clusters.\(^{30}\) M06-L\(^{31}\) in its unrestricted formalism (U) was used in combination with the def2-TZVP basis sets.\(^{32-33}\) This level of theory has previously been shown to be accurate, when compared to multireference wave function theory, for the electronic structure of single iron centers in ethane and methane oxidation studies.\(^{30}\) Preliminary calculations performed at the M06-L level for the interaction of probe molecules with FeFeFe accurately reproduced the experimental vibrational shifts of NO and CO following adsorption on Fe(II) sites in MIL-100-Fe.\(^{34-35}\) suggesting that the M06-L model properly captures the combination of donation and back-donation occurring at the Fe(II) centers in these MOFs, which will figure critically in their catalytic activity.\(^{36}\)

For each intermediate of the catalytic cycle in Figure 1, the spin ladder was determined using a smaller basis set, with all-electron def2-SVP basis sets\(^{36}\) on C, H, and O. Geometry optimization was carried out by means of the Berny optimization algorithm with analytical gradient and default convergence thresholds. A (99,590) pruned grid was used (i.e. 99 radial points and 590 angular points per radial point). All the energetic data have been corrected for basis set superposition error (BSSE) following the a posteriori method proposed by Boys and Bernardi\(^{37}\) as implemented in Gaussian 09. The BSSE corrected energetic values are indicated by a c superscript and were obtained from the computed Y values as $Y^c = Y -$ BSSE.

Unscaled, harmonic vibrational frequencies were computed analytically. Enthalpies and Gibbs free energies were calculated at 1 atm and 298 K from conventional ideal gas, rigid rotor, particle in a box, quantum mechanical harmonic oscillator partition functions, except that low vibrational frequencies (<5 cm$^{-1}$) were replaced by a cut-off value (50 cm$^{-1}$) accounting for limitations in the harmonic oscillator approximation for very low frequency vibrations.\(^{38-42}\) Charge and spin densities were obtained using Charge Model 5 (CM5)\(^{43}\) and Hirshfeld population analysis,\(^{44}\) respectively.
other oxidants (e.g., O₃), although one may generate the ferryl species by many approaches. Three transition states are of special interest: TS₁ (ferryl formation), TS₂ (C-H bond scission) and TS₃ (alkyl radical rebound). All energetics, unless otherwise specified, are referenced to the total energy of the separated reactants (A, N₂O, alkane).

The reaction profiles for methane oxidation to methanol and ethane oxidation to ethanol are reported in Figure 2a and b, respectively. All relevant energy values are compiled in Tables S12–S21 and relevant electronic and geometrical parameters are compiled in Table S1–S11. For the particular case of the ALAIrFe cluster, structures of the optimized geometries along the reaction path are also presented in Figure 3.

Considering the possible spin states, all Fe and Cr centers were found to prefer high-spin configurations, as expected given the weak ligand field associated with the coordinating oxygen atoms. These energetic preferences were substantial: for example, in the A structure for ALAIrFe node, the triplet Fe is predicted to be less stable than the quintet Fe by 100 kJ mol⁻¹ at the M06-L level and by >180 kJ mol⁻¹ at both the CASCF and CASPT2 levels (see Table S26); a similar difference was reported for isolated Fe(II) in MOF-74.²⁰ The quintet state persists as the lowest spin state along the entire reaction coordinate (i.e., there is a single-state reactivity), for both methane and ethane conversion, again in analogy to Fe(II) in MOF-74.²⁰ This differs with other non-heme complexes in which a spin crossing between the triplet and the quintet surfaces can occur along the reaction coordinate.⁵¹-⁵²

Although the individual Cr and Fe atoms are in their highest spin state, the fully coupled high spin state (HS) is the ground state only for the trivial case of ALAIrFe (spin ground state: S = 2) and AlFeFe (S = 9/2). For FeFeFe, CrCrFe and CrFeFe, by contrast, the most stable spin state is one with antiferromagnetic coupling between the M₁ and M₂ centers. These correspond to intermediate spin states requiring a broken symmetry (BS) treatment within single-determinantal KS DFT, namely the septet for CrCrFe and the quintet for FeFeFe and CrFeFe. For the bare cluster, the BS states are more stable than the HS state in these three systems by more than 20 kJ mol⁻¹.

While a BS approach can provide accurate energetics, it provides an unphysical description of the spin density.⁵³-⁵⁴ Moreover, we observed in many instances that the convergence to a particular broken symmetry solution was highly dependent on the specific initial guess of the KS determinant, making quite difficult to follow the reaction profile reliably. In such instances, so long as the intermediate-spin state derives from relatively weak coupling of locally high-spin centers that are themselves primarily spectators to a particular process, it can be equally effective to compute the energetics of the reaction coordinate on the HS surface. CASPT2 calculations on A of FeFeFe, show that all the spin states lay within 22 kJ mol⁻¹ (see Table S25). This suggests that following the high spin surface is an appropriate choice. The CASPT2 results also show that the three iron centers have a different oxidation state, namely there are two Fe(III) and one Fe(II) (see Table S26). This is in agreement with Mossbauer measurements showing the presence of a Fe(II) center in reduced MIL-100(Fe). Motion functional calculations, on the other hand, indicate three equivalent Fe in an intermediate (II)-(III) oxidation state (see Table S1). The activation enthalpies associated with TS₁ and TS₂ for ethane computed at the M06-L level for FeFeFe were indeed found to be very similar on both the quintet and the pentadectet surfaces, with computed values for the former of Δ H₂₉₈=122.8 and for the latter of 140.5 kJ mol⁻¹ and Δ H₂₉₈=28.6 and 39.0 kJ mol⁻¹, respectively. Again, we expect similarity in these energetics because the difference between the

### 3. RESULTS AND DISCUSSION

Figure 1 shows the catalytic cycle studied for ethane hydroxylation by M₃M₄Fe clusters (an equivalent cycle was considered for methane). Similar mechanisms have been suggested for other Fe(II)-containing MOFs. The reaction sequence involves four elementary steps: (i) Fe(IV)=O formation (from AO to B in Figure 1), (ii) C-H bond activation (from C to D), (iii) formation of ethanol (from D to E), (iv) desorption of ethanol, which corresponds to regeneration of the catalyst (from E to A). With respect to the formation of the Fe(IV)=O species, we employ N₂O as the oxygen source because it is more effective and selective for Fe than
two spin states is associated with the Fe(III) sites (see spin map in Figure S1), not the active Fe(II) site; similar results have been obtained in other studies of catalysts involving analogous coupling among multiple iron centers. With respect to the ~11 kJ mol⁻¹ lower barriers predicted on the BS surface, these may be attributable more to instabilities associated with the final BS solutions for the various stationary points than to an actual difference between reactivity on the two spin-state surfaces. But, even if the lower barriers are accurate, that suggests that calculations on the HS surface will only be more conservative in terms of predicting C-H bond activation energies, and favorable results may be taken as upper bounds to actual reactivity. In any case, noting our own testing and precedent, the energies reported hereafter are for the HS configurations of all clusters, \( S = 7 \) for FeFeFe, \( S = 5 \) for CrCrFe, and \( S = 6 \) for CrFeFe).

**Figure 2.** Reaction enthalpies for oxidation of (a) methane to methanol and (b) ethane to ethanol as computed at the UM06-L/def2-TZVP level following the cycle reported in Figure 1 for all M:M:Fe clusters on their high spin surfaces taking separated reactants as zero (data in Tables S12-S21).

**N\(_2\)O activation.** The first step in the catalysis is the formation of the active Fe(IV)=O species (B) from Fe(II) (A) using N\(_2\)O as oxygen source. Nitrous oxide first coordinates to the Fe(II) center (AO intermediate in Figure 1) and then dissociates to molecular nitrogen through TS\(_1\) generating the ferryl.

For all AO clusters, the adsorption of N\(_2\)O on the Fe(II) site was found to be exothermic by 20-30 kJ mol⁻¹ (see Table S3). Similar adsorption energies for N\(_2\)O have been reported for other Fe-based MOFs. In all cases, adsorption at the N terminus of N\(_2\)O was favored over adsorption at the O terminus, but by less than 4 kJ mol⁻¹. The geometry of N\(_2\)O adsorption involves Fe-O-N or Fe-N-N angles greater than 130°, which are less acute than those reported for some other Fe(II)-MOFs, e.g. MOF-74 (120°) and Fe-BTC (111°). Competitive adsorption of N\(_2\)O on Al\(_{16}\) and Cr\(_{16}\) sites was evaluated for the AlAlFe and the CrCrFe clusters. While N\(_2\)O was not found to bind significantly to Al\(_{16}\), adsorption on Cr\(_{16}\) was computed to be more favorable than on Fe\(_{24}\) by 14 kJ mol⁻¹. In the Fe/Cr systems a larger N\(_2\)O pressure should be then used in order to allow the saturation of both the chromium and the iron sites.

The AO → B step is predicted to be exothermic (and exergonic) for all clusters. The relative stabilization of B and the corresponding reaction enthalpies of the AO → B process (\( \Delta H_{AO \rightarrow B} \)) are quite sensitive to the cluster composition varying as AlAlFe (\( \Delta H_{AO \rightarrow B} = -52 \) kJ mol⁻¹) < CrCrFe < AlFeFe < CrFeFe < FeFeFe (-0.7 kJ mol⁻¹). The magnitude of \( \Delta H_{AO \rightarrow B} \) decreases on increasing the Lewis acidity of the trivalent ions (Al\(_{16}^3+\) < Cr\(_{16}^3+\) < Fe\(_{16}^3+\)). These reaction enthalpies are all less negative than those computed previously at the same level of theory for isolated Fe(II) sites in Fe\(_n\)M\(_2\)Cr\(_2\)(dobsdc)\(_2\) (-76 kJ mol⁻¹) and Fe-BTC (-58 kJ mol⁻¹), while for Fe-BTC, where there is a Fe-Fe bond, a less negative \( \Delta E \) has been reported (-27.6 kJ mol⁻¹), to be compared with the values in Tables S3, consistent with our noted sensitivity to coupled redox centers.

Considering the ferryl species in more detail, it has previously been noted that the Fe=O bond is shorter and stronger in the absence of a ligand trans to the oxo thanks to the larger stabilization of the Fe 3d\(_e^2\) in a square pyramidal geometry compared to an octahedral one. In Fe-BEA, an unusual short Fe=O bond of 1.59 Å in the α-Fe species has been attributed to such a lack of ligands trans to O. Interestingly, the calculated Fe-O(rem) distance in Fe\(_n\)M\(_2\)Cr\(_2\)(dobsdc) is 2.05 Å, a value considerably larger than any predicted for the clusters computed here (see Table S1), and this weak ligation is consistent with the more exothermic formation of B reported for this MOF. For species A the reactivity of the Fe(II) leading to B correlates with the partial charges on O\(_2\), \( \varphi(O_2) \), (Table S1 and S2 and Figure 4a and S2b; \( R^2 = 0.95 \)). A similar correlation was derived also for the spin density of O\(_2\), \( \varphi(O_2) \) (see Figure S2a). The CASSCF calculations (see Table S27) also confirm larger charges on O\(_2\) for FeFeFe than for AlAlFe (the systems with the largest and the lowest \( \varphi(O_2) \) according to DFT calculations, respectively; see Tables S1).
Figure 3. Reaction profiles for oxidation of methane to methanol (orange) and ethane to ethanol (dark red) calculated at the UM06-L/def2-TZVP level for the AlAlFe cluster on the quintet energy surface with separated reactants as the zero of enthalpy. Selected geometrical parameters are reported for optimized stationary points (only the reacting Fe center and its first coordination sphere are depicted). Color code: red (oxygen), orange (iron), blue (nitrogen), grey (carbon), white (hydrogen).

The activation enthalpy $\Delta H_{TS1}^c$ for $AO \rightarrow B$ is predicted to be significant ranging from 92.6 (for AlAlFe) to 140.5 kJ mol$^{-1}$ (for FeFeFe). These values are close to those reported for the same reaction in other iron-based MOFs and zeolites.$^{17, 20, 56, 58}$ The reaction $AO \rightarrow B$ shows Brønsted–Evans–Polanyi behavior with $\Delta H_{TS1}^c$ being linearly correlated with the reaction enthalpy $\Delta H_{AO}^{c} \rightarrow B$ (Figure 4b, $R^2 = 0.99$). Results reported for Fe$_{0.1}$Mg$_{1.9}$ (dobdc)$_2$ also fall on this correlating line, while those reported for Fe-BTC and Fe-BTT deviate (Figure 4b), the latter deviation being consistent with the different heteroatoms in the Fe coordination shell in Fe-BTC (1 Fe, 4 O) and Fe-BTT (1 Cl, 4 N) compared to 5 O atoms.

Figure 4. Reaction enthalpy for $AO \rightarrow B$, $\Delta H_{AO}^{c} \rightarrow B$ vs. (a) charge of the central oxygen of the cluster, $q(O_c)$, in A and (b) the activation enthalpy, $\Delta H_{TS1}^c$, for M:MzFe clusters at the UM06-L/def2-TZVP level. Best linear fits are shown as solid lines. In (b), literature values reported for Fe$_{0.1}$Mg$_{1.9}$ (dobdc)$_2$,$^{59}$ (blue square), Fe-BTC$^{56}$ (green triangle), and Fe-BTT$^{17}$ (pink diamond), are also shown.
Relevant electronic, geometrical and energetic data for Φ after desorption of N₂ (AB) are reported in Table S2. Interestingly, for all of the Fe(IV)=O species studied here, the spin densities, charges and Fe-O bond lengths are identical within very small variations. All Fe=O bond lengths are 1.61 Å, which may be compared to 1.61 Å in Fe-BTC⁵⁶ and 1.63-1.64 Å in Fe₂O₃Mg₁.s(dobdc)₂;²⁰-⁵⁰ (and very similar experimental values reported for other heme and non-heme complexes).²⁰ Similarly, the hydrogen affinity E₉ of the Fe(IV)=O (as defined in Section S2), which has been suggested in previous works⁵¹-⁶¹ to be a good descriptor for catalytic activity for C-H bond activation, is computed to be about -80 kJ mol⁻¹ for all clusters (see Table S2). While we do not observe much variation, such a large negative value of E₉ would portend low barriers for C-H bond activation, even for methane. This independence of the Fe=O bond length and hydrogen affinity on the chemical composition of the node can be explained by the dominant impact of the oxyl ligand on the electronic structure at the Fe center, as opposed to the negligible impact of the weak ligand-field, equatorial oxygen ligands and O₆.⁶²

C-H bond activation. In this step, a C-H bond of a reacting ethane/methane is cleaved to produce an alkyl radical and a Fe(III)-OH group (D). The total spin does not change as the alkyl radical is antiferromagnetically coupled with the Fe(III)OH (for Hirshfeld spin densities on C and Fe see Tables S6 and S7). The reaction follows a so-called σ pathway, which is typical for non-heme oxoferryl species.²⁰, ⁶³-⁶⁴

Structural data for all cases may be found in Tables S4-S7 (cf. Figure 3 for AlAlFe). The C-H bond cleavage step itself is predicted to be endothermic for all clusters by roughly 20 and 45 kJ mol⁻¹ for ethane and methane, respectively (Tables S3-S7 and Figure 2). The difference among these two values is close to the computed difference in absolute C-H bond dissociation energies for the two alkanes at the M06-L/def2-TZVP level, 23.8 kJ mol⁻¹. These reaction enthalpies are slightly less endothermic than those reported previously for Fe₀₁Mg₁.s(dobdc)₂ (31 and 47 kJ mol⁻¹) while for Fe-BTT, this step was reported to be endothermic for ethane by only 2 kJ mol⁻¹,¹¹ and for the highly reactive Fe(IV)=O in BEA zeolite this step is reported to be exothermic by 16 kJ mol⁻¹ for methane.¹¹

Activation enthalpies ΔH₅₃² for the C-H bond dissociation are listed in Tables S4-S5, along with additional electronic and geometrical data. ΔH₅₃² are very similar for all the clusters, amounting to 39-47 kJ mol⁻¹ for ethane and 55-62 kJ mol⁻¹ for methane, differing again by roughly the C-H bond dissociation energies of the two alkanes. The insensitivity of the C→D energy profile to the chemical composition of the node indicates the Fe(IV)=O site to be effectively isolated, suggesting no need for iron dilution to avoid undesirable polynuclear reactivity, as observed for MIL-53 and MOF-74. Interestingly, the predicted MnMFe barriers are lower than those computed at the same level of theory for Fe₀₁Mg₁.s(dobdc)₂ (ΔH₅₃² = 58 and to 69 kJ mol⁻¹, respectively) albeit higher than those computed for methane in zeolite Fe-BEA (15 kJ mol⁻¹).¹¹ The higher barrier for the MIL model compared to the zeolite system may be attributed to the absence of a trans oxygen ligand in the Fe coordination sphere of the latter. Such a trans ligand has been shown to decrease the strength of the forming FeO-H bond in heterogeneous catalysts.¹¹ Because of that, unlike in the zeolite, where the strength of the formed O-H bond is equivalent to that of the activated C-H bond, in the MnMFe clusters it is about 407-412 kJ mol⁻¹. It is interesting to speculate that replacement of the central oxygen in the MnMFe clusters studied here with some other trans ligand, might lead to an even more active catalyst.

Alkyl rebound. Rebound of the alkyl radical to the Fe(III)-OH group forms metal-bound ethanol (or methanol) (E) with reduction of the metal back to Fe(II) (changes in spin densities on the iron and carbon centers going from D to E are listed in Tables S6-S7 and S10-S11).

This step has low activation enthalpies (TS₃) as expected for a radical rebound reaction. For Fe-BTT and Fe₀₁Mg₁.s(dobdc)₂, the analogous reactions have been reported to have activation enthalpies of only 5 and 7 kJ mol⁻¹ for ethyl, respectively. In the MnMFe clusters, ΔH₅₃³ varies from 7.8 (AlFeFe) to 0.9 kJ mol⁻¹ (FeFeFe) for ethyl and from 10.5 (AlAlFe) to 4.7 kJ mol⁻¹ (CrFeFe) for methyl.

Alternatives to rebound can lead to reduced activity and the formation of by-products. If the radical desorbs from the active site (i.e. dissociates)⁹⁵ with its high reactivity, it can readily react with other components present in the MOF, e.g. by abstracting hydrogen atoms from organic linkers, adding to aromatic linkers, or at sufficiently high concentrations coupling with other radicals. Enthalpies of dissociation are reported in Tables S6-S7 and are about -9 kJ mol⁻¹ for methyl and -13 kJ mol⁻¹ for ethyl. While these values are larger than corresponding ΔH₅₃³ values, they are sufficiently close to suggest that dynamical effects may permit some alkyl radicals to avoid alcohol formation via rebound.

An alternative unproductive pathway available in the case of the ethyl radical is removal of an additional hydrogen atom from the β position to form ethylene and water (see TS₅₋₆ and E₆₋₇ in Figure 5). This is a reaction of potential interest, as ethylene is more valuable than ethane. The reaction activation enthalpies are all lower than 21 kJ mol⁻¹ (see Table S22 and Figure 5), leading to similar conclusions to what has been reported for MOF-74.²⁰ These are again larger, and now by a more substantial margin, than corresponding ΔH₅₃³ but at higher temperatures dynamical effects might permit reasonable partitioning into this pathway.

Figure 5. Reaction profiles of ethyl radical rebound (dark red line) and second C-H bond activation (desaturation mechanism, gold line) calculated at the U06-L/def2-TZVP level for the AlAlFe cluster on the quantum energy surface with separated reactants as the zero of enthalpy. Selected geometrical parameters are reported for optimized stationary points (only the reacting Fe center and its first coordination sphere are depicted). Color code: red (oxygen), orange (iron), blue (nitrogen), grey (carbon), white (hydrogen).

Catalyst regeneration. Regeneration is the last step of the catalytic cycle and requires desorption of the alcohol from the Fe(II)
center. The adsorption enthalpies on the Fe(II) sites range from 77.7 to 91.5 kJ mol\(^{-1}\) for methanol and from 69.6 to 84.3 kJ mol\(^{-1}\) for ethanol (see Tables S10 and S11). These values are slightly higher than those reported experimentally for the adsorption of methanol and ethanol\(^{66}\) in MIL-100-Fe (72 and 56 kJ mol\(^{-1}\), respectively). The differences can be related to an overestimation of the alcohol affinity by the DFT method. Nevertheless, in Ref. 66 it is pointed out that the experimental values were obtained using only few data points.

The activation enthalpy for desorption is not as high as that for the formation of the Fe(IV)=O, but it is sufficiently high relative to the adsorption enthalpy of N\(_2\)O (20-30 kJ mol\(^{-1}\)), suggesting that a deliberate process for alcohol removal will need to take place before a new catalytic cycle can begin. Although steam is sometimes used in zeolites to remove alcohols,\(^{13}\) experiments have indicated methanol and ethanol to be removed from MIL-100 and MIL-101-Fe, without affecting the framework at 150 °C.\(^{66}\) Thermal re-activation at such a relatively low temperature would be an attractive feature for catalysis.

4. CONCLUSIONS

Tririon oxo-centered clusters Fe(II)-Fe(III)(μ-O)(COOH)\(_6\) are structural units recurrently found in various MOFs, including MIL-100(Fe), MIL-101(Fe), MIL-127,\(^{67}\) and PCN-250.\(^{68}\) These MOFs have been extensively studied because of their thermal and chemical stability as materials for adsorption, separation and more recently also for catalysis. Based on Kohn Sham density functional calculations, Fe(IV)=O units generated from the Fe(II) centers are predicted to oxidize methane to methanol and ethane to ethanol with C-H bond activation enthalpies of only 63.3 and 39.3 kJ mol\(^{-1}\), respectively. Such values suggest that MOFs based on tririon oxo-centered clusters are promising catalysts for these reactions under relatively mild conditions. Moreover, the Fe sites are predicted to function in an isolated manner, so that it should not be necessary to dilute the Fe concentration to maintain high catalytic activities, unlike in other Fe MOFs previously shown to carry out such oxidations.\(^{21,69}\) Multireference calculations show that all spin states are very close in energy and that in the system with three Fe centers the formal oxidation states of the three Fe is Fe(III), Fe(III) and Fe(II). The highest activation enthalpy for the catalysis, here, is that for the formation of the Fe(IV)=O species from N\(_2\)O as oxidant (140 kJ mol\(^{-1}\)). Doping the node with other metals (M = Al and Cr) strongly impacts N\(_2\)O activation energy while it has a relatively little effect on the energetics for C-H bond activation by the Fe(IV)=O unit. Comparison of the present results to prior experiments for MIL-100 suggests that it should be possible to desorb product alcohols from the catalysts by thermal activation without compromising the structure of the MOF. Thus, MOFs based on this tri-iron oxide node merit further investigation as potentially promising catalysts for the conversion of light alkanes to alcohols.

ASSOCIATED CONTENT

Supporting Information

Relevant geometrical, electronic and energetic parameters for all the structures, results of the multireference calculations, coordinates for the all the optimized geometries. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

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ABBREVIATIONS

DFT, density functional theory; MIL, Materials Institut Lavoisier; MOF, metal organic framework; CASSCF, complete active space self consistent field; CASPT2, complete active space perturbation theory to second order.

REFERENCES


