Aerobic oxidation of hydrocarbons in Mn-doped aluminophosphates: a computational perspective to understand mechanism and selectivity

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We discuss the mechanism and energetics for the aerobic oxidation of hydrocarbons catalysed by Mn-doped nanoporous aluminophosphates with the AFI structure (Mn-APO-5), obtained computationally using electronic structure techniques. Calculations have been performed employing hybrid exchange density functional theory methods under periodic boundary conditions. The active sites of the catalyst are tetrahedral Mn ions isomorphously replacing Al in the microporous crystalline framework of the AlPO host. Since all Al sites in AFI are symmetry equivalent, all Mn dopants are in an identical chemical and structural environment, and hence satisfy the definition of a single-site heterogeneous catalyst. We focus in particular on the atomic-level origin of selectivity in this catalytic reaction.

Keywords: catalysis; modelling; oxidation; alkanes; zeolites; selectivity

1. Introduction

The use of catalysis is widespread in the chemical industry, not only to optimize economic operations and minimize their environmental impact, but also as a way to control selectivity in reactions where the required products are not the thermodynamically stable combination of the reagent molecules in the gas phase. Among the available options, heterogeneous solid catalysts offer operational advantages over homogeneous catalytic alternatives, in particular for the ease of handling and reprocessing, but they often suffer from inferior selectivity. This feature is associated with the multitude of structurally and chemically different active sites that are usually exposed in catalytically active solid surfaces, as opposed to the molecular precision by which homogeneously active catalytic sites can be replicated. As a general rule, selectivity is obtained with the introduction of stereochemical constraints in the catalyst region surrounding the active site. The broader the spatial extension and complexity of the constrained region, the higher we can expect the resulting selectivity. Not surprisingly, the unsurpassed
example of molecular recognition efficiency is found in enzymes, where the active
site is surrounded by a large number—often several hundreds—of amino acid
residues.

A grand challenge for current catalysis is to replicate the selectivity features,
if not of enzymes then at least of homogeneous catalysts, in stable solid materials
that combine them with the operational advantage of heterogeneous catalytic
processes. A first logical step in this direction is the ability to synthesize
catalytically active solids in which all active sites are in an identical chemical
and structural environment, and thus all operate in the same way. The concept
of single-site heterogeneous catalysts (SSHCs), to which this Special feature
is dedicated, effectively identifies such materials. Clever synthetic design has
ensured that SSHCs do exist; a classification can be found in the review by
Thomas et al. (2005), where four classes of known SSHCs are discussed. Of
these, three are obtained with post-synthetic modifications of high-surface-area
solid supports, by grafting or tethering identical replicas of an active molecular
species on the available surface sites of the support. If appropriately chosen
and manipulated these SSHCs retain the activity and selectivity properties of
the starting molecular species, including enantioselectivity (Hutchings 2005),
and thus enable a direct transfer to heterogeneous catalysis of the knowledge
accumulated in homogeneous catalytic studies. In the fourth type of SSHC,
represented by open-structure microporous solids, the active sites are instead
dopant ions incorporated isomorphously in the framework sites of the host system,
and are an integral part of the solid catalyst ever since its synthesis. Their
understanding and optimization requires an entirely solid state-based approach.
The constraints responsible for the catalytic selectivity of these microporous
SSHCs are associated with the well-defined crystalline nature of the solid matrix,
whose internal dimensions (in the range of approx. 3–12 Å) are comparable
to those of common organic molecules, which can therefore be differentiated
according to size and shape. Selectivity can be tailored by an appropriate choice
do dopant type and host framework, in a fashion that is often guided by reference
to the functioning of known homogeneous catalysts; however, the behaviour of
an ion in an inorganic solid matrix is often substantially different from that of
the same ion in a molecule. A rational optimization of activity and selectivity of
such SSHCs requires an atomic-level understanding of the reaction mechanism.

Since all sites of a microporous solid are, at least in principle, accessible
to suitable reagent molecules and the dopant ions are distributed across the
solid, these heterogeneous catalysts offer a unique medium for experimental
studies (Thomas 1988) open not only to surface-specific probes but also to all
those spectroscopic techniques that are dominated by the bulk response. Even
in such a favourable situation, important details of the reaction mechanism,
especially those associated with the presence of competitive transition states (TSs;
ultimately responsible for the selectivity) and short-lived intermediates, cannot
always be detected by experiment alone. Computational chemistry is increasingly
able to complement experiment in gathering such crucial information.

In the present contribution, we are concerned with the role that modelling
can play in the mechanistic characterization of complex heterogeneous catalytic
cycles, and how this information can be used to design new SSHCs with improved
selectivity for desired applications. We make reference to a particular reaction,
the aerobic oxidation of saturated hydrocarbons in Mn-doped AlPO-5 (AFI),

Microporous aluminophosphates (AlPOs) are structural analogues of zeolites, in which the inorganic framework is formed by a strict alternation of $\text{Al}^{3+}$ and $\text{P}^{5+}$ ions (or $\text{Al}^{3+}$ and $\text{PO}_4^{3-}$ when taking into account the molecular–ionic nature of the solid (Corà & Catlow 2001)) in a corner-sharing tetrahedral environment. The catalytic activity of Mn-doped AlPO catalysts in selective oxidation catalysis was first demonstrated in the late 1990s (Thomas & Raja 1998). The Mn ions, once incorporated into the tetrahedral sites of the AlPO framework, are able to vary reversibly their oxidation state; the catalytic activity of Mn-APO materials has been shown to correlate with the fraction of redox-active Mn ions in the solid (Corà et al. 2002; Modén et al. 2004). AlPOs doped with transition metal ions such as Mn, but also Co and Fe, are now recognized as efficient and selective catalysts for a wide range of oxidation reactions, including the industrially relevant selective oxidations of $n$-hexane (Thomas et al. 1999; Raja et al. 2000; Modén et al. 2004, 2007) and cyclohexane (Vanoppen et al. 1995; Conception et al. 1996; Luna et al. 1997; Raja et al. 1999a; Dugal et al. 2000; Modén et al. 2006; Zhou et al. 2008), the epoxidation of alkenes (Raja et al. 1999b) and the Baeyer–Villiger oxidation of ketones to lactones (Raja et al. 1999c), all using $\text{O}_2$ as the oxidant. The AFI structure (figure 1) examined here comprises one-dimensional, non-interconnected, 12-membered ring (MR) channels, whose walls are formed by 6-MR windows. These large channels are surrounded by smaller 6- and 4-MR voids, which are too small to permit the diffusion of the hydrocarbon reactants. Mn dopants are introduced during the synthesis as $\text{Mn}^{2+}$ ions, which replace $\text{Al}^{3+}$ but not $\text{P}^{5+}$ in the host framework. All Al sites in the AFI structure are symmetry equivalent, hence all the Mn ions incorporated in the AFI framework are in an

Figure 1. Structure of the AlPO-5 aluminophosphate (AFI) highlighting the different pores available.
identical environment and obey in a strict way the definition of SSHC given earlier. As is typical of crystalline solids, the presence of alternative active sites at least in small quantities, such as intrinsic defects, extraframework ions or Mn clusters, cannot be entirely ruled out; however, activation by doping ensures that substitutional Mn in the AFI framework is present in a much higher concentration than at any other site, and is thus the major active site of the system. The catalytic oxidation reactions take place in the 12-MR channels, where the MnO$_4$ tetrahedra are part of the channel walls.

2. Methodology

The computational characterization of a system, be it a molecule or a solid, takes place through the evaluation and analysis of its potential energy surface (PES), i.e. the calculated energy as a function of all structural coordinates. While the study of a system under equilibrium conditions is only concerned with the location of minima in the PES, the characterization of reactivity is more demanding, in that it also requires us to identify the barriers (saddle points) between the stable basins. In this case, minima represent stable and metastable reaction intermediates, while each path connecting two adjacent stability basins through a saddle point represents a possible elementary reaction step in the chemical transformation studied. Despite many recent advances, at present there still is no systematic way of enumerating all possible minima and saddle points for a system of given complexity; in the absence of experimentally derived references, the computational search for TSs is therefore still largely driven by chemical intuition, but modelling enables an accurate quantification of intuition-driven hypotheses, in a way that is still inaccessible to experiment.

Two additional choices differentiate computational studies of heterogeneous catalysis. The first concerns the description of the extended nature of the solid catalyst, with common options being isolated and embedded cluster models (Catlow et al. 2005) and the use of periodic boundary conditions (PBCs) typically employed for the study of crystalline materials. Second, the energy can be computed at different levels of theory (Hamiltonians), with the availability of options closely linked to the model of the solid.

In our work, we have employed the PBC model, which we consider more faithful to the real-life conditions under which microporous SSHCs operate. The Mn-doped AFI framework is described using the crystallographic unit cell (72 atoms) containing 1 Mn ion in the tetrahedral position. Even at this relatively high doping level, Mn sites are separated by at least 8 Å from one another, which prevents strong interactions between the reactants in adjacent cells. The quantum mechanical method of choice for such PBC calculations is density functional theory, and we have employed the hybrid-exchange functional B3LYP (Becke 1993), which is suitable to describe the chemistry of the unpaired electrons on Mn (Corà et al. 2004) as well as the hydrocarbon thermochemistry (Becke 1993). We employed the computer code CRYSTAL (Dovesi et al. 2009), in which the electronic distribution is described as a linear combination of atomic orbitals; full technical details can be found in our earlier papers (Gómez-Hortigüela et al. 2010, 2011a–d). Once incorporated in the AlPO matrix the
Mn ions in both $2 + (d^5)$ and $3 + (d^4)$ oxidation states are stable in high-spin electronic configuration, as expected, owing to the low ligand field splitting caused by the $\pi$ donor character of O-based ligands and the tetrahedral coordination of the Mn ions. The spin density of Mn in the different intermediates is therefore a clear indication of the Mn oxidation state at each stage of the catalytic cycle.

In our initial computational study, we employed ethane as the model hydrocarbon substrate; while this choice does not enable us to discriminate the reactivity of primary and secondary carbon atoms to oxidation, which is of interest for industrially relevant applications (e.g. oxidation of hexane or cyclohexane), it enables a much more in-depth study of the elementary reaction steps involved in the catalytic cycle. Only those where selectivity originates will need to be repeated with more complex substrates to investigate the atomic-level cause of selectivity. Such simplification is a common strategy in computational studies.

In order to find the reaction pathway and locate reliably all stable intermediates and activation energies in the catalytic cycle, we made initial reference to the mechanism proposed by Modén et al. (2006) and tested computationally a large number of alternative mechanisms corresponding in practice to the interaction of each reasonable combination of reagent molecules and intermediates with the Mn sites. For each elementary reaction step, the reactant species were moved in discrete steps (of 0.1 Å or less) along the relevant reaction coordinate. At each step, we performed constrained geometry optimizations, keeping the selected reaction coordinate frozen but relaxing all other degrees of freedom; this methodology allowed us to obtain the energy profile for each elementary step. For selected reaction steps, the location of the TS has been refined using eigenvector-following techniques based on calculated second derivatives. We invariably found that the approximate TS identified in the constrained search is very close to that obtained in the refinement both in geometry (to within the step size chosen) and in energy (usually less than 4 kJ mol$^{-1}$).

3. Results

Our calculations confirm experimental indications that the aerobic catalytic oxidation considered here proceeds via a radical mechanism on the Mn active sites. A summary of the reaction cycle derived computationally with calculated reaction enthalpies and activation energies of each elementary reaction step is reported in figures 2 and 3 and is expressed in the scheme below:

1) $\text{CH}_3\text{CH}_2\text{H} + \text{Mn}^{\text{III}} \rightarrow \text{CH}_3\text{CH}_2\cdot + \text{Mn}^{\text{II}}(\text{H})$
2a) $\text{CH}_3\text{CH}_2\cdot + \text{O}_2 \rightarrow \text{CH}_3\text{CH}_2\text{OO}\cdot$
2b) $\text{CH}_3\text{CH}_2\text{OO}\cdot + \text{Mn}^{\text{III}} \rightarrow \text{CH}_3\text{CH}_2\text{OO}\cdot(\text{Mn}^{\text{III}})$
3) $\text{CH}_3\text{CH}_2\text{OO}\cdot(\text{Mn}^{\text{III}}) + \text{CH}_3\text{CH}_2\text{H} \rightarrow \text{CH}_3\text{CH}_2\text{OOH}(\text{Mn}^{\text{III}}) + \text{CH}_3\text{CH}_2\cdot$
4a) $\text{CH}_3\text{CH}_2\text{OOH} + \text{Mn}^{\text{II}}(\text{H}) \rightarrow \text{CH}_3\text{CH}_2\text{O}\cdot(\text{Mn}^{\text{III}}) + \text{H}_2\text{O}$
4b) $\text{CH}_3\text{CH}_2\text{OOH} + \text{Mn}^{\text{II}}(\text{H}) \rightarrow \text{HO}\cdot(\text{Mn}^{\text{III}}) + \text{CH}_3\text{CH}_2\text{OH}$
5a) $\text{CH}_3\text{CH}_2\text{O}\cdot(\text{Mn}^{\text{III}}) + \text{CH}_3\text{CH}_2\text{H} \rightarrow \text{CH}_3\text{CH}_2\text{OH}(\text{Mn}^{\text{III}}) + \text{CH}_3\text{CH}_2\cdot$

Figure 2. Preactivation mechanism for the production of CH$_3$CH$_2$OOH from RH and O$_2$ without (top) and with the assistance of Mn$^{III}$ (middle). Boxed species represent initial catalyst and reactant molecules, and intermediates produced here which are necessary to initiate the propagation cycle (figure 3). Enthalpies and activation energies if any (in brackets) are shown for each elementary step in kJ mol$^{-1}$. (Online version in colour.)

5b) HO·(Mn$^{III}$) + CH$_3$CH$_2$H → H$_2$O(Mn$^{III}$) + CH$_3$CH$_2$·.

6) CH$_3$CH$_2$OO·(Mn$^{III}$) + CH$_3$CH$_2$OH → CH$_3$CH$_2$OOH + Mn$^{II}$ (H) + CH$_3$CH(=O),

where L(Mn$^x$) indicates complexation of intermediate L on a Mn$^{x+}$ site; Mn$^{II}$(H) indicates that the Mn$^{II}$ active site has a proton attached to a nearest neighbour framework O.

Starting from the calcined Mn-AFI catalyst with only oxidized Mn$^{III}$ sites the onset of the catalytic cycle requires a slow activation step (1) with a high activation energy of 135 kJ mol$^{-1}$ in which Mn$^{III}$ abstracts a H radical from the hydrocarbon yielding a reduced Mn$^{II}$ site and an ethyl radical that remains chemisorbed on Mn$^{II}$. We refer to this reaction as the preactivation step (Gómez-Hortigüela et al. 2011a). The alkyl radicals R$^\cdot$ (when possible here and in the following, we identify the ethyl chain CH$_3$CH$_2$ simply as R) are subsequently stabilized by a barrierless addition of O$_2$ (2a) yielding peroxo radicals ROO$^\cdot$. 

Figure 3. Propagation mechanism of the aerobic oxidation. (Online version in colour.)
that desorb from Mn$^{\text{II}}$ and form a complex with a new Mn$^{\text{III}}$ site (2b). The propagation phase of the catalytic reaction proceeds from Mn$^{\text{II}}$ and ROO·(Mn$^{\text{III}}$). ROO·(Mn$^{\text{III}}$) complexes are responsible for the production of the hydroperoxide intermediate (ROOH) through H abstraction from hydrocarbon molecules (3), yielding in turn alkyl radicals R· that undergo again steps 2a and 2b. The subcycle (2 + 3) provides a catalytic source of ROOH. The decomposition of the ROOH intermediate can only occur on reduced Mn$^{\text{II}}$ sites (4a and 4b) (Gómez-Hortigüela et al. 2011b) and has two alternative mechanistic pathways depending on the stereochemistry of the adsorption of ROOH on Mn$^{\text{II}}$, yielding either RO·(Mn$^{\text{III}}$) and H$_2$O (4a) or HO·(Mn$^{\text{III}}$) and ROH (4b) both resulting in the oxidation of Mn. Subsequent propagation reactions take place from these Mn$^{\text{III}}$ complexes via H abstraction from new hydrocarbon molecules by the radical O atom of RO·(Mn$^{\text{III}}$) or HO·(Mn$^{\text{III}}$) (5a and 5b) (Gómez-Hortigüela et al. 2011c), analogous to step (3) on ROO·(Mn$^{\text{III}}$), to yield the primary oxidative products (ROH, H$_2$O, and ROOH). Reduction of the Mn$^{\text{III}}$ sites is required to close the reaction cycle, a step that we referred to as regeneration (Gómez-Hortigüela et al. 2011d). The most favoured regeneration route takes place through a mechanism consisting of two H abstractions from the alcohol ROH to give the aldehyde/ketone (R(=O)) and Mn$^{\text{II}}$(H) sites (6). Secondary oxidation reactions (Gómez-Hortigüela et al. in press) follow the same mechanism but H is abstracted in steps (3) and (5) from an already oxidized product (alcohol and aldehyde/ketone). A common feature in this reaction cycle is that whenever a new hydrocarbon radical is formed it is stabilized by addition of O$_2$; this step is always highly exothermic and barrierless and it is the main thermodynamic driving force for the reaction to proceed. At the high O$_2$ partial pressure that these catalytic oxidations usually operate at, we can expect the O$_2$ addition to occur promptly upon formation of a new C-based radical.

In the catalytic cycle, we distinguish two types of elementary reaction steps: those in which the Mn dopant changes its oxidation state, which are therefore directly enabled by the redox activity of the transition metal ion, and those in which Mn is involved in complexing one of the reaction intermediates but does not itself participate directly in the bond-breaking and -making processes. Here, we examine a representative example of each type of reaction step to highlight the wealth of information provided by the computational study. The former case is exemplified by the preactivation step (1), where Mn$^{\text{III}}$ abstracts a H radical from the hydrocarbon effectively initiating the catalytic process. The energy diagram for this reaction step as well as the evolution of the spin on Mn are shown in figure 4a. Here, the reaction coordinate is the distance between the dissociating H and the framework O atom forming the new O–H bond. The C–H bond remains stable as the hydrocarbon approaches the framework O (i.e. the active site) up to a (R)H–O(Mn) distance of 1.7 Å, when the bond starts to dissociate. At the TS, we observe an abrupt change of the Mn spin from 3.79 (corresponding to Mn$^{\text{III}}$) to 4.83 (corresponding to Mn$^{\text{II}}$), indicating the reduction of Mn in this step. The homolytic mechanism is also clear from the spin density maps of the TS and the ethyl radical intermediate produced in this elementary step shown in figure 5. In the TS, the β spin-density from the C–H bond is shared between the C atom (which is becoming a radical) and the framework O nearest-neighbour to Mn. The H atom has much smaller spin density: it mediates the radical transfer from C to the framework but does not itself become spin polarized. The H donated to

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the framework in this elementary step becomes a Brønsted acid proton typical of a hydrogen neighbouring low valent dopant ions (MnII in this case) in zeolites and AlPOs. The alkyl intermediate formed retains a strong stabilizing interaction with the transferred H atom, now the Brønsted acid site in the framework. The radical C atom has planar geometry; since one side is engaged in the interaction with the framework, addition of O\textsubscript{2} can only occur from the opposite side with stereospecific features.

Figure 4. Characterization of the preactivation step. (a) Energy diagram and evolution of Mn spin along the reaction coordinate (represented as the H(CH\textsubscript{3}CH\textsubscript{3})-O(OMn) distance). (b) Energy diagram for the activation of ethane by MnAPO-5 by undoped AlPO-5 and by O\textsubscript{2} to give CH\textsubscript{3}CH\textsubscript{2}- and ·OOH.

The preactivation step is directly enabled by the redox activity of Mn; upon repeating the calculations in an undoped AFI system the energy (open squares in figure 4b) increases upon elongation of the C–H bond without showing any
indication of reaching a TS. We also studied the non-catalytic activation of the hydrocarbon by O$_2$ without assistance of the Mn active site but still occurring within the Mn-AFI channels. In this case, the H atom of the dissociating C—H bond is taken up by O$_2$, giving place to one ethyl (R·) and one hydroperoxo (·OOH) radical—again stabilized by a strong interaction between the transferred H and the radical C in R·. Such a H-transfer reaction involves a reaction enthalpy of 188 kJ mol$^{-1}$—much higher than even the activation energy corresponding to the Mn-catalysed ethane activation (135 kJ mol$^{-1}$). This non-catalytic activation
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mechanism will not therefore operate, confirming the essential role of the redox activity of Mn in the initial activation of the hydrocarbon molecules. A similar dependence on the Mn redox activity is observed in the hydroperoxide decomposition step (4a and 4b), where the calculated activation barriers are 86 and 82 kJ mol\(^{-1}\) on redox-active Mn\(^{II}\) while in absence of Mn\(^{II}\) the calculated reaction enthalpy is 187 kJ mol\(^{-1}\).

Instead, in the propagation stage of the catalytic cycle (figure 6) responsible for the production of the hydroperoxide intermediates (3 and 5), the Mn ions remain in the 3+ oxidation state. Here, an O-based radical (ROO\(^{·}\), RO\(^{·}\) or HO\(^{·}\)) is coordinated to Mn\(^{III}\) and abstracts a H from a new hydrocarbon molecule; the resulting radical is stabilized by the addition of O\(_2\) to yield new peroxide radicals that re-enter the cycle, having as a net result the insertion of O\(_2\) into a CH bond (R−H + O\(_2\) → ROOH). The Mn spin during this reaction step does not vary as reported in figure 7; however, even if Mn remains in the 3+ oxidation state its presence lowers the activation barrier (figure 7b). The H abstraction step by a free peroxo radical ROO\(^{·}\) in the AFI pores has a reaction enthalpy and activation barrier of 83 and 97 kJ mol\(^{-1}\), respectively, reduced to 78 and 88 kJ mol\(^{-1}\), respectively, for ROO\(^{·}\) complexated on Mn\(^{III}\); Mn thus facilitates this reaction step by stabilizing the intermediate formed.

4. Selectivity issues

Let us now examine how the atomic-level detail on the mechanism derived computationally and discussed above can be employed to analyse selectivity issues related to this catalytic oxidation. Our work shows that selectivity features occur at three complementary levels that we identify as (i) the stereochemistry of the O\(_2\) addition; (ii) the C atom of the substrate which is oxidized; and (iii) the extent of oxidation.

(a) Stereochemistry of the O\(_2\) addition

Whenever a C-based radical R\(^{·}\) is formed in the catalytic cycle (steps 1, 3 or 5) it transforms into the corresponding peroxide by barrierless addition of O\(_2\). After its formation, the radical C atom is always engaged in H-like bonding with the transferred H atom that stabilizes the radical and creates barriers for internal rearrangements. In the operating conditions with high oxygen partial pressure, the radical is unlikely to disengage from the H bonding before the O\(_2\) addition step. The planar structure of the radical C atom with one side blocked by the H bond may therefore give stereospecific character to the O\(_2\) addition that proceeds with inversion of configuration at the C site. Upon formation of ROO\(^{·}\), the radical C atom engaged in the H-bond interaction becomes saturated (the radical is located on the terminal oxygen and points away from the active site); formation of the peroxy radical is therefore simultaneous with its desorption from the Mn\(^{II}\) site. The possible stereospecific nature of the O\(_2\) addition is unlikely to have immediate practical applications and requires the H abstraction to take place from a chiral C atom to be observed, but it has not yet been discussed and its experimental investigation may provide precise information to validate the computational analysis.

Figure 7. (a) Energy diagram and evolution of the C, O and Mn spin along the propagation step of the reaction. (b) Energy profile for the H transfer from RH to ROO· without and with the assistance of Mn showing the corresponding activation energies and reaction enthalpies. The adsorption energy of ROO· on MnIII is 60 kJ mol⁻¹.

(b) C oxidation: primary versus secondary C atom reactivity

In the catalytic cycle examined, the hydrocarbon molecules are invariably oxidized at the C atom that undergoes the initial H abstraction reaction to produce the alkyl radical R·. Selectivity arises therefore in the H abstraction step. The C–H bonds of the substrate are cleaved homolytically in two stages of the reaction cycle, namely preactivation (1) and propagation (3 or 5). The calculated reaction enthalpies and activation barriers for processes (3, 5) are summarized in table 1. The relatively high activation energy of 135 kJ mol⁻¹ in the preactivation step compared with 84 kJ mol⁻¹ at most in the propagation step suggests that preactivation is necessary to initiate the catalytic cycle but will play a small
Table 1. Summary of the energies (reaction enthalpies $\Delta H$ and activation energies $E_a$ in kJ mol$^{-1}$) of the alternative H abstractions from ethane, ethanol and ethanal to radical O atoms in ‘OX ligands of complexes Mn$^{\text{III}} \cdot \cdot \cdot$OX.

<table>
<thead>
<tr>
<th>complex</th>
<th>H abstraction from ethane (RH)</th>
<th>H abstraction from ethanol (ROH)</th>
<th>H abstraction from ethanal (R(=O)H)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\Delta H$</td>
<td>$E_a$</td>
<td>$\Delta H$</td>
</tr>
<tr>
<td>C$-\text{H}$ bond strength</td>
<td>454</td>
<td>-70</td>
<td>417</td>
</tr>
<tr>
<td>Mn$^{\text{III}} \cdot \cdot \cdot$OH</td>
<td>-70</td>
<td>no</td>
<td>-112</td>
</tr>
<tr>
<td>Mn$^{\text{III}} \cdot \cdot \cdot$OR</td>
<td>-27</td>
<td>32</td>
<td>-35</td>
</tr>
<tr>
<td>Mn$^{\text{III}} \cdot \cdot \cdot$OOR</td>
<td>+78</td>
<td>84</td>
<td>+29</td>
</tr>
</tbody>
</table>

role in the overall product formation. The propagation reactions correspond to a common transformation described as $(\text{XO}^+ + \text{RH} \rightarrow \text{XOH} + \text{R})$. Calculations clearly demonstrate that these steps occur not on a bare Mn site but on an O-based radical ligated to Mn$^{\text{III}}$ and require the presence of two molecular species (XO$^+$ and RH). In the confined space provided by the microporous framework of the SSHC, the presence of the radical ligand in the XO$^+$(Mn$^{\text{III}}$) complex may modify substantially the steric requirements of the C$-\text{H}$ bond cleavage; it is therefore important to include the XO$^+$ intermediate when examining the relative reactivity of primary and secondary C atoms of the substrate in this reaction step.

For an isolated molecule of a saturated hydrocarbon, inductive effects cause the strength of C$-\text{H}$ bonds to decrease when moving from primary to secondary and tertiary C atoms, which in turn results in a more facile abstraction of H from secondary (tertiary) atoms. Similarly, oxidation at secondary over primary C atoms is thermodynamically favoured in the gas phase, while the terminal oxidation at primary C atoms yields more desirable products. Modification of the relative reactivity of primary and secondary C atoms of the substrate is therefore a useful outcome of the catalytic process and one that can at least in principle be achieved in microporous SSHCs. As shown in figure 8, the TS originating from the activation of secondary C atoms is in fact more bulky than that from the activation of primary C atoms, which is an important effect especially when the space neighbouring the active site is already occupied by the XO$^+$ intermediate ligated to the Mn ion whose radical O atom can itself be bonded to a primary or secondary C atom.

While our use of ethane as the model hydrocarbon prevents us from discussing this issue directly, we have examined the activation of differently functionalized substrates in the study of oxidation reactions beyond the alcohol (table 1). The calculated activation energies in the catalytic cycle show a good correlation with the C$-\text{H}$ bond strengths calculated for the gas-phase molecules; hence in the AFI/ethane case examined here the catalyst does not alter the reactivity typical of the gas-phase hydrocarbon molecules. In other words, it does not impose selectivity constraints. This result is not surprising given the relatively large dimension of the AFI channels, which exert only limited steric control over the TS energetics. It is, however, reasonable to expect that microporous frameworks with smaller pore dimensions impose more stringent constraints on
Figure 8. Reaction scheme showing the TSs in reaction step (3) corresponding to selectivity to oxidation at (a) primary and (b) secondary C atoms. While thermodynamically favourable the secondary C oxidation requires a bulkier TS that can be blocked in small-pore microporous SSHCs.

the bulkier TS originating from activation of secondary C atoms and hence offer a better opportunity to direct oxidation selectively towards the terminal C atoms. Importantly, by computationally identifying the exact mechanistic mode of action of the catalyst, we are now able to focus future research on only one elementary reaction step where selectivity is introduced, which streamlines the search for catalysts of improved selectivity.

(c) Extent of oxidation

A further product selectivity of interest in the aerobic oxidation reaction examined here arises not from the C atom of the substrate that is functionalized, discussed in §4b above, but from the extent of its oxidation leading to the formation of alcohol, aldehyde (ketone) or carboxylic acid functionalities. We note in this respect that formation of both alcohol and aldehyde molecules occurs in the main catalytic cycle of the primary oxidation reaction: the alcohol is formed in the hydroperoxide decomposition step (4) responsible for the oxidation of MnII sites into MnIII (Gómez-Hortigüela et al. 2011b), while the aldehyde is formed in the regeneration step (6) that converts MnIII back into MnII (Gómez-Hortigüela et al. 2011d). Even excluding the occurrence of further (secondary) oxidation reactions the simultaneous production of alcohols and aldehydes in the catalytic oxidation is an intrinsic requirement of the reaction mechanism which cannot be avoided. In other words, the production of alcohols alone is impossible with the Mn-APO catalysts examined here. In the presence of the primary oxidative products, secondary oxidation reactions can further convert the alcohol into the aldehyde first and then into carboxylic acid (Gómez-Hortigüela et al. in press). The calculated activation energies for the secondary oxidation steps are summarized in table 1, which shows that the C−H bond cleavage becomes progressively easier (in terms of both reaction enthalpies and activation energies) when increasing the degree of oxidation of the substrate C atom. It is therefore impossible to prevent secondary oxidations on thermodynamic grounds alone. In addition, the products resulting from subsequent oxidations at the same C atom (for instance, the alcohol R−CH$_2$OH, the aldehyde R−CHO and the carboxylic acid R−COOH when considering the oxidation at a terminal C atom) have very similar size and shape, which indicates that it is very difficult to prevent further oxidation steps also using steric constraints in the catalyst around the active site. The best way to control the extent of oxidation appears therefore to be to vary the residence time of the hydrocarbon substrate in the microporous catalyst; long residence times
favour further oxidation reactions that enrich the product in aldehydes/ketones and carboxylic acids at the expense of the alcohols while the maximum fraction of alcohol is obtained for short residence times. The evolution of products with time discussed above is consistent with experimental observations (Modén et al. 2006).

5. Conclusions

By making reference to the aerobic oxidation of hydrocarbons in microporous Mn-doped aluminophosphates, we have discussed how modern computational methods can contribute to the understanding and rational design of heterogeneous catalysts and catalytic reactions. The particular system examined—Mn-AFI—obeys strictly the definition of a SSHC in that all Mn ions are in an identical environment in the crystalline microporous inorganic matrix. We first presented an overview of the catalytic mechanism obtained computationally with electronic structure methods, which enabled us to discuss the entire catalytic cycle with atomic-level detail. The active sites for the reaction are substitutional Mn ions in tetrahedral coordination in the AlPO framework. Some of the elementary reaction steps are directly enabled by the redox activity of Mn while other steps do not require direct involvement of Mn but are facilitated by its presence through the ligation of reaction intermediates. We have employed the mechanistic detail on the reaction cycle to discuss three types of selectivity that can be accomplished in this catalytic reaction. The one of highest practical interest refers to the C atom of the substrate which is functionalized. We have shown that this is the C atom that undergoes the initial H abstraction. The relevant step involves two substrate molecules both contributing to the steric constraints. Analysis of the TS for this elementary reaction step can at least in principle enable a rational design of new catalysts in which the atomic-level features of the TS are suitably constrained to direct selectively towards oxidation of primary or secondary C atoms. The extent of oxidation is a second selectivity issue relevant to the reaction studied; we have shown that the simultaneous formation of both alcohol and aldehyde (ketone) molecules is intrinsic to the reaction mechanism and cannot be avoided; secondary oxidation reactions cannot be prevented on thermodynamic grounds but can be controlled by varying the residence time of the substrate in the microporous catalyst. We have also shown that the O$_2$ insertion step has stereospecific features that may lead to interesting applications in chiral synthesis.

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