

Biomimetic Oxidation with Fe-ZSM-5 and H₂O₂? Identification of an Active, Extra-Framework Binuclear Core and an Fe^{III}–OOH Intermediate with Resonance-Enhanced Raman Spectroscopy

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Developing inorganic materials that can mimic nature's ability to selectively oxidise inert C–H bonds remains a topic of intense scientific research. In recent years, zeolitic materials containing Fe and/or Cu have been shown to be highly active, heterogeneous catalysts for the selective oxidation of alkanes (including methane), amongst a range of other related oxidation challenges. By using resonance-enhanced Raman spectroscopy, we demonstrate that, following high-temperature pretreatment (activation), Fe-containing ZSM-5 possesses an active binuclear core, and forms a key Fe–OOH intermediate upon activation with H_2O_2 . Both factors are reminiscent of biological oxidation catalysts, and may account for the unique ability of this material to selectively oxidise methane to methanol at low temperature.

The activation and selective oxidation of C-H bonds remains one of the most elusive targets in catalysis, the most challenging reaction of this type being the selective oxidation of methane to methanol. Methane, the major constituent of natural gas, is a hugely abundant and promising feedstock^[1] but its direct utilisation is hampered, given the difficulties associated with selectively upgrading this most unreactive of hydrocarbon substrates ($\Delta H_{C-H} = 104 \text{ kcal mol}^{-1}$).^[1] Tantalisingly, naturally occurring metalloenzymes are able to perform this and related oxidation reactions with ease even under mild reaction conditions, with exquisite chemo- and stereoselectivity, and with molecular oxygen as the sole, terminal oxidant.^[2] Typically, these monooxygenase enzymes possess Fe or Cu active centres, and are able to oxidise substrates through the reductive activation of dioxygen with stoichiometric reductive cofactors.^[3] During this process, various superoxo, (hydro)peroxo

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and oxo intermediates are formed, each possessing various levels of oxidising ability,^[4] although much of the cycle can be bypassed (shunted) by using more-activated oxygen donors, such as H_2O_2 .^[5]

Recently, a zeolite catalysts, CuFe-ZSM-5, was found to mediate the selective and catalytic oxidation of methane to methanol at high levels of activity and selectivity with H₂O₂ as a green oxidant.^[6] In contrast to previous zeolitic systems,^[7] this new peroxide-mediated system was both catalytic (turnover number > 10 000) and selective to the desired product, methanol (selectivity >90%), even at high levels of methane conversion.^[6a] Furthermore, in contrast to the most active and/ or selective methane oxidation catalysts reported to date,^[1] this catalytic system was found to be highly active under benign reaction conditions, and was able to catalyse the selective oxidation of methane to methanol in the aqueous phase, in the absence of any acidic promoters, at temperatures between 2 and 70 °C.^[6a]

The key to this system appears to be the heterolytic activation of H_2O_2 by active Fe species within the zeolitic micropores. Through various spectroscopic and computational methods, some of us recently demonstrated that the active Fe species for this reaction are cationic, extra-framework Fe oligomers, with the resting state of the catalyst most likely possessing two μ -hydroxo-bridged Fe atoms: $[Fe_2(\mu_2-OH)_2(OH)_2 (H_2O)_2]^{2+}$.^[6a,c] Upon activation by the oxidant, DFT calculations predict that this resting state is converted into a bifunctional active site possessing both iron-oxo and iron-hydroperoxo intermediates.^[6a,b] Such intermediates are reminiscent of many formed in biological systems, and raise the enticing prospect that this catalytic system operates in a biomimetic peroxide shunt-type process.^[2] Nevertheless, in situ characterisation of the catalyst has not yet been achieved, without which definitive identification of 1) the reactive intermediates, and 2) the precise speciation of the active site(s) operating during the reaction, cannot be obtained. This precludes further comparison to biological oxidation catalysts.

In contrast to well-defined homogeneous model catalysts, the in situ spectroscopic analysis of a heterogeneous catalyst is considerably more challenging because heterogeneous catalysts do not contain a homogeneous distribution of a single active site or species. Rather, a heterogeneous distribution of species, each displaying various levels of activity and/or selectivity, is typically found. As such, the percentage of active species may be very low, and features arising from spectator spe-



cies and/or competitive active sites may dominate or mask the spectroscopic data of interest. Unfortunately, many spectroscopic techniques are unable to differentiate between the active and spectator species, and therefore only provide an averaged signal of many different species.

To overcome this limitation, we have extended our study of this system by using resonance-enhanced UV/Raman spectroscopy.^[8] Recently, we demonstrated that the catalytic activity of Fe-containing zeolites for methane oxidation correlated to the fraction of Fe species experiencing electronic transitions between $\lambda_{(abs)} = 250$ and 350 nm, as determined by UV/Vis spectroscopy.^[6d] Indeed, more recent kinetic studies demonstrate that the initial rate of methane oxidation is intimately linked to the fraction of these extra-framework species, which are formed through high-temperature pre-treatment of the as-synthesised zeolite (Figure 1). By tuning the Raman excitation



Figure 1. Initial rate of methane oxidation with various samples of A) 0.5 Fesilicalite-1 and B) 0.5 Fe-ZSM-5, each of which contained different amounts of extra-framework Fe^{3+} . Increased formation of extra-framework Fe^{3+} was achieved by increasing the pre-treatment temperature employed (550– 900 °C) and was determined by using UV/Vis spectroscopy.

wavelength into this particular electronic transition feature (λ_{exc} =325 nm), it is possible to selectively enhance any Raman vibrations associated with those electronic transitions, thereby selectively enhancing only the species of interest, even if these species only constitute a fraction of the total metal content. Furthermore, given the low Raman cross-section of H₂O, Raman spectroscopy offers a convenient means of studying the chemistry of this catalyst in situ, despite the presence of the aqueous solvent.

Preliminary investigations focused on Fe-silicalite-1, an MFItype zeolite containing 0.5 wt% Fe and pre-activated at 550 °C (denoted henceforth 0.5 Fe-silicalite-1₅₅₀), which is both an active and selective catalyst for the oxidation of methane in the absence of additional metal promoters. It is also an active catalyst for other oxidation processes, such as that of benzene to phenol.^[6a] Full characterisation of this material by conventional methods [UV/Vis, X-ray absorption (XAS) and FTIR spectroscopies and XRD and BET analyses] was described recently.^[6c] As can be seen in Figure 2, tuning the excitation wave-





Figure 2. Raman analysis of 0.5 Fe-silicalite-1 $_{\rm 550}$ with A) 785, B) 514, and C) 325 nm laser lines.

length into the UV region ($\lambda = 325$ nm) leads to four new Raman-active bands that are not observed by using visible (λ = 514 nm) and IR (λ = 785 nm) Raman excitation sources. Thus, in addition to the signals arising from the silicalite-1 matrix, that is, heteroatom free MFI-type zeolite (at $\tilde{\nu} = 290$, 380 and 800 cm⁻¹; Figure S1, Supporting Information), a relatively broad feature between $\tilde{\nu} = 500$ and 600 cm⁻¹, with a maximum at $\tilde{\nu} = 521 \text{ cm}^{-1}$, and additional features at $\tilde{\nu} = 1013$, 1120 and 1165 cm⁻¹ are now observed. Previously, all of these bands have been assigned to tetrahedrally coordinated, isomorphously substituted framework Fe³⁺ species [Fe(OSiO₃)₄] by Bonino et al.^[9b] and Li and co-workers,^[9c] suggesting that Fe³⁺ was present exclusively in the zeolite framework. However, it is believed that such saturated framework Fe³⁺ sites are unable to coordinate reacting species, and are thus unable to participate in catalytic reactions, which is seemingly at odds with the known activity of this catalyst for methane oxidation and other reactions.^[10] Consequently, further Raman spectroscopy analysis of the Fe³⁺ speciation in Fe-containing zeolites and particularly the evolution of these species as a function of pre-treatment temperature, is required.

It is well established that, despite the initial presence of Fe³⁺ in the framework of Fe-silicalite-1 and related materials after hydrothermal synthesis, considerable changes to the speciation of Fe³⁺ occur following the high temperature treatments required to 1) remove the organic template (at 550 °C), and 2) pre-activate the catalyst for reaction (typically at temperatures between 550 and 1100 °C).^[6c, 11] In fact, recent studies by our team and other research groups have found that, even after removal of the template, a large percentage of Fe³⁺ in Fe-siliaclite-1 and Fe-ZSM-5 is located in extra-framework positions of the zeolite material^[11] and is present typically as isolated or oligomeric (hydr)oxo clusters, or even bulk Fe oxides, depending on the exact procedure employed.^[6c] To establish the influence of this migration on the Raman spectrum of 0.5 Fesilicalite-1, and to further corroborate the results obtained in Figure 1, a series of catalysts at various stages of pre-treatment were examined by using UV/Raman spectroscopy.

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Figure 3. Effect of pre-treatment on the Raman spectrum of 0.5 Fe-silicalite-1. A) As-synthesised zeolite containing template, B) NH₄-form, C) H-form, after calcination of NH₄-form at 550 °C, D) H-form, after calcination of NH₄form at 750 °C and E) H-form, after calcination of NH₄-form at 900 °C.

In good agreement with the known chemistry of these materials, considerable changes in the Raman spectra of 0.5 Fe-silicalite-1 are observed during pre-treatment, suggesting major changes in the speciation of Fe (Figure 3). The first stage in the preparation of active samples of Fe-silicalite-1 involves the removal of the organic template (tetrapropylammonium hydroxide) and conversion to the NH₄ form. During this step, the vibrations arising from the template are lost, and the spectrum already looks similar to that of 0.5 Fe-silicalite-1₅₅₀, possessing the features of the silicalite-1 framework ($\tilde{\nu}$ = 290, 380 and 800 cm⁻¹) and the Fe modes described above ($\tilde{\nu}$ = 521, 1013, 1120 and 1160 cm⁻¹).

Although the vibrations of the organic template overlap with the Fe³⁺ features in the as-synthesised material (Figure S2) and thus prohibit a full comparison, it is clear that the lower energy signal at $\tilde{\nu} = 521 \text{ cm}^{-1}$ increases in intensity upon pre-treatment relative to the silicalite-1 framework modes. Upon further pre-treatment of the catalyst, it is also clear that there is a steady increase in intensity of the $\tilde{\nu} = 521 \text{ cm}^{-1}$ band, with the relative intensity of this band at its greatest following pre-treatment at 750 °C, after which the band broadens and erodes. Conversely, it is also clear that with increasing pretreatment temperature, the $\tilde{\nu} = 1013 \text{ cm}^{-1}$ band is eroded steadily and experiences a red shift of $\pm 35 \text{ cm}^{-1}$ following pre-treatment at 750 °C. By 900 °C, this band is lost almost completely from the Raman spectrum. This indicates that the species responsible for this signal decrease in concentration with pre-treatment, which is in line with their assignment as framework Fe³⁺ species.^[9b,c] The observed red shift also indicates a relaxation in the coordinative strain of the Fe³⁺ species responsible for this vibration,^[12] further indicating the removal of Fe³⁺ from the highly strained framework positions. Changes in the position and intensity of the $\tilde{\nu} = 1120$ and 1165 cm⁻¹ vibrations are also evident and their steady decrease in intensity suggests that these species are also related to tetrahedrally coordinated framework Fe³⁺ species, in line with previous studies.^[9b,c]

It is apparent at this stage that, despite the previous assignment of all four Fe bands to framework Fe³⁺ species,^[9b,c] the story is much more complex and the Raman spectrum of 0.5 Fe-silicalite-1 contains signals arising from multiple species. We have recently established that, during the heat treatment process, several changes in the speciation of Fe³⁺ are observed.^[6c] Initially, there is a homogeneous distribution of framework Fe³⁺ after the synthetic procedure. During template removal, a large amount of Fe³⁺ migrates from the framework and initially forms a broad distribution of isolated and/or oligonuclear extra-framework cationic complexes within the zeolite micropores, which are characterised by intense electronic transitions between $\lambda = 250$ and 350 nm. These species, which correlate with catalytic activity for methane oxidation (Figure 1),^[6c,d] are maximised following pre-treatment at 750°C, with increased temperatures thereafter (900°C) only causing further agglomeration of ${\rm Fe}^{3+}$ into bulk ${\rm Fe}_2O_3.$ To date, our spectroscopic (XAS) and theoretical studies indicate that these active, extra-framework oligomers are most likely hydroxobridged binuclear Fe clusters,^[6] with the resting state of the catalyst best described as a di-µ-hydroxo-bridged Fe complex: $[Fe_2(\mu_2-OH)_2(OH)_2(H_2O)_2]^{2+}$. Notably, the self-organisation of extra-framework metal complexes into bridged, binuclear complexes was proposed recently by Pidko et al. to be spontaneous for many metallozeolites.[13]

In light of these results, it is clear that the $\tilde{\nu}\!=\!1013\ \text{cm}^{-1}$ band behaves as we would expect for a band arising from tetrahedrally-coordinated framework Fe3+: during template removal and pre-activation, the band is continually eroded as the fraction of framework Fe³⁺ diminishes. The steady, albeit slower, erosion of the $\tilde{\nu} = 1120$ and 1165 cm⁻¹ bands indicates that these bands are also related to the framework Fe³⁺ component. Their slower rate of erosion upon pre-treatment likely relates to their (partial) reliance on neighbouring Si-O-Si vibrations;^[9c] previous work has indicated that Si-O-Si vibrations in the vicinity of the framework Fe³⁺ species partially drive this Fe-O vibration and thus account for some of its spectral intensity. Nevertheless, the increase in the $\tilde{\nu} =$ 521 cm⁻¹ band as a function of pre-treatment is contrary to what we would expect for framework Fe³⁺ species. Indeed, its steady increase in intensity, especially in comparison to the negligible level found in the as-synthesised material, suggests that this feature does not arise from framework Fe³⁺ but from extra-framework Fe³⁺ species, the proposed active species for methane oxidation, which are known to increase in concentration during heat treatment.^[6c] Notably, this is the first systematic Raman spectroscopy study that follows the changes in Fe³⁺ speciation (framework vs. extra-framework) in Fe-containing zeolites as a function of essential heat pre-treatment.

To further probe this hypothesis, 0.5 Fe-ZSM-5₅₅₀ [containing 0.5 wt% Fe and 0.6 wt% Al (SiO₂/Al₂O₃ = 90), pre-activated at 550 °C] was studied subsequently by using UV/Raman spectroscopy. Recently, we established that this catalyst was substantially more active for methane oxidation than its Al-free analogue 0.5 Fe-silicalite-1₅₅₀, and that it contained substantially more extra-framework (and catalytically active) Fe³⁺ species at any given pre-treatment temperature.^[6d] In line with the hy-

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pothesis that the $\tilde{\nu} = 521 \text{ cm}^{-1}$ band arises from the extraframework and catalytic Fe³⁺ content of these materials, this band is substantially more intense and prominent in 0.5 Fe-ZSM-5₅₅₀ than in 0.5 Fe-silicalite-1₅₅₀ (Figure 4).



Figure 4. Comparison of A) 0.5 Fe-ZSM-5 and B) 0.5 Fe-silicalite-1, both after calcination at 550 $^\circ$ C. C) 0.5 Fe-ZSM-5_{550} after treatment with H_2O_2.

The assignment of the $\tilde{v} = 521 \text{ cm}^{-1}$ band to extra-framework Fe³⁺ complexes is well-supported by Raman and IR spectroscopic analysis of model homogeneous compounds and DFT calculations. For instance, the Raman-active (symmetric) stretching mode of various bridged binuclear Fe complexes has been shown to appear between $\tilde{\nu} = 400$ and $600 \text{ cm}^{-1[14]}$ and is known to be resonance-enhanced by low-wavelength lasers ($\lambda = 300-400$ nm).^[15] Indeed, Sanders-Loehr et al. identified that the exact location of this Raman active stretching mode was highly dependent upon the precise Fe-O(H)-Fe angle of the binuclear Fe complex under study,^[15] with smaller angles shifting the stretching frequency to higher energy. By graphically plotting the data of Sanders-Loehr et al., a correlation between the Fe–O(H)–Fe angle and stretching frequency was obtained.^[15] Our previous DFT and spectroscopic studies have indicated that the potential active site for methane oxidation is consistent with a di-bridged, µ-hydroxo diiron complex, possessing Fe–O(H)–Fe angles between \pm 95 and 110°.^[6a,b] A comparison of this DFT-calculated Fe-O(H)-Fe angle in 0.5 Fe-ZSM-5₅₅₀^[6a,b] with the systematic data of Sanders-Loehr et al. reveals that an Fe–O(H)–Fe stretching frequency between $\tilde{\nu} =$ 539 and 580 cm⁻¹ should be observed in this material. As can be seen, this is in excellent agreement with the experimental data. To further validate this assignment, the Raman spectrum of a cation-exchanged $[Fe_2(\mu_2-OH)_2(OH)_2(H_2O)_2]^{2+}$ complex was also calculated by DFT. These simulations predicted that two Fe–O(H)–Fe stretching vibrations at 521 and $\tilde{v} = 574 \text{ cm}^{-1}$ should be observed in 0.5 Fe-ZSM-5550, in full agreement with the experimental data (Figure S3 and Ref. [6b]). Thus, in combination with our previous XAS results,^[6a] which imply that a large fraction of dimeric Fe species is present in this material,^[6a] we propose that the $\tilde{\nu} = 521 \text{ cm}^{-1}$ feature arises from binuclear Fe species and not from catalytically inactive framework Fe³⁺ species, as proposed previously. In regards to the broadness of the $\tilde{\nu}$ =521 cm⁻¹ feature, which has a span of approximately $\tilde{\nu}$ =100 cm⁻¹, we propose that this catalyst likely contains a number of bi- and/or oligonuclear Fe complexes of various geometry and speciation, each of which would possess slightly different stretching frequencies. Although this phenomenon is unfortunately undetectable by using XAS, which provides only an averaged signal of all the species present in a heterogeneous catalyst, it further demonstrates the potential of resonance-enhanced Raman spectroscopy for studying heterogeneous catalysts that contain complex active-site distributions.

To determine whether the species responsible for this stretch is active in H₂O₂-based oxidations and if it may be the active site for C-H activation and methane oxidation, treatment of the catalyst with aqueous H₂O₂ was subsequently examined. As can be observed, this resulted in the complete loss of the proposed Fe–O(H)–Fe stretch from the Raman spectrum and strongly suggested that this species was responsible both for H₂O₂ activation and subsequent methane oxidation (Figure 4C). The complete loss of the $\tilde{\nu} = 521 \text{ cm}^{-1}$ vibration indicated that, upon coordination and activation of H_2O_2 , the bridges between the two Fe atoms were cleaved, likely through protonation following heterolysis of H₂O₂. This would lead to the formation of two transient, mononuclear Fe³⁺ sites, which would operate in a cooperative manner in the remaining catalytic cycle. Nevertheless, this cleavage of the Fe–O(H)–Fe core of the catalyst was reversible, as even moderate irradiation under the UV laser regenerated the $\tilde{\nu}$ = 521 cm⁻¹ band to some extent, and reheating the sample to 110°C completely restored the same band (Figure S4). The shift between dimer and transient monomeric structure (and vice versa) demonstrated the flexibility of the Fe³⁺ sites for mediating this complex catalytic mechanism. Similar "transient self-organisation" also played a role in the activation of glucose by transient Cr²⁺ dimers, as identified by Pidko et al.^[16]

Nevertheless, no new vibrations corresponding to potential iron–(hydro)peroxo or iron–oxo complexes are observed in the UV/Raman spectrum of $H_2O_2/0.5$ Fe-ZSM-5₅₅₀, preventing the acquisition of further mechanistic insight. This might be due to the known instability of various metal–(hydro)peroxides and metal–oxo species, which are notoriously difficult to characterise under the intense Raman beam. However, it is also possible that the potential metal–oxygen intermediates formed in this system do not undergo resonance enhancement under the same conditions as the Fe³⁺ species present within the Fe-containing zeolites themselves. Indeed, iron–oxo, iron–superoxo and iron–(hydro)peroxo complexes typically experience intense electronic transitions in the visible and/or IR regions.^[17–21]

Although shifting the excitation wavelength to the visible region (λ_{exc} =514 nm) leads to the loss of Fe-specific modes at $\tilde{\nu}$ =521, 1013, 1120 and 1160 cm⁻¹ through a lack of resonance enhancement, two new H₂O₂-related features are observed under visible light excitation (Figure 5). The first of these features arises from the v(O–O) of physisorbed H₂O₂ ($\tilde{\nu}$ = 874 cm⁻¹) and is unrelated to any Fe coordination (Figure 5C, Figure S1B). However, the vibration observed at $\tilde{\nu}$ =631 cm⁻¹



Figure 5. Vis/Raman spectrum of A) 0.5 Fe-ZSM-5 $_{550}$ B) $H_2O_2/0.5$ Fe-ZSM-5 $_{550}$ and C) $H_2O_2/silicalite-1_{550}.$

is consistent with a v(Fe–O) stretch, as demonstrated through numerous sophisticated labelling studies,^[18-21] and is characteristic of model Fe^{III}-OOH complexes, such as [Fe(bbpc)-(MeCN)(OOH)]SbF₆ (bbpc = N,N'-di(phenylmethyl)-N,N'-bis-(2-pyridinylmethyl)-1,2-cyclohexanediamine, $\tilde{\nu} = 632 \text{ cm}^{-1}$),^[17] $(\tilde{\nu} = 632 \text{ cm}^{-1}),^{[19]}$ $[(N_4Py)Fe(OOH)]^{2+}$ $[(H_2 bppa)Fe(OOH)]^{2+}$ (bppa = bis(2-picolyl)(2-hydroxy-3,5-di-tert-butylbenzyl)amide, $\tilde{\nu} = 621 \text{ cm}^{-1})^{[20]}$ and $[(TMC)Fe(OOH)]^{2+}$ (TMC = 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane, $\tilde{\nu} = 658 \text{ cm}^{-1}$).^[21] This indicates that an Fe^{III}-OOH intermediate is present in 0.5 Fe-ZSM-5₅₅₀ following activation of the catalyst with aqueous H_2O_2 . Although the accompanying v(O–O) stretch of Fe^{III}–OOH is not discernible between $\tilde{v} = 750$ and 800 cm⁻¹, this is likely due to its extremely weak Raman scattering intensity compared to the v(Fe-O) stretch^[18] and the unfortunate overlap with the $\tilde{\nu} = 800 \text{ cm}^{-1}$ vibration of the MFI framework, decreasing the detection limit.

Nevertheless, to further verify the identity of the intermediate, we investigated the activation of other peroxides known to undergo heterolysis in the presence of Fe³⁺.^[22] Upon substitution of the H atom of H₂O₂ for a *tert*-butyl group (*tert*-butyl hydroperoxide), bands at $\tilde{\nu} = \pm 495$, 715 and 798 cm⁻¹ were observed (Figure S5). These were consistent with those found in other Fe–OO(tBu) complexes^[23] and confirmed the ability of the Fe species in Fe-ZSM-5/Fe-silicalite-1 to mediate the formation of (hydro/alkyl)peroxides by heterolysis. These band have been attributed to tert-butyl deformation containing considerable v(Fe–O) character ($\tilde{\nu} = 492 \text{ cm}^{-1}$) and the v(Fe–O) ($\tilde{\nu} =$ 715 cm⁻¹) and v(O-O) stretches ($\tilde{v} = 798 \text{ cm}^{-1}$) of Fe–OO(tBu).^[23] Notably, these vibrations are not observed upon treatment of Fe-free zeolites (such as silicalite-1 and H-ZSM-5) with tert-butyl hydroperoxide, confirming that the presence of Fe³⁺ is critical to the formation of this reactive intermediate, in excellent agreement with our catalytic studies.

Conclusions

Fe-containing zeolites, such as Fe-silicalite-1 and Fe-ZSM-5, are well-known catalysts for various selective oxidation processes,

including the low-temperature oxidation of methane to methanol. In the first part of this study, in depth characterisation of these materials with resonance-enhanced Raman was performed. Our full, systematic study of the heat pre-treatment process has revealed that the active site speciation of Fe³⁺ in these materials is particularly complex and that a range of both framework and extra-framework Fe³⁺ species are present in these materials. The precise ratio of these species is highly dependent on the pre-treatment temperature. Notably, this provides significantly greater levels of insight than previously reported Raman studies of these materials, which did not fully monitor the heat pre-treatment processes and consequently proposed that a homogeneous distribution of framework Fe³⁺ sites was present. Most important amongst the Raman features is a prominent, broad band at $\tilde{\nu} = 521 \text{ cm}^{-1}$, which correlates favourably to the catalytic activity of these materials for methane oxidation. Comparison of the Raman spectra against literature studies of model compounds, our DFT calculations, our previous X-ray absorption, and UV/Vis spectroscopy studies reveals that the species responsible for this feature is both extraframework and binuclear in nature. Treatment of the catalyst with aqueous H₂O₂ also reveals this species to be responsible for H₂O₂ coordination during methane oxidation.

This work also provides the first in situ spectroscopic study of the Fe-containing zeolites that are able to catalyse methane oxidation in the aqueous phase. Our in situ Raman spectroscopy studies monitoring the treatment of Fe-ZSM-5 with H_2O_2 (tert-butyl hydroperoxide) reveal that the analogous Fe-OOH (Fe–OO(tBu)) intermediates are present during the reaction cycle and that these intermediates are formed by heterolysis of the peroxide by the binuclear Fe³⁺ species. The identification of an Fe^{III}-OOH intermediate in Fe-containing zeolites gives further support to our previously calculated reaction mechanism^[6a] and provides spectroscopic evidence that this catalytic system contains at least some similarities to biological oxidation systems. Fe^{III}-OOH is known to be a key precursor to the most potent C-H activating oxidant in biological catalystshighly electrophilic iron-oxo species-and its conversion to the iron-oxo moiety through O-O homolysis or heterolysis is well-established. $^{\mbox{\tiny [2-4]}}$ We reason that the lack of evident signals associated with the oxo species arises from 1) the overlap of the MFI framework feature at $\tilde{\nu} = 800 \text{ cm}^{-1}$ and 2) its extremely short lifetime under the conditions employed in this study (τ < 7 s at 25 $^{\circ}$ C in water).^[24] Indeed, although H₂O is a relatively benign solvent for catalytic applications, it severely restricts the possibility of detecting the ultimate high-valent iron-oxo species, which to date has been detected only at sub-ambient temperatures with soluble catalysts.^[25] Identification of the elusive iron-oxo species, and detailed microkinetic analysis of the reaction intermediates formed, are therefore required to gain deeper insight into the potential biomimetic properties of this catalytic system, and are the target of future research studies with additional, advanced in situ spectroscopic techniques.



Experimental Section

Catalyst preparation

Fe-containing ZSM-5 and silicalite-1 were prepared as described elsewhere.^[6a] Tetraethylorthosilicate (Sigma–Aldrich, 99.999%, trace metal basis), iron nitrate (Sigma–Aldrich, 98%) and sodium aluminate (Sigma–Aldrich, 50–55 wt% Al₂O₃) were used as the Si, Fe and Al sources, respectively. Tetrapropylammonium hydroxide (Sigma–Aldrich, 20 wt% in water) was used as a structure-directing agent. Crystallisation was performed in a stainless-steel autoclave at 175 °C for 120 h. The as-synthesised materials were pre-treated at various temperatures (550 °C–900 °C) to induce migration of Fe³⁺ sites to the extra-framework, following prior occlusion of the organic template and ion exchange with NH₄NO₃.

Catalyst testing

Catalytic evaluation was performed in a 50 mL stainless-steel autoclave (working volume 35 mL). The vessel was charged with an aqueous solution of H_2O_2 (10 mL, 0.5 M) and the desired amount of catalyst (27 mg). The reactor was pressurised with methane (3.05 MPa) and the autoclave heated to the reaction temperature (50 °C) with stirring at 1500 rpm once the desired temperature was obtained. Following the appropriate reaction time, the vessel was cooled in ice (12 °C) and the resultant solution filtered and analysed by using ¹H NMR spectroscopy. Analysis was performed on a Bruker 500 MHz Ultra-Shield NMR spectrometer and reactant products were quantified against a 1 vol% TMS/CDCl₃ internal standard.

Catalyst characterisation

Raman spectroscopic analysis was performed on a Renishaw inVia Raman microscope with laser excitation wavelengths of $\lambda = 325$, 514 and 785 nm. Solid sample measurements were performed inside a Raman cell at 10 mW power, with a total of 256×2 s accumulations. No organic species were present in the material. H₂O₂treated samples were measured at 1 mW power, with 50×2 s scans performed. Metal contents were determined by using inductively coupled plasma atomic emission spectroscopy to an accuracy of 10%. Supporting characterisations have been described elsewhere.^[6c,d]

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Biomimetic Oxidation with Fe-ZSM-5 and H₂O₂? Identification of an Active, Extra-Framework Binuclear Core and an Fe^{III}–OOH Intermediate with Resonance-Enhanced Raman Spectroscopy



A pre-ferryl cat: Through in situ resonance-enhanced Raman spectroscopy, we identify an active, binuclear Fe–O(H)–Fe core and an Fe^{III}–OOH intermediate in Fe-containing ZSM-5 following activation with H_2O_2 . The preferryl nature of this biomimetic intermediate may account for the unique ability of this solid catalyst to selectively oxidise methane to methanol under mild conditions.