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Aqueous phase methane oxidation over Fe-MFI zeolites; promotion through isomorphous framework substitution

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ABSTRACT: Fe and Cu-containing zeolites have recently been shown to be efficient catalysts for the one-step selective transformation of methane into methanol in an aqueous medium at only 50 °C, using H_2O_2 as green oxidant. Previously, we have observed that Fe species alone are capable of catalysing this highly selective transformation. However, further catalytic testing and spectroscopic investigations demonstrates that although these extra-framework Fe species are the active component of the catalyst, significant promotion is observed upon the incorporation of other trivalent cations *e.g.* Al³⁺, Ga³⁺, into the MFI-framework. Whilst these additional framework species do not constitute active catalytic centres, promotion is observed upon their incorporation as they (1) facilitate the extraction of Fe from the zeolite framework, and hence increase the formation of the active Fe species, and (2) provide an associated negatively-charged framework, which is capable of stabilizing and maintaining the dispersion of the catalyst (Fe *and* Al), we have subsequently been able to prepare a catalyst of equal intrinsic activity (*i.e.* TOF) but five-times higher productivity (*i.e.* space-time-yield) to the best catalysts reported for this reaction to date.

1 Introduction

Natural gas is a highly abundant source of hydrocarbons that is primarily composed of methane (*ca.* 85 vol. %), and represents one of the major building blocks of the present day chemical industry.¹⁻³ Nevertheless, its conversion to various chemicals and fuels currently requires the intermediate manufacture of synthesis gas, and subsequent conversion to higher hydrocarbons or commodity chemicals through Fischer-Tropsch type chemistry.⁴ During various stages of these processes, extremely high temperatures and pressures are required, thus resulting in high operational costs and significant capital investment.

As such, the development of alternative and less economically intensive routes for the selective transformation of natural gas, or methane in particular, to various value-added products is of particular interest. Of greatest promise is the transformation of methane to more energy dense liquid derivatives, such as methanol, formic acid or mid-range hydrocarbons. Along with being useful as chemical building blocks *e.g.* methanol-toolefin technology,⁵ these liquid derivatives are significantly easier and cheaper to transport around the globe; like many fossil reserves, a large fraction of the natural gas reserves is inconveniently located in various inaccessible parts of the globe. In contrast to crude oil, the transportation of this volatile and flammable gas to existing technological sites presents considerable safety and economic issues. The conversion of methane to more energy dense liquid derivatives, particularly at the point of origin, could lead to significant breakthroughs in the utilisation of natural gas as a primary feedstock.

The primary obstacle and more challenging aspect of this reaction stems from the fact that methane is the least reactive of all hydrocarbons, with very high C-H bond strengths of 438.8 kJ mol⁻¹. Consequently, conditions that are sufficient to activate methane also have the undesired effect of activating the partial oxidation products toward deeper oxygenated products (CO_x), since bond strengths in these oxygenated species are typically much lower ($\Delta H_{C-H} = 373.5$ kJ mol⁻¹ for methanol). Thus, at high temperatures the formation of deeper oxygenated products such as CO and CO₂ is generally unavoidable, which limits the overall reaction selectivity. In view of this, it is apparent that the selective oxidation of methane can only be achieved by developing new catalytic systems that are able to oxidise methane at mild temperatures (≤ 200 °C), as this may provide some inherent selectivity to the partial oxidation products by operating under kinetic rather than thermodymanic control.

Whilst a number of low temperature approaches have been proposed in recent times, each approach is typically limited by low catalytic rates *i.e.* low turnover frequencies/space-timeyields, or environmental issues concerning the solvent system or chosen oxidant.¹ For example, whilst the electrophillic activation of methane by bipyramidal platinum complexes yields methyl bisulphate at high selectivity (81 % at > 90 % conversion), this and related systems are limited by the highly corrosive solvent system (oleum), low intrinsic activity (TOF < 10 h^{-1}) and the lack of a fully-closed catalytic cycle.^{6,7} An alternative approach has focused upon on the use of Fe(Cu)containing zeolites for the selective oxidation of methane with ¹³ Whilst these materials do exhibit a remarkable $N_2O(O_2)$. ability to activate methane, the product in both cases is a strongly chemisorbed methoxy species that cannot readily desorbed or be isolated without destruction of the catalytic active sites, thus resulting in a non-catalytic process. Alternative approaches using both encapsulated¹⁴ or supported^{15,16} Fephthalocyanine complexes have also been proposed, but these systems are limited by very low intrinsic activities, maximum methanol selectivities of 50 %, and catalyst stability issues.¹⁷

We have demonstrated that Fe-containing MFI-type zeolites are capable of not only oxidising methane at high catalytic rates ($\leq 14,500 \text{ h}^{-1}$) and partial oxygenate selectivity *i.e.* selectivity to oxidation products not including CO and CO₂ (≥ 90 %), but that this favourable transformation can be carried out in an environmentally benign process at only 50 °C, in the aqueous phase and with hydrogen peroxide as the chosen oxidant.¹⁸ Moreover, although the Fe-only system was primarily selective to formic acid, we have demonstrated that the addition of Cu²⁺ to these highly reactive Fe-containing zeolites eliminates the methanol over-oxidation process, thereby allowing methanol to be obtained at over 90 % selectivity at methane conversions of up to 10 %.^{18,19}

Recently, we demonstrated that the catalytic activity of these materials corresponds to the formation of extra-framework Fe³⁺ species that reside within the zeolite micropores.²⁰ Whilst bearing some resemblance to the solid-state chemistry exhibited by these materials during activation for N2O-based oxidations, key evidence has indicated that the active species formed in this system for selective and catalytic methane oxidation with H₂O₂ are fundamentally different to those found for these other stoichiometric oxidation systems, given the different pre-activation procedures employed.²⁰ However, a major question remains. Whilst Fe alone in Fe-silicalite-1 is capable of catalysing the reaction, significantly higher turnover frequencies have been observed for an Fe and Alcontaining systems (such as commercial zeolite ZSM-5), despite the catalytic inactivity of Al³⁺ and its related properties for this reaction.¹⁸ In this publication we now focus on this key aspect in order to develop a more detailed understanding of this unique methane oxidation catalyst, and subsequently produce significantly more active catalysts for this challenging reaction.

2 Results and Discussion

Material synthesis. To determine the precise role(s) of Al³⁺. analogous samples of silicalite-1, ZSM-5, Fe-silicalite-1 and Fe-ZSM-5 were first prepared by hydrothermal synthesis. In particular, this was necessary in order to avoid issues associated with comparing samples obtained from different sources (commercial material vs. laboratory prepared material) and that contained different Fe loadings. To achieve this comparison, Al-only (ZSM-5), Fe-only (Fe-silicalite-1), Fe and Alcontaining (Fe-ZSM-5) and metal-free (silicalite-1) analogues were prepared by an identical, benchmarked²⁰ hydrothermal synthesis procedure (Table 1), and later screened for activity (Table 2). We note here that the pre-treatment temperature employed during activation of the catalyst is provided as a subscript following the description of the catalyst, and that the SiO₂/Al₂O₃ ratio – where applicable – is provided in parenthesis. Additionally, the Fe loading of the catalyst – where applicable – is provided prior to the catalyst description e.g. Fecontaining ZSM-5, containing 0.5 wt. % Fe and a SiO₂/Al₂O₃ mole ratio of 84, and pre-treated at 550 °C, is denoted 0.5Fe-ZSM-5 (84)550. As demonstrated by XRD analysis (Extended Supplementary Information (ESI) Figure S1), each of the synthesised samples possesses the crystalline MFI structure. Coupled with the similar surface areas $(\pm 330 \text{ m}^2 \text{ g}^{-1})$ and microprorous volumes (± 0.13 cm⁻³ g⁻¹), it can be concluded that each synthesised solid possesses comparable physical properties. In view of this, each sample was subsequently evaluated for catalytic activity following activation at 550 °C.

Table 1. Physical and chemical properties of a series of Aland Fe-containing MFI-type zeolites, prepared by hydrothermal synthesis.

Catalyst	Fe content (wt. %) [‡]	Molar ratio		$\mathbf{S}_{\mathrm{BET}}$	V _{MICRO}
		SiO ₂ /	SiO ₂ /	$(m^2 g^{-1})$	$(cm^3 g^{-1})$
		Fe_2O_3	Al ₂ O ₃		
silicalite-1550	< 0.001	-	-	330	0.13
ZSM-5 (86)	0.003	-	86	340	0.14
550					
Fe-silicalite-	0.52	250	-	330	0.13
1 ₅₅₀					
Fe-ZSM-5(84)	0.49	254	84	310	0.14
550					

 \ddagger Determined by ICP-OES. Values are accurate to ± 10 %.

In line with our previous studies, the synthesis of metal-free silicalite- 1_{550} and Al-only ZSM-5 (86)₅₅₀ does not lead to materials with any significant activity for this reaction.¹⁸⁻²⁰ This is in agreement with our previous observations that catalytic activity for methane oxidation with H₂O₂ can only be achieved when sufficient quantities of Fe³⁺ are present within the catalyst, and that the presence of Brønsted and Lewis acid sites (from framework Al³⁺), and/or a microporous framework alone, are insufficient for catalysis to be observed. In fact, we have previously attributed the very minor catalytic activity of our synthesised ZSM-5 materials to be related to their low but non-negligible Fe³⁺ content (Table 1).²⁰

 Table 2. Catalytic activity of analogous samples of a series of
Al- and Fe-containing MFI-type zeolites, prepared by hydrothermal synthesis.

Catalyst	Product	Sum of products	Oxy. sel.			
	МеОН	НСООН	MeOOH	$CO_2(g)$	(μmol)	(%)
silicalite-1550	0.0	0.0	0.0	0.0	0	-
ZSM-5 (86)	1.5	0.8	2.3	1.6	6.2	74
Fe-silicalite- 1 ₅₅₀	17.6	56.1	11.0	6.4	91.1	93
Fe-ZSM- 5(84) ₅₅₀	20.1	158.5	3.0	15.8	197.4	92

Reaction conditions; cat: various (27 mg); P_(CH4): 30.5 bar; [H₂O₂]: 0.5 M; temp: 50 °C; time: 30 min; stirring speed: 1500 rpm; Note: Each catalyst was calcined at 550 °C for 3 h in air prior to use.

The requirement for Fe^{3+} is well emphasised by comparing entries 1 and 3 of Table 2, where it can be observed that the incorporation of a low amount of Fe3+ (0.5 wt. %) into the inactive silicalite-1 material leads to large increases in catalytic activity. As expected in the absence of a Cu²⁺ additive, which we have shown to be critical for maintaining MeOH selectivity,¹⁸⁻²⁰ the major product formed with 0.5Fe-silicalite-1 is HCOOH (at 62 % selectivity), though the selectivity to partial oxygenates (MeOOH, MeOH and HCOOH) remains high (93 %) and the selectivity to CO_2 (7 %) remains very low. Nevertheless, in spite of the minimal catalytic activity of Alonly ZSM-5 (Entry 2, Table 2), 0.5Fe-ZSM-5 (84), again comprising only 0.5 wt. % Fe, is over two-times more active than the analogous sample of 0.5Fe-silicalite-1, following the addition of only 0.6 wt. % Al (Table 2, compare entry 4 vs. 3). Additionally, although the catalyst is over twice as active, no significant loss of partial oxygenate selectivity was observed (92 %), though HCOOH selectivity was marginally higher (80 %), likely as a consequence of the increased conversion. Given that these samples were prepared by the same method, and contain similar physical and chemical properties (Fe content, surface areas and pore volumes), it is highly unlikely that the reactivity differences observed can be related to changes in the physical properties of the zeolite, or potential secondary factors such as diffusion. Indeed, it can be assumed that the only difference in these samples is the Al³⁺ content, and hence the simultaneous presence of Fe³⁺ and Brønsted/Lewis acid sites. This conclusively demonstrates that the presence of Al^{3+} is highly beneficial to the activity of the catalyst. Whilst it cannot be forgotten that the addition of Al³⁺ does increase the hydrophilicity of the MFI-framework, the very dilute levels of Al^{3+} in 0.5Fe-ZSM-5 (84)₅₅₀ (SiO₂/Al₂O₃ = 84) does not majorly change the hydrophobic nature of the sample, and since the diffusion of both a hydrophobic (methane) and hydrophilic (H₂O₂) reactant is required for reaction, changes in the hydrophil-/phob-icity of the samples is unlikely to be responsible for the observed difference in catalytic activity. We stress here that in agreement to our previous publications,¹⁸⁻²⁰ each catalyst was found to be heterogeneous *i.e.* leaching of an active homogeneous catalyst into solution did not occur (Figure S2).

This raises the important question regarding the precise role(s) of Al^{3+} . Indeed, even for the more thoroughly established N₂Obased oxidations, the role(s) of Al³⁺ in the same or similar materials is still the subject of much debate. For instance, Hensen et al. have reported that only MFI materials containing both Fe and Al exhibit catalytic activity for N₂O-based oxidations, as the active site in these cases is an extra-framework mixed oxide (Fe-O-Al).²¹ A number of other reports also conclude that Al³⁺ itself, or the Brønsted acid sites associated with framework Al³⁺ also constitute active catalytic centres for such reactions.²² It has also been reported that Al³⁺ facilitates the auto-reduction of Fe^{3+} to Fe^{2+} , which is the active state of Fe for both benzene hydroxylation and N2O decomposition. Furthermore, the ability of Al^{3+} to aid the extraction of Fe^{3+} from the framework of the zeolite (and thus form active extraframework species) is also widely reported.²³ Finally, it is also known that the associated cation-exchange site of the AlO_4 tetrahedron is able to stabilise cationic extra-framework complexes.^{24,25} Nevertheless, it should not be overlooked that the activation procedures employed for this reaction are fundamentally different to those utilised for N₂O-based oxidations, and that different Fe species apparently catalyse these different reactions.

Extraction of framework Fe³⁺. We have previously demonstrated that although a homogeneous distribution of framework Fe³⁺ is found within as synthesised zeolite, significant changes to the speciation of Fe3+ are observed following the two heat pre-treatment procedures required to (1) remove the residual organic template, and (2) to further activate the material prior to catalysis (Scheme 1).²⁰ Specifically, we observed that during removal of the organic template (pre-treatment 1) and further activation (pre-treatment 2), Fe³⁺ migrates from coordinatively saturated framework sites, to form extraframework Fe³⁺ cations that take up position within the zeolite channels. Indeed, this migration to the extra-framework was found to be a pre-requisite for attaining high levels of activity, and a positive correlation ($R^2 = 0.92$) between the fraction of these species and catalytic activity was observed.²⁰ Considering this, it seemed important to us to establish whether the migration of Fe³⁺ to the extra-framework is greater when Al³⁺ is also present in the structure. In fact, it has previously been reported that along with Fe³⁺ being less stable than Al³⁺ in the ZSM-5 framework, the stability of Fe³⁺ within the MFI framework is significantly lower in ZSM-5 than in silicalite- $1.^{21}$



Scheme 1. Activation procedures employed for 0.5Fe-silicalite-1 and 0.5Fe-ZSM-5 (84). Removal of the template at 550 °C and ion-exchange with NH₄NO₃ leads to an NH₄-form zeolite. Further activation (\geq 550 °C) yields the H-form of the zeolite. This scheme was originally published in reference 20.

The ligand to metal charge transfer (LMCT) bands (Fe³⁺ \leftarrow O) within the UV-Vis spectra of Fe-containing zeolites is an ideal method for studying the extraction of Fe³⁺ from the framework of the zeolite, due to the distinct absorbances found for Fe species in different geometrical positions and coordination environments within the zeolite.²⁶⁻³¹ There are of course some inherent limitations in regards to utilising UV-Vis as a fully quantitative tool. For example, deviations in the precise molar extinction coefficients (ϵ) of various absorbing species, and the presence of (multiple) broad, overlapping bands, make full quantification an extreme challenge. Nevertheless, for Fecontaining zeolites, it has been shown that the ε values are equal to the same order of magnitude,³² and that the multiple bands can adequately be fitted by using single bands corresponding to (1) framework Fe species (200-250 nm, λ_1), (2) isolated and oligomeric extra-framework Fe cations within the zeolite channels (250-350 nm, λ_2), (3) larger Fe clusters (350-450 nm, λ_3) and finally (4) bulk Fe oxides on the surface of the zeolite (> 450 nm, λ_4). Moreover, any deviations of these factors will also be systematic over the entire series of pretreated catalysts, and will still provide empirical and semiquantitative insights in regards to the precise changes in speciation of Fe³⁺ in these materials as a function of preatment and/or A1³⁺ incorporation



Figure 1. Diffuse Reflectance UV-Vis spectra for 0.5Fe-silicalite- 1_{550} (blue/solid) and 0.5Fe-ZSM-5 (84)₅₅₀ (red/dashed) both containing \pm 0.5 wt. % Fe³⁺ and calcined at 550 °C in air.

Given the increased levels of absorbance at wavelengths at or above 250 nm - which correspond to extra-framework Fe³⁺ species – it is clear that following template removal and identical activation procedures (550 °C, 3 h in air), more extensive Fe³⁺ migration has indeed taken place in 0.5Fe-ZSM-5 (84)₅₅₀ versus 0.5Fe-silicalite-1₅₅₀ (Figure 1). Given that our previous studies correlated catalytic activity to extra-framework Fe species within the zeolite micropores,²⁰ it is logical that the increased dislodgement of framework Fe³⁺ to the extraframework observed for 0.5Fe-ZSM-5₅₅₀ at identical pretreatment temperatures would result in an increase in catalytic activity.

The relationship between extra-framework Fe species within the micropores and catalytic activity, especially in regards to the disparate activities of 0.5Fe-ZSM-5 (90) and 0.5Fesilicalite-1, is even more clearly displayed through full deconvolution of the observed UV-Vis spectra into the four relevant sub-bands (Table 3).

Table 3. Deconvolution data for 0.5Fe-silicalite- 1_{550} and 0.5Fe-ZSM-5 (84)₅₅₀, both containing \pm 0.5 wt. % Fe³⁺, after template removal and heat pre-treatment at 550 °C.

Catalyst	Relative contribution of each λ range (nm)			
	λ_1	λ_2	λ_3	λ_4
0.5Fe-silicalite- 1 ₅₅₀	0.627	0.337	0.025	0.011
0.5Fe-ZSM-5 (84) ₅₅₀	0.422	0.542	0.027	0.009

Although the aforementioned issues do not allow us to calculate an exact percentage of each type of Fe species, calculating the relative contributions of each area of the UV-Vis absorption spectra demonstrates that whilst significant Fe³⁺ migration is observed for the activated form of 0.5Fe-silicalite-1₅₅₀, it is evident that following identical heat pre-treatment procedures, significantly more Fe³⁺ has migrated from the tetrahedral framework sites in 0.5Fe-ZSM-5 (84)₅₅₀. In fact, following template removal and activation at 550 °C, the majority of Fe³⁺ can be assigned to extra-framework species in 0.5Fe-ZSM-5 (84)₅₅₀, clearly displaying the remarkably low stability of framework Fe³⁺ in this sample. This also demonstrates the lower stability of framework Fe³⁺ in ZSM-5 than in silicalite-1, an observation that is supported by the available literature.²¹

Most notably, a significantly higher fraction of extraframework Fe cations within the micropores is present in 0.5Fe-ZSM-5 (84)₅₅₀ than in 0.5Fe-silicalite-1₅₅₀. This is highly significant, as we have previously demonstrated through computational¹⁸ and spectroscopic²⁰ studies that these Fe³⁺ species are most likely the species that are responsible for the catalytic activity displayed by this catalyst the for selective oxidation of methane. In fact, if one were to assume that all of these Fe species in these samples were active, and that no other Fe species impact catalytic activity whatsoever, we would expect 0.5Fe-ZSM-5 (84) 550 to be around 1.6 times more active than 0.5Fe-silicalite-1₅₀ under these conditions, which is in good, but not perfect, agreement to the observed activities; 0.5Fe-ZSM-5 (90)₅₅₀ being 2.1 times more active than 0.5Fesilicalite-1₅₅₀ (Table 2). We stress here that through UV-Vis spectroscopy alone it is not possible to be more specific regarding the nature and composition of these extra-framework species, as there are a large number of potential species that could contribute to this broad absorbance feature *i.e.* isolated extra-framework Fe³⁺ species, dimers, trimers and small oligomers are all expected to absorb within this region. However, whilst not the purpose of this publication, our previous EXAFS studies and DFT calculations have suggest that the active extra-framework clusters contain between one and three Fe atoms, with the best match for experiment and theory being obtained for Fe₂(μ_2 -OH)₂(OH)₂(H₂O)₂]²⁺₁₈, a binuclear active site that comprises an overall +2 charge.

It seems reasonable, therefore, that, since greater Fe^{3^+} migration is observed in 0.5Fe-ZSM-5 (84)₅₅₀ than in 0.5Fesilicalite-1₅₅₀ following identical activation procedures, the Alcontaining analogue would display higher levels of activity. In such a case, Al³⁺ would not so much act as a catalytic promoter, but behave as a structural promoter for increasing the probability of forming the active species. In such a case, it should be possible to form an equally active sample of 0.5Fesilicalite-1₅₅₀ just by increasing the pre-treatment (activation) temperature, in order to obtain a similar distribution of Fe³⁺ species. To verify whether the increased activity observed for 0.5Fe-ZSM5 (84)₅₅₀ over 0.5Fe-silicalite-1₅₅₀ was simply due to an insufficient pre-treatment of Fe-silicalite-1 *i.e.* whether Al³⁺ did indeed promote the catalyst, or if the pre-treatment of Fe-silicalite-1 was simply not optimised to achieve the same level of extra-framework Fe³⁺, and hence activity, both NH₄-form samples of 0.5Fe-ZSM-5 (84) and 0.5Fe-silicalite-1 were pre-treated at different temperatures, in order to determine the maximum activity possible for each sample (Figure 2).



Figure 2. Catalytic activity of 0.5Fe-silicalite-1 (blue bars/left) and 0.5Fe-ZSM-5 (84) (red bars/right), following high temperature pre-treatment. The temperature of pre-treatment is denoted in parenthesis. Reaction conditions; cat: various (27 mg); $P_{(CH4)}$: 30.5 bar; $[H_2O_2]$: 0.5 M; temp: 50 °C; time: 30 min; stirring speed: 1500 rpm; catalyst pre-treatment: various °C, 3 h, air.

As we previously demonstrated for 0.5Fe-silicalite-1, both ammonium-form samples of 0.5Fe-silicalite- 1_{NH4} and 0.5Fe-ZSM- 5_{NH4} show considerable levels of activity, due to the migration of Fe³⁺ from the framework sites that occurs during removal of the organic template (Scheme 1). Nevertheless, considerable increases in catalytic activity of both materials can be achieved following a second high-temperature pretreatment. However, whilst it is clear that an activation temperature of 550 °C is optimal for 0.5Fe-ZSM-5 (84)₅₅₀, 0.5Fe-silicalite-1 does not reach its maximum catalytic activity until a pre-treatment temperature of 750 °C is utilised. At significantly higher pre-treatment temperatures (900 °C), both 0.5Fe-silicalite-1 and 0.5Fe-ZSM-5 (84) decrease in activity, though the observed decrease is significantly greater for Fe-silicalite-1.

Nevertheless, in spite of the fact that the optimal pre-treatment of Fe-silicalite-1 is *ca.* 200 °C higher than for Fe-ZSM-5, 0.5Fe-silicalite-1 is *always* less active than 0.5Fe-ZSM-5 (84), even following optimisation of both catalyst pre-treatment procedures. This is in direct contrast to previous studies focusing on Fe-containing zeolites for N₂O decomposition, which demonstrated that the catalytic activity of Fe-silicalite-1 and Fe-ZSM-5 are identical for NO_x decomposition following optimisation of the pre-treatments.²⁸ This clearly indicates that in the case of Fe-containing zeolites for aqueous-phase methane oxidation, there is an additional promotional role of Al³⁺ in the catalyst beyond simply facilitating the extraction of Fe³⁺ species to the extra-framework. This is further emphasized from the deconvolution analysis of 0.5Fe-ZSM-5 (84) and 0.5Fe-silicalite-1, following heat pretreatment (ESI Table S1 and Figure S3 and reference 20, respectively). Previously, we have demonstrated that the activity of 0.5Fe-silicalite-1 correlates well with the amount of extraframework Fe within the zeolite micropores *i.e.* λ_2 . A similar interpretation of the UV-Vis data of 0.5Fe-ZSM-5 (84) also produces a positive correlation between the percentage of these species and catalytic activity (Figure 3). Nevertheless, it is clear that per 'active' Fe species, 0.5Fe-ZSM-5 (84) displays over 20 % higher



Figure 3. Relationship between the % of extra-framework Fe species within the zeolite micropores (the proposed active species) and catalytic activity for 0.5Fe-silicalite-1 (\blacktriangle) and 0.5Fe-ZSM-5 (84) (\bullet) following various pre-treatment procedures. The data for 0.5Fe-silicalite-1 was previously published in reference 20.

Role of cation-exchange sites. An additional promotional role of Al³⁺ was inferred by visual inspection and kinetic evaluation of the samples calcined at 900 °C; whilst the 0.5Fe-ZSM-5 (84)₉₀₀ sample was still white in colour, and comparable in activity to those samples pre-treated at 550 °C, the 0.5Fesilicalite-1900 sample was a dark orange/brown colour and significantly less active than the samples calcined at 550 and 750 °C. This implies that excessive clustering to catalytically inactive bulk Fe oxides is more evident in the Fe-only sample, in spite of the fact that Fe^{3+} is initially more easily extracted from the Fe- and Al-containing system. We have previously identified bulk Fe oxides to not only be incapable of methane activation, but responsible for the formation of carbon oxide species and increased non-selective H₂O₂ decomposition.²⁰ Thus, the decrease in the percentage of 'active' Fe species, coupled with the increased formation of 'inactive' and undesirable spectator species would correlate favourably with the observed activities.

As we recently reported,²⁰ UV-Vis analysis confirms that 0.5Fe-silicalite-1₉₀₀ has 'over-clustered' to Fe oxide species upon the excessive thermal pre-treatment (ESI Table S1). Indeed, a remarkable increase in the fraction of undesirable larger clusters and bulk oxides is observed following pre-treatment at 900 °C. This agrees well with the colour of the sample (orange/brown) and the significant decrease in observed activity (Figure 2). It is apparent, therefore, that once a given amount of Fe migrates from the framework of 0.5Fe-silicalite-1, the formation of larger clusters and bulk Fe oxides is triggered, and the catalyst rapidly decreases in activity.

In contrast, despite Fe³⁺ apparently being more readily extracted from the MFI framework in 0.5Fe-ZSM-5 (84) than 0.5Fesilicalite-1 to begin with, the pre-treated samples of 0.5Fe-ZSM-5 (90)750 and 0.5Fe-ZSM-5 (84)900 do not possess significantly different Fe speciation to the sample calcined at 550 °C, and the fraction of 'active' extra-framework Fe³⁺ species within the zeolite micropores does change significantly. This correlates favourably with the miminal decrease in activity observed with these samples. Although the pre-treatment of 0.5Fe-ZSM-5 (84) at high temperatures (> 550 °C) will also lead to some dealumination *i.e.* the formation of extraframework Al³⁺, the fraction of such octahedral Al³⁺ remained low, in agreement with the known stability of framework Al³⁺ in MFI frameworks. Furthermore, the pre-treatment of ZSM-5 (86) at such temperatures still did not lead to any relevant catalytic activity, thus demonstrating that the changes in Fe³⁺ speciation are the dominant factor in the activity of these materials.

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59 60 The observation that the 'over'-clustering of Fe³⁺ to larger clusters and bulk Fe oxides is less prevalent for 0.5Fe-ZSM-5 (84) than for 0.5Fe-silicalite-1 suggests that an alternative promotional role of Al³⁺ may be its ability to stabilise or disperse the active extra-framework cationic Fe species, as previously observed by groups focusing on gas phase oxidation of higher hydrocarbons and NO_x decomposition.^{21,29-31} Should this be the case, it would be expected that this would particularly apply for active catalytic materials prepared by postdeposition methods; although we have shown these samples to be less active per mole of Fe^{3+} , they contain the entire Fe^{3+} fraction in extra-framework positions, and thus allow the discrimination of Al³⁺ promotion through dispersion/stabilisation and the increased extraction phenomena observed for the hydrothermally prepared samples. Thus, samples of 2.5 wt. % Fe³⁺/ZSM-5 (86) and 2.5 wt. % Fe³⁺/silicalite-1 were prepared by solid-state ion-exchange and screened for catalytic activity. The higher metal loading (2.5 wt. % vs. 0.5 wt. %) was chosen given the lower intrinsic activity of post-synthetic deposition compared to hydrothermal incorporation. We note here that post-synthetic Fe³⁺ deposition is denoted Fe³⁺/ZSM-5, whereas hydrothermal incorporation is defined Fe-ZSM-5.



Figure 4 Catalytic activity of 2.5 wt % Fe/ZSM-5 (86) and 2.5 wt. % Fe/silicalite-1, prepared by solid-state ion-exchange. Reaction conditions; cat: various (27 mg); $P_{(CH4)}$: 30.5 bar; $[H_2O_2]$: 0.5 M; temp: 50 °C; time: 30 min; stirring speed: 1500 rpm; Note: Catalyst pre-treatment: 550 °C, 3 h, static air.

Catalyst	Relative contribution of each λ range (nm)			
	λ_1	λ_2	λ_3	λ_4
2.5Fe ³⁺ /silicalite -1 ₅₅₀	0.204	0.164	0.236	0.395
2.5Fe ³⁺ /ZSM-5 (86) ₅₅₀	0.169	0.512	0.192	0.127

Data calculated from UV-Vis spectra in ESI Figure S4.

Figure 4 demonstrates that in spite of identical Fe³⁺ loadings (2.5 wt. %) and pre-treatment conditions (550 °C, 3 h, static air), the $2.5\text{Fe}^{3+}/\text{ZSM-5}$ (86)₅₅₀ sample is more than one order of magnitude more active than the analogous $2.5\text{Fe}^{3+}/\text{silicalite-}1_{550}$. This clearly emphasises that there is a beneficial role of Al³⁺ that is not related to its ability to facilitate the extraction of Fe³⁺ from the framework of the zeolite, as both samples were prepared by post-deposition methods and did not therefore contain any (initial) framework Fe³⁺.

Following deconvolution of the relevant UV-Vis spectra of $2.5 \text{Fe}^{3+}/\text{silicalite-1}_{550}$ and $2.5 \text{Fe}^{3+}/\text{ZSM-5}$ (86)₅₅₀, it is clear that 2.5Fe^{3+} /silicalite-1₅₀ possesses a significantly lower fraction of 'active' Fe species than 2.5Fe³⁺/ZSM-5 (86)₅₅₀ (Table 4). Whilst we could expect 2.5Fe³⁺/silicalite-1 to thus be around 1/3 the activity of $2.5 \text{Fe}^{3+}/\text{ZSM-5}$, based on the relative contributions within each sample, it cannot be overlooked that the UV-Vis spectrum of 2.5Fe³⁺/silicalite-1 is dominanted by larger Fe clusters and bulk Fe oxides, which are responsible for non-selective H_2O_2 decomposition (Entry 2).²⁰ On the other hand, the fraction of such undesirable spectator species in $2.5 \text{Fe}^{3+}/\text{ZSM-5}$ (86) is much lower. The lack of active sites, coupled with the large amount of undesirable Fe species, results in this sample showing little activity whatsoever. It is clear therefore that Fe³⁺ is significantly more dispersed within/on the MFI material when Al^{3+} is also present in the zeolite structure, as significantly less bulk oxides (and thus less clustering) is observed in $2.5 \text{Fe}^{3+}/\text{ZSM-5}$ (86)₅₅₀ than in $2.5 \text{Fe}^{3+}/\text{silicalite-1}_{550}$.

Based on these experiments, it is evident that the inclusion of Al^{3+} within the zeolite leads to higher levels of activity, due to both an increased extraction of Fe³⁺ from the zeolite framework (where applicable), and an increased dispersion of the extra-framework Fe species, which maximises the fraction of extra-framework Fe species within the zeolite micropores and minimises the fraction of undesirable clusters and bulk oxides. Nevertheless, the exact nature of this increased dispersion is not yet evident. Previously, it has been proposed that Al^{3+} aids the dispersion of Fe³⁺ in similar zeolite materials even when deposited by post-synthesis methods; from this, it has been proposed that extra-framework Al^{3+} species are able to aid dispersion.²¹ Alternatively, the cation-exchange sites associated with framework Al³⁺ may also be responsible for dispersion, given the ability of the negative lattice charge to coordinate and stabilize cationic complexes.^{24,25} Nevertheless, each of these studies utilized Fe-containing zeolites for hightemperature (> 250 $^{\circ}$ C) gas phase oxidation chemistry, which we have shown to be unrelated to our present system. Furthermore, both reported catalytic systems required pretreatment at significantly higher temperatures to the catalysts reported herein, and in a vacuum or an inert atmosphere, in 1

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59 60 order to facilitate the formation of Fe^{2+} species that are responsible for activity in such cases. Thus, the extrapolation of these previous studies to the present system, which focuses on the low temperature, aqueous phase methane oxidation with Fe^{3+} active sites cannot be presumed.

To probe whether framework or extra-framework Al^{3+} species were responsible for the promotion, Al^{3+} was incorporated into 0.5Fe-silicalite-1 by three different techniques; namely hydrothermal synthesis, solid-state ion-exchange and impregnation. From the data presented (Figure 5), it is clear that the addition of Al^{3+} to 0.5Fe-silicalite- l_{550} by solid-state ion-exchange or impregnation does not lead to any improvements in catalytic activity. It can thus be firmly concluded that extra-framework Al^{3+} species do not promote the catalytic activity of Fe³⁺, and that an extra-framework mixed oxide (Fe-O-Al) is highly unlikely to be responsible for catalytic activity, as has previously



Figure 5. Influence of AI^{3+} addition on the catalytic activity of 0.5Fe-silicalite-1₅₅₀. For the post-synthesis samples, AI^{3+} was added to a pre-synthesised sample of 0.5Fe-silicalite-1. For 0.5Fe-ZSM-5 (X) prepared by hydrothermal synthesis, Fe *and* Al were concurrently incorporated into the framework by the addition of the relevant precursors to the synthesis gel. In hydrothermal incorporation, \blacktriangle impregnation, \blacklozenge solid-state ion-exchange. Reaction conditions; volume: 10 mL; time: 30 min; temp: 50 °C: P_(CH4): 30.5 bar; [H₂O₂]: 0.5M; catalyst: 27 mg; stirring speed: 1500 rpm; Catalyst pre-treatment: calcination (550 °C, 3 h, static air).

In contrast, the incorporation of Al³⁺ into the framework of 0.5Fe-silicalite-1550 during hydrothermal synthesis leads to significant increases in catalytic activity, that are directly proportional to the Al³⁺ content up to 2.2 wt. %. Given that this method is the only method capable of incorporating Al³⁺ into the zeolite framework, and is thus the only method capable of increasing the number of cation-exchange sites, it can be proposed that the increased cation-exchange site density is responsible for the promotion displayed by Al³⁺, presumably by the stabilisation and dispersion of the active Fe³⁺ cations onto the negative framework charge associated with the AlO₄⁻ tetrahedron. This would lead to a more significant interaction between extra-framework Fe³⁺ and the zeolite framework (anchoring) and would limit the formation of bulk and undesirable oxide species upon pre-treatment. We note here that whilst the observed TOF for the most active sample (0.5Fe-ZSM-5

 $(28)_{550}$ is still around 5-10 times lower than the highest obtained with commercial 0.014ZSM-5 $(30)_{550}$ under identical reaction conditions,¹⁸ we reason that the probability of obtaining the highest percentage of active Fe sites whilst concurrently minimising the formation of undesirable Fe oxides is likely to be increased at lower Fe loadings. This will be described in depth in the following section.

To substantiate the proposed interaction of cationic extraframework Fe³⁺ and framework Al³⁺, 2.5Fe³⁺/ZSM-5 (86)₅₅₀ was investigated with FT-IR spectroscopy. It is well-known that when in the H⁺-form, the cation-exchange sites associated with framework T³⁺ atoms give rise to clear stretches between $3700 - 3600 \text{ cm}^{-1}$, the exact values of which depend entirely on the identity of the T³⁺ atom. If cationic Fe complexes are indeed dispersed on the cation-exchange sites, the intensity of the Al-O(H)-Si stretch (3610 cm⁻¹) should diminish taking into account that some (or all) of the protons would be replaced by cationic Fe complexes. This was subsequently verified experimentally, as the Al-O(H)-Si band in ZSM-5 (86) (Figure 6, A/blue) is completely eliminated from the FT-IR spectrum upon solid-state ion-exchange with Fe³⁺ (B/red). This indicates the substitution of all of the cation-exchange sites with Fe³ during catalyst synthesis, and confirms the association of extra-framework Fe^{3+} with the cation-exchange sites associated with framework $A1^{3+}$. Nevertheless, in spite of the excess of Fe to Al in these samples, a partial restoration of the Al-O(H)-Si band is observed after calcination the final catalyst at 550 °C. The lack of 100 % exchange i.e. complete loss of O-H band, in this sample, which is the active catalyst, is likely due to increased clustering of Fe³⁺ into larger clusters or bulky iron oxides upon calcination.



Figure 6. O-H stretching region of the FT-IR spectra of ZSM-5 (30) (A/blue), uncalcined/as synthesised 2.5 wt. % $Fe^{3+}/ZSM-5$ (30) (B/red) and calcined 2.5 wt. % $Fe^{3+}/ZSM-5$ (30) (C/green). Absorbances were normalised to the Si-O-Si stretches of the zeo-lite framework.

To further substantiate the hypothesis that framework AI^{3+} maximises the formation of the active Fe³⁺ species, a final analogous sample of [Fe,Ga]-silicalite-1 was prepared by hydrothermal synthesis. This substitution of Si⁴⁺ by Ga³⁺ also gives rise to cation-exchange sites in a similar manner to AI^{3+} , and a significant increase in catalytic activity versus the Feonly analogue (Figure 7). This strengthens the identification of cation-exchange sites as the promoting functionality of the

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Figure 7. Catalytic activity of various Fe-containing zeolites at a fixed Fe loading (0.5 wt. %). Ga³⁺ and Al³⁺, where applicable, were added to the material at an SiO₂/M₂O₃ ratio of \pm 85. Reaction conditions; cat: various (27 mg); P_(CH4): 30.5 bar; [H₂O₂]: 0.5 M; temp: 50 °C; time: 30 min; stirring speed: 1500 rpm; Note: Catalyst pre-treatment: 550 °C, 3 h, static air.

Optimised material synthesis. At this point, we have established that (1) the catalytic activity of (Fe)-ZSM-5 correlates to the presence of extra-framework Fe^{3+} species within the zeolitic micropores (work herein and reference 20), (2) that the clustering of extra-framework Fe³⁺ to larger clusters and bulk oxides leads to a decrease in activity and C- and H₂-based selectivity,²⁰ and (3) that the co-presence of Al^{3+} or Ga^{3+} is critical for maximising the activity of each Fe³⁺ atom, first by facilitating its extraction from the zeolitic framework, and secondly by providing cation-exchange sites which are capable of acting as stabilising ligands to the cationic Fe^{3+} species, thereby inhibiting the formation of undesirable side species and maximising the fraction of active species. Nevertheless, the TOFs exhibited by the optimal material so far, 0.5Fe-ZSM-5 (28)₅₅₀, are still around 5-10 times lower than those exhibited by commercial ZSM-5 (30), containing only 0.014 wt. % Fe.¹⁸

By considering these factors, we reasoned that the extremely high TOFs of the commercial sample might be due primarily to its low Fe loading (0.014 wt. %) but high Al loading (2.3 wt. %); a large amount of Al³⁺ would maximise the extraction of framework Fe³⁺ (thereby forming a greater number of active sites), and provide sufficient cation-exchange sites to stabilise *all* of the extracted Fe³⁺ (thereby inhibiting the formation of undesirable side species). The low Fe loading would also maximise the percentage of 'active' Fe species, as the spatial distribution of Fe would be maximised, and the formation of bulk oxides inhibited. In view of this, a number of Fe- and Alcontaining ZSM-5 samples were prepared (Figure 8).

Many important features are immediately evident from the data shown in Figure 8. First, it is clear that as the Al-content of the material increases, the activity of each catalyst at a given Fe loading is higher, likely due to the more facile extraction of framework Fe³⁺ at higher Al contents. Furthermore, it is clear that at higher Al contents, the optimal Fe loading decreases. It is likely that due to the increased extraction, the possibility of forming inactive larger clusters and bulk oxides is enhanced at higher loadings. Finally, it is apparent that above the optimal Fe loading of each Fe-ZSM-5 (X) series, catalytic activity decreases, yet the apparent decrease in activity is much lower at higher Al³⁺ content. This is in excellent agreement to our previous observations and confirms that Al³⁺ inhibits the formation of larger Fe clusters and Fe oxides, thus maximising the amount of active Fe species, and minimising the amount of undesirable side species. Each of these observations fully supports the hypothesis that the key to attaining the highest levels of activity is maximising the content of Al³⁺, and subsequently optimising the Fe content. We note here that we have previously proposed through EXAFS analysis and DFT calculations that catalytic activity is due to an extraframework species, $Fe_2(\mu_2-OH)_2(OH)_2(H_2O)_2]^{2+}$, a binuclear active site that comprises an overall +2 charge.¹⁸ The coordination of such a species on to the cation-exchange sites would require two exchange sites within a critical distance of $\sim 5-6$ Å, or two Al^{3+} atoms within the 10 membered MFI ring. The probability of having two exchange sites within this distance would improve significantly upon the incorporation of additional Al³⁺ into the framework, and has been shown by Feng and Hall to be very high for zeolites with a SiO₂/Al₂O₃ mole ratio approaching 40, but negligible for zeolites with a SiO_2/Al_2O_3 much greater than 100.³⁴ This correlates favourably with the observed activity.



Figure 8. Catalytic activity of various Fe-ZSM-5 samples containing different Fe- and Al-contents. Reaction conditions; cat: ZSM-5 (27 mg); $P_{(CH4)}$: 30.5 bar; $[H_2O_2]$: 0.5 M; temp: 50 °C; time: 30 min; stirring speed: 1500 rpm; Note: Catalyst pretreatment: 550 °C, 3 h, static air.

It is important to stress here that by understanding the critical role(s) of each component of the catalyst, we have been able to optimise the catalytic activity of Fe-ZSM-5 enormously. The TOFs displayed by the Fe-ZSM-5 (28) series – containing 2.2 wt. % Al – are two orders of magnitude higher than those of the Fe-only series *i.e.* 0.5Fe-silicalite-1. Thus, the TOFs exhib-

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58 59 60 ited by this series are now very similar to the TOFs obtained for the original commercial ZSM-5 (30) catalyst, the most intrinsically active catalyst to date. For example, 0.045Fe-ZSM-5 (28)₅₅₀ and 0.095Fe-ZSM-5 (28)₅₅₀ oxidises methane at a TOF of *ca.* 1,600 h⁻¹, comparable to the *ca.* 2,000 h⁻¹ that we have observed for commercial ZSM-5 (30)₅₅₀. More importantly, however, is that these levels of TOF have been maintained at significantly higher Fe loadings (0.095 wt. % *vs.* 0.014 wt. %). Thus, along with possessing similar intrinsic activity, 0.095Fe-ZSM-5 (28) is around 5-times more productive in terms of volumetric productivity (1.92×10^{-8} mol (product) cm⁻³ s⁻¹ after 30 minutes) than commercial ZSM-5 (30) (4.2×10^{-9} mol cm⁻³ s⁻¹ after 30 minutes).

Conclusions. Through catalytic measurements and spectroscopic investigations, we have demonstrated that, whilst extraframework Fe³⁺ species are the active component of Fecontaining MFI-type zeolites for selective aqueous-phase methane oxidation, significant promotion is observed upon the incorporation of other non-catalytic trivalent cations (e.g. Al^{3+} , Ga³⁺) into the MFI-framework. We have rationalised this promotion in terms of two co-operative effects. Firstly, the coaddition of Al³⁺ or Ga³⁺ to the framework leads to an increased migration of (initially) framework Fe³⁺ to the extra-framework during heat pre-treatment. Concurrently, the cation-exchange sites associated with framework M³⁺ species also are able to stabilise and disperse the so-formed extra-framework Fe³⁺ species that are responsible for catalytic activity. In this case, the dispersion of Fe^{3+} is a consequence of both the dispersed nature of Al³⁺ within the zeolite (Lowenstein's rules ensuring maximum dispersion), and an 'anchoring' process whereby Fe is inhibited towards agglomeration into bulk oxides due to the stabilisation provided by the negative framework charge. By understanding these key roles exhibited by each aspect of the solid catalyst, significant improvements in catalytic activity (one order of magnitude) have been obtained by the careful and rationalised design of new catalysts. Optimal activity has thus been obtained with a catalyst comprising of 0.095 wt. % Fe, and 2.2 wt. % of Al³⁺. This catalyst performs this highly desirable reaction at volumetric productivities of 1.92×10^{-8} mol cm⁻³ s⁻¹, and at TOFs comparable to the commercial catalyst previously reported (*ca.* 2,000 h^{-1}), and is therefore the most active catalyst reported for this challenging reaction to date.

Experimental Section

Catalyst synthesis and pre-treatment. MFI-type zeolites containing various amounts of Fe, Al and Ga were prepared by a hydrothermal synthesis method in a batch autoclave. The procedure used is more completely described previously.^{18,20} Crystallisation was performed in a stainless-steel autoclave at 175 °C for 120 h. The as synthesised materials obtained were calcined at 550 °C (1 °C min⁻¹), first in a flow of nitrogen (5 h), and later air (3 h) in order to remove the organic template. The de-templated sample was subsequently ion-exchanged three-times with NH₄NO₃ (1.0 M) at 95 °C, and later dried for 16 h at 110 °C. Activation was achieved by calcination in flowing air (30 mL min⁻¹) at 550 °C (750 °C or 900 °C for 3 h. Following this route, ferrigallosilicate ([Fe, Ga]), ferrisilicate ([Fe]), aluminosilicate ([AI]) and silicate (no heteroatom) were also prepared.

Silicalite-1, Fe-silicalite-1 and ZSM-5 were also used as precursors for the incorporation of Al³⁺, Fe³⁺ and Ga³⁺ by postsynthesis deposition methods (impregnation, solid-state and aqueous ion-exchange). To this end, 2.5 wt. %Fe/ZSM-5 was prepared by impregnation through the addition of support $(1.95g, NH_4$ -ZSM-5, SiO₂/Al₂O₃ molar ratio = 30, ZeolystTM) to an aqueous solution of Fe(NO₃)₃.9H₂O (3.613mL, 13.828g dissolved in 1L). The solution was stirred until a homogeneous solution was obtained. The slurry was dried (16 h, 110 °C) before calcination at 550 °C for 3 h in static air. 2.5 wt. % Fe/ZSM-5 was also prepared by solid-state ion-exchange by adding the desired amount of $Fe(acac)_3$ (0.158g, 0.45 mmol) to NH₄-ZSM-5 (0.975g, SiO₂/Al₂O₃ molar ratio = 30, ZeolystTM) prior to mechanical grinding for 30 minutes. Finally, aqueous ion-exchange of was performed by the addition of NH₄-ZSM-5 (2g, SiO₂/Al₂O₃ molar ratio = 30, ZeolystTM) to an aqueous solution of Fe(NO₃)₃.9H₂O (30 mL, 0.02 M, 20.2g Fe(NO₃)₃.9H₂O dissolved in 250 mL deionised water). The suspension was stirred vigorously (85 °C, 24 h) under reflux. The catalyst was filtered, washed with deionised water and dried (16 h, 110 °C). Prior to testing, the catalyst was activated by calcination at 550 °C for 3 h in static air.

Catalyst characterisation. Powder X-ray diffraction (XRPD) was performed using a PANalytical X'PertPRO X-ray diffractometer, with a CuK_a radiation source (40 kV and 40 mA). Diffraction patterns were recorded between 6-55° 20 at a step size of 0.0167° (time/step = 150 s, total time = 1 h). FT-IR spectroscopy was performed by forming self-supporting wafers from a small amount of sample and KBr. The spectra were recorded on a Jasco FT-IR660 Plus over a range of 4000-400 cm⁻¹ at a resolution of 2 cm⁻¹. UV-Vis analysis was performed on an Agilent Cary 4000 UV-Visible Spectrophotometer equipped with Diffuse Reflectance set-up. Samples were scanned between 190 and 900 nm at a scan rate of 600 nm min⁻¹. Na, Si and Al content was determined by Neutron Activation Analysis (NAA). Metal contents were determined by ICP-OES to an accuracy of \pm 10 %.

Kinetic evaluation. Micro-kinetic analysis was carried out in a batch stainless-steel autoclave containing a Teflon liner vessel and a working volume of 35 mL. The vessel was charged with an aqueous solution of H_2O_2 (10 mL, 0.5 M, 5000 µmol) and the desired amount of catalyst (typically 27 mg). After evacuation of contaminant gases, the autoclave was heated to the reaction temperature (typically 50 °C), and vigorously stirred at 1500rpm once the desired temperature was obtained. The vessel was cooled in ice (12 °C) following the appropriate reaction time, and the resultant solution was filtered and analysed. Experimental error was determined to be \pm 7 %.

Analytical methods. Aqueous-phase products were identified through ¹H-NMR spectroscopy on a *Bruker 500MHz Ultra-Shield NMR spectrometer*, and quantified against a 1 vol. % TMS/CDCl₃ internal standard, previously calibrated against authentic standards. The detection limit was optimised to a level corresponding to a product yield of 0.1 μ mol.²⁰ End H₂O₂ concentrations were determined by titration against acidified Ce(SO₄)₂ solution. Gaseous phase products were quantified by means of an FID-GC (*Varian 450-GC*) fitted with a CP-Sil 5CB capillary column (50m length, 0.32mm ID). The GC was equiped with a methaniser unit, and CO₂ was quantified against a calibration curve constructed from commercial standards (*BOC*).

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ABBREVIATIONS AND DEFINITIONS

Partial oxygenated products;

methyl hydroperoxide (CH $_3$ OOH), methanol (CH $_3$ OH) and formic acid (HCOOH).

Total product formed; partial oxygenates + CO₂.

Oxygenate selectivity;

moles (partial oxygenates)moles (total oxygenated product)× 100

Turnover frequency;

moles (oxygenated species formed) mol⁻¹ (Fe) h⁻¹.

Volumetric productivity;

moles (oxygenated species formed) cm⁻³ (reactor volume) s⁻¹. Volumetric productivity and TOFs were calculated based on the final yield at the end of the reaction *i.e.* they are an averaged value over the entire time scale of the reaction. Typically, the initial productivities and TOFs *i.e.* productivities at 2 and 5 minutes of reaction, were one to two orders of magnitude higher.

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