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Methane oxidation using silica-supported N-bridged di-iron phthalocyanine catalyst

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ABSTRACT

Methane oxidation in water using hydrogen peroxide with a μ-nitrido iron phthalocyanine complex grafted on silica has been investigated in detail. Methyl hydroperoxide is identified as the main primary reaction product from methane oxidation. The catalyst is unstable under reaction conditions and this is discussed. However, the unmodified silica support is also found to be active for this reaction, and in particular, a Fe/SiO_2 catalyst prepared by wet impregnation is also found to be as effective as the μ-nitrido iron phthalocyanine complex grafted on silica, with higher selectivity to useful oxygenates (>80%) and displays minimal leaching or instability. A method for the reliable quantification of CO_2 in both the gas and aqueous phase is reported as this presents a key experimental difficulty in the oxidation of methane in aqueous media.

1. Introduction

Recent work by Sorokin and co-workers has raised the interesting possibility that a μ-nitrido iron phthalocyanine complex grafted on silica can be an effective bio-inspired catalyst for the selective oxidation of methane using hydrogen peroxide as the terminal oxidant under mild reaction [1,2]. The demonstration of a truly heterogeneous catalyst for the selective low-temperature oxidation of methane to methanol can still be considered one of the remaining grand challenges of catalysis, and consequently, the work presented by Sorokin and co-workers represents a potentially interesting new development. To date the activation of methane has been a very active field, but over a century of research has not yet led to a process with commercial potential which can be classified as ‘green catalysis’ for the direct conversion of methane in the liquid phase with a heterogeneous catalyst. The relative strength of the C–H bond in methane (435 kJ mol^{-1}) as compared to bonds in its oxygenated products is one of the reasons often considered as responsible for the low selectivity achieved in this oxidation reaction. Whilst the direct conversion of methane to methanol has not yet been achieved in a viable manner, the current indirect method involving the production of syngas and its conversion to methanol has been fine tuned over many decades of operation and gives a high selectivity to methanol. The indirect process, therefore, represents a difficult process to improve upon. A process based on the direct conversion of methane to methanol in a single step might provide advantages if high selectivity can be achieved at a sufficient level of conversion with the appropriate terminal oxidant, which for commercial purposes has to be molecular oxygen.

A number of materials have been proposed for the low-temperature activation of methane [3–8]. Most of these are homogenous catalysts and use strong acidic conditions for the transformation. For example, Periana and co-workers [8] have utilised a bipyrimidyl Pt complex in oleum, which shows both high selectivity and methane conversion (~90%). From an industrial standpoint, the associated issues of waste disposal, difficulties with the recyclability of the acidic media, capital outlay to build large scale plants with acid stable materials and the price volatility of energy resources means this sort of chemistry cannot be implemented.

Many studies have sought to emulate natural enzymes in the design approach for catalysts capable of methane oxidation using bio-inspired or bio-mimetic approaches. However, to be classified as effective, these bio-inspired catalysts have to show that they can compete with the real bench mark which is that displayed by methane monooxygenase (MMO) [9,10], that is, the catalysts should be stable under mild reaction conditions and display high selectivity to methanol, although it is recognised that the catalysts will necessarily operate by a different mechanism. It is known that the soluble form of MMO (sMMO) could oxidise C_1–C_8 hydrocarbons efficiently to the corresponding alcohol [11]. It is important to note that *in vivo* this enzyme does not produce carbon dioxide or other over-oxidation products and is therefore highly specific. Detailed *in vitro* studies by Dalton and co-workers [11] have shown that the activity for methanol synthesis is 5 mol (CH_3OH) kg

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$(\text{catalyst})^{-1}\,h^{-1}$ for sMMO (C.bath) as a complete enzyme with NADH present (5 μmol NADH, 45 °C, 12 min, 2 mg protein, pH 7, CH_4 6 ml at atmospheric pressure) and this represents the benchmark by which bio-inspired or bio-mimetic catalysts should be judged. However, no data on CO_2 production *in vitro* have been given. sMMO cannot use hydrogen peroxide in its native form and molecular oxygen is activated to the reactive peroxy species by NADH. However, when the NADH cofactor is removed, H_2O_2 can be used as the terminal oxidant with the enzyme but the catalytic activity decreases to 0.076 mol $(CH_3OH)\ h^{-1}\ kg(MMOH)^{-1}$ (120 μmol sMMO hydroxylase, 100 mmol H_2O_2, 15 min, 45 °C) [12]. It is this observation that often leads researchers to use H_2O_2 as an oxidant for methane oxidation. However, it should be noted that the cost of H_2O_2 precludes is use in any commercial direct methane oxidation process. Indeed, H_2 is the expensive reagent in the production of H_2O_2 and this is derived from methane commercially.

The main approach utilised in bio-mimetic alkane oxidation catalysts uses organometallic complexes to activate oxidants such as H_2O_2 [13]. Usually, V, Fe, Ru, Co, Cu and Mn complexes of porphyrins, phthalocyanines and Schiff bases [13–26] have been employed for the oxidation of many alkanes but they have not been extensively used for methane activation. It is apparent from the recent literature that efforts to produce a bio-mimetic methane oxidation catalyst have been focussed on using phthalocyanine-based complexes either as homogeneous or as heterogeneous catalysts. This is based, in part, on the observation that in cytochrome P-450 enzymes an iron porphyrin complex inserts an O atom into the C–H bond via an abstraction-radical rebound mechanism to give the hydroxylated product using an oxy-ferryl porphyrin radical intermediate generated from the activation of molecular oxygen [27,28]. It is well known that in most cases anchoring organometallic complexes onto supports can remove issues of catalyst recyclability, loss of catalytic activity with time due to complex auto-oxidation or polymerisation [29,30] and may increase selectivity to desired products. Encapsulation into microporous and mesoporous materials, as well as grafting onto inorganic or polymer supports is used for this purpose. Two reported studies are of note for methane oxidation and both use heterogenised phthalocyanine catalysts anchored to supports in different ways [1,2,31]. The system reported by Raja and Ratnasamy [31] utilised Cu, Co and Fe complexes encapsulated in a zeolite to achieve partial oxidation of methane with selectivity of 15.1%, 52.9% and 19.5% to methanol, formic acid and CO_2 respectively, when using tertiary butyl hydroperoxide (TBHP) as oxidant and water as solvent. However, isotopic labelling studies were not performed for validation of the results and it should be noted that TBHP can decompose to give methanol under these reaction conditions. Chloro-substituted phthalocyanines, as opposed to alkyl-substituted phthalocyanines, were employed to increase catalytic activity and stability [32,33]. The recent reports by Sorokin and co-workers [1,2] also show that a phthalocyanine complex can be effective in the oxidation of methane under mild reaction conditions. In view of the continued interest in these catalysts, we have undertaken to study the catalyst used in the Sorokin study, namely μ-nitrido diiron tetra-tert-butylphthalocyanine grafted onto high surface area silica ($(FePc^tBu_4)_2N@SiO_2$) for the aqueous phase oxidation methane with hydrogen peroxide. We were primarily concerned with the stability of the catalyst, due to reports of possible catalyst degradation [1], and the overall selectivity of the process, since it is indicated that CO_2 is not expected to be a product using this catalyst [1]. To carry out this work, we have established a full analytical protocol to determine the nature of all the products formed when $(FePc^tBu_4)_2N@SiO_2$ is used as a catalyst for methane oxidation with H_2O_2 in water. In this study, we present our detailed findings and we compare the activity and selectivity of the catalyst with a silica-supported Fe catalyst prepared by impregnation of ferric nitrate or iron(III) acetylacetonate followed by calcination.

2. Experimental

2.1. Synthesis and characterisation of μ-nitrido-bis[tetra(tert-butyl) phthalocyaninatoiron on silica

The μ-nitrido-bis[tetra(tert-butyl)phthalocyaninatoiron] was synthesised in two steps according to the literature [1,34].

2.1.1. Synthesis of tetra(tert-butyl)phthalocyaninatoiron ($FePc^tBu_4$)

Following the procedure of Hanack and co-workers [34], $Fe(CO)_5$ (0.675 g, 3.45 mmol) was added in small portions to a solution of 4-*tert*-butylphthalonitrile (2.5 g, 13.8 mmol) in ethylene glycol (18 ml) maintained at 200 °C. After 1 h, the reaction mixture was cooled and water added (30 ml). The resulting blue solid was collected by filtration, washed with water and methanol, dried under vacuum and finally heated at 300 °C under N_2 atmosphere (2.05 g, 75%). LRMS, (ES+), m/z: 792.31 ($M^{\cdot +}$, 100%).

2.1.2. Synthesis of μ-nitrido-bis[tetra(tert-butyl)phthalocyaninatoiron] ($(FePc^tBu_4)_2N$)

Following the procedure of Sorokin et al. [1], $FePc^tBu_4$ (0.8 g, 1 mmol), and NaN_3 (3 g, 46 mmol) were suspended in 70 ml of oxygen-free xylene under N_2. The mixture was heated for 6 h at 150 °C with stirring. On cooling, the reaction mixture was filtered to remove solid impurities and the solvent was removed by distillation under reduced pressure. The crude product was added to a column of neutral alumina with CH_2Cl_2 and then a blue fraction was eluted using a mixture of CH_2Cl_2 and EtOH (starting with 100:1 ratio and increasing the amount of EtOH). The product still contained impurities and further purification was achieved by chromatography using silica as substrate and a mixture of CH_2Cl_2 and EtOH as eluent (starting with 10:1 ratio and increasing the amount of EtOH). The solvent was evaporated and the solid dried in a vacuum oven to afford pure $(FePc^tBu_4)_2N$ (0.31 g, 39%). MS (MALDI-TOF): cluster centred at *m/z* 1599 (M^+) and cluster centred at *m/z* 1615 (M + O). UV/vis, ^1H NMR and IR spectra all identical to those reported by Sorokin et al. [1].

2.1.3. Synthesis of $((FePc^tBu_4)_2N)@SiO_2$

The SiO_2-supported complex $(FePctBu_4)_2N@SiO_2$, was prepared according to the published method of Sorokin and co-workers [1]. The Fe content was measured by dissolving the catalyst first in hydrogen peroxide (50% in water) and then in concentrated HNO_3 to afford complete dissolution of the silica. Metal loading was 0.2 wt.% Fe which corresponds to a loading of 18.5 μmol/g of the supported complex. Note regular dissolution in aqua regia was ineffective.

IR spectrometry was performed by a Jasco FTIR 660 Plus instrument using discs (10 mg) prepared from catalyst (5 mg) in KBr (50 mg) after extensive drying and stored in a humidity controlled dessicator. The spectra were taken at ambient temperature in air. All UV–Vis spectra of solutions were performed on a JascoV-570 UVVis–NIR instrument at ambient temperature in air. Solid state diffuse reflectance spectra were recorded on a Perkin Elmer Lambad900 instrument. MS-ESI was measured on a Waters LCT Premier Xe instrument and Maldi-TOF spectra were acquired on a Waters Maldi Micro MX instrument.

2.2. Synthesis of Fe/SiO_2 by wet impregnation

A 0.2 wt.% Fe on silica was made by stirring silica (1.996 g, Degussa, which contains 20 ppm Fe as an impurity) in $Fe(NO_3)_3(aq)$

(Sigma, 10 ml, 0.072 mol) for 1 h and then the water evaporated at 110 °C by drying in an oven for 16 h. The sample obtained was calcined at 400 °C for 3 h in static air. A second sample with 2.5% Fe loading was prepared in the same way but changing the $Fe(NO_3)_3$(aq) concentration. This method was also used to prepare Fe/SiO_2 using iron(III) acetylacetonate (Sigma, purity > 99.5%) as the precursor and a 60–40 mixture of acetone–water as the solvent. The dried sample was calcined at 400 °C before use.

2.3. Oxidation of methane

The catalytic oxidation of methane was carried out using a stainless steel autoclave (Parr reactor) containing a Teflon liner vessel with total volume of 50 ml (working volume of 35 ml). In a typical experiment, catalyst (50 mg) was added to pure water (10 ml) containing a measured amount of H_2O_2 (50 wt.% H_2O_2). The system was pressurised with methane to a fixed pressure (32 bar, 0.033 mol) after air in the reactor was removed by purging three times with methane. The autoclave was heated to the desired reaction temperature of 50 °C. Once the reaction temperature was attained, the solution was vigorously stirred at 1500 rpm and maintained at the reaction temperature for a fixed period (0.5–20 h). At the end of the reaction, the autoclave was cooled in ice to a temperature below 10 °C to minimise loss of volatile products and the reaction gas removed for analysis in a gas sampling bag. The reaction mixture was filtered and analysed by ^{1}H NMR using D_2O as a solvent and a calibrated TMS in $CDCl_3$ insert (see Supplementary information).

Some reactions were also performed in a smaller stainless steel reactor with internal volume of 15 ml. For these reactions catalyst (50 mg) was used in water (2 ml) charged with an appropriate amount of H_2O_2 (50% in water). Methane (44 bar, 0.023 mol) was used for these reactions in an effort to closely match the published conditions for this catalyst [1]. The analysis of products was the same as for the 10 ml reactions. All reactions with $FeCl_3$(aq), SiO_2 or Fe/SiO_2 were performed as for the 10 ml reaction volume previously described. Fe analysis of both liquid and solid samples was carried out using ICP and AAS analyses.

2.4. Analysis of products

Gas phase CO_2 was determined by GC analysis on Varian 450-GC equipped with aCP-SiL5CB column (50 m, 0.33 mm diameter, He carrier gas) using a methaniser and an FID. Liquid products could be analysed by liquid GC injection using the same equipment but it was not sensitive enough to detect the low levels of HCOOH and CH_3COOH produced in some of these reactions. For this reason ^{1}H NMR was the method of choice for liquid analysis. However, CO_2 in the liquid phase was suitably analysed using our GC-FID method. For this, the initial water solvent was degassed with N_2 until a steady peak for CO_2 was observed upon GC analysis of the gas phase. An aliquot (10 ml) was used as detailed previously for the reaction. The reaction mixture was analysed immediately after depressurisation once enough filtrate had been collected for analysis (usually within 1 min). For this procedure, the gas and liquid injection ports of the instrument were first flushed with N_2 and kept under low N_2 flow to prevent injection of ambient air which would contribute significantly to the CO_2 in the analysis. A standard saturated solution of CO_2 in water was prepared by stirring water in a pressurised atmosphere of CO_2/N_2 to confirm the CO_2 in water assignment.

^{1}H NMR (500 MHz Bruker spectrometer) unambiguously identified all major liquid phase reaction products including CH_2O that is observed as hydrated CH_2O (depending on the concentration). An internal standard containing 1% TMS in $CDCl_3$ was placed in a sealed tube and used to quantify the product amount after calibration against known standards. The detection limit of this method was *ca.* 0.1 μmol of oxygenate products and the accuracy was *ca.* ±0.1 μmol of oxygenate product. CH_2O was also quantified by the Nash method [35] immediately after filtering the reaction mixture.

3. Results and discussion

3.1. Product identification for methane oxidation using $(FePctBu_4)_2N@SiO_2$

The $(FePctBu_4)_2N@SiO_2$ catalyst was synthesised and analysed by MS, IR, UV–VIS and XPS (see Supplementary information Figs. S1–S9). An attempt to study the single crystal structure of the organometallic complex was unsuccessful due to an inability to obtain suitable crystals for the diffraction study. However, all other techniques show the material to be identical to that reported by Sorokin and co-workers [1]. The catalyst was then used for the oxidation of methane under the standard reaction conditions for 20 h. Our initial studies focussed on ensuring complete analysis of the reaction products. In particular, it is necessary to determine the levels of CO_2 in both the liquid and the gas phases as the reaction is conducted in a three phase system (solid catalyst, solvent with H_2O_2 and methane gas). Analysis was, therefore, carried out using a combination of NMR and GC methods to achieve the necessary sensitivity. ^{1}H NMR was used for the identification and quantification of liquid phase oxygenated products. This method has the advantage of being unambiguous when compared to GC methods of analysis which typically have low sensitivity to C_1–C_2 acids and formaldehyde. We observed no overlapping signals in the ^{1}H NMR spectra and we identified methyl hydroperoxide as a reaction product (Fig. 1) along with hydrated CH_2O, formic acid, methanol, acetic acid and acetone. No ethane is observed in the reaction products. The assignment of methyl hydroperoxide was based on the work of Suss-Fink and co-workers [36]. As noted by Shul'pin [37], alkyl hydroperoxy species can be reduced using suitable reducing agents, and in the case of methyl hydroperoxide, methanol is the only product. Methyl hydroperoxy cannot be directly measured by GC analysis without reduction and these values can be compared with those obtained before reduction. However, methyl hydroperoxide is sufficiently stable to be quantified by ^{1}H NMR for up to 2–3 days after the reaction if stored below 5 °C. We consider this species to be the initial product of methane oxidation in this catalytic system. Interestingly, methyl hydroperoxide has not been directly observed in the previous studies with this catalyst [1,2].

Formaldehyde was not observed in the 2 ml reaction (entry 2 Table 2) by either ^{1}H NMR spectroscopy or GC analysis and was therefore quantified by the Nash method [35]. However, this method was complicated by interference with leached Fe from $(FePctBu_4)_2N@SiO_2$ present in the solution that can react with the Nash reagent giving a false-positive result for this analysis (see Supplementary Table S1). We were able to correct for the contribution of the leached Fe in small scale reactions (2 ml) reactions after dilution of an aliquot of the reaction mixture to ensure negligible Fe in solution. This was not possible for most of the larger scale (10 ml) reactions where the combination of low concentration of formaldehyde and high concentration of leached Fe precluded this correction being feasible. However, it should be noted that low concentrations of hydrated formaldehyde was observed by ^{1}H NMR using $(FePctBu_4)_2N@SiO_2$ as a catalyst for methane oxidation in our 10 ml reactions.

We developed two methods for the analysis of CO_2 as this can be present in both the gas and the liquid phases following reaction. For the gas analysis of CO_2, an aliquot of the gas following reaction was analysed directly by GC (see Supporting Fig. S10). This was

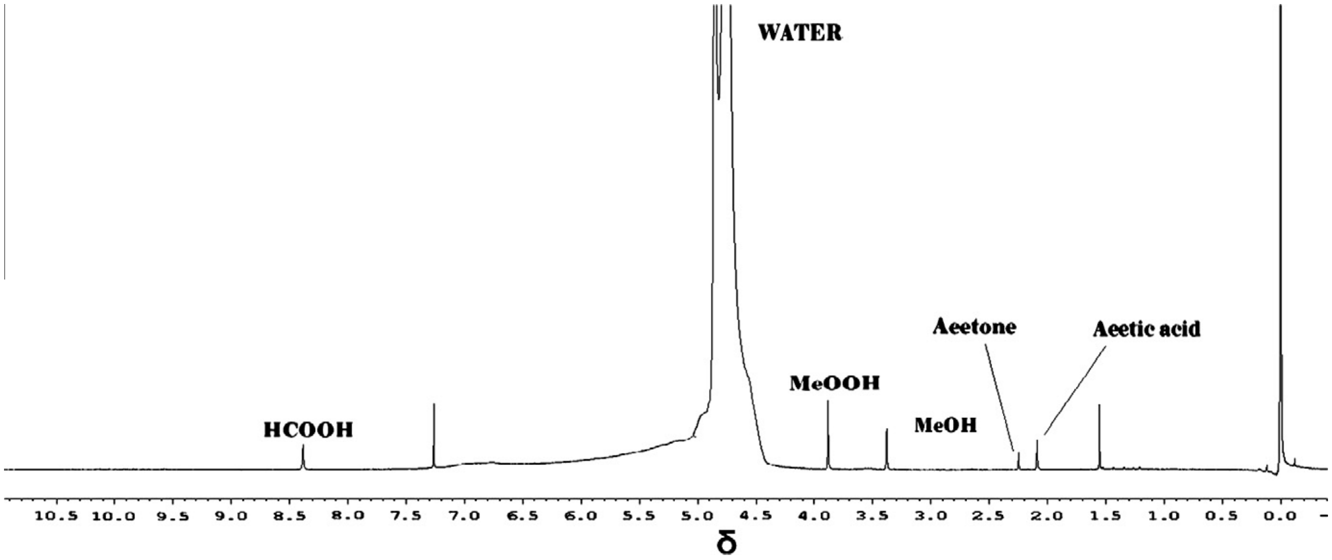

Fig. 1. ^{1}H NMR spectra of the reaction mixture obtained from the oxidation of methane using $(FePc^tBu_4)_2N@SiO_2$ and H_2O_2 following reaction for 20 h. The signals at 0, 1.55 and 7.26 are due to the TMS standard and solvent contained in the calibration insert. In this example hydrated CH_2O cannot be observed but it would be observed at δ = 5.1 ppm in the spectrum.

Table 1
Results of using the two protocols for total CO_2 analysis.

Entry	Experiment	Products (μmol)		Ratio CO_2 liquid/gas
		CO_2 in liquid	CO_2 in gas[a]	
1	GC analysis of reaction liquid + gas	5.31[b]	55.7	1:10.5
2	Out gassing of reaction mixture. Gas only analysis	6.61[c]	63.7	1:9.6

Catalyst: acidified $Fe(NO_3)_3$(aq), 10 ml water, 0.5 M H_2O_2, 0.5 h, 30 bar CH_4, 1500 rpm.

[a] Measured by GC-FID method using first reaction gas extracted.

[b] Measured by modified liquid analysis under a N_2 atmosphere.

[c] Estimated by the sum total of CO_2 in the reaction gas mixture after four degassing steps. Note these data do not include the analysis of oxygenated liquid phase products entries 1 and 2 were performed separately using the same experimental as described. pH of the final reaction mixture was 3–4.

compared with a similar analysis prior to reaction as the high-purity methane we utilised contained a very minor CO_2 impurity which required correction. For quantification of CO_2 in the liquid phase, we developed a method of GC analysis where CO_2 was quantified reliably after flushing the gas in the reactor with N_2 and then analysing the liquid by GC. It is essential that this procedure is carried out immediately after the reaction mixture is removed from the reactor. To validate this method, we also performed an outgassing experiment in which the reactor was initially vented to remove the gas, which was analysed for CO_2 as described earlier, and then, the reactor was refilled with CH_4 to the reaction pressure (30 bar total pressure) and vented again with analysis of the gas mixture for CO_2. This procedure was repeated, usually 5–6 times, until the CO_2 level observed was identical to that observed at the start of the reaction (approximately 0.5 μmol in the gas mixture). This method gave results in agreement with the combined gas and liquid phase analysis method (Table 1). It

Table 2
Results of aqueous phase methane oxidation using the $(FePc^tBu_4)_2N_2@SiO_2$ and H_2O_2.

Entry	Products/mM[g]						Products/ μmol[h]		%Fe leached[i]	TON[k]
	CH_3COOH	CH_3OH	CH_2O[j]	HCOOH	CH_3COOH	$(CH_3)_2CO$	CO_2	CO_2 (aq)		
1[a]	n.r.	n.r.	4.7 (9.4)	9.2 (18.4)	n.r.	n.r.	n.r	0	n.r	7.8
2[b]	0.84 (1.67)	0.65 (1.29)	4.73 (9.46)	1.55 (3.09)	2.70 (5.39)	4.98 (9.96)	19.55	0.85	40.2	29
3[c]	1.77 (17.7)	1.16 (11.6)	1.27 (12.7)	1.39 (13.9)	0.90 (9.02)	0.44 (4.42)	31.50	2.65	94.2	59
4[d]	1.03 (10.3)	0.75 (7.50)	0	Trace	0.88 (8.8)	0.90 (9.0)	7.4	n.d	19.4	24
5[e]	1.24 (12.4)	0.36 (3.6)	0.36 (3.6)	0.77 (7.7)	0.47 (4.7)	0.39 (3.9)	28.9	n.d	n.d	37
6[f]	0.84 (8.4)	0.2 (2.0)	0	4.4 (44.0)	0.47 (4.7)	0.23 (2.3)	35.1	n.d	25	55
7[f*]	1.29 (12.9)	0.32 (3.2)	0.59 (5.9)	2.76 (27.6)	0.13 (1.3)	0.03 (0.3)	13.0	n.d.	n.d	48

Entries 1–4 ran for 20 h at 50 °C using 50 mg of catalyst.

[a] Data calculated from the literature.

[b] 2 ml water, 44 bar CH_4 (0.023 mol), 0.35 M H_2O_2.

[c] 10 ml water, 32 bar CH_4 (0.033 mol), 0.5 M H_2O_2.

[d] 10 ml water, 32 bar CH_4 (0.033 mol), 0.07 M H_2O_2.

[e] 10 ml water, 23 bar CH_4 (0.023 mol), 0.35 M H_2O_2, 60 °C.

[f] 10 ml water, 23 bar CH_4 (0.023 mol), 0.35 M H_2O_2, 0.075 M H_2SO_4, 60 °C.

[f*] Reuse of catalyst from 6f under the same conditions.

[g] Analysis using ^{1}H NMR except for CH_2O.

[h] Analysis using GC-FID. Trace products taken was less than 0.1 μmol as detected using ^{1}H NMR.

[i] Quantified using AAS based on detected Fe in reaction filtrate relative to Fe in catalyst at start of experiment.

[j] Analysed as hydrated CH_2O using ^{1}H NMR and the Nash method.

[k] Turnover number calculated on total Fe including the support. () = product amount in μmol for that specific reaction volume; 'n.r' = not reported, 'n.d' = not determined.

should be noted that most of the CO_2 is observed in the gas phase (Table 1). As these methods of CO_2 analysis require extensive analytical time (*ca.* 4 h per analysis), we report the full quantification for key reactions to demonstrate the full selectivity data.

3.2. Methane oxidation using $(FePctBu_4)_2N@SiO_2$

Table 2 shows the results for the oxidation of methane using $(FePctBu_4)_2N@SiO_2$ as catalyst carried out under different conditions. When the reaction conditions are identical (entry 2) to those reported previously in the literature (entry 1), we observed the same values of formaldehyde as reported. However, after repeated attempts and checking the possibility of H/D exchange issues with the ^{1}H NMR procedure, we could not obtain the value of HCOOH previously reported [1,2] and we observed significantly lower concentrations of HCOOH (9.2 mM for entry 1 vs. 1.55 mM for entry 2 Table 2). Low amounts of methanol and methyl hydroperoxide were detected for the 20 h reaction as shown in entry 2, Table 2. Using these reaction conditions that are identical to those used by Sorokin and co-workers [1], substantial amounts of CO_2 were also produced (20.4 μmol, entry 2 Table 2) giving a total oxygenate selectivity of only 43%. Coupled with the low levels of products (total methane conversion of 0.16% or oxygenate productivity of 0.016 mol (C_1 oxygenates) kg (catalyst)$^{-1}$ h^{-1}) these results demonstrate that the $(FePc^tBu_4)_2N@SiO_2$ catalyst gives a performance in methane oxidation that is very far from the activity of the benchmark provided by sMMO. Furthermore, products resulting from the decomposition of $(FePc^tBu_4)_2N@SiO_2$, namely the C_2 compounds of acetone and acetic acid, are observed even at very low methane conversions.

The presence of acetic acid and acetone, previously reported as not being derived from CH_4 oxidation in labelling studies by Sorokin and co-workers [1,2] demonstrates that decomposition of the silica-supported organometallic complex is occurring as the catalysis proceeds. This indicates that Fe could be leached into the solution as the reaction proceeds, and therefore, we analysed reaction mixtures for solubilised Fe. It should be noted that $(FePctBu_4)_2N@SiO_2$ is highly insoluble in water, the solvent for the reaction, but is decomposed by reaction with H_2O_2. In entry 2, the leached Fe accounts for ca. 40% of the initial Fe present in the catalyst, and the sum total of acetone and acetic acid accounts for about 46% of the starting carbon present in the catalyst. These data indicate that the $(FePctBu_4)_2N@SiO_2$ catalyst is unstable under these reaction conditions and clearly cannot be recovered and re-used.

At a higher oxidant level (entry 3, 500 mM H_2O_2), a higher level of gas phase CO_2 is detected. Even for a very low oxidant concentration (entry 4, 70 mM H_2O_2), the catalyst still shows substantial decomposition products (acetone and acetic acid) and partial selectivity to oxygenates of 71%. By comparing the data in entry 3–4, it is apparent that decreasing the oxidant concentration effectively prevents over-oxidation of the primary products to HCOOH and CO_2. Due to similarities in the CO_2 results between the 2 ml and 10 ml reactions, entries 2 and 3 in Table 2, we were prompted to consider that the catalyst decomposition was responsible for the formation of some of the CO_2 and/or the useful oxygenates rather than being derived from CH_4. This aspect of the stability of the $(FePctBu_4)_2N@SiO_2$ catalyst is explored further in a subsequent section. It is important to note that the catalyst showed total loss of its original blue–green colour after 20 h reaction under the conditions in entry 3 and major loss of colour for the data reported in entries 2,4 (see Supporting information Fig. S14).

Finally, we studied the catalyst under (0.075 M H_2SO_4) since it was reported that the catalyst had higher activity and stability under acidic conditions [1,2]. We modified the reaction conditions so that similar levels of oxidant, catalyst and substrate as in the '2 ml' reaction were employed. The freshly prepared material was used in the absence of acid, entry 5 Table 2, and gave 49% oxygenate selectivity together with C_2 decomposition products. When an aqueous 0.075 M H_2SO_4 solution was used as the solvent, entry 6 Table 2, the activity improved dramatically as a twofold increase in C_1 oxygenates was observed as compared to the test performed in the absence of acid. Additionally, the oxygenate selectivity was improved from 49% to 62% in the presence of acid though there was total consumption of the hydrogen peroxide. Visually the loss of blue colour in the recovered material was not as severe which prompted us to perform a re-use test under acidic conditions. The data presented in entry 7 Table 2 show product amounts similar to that observed in entry 6 but with different product distribution and higher oxygenate selectivity. However, in this case, the recovered catalyst was completely decolourised and XPS analysis of the used material showed no Fe was present on the surface of the used catalyst (see Supporting information Fig. S11). Thus, we proposed that the result of the reuse test was probably due to leached Fe which under acidic conditions has appreciable activity with good selectivity for methane oxidation (refer to entry 3 Table 3 for an example of this). Thus, it is apparent that $(FePc^tBu_4)_2N@SiO_2$ is unstable under reaction conditions and that catalyst decomposition or homogeneous Fe based methane oxidation may be responsible for a major proportion of the products observed due to its reaction with H_2O_2 over the extended reaction time.

3.3. Methane oxidation using components in the $(FePc^tBu_4)_2N_2@SiO_2$ catalyst

The results of Section 3.2 demonstrate that the catalyst is unstable under reaction conditions. It is, therefore, useful to know the activity of a number of the components of the catalyst for this reaction. The blank reaction can be considered to be the reaction catalysed by the H_2O_2 (auto-oxidation) or the silica used as a support for the complex. CH_4 oxidation by H_2O_2 in the absence of any added catalyst was not observed under the reaction conditions. However, we observed that the silica support was active for methane oxidation (entry 1, Table 3) and was also active for the decomposition of H_2O_2 as very little remained at the end of the reaction. However, it should be noted that the C_1 oxygenate selectivity observed with the SiO_2 support alone is high (80.4%) compared with the $(FePc^tBu_4)_2N@SiO_2$ catalyst (entry 3, Table 2). Under these reaction conditions, the phthalocyanine-based catalyst leached a total concentration of 10 ppm Fe into the reaction mixture after 20 h. The leached Fe could be in the form of intact $(FePc^tBu_4)_2N$ (i.e. the organometallic complex being wholly leached off the silica support) or as un-complexed aqueous Fe which would then act as a homogeneous catalyst. However, we did not observe the intact complex in solution after the reaction and in view of its high affinity for silica we do not consider that the complex leaches in this way.

We therefore investigated the reaction of this concentration of Fe using $FeCl_3$ and the results (entry 2, Table 3) show that soluble Fe can catalyse the reaction and CH_3OOH and CH_3OH are both observed. However, large amounts of CO_2 are produced. Of course the catalyst could leach this amount of Fe as a maximum amount over the course of the 20 h reaction and so this experiment possibly overestimates the contribution of the homogeneously catalysed component of the reaction; but the experiment demonstrates that the reactions with $(FePc^tBu_4)_2N@SiO_2$ are not wholly heterogeneously catalysed. Furthermore, under acidic conditions (entry 3 Table 3), homogeneous Fe based oxidation shows higher catalytic activity and oxygenate selectivity but in all reactions high hydrogen peroxide usage occurs. It is well known that Fenton chemistry [37–39] principally proceeds through hydroxyl and hydroperoxy radicals, and thus, we postulate the possible involvement of these species not only in methane activation, in a similar way to benzene

Table 3
Comparison of the oxidation activity of components of $(FePc^tBu_4)_2N@SiO_2$ for methane oxidation[a].

Entry	Catalyst	Products (μmol)					Oxygenate productivity[e]	Oxygenate selectivity[f]	Unused H_2O_2 (μmol)[g]	TON[h]
		CH_3OOH[b]	CH_3OH[b]	CH_2O[c]	HCOOH[b]	CO_2 in gas [d]				
1	SiO_2	4.14	3.08	0	0	1.76	0.007	80.4	<200	503
2	10 ppm Fe(aq)[i]	2.35	6.81	0	27.5	66.4	18.3	35.6	<50	58
3	30 ppm Fe(aq)[i]	10.0	4.4	7.3	40.3	18.5	413	77	1875	15

[a] Conditions entries 1, 2 – reaction time 20 h; temperature 50 °C; $[H_2O_2] = 0.5$ M, P $(CH_4) = 32$ bar, mass of solid catalysts used was 50 mg. Conditions entry 3 – reaction time 0.5 h; temperature 50 °C; $[H_2O_2] = 0.5$ M, P $(CH_4) = 32$ bar, pH3.
[b] Analysis using ^1H NMR.
[c] Analysed as hydrated CH_2O by ^1H NMR.
[d] Analysis using GC-FID with a methaniser.
[e] Oxygenates productivity = mol of oxygenates (MeOOH + CH_3OH + CH_2O HCOOH)/kg_{cat}/reaction time (h).
[f] Total C_1 oxygenates/total C_1 oxygenates + CO_2 in gas.
[g] Assayed by Ce^{+4}(aq) titration.
[h] Turnover number calculated on total Fe including the support.
[i] Using $FeCl_3$, For entry 1 [Fe] in filtrate was < 1.25 ppm.

oxidation with Fenton's reagent [40], but also in catalyst degradation. Though it was reported that the initial interaction of H_2O_2 with $(FePc^tBu_4)_2N$ does not produce hydroxyl radicals [1,2], if leached iron results in hydroxyl radicals being formed then these could play a major role in the observed chemistry. Hence, we can conclude that leached Fe can contribute significantly to the oxidation activity observed when using $(FePc^tBu_4)_2N@SiO_2$ as a catalyst. It is also possible that the action of silica in the presence of hydrogen peroxide initiates catalyst degradation since silica has been shown to be active for the methane oxidation.

3.4. Catalyst decomposition

As we have observed catalyst decomposition during the reaction, it follows that we have only partially answered the question concerning catalyst selectivity as to whether or not all the CO_2 or C_1 products observed in the reaction originate from methane oxidation or from the methyl groups in the catalyst? We therefore studied the decomposition of both the ligand and the catalyst by stirring under reaction conditions in the absence of methane. In this case, methane was replaced with He or N_2. First, we investigated the supported ligand in the absence of complexed Fe (entry 1, Table 4) and this was found to produce a range of products including methanol and formic acid as well as acetone, acetic acid and acetaldehyde. These products result from the oxidation of the *tert*-butyl groups of the ligand and the colour of the complex was retained after reaction (see Supplementary Fig. S12). It is known that organic compounds with t-butyl groups or other OH groups are also either autoxidised by H_2O_2 or oxidised by homogeneous metal catalysed reactions. For example, use of tertiary butyl hydroperoxide as oxidant can give products that are easily misidentified as coming from methane oxidation (see Supplementary Fig. S13). We then added soluble Fe^{3+} and observed that the decomposition of the ligand was enhanced by the addition of this non-complexed Fe^{3+} (entries 2–4, Table 4) but the phthalocyanine ring remained intact as evidenced by the retention of colour following reaction (see Supplementary Fig. S12). We then reacted the supported complex $(FePctBu_4)_2N@SiO_2$ under the same reaction conditions (entry 5, Table 4) and now we observe that the phthalocyanine breaks down and CO_2 is observed in significant amounts. The C_2 products are derived from the reaction of the *tert*-butyl groups of the phthalocyanine and the additional CO_2 observed originates from the degradation of the ligand as evidenced by the loss of colour after the reaction (see Supplementary Fig. S12). The observation of small amounts of C_1 products in these experiments could mean that the selectivity observed for the C_1 products during the reaction of the catalyst with methane (Table 2) may be overestimated. The observation of enhanced phthalocyanine decomposition when

Table 4
Reactions of SiO_2-supported $^tBu_4Pc$ and $(FePc^tBu_4)_2N$ with aqueous H_2O_2[a].

Entry	Setup	Aqueous phase products (μmol)						Gas Phase product μmol	Total Aqueous Products (μmol)	Carbon balance%
		HCOOH[b]	CH_3OH[b]	$(CH_3)_2CO$[b]	CH_3COOH[b]	CH_3CHO[c]	CH_2O[d]	CO_2[e]		
1	$^tBu_4Pc - SiO_2 + H_2O_2$	0.36	0.29	2.86	1.90	1.57	n.d	2.63	6.98	21.2
2	$^tBu_4Pc - SiO_2 + H_2O_2 + 0.2$ ppm Fe (aq)	0.71	0.43	2.57	2.00	1.00	n.d	6.39	6.71	23.6
3	$^tBu_4Pc - SiO_2 + H_2O_2 + 5$ ppm Fe (aq)	0.71	0.29	2.58	2.14	3.00	n.d	5.00	8.72	26.9
4	$^tBu_4Pc - SiO_2 + H_2O_2 + 10$ ppm Fe (aq)	0.43	0.29	2.00	1.29	5.57	n.d	4.18	9.58	26.6
5	$(FePc^tBu_4)_2N - SiO_2 + H_2O_2$	n.d	n.d	4.57	5.29	n.d	n.d	20.14	8.86	53.7
6	$(FePc^tBu_4)_2N - SiO_2 + H_2O_2$	1.09 (0.23)	0.89	(1.33)	(1.9)	(1.71)	(1.28)	11.1	6.45*	45.7*

[a] Conditions entries 1–5; water (10 ml), 50 mg of supported materials, $[H_2O_2] = 0.5$ M, 50 °C, 20 h, 1500 rpm, P $(N_2) = 32$ bar; conditions entry 6; water (10 ml), catalyst (17.8 mg), $[H_2O_2] = 0.16$ M, 60 °C, 20 h, 1500 rpm, P $(^{13}CH_4) = 8$ bar; Fe(aq) from $Fe(NO_3)_3$.
[b] Analysed using ^1H NMR.
[c] Analysed as hydrated CH_3CHO by ^1H NMR.
[d] Analysed as hydrated CH_2O by ^1H NMR.
[e] Analysed using GC-FID. () refer to ^{12}C products.
[*] Based solely upon ^{12}C products. n.d not detected.

the Fe^{3+} is complexed is an important observation and, as discussed subsequently, indicates the iron phthalocyanine complex is a catalyst for its own oxidative decomposition.

In these studies, we have shown that the Fe in the catalyst can be leached and it is known that Fe^{3+} in the presence of H_2O_2 can generate OH radicals by Fenton's reaction [37–39] which can then react with the phthalocyanine leading to its degradation. Hence, we have investigated the effect of adding a scavenger for OH radicals. In the presence of a hydroxyl radical scavenger, sodium sulphite, we observed that the catalyst decomposition decreased by approximately 30% with H_2O_2: sulphite ratio of 2:1 (see Supplementary Fig. S14). Hence, the catalyst becomes more stable in the presence of a hydroxyl radical scavenger. Previous studies have proposed that the reaction mechanism does not include hydroxyl radical formation by homolysis of the O–O bond from the iron hydroperoxy species initially formed by interaction of H_2O_2 with the iron centre [1,2,41,42]. Rather a high valent iron oxo species was put forward as the active oxidising species, but this result does indicate the possible involvement of hydroxyl radicals in the overall chemistry observed, and we consider that this is potentially important for the mechanism of the catalyst decomposition. Considering the role of OH radicals in the decomposition of the phthalocyanine, two pathways might be possible: (i) generation of OH radicals by the iron phthalocyanine (this would lead to inherent instability) and (ii) generation of OH radicals in the close vicinity of the adsorbed complex leading to its decomposition which, in turn, provides more iron sites leading to autocatalytic decomposition. The SiO_2 support alone, which contains 20 ppm Fe as an impurity, (entry 1, Table 3) shows significant H_2O_2 decomposition which will lead to OH radical formation. It is clear therefore that there is probably a significant contribution from pathway (ii). However, the observation that complexed Fe is more reactive in the decomposition of the phthalocyanine clearly also shows that pathway (i) is also operating. Hence, at this stage, it is considered that both pathways are operating under the reaction conditions we have used.

We then used $^{13}CH_4$ to indicate the contribution to C_1 oxygenates from catalyst degradation since any non-^{13}C products must originate from carbon in the catalyst under these conditions. As shown in entry 6 Table 4, methyl hydroperoxide, methanol and formic acid contain the ^{13}C label. We also detected ^{12}C formic acid, hydrated formaldehyde as well as acetic acid, acetone and acetaldehyde under these conditions. The products containing ^{12}C accounted for *ca.* 46% of the initial carbon in the catalyst, whilst the actual oxygenate productivity of the catalyst based on ^{13}C products was 0.014 mol oxygenates kg $(cat)^{-1}$ h^{-1}. This experiment shows unambiguously that formic acid, formaldehyde, acetic acid, acetone and acetaldehyde can be derived from the degradation of the catalyst. Although the ratio of $^{13}CO_2$ to $^{12}CO_2$ formed could not be determined by our analytical methods, there is clear evidence for the formation of CO_2 from the catalyst since in the absence of methane (entry 1, 2 Table 4) CO_2 is produced.

Finally, the effect of the reaction time on product formation was investigated (Fig. 2). It is apparent that even at low reaction times, when the amount of methane oxidation products is low, appreciable amounts of the C_2 catalyst decomposition products are observed. As time proceeds, the activity of the catalyst levels off then shows increased activity after 6 h. We propose that the contribution from homogeneous iron catalysed reactions is significant after this time as about 6 ppm of Fe was detected in the reaction filtrate for the 6 h reaction. We observed that CH_3OOH was the major product throughout the entire reaction as one would expect from the interaction of a metal bound hydroperoxy species and methane under suitable conditions. As noted before, this species can be generated by homogeneous Fe reactions (entry 3, Table 3) and hence it is not unique to the $(FePctBu_4)_2N@SiO_2$ catalyst. Colour loss is always observed with this catalyst and this is pronounced using 0.5 M H_2O_2 in our 10 ml reaction (see Supplementary Fig. S15).

3.5. Reactions using Fe/SiO_2

In Section 3.3, we noted that the silica support showed some activity for the oxidation of methane possibly originating from transition metal impurities. Therefore, we tested a 0.2% Fe/SiO_2 catalyst prepared by an impregnation procedure. The metal loading matches the metal content of the phthalocyaninato-based catalyst though the metal sites in both systems will be significantly different. Interestingly, this catalyst was very selective to oxygenates and when compared to the phthalocyanine-based system it has superior selectivity and high hydrogen peroxide utilisation, though the productivity of C_1 oxygenates is lower (entry 1 Table 5).

We prepared and studied wet impregnation catalysts for 4 h reactions as the reference phthalocyanine-based system has appreciable Fe leaching after this reaction time. XRD characterisation of the Fe/SiO_2 sample prepared from $Fe(NO_3)_3$ showed that haematite was present with an estimated particle size of 16 nm, whilst the sample prepared from $Fe(acac)_3$ was amorphous to X-rays indicating that any oxide present must have a particle size of below 5 nm (see Supplementary Fig. S16). The metal loadings were 2.58 and 2.43 wt.% Fe, respectively, as determined by AAS. Both these samples were active for methane oxidation with high selectivity to oxygenates >85% (entries 1 and 3 Table 5). The leaching observed under these reaction conditions is minimal indicating catalyst stability is superior to the $(FePc^tBu_4)_2N@SiO_2$ catalyst. These data demonstrate

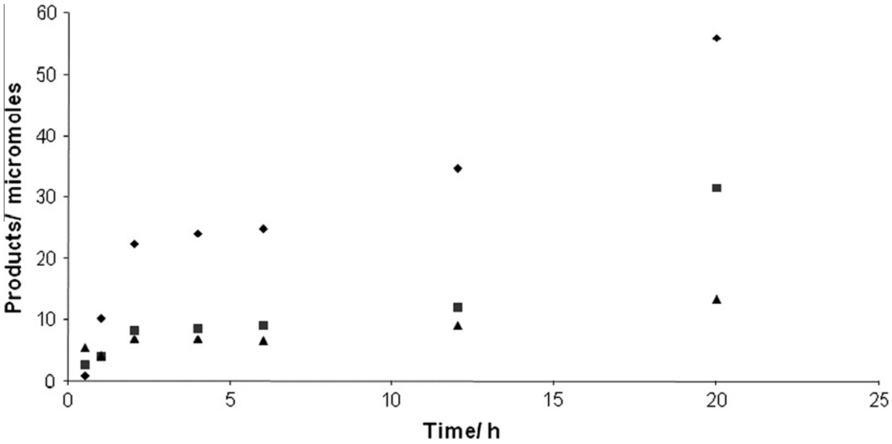

Fig. 2. Product reaction profile for the $(FePctBu_4)_2N@SiO_2$ catalyst using H_2O_2 for methane oxidation. All conditions as in Entry 3 Table 2. ◆ Total C_1 oxygenates; ▲ total C_2 oxygenates; ■ CO_2 in the gas phase.

Table 5
Comparison of activities of various Fe/SiO_2 catalysts for CH_4 oxidation.

Entry	Catalyst	Products (μmol)					Oxygenate productivity [d]	Oxygenate selectivity[e]	Unused H_2O_2 (μmol)[f]	Leached Fe(aq) ppm [g]	TON[h]
		MeOOH[a]	MeOH[a]	CH_2O[b]	HCOOH[a]	CO_2 in gas[c]					
1	$(FePc^tBu_4)_2N@SiO_2$	17.7	11.6	12.7	13.9	26.6	0.056	67.7	2600	9.7	47
2	0.2 wt.% Fe/SiO_2 (from $Fe(NO_3)_3$)	13.5	1.90	0	0.61	2.59	0.016	86.1	3620	<0.1	10
3	$(FePc^tBu_4)_2N@SiO_2$	19.3	2.32	Trace*	2.58	8.7	0.121	73.5	3660	3.9	19
4	2.43 wt.% Fe/SiO_2 (from $Fe(acac)_3$)	13.6	4.11	11.3	2.04	4.85	0.155	86.5	2220	0.1	1.7
5	2.58 wt.% Fe/SiO_2 (from $Fe(NO_3)_3$)	4.94	12.4	4.49	2.71	4.03	0.123	85.9	3900	0.28	1.2

Conditions entry 1, 2: 20 h, 50 mg catalyst, 0.5 M H_2O_2, 32 bar CH_4, 10 ml reaction volume. Conditions entries 3–5: 4 h, 50 mg catalyst, 0.5 M H_2O_2, 32 bar CH_4, 10 ml reaction volume. All catalysts calcined at 400 °C, 3 h in static air except $(FePc^tBu_4)_2N@SiO_2$.

[a] Analysis using ^{1}H NMR.

[b] Observed as hydrated CH_2O by ^{1}H NMR.

[c] Analysis by GC-FID.

[d] moles (MeOOH + MeOH + CH_2O + HCOOH) h^{-1} kg(catalyst)$^{-1}$.

[e] Total C_1 oxygenates/(total C_1 oxygenates + CO_2 in gas).

[f] Assayed by Ce^{+4} (aq) titration.

[g] Analysed by AAS of the reaction filtrate with 0.1 ppm being the lowest calibration point.

[h] Turnover number calculated on total Fe including the support.

[*] Trace taken as <0.1 μmol.

Table 6
Activity of 2.43 wt.% Fe/SiO_2 catalyst made by impregnation method from Fe $(acac)_3$ calcined at 400 °C.

Entry	Catalyst mass (mg)	Rxn. time (h)	Products (μmol)					Oxygenate productivity[d]	Oxygenate selectivity[e]	Unused H_2O_2 (μmol)[f]	Leached Fe(aq) ppm[g]	TON[h]
			MeOOH[a]	MeOH[a]	CH_2O[b]	HCOOH[a]	CO_2 in gas[c]					
1	22.5	4	9.89	2.00	0	0.83	2.64	0.141	82.8	3526	<0.1	1.6
2	22.5	20	12.0	6.04	8.03	8.86	8.59	0.078	80.3	1433	0.71	4.5
3	50	0.17	6.0	1.51	0	0	1.05	0.901	87.7	4126	<0.1	0.4

Conditions: 32 bar CH_4, 10 ml reaction volume, 50 °C.

[a] Analysis using ^{1}H NMR.

[b] Observed as hydrated CH_2O by ^{1}H NMR.

[c] Analysis by GC-FID.

[d] moles (MeOOH + MeOH + CH_2O + HCOOH) h^{-1} kg(catalyst)$^{-1}$.

[e] Total C_1 oxygenates/total C_1 oxygenates + CO_2 in gas.

[f] Assayed by Ce^{+4}(aq) titration.

[g] Analysed by AAS of the reaction filtrate with 0.1 ppm being the lowest calibration point.

[h] Turnover number calculated on total Fe including the support.

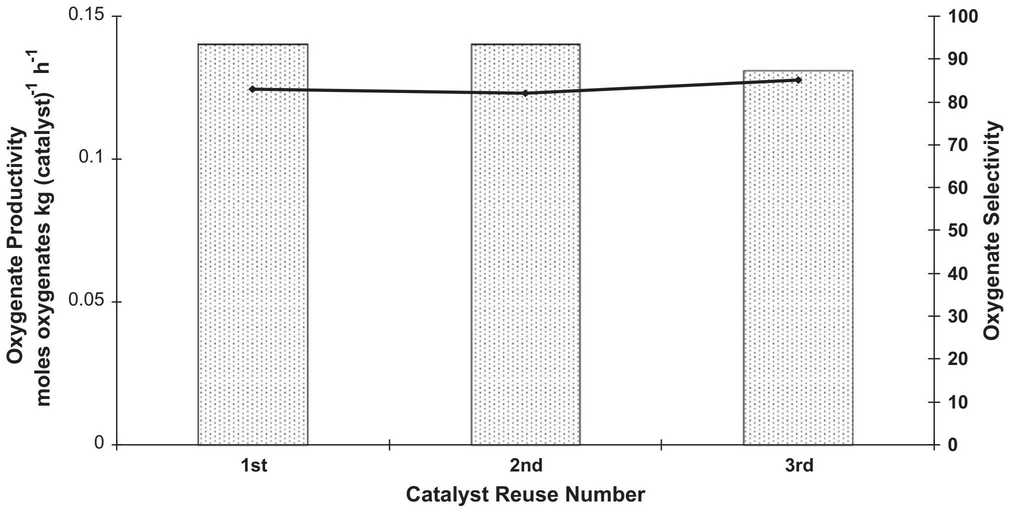

Fig. 3. Reuse testing for 2.43 wt.% Fe/SiO_2 calcined at 400 °C in static air. Conditions P (CH_4) = 30 bar, [H_2O_2] = 0.5 M, T = 50 °C, t = 4 h, 1500 rpm, catalyst mass = 22.5, 22.5, 13 mg for tests 1,2,3 respectively. The recovered catalyst was dried in air at ambient temperature after washing with distilled water in between uses.

that the relatively simple supported metal oxide catalysts, prepared by wet impregnation, can perform selective methane oxidation using H_2O_2 as the oxidant. Also we observe that the catalyst containing the smaller iron oxide particles gives a higher yield of methyl hydroperoxide vs. methanol (entries 2 and 3 Table 5).

Further study of these catalysts showed that even after 20 h the selectivity to oxygenates is still 80% with a similar productivity to the unstable $(FePc^tBu_4)_2N@SiO_2$ system (entry 2 table 6 vs. entry 3 Table 2). At longer reaction times or with higher catalyst mass, we observe the sequential oxidation of methyl hydroperoxide to formic acid *via* the alcohol and aldehyde (Table 6). Finally, we compared the Fe/SiO_2 catalyst to MMO by carrying out a 10 min reaction (entry 3 Table 6). For Fe/SiO_2, the productivity is one-fifth of that observed with the whole native sMMO enzyme for methane to methanol conversion. Additionally, the Fe/SiO_2 catalyst does not show an induction period that is a hallmark of the $(FePc^tBu_4)_2N@SiO_2$ catalyst, and also no formaldehyde or formic acid was detected for this short reaction (entry 3 Table 6). We note that these Fe/SiO_2 catalysts are stable and reusable even after prolonged reaction times as demonstrated by almost identical productivity and selectivity even after three reuse tests (Fig. 3). It should be noted that without further modification the Fe/SiO_2 is not stable under acidic conditions and shows appreciable leaching in similar manner as the supported phthalocyanine catalyst. Further tuning of this catalyst was not performed.

It is useful to compare the turn over frequency of these systems to sMMO hydroxylase using aqueous H_2O_2 as oxidant. Considering there are two mol of active Fe per mol of sMMO hydroxylase (i.e. a di-iron active site) the TOF is 2.38 mol oxygenates per (h × mol (Fe)) at 0.5 h reaction time. For 2.43 wt% Fe/SiO_2 reported in Table 6 the TOF is 2.0 mol oxygenates per (h × mole (Fe)), whilst for $(FePc^tBu_4)_2N@SiO_2$ which had 0.2 wt.% Fe the TOF is 1.03 mol oxygenates (h × mole (Fe)) at 0.5 h reaction time. These data show that the catalyst prepared by impregnation is both stable and is comparable in activity to the phthalocyanine catalyst for methane oxidation with H_2O_2 and also highlights that traditional heterogeneous metal oxide catalysts can compete with the enzyme systems for low temperature methane oxidation.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jcat.2012.03.013.

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