The Partial Oxidation of Propane under Mild Aqueous Conditions with H₂O₂ and ZSM-5 Catalysts

Virginie Peneau[a], Greg Shaw[a], Robert D. Armstrong[a], Robert L. Jenkins[a], Nikolaos Dimitratos[a], Stuart H. Taylor[a], Horst W. Zanthoff[b], Stefan Peitz[b], Guido Stochniol[b], and Graham J. Hutchings*[a]

[a]Cardiff Catalysis Institute, School of Chemistry, Cardiff University, Main Building, Park Place, Cardiff, CF10 3AT, United Kingdom. Tel: +44 (0) 2920874059, Fax: +44(0) 2090874 030

[b] Evonik Industries AG, 45764 Marl, Germany

*Corresponding author: Hutch@cf.ac.uk

Abstract

We report the oxidation of propane under mild aqueous conditions using H_2O_2 as the oxidant. Various reaction conditions have been studied with a view to optimising the conversion of propane in the presence of a Fe/ ZSM-5 (30) catalyst. Process optimisation afforded 52% propane conversion in 0.5 h at a temperature of 70 °C. C_3 products are shown to undergo sequential catalytic C-C scission and oxidation reactions in the presence of the catalysts, yielding C_2 and C_1 products. This leads to an inverse relationship between propane conversion and reaction selectivity. Addition of Cu to Fe /ZSM-5 (30) shifted reaction selectivity towards propene ($\leq$ 34 %) with increasing conversion.

1. Introduction

Increasingly stringent environmental restrictions, depleting crude oil reserves and burgeoning demand are driving the search for alternate, greener routes to bulk chemicals from non-traditional feedstocks. Given their abundance, relatively low cost and global distribution natural and shale gases are promising feedstocks for such a transition, however these are as yet an underutilised resource. Valorisation of the short chain alkane constituents; present within these reserves, is a promising route, however, it is hampered by low substrate reactivity with C-H bond enthalpies in methane (ΔH_{C-H} = H-CH$_3$ 439.6 kJmol^{-1}), ethane (H-CH$_2$CH$_3$ 423.3 kJmol^{-1}) and propane (H-CH$_2$CH$_2$CH$_3$ 422.2/ CH$_3$CH(H)CH$_3$ 409.2 kJmol^{-1})[1, 2]. An additional barrier to selective oxidation is that primary reaction products are often more reactive than the substrate, thereby limiting reaction yield. An example of this is the oxidation of propane to acrolein, whereby the weakest C-C bond in acrolein (ΔH_{C-C} = 347 kJ mol^{-1}) is inherently more reactive than the weakest C-H bonds in either acrolein (ΔH_{C-H} = 364.4 kJ mol^{-1}) or propane [3]. Consequently, technologies for natural gas upgrading are often energy intensive. A low energy, atom efficient route to the upgrading of these aliphatic hydrocarbons would therefore represent a significant step towards realising the potential of natural gas as a chemical feedstock.

Previously, technologies have focused upon conversion of the lower (C$_2$ – C$_4$) alkanes to their corresponding olefins through steam cracking [4]. Olefins, being intrinsically more reactive than the corresponding alkane, are then converted to value added products. In this way acrolein and acrylic acid are produced commercially from propane via a 2 step process which proceeds through propene [5]. Whilst the oxidation reaction is high yielding, propene production is highly energy intensive and although progress has been made in alternative routes for propene production such as propane dehydrogenation [6], the direct oxidation of propane is preferable [4]. Propene is also an important feedstock for the production of isopropanol [7] and in the cumene process, where benzene is alkylated to yield acetone and phenol. Indeed > 80% of acetone is produced in this way, leading acetone- output to be dictated by global demand for phenol [8]. The direct catalytic transformation of propane to oxygenated products is therefore a growing field of research. Indeed, the direct production of

isopropanol [7, 9], acetone [9, 10], acrylic acid [11-17] and acrolein [18] has been reported. The most promising reactions appear to be propane ammoxidation to acrylonitrile [19] and direct propane oxidation to acrylic acid [20] which have both been trialled at pilot plant scale but are yet to replace existing production routes. However, owing to low liquefaction pressures and low substrate reactivity, the low temperature, liquid phase oxidation of propane has been less extensively studied [7, 9, 21].

A key obstacle to the selective partial oxidation of propane is that high C-H bond energies at both 1° and 2° positions render propane less reactive when compared with its partial oxidation products. Indeed, this is common to the lower alkanes. Therefore, a catalytic system must have sufficiently high rates of C-H activation, whilst inhibiting further oxidation of desirable products. A number of studies have reported the selective oxidation of n-alkanes at low reaction temperatures using the green oxidant H_2O_2 and MFI- type zeolites [22-32]. ZSM-5 type aluminosilicate zeolites have recently been reported as active catalysts for the oxidation of methane [24, 25] and ethane [22, 23] at temperatures of < 70 $^\circ$C using H_2O_2 in the aqueous phase. Catalytic activity was attributed to contaminant iron species present within commercial zeolites (< 100 ppm), which migrate to extraframework positions upon thermal activation to form dimeric μ- oxo- hydroxo iron sites [24]. These sites catalyse H_2O_2 conversion and also C-H activation reactions, with alkane TOFs ($mol_{activated}$ mol_{Fe}^{-1} h^{-1}) of greater than 1200 reported [22]. Furthermore, it was reported that simultaneous deposition of post synthesis Fe and Cu onto these catalytically active materials increases productivity and selectivity. In this way reaction selectivity might be tailored to methanol (14.0 $mol_{methanol\ formed}$ $kg_{cat}^{-1}h^{-1}$, 85 % selectivity) from methane, with either acetic acid (25.7 $mol_{acetic\ acid\ formed}$ kg_{cat}^{-1} h^{-1}, 55% selectivity) or ethene (7.8 $mol_{ethene\ formed}$ kg_{cat}^{-1} h^{-1}, 34% selectivity) formed from ethane at 50 $^\circ$C [22, 24]. Alkane activation has also been reported using the titanosilicate zeolite TS-1 [28-32]. Indeed, Shul pin and co-workers reported the selective oxidation of propane, amongst other n-alkanes, with acetone (0.25 $mol_{acetone}$ kg_{cat}^{-1} h^{-1}) and isopropanol (0.12 $mol_{isopropanol}$ kg_{cat}^{-1} h^{-1}) being the favoured reaction products [32]. Preferential oxidation of secondary C-H bonds, in particular those adjacent to terminal CH_3 groups in TS-1/ H_2O_2 alkane oxidation systems, is consistent with previous theoretical [33] and experimental

studies [28, 30]. However, whilst these studies show the reaction to be feasible, failure to address the efficiency of H_2O_2 use impacts upon atom efficiency and economic viability.

In this study we aim to assess Fe- and Cu- modified ZSM-5 catalysts for activity in the low temperature partial oxidation of propane with H_2O_2. A systematic study of reaction conditions targets reaction optimisation. Based on initial findings, catalysts are then selected in order to maximise the yield of partially oxygenated C_3 products

2. Experimental

2.1 Catalyst preparation

NH$_4$-ZSM-5 (SiO$_2$/Al$_2$O$_3$ = 30) was obtained from a commercial source (Zeolyst) and was activated in flowing air prior to use (550 °C, 3 h, 20 °C min^{-1}). Where applicable, Fe and/or Cu were deposited to the desired loading by Chemical Vapour Infiltration (CVI) with the appropriate acetylacetonate precursor [34]. This preparation technique has been studied previously, and was shown to give strict control of actual metal loadings [35]. A typical procedure is that prior to the addition of the metal H-ZSM-5was dried (160 °C, 3 h) under vacuum (10^{-3} mbar) prior to sieving (40 mesh). H-ZSM-5 and the appropriate amount of metal acetylacetonate were physically mixed and transferred to a Schlenk flask. The flask was then evacuated (10^{-3} mbar) and heated under vacuum (150 °C, 2 h). The sample was removed after cooling to ambient temperature and then calcined in static air (550°C, 3 h, 20 °C min^{-1}).

2.2 Propane oxidation

Batch catalyst testing for the oxidation of propane with H_2O_2 was carried out in a 50 ml stainless-steel Parr autoclave fitted with a Teflon liner and a total workable volume of 35 ml. In a typical experiment, 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 purging with helium, the system was charged with propane (4 bar, 4000 µmol) and then the total pressure was increased to 20 bar with helium as

diluent. The autoclave was then heated to the desired reaction temperature (typically 50 °C) and vigorously stirred (1500 rpm) and maintained at a constant temperature for the desired reaction time (typically 0.5 h). After completion of the reaction, the vessel was cooled in ice to *ca.* 12 °C and the gas phase vented into a gas sampling bag. Following this the liquid phase was recovered and filtered prior to analysis.

Liquid products were identified through a combination of ^{1}H NMR spectroscopy, on a Bruker 500 MHz Ultra-Shield NMR spectrometer (assigned NMR spectra, figure S1), and GC-MS. The products were subsequently quantified against a 1 vol% TMS/CDCl$_3$ internal standard, which was calibrated against authentic standards of each reaction product using ^{1H} NMR spectroscopy due to the level of sensitivity required and the use of water as solvent. The ^{1}H NMR method contained a suppression of the water peak to negate its contribution. Gaseous phase products were analysed using a Varian 450-GC fitted with a CP-Sil 5CB capillary column (50 m length, 0.33 mm ID), a methaniser and FID detector. Products were identified and quantified against standards. The amount of H$_2$O$_2$ remaining after reaction was quantified by titration of aliquots of the final solution against Ce(SO$_4$)$_2$ using Ferroin indicator. This allowed quantification of (a) % H$_2$O$_2$ conversion such that % H$_2$O$_2$ converted = ((mol $_{start}$ − mol$_{end}$)/ mol$_{start}$ x 100) and (b) % H$_2$O$_2$ utilisation, such that % H$_2$O$_2$ utilised = ((mol $_O$ (products)/ mol$_O$ (converted H$_2$O$_2$) x 100)

3. Results and Discussion

3.1 Preliminary catalyst studies

Previous studies into ZSM-5 catalysed alkane oxidation systems have shown iron impurities within the zeolite framework to be the source of active sites [24]. These migrate to extra-framework sites to form catalytically active dimeric μ- oxo- hydroxo iron species upon high temperature activation [24]. From our earlier studies for methane and ethane oxidation, the most intrinsically active catalyst (in terms of TOF mol$_{Fe}^{-1}$ h^{-1}) was H-ZSM-5 (SiO$_2$:Al$_2$O$_3$ = 30), and hence was investigated for the oxidation of propane under mild reaction conditions ([H$_2$O$_2$] = 0.5 M, 50°C, 0.5 h). Over the 0.5 h

testing period 0.9 % propane conversion was achieved with 88.7 % selectivity to oxygenated products and the product distribution is shown in Figure 1.

With the aim of increasing propane conversion, iron was deposited post- synthesis onto ZSM-5 by CVI. Fe/ZSM-5 catalysts prepared via this method have been fully characterised previously [23]. HR-TEM has shown that Fe deposits as a porous iron oxide film on the zeolite surface and within its pores [22, 23]. Additionally, UV-Vis spectroscopy indicated the presence of isolated iron clusters, oligomeric iron species, and cationic species at exchange sites within the zeolite pores [22, 23]. The concentration of all Fe species was shown to increase with Fe loading, showing Fe- deposition via CVI to be non-selective [22, 23]. XPS shows the presence of Fe^{3+} characteristic of Fe_2O_3 particles [23].

Deposition of Fe onto H-ZSM-5 led to a significant increase in catalyst productivity relative to H-ZSM-5 (Figure 2). A beneficial effect on propane conversion was observed up to an iron loading of 2.5 wt%, with propane conversion increasing from 0.9% to 7.9%. This constituted a catalyst productivity increase from 2.7 to 23.5 $mol_{propane\ converted}.kg_{cat}^{-1}h^{-1}$. Whilst the oxygenate selectivity remained at *ca.* 90% across this range, the amount of oxygen from converted H_2O_2 which was utilised in the products increased from 20 to 43%. This is an important result as high efficiency of utilisation is an important economic requirement when using H_2O_2. It should however be noted that 43 % utilisation is itself not commercially viable due to economic and safety considerations.

Although catalyst productivity increased with iron loading, the increase was not linear and no further enhancement was observed at loadings of > 2.5 wt%. With increasing Fe loading it is probable that the ion exchange sites within the ZSM-5 framework become increasingly populated with cationic Fe species or blocked by Fe_xO_y particles. We have recently reported that iron oxide species on the external zeolite surface are spectator species in the oxidation of ethane using Fe/ZSM-5 catalysts and H_2O_2 [36]. Figure 2 therefore suggests that Fe species deposited at loadings of > 2.5 wt% behave in much the same way for propane oxidation reactions.

3.2 Optimisation of reaction conditions to favour high propane conversion

To better understand the reaction mechanism, and further increase propane conversion, a systematic study of catalyst testing parameters was conducted using 2.5% Fe/ZSM-5 prepared by CVI.

As shown in Figure 3, propane conversion increased with time up to 0.5 h. However, the rate of propane conversion decreased from 4 h on-line with a maximum of 17.2 % propane converted. With increasing reaction time, a gradual decrease in selectivity to oxygenated products was observed, from 93.6 % at 0.1 h to 89.1% at 6 h, and this corresponded to an increase in CO_2 selectivity of 2.8 % to 4.6 %. A decrease in the rate of reaction at times greater than 4 h is consistent with decreasing availability of H_2O_2, indeed 63.9 % H_2O_2 was converted over the initial 4 hours of reaction. Time on line analysis (Figure 4) shows decreasing selectivity towards the C_3 products propene, n-propanol and isopropanol with increasing reaction time. Meanwhile a corresponding increase in selectivity towards acetic acid, formic acid and CO_2 was observed. Our previous studies into the selective oxidation of ethane over the same catalyst system yielded two primary products (ethanol and ethene) for which analogous C_3 products (n-propanol, isopropanol and propene) were formed (Figure 4) [22]. Hydration of propene is a commercialised route to isopropanol production, and therefore propene is likely to be both a primary and intermediate product to C_3 oxygenated products. Given the high n-propanol and isopropanol selectivities observed at t = 0.1 h, Figure 4 indicates that they are probably both primary products of propane oxidation as well as potential propene oxidation products. The presence of C_2 and C_1 oxygenated products, as well as CO_2 is clear evidence of the catalytic C-C scission of these primary products, and also indicates the presence of carbon centred radical species in solution, consistent with our previous studies [22]. These catalytic transformations are explored in detail later.

The effect of varying $[H_2O_2]$, within the range of 0.2 M to 1.8 M, on the propane oxidation was investigated and the results are shown in Figure 5. As expected propane conversion increased with increasing $[H_2O_2]$ but oxygenate selectivity remained constant across the whole range at 92% $\pm$ 0.8. Above 1.2 M H_2O_2 an increase to 1.8 M H_2O_2 led to no increase in conversion which suggests that either the system was propane limited or that competing H_2O_2 decomposition reactions were limiting oxidant availability. Indeed, the % utilisation of converted H_2O_2 decreased across the range, from 49.0 % at 0.2 M to 27.0 % at 1.8 M, which suggests that competing H_2O_2 decomposition reactions become

more favourable in the absence of propane. Such an effect was previously reported for ethane/ H_2O_2 [36]. An alternate mode of deactivation is through formation of intermediate Fe-OOH species, which previous studies have suggested block access of the alkane substrate to the active site [37]. Moreover, the Fenton's type decomposition of H_2O_2 leads to a change in the oxidation state of Fe, which could also result in deactivation of the active site for propane [38]. Hence, it is assumed that the low increase of conversion at high H_2O_2 concentration could be due to H_2O_2 saturating or deactivating sites that are active for propane activation.

The attainable partial pressure of propane in the current reactor is limited to a P_{max} of 4 bar. Therefore under our standard conditions (4 bar propane, 50 ºC) Henry's law predicts an aqueous propane concentration of 0.00298 M (Supplementary Figure S2). To determine the reaction order with respect to propane concentration, reactions were carried out at 0.8 and 2 bar propane partial pressure. A pseudo zero order dependence is observed across this pressure range (Figure 6), with the rate of propane conversion showing a slight decrease from 26.0 to 23.5 $mol_{propane\ converted}$ kg_{cat}^{-1} h^{-1} upon moving from 0.8 bar (800 $\mu mol_{propane}$) to 4 bar (4000 $\mu mol_{propane}$). Consequently, propane conversion increased from 7.9 % to 45.6 % moving from 4 bar to 0.8 bar. Lowering the propane partial pressure from 4 to 0.8 bar led to a decrease in selectivity to primary oxidation products (acetone, isopropanol and n-propanol)(product selectivities not illustrated in Figure 6), indeed total C_3 selectivity decreased from 38.9 % to 22.9%. This was reflected in an increase in selectivity to secondary oxidation products; acetic acid (10.3 % to 21.0%), formic acid (29.1 % to 44.1%) and CO_2 (1.3 % to 5.0%).

Increasing the catalyst mass from 15 mg to 160 mg led to an increase in propane conversion from 5.3 % to 10.9 % over 0.5 h as shown in Figure 7. Increasing the catalyst mass increased the population of active sites available in the reaction, thus increasing the conversion of H_2O_2 and propane. At the lowest loadings tested (0 – 27 mg) the catalyst operated within the kinetic regime, whilst at loadings of > 27 mg diffusion limitation of H_2O_2 and/ or propane is implied by a decrease in catalyst productivity (23.5 to 10.6 $mol_{propane\ converted}$ kg_{cat}^{-1} h^{-1} for 27 mg and 62 mg respectively). Isopropanol selectivity was observed to decrease with increasing catalyst mass, from 8.4 % at 15 mg loading to 3.7 % with 160 mg of catalyst. Across the same range, selectivity towards n-propanol also decreased from

17.8 to 5.2% respectively, with corresponding increases in formic acid selectivity (24.7 % to 40.5 %) and acetic acid selectivity (8.3 % to 16.9 %). Cracking of primary C_3 to secondary C_2 and C_1 products was clearly catalytic in nature, and these transformations are studied later in this article.

Another approach to increase the rate of propane and H_2O_2 conversion was through increasing the reaction temperature (Figure 8). Increasing the reaction temperature from 30 to 70 °C afforded an increase in conversion from 1.9% to a χ_{max} of 20.0 %, as shown in Figure 8. Given that 100 % H_2O_2 conversion was observed within 0.5 h at 90 °C, the effect of further increasing the reaction temperature was not studied. An Arrhenius plot of this data allowed calculation of an activation energy for propane oxidation as 52.7 kJ mol^{-1} (Supplementary information Figure S3). The deviation from linearity observed in the Arrhenius plot (70 °C), is probably due to (a) the system becoming oxidant limited, with 87 % H_2O_2 conversion observed after 0.5 h and (b) competing thermal H_2O_2 decomposition. Indeed, it is well known that thermal conversion of H_2O_2 occurs at temperatures of > 60 °C. Selectivity towards C_3 products decreased when increasing the reaction temperature from 30 °C to 70 °C, indeed selectivity to isopropanol decreased from 14.8 % to 2.1 % across this range. A corresponding increase of acetone selectivity, from 3.7 % to 8.6 % is consistent with consecutive oxidation pathways. A significant increase in formic acid selectivity was also observed with increasing temperature, from 13.7 % at 30 °C to a maxima of 43.6 % at 90 °C. These selectivities appear to be inherent of this catalytic reaction system and arise relative to changes in the propane conversion. Therefore, if high C_3 selectivity is to be realised under these testing conditions then operation at low temperatures/ low conversion is preferred. These trends are borne out of conversion vs selectivity plots that are described later.

To optimise propane conversion, reaction conditions were selected to reflect the findings of these systematic studies. The conditions used were; 0.1 g 2.5 wt% Fe / ZSM-5, [H_2O_2] = 1 M (10,000 µmol), 70 °C (Table 2 Entry 2). Under these conditions 33 % propane conversion was observed after 0.5 h of reaction. Further increasing the reaction time had no beneficial effect upon conversion, as 99 % H_2O_2 was converted within the initial 0.5 h of reaction and therefore the system was be oxidant limited. However, by lowering the partial pressure of propane to 1 bar *ca.* 52 % conversion was

attained (Table 2 Entry 5). Low C_3 selectivities were observed under these high conversion conditions, with reaction selectivity favouring the secondary oxidation products; acetic acid, formic acid and CO_2.

Conversion versus selectivity plots were constructed using the combined 2.5 % Fe/ZSM-5 (30) optimisation studies. This provided insight into the catalytic transformations which yielded the observed C_3, C_2 and C_1 products. (Supplementary Information Figures S4, S5 and S6). Three primary C_3 products were considered possible; n-propanol, isopropanol and propene (Supplementary Information Figure S4). Selectivity to these products decreased with increasing conversion, with corresponding increases in acetone and propanoic acid selectivity. C-C scission is evident, with both C_2 and C_1 products formed. Our previous studies into the oxidation of ethane over ZSM-5 catalysts showed that ethane underwent catalytic transformation to ethanol, ethene and ethylhydroperoxide (EtOOH, not observed here) [22]. These primary products underwent secondary oxidation to acetic acid and C-C scission yielded carbon centred radicals, which were either oxidised to form C_1 products; formic acid, methanol, methylhydroperoxide (MeOOH, not observed here) and CO_2 or recombined to reform ethane [22]. We propose that the C_2 and C_1 oxidation pathways are consistent with previously reported ethane and methane studies [22, 24]. Consistent with a consecutive oxidation/ C-C scission reaction profile, selectivity towards formic acid and CO_2 increased with increasing propane conversion.

To better understand the source of secondary reaction products, the reactivity of C_3 oxygenated products was studied under standard conditions (0.5 M H_2O_2, 27 mg 2.5% Fe/ZSM-5 (30), P = 20 bar, 50 ℃, 1500 rpm) using an atmosphere of 100 % He. The starting concentration of the products was 0.05 M, which is similar to the concentration range obtained during a reaction. Oxidation of n-propanol gave propanoic acid (30 % selectivity) and formic acid (49 % selectivity) as major products. Meanwhile isopropanol was oxidised to acetone (29 % selectivity), acetic acid (33 % selectivity) and formic acid (36 % selectivity). C-C scission of all C_3 oxygenate products (n-propanol, isopropanol, acetone and propanoic acid) gave acetic acid, formic acid and CO_2 as reported in Table 3. High rates of catalytic conversion of C_3 oxygenated products are shown in Table 3. When compared with the rate

of propane conversion under our standard conditions (23.5 $mol_{propane\ converted}$ kg_{cat}^{-1} h^{-1}) it is apparent that high yields of partially oxygenated C_3 products might not be realised using 2.5 % Fe/ZSM-5 (30), which is consistent with trends in Supplementary Figures S4-S6. These data were used to propose a reaction scheme for the liquid phase oxidation of propane as shown in Figure 9.

Interestingly, the molar rate of H_2O_2 conversion ($mol_{converted}$ h^{-1}) correlated differently with increasing propane conversion depending on reaction conditions (Supplementary Information Figure S7). Figure S7 shows that propane conversion might be increased through increasing catalyst mass or reaction time, but that a high degree of propane conversion and relatively low H_2O_2 conversion is achieved only at long reaction times. This is likely because increasing the catalyst mass increases, not only the rate of propane activation and H_2O_2 utilisation, but also the rate at which H_2O_2 is decomposed. Hence, propane activation cannot be correlated with H_2O_2 conversion in a generalised way.

3.3 Increasing C_3 product selectivity through catalyst development

Previously, we have shown the promoting effect of the addition of copper towards enhancing selectivity towards primary reaction products in the oxidation of both methane and ethane [22, 24], demonstrating increased selectivity for methanol and ethene respectively. It has been reported that Cu effectively inhibits secondary oxidation pathways by scavenging ·OH radicals [22, 24, 25, 39]. We therefore investigated whether co-deposition of Fe and Cu onto H-ZSM-5 (30) might produce higher selectivity towards primary C_3 products. At a constant Fe loading of 1.25 wt%, a decrease of propane conversion was observed with increasing Cu loading. Indeed, propane conversion decreased from 5.9% for 1.25% Fe/ZSM-5 (30) to 2.6 % for 1.25% Fe 2.5% Cu/ZSM-5 (30) as shown in Table 4. Hence, we suppose that the addition of Cu either (i) blocks active iron sites, thus decreasing the capacity of Fe to activate propane or (ii) the Cu sites catalytically terminate oxygen- based radicals, thereby lowering the rate of propane oxidation. Decreased conversion with increasing Cu loading is consistent with propane activation being at least in part a radical based mechanism, with Cu suppressing propane activation through scavenging of oxygen centred radicals (·OH). In this way propane oxidation would be behaving differently from methane oxidation over the same catalysts,

whereby methane was oxidised to MeOOH in a molecular mechanism, with free $\cdot$OH radicals implicated in subsequent oxidation steps only [25]. Total C_3 product selectivity increased from 38 % for 0 wt% Cu to 71 % at 2.5 wt% Cu loading. Key to this was the change in propene selectivity, which increased from 2% to 34% at 2.5 wt% Cu. (Table 4), with a corresponding decrease in acetic and formic acid selectivities. It can therefore be concluded that supported Cu species suppress the oxidation of propene (a primary product), as they were previously reported to suppress the oxidation of ethene under comparable ethane/ H_2O_2 oxidation conditions [22]. A comparison of the catalytic performance of H-ZSM-5 (30) and 2.5 % Cu/ZSM-5 (30) prepared by CVI is shown in Supplementary Table S1. It is apparent that deposition of 2.5 wt% Cu has no net benefit upon propane conversion, which actually decreased from 0.9 % to 0.36 % at isoconversion of H_2O_2. Consistent with data in Table 5, post-synthesis deposition of Cu had a significant effect on C_3 selectivity which increased from 48 to 72 %. Indeed, the product distributions shifts, from that shown in Figure 1 to favour isopropanol (19.8 % selectivity), n-propanol (18.8 %) and propene (21 %) as major reaction products. Our previous EPR studies have shown that ZSM-5 – supported Cu sites catalytically terminate oxygen based radicals in methane / ethane oxidation systems and thereby afford higher selectivity towards primary products, methanol and ethene respectively at isoconversion. It is likely that Cu sites fulfil a similar role within the current propane oxidation reaction. Decreased propane conversion is consistent with data in Table 5 and further suggests that the rate of propane conversion is at least partly dependent upon the concentration of $\cdot$OH radicals. A spectroscopic investigation of the nature of Cu species and their role within this catalytic system will be addressed in a future publication.

To determine whether high C_3 yields might be realised, 1.25 % Fe 1.25 % Cu/ ZSM-5 (30) was tested under the previously optimised reaction conditions (70 ^oC, 100 mg catalyst and 1 M H_2O_2). Results are shown in Table 5. Under optimised reaction conditions (Table 5 Entry 2) 17.6 % propane conversion was observed. The same catalyst gave 3.9 % conversion under standard conditions. With 2.5% Fe/ZSM-5 (30) a significant decrease in C_3 selectivity (33 % to 17 %) was observed, when changing from standard to optimised reaction conditions (Table 2 Entries 1 and 2). C_3 selectivity also

decreased for 1.25 % Fe 1.25 % Cu/ZSM-5 (30), from 64 % to 40 % under the same conditions (Table 5 Entries 1 and 2). The full C_3 product selectivity breakdown under optimised conditions was; acetone 11.8%, propene 13.1%, propanoic acid 7.2%, n-propanol 6.3% and isopropanol 2% with a total catalyst productivity of 14 $mol_{propane\ converted}$ kg_{cat}^{-1} h^{-1}.

It is important to note that in this study 4 bar (4000µmol) propane was used to ensure that propane was not the limiting reagent. As shown previously with ZSM-5, increased propane conversion might be achieved with no significant loss in catalyst productivity, through decreasing the partial pressure of propane. Future studies will seek to increase C3 selectivity and the efficiency with which H_2O_2 is utilised in these zeolite- catalysed systems.

4. Conclusions

This work demonstrates that propane can be converted selectively into oxygenated products, typically > 95 % selectivity, using H_2O_2 as the oxidant and MFI zeolite catalysts. The activity of a ZSM-5 zeolite has been increased by post deposition of iron, and reaction conditions optimised to achieve propane conversions of up to 52%. Combined optimisation and mechanistic studies have resulted in the identification of the reaction scheme. The selectivity to specific products achieved is inherently linked to propane conversion in this catalytic reaction. A route to increasing C_3 selectivity has been shown, through addition of Cu to Fe/ZSM-5 (30) to favour propene as a major product (33.7 % selectivity).

5. Acknowledgement

6. References

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Catalytic and mechanistic insights of the low-temperature selective oxidation of methane over Cu-promoted Fe-ZSM-5, Chemistry-A European Journal, 18 (2012) 15735-15745.

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Table 1 A summary of current literature on the direct catalytic oxidation of propane

Entry	Catalyst	Solvent	Reactor Temp / °C	$P(C_3H_8)$/ bar	Oxidant	S (major C_3 products)	Mass normalised rate / mol $_{propane\ converted}$ kg$_{cat}^{-1}$ h^{-1}	Total Oxygenate Selectivity / %[a]	Ref.
1	TS-1	95% MeOH, 5% H_2O	55	n.d	H_2O_2	Acetone (66), *i*-PrOH (34)	2.25	n.d	[28]
2	TS-1	-	60	5	H_2O_2	Acetone (68), *i*-PrOH (32)	0.37	n.d	[32]
3	0.52% Au/TS-1	Gas Phase	170[b]	0.127	H_2O_2[c]	Acetone (92), *i*-PrOH (4)	3.17	97.0	[40]
4	0.11% Au- Ba/ TS-1[d]	Gas Phase	170[b]	0.15	H_2O_2[c]	Acetone (90), *i*-PrOH (5)	0.63	95.0	[41]
5	Au- TiO_2/SiO_2	Gas Phase	80[b]	0.05	H_2O_2[c]	Acetone (59)	0.039	58.8	[42]
6	2.4 wt% Co_3O_4-SiO_2	sc CO_2	280	1	O_2	Acetone (7), C_3H_6 (5)	n.d	49.6	[43]
7	1.25% Fe 1.25% Cu/ZSM-5 (30)	H_2O	50	4	H_2O_2	C_3H_6 (24), *n*-PrOH (16), *i*-PrOH (16)	11.6	64.9	Current Article

[a] Total oxygenate selectivity where reported, [b] Reaction carried out in the gas phase, [c] H_2O_2 generated *in situ* from O_2 and H_2, [d] Ba loading not defined, [n.d] signifies not defined
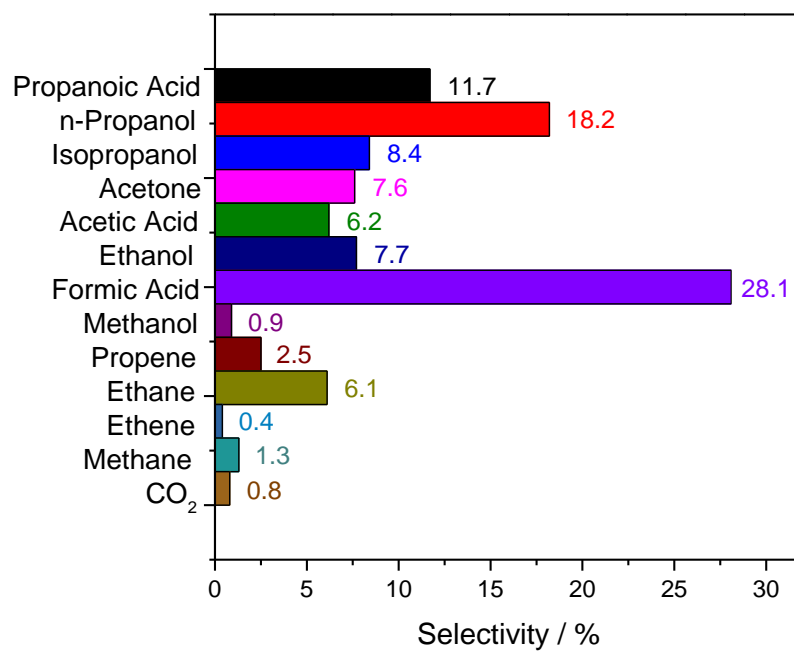
Figure 1 – The product distribution for a propane oxidation reaction catalysed by H-ZSM-5 (30). Reaction conditions: Propane (4000 µmol), $[H_2O_2] = 0.5$ M (5000 µmol), 27 mg H-ZSM-5 (30), 50 ºC, 0.5 h, 1500 rpm.

Figure 2 – Effect of Fe loading for propane oxidation. Propane conversion (♦), oxygenate selectivity (■), H_2O_2 converted (▲) and H_2O_2 utilised (●). Reaction conditions: Propane (4000 μmol), $[H_2O_2]$ = 0.5 M (5000 μmol), catalyst (27 mg), 50 ℃, 0.5 h, 1500 rpm.
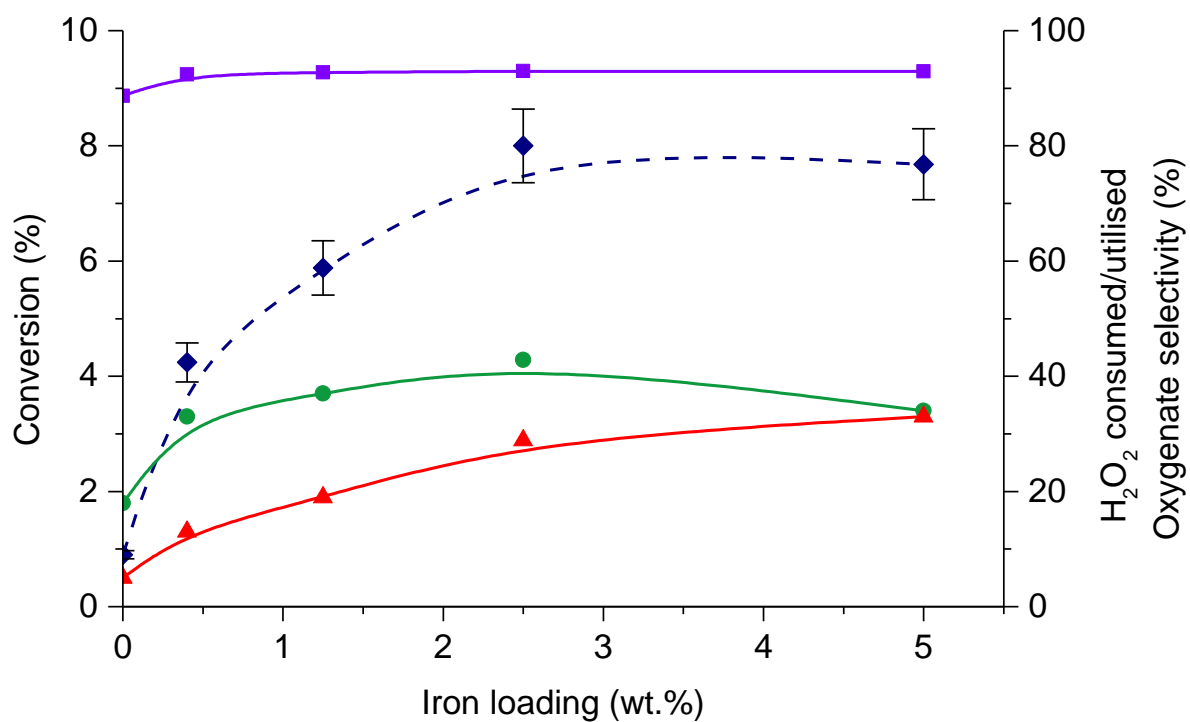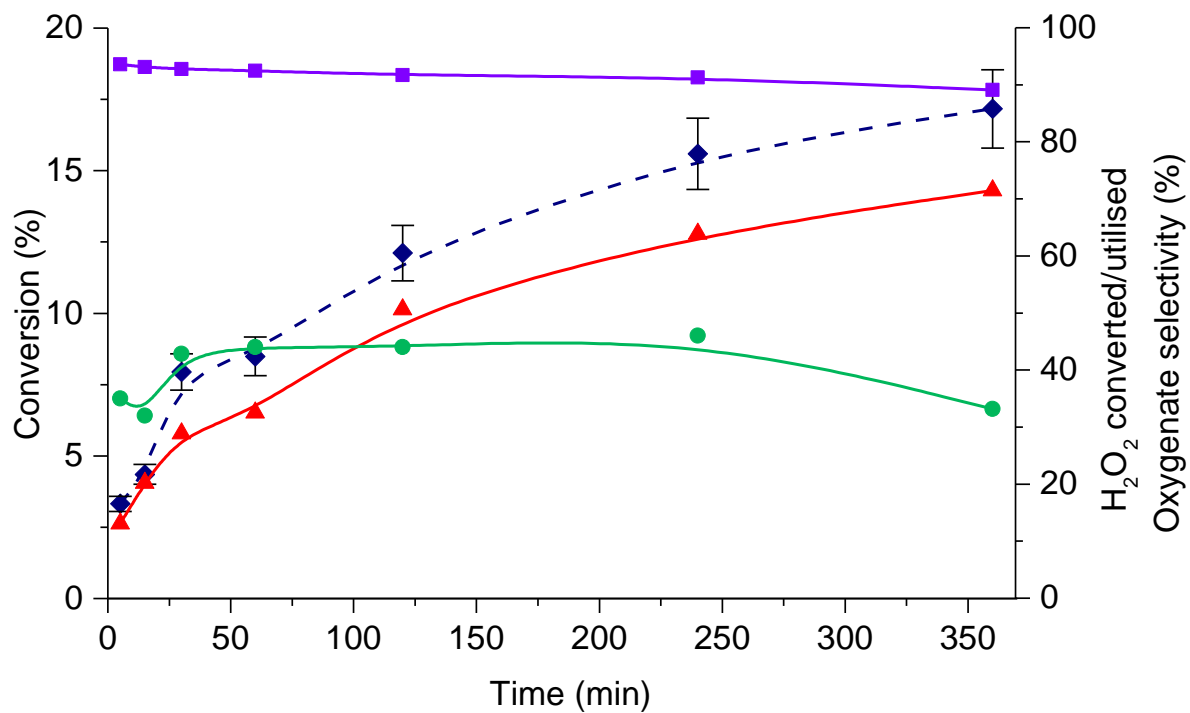
Figure 3 – Effect of time for propane oxidation. Propane conversion (♦), oxygenate selectivity (■), H_2O_2 converted (▲) and H_2O_2 utilised (●). Reaction conditions: Propane (4000 μmol), $[H_2O_2]$ = 0.5 M (5000 μmol), 2.5 % Fe/ZSM-5 (30) (27 mg), 50 ºC, 1500 rpm.

Figure 4 – Temporal evolution of propane oxidation reaction products.

(a) Major reaction products: formic acid ($\blacklozenge$), acetic acid ($\blacktriangleright$), ethanol ($\diamondsuit$), n-propanol ($\star$), propanoic acid ($\bigcirc$), acetone ($\newmoon$) and isopropanol ($\triangledown$).

(b) Minor reaction products: CO_2 ($\blacktriangledown$), C_3H_6 ($\square$), C_2H_6 ($\newmoon$), methanol ($\bigstar$) and C_2H_4 ($\triangledown$).

Reaction conditions: Propane (4000 µmol), [H_2O_2] = 0.5 M (5000 µmol), 2.5 % Fe/ZSM-5 (30) (27 mg), 50 °C, 1500 rpm.

Figure 5 – Effect of H₂O₂ concentration for propane oxidation. Propane conversion (♦), oxygenate selectivity (■), H₂O₂ converted (▲) and H₂O₂ utilised (●). Reaction conditions: Propane (4000 μmol), H₂O₂, 2.5 % Fe/ZSM-5 (30) (27 mg), 50 ℃, 0.5 h, 1500 rpm.

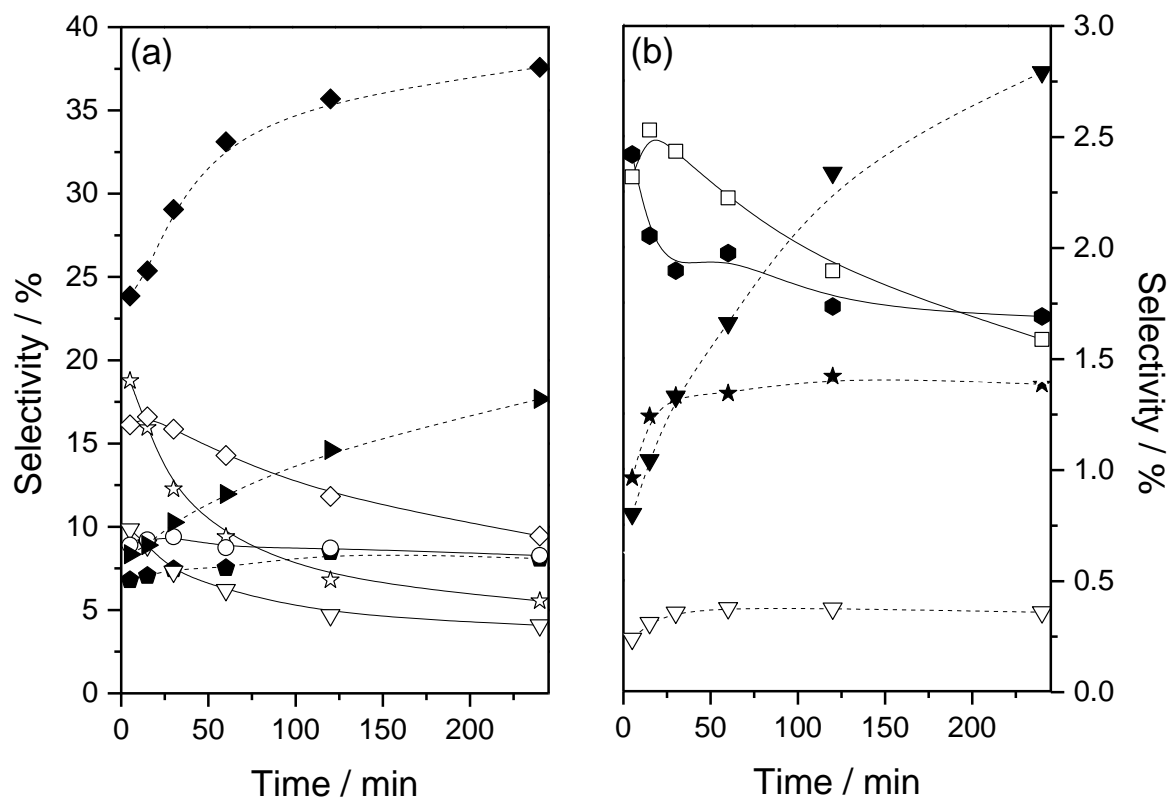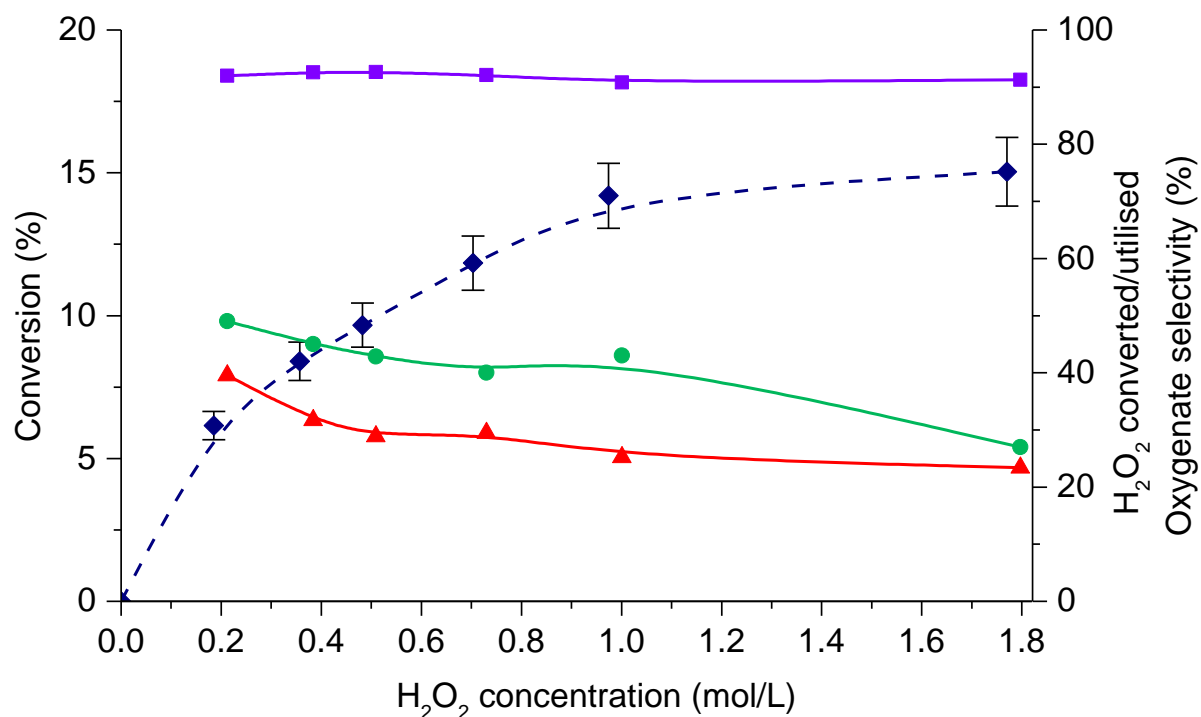**Figure 6** – Effect of partial pressure of propane for propane oxidation. Propane conversion (♦), oxygenate selectivity (■), H_2O_2 converted (▲) and H_2O_2 utilised (●). Reaction conditions: Propane (4000 µmol), $[H_2O_2]$ = 0.5 M (5000 µmol), 2.5 % Fe/ZSM-5 (30) (27 mg), 50 ºC, 0.5 h, 1500 rpm.

Figure 7 – Effect of mass of catalyst for propane oxidation. Propane conversion (♦), oxygenate selectivity (■), H_2O_2 converted (▲) and H_2O_2 utilised (●). Reaction conditions: Propane (4000 µmol), $[H_2O_2] = 0.5$ M (5000 µmol), 2.5 % Fe/ZSM-5 (30), 50 °C, 0.5 h, 1500 rpm.
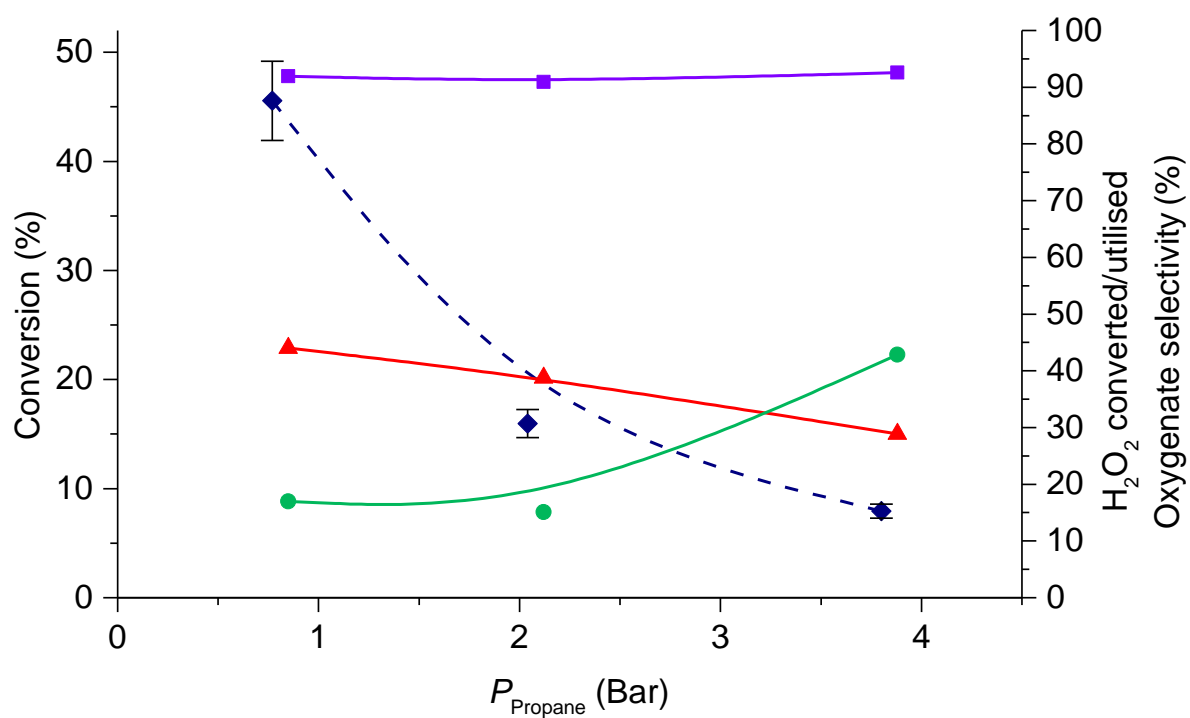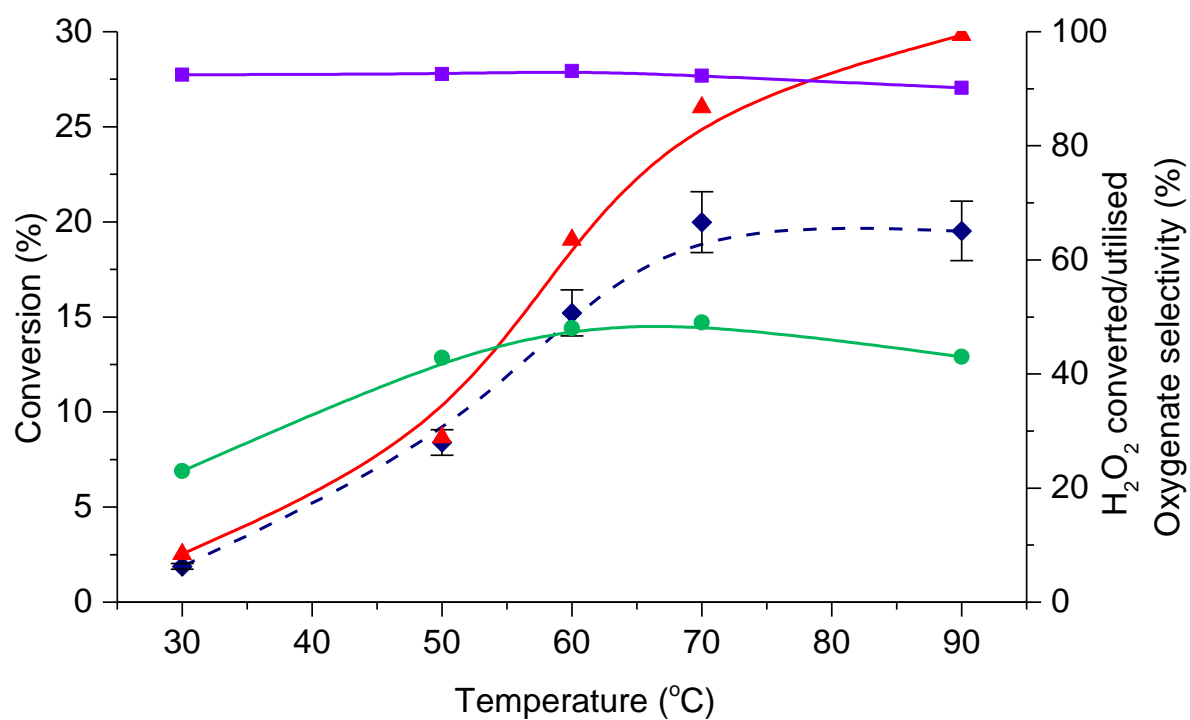
Figure 8 – Effect of temperature for propane oxidation. Propane conversion (♦), oxygenate selectivity (■), H_2O_2 converted (▲) and H_2O_2 utilised (●). Reaction conditions: Propane (4000 μmol), $[H_2O_2]$ = 0.5 M (5000 μmol), 2.5 % Fe/ZSM-5 (30) (27 mg), 0.5 h, 1500 rpm.
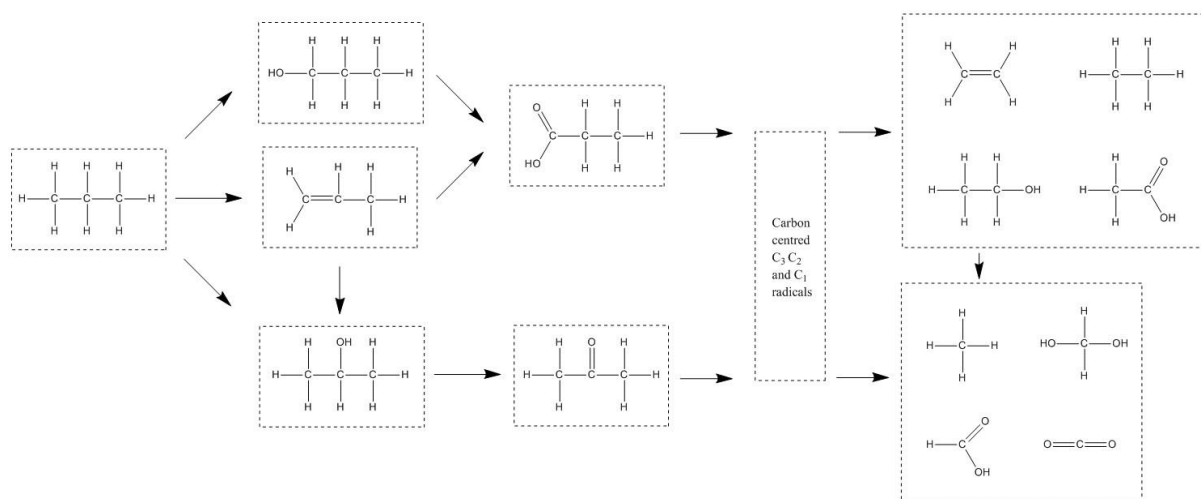
Figure 9 – Reaction scheme for the oxidation of propane using H_2O_2 in an aqueous medium.

Table 2 Catalytic oxidation of propane under high conversion conditions using 2.5% Fe/ZSM-5 (30)

Entry	Propane conversion / %	H_2O_2 Conversion / %	H_2O_2 Utilisation / %	C3 Products				C_3H_6	C_2 Products				MeOH	C_1 Products	CH_4	CO_2	Combined Product Selectivity/ %		
				Acetone	i-PrOH	n-PrOH	Propanoic Acid		EtOH	Acetic Acid	C_2H_4	C_2H_6		Formic Acid			C_3	C_2	C_1
1	7.9	29	43	6.4	5.7	8.8	11.4	2	14.1	11	0.6	1.5	1.3	34.6	0.9	1.4	33	28	39
2	33	99	29	8.0	0.2	0.8	7.0	0.6	1.2	25.3	0.2	0.7	0.8	43.8	0.4	10.7	17	27	56
3	19	52	27	9.7	1.8	2.9	8.7	1.4	5.4	20.1	0.3	2.0	1.2	40.4	1.1	5.0	24	28	48
4	23	75	26	10.1	1.9	2.3	7.7	0.9	3.6	23	0.3	1.6	1.1	40.4	1.5	5.5	23	28	49
5	52	97	12	1.6	0.0	0.0	0.0	0.02	0.0	33.9	0	0.2	0.2	29.5	0.2	34	2	34	64

Reaction conditions for Entry 1: Propane (4000 μmol), [H_2O_2] = 0.5 M (5000 μmol), 27 mg catalyst, 50 °C, 0.5 h, 1500 rpm.
Entry 2: Propane (4000 μmol), [H_2O_2] = 1 M (10,000 μmol), 100 mg catalyst, 70 °C, 0.5 h, 1500 rpm.
Entry 3: Propane (4000 μmol), [H_2O_2] = 1 M (10,000 μmol), 100 mg catalyst, 50 °C, 0.5 h, 1500 rpm.
Entry 4: Propane (4000 μmol), [H_2O_2] = 1 M (10,000 μmol), 100 mg catalyst, 50 °C, 2 h, 1500 rpm.
Entry 5: Propane (800 μmol), [H_2O_2] = 1 M (10,000 μmol), 100 mg catalyst, 70 °C, 2 h, 1500 rpm.

Table 3 Catalytic conversion of C$_3$ products under propane reaction conditions.

Reactant	Conversion / %	Amount of Product/ μmol					Rate / mol$_{converted}$ kg$_{cat}^{-1}$ h^{-1}	TOF / mol$_{converted}$ mol$_{Fe}^{-1}$ h^{-1}
		Acetone	Propanoic	Acetic Acid	Formic Acid	CO$_2$		
n-PrOH [a]	47	0.6	19	13	92	12	261.1	583.3
i-PrOH [a]	93	58	-	99	218	14	516.7	1154.1
Acetone [a]	62	-	-	70	62	17	344.4	769.4
Propanoic acid [a]	12	-	-	17	22	9	66.7	148.9
Propanoic acid[b]	43	-	-	47	108	38	16.0	35.6

Reaction conditions: [H$_2$O$_2$] = 0.5 M (5000 μmol), 27 mg 2.5% Fe/ZSM-5 (30), P(He) = 20 bar, 50 ºC, 1500 rpm. [a]Reaction time: 2 min, [b] Reaction time: 0.5 h

Table 4 The effect of copper addition upon the catalytic performance of 1.25% Fe/ZSM-5 (30) in propane oxidation

Entry	Cu loading / wt%	Propane conversion / %	H_2O_2 conversion / %	H_2O_2 utilisation / %	Acetone	i-PrOH	n-PrOH	Propanoic Acid	C_3H_6	EtOH	Acetic Acid	C_2H_4	C_2H_6	MeOH	Formic Acid	CH_4	CO_2	C_3	C_2	C_1
					C3 Products				C2 Products					C1 Products				Combined Product Selectivity / %		
1	0	5.9	19	56	6.8	7.5	12.6	9.0	1.8	18.0	9.2	0.3	2.0	1.3	29.0	1.1	1.3	38	31	33
2	0.4	4	22	30	6.4	8.3	18.1	7.9	0.8	21.3	6.6	0.2	1.4	1.2	27.2	0.3	0.2	42	31	29
3	1.25	3.9	27	13	6.7	8.5	16.4	9.2	24.3	16.3	6.5	5.2	1.3	1.3	0.0	3.1	1.1	64	30	6
4	2.5	2.6	7	36	7.8	8.8	14.9	5.4	33.7	9.6	0.0	5.0	1.7	1.0	10.7	0.1	1.1	71	16	13

Reaction conditions: Propane (4000 μmol), $[H_2O_2]$ = 0.5 M (5000 μmol), 27 mg catalyst, 50 ºC, 0.5 h, 1500 rpm

Table 5 Propane conversion catalysed by 1.25 %Fe-1.25 %Cu / ZSM-5 (30) under high conversion conditions.

Entry	Propane conversion / %	H_2O_2 conversion / %	H_2O_2 utilisation / %	Product Selectivities / %														Combined Product Selectivity / %		
				C3 Products					C2 Products				C1 Products							
				Acetone	i-PrOH	n-PrOH	Propanoic Acid	C_3H_6	EtOH	Acetic Acid	C_2H_4	C_2H_6	MeOH	Formic Acid	CH_4	CO_2	C_3	C_2	C_1
1	3.9	27	6	6.7	8.5	16.4	9.2	24.3	16.3	6.5	5.2	1.3	1.3	0.0	3.1	1.1	64	30	6
2	17.6	89	8	11.8	2.0	6.3	7.2	13.1	9.1	30.4	6.1	0.8	3.9	0.0	0.8	7.9	40	46	13
3	9.2	40	7	10.0	4.4	10.8	7.9	20.6	13.8	16.9	6.8	1.3	3	0.0	0.7	3.5	53	39	8
4	12.3	58	8	10.7	3.8	8.7	9.2	15.4	11.7	22.3	6.3	1.7	3.2	0.0	1.2	5.7	48	42	10

Reaction conditions for Entry 1: Propane (4000 μmol), $[H_2O_2]$ = 0.5 M (5000 μmol), 27 mg catalyst, 50 ºC, 0.5 h, 1500 rpm.
Entry 2: Propane (4000 μmol), $[H_2O_2]$ = 1 M (10,000 μmol), 100 mg catalyst, 70 ºC, 0.5 h, 1500 rpm.
Entry 3: Propane (4000 μmol), $[H_2O_2]$ = 1 M (10,000 μmol), 100 mg catalyst, 50 ºC, 0.5 h, 1500 rpm.
Entry 4: Propane (4000 μmol), $[H_2O_2]$ = 1 M (10,000 μmol), 100 mg catalyst, 50 ºC, 2 h, 1500 rpm