1 Introduction

The direct conversion of methane to methanol has been attracting considerable attention because of its great potential application in the efficient utilization of abundant natural gas reserves. In the last decade a number of interesting approaches was suggested for the effective implementation of this difficult transformation. A most attractive approach is to convert the natural gas into products such as methanol, which under ambient temperature and pressure is a liquid. However, over the past few decades, the conversion of methane to methanol has remained as one of the major unrequited challenges in chemistry. To activate methane, usually high temperatures are required. At these temperatures, formed methanol undergoes further oxidation to CO2 and H2O, as illustrated below:

\[
\begin{align*}
\text{CH}_4 + \frac{1}{2}\text{O}_2 & \rightarrow \text{CH}_3\text{OH} + \frac{1}{2}\text{O}_2 \\
\text{CH}_3\text{OH} + \frac{1}{2}\text{O}_2 & \rightarrow \text{HCHO} + \text{HCOOH} \\
\text{HCOOH} + \frac{1}{2}\text{O}_2 & \rightarrow \text{CO}_2 + \text{H}_2\text{O} \\
\end{align*}
\]

Methanol is formed via methane oxidation by \(\alpha\)-oxygen, \(\text{CH}_4 + (\text{M}^\text{n-}\text{O}^\text{=} \text{O}^\text{=})_\alpha\), migrated from \(\alpha\)-oxygen sites. It is generally accepted that \(\alpha\)-sites perform the oxidation via the reversible...
redox transition $M^+ \leftrightarrow M^{0+1.3}$. Much of the work on the variety of catalysts that have been investigated for partial oxidation of methane to methanol has been summarized in recent literature reports.5–7 The majority of the studies involved supported metal oxide catalysts, primarily vanadium and molybdenum oxide.1,2 Higher activity and selectivity to the desired products over mixed metal oxide catalysts can be attributed to the formation of easily reducible metal oxide species caused by interactions between the metals. Loading of supported phase below the monolayer coverage has been shown to be preferable for the high production of formaldehyde and methanol from methane.6,9 Otsuka et al.10 reported that the conversion of methane is accelerated by co-feeding hydrogen with oxygen over several iron containing catalysts. The co-feeding of hydrogen induces the formation of methanol over FePO4, FeAsO4 and FAPO-5 (Fe : Al : P = 0.1 : 0.9 : 1.0) catalysts at atmospheric pressure and in the temperature range of 350–500 °C. Thus, in order to design a better catalyst, it is quite important to understand which the effective and/or ineffective iron sites are in the selective oxidation of methane to methanol.

A low temperature (150 °C), isothermal, gas-phase recyclable process was described for the partial oxidation of methane to methanol over Cu/ZSM-5 by Sheppard et al.,11 which showed a stable formation of methanol for a long period of time. Depending on the iron content and activation conditions, a variety of Fe species may be available in the zeolite, ranging from isolated Fe$n$ and Fe$m$ cations and oligonuclear Fe complexes up to large agglomerates of iron oxide. FeZSM-5 zeolites have a long application history as catalysts for oxidations by N2Oa s first row MO+ complexes (M = Sc, Ti, V, Cr, Mn, Fe, Co, Ni and Cu) and methane, which can competitively form methanol and methyl radical. Anderson et al.16 carried out a systematic study of the conversion of methane using a number of metal oxide catalysts. They demonstrated that cobalt oxide is the most active single component catalyst which resulted in a high conversion, but with a very low selectivity towards methanol synthesis.

Stolcová and co-workers17,18 examined the influence of structure and reactivity of copper iron pyrophosphate catalysts for the selective oxidation of methane using O2 and N2O as oxidizing agents. These oxidants showed appreciable impact on the onset of both methane conversion and the primary oxidation products. The catalytic results showed that the lattice oxygen of the catalyst could react with methane molecules producing methanol and that replenishment of the lattice oxygen by N2O takes places rather readily and rapidly. Wang et al.13 showed the use of N2O oxidant for the epoxidation of C2H6 over iron-containing catalysts. Iron is peculiar for obtaining high selectivity to propylene oxide, and the modification of the iron sites with an alkaline metal salt can promote the C2H4 epoxidation. Christos et al.19 have shown that the reactivity of commercial zeolite-based catalysts containing Fe and/or Cu cations for the partial oxidation of methane is influenced by the acid sites strength and concentration in the catalyst which depends on the Si/Al molar ratio and type of zeolite. It was shown that the Fe cations are responsible for the superior oxygenates productivity, while the crucial role of Cu is to maintain high MeOH selectivity by suppressing the production of the deeper oxidation product, HCOOH. Partial oxidation of methane over iron phosphate supported on silica produced high formaldehyde yields.17,20 In the literature,18,21 it has been shown that the nature of the oxidant, however, was observed to play a vital role in favoring yield towards methanol. In line with the state of the art direct conversion of methane to methanol, we have undertaken this work with the aim to investigate which of the oxidant species, O2, H2O or N2O, would lead to achieving a high yield of methanol over FePO4 catalysts. As an attempt to achieve this objective, an ammonia gel method was employed to synthesize FePO4 catalyst, the resulting catalyst structures were then revealed by different characterisation techniques and the influence of oxidants on the structure and phase of FePO4 during the reaction was examined.

2. Experiment

2.1 Synthesis of the catalyst

The catalysts were synthesized by the ammonia gel method described by Friedrich et al.22–24 This catalytic preparation methodology was chosen because of its simplicity and to achieve a better control of particle size and morphology of the active phase. In essence, an appropriate amount of ferric nitrate, Fe(NO3)3·9H2O (99%, Sigma Aldrich) was dissolved in water and then a dilute ammonium solution (25% NH3 in H2O, Sigma Aldrich) was added. This led to precipitation and formation of iron(III) hydroxide (brown gel). Orthophosphoric acid (85% H3PO4, Sigma Aldrich) was added while stirring the gel, followed by a 40 wt% silica solution. The stirred mixture was then heated to 60 °C and kept at this temperature for 2 h. The obtained gel was then heated at 90 °C for 12 h, and the dried solid achieved was then calcined at a temperature 500 °C for 4 h in a 2 bar flow of air.

2.2 Characterization of catalysts

The characterizations of fresh and used catalysts are described below. Nitrogen physisorption analyses were carried out by degassing the catalysts under N2 flow for 4 h at 200 °C. The degassed samples were analysed in the Micromeritics ASAP 2020 multi-point surface area and porosity analyser. Powder X-ray diffraction (XRD) studies were conducted using the PANalytical X'Pert Pro instrument. Scanning from 10 to 90° was carried out using the CuKα-radiation source with the wavelength of 0.15406 nm. Temperature programmed reduction-oxidation (TPRO) was performed using the Micromeritics 2920
Autochem II Chemisorption Analyser. Initially, the reduction of the catalyst was done using 4.9 mol% H₂ in Ar as a reducing agent as in the method described in. Temperature programmed desorption (TPD) was carried out using the Micro-meritics 2920 Autochem II Chemisorption Analyser as well. After reduction, the catalysts were pre-treated at 350 °C under the stream of helium for 60 min. The temperature was consequently decreased to 80 °C. Appropriate pre-chosen gas was passed over the catalysts (10 mol% CO₂ in He or 4.9 mol% H₂ in Ar) at the flow rate of 30 mL min⁻¹ for 60 min. The excess gas was removed by purging with helium for 30 min. The temperature was thereafter gradually raised to 900 °C by ramping at 10 °C min⁻¹ under the flow of helium, wherein the desorption data of CO₂ or H₂ was recorded. The desorption data of O₂, H₂O and N₂O were also recorded in the same procedure. Metal dispersion is calculated using CO chemisorption which is illustrated in literature²⁵,²⁶

The structural morphology of the prepared catalysts was studied using field-emission scanning electron microscope (Carl Zeiss, FE-SEM SUPRA 35VP), equipped with energy-dispersive X-ray spectroscopy hardware (Oxford Instruments, model INCA 400). Particle size, morphology and elemental mapping performed by EDXS analyses were investigated using Cs corrected scanning transmission electron microscope JEOl ARM 200 CF equipped with JEOl Centurio 100 mm² EDXS system. Fe-Mössbauer spectroscopy measurements were made at room temperature (RT) in conventional transmission geometry with a Co source embedded in Rh matrix.

### 2.3 Partial oxidation of methane

The catalytic partial oxidation runs using the FePO₄ catalysts were carried out in a horizontal fixed-bed U-shaped quartz reactor as described in.⁷⁻²⁸ The catalyst (~0.4 g) was placed in the middle of the reactor and a flow of N₂ (30 mL min⁻¹) was introduced into the reactor at a temperature of 200 °C in order to remove the physisorbed gases from the surface of the catalyst. The catalytic runs were carried out under atmospheric pressure at the temperature range of 200–500 °C using undiluted high purity CH₄ (99.95%) and the appropriate oxidant (O₂, N₂O or H₂O) at flow rate of 60 mL min⁻¹, corresponding to the gas hour space velocity (GHSV) of 3600 h⁻¹ with a methane to oxidant ratio of 1 : 1. The gas products were analysed using an Agilent 490 Micro GC TCD equipped with CP-Molsieve and PoraPolt U columns. Reported values are given after 5 h of the reaction under steady-state conditions. The product mixture including methane, methanol, carbon oxides and nitrogen were analysed by online quadrupole mass spectrometry (MS). The signals in the MS are calibrated with different mole fractions of methane, methanol, carbon oxides and nitrogen in order to determine the mole composition of gases in the outflow. No other gaseous products were detected during the reaction. All the data points were recorded in duplicate with a standard deviation of ± 2%. The carbon mass balances are in the range of 98–99%.

The methane conversion (δ) was calculated using the following equation:

\[ \text{CH}_4 \text{ conversion} (\delta_{\text{CH}_4} \text{ mol } \%) = \frac{[\text{CH}_4]_{\text{in}} - [\text{CH}_4]_{\text{out}}}{[\text{CH}_4]_{\text{in}}} \times 100 \]

Oxidant conversion (δox%mol) = \[ \frac{\text{moles of oxidant}}{\text{moles of oxidant}}\times \frac{100}{\text{mol}} \]

CH₃OH selectivity (SCH₃OH mol%) = \[ \frac{[\text{CH}_3\text{OH}]_{\text{out}}}{[\text{CH}_4]_{\text{in}} - [\text{CH}_4]_{\text{out}}} \times 100 \]

### 3 Results and discussion

The effect of reaction temperature on methane conversion over FePO₄ catalyst with different oxidative environments was investigated as shown in Fig. 1. Methane conversion with N₂O and O₂ increases with temperature; however when H₂O is used as an oxidant, methane conversion increases at much lower linear rate with temperature. Furthermore, the maximum methane conversion (17%) was obtained when oxygen is used as an oxidant at a temperature of 500 °C, the highest reaction temperature in this study. The differences in conversion rates clearly show that selective oxidation of methane on FePO₄ is influenced by the nature of the oxidant. These facts strongly suggest that the reaction mechanisms are different.¹ This conclusion is strengthened by the greater conversions with O₂ than N₂O, which is in agreement with the reaction thermodynamics and the activation energy differences between these two oxidants.¹ This means that there exists a lower kinetic barrier for O₂ than N₂O in catalytic selective oxidation of methane.

When considering the effect of temperature on the methane conversion, two factors need to be considered. Firstly, methane conversion will depend on the oxidant feed concentration, secondly, even if total oxidant consumption occurs, methane conversion can change with a change in selectivity. Most of the studies²⁻¹,¹⁴,¹⁶,¹⁸,¹⁹,²⁰,²¹ reported in literature have examined the effect of temperature over a range varying from approximately 300 to 500 °C. It has been found that very low conversion occurs until a critical temperature is reached, after which a very rapid rise in conversion is observed (Fig. 1). This usually corresponds to total oxidant consumption. Typically the products obtained in the partial oxidation of reaction consist of CH₃OH, CO, CO₂, HCHO and H₂O. CO₂ and H₂O are formed initially at temperatures below 300 °C. At 400 °C both selectivity and yield of methanol are found to pass through a maximum before decreasing as the temperature is increased further (Fig. 2). Methanol formation is accompanied by the production of CO along with CO₂ and H₂O. It was generally found that increasing the temperature well above the self-ignition temperature of methanol favors the production of CO, CO₂ and H₂O at the expense of methanol.¹,¹⁰,¹⁸

To make a better comparison of catalytic performance among the oxidants, we further carried out the reactions with various flow rates between a GHSV of 2000 and 7000 h⁻¹. The conversion of methane increased and the selectivity to
methanol decreased with decrease in the flow rate as expected (ESI, Fig. S1†). From these data, the plot (Fig. 3) of methanol selectivity versus methane conversion was constructed. The selectivity towards methanol was very high at lower methane conversion at higher flow rate. However, when the comparison was made at higher methane conversion, the selectivity towards methanol was the highest when N₂O is used as oxidant. In addition to that, the selectivity of methanol at low conversions (<2%) of methane was almost identical (see first two data points at nearly 100% selectivity in Fig. 3). By elevating the reaction temperature at these conditions also, methanol selectivity gradually dropped and raised the CO production. This was
a consequence of the low stability of methanol at higher temperatures and thereby it over oxidised to carbon oxides. It has been well recognized that the selective oxidation of methane proceeds \textit{via} redox mechanism, but the pathways and product distribution depend on the nature of the oxidant and the reaction conditions.\textsuperscript{16,29}

Activation of methane may occur by both hemolytic and heterolytic mechanisms.\textsuperscript{7,27} Thus the investigations of used catalysts of FePO$_4$ might give an insight into the modified

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**Fig. 3** Selectivity towards methanol varying with methane conversion over FePO$_4$ catalyst at the temperatures of (a) 300 °C and (b) 400 °C (GHSV = 2000–7000 h$^{-1}$, methane to oxidant ratio of 1 : 1).
physicochemical properties of the catalysts which further influenced the conversion and selectivity in the partial oxidation of methane. The rate determining step would be the rupture of the C–H bond and the formation of CH$_3$ and HO radicals were postulated as the initial step.\textsuperscript{1,29} For methane oxidation to methanol, the most strongly supported mechanism consists of consecutive conversion scheme as shown in eqn (1). The methoxy radical is an important intermediate in the reaction pathway.\textsuperscript{19} Elimination of hydrogen from methoxy radical in a reaction such as oxidative dehydrogenation gives formaldehyde which is easily converted to CO and CO$_2$. Hydrogenation of the methoxy radical yields methanol.\textsuperscript{1} Stabilization of the methoxy radical by hydrogenation is a key step to achieve a high methanol yield.\textsuperscript{18} Fig. 4 shows the selectivity towards products in the partial oxidation of methane at iso-conversions of 10% and 5%. At both iso-conversion conditions (similar conversions at the same temperature), methanol was formed in high quantity when N$_2$O used as an oxidant. CO$_2$ is the major product.

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Fig. 4 Selectivity towards products in the partial oxidation of methane at an iso-conversion of (a) 5% and (b) 10% over FePO$_4$ catalyst with various oxidants (temperatures of 400 °C and methane to oxidant ratio of 1 : 1).
with both O2 and H2O. This could be either due to the further oxidation of methoxy radical to CO2 or the direct combustion of methane to CO2. On the other hand, when N2O was used, these effects were less systematic; the production rate of methanol was approximately doubled (Fig. 4). Using N2O, methanol selectivity was higher, with decreased CO2 selectivity. The catalytic differences have been ascribed to the differing oxidizing power of O2, N2O and H2O. In accordance with the Mars–van Krevelen mechanism,13,29 which has been proposed, the re-oxidation of the catalyst will be less effective with N2O and H2O compared to O2. At all conditions, formaldehyde is formed in very minor quantities, which could also be due to a secondary oxidation of formaldehyde to CO or CO2.

Fig. 5 shows the SEM images of FePO4 catalysts treated under various conditions. The fresh catalyst possesses rough crystalline morphology with a particle sizes ranging from 50–80 nm with a homogeneous dispersion of the particles. After reduction, the agglomeration of these particles was observed. After oxidation with oxygen the crystalline nature is retained with a separate agglomerated bulk particles. After oxidation with N2O and H2O, the catalysts showed a relatively poor crystalline structure and an amorphous like morphology (Fig. 5d and e). The BET surface areas, measured by the physical nitrogen adsorption for all of the samples, are presented in Table 1. The specific surface area of fresh FePO4 was found to be 19 m2 g−1. However, BET surface area decreased after reduction and oxidation treatments. After reduction, the surface area of the catalyst reduced drastically to 9 m2 g−1, due to the blocking of the pores of the FePO4 by the amorphous carbon which formed large crystallites, as evidenced by XRD and pore-size distribution measurements.

![Fig. 5 Scanning electron micrographs (SEM) of FePO4 catalysts under various conditions (a) fresh, (b) reduced under CH4, (c) oxidized with O2, (d) oxidized with N2O and (e) oxidized with H2O.](image-url)
The N₂ adsorption–desorption isotherms of the fresh, reduced and oxidised catalysts (ESI, Fig. S2†) can be categorised as the type IV isotherms, with a distinct hysteresis loop, observed in the relative pressure (P/P₀) range of 0.47–0.79. The pore-size distribution, calculated from the desorption counterpart using Barrett–Joyner–Halenda (BJH) method, showed a dominant peak in the mesoporous range (ESI, Fig. S3†). The metal dispersion of Fe species was calculated from CO chemisorption. Metal dispersion showed the similar trend to surface area, as the fresh catalyst showed a high metal dispersion compared to the reduced and oxidised catalysts. Among the oxidised catalysts, the catalyst oxidised with oxygen showed a higher metal dispersion compared to the catalysts oxidised with N₂O or H₂O. This could be due to the amount of available oxygen present in N₂O or H₂O. This shows that the nitrous oxide or water provides adequate oxidation of reduced sites of the catalyst. This may explain the fact that the number of active sites is altered and the nature of the active sites of the oxidised catalyst remained unchanged.

To investigate the phase transformations occurred during reduction and oxidation, powder XRD and Mössbauer analysis of the reduced and oxidised samples were carried out. The reduced sample was obtained using reducing the fresh FePO₄ catalyst under 10% CH₄ in Ar. In the TPR profile, the catalyst showed three peaks at the temperatures of 492, 625 and 815 °C (Fig. 6). These peaks represent reduction of FePO₄ to Fe₂P₂O₇ as suggested in:

\[
\text{FePO}_4(\text{tridymite}) \xrightarrow{400\text{–}650\;^\circ\text{C}} \beta\text{-Fe}_3(\text{P}_2\text{O}_7)_2
\]

\[
\xrightarrow{700\text{–}850\;^\circ\text{C}} \text{Fe}_2\text{P}_2\text{O}_7(\text{pyrophosphate})
\]

As reported in the literature, the first step in the reduction occurs above the temperatures of 500 °C. The use of CH₄ as reductant in this study accelerated the reduction, probably due to the activation and spill over of hydrogen from the metal centers to the iron phosphate.

After the reduction, the oxidation was conducted using O₂, N₂O and H₂O as oxidants (10% of oxidant in Ar), separately. The TPR profile under H₂O exhibited a very wide range of oxidation profile in the temperature ranging from 200–370 °C (Fig. 7). When N₂O is used an oxidant, only one peak was exhibited and
two peaks in the profile occurred with O2 as oxidant. There were no peaks observed above 500 °C, in the TPRO profiles. Various literature reports37,38 stated that the oxidative transformation of iron pyrophosphate phase to quartz phase occurs in two steps as below:

\[
\text{Fe}_2\text{P}_2\text{O}_7 (\text{pyrophosphate}) \xrightarrow{\text{above } 500 \degree \text{C}} \text{a-Fe}_3(\text{P}_2\text{O}_7)_2
\]

\[
\xrightarrow{\text{above } 500 \degree \text{C}} \text{FePO}_4 (\text{quartz})
\]

The formation of the quartz type phase has been reported in the literature; however, it was formed at temperatures above 500 °C.39 However, it was also observed that the transformation between the \( \alpha \)-phase and \( \text{Fe}_2\text{P}_2\text{O}_7 \) is reversible. Thus, from TPRO profiles, it is evident that the type of oxidant used in the re-oxidation influenced the re-oxidation pathway of reduced FePO4 catalyst. The powder XRD patterns of the fresh, reduced and oxidized catalysts are shown in Fig. 8.

The fresh catalyst showed the presence of the FePO4 trydimite-like (tdm) phase by exhibiting a main peak at a \( 2\theta = 34\degree \) and minor peaks in the range of 24–30\degree. The XRD pattern of the reduced catalyst (with methane) shows two distinct peaks at \( 2\theta \) values of 24\degree and 30\degree, confirming the formation of the \( \text{Fe}_2\text{P}_2\text{O}_7 \) phase range (ESI, Fig. S4†). The formation of this phase is also observed in literature22,37 when FePO4 is reduced under various hydrocarbon reduction atmospheres. When the reduced catalyst is oxidized in the presence of oxygen, the formation of the \( \alpha \)-phase (\( \alpha \)-\( \text{Fe}_3(\text{P}_2\text{O}_7)_2 \)) is observed. The XRD profile of this catalyst showed two characteristic major peaks in the region of \( 2\theta = 33–36\degree \) indicating the presence of \( \alpha \)-phase (\( \alpha \)-\( \text{Fe}_3(\text{P}_2\text{O}_7)_2 \)) along with some minor peaks. Some of the XRD peaks in this region also coincide with peaks characteristic of the \( \beta \)-phase.22,37

The XRD profile of the catalyst oxidized with \( \text{N}_2\text{O} \) also showed the presence of the \( \alpha \)-phase along with \( \text{Fe}_2\text{P}_2\text{O}_7 \) phase, but absence of the \( \beta \)-phase which would give a peak at \( 2\theta = 36\degree \) range (ESI, Fig. S4†). Oxidation of the catalyst in \( \text{H}_2\text{O} \) showed a similar pattern to the catalyst oxidized with oxygen, but with
the notable absence of a peak at a $2\theta = 28^\circ$, indicating the absence of the $\beta$-phase under $H_2O$ oxidation also. This could be due to a high oxidizing atmosphere being required for the formation of $\beta$-phase and the low oxidizing strength of $H_2O$ compared to $O_2$.\textsuperscript{22,37}

Mössbauer spectra of fresh, reduced (with $CH_4$) and oxidized (with $N_2O$, $O_2$ and $H_2O$) FePO$_4$ catalysts are shown in Fig. 8. The spectra were corrected for thickness effects and then fitted with the analysis code RECOIL\textsuperscript{51} using Lorentzian line shapes for the spectral components. The spectral fit parameters (isomer shift

<table>
<thead>
<tr>
<th>Sample</th>
<th>IS (mm s$^{-1}$)</th>
<th>QS (mm s$^{-1}$)</th>
<th>$\Gamma$ (HWHM) (mm s$^{-1}$)</th>
<th>Fe species</th>
<th>Area (%)</th>
<th>Attributed phase</th>
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<td>Fresh catalyst</td>
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<td>Fe$_5$(PO$_4$)$_6$</td>
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<td>0.67(8)</td>
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<td>2.53(8)</td>
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<td>Fe$_3$P$_2$O$_7$</td>
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$^a$ The isomer shifts are expressed relative to $\alpha$-Fe at room temperature.
The phase assignments were made on the basis of parameters reported in ref. 36, 37 and 40. The phase parameters of the fresh catalyst confirm that only the FePO₄-tdm phase is present in the catalyst, in agreement with literature and previous work.²³,²⁴,³⁷ Two Fe²⁺ species which are observed after the reduction of the fresh catalyst under methane at 500 °C, are attributable to the Fe₂P₂O₇ phase.²² A 17% contribution from a FePO₄ low quartz phase is evident, most likely the result of the unreduced phase present in the catalyst.³⁷ The effect of oxygen atmosphere on the phase formation is reflected by the Mössbauer spectrum for the O₂ oxidized catalyst (Fig. 8), which shows a 74% spectral area due to a Fe³⁺ iron phase and a weaker Fe²⁺ component with IS of 1.15 mm s⁻¹ and QS of 2.71 mm s⁻¹. These values are in accordance with the values of Fe³⁺ and Fe²⁺ components in the ß-phase of the catalyst, ß-Fe₃(P₂O₇)₂. The XRD profile of the catalyst also supports this assignment. In addition, a tdm-like FePO₄ phase is observed with a spectral area of 13%.

The Mössbauer spectrum obtained for the oxidized catalyst with N₂O (Fig. 8), showed a 12% contribution from components with IS and QS values characteristic of Fe²⁺ (Fig. 9 and Table 2) which can be assigned to the Fe₃P₂O₇ phase. In addition, the spectrum showed a 18% Fe³⁺ component with parameters corresponding to the ß-phase together with a mixture of 44% Fe²⁺ in the Fe₂P₂O₇ phase. A Fe³⁺ species, with IS and QS values which were not characteristic of a typical FePO₄-tdm phase in the oxidized catalyst, with a 26% site fraction is observed.²²,³⁷ The Mössbauer spectrum of the catalyst oxidized with H₂O, showed Fe³⁺ components with a combined 11% intensity, which can be assigned to the Fe₂P₂O₇ phase. The spectrum also shows the presence of the Fe³⁺ species with a 88% site fraction (Fig. 10). The respective IS and QS values of this ferric species are in agreement with the Fe³⁺ species in the various iron phosphate type phases, namely the ß-phase.²⁰,²₂,²₃

In the Powder XRD diffractogram of the used catalyst after the reaction with O₂ atmosphere, two major peaks are evident at Table 3 Mössbauer parameters, isomer shift (IS), electric quadrupole splitting (QS), line width (HWHM) and the attributed phases of the spent catalyst after oxidation in O₂, N₂O and H₂O atmospheres.

<table>
<thead>
<tr>
<th>Oxidizing atmosphere</th>
<th>IS (mm s⁻¹)</th>
<th>QS (mm s⁻¹)</th>
<th>Γ (HWHM) (mm s⁻¹)</th>
<th>Fe species</th>
<th>Area(%)</th>
<th>Attributed phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>O₂</td>
<td>0.40(1)</td>
<td>0.61(2)</td>
<td>0.23</td>
<td>Fe³⁺</td>
<td>51(2)</td>
<td>ß-Fe₃(P₂O₇)₂</td>
</tr>
<tr>
<td></td>
<td>0.41(2)</td>
<td>1.04(2)</td>
<td>0.20</td>
<td>Fe²⁺</td>
<td>23(2)</td>
<td>Fe₂P₂O₇</td>
</tr>
<tr>
<td></td>
<td>1.03(8)</td>
<td>2.20(5)</td>
<td>0.25</td>
<td>Fe²⁺</td>
<td>7(1)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.11(4)</td>
<td>2.74(4)</td>
<td>0.18</td>
<td>Fe²⁺</td>
<td>5(1)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.29(1)</td>
<td>0.21(2)</td>
<td>0.14</td>
<td>Fe³⁺</td>
<td>12(2)</td>
<td>FePO₄-tdm</td>
</tr>
<tr>
<td></td>
<td>0.38(1)</td>
<td>0.68(3)</td>
<td>0.23</td>
<td>Fe³⁺</td>
<td>44(3)</td>
<td>ß-Fe₃PO₄₆</td>
</tr>
<tr>
<td></td>
<td>0.40(2)</td>
<td>1.09(3)</td>
<td>0.20</td>
<td>Fe³⁺</td>
<td>18(3)</td>
<td>FePO₄-low quartz</td>
</tr>
<tr>
<td></td>
<td>1.19(4)</td>
<td>2.00(5)</td>
<td>0.15</td>
<td>Fe²⁺</td>
<td>6(1)</td>
<td>Fe₂P₂O₇</td>
</tr>
<tr>
<td></td>
<td>1.13(2)</td>
<td>2.78(4)</td>
<td>0.16</td>
<td>Fe²⁺</td>
<td>6(1)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.30(1)</td>
<td>0.22(8)</td>
<td>0.17</td>
<td>Fe³⁺</td>
<td>26(1)</td>
<td>FePO₄-tdm</td>
</tr>
<tr>
<td>N₂O</td>
<td>0.30(1)</td>
<td>0.65(5)</td>
<td>0.22</td>
<td>Fe³⁺</td>
<td>45(2)</td>
<td>ß-Fe₃(P₂O₇)₂</td>
</tr>
<tr>
<td></td>
<td>0.50(1)</td>
<td>0.63(1)</td>
<td>0.17</td>
<td>Fe³⁺</td>
<td>26(1)</td>
<td>ß-Fe₃(P₂O₇)₂</td>
</tr>
<tr>
<td></td>
<td>0.39(1)</td>
<td>1.20(2)</td>
<td>0.18</td>
<td>Fe²⁺</td>
<td>17(2)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.14(2)</td>
<td>2.75(5)</td>
<td>0.22</td>
<td>Fe²⁺</td>
<td>6(1)</td>
<td>Fe₂P₂O₇</td>
</tr>
<tr>
<td></td>
<td>1.25(3)</td>
<td>2.54(8)</td>
<td>0.20</td>
<td>Fe²⁺</td>
<td>5(1)</td>
<td></td>
</tr>
<tr>
<td>H₂O</td>
<td>0.30(1)</td>
<td>0.30(1)</td>
<td>0.22</td>
<td>Fe³⁺</td>
<td>12(2)</td>
<td>FePO₄-tdm</td>
</tr>
<tr>
<td></td>
<td>0.50(1)</td>
<td>0.63(1)</td>
<td>0.17</td>
<td>Fe³⁺</td>
<td>26(1)</td>
<td>ß-Fe₃(P₂O₇)₂</td>
</tr>
<tr>
<td></td>
<td>0.39(1)</td>
<td>1.20(2)</td>
<td>0.18</td>
<td>Fe²⁺</td>
<td>17(2)</td>
<td></td>
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<tr>
<td></td>
<td>1.14(2)</td>
<td>2.75(5)</td>
<td>0.22</td>
<td>Fe²⁺</td>
<td>6(1)</td>
<td>Fe₂P₂O₇</td>
</tr>
<tr>
<td></td>
<td>1.25(3)</td>
<td>2.54(8)</td>
<td>0.20</td>
<td>Fe²⁺</td>
<td>5(1)</td>
<td></td>
</tr>
</tbody>
</table>

* The isomer shifts are expressed relative to ß-Fe at room temperature.

![Mössbauer spectra of used catalysts after reaction with (a) O₂, (b) N₂O and (c) H₂O.](image-url)
43% and 21% which can be attributed to the Fe₂P₂O₇ phase, but this region also coincides with an overlap of the most intense peak of the α-phase. In the Mössbauer data of the used catalysts (Fig. 10), the α-Fe₃(P₂O₇)₂ phase, with a Fe³⁺ spectral component, was the dominant phase (74%). The appearance of the Fe₂P₂O₇ phase was also observed, with ferric and ferrous species each contributing towards an 11% total site fraction. The formation of the α-phase results from the transformation between the FePO₄-tdm and Fe₂P₂O₇ phases, which takes place reversibly, depending on strength of the redox atmosphere and the fact that the α-Fe₃(P₂O₇)₂ phase is a mixed ferric and ferrous pyrophosphate consisting of both Fe₃(P₂O₇)₂ and Fe₂P₂O₇.

The diffractogram obtained for the used catalyst after the reaction with N₂O (ESI, Fig. S5†), showed an intense, sharp peak at 2θ = 34.5°. The Mössbauer data (Fig. 10) for the used catalyst after the reaction with N₂O showed typical of Fe⁴⁺ species (88%) and a Fe²⁺ species (12%) with parameters which correlate with the FePO₄-low quartz and Fe₃(PO₄)₁₆ phases. In addition, there is a component (22%) with IS and QS values corresponding to Fe²⁺ which we identified as Fe₂P₂O₇ phase. These results showed an enhancement towards the α-phase after reaction with N₂O atmosphere. The absence of the β-phase during the oxidation reactions has been observed in previous studies, especially during the oxidative dehydrogenation of isobutyric acid with a water co-feed over FePO₄ catalyst. In literature, it has been reported that an FePO₄ catalyst consisting of the quartz type phase as the precursor, undergoes phase transformation during a catalytic reaction involving the oxidative dehydrogenation of isobutyric acid to form Fe₃(PO₄)₁₆ and the α-phase (Table 3).

The diffractogram of the used catalyst using H₂O as an oxidant showed the presence of Fe₂P₂O₇ phase along with α-phase. The Mössbauer spectrum, after using H₂O as an oxidant (Fig. 10), showed Fe²⁺ and Fe³⁺ components with a relative intensities of 11% and 71% (Fig. 11), which can be assigned to the α-Fe₃(P₂O₇)₂ phase. Similar to the catalyst obtained after reaction under N₂O atmosphere, no evidence of β-phase was observed after the reaction with H₂O also. It has been reported that formation of the β-phase is dependent on the catalyst structure and redox atmosphere. Obviously, water plays a role in avoiding high reduction atmospheres. Similar observation was reported in literature, that the addition of the water co-feed in the reaction, blocks the formation of the less selective β-phase. In summary, the XRD and Mössbauer spectra of the fresh and used catalysts oxidized in the presence of N₂O and H₂O showed that the α-phase was formed in high quantity when the formation of β-phase was suppressed.

Panov et al. assessed the methane partial oxidation by nitrous oxide in the processes in which the α-oxygen sites were created at 160 °C temperature over FeZSM-5 zeolite. They discovered that the reactions occur through a hydrogen abstraction mechanism, making methoxy or hydroxy groups bounded to the α-sites. When the same reaction is performed with heating to 160 °C, they verified that at CH₄:N₂O molar ratio equal to 1:1, the reactions directly provide methanol. Wood et al. studied the mechanism of “catalytic” oxidation reactions of methane by nitrous oxide over Fe-ZSM-5 zeolite, and concluded that the primary products of methane oxidation are methoxy groups bounded to active iron (i.e., Fe–OCH₃). As can be seen, the Fe⁵⁺ cations of α-sites are activated by nitrous oxide generating adsorbed oxidant species (i.e., Fe⁵⁺–O⁻–)α sites, which convert methane to adsorbed methanol. Afterwards, adsorbed methanol can be converted to dimethyl ether and water. Beznis et al. assessed the activity of Co–ZSM-5 solid catalysts on reactions of partial oxidation of methane. They found that methanol production proportionally increased in relation to surface area of catalyst, which can be increased treating the catalyst with NaOH. These authors discovered that the active sites (i.e., cobalt oxidic species, such as Co₃O₄ and
CoO, present on catalyst external surface) were also proportionally formed in relation to surface area of solid catalyst. In the presence of N2O, CH4 would be oxidized by peroxy species MO2 formed by the reaction of N2O with a Fe=O centre. Fe=O centres may be the active sites for methanol formation.\(^3,17,46\) The kinetic results obtained on the oxidation of CH4 by N2O showed that carbon oxides are probably primary products and may also stem from methanol or formaldehyde as secondary products. The direct pathway to carbon oxides could be ascribed to the existence of surface sites where the intermediate oxygenates are strongly attached and not allowed to desorb in the gas phase. In contrast, formation of methanol or formaldehyde would rather correspond to oxygenate precursors more easily desorbed because less retained at the catalyst surface.

In literature, it is well established that Fe based catalysts entail different chemical properties considering those of their other individual monometallic components, e.g. achieving the synergistic effects in methane activation reactions. In general, ZSM-5 catalysts show a higher activity for methane activation than other supports. Panov and co-workers\(^4,4\) showed the methane oxidation over Fe-ZSM-5 catalysts by N2O at 200 °C and showed that methanol that formed via methane oxidation by α-oxygen, CH4 + [Fe(III–O)\(^\text{2−}\)]\(_2\), migrated from α-sites, initiating new reaction cycles. At 200 °C, a 4 h run provided a turn over frequency (TOF) of 5.5 × 10\(^{-3}\) \(\text{molMeOH g}_{\text{cat}}^{-1} \text{ h}^{-1}\). Beznis and co-workers\(^3,17,46\) showed that the selective activation of methane towards methanol over Co-ZSM-5 can be influenced by altering the micro-and meso-porosity of the zeolite material. They showed a linear relationship between the ZSM-5 surface area and the amount of methanol produced (5.5 × 10\(^{-3}\) \(\text{molMeOH g}_{\text{cat}}^{-1} \text{ h}^{-1}\)) over Co-ZSM-5 from methane and oxygen at 250 °C (Table 4).

Zhang and co-workers\(^38–50\) showed that the iron species introduced into mesoporous silica SBA-15 could catalyze the selective oxidation of CH4 to methanol by O2 and that the catalyst with a Fe content of 0.5 wt% provided the highest single-pass yield (2.1 × 10\(^{-4}\) \(\text{molMeOH g}_{\text{cat}}^{-1} \text{ h}^{-1}\)). The TOF towards methanol formation decreased with increasing Fe content. They also studied SBA-15-supported iron phosphate (FePO\(_4\)) for the partial oxidation of CH4 with O2. The SBA-15-supported FePO\(_4\) catalysts exhibit higher CH4 conversion and MeOH selectivity than the unsupported and the MCM-41-supported ones in the partial oxidation of CH4 with O2.\(^14,48,50\)

The catalyst with a loading amount of 5 wt% shows the highest MeOH selectivity at a given CH4 conversion and the highest MeOH formation rate based on the amount of FePO\(_4\) in the catalyst. It is likely that the improved catalytic performances of the SBA-15-supported samples are related to the enhanced redox properties of FePO\(_4\) species, the large porous diameter and the high inerteriness of SBA-15.\(^48\) With compared to the other catalysts reported in literature, the FePO\(_4\)-tdm phase catalysts showed in this work exhibited a high activity towards methanol i.e., 12.3 × 10\(^{-3}\) \(\text{molMeOH g}_{\text{cat}}^{-1} \text{ h}^{-1}\) using N2O as an oxidant. This catalyst also showed a high activity with O2 as an oxidant (5.3 × 10\(^{-3}\) \(\text{molMeOH g}_{\text{cat}}^{-1} \text{ h}^{-1}\)).

### 4 Conclusion

A high yield of methanol was observed over FePO\(_4\) when using N2O as oxidant. The methane conversion with O2 and N2O increased steeply with temperature but increased much slower when H2O was applied as an oxidizing agent. Furthermore, the maximum CH4 consumption (17 mol%) was obtained when oxygen had been used as the oxidant at 500 °C, the highest in this study. The selectivity towards methanol was very good at lower methane conversions (elevated flow rates). Additionally, when a comparison was made at all the levels of CH4 consumption, it was the highest when N2O was used as an oxidant. The present results clearly show that the selective oxidation of methane over FePO\(_4\) is influenced by the nature of the oxidizing agent. Furthermore, the fresh catalyst possessed a rough crystalline morphology with particle sizes ranging from 50 to 80 nm, and with a homogeneous dispersion of crystallites. After reduction, agglomeration of these nanoparticles was observed. After the oxidation with O2, the crystalline nature was retained, but with separate agglomerated bulk particles present. From TPRO profiles, it was evident that the type of oxidant, used in re-oxidation, influenced the pathway of oxidation for a reduced FePO\(_4\) catalyst.

Mössbauer spectroscopy, complemented with powder X-ray diffraction, proved to be a very sensitive tool in providing an understanding of the phase transformations of FePO\(_4\) material.

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**Table 4** Comparison of catalytic performance of Fe based catalysts for methane activation reaction reported in literature

<table>
<thead>
<tr>
<th>S. no</th>
<th>Catalyst</th>
<th>Oxidant</th>
<th>Temperature (°C)</th>
<th>Methanol TOF ((\text{molMeOH g}_{\text{cat}}^{-1} \text{ h}^{-1}))</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2% Fe-ZSM5</td>
<td>O2</td>
<td>300</td>
<td>6.3 × 10(^{-4})</td>
<td>4</td>
</tr>
<tr>
<td>2</td>
<td>2% Fe-ZSM5(^a)</td>
<td>N2O</td>
<td>200</td>
<td>5.5 × 10(^{-3})</td>
<td>3</td>
</tr>
<tr>
<td>3</td>
<td>2% Fe-ZSM5</td>
<td>N2O</td>
<td>550</td>
<td>7.1 × 10(^{-3})</td>
<td>19</td>
</tr>
<tr>
<td>4</td>
<td>0.5% Fe–SiL-1</td>
<td>N2O</td>
<td>550</td>
<td>8 × 10(^{-3})</td>
<td>2</td>
</tr>
<tr>
<td>5</td>
<td>FePO(_4)/MCM-41</td>
<td>O2</td>
<td>400</td>
<td>7.5 × 10(^{-4})</td>
<td>14</td>
</tr>
<tr>
<td>6</td>
<td>FePO(_4)/SBA-15</td>
<td>O2</td>
<td>500</td>
<td>1.2 × 10(^{-4})</td>
<td>48</td>
</tr>
<tr>
<td>7</td>
<td>2% Co–ZSM5</td>
<td>O2</td>
<td>250</td>
<td>1.5 × 10(^{-4})</td>
<td>45 and 47</td>
</tr>
<tr>
<td>8</td>
<td>0.5% Fe–SiO(_2)</td>
<td>O2</td>
<td>500</td>
<td>2.1 × 10(^{-4})</td>
<td>49 and 50</td>
</tr>
<tr>
<td>9</td>
<td>FePO(_4)-tdm</td>
<td>O2</td>
<td>300</td>
<td>5.3 × 10(^{-3})</td>
<td>This work</td>
</tr>
<tr>
<td>10</td>
<td>FePO(_4)-tdm</td>
<td>N2O</td>
<td>300</td>
<td>12.3 × 10(^{-3})</td>
<td>This work</td>
</tr>
</tbody>
</table>

\(^a\) Batch reactor, under a pressure of 2 bar.
using O₂, H₂O and N₂O as oxidizing agents for the selective conversion of methane to methanol. The Mössbauer data provided evidence that the Fe₅P₃O₁₀ phase was dominant in the reduced catalyst sample, while its amount decreased five-fold after the oxidation with O₂ due to the formation of α-domains. In the Mössbauer data of the used catalysts, the α-Fe₂P₂O₇ phase, with a Fe³⁺ spectral component, was the dominant phase (74%). The appearance of the Fe₂P₂O₇ phase was also observed, with ferric and ferrous species each contributing towards an 11% total site fraction. The formation of this phase is evidenced by differences in the FePO₄-tdm and Fe₂P₂O₇ phases, which take place reversibly, depending on the redox atmosphere and the fact that the α-Fe₂P₂O₇ phase is a mixed ferric and ferrous pyrophosphate consisting of both Fe₄(P₂O₇)₃ and Fe₂P₂O₇.

In the Mössbauer data of the used catalysts, the presence of the Fe₅P₃O₁₀ phase was also investigated in the presence of N₂O and H₂O. This work exhibited a high activity towards methanol conversion of methane to methanol. The Mössbauer data also showed a high activity with O₂ as an oxidant (5.3 × 10⁻³ μmolMeOH g⁻¹ h⁻¹ using N₂O as an oxidant. This catalyst also showed a high activity with O₂ as an oxidant (5.3 × 10⁻³ μmolMeOH g⁻¹ h⁻¹).

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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