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COMMUNICATION

A low temperature, isothermal gas-phase system for conversion of methane to methanol over Cu-ZSM-5

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A low temperature, isothermal, gas-phase, recyclable process is described for the partial oxidation of methane to methanol over Cu-ZSM-5. Activation in NO at 150 °C followed by methane reaction and steam extraction (both at 150 °C) allowed direct observation of methanol at the reactor outlet.

Partial oxidation of methane constitutes a formidable challenge in modern chemistry but the incentive of obtaining a source of valuable chemical precursors and fuels, including methanol and formaldehyde, sustains a high interest in this process.¹ The high C-H bond strength and symmetry within the methane molecule render it highly resistant to chemical attack and, with the products of oxidation generally being more reactive, the conditions required to activate this bond result in loss of selectivity to total oxidation products. Several examples of catalytic methane partial oxidation have been demonstrated in the literature. However these suffer from drawbacks such as low selectivity, as with V₂O₅/SiO₂,² or harsh reaction conditions as when using bipyrimidyl Pt (II) complexes, in concentrated H₂SO₄.^{3,4}

In contrast, methanotrophs, such as particulate methane monooxygenase (pMMO) perform enzymatic methane partial oxidation selectively to methanol under mild conditions.^{5,6} The proposed active dicopper species in pMMO was suggested to be similar in structure to the bent mono(μ -oxo) dicopper core stabilised in the structure of Cu-ZSM-5 and Cu-MOR. The dicopper core has been shown to be the active site for partial oxidation of methane providing a biomimetic link for this inherently challenging reaction.⁷ The mono(μ -oxo) dicopper core which can be observed by UV-vis analysis typically after high temperature (>350 °C) activation in oxygen has been correlated to the amount of methanol formed after reaction with methane (130-200 °C).^{8,9} However, strong adsorption of the methoxy-type product formed on the copper sites requires the presence of a proton for product removal, which can be by ex-situ solvent extraction or by steam extraction below 200 °C to prevent methanol decomposition and loss of selectivity.¹⁰ Thermal

desorption results in complete decomposition of the product. A second high temperature activation in oxygen is then needed to remove the water from the extraction step and re-form the dicopper core to close the cycle. Therefore, due mainly to the discrepancy between the high temperature required for core formation and lower temperatures required to ensure methanol stability, at present, this reaction cannot be considered catalytic. Although low temperature activation (>175 °C) in oxygen has also been described via the formation of a precursor species to the active core, prior autoreduction of the catalyst at elevated temperatures is still required to facilitate this.¹¹ Analysis of the temperature profile of the reaction using O₂ as oxidant shows that a reduction in the temperature required for core formation is needed before an isothermal process can be achieved. Hutchings et al. addressed the problems of product removal and high temperature activation by carrying out the reaction in the aqueous phase, allowing facile product extraction and use of hydrogen peroxide as the oxidant.^{12,13} Although an excess of peroxide was required and the concentration of methanol in the final solution was low, the reaction was successfully carried out isothermally under mild conditions of 50 °C and was observed to be catalytic with TOF greater than many comparable processes. However, with operation in the liquid phase requiring an additional product separation step, and the relative cost of H₂O₂ in comparison to the products, the authors reported that this route is too expensive for commercial use with methane.

It has been known for some time that the bent mono(μ -oxo) dicopper core observed in ZSM-5 after high temperature oxidation in oxygen is also formed during the catalytic decomposition of NO_x over Cu-ZSM-5.¹⁴⁻¹⁶ Another reactive species has been reported through the interaction of N₂O with Fe-ZSM-5.¹⁷ Anderson and Tsai reported the use of N₂O with Cu-FeZSM-5 for the oxidation of methane to methanol, however due to the high temperatures required for reaction; loss of selectivity to further oxidation resulted in reasonable selectivity being obtained only at almost negligible conversions of 0.25%. Without the presence of Fe in the framework only total oxidation products were formed.¹⁸ Here we present a gas

phase process carried out isothermally under mild conditions (150 °C), to retain the methanol product, with product extraction using steam and re-formation of the copper core completing the catalyst cycle using NO as the oxidant. While not an ideal oxidant for this process, NO is produced commercially via ammonia oxidation.

Catalyst samples prepared† had a copper loading of 1.88 wt.% Cu. BET showed a uniform decrease in total surface area (320 m²g⁻¹) compared to the precursor NH₄-ZSM-5 (380 m²g⁻¹), attributed to the introduction of copper to the zeolite channel structure. TEM confirmed the presence of finely dispersed copper particles together with small clusters on the external zeolite surface (<10 nm). To develop an isothermal process, it was first necessary to define the maximum temperature at which methanol would remain stable over the catalyst. On-line GC analysis of a methanol-saturated Ar stream passed over the catalyst showed that the temperature should remain below 200 °C to prevent methanol decomposition (S6, ESI) which is below the typical temperature required for core formation in oxygen.

UV-vis analysis of Cu-ZSM-5 activated with NO or N₂O above 100 or 200 °C respectively showed the presence of an absorption band at 455 nm (S3, ESI), near the reported position of the bent mono(μ -oxo) dicopper core.¹⁹ The band was removed following contact with methane at 150 °C, indicative of a reaction occurring and was also removed on contact with steam at 150 °C. Notably, regardless of prior contact with methane and then steam, reintroduction of NO at 150 °C resulted in re-formation of the 455 nm band, indicating successful re-formation of the bent mono(μ -oxo) dicopper core (S7, ESI). UV-vis analysis of Cu-ZSM-5 during sequential treatment with NO, CH₄ and H₂O is shown in Figure 1.

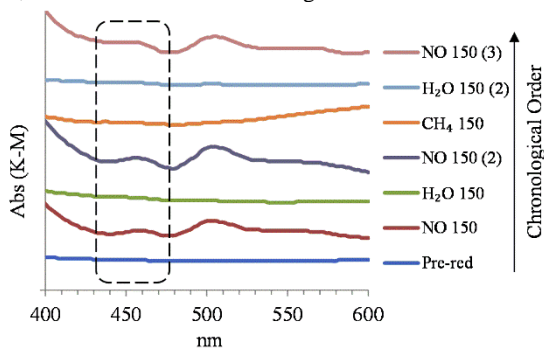


Figure 1 - UV-vis spectra of Cu-ZSM-5 after pre-reduction at 500 °C in Ar and treatment in NO, steam and CH₄. A constant temperature of 150 °C was used during treatment with each gas. Spectra were recorded in chronological order for a single sample in-situ at room temperature. The band attributed to the dicopper core is highlighted.

Following reaction with methane; displacement of the catalyst bed, aqueous extraction and GC analysis showed methanol as the sole product. From activation of the catalyst in NO at 150 °C or N₂O at 300 °C, the methanol yields were 0.103 and 0.331 μmolg^{-1} respectively. Both the methanol yields and UV-vis absorption band intensity at 455 nm (NO: 0.09, N₂O: 0.58 K-M) were distinctly lower than those observed following comparable activation of the catalyst in O₂ at 500 °C (methanol yield of 1.97 μmolg^{-1} and 0.95 K-M).⁸ Separate test reactions in O₂ with activation at 150 and 200 °C did not yield methanol (S4, ESI).

To demonstrate a complete catalytic cycle, the reaction was monitored by in-situ MS. Samples were first activated in NO at 150 °C, followed by interaction with methane at the same temperature. Steam was then introduced via a wet argon stream also at 150 °C and

$m/z = 18$ (H₂O), 31 (CH₃O⁺), 28 (CO) and 44 (CO₂) were monitored by in-situ MS at the reactor outlet. Figure 2 shows the mass spectra observed during contact of an activated, methane exposed Cu-ZSM-5 catalyst with steam.

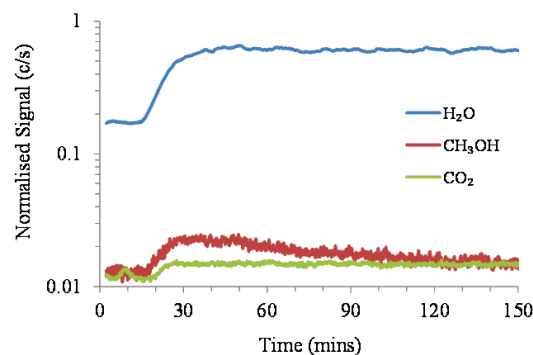


Figure 2 - In-situ mass spectrometry following H₂O, CH₃O⁺ and CO₂ traces ($m/z = 18, 31$ and 44 respectively), during exposure of Cu-ZSM-5 to wet argon at 150 °C. The catalyst was previously activated in NO at 150 °C and reacted with CH₄ at 150 °C.

The simultaneous increase in both H₂O and CH₃O⁺ signals (the latter attributed to methanol) is indicative of methanol desorbing from the catalyst surface and being removed by steam as it exits the reactor.¹⁰ The subsequent steady decrease in the CH₃O⁺ signal to a constant minimum value after 150 mins of exposure to steam, while the H₂O signal remains constant, confirms the increase in 31 (CH₃O⁺) is due to methanol in the stream. The initial increase observed for the $m/z = 44$ (CO₂) signal, which mirrored the 18 (H₂O) signal throughout, was due to a small amount of CO₂ in the water saturator present as traces of carbonic acid. During activation, reaction and product extraction, no methanol decomposition products were observed at any point (S8, ESI).

Subsequent heating of the spent catalyst to 500 °C in Ar after interaction with steam revealed only water desorption, indicating complete extraction of the product with steam, as shown in Figure 3.

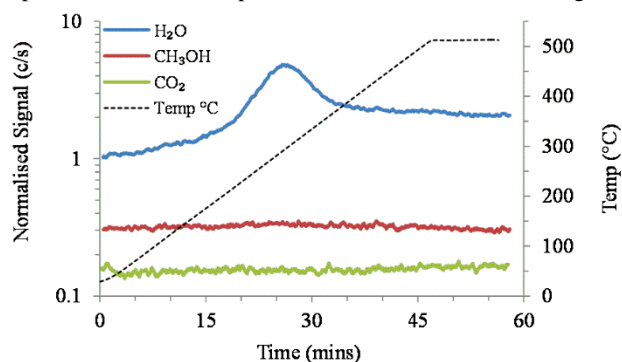


Figure 3 - In-situ mass spectrometry following H₂O, CH₃O⁺ and CO₂ traces ($m/z = 18, 31$ and 44 respectively), during thermal treatment of spent Cu-ZSM-5 in dry argon from 20-500 °C at 10 °C/min.

The yield of methanol obtained through steam extraction was 0.629 μmolg^{-1} , significantly greater than that obtained by ex-situ washing of the catalyst. Without an additional high temperature treatment, direct introduction of NO to the spent catalyst isothermally at 150 °C resulted in desorption of water (S8, ESI) and reformation of the dicopper core, Figure 1. High temperature treatment to remove water from the catalyst surface prior to reactivation was therefore not

required with NO, in contrast to the use of O₂ as oxidant.¹⁹ Following the second cycle of activation, reaction and steam extraction (S8, ESI), methanol was observed in comparable quantities at 0.589 μmolg⁻¹, thereby demonstrating the sustainability of the present isothermal NO activated process.

Cu-ZSM-5 was then activated using N₂O at 300 °C, followed by reaction with methane and exposure to a wet argon stream at 150 °C as previously described. Figure 4 shows that in-situ MS analysis detected the presence of methanol in the outlet stream with a yield of 0.690 μmolg⁻¹.

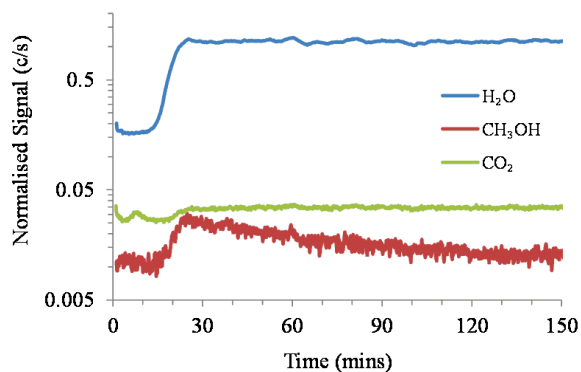


Figure 4 - In-situ mass spectrometry following H₂O, CH₃O⁺ and CO₂ traces (*m/z* = 18, 31 and 44 respectively), during exposure of Cu-ZSM-5 to wet argon at 150 °C. The catalyst was previously activated in N₂O at 300 °C and reacted with CH₄ at 150 °C.

Again no methanol decomposition products were detected at any stage. Activation in N₂O was also repeated at 200 °C, where minor UV-vis absorbance was still observed. After treatment with methane followed by a wet argon stream both at 150 °C, 0.137 μmolg⁻¹ methanol was recovered (S8, ESI). Notably, only CO₂ was observed when steam extraction was carried out at 200 °C and as no methanol was detected when activated with N₂O at 175 °C the reaction could not be run isothermally using N₂O. Recovery of methanol was therefore possible in a pulsed gas catalytic process following activation at a minimum possible temperature of 150 °C in NO or 200 °C in N₂O (S9, ESI). With the application of NO, repeated activation isothermally at 150 °C without the need for high temperature pre-treatment demonstrates the possibility of an isothermal process. Throughout this investigation, the same sample of Cu-ZSM-5 was employed continuously through the cycle of activation (in NO and N₂O), reaction and product desorption. Continued observation of methanol after at least three consecutive runs therefore confirms the recyclability of the catalyst.

Conclusions

In conclusion, a successful isothermal process for direct conversion of methane to methanol has been shown at lower temperatures than have been previously described in the gas phase. Although the use of NO or N₂O as oxidant is expensive and product yields are marginally lower than those reported with O₂, the large reduction in maximum operating temperature achieved, using NO in particular, is highly desirable. The ability of NO to facilitate activation at 150 °C regardless of previous catalyst treatment offers the potential for the process to be run isothermally and continuously; while operation in the gas phase allows facile separation of products. It is proposed that this method may be applicable to other metal zeolite materials which support formation of active copper sites.

Notes and references

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†Experimental: Cu-ZSM-5 samples were synthesised by wet ion exchange and characterised by ICP, BET and TEM (S1 and S2, ESI). Samples were exposed to NO or N₂O in argon from 25 to 400 °C and monitored by in-situ UV-vis for the presence of the bent mono(μ-oxo) dicopper core (S3, ESI). Methane was passed at 150 °C, followed by removal of the catalyst and aqueous extraction in deionised H₂O at room temperature, with the products observed by GC (S4, ESI). In a separate gas phase system, activation and methane reaction as above were followed by product extraction with steam at 150 °C, while the products were directly observed by in-situ MS (S5, ESI).

Electronic Supplementary Information (ESI) available: [Catalyst preparation and characterisation, experimental details and background data from DR-UV-vis, solvent extraction, mass spectrometry, determination of methanol stability, re-formation of dicopper core using NO and recyclability of Cu-ZSM-5.]. See DOI: 10.1039/c000000x/

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