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

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### Introduction

Selective, partial oxidation of methane constitutes a formidable challenge in catalysis, but the incentive of obtaining a source of valuable chemical precursors and fuels including methanol and formaldehyde generates high interest in this process. Metal-zeolite species including Cu-ZSM-5 and Cu-MOR are well known for facilitating selective partial oxidation of methane to methanol by stabilising the active species, the bent mono( $\mu$ -oxo) dicopper core. However, typically operation in the gas phase requires high temperature activation in O<sub>2</sub> and large changes in temperature during subsequent reaction with methane and product extraction using H<sub>2</sub>O<sub>(g)</sub>/H<sub>2</sub>O<sub>(D)</sub>.<sup>1</sup> While low-temperature operation in the liquid phase is possible with H<sub>2</sub>O<sub>2</sub> as the oxidant, this requires a further product separation step.<sup>2</sup> Partial methane oxidation is therefore usually performed in discrete batch-type processes.

In this work, we present an isothermal gas phase process carried out under mild conditions of 150 °C with product extraction using steam and simple re-formation of the copper core, thereby completing the catalyst cycle using  $NO_x$  as the oxidant. Product analysis, quantification and determination of catalyst recyclability was performed using GC and MS.

### **Materials and Methods**

1.9 wt.% Cu-ZSM-5 catalysts were prepared by wet ion exchange of an Na-ZSM-5 precursor with  $Cu(CH_3COO)_2$  solution, followed by drying and calcination at 500 °C. *In-situ* UV-vis analysis via fibre-optic probe (Hellma) was used to monitor the formation of the active copper core during exposure to NO (25 sccm, 1% in Ar) from 100-350 °C or N<sub>2</sub>O (25 sccm, 5% in Ar) from 100-400 °C respectively. Following activation, methane (50 sccm, 1% in Ar) was passed at 150 °C for 1 hour, the catalyst bed was removed and products extracted in deionised H<sub>2</sub>O at RT for 24 hours, then analysed by GC. This method was used to determine the temperature conditions for successful formation of the active copper species with NO<sub>x</sub>.

Catalytic activity tests were performed in a separate gas-phase system with *in-situ* MS analysis, NO and N<sub>2</sub>O were investigated separately. The total flow rate was 50 sccm, with Kr (10 sccm, 5% in Ar) as internal standard and the balance made up with Ar. Cu-ZSM-5 samples were activated in NO (150 °C) or N<sub>2</sub>O (200, 300 °C) for 2 hours, followed by reaction with methane as previous. Steam (1% total flow) was introduced at 150 °C via water saturator and the desorbed products observed. Quantification was performed by calibration curve. Catalyst recyclability was tested by repeatedly cycling NO/N<sub>2</sub>O, methane then steam as detailed above.

## **Results and Discussion**

Activation of pre-reduced Cu-ZSM-5 in NO or  $N_2O$  above 100 or 200 °C respectively caused the formation of a UV-vis absorption band at 455 nm, indicative of the active copper core. The band was removed following contact with CH<sub>4</sub> at 150 °C, suggesting a reaction, and also on contact with steam at 150 °C. Regardless of prior contact, reintroduction of NO at 150 °C always reformed the 455 nm band,<sup>3</sup> indicating successful reactivation as

shown in Figure 1. Aqueous extraction of the catalyst bed allowed detection of methanol as the sole product by GC.

With *in-situ* MS analysis, samples were exposed to NO then CH<sub>4</sub> at 150 °C. Steam was introduced via wet argon stream at 150 °C and traces of m/z = 18 (H<sub>2</sub>O), 31 (CH<sub>3</sub>O<sup>+</sup>), 28 (CO) and 44 (CO<sub>2</sub>) were observed, as shown in Figure 2. The increase and subsequent decrease in CH<sub>3</sub>O<sup>+</sup> signal to a constant minimum after 150 mins of steam exposure while the H<sub>2</sub>O signal remained constant, indicates methanol desorption and removal by steam as it exits the reactor. No combustion products were observed at any point, while heating the spent catalyst to 500 °C in Ar after contact with steam revealed only water desorption, indicating complete product extraction.<sup>3</sup> Cycling of NO, CH<sub>4</sub> and steam isothermally at 150 °C allowed repeated observation of methanol in similar volumes. An analogous process with activation in N<sub>2</sub>O at 200 °C also allowed observation of methanol following steam extraction at 150 °C.

Recovery of methanol was therefore possible in a pulsed gas catalytic process following activation at a minimum temperature of 150 °C in NO or 200 °C in N<sub>2</sub>O. The process was isothermal using NO. Continued observation of methanol after at least three consecutive runs confirms the recyclability of the catalyst, closing the catalytic cycle.



Figure 1 UV-vis spectra of Cu-ZSM-5 during treatment in NO, steam and CH<sub>4</sub>. A constant temperature of 150  $^{\circ}$ C was used throughout. Spectra were recorded in chronological order for a single sample *insitu* at room temperature.

**Figure 2** *In-situ* MS following  $H_2O$ ,  $CH_3O^+$ and  $CO_2$  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 CH<sub>4</sub> at 150 °C.

#### Significance

A successful catalytic process is detailed for direct conversion of methane to methanol at lower temperatures than have been previously described in the gas phase. The large reduction in temperature achieved using NO<sub>x</sub> in comparison to O<sub>2</sub> as oxidant 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. This method may be applicable to other metal zeolite materials which support formation of active copper sites.

#### References

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