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# Studies on the formation of primary olefins from methanol: Decoupling adsorption, desorption and activity using a TAP reactor

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## Introduction

The use of non-conventional carbon sources such as biomass is receiving growing interest for the sustainable production of fuels and chemicals. Methanol is readily accessed after gasification of biomass and can be further converted over ZSM-5 zeolites at 450°C to produce light olefins (MTO). MTO's chemistry involves chain growth and cracking where larger molecules obtained through methylation crack to give a product distribution rich in light olefins. To fully appreciate this chemistry, it is important to clarify the primary reactant, understand the formation of the first carbon-carbon bond and reveal primary products. Methanol forms its equilibrium products (DME, H<sub>2</sub>O) very rapidly over ZSM-5<sup>1</sup> and initially present oxygenates compete for active sites. The carbonylation of surface methoxy groups is a feasible pathway towards the direct formation of olefins due to low activation energies (80 kJ/mol).<sup>2</sup> Si/Al ratio, reaction temperature and DME/methanol ratio influence the primary product formed over fresh ZSM-5 catalysts.<sup>3</sup> Here, we quantify the influence of these parameters on primary olefin formation over fresh and activated ZSM-5 catalysts.

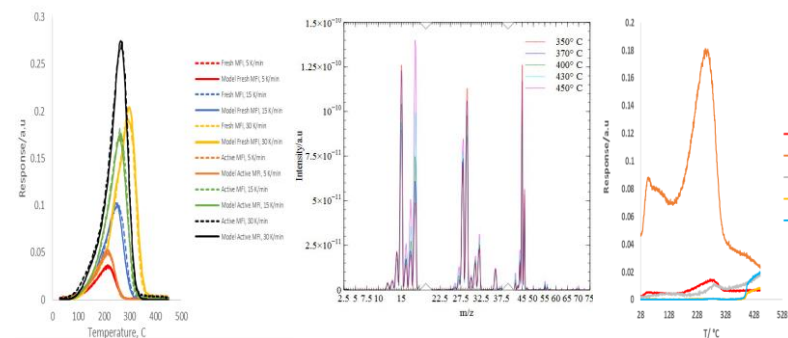
## Materials and Methods

Experiments used ZSM-5 of different Si/Al ratios (25, 36 and 135), here referred to as ZSM-5 (25), ZSM-5 (36) and ZSM5 (135) respectively. The ammonium form of zeolites was pressed, crushed and sieved to obtain particles sizes of 250 – 500 µm. Anhydrous DME (99.999%), Argon (99.999%) and ultra-high purity methanol (99.8%) were used. H-forms were obtained by thermal treatment under 30% O<sub>2</sub>/N<sub>2</sub> in a fixed bed reactor, ramping at 10 °C/min to 450°C, holding for 30 min before being subsequently cooled at 25 °C/min. Optional atmospheric sample activation involved steady state methanol to hydrocarbon conversion at 370 °C with 12 vol% of methanol flow at 10 mL/min. Samples were withdrawn after two hours TOS. Temperature programmed desorption (TPD), temperature programmed surface reaction (TPSR) and step response experiments were conducted over fresh and activated ZSM-5 catalysts to study the formation of primary olefins from methanol. Kinetic parameters (pre-exponential factors, activation energies and relative yields) were obtained by comparing experiments with prediction of a kinetic model implemented in FORTRAN.

## Results and Discussion

Contributions of three different sites were resolved from the desorption spectrum and individually analyzed following the Redhead method (Fig 1).<sup>4</sup> A mechanistic model corresponding to molecular desorption on a lower temperature site and dissociative desorption on higher temperature sites agrees well with experimental data. TPD results indicate that methanol adsorbs stronger than DME on ZSM-5 (25) while DME adsorbs more strongly than methanol to ZSM-5 (36) and ZSM-5 (135). For high temperature sites, amounts of species desorbed (DME or methanol) from activated samples in comparison to fresh samples follow an

inverse u-curve. The behavior likely relates to a competition between the rising cracking intensity of the zeolites and the increasing tendency of coke formation, both in respect to a decreasing Si/Al ratio. Following TPSR studies, DME formation is activated at a constant temperature with a dilute methanol feed. However, with a dilute DME feed, the temperature at which primary hydrocarbons form reduces as Si/Al ratios increase. Propene is the first olefin formed under TAP conditions. Equilibration times obtained from the step experiments show two temperature regimes during catalytic activity where either DME or methanol is more reactive in accordance to TPD profiles. A reaction sequence is developed showing CO<sub>2</sub>, CO, H<sub>2</sub> and CH<sub>4</sub> as key intermediates in the formation of primary olefins via the CO mechanism over ZSM-5 zeolites.



**Figure 1** (From left to right): TPD profile with 5 vol% DME over fresh and active ZSM-5 (36), Evolution of products at 15 TOS after step-up of 5 vol% DME over fresh ZSM-5 (36), TPSR profile with 5 vol% DME over fresh ZSM-5 (36).

## Significance

Conventionally, due to the exothermicity of the initial equilibrium stage of MTO conversion, pre-converters are used to separate DME from methanol which is subsequently used as initial feed into the reactor. This work lays further mechanistic proof for the utilization of DME as a primary reagent over fresh ZSM-5 catalysts. Also, the mechanisms by which olefin formation is regulated by the already formed hydrocarbon pool over active ZSM-5 catalysts is elucidated.

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