

Towards Understanding Primary Olefin Formation from Methanol over ZSM-5 Catalysts

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Highlights

- The conversion of methanol to hydrocarbons is autocatalytic in nature
- Propene is primary olefin formed under kinetic regime of MTH conversion
- Ethene is produced under mass transfer conditions during MTH conversion
- Dimethyl ether (DME) propagates the olefin cycle of the hydrocarbon pool mechanism

1. Introduction

There exist two fundamental challenges in understanding the early stages of the conversion of methanol to hydrocarbons (MTH) over ZSM-5 catalysts: (i) identification of the first C-C formed and (ii) the dominating mechanism leading to it. Our recent work shows that dimethyl ether (DME), a derivative of methanol, is the key surface reactant involved in MTH conversion [1]. Direct mechanisms involving surface carbenes, trimethyloxonium ion, methane-formaldehyde, and CO as well as indirect mechanisms involving impurities have been suggested. These mechanisms lead to the pre-formation of a hydrocarbon pool responsible for steady state MTH conversion. Olefins (ethene and/or propene) are the first C-C bonds detected in the gas phase. There are fundamental discrepancies in the literature on whether ethene or propene are formed alone or together due to lack of specificity on experimental conditions (kinetic regime, mass-transfer controlled or heat-transfer controlled conditions). In this contribution, using a combined experimental and kinetic modelling approach, the influence of mass transfer on early product distribution during MTH conversion is elucidated and a Langmuir-Hinshelwood-Hougen-Watson kinetic model using a lumped methodology is used to verify the dominating mechanism leading towards primary olefin formation.

2. Methods

Anhydrous DME (99.99 vol%), methanol (99.93 wt%), NH₄-ZSM-5 (Si/Al=36) powder with particle diameter of 10µm and extrudate forms obtained after being pressed, crushed, and sieved to give particles sizes of 250 – 500 µm were used. The protonic forms were obtained by thermal treatment under 30 vol% O₂/N₂. The product gases were insulated and sampled through an online gas chromatography–flame ionization detector equipped with an Equity™ –1 fused silica capillary column. Internal and external heat and mass transfer effects were checked using experimental criteria such as Wheeler-Weisz modulus, Carberry number and the internal and external Prater numbers. A lumped kinetic model was built using MATLAB to study the dominating mechanism that controls product distribution. Sensitivity analysis technique was used to reduce the number of parameters. Parameter optimization was carried out using the Levenberg-Marquardt routine and confidence intervals were obtained using Monte-Carlo methods.

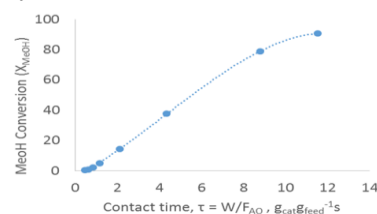


Figure 1: Evolution of methanol at full conversions

3. Results and discussion

MTH conversion was first studied using 25 wt% inlet methanol feed at 370°C with pelletized ZSM-5. Methanol transformation shows autocatalytic behaviour as shown by the S-shaped curve (Figure 1). The S-shaped curve shows the initial characteristic induction phase at low conversions, the intermediate autocatalytic regime and slow termination phase at high conversions. The presence of an induction phase supports the initial transformation of methanol through a high activation energy barrier particularly *via* the direct mechanisms. During the induction phase (up to 5% conversion), the formation of aromatics and

paraffins were minimal indicating that the formation of primary olefins and the methylation of olefins controlled the product distribution. Ethene and propene were formed initially at approximately equal yields (Figure 2). The analysis of the experimental criteria showed that the reaction kinetics were affected by external heat and mass transfer as well as internal mass transfer limitations.

Further studies compared MTH conversion using inlet feeds of 1 wt% DME to 1 wt% methanol over powder ZSM-5 catalysts. At contact times of less than $2 \text{ g}_{\text{cat}}\text{g}_{\text{feed}}^{-1}\text{s}$, very low conversions were obtained. With a 1 wt% methanol feed, internal and external heat and mass transfer limitations were negligible. Twice the contact time for similar methanol conversions at 370°C was required than at 450°C . Propene was the major olefin formed at both temperatures, although methane was the first product observed (Figure 3,4). This observation supports the proposal that ethene, which has been linked to the dominance of the aromatic cycle at low conversions [2] is formed under mass transfer limitations. With an inlet feed of 1 wt% DME, propene, butene and pentene are the major olefins formed although experimental criteria shows that internal and external mass transfer affected the reaction kinetics due to low DME diffusivities and mass transfer coefficients respectively. DME propagates the olefin cycle of the hydrocarbon pool.

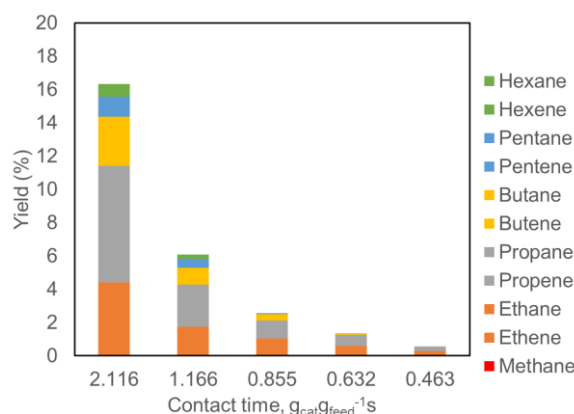


Figure 2: Conversion of 25 wt% inlet methanol at 370°C

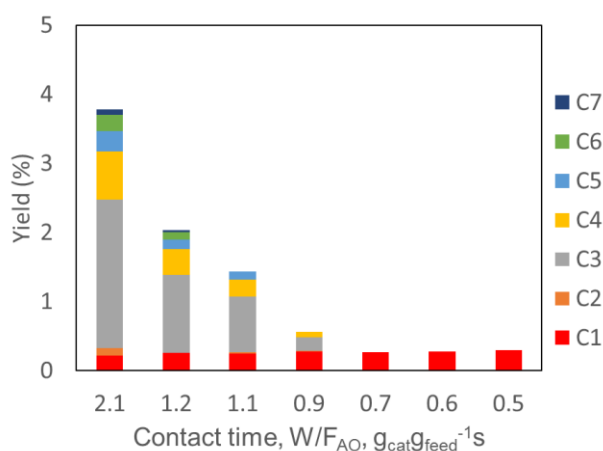


Figure 3: Conversion of 1wt% methanol at 370°C

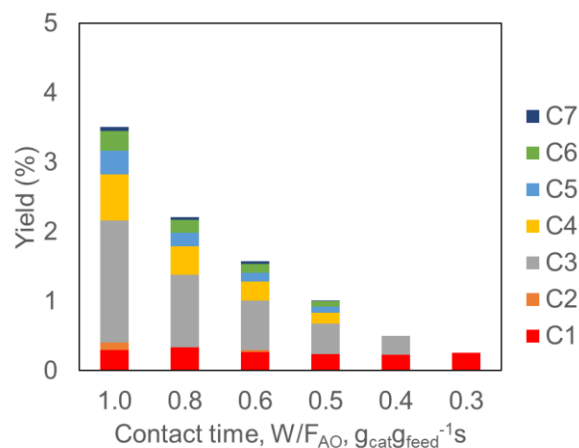


Figure 4: Conversion of 1wt% methanol at 450°C

4. Conclusions

Here, it is shown that under transport limitations, ethene is formed as a primary product from methanol while DME propagates the olefin cycle. A comprehensive study that includes the use of a microkinetic model for the estimation of parameters under kinetic regime as well as Maxwell-Stefan equations under mass transfer regime is underway and likely to provide clearer insights into the influence of transport effects on product distribution.

References

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Keywords

Methanol-to-hydrocarbons, first C-C bond, primary olefin formation, ZSM-5 zeolite