

Studies on Primary Olefin Formation from Methanol using Short-Contact-Time Reactors

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Highlights

- ZSM-5 particles are compared to monoliths as short-contact-reactors for MTH conversion
- Propene is the first olefin formed over ZSM-5 particles
- Influence of heat and mass transport on kinetics of MTH conversion is studied

1. Introduction

The conversion of methanol to hydrocarbons (MTH) over ZSM-5 catalysts exists within the framework of obtaining gasoline and high-value olefins sustainably from bio-feedstock. At steady state, MTH conversion is regulated by a hydrocarbon-pool mechanism consisting of olefin and aromatic cycles whose propagation is tunable depending on operating conditions. C₃₊ are the main products of the olefin cycle while C₂ and aromatics are the products of the aromatic cycle. Low conversions are required to achieve a high selectivity of olefins over ZSM-5 catalyst. This is particularly important as current projections for market demand for propylene exceed ethylene. ZSM-5 monoliths can be used as short-contact-time reactors for the achieving optimum olefin production. Detailed kinetic modelling is required to understand the complex interaction between transport and kinetics in these systems and for their industrial applications. In this contribution, using a combined experimental and kinetic modelling approach, MTH conversion over powdered ZSM-5 catalysts are compared to ZSM-5 monolith to study the effect of transport on product distribution at short contact times and at temperatures relevant for olefin production.

2. Methods

A commercial ZSM-5 zeolite (Si/Al of 25, Zeolyst International) was mixed with 20 – 50 wt% sodium bentonite (RS minerals Ltd) to form a solid mixture. A paste was obtained using distilled water and the optimum water content varied from 0.9 to 1.2 times the solid mixture weight. The wet paste was further stirred in a high shear mixture for 2 mins to form a homogenous textured mixture. Mesoporosity was induced using 10 wt% carbon and the pore volumes were changed using surplus water in some experiments. The wet paste was kneaded and extruded manually using a bench mounted press. The fabricated extrudates were characterized using X-ray diffraction (XRD), nitrogen physisorption, scanning electron microscopy (SEM) and thermogravimetric analysis (TGA). Further kinetic studies were carried out by comparing ZSM-5 monoliths to particles in a fixed bed reactor during MTH conversion. Anhydrous DME (99.99 vol%) and methanol (99.93 wt%) were also 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 EquityTM –1 fused silica capillary column. A lumped kinetic model is being built in MATLAB to study the mechanism that controls product distribution at short contact times.

3. Results and discussion

The zeolite monolith samples were studied using X-ray diffraction (XRD) with a Bruker Advance D8 diffractometer using Cu K_{α1} radiation equipped with standard Bragg-Brentano geometry. ZSM-5 monolith maintained their crystallinity and catalytic function with up to 50 wt% bentonite (Figure 1). TGA experiments (Figure 2) validated calcination temperatures at 450 °C preserving the ratio of Bronsted acid sites to Lewis acid sites as well as preventing further degradation of the bentonite binder. Using SEM, it was observed that ZSM-5 zeolite particles are dispersed on the bentonite binder (Figure 3). This helped to enhance heat dissipation in comparison to wash-coat systems and further prevent hot spots. High bentonite content would prevent further propagation to olefins and aromatics/paraffins.

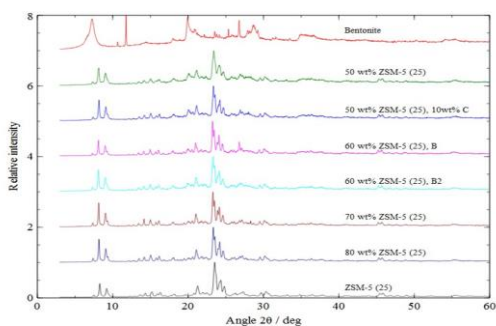


Figure 1: X-ray diffraction of ZSM-5 monoliths

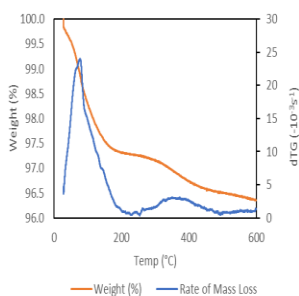


Figure 2a: TGA of ZSM-5 (25) used for monolith preparation

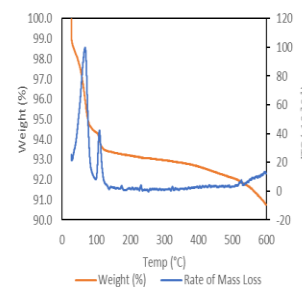


Figure 2b: TGA of bentonite used for monolith preparation

Firstly, the effect of the binder on MTH conversion was checked by comparing ZSM-5 monoliths of different lengths but similar catalyst weight. The bentonite binder with Si/Al=1.5 is of high acidity and would obviously lead to an initial conversion of methanol to DME. In view of DME as an alternative fuel, first set of studies investigated its in-situ formation from methanol in a ZSM-5 monolith. Studies were carried out from 200 – 300 °C at 1 atm.

Our recent work showed DME as the key methylating specie during MTH conversion [1]. A second series of studies compared DME transformation to primary olefins over ZSM-5 particles and monoliths. Heat transfer effects were obtained by increasing binder weight while keeping active zeolite weight constant in powder form. Mass transfer effects were obtained by comparing powder to structured forms.

Under the kinetic regime of MTH conversion, development of a Langmuir-Hinshelwood-Hougen-Watson model using the lumped methodology to estimate rate parameters is currently underway. The model is used to investigate the dominating mechanism that controls product distribution at short contact times. Parameter optimization was carried out using the Levenberg-Marquardt routine and confidence intervals were obtained using Monte-Carlo methods.

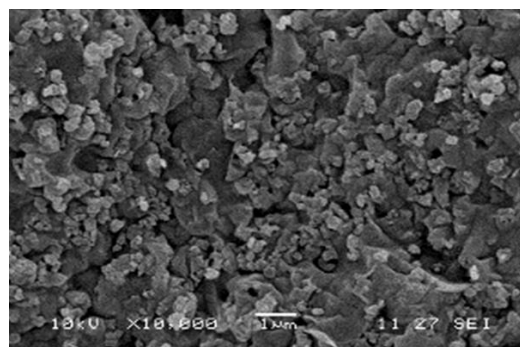


Figure 3: SEM image of a channel cross-section of 50 wt% ZSM-5 on bentonite

4. Conclusions

ZSM-5 monoliths have been fabricated and characterized. They were further tested as short-contact-time reactors for the conversion of methanol to hydrocarbons. These studies were used to compare MTH conversion over zeolite particles to determine effectiveness of the monolith system. Understanding the tunability of the hydrocarbon pool mechanism over ZSM-5 monoliths is key to investigating the factors that control product distribution under steady state at short contact times.

References

- [1] T. Omojola, N. Cherkasov, A.I. McNab, D.B.Lukyanov, J.A.Anderson, E.V.Rebrov, A.C.van Veen. Submitted (2017).

Keywords

ZSM-5 monoliths, mass transfer, primary olefin formation, short-contact-time reactors