On the induction period of propylene formation from methanol over ZSM-5 catalysts

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Highlights

- A DFT-based methoxy methyl mechanism describes the induction period of propylene formation
- Parallel adsorption mechanism describes the induction period based on the same global stoichiometry
- Dynamic site-interconversion reduces, and acid site density distribution controls the induction period
- The source terms for catalyst design are integrated with those for reactor design

1. Introduction

The mechanism required for the formation of the first C-C bond during the induction period of methanol conversion has been debated for 50 years. Several mechanisms based on density functional theory (DFT) calculations and spectroscopic measurements have been proposed. Limited kinetic evidence exists on the induction period of methanol conversion. Ultimately, deciphering the mechanism of the formation of the first C-C bond requires an intricate understanding of (i) key oxygenate i.e., methanol or dimethyl ether, (ii) the primary olefin i.e., ethylene, propylene or both, and (iii) the mechanism leading from the key oxygenate to primary olefin. Consequently, in this work, transient kinetic experiments are combined with microkinetic models (DFT-based) and rational kinetic models to describe the behaviour of the induction period during methanol conversion.

2. Methods

Temperature-programmed desorption (TPD), and temperature-programmed surface reaction (TPSR) studies were conducted with 5 vol% methanol (balance argon), or 5 vol% DME (balance argon) over ZSM-5 (Si/Al=25) catalysts in a temporal analysis of products (TAP) reactor. TPD studies were conducted at various heating rates and initial coverages on fresh and working catalysts, while TPSR studies were carried out at 15 K min^{-1} on fresh and working catalysts. Step response cycles (single-, multiple-, consecutive) were carried out over ZSM-5 (Si/Al=25) catalysts at 300 °C and 330 °C. Quasi-elastic neutron scattering (QENS) studies were conducted for methanol, DME, and water over ZSM-5 catalysts of different compositions. The combination of transient kinetics, QENS, and numerical modelling decouples adsorption, desorption, reaction, diffusion and dynamics.

3. Results and discussion

Dimethyl ether (DME) has higher activation energies of desorption than methanol, as evidenced by the shift of desorption profiles to the right (figure 1 [1]) and transient kinetic modelling results (121 kJ mol^{-1} compared to 112 kJ mol^{-1}). Methanol occupies a higher site density than DME [2]. The DFT-based methoxy methyl mechanism describes the formation of propylene from methanol (figure 2 [3]). The dynamic site-interconversion mechanism across three site ensembles reduces the induction period of propylene formation over ZSM-5 catalysts (figure 3 [4]). Based on the same global stoichiometry, the induction period of propylene formation can be described by the parallel adsorption mechanism (figure 4 [5]). Although the induction period is readily described with the methoxymethyl mechanism by the conversion of DME (figure 5 [6]), extra reaction steps must be included for the induction period of methanol conversion (figure 6 [2]). The reaction barriers to propylene formation from methanol, and dimethyl ether are 141 kJ mol^{-1}, and 200 kJ mol^{-1} in agreement with DFT calculations. Also, rational kinetic models show a first-order rate increase with C_{DME} and a maximum in the concentration of methanol [5]. QENS studies show that methanol and water are located primarily in the pore channels and dimethyl ether is in the pore intersections [7, 8]. The diffusion of methanol, dimethyl ether, or water does not limit the kinetics of the induction period of propylene formation.

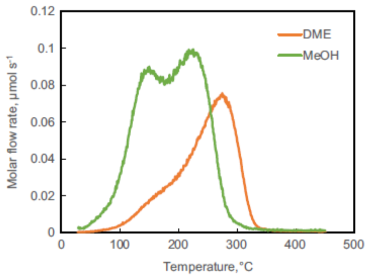

Figure 1: A comparison of the desorption of methanol to dimethyl ether over ZSM-5 catalysts

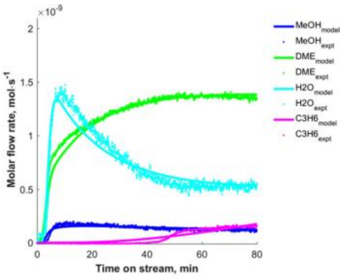

Figure 2: Modelling of a step response of dimethyl ether based on the methoxymethyl mechanism

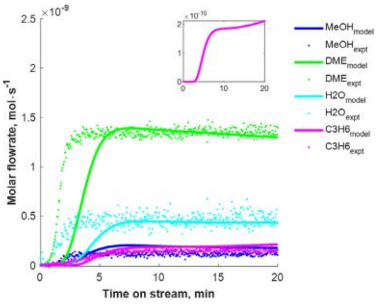

Figure 3: Modelling of the reduction in the induction period using the dynamic site-interconversion mechanism

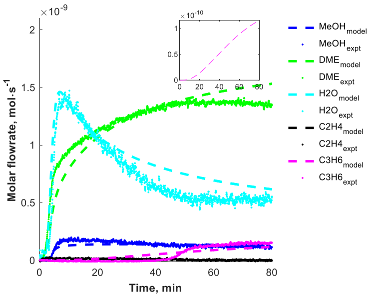

Figure 4: Step response cycle and the parallel adsorption mechanism

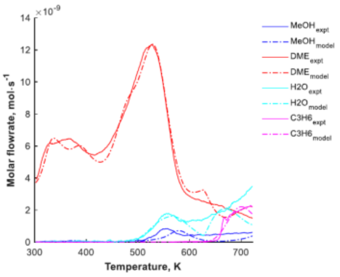

Figure 5: TPSR of dimethyl ether over ZSM-5 catalysts

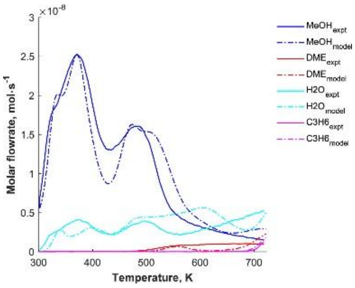

Figure 6: TPSR of methanol over ZSM-5 catalysts

4. Conclusions

The induction period of primary olefin formation from methanol has been debated for 50 years. Evidence is presented that primary olefins form directly from methanol. Dimethyl ether is the key oxygenate, and propylene is the primary olefin. The detailed methoxymethyl mechanism and the global parallel adsorption mechanism describe the formation of propylene from dimethyl ether. Understanding this kinetic information is important for the development of the working catalyst used in industrial processes.

References

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Keywords

Surface chemistry, transient kinetics, numerical modeling, catalysis