

Kinetic Modeling of Methanol-to-Olefins on ZSM-5: From Macrokinetics to the Single-Event Approach

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Highlights

- Single-event kinetic model for olefins cracking optimized.
- Transfer of olefins cracking model to MTO after implementation of paraffin formation.
- Evaluation of kinetic MTO data with literature models and the single-event case.
- Comparison between macrokinetics and microkinetics for MTO.

1. Introduction

Alternative concepts for producing lower olefins on demand have gained in importance. The established synthesis routes like steam cracking or fluid catalytic cracking show only limited flexibility and cannot be adapted to suffice current demands [1]. One of the proposed alternatives is the methanol-to-olefins process (MTO) where methanol reacts on shape-selective zeolites like ZSM-5, leading to a mixture of olefins [2]. Both reaction conditions and the pore structure of the zeolite determine whether paraffins and aromatics evolve to a significant amount [3]. This influences propene yields which can be further increased by recycling all products besides ethene and propene (methanol-to-propene, MTP) [2]. Kinetic modeling is an indispensable tool to assess the crucial reaction parameters. When performed on a microkinetic level, it can be further used to optimize both the catalyst and the process [4]. In this work, different approaches to simulate the output of MTO experiments are analyzed and compared. This comprises macrokinetic concepts from literature as well as a self-developed microkinetic model where the single-event methodology is applied.

2. Methods

All kinetic models are evaluated with experimental data stemming from a single tube quartz glass reactor filled with ZSM-5 and SiC. The feed consists of a mixture of methanol and butanol (water and nitrogen as diluents). Different combinations of temperature, total flow rate, methanol and butanol partial pressures and conversion levels of methanol are investigated to obtain a comprehensive description of the reactivity.

Several kinetic models for MTO from literature (e.g., [5,6]) are implemented and validated. These are applied to the experimental data which allows an assessment of the methodology. With this knowledge, a single-event model originally developed for 1-pentene cracking [7] is extended to MTO. Before, its adsorption description is analyzed and optimized with special attention to the nature of the protonated intermediates. Such mechanistic insights are also obtained for MTO by creating different versions of the single-event model: for example, the methylation can be implemented as step-wise or as concerted mechanism. Furthermore, it is possible to allow DME as competing methylation reactant or not. The methylation can be expressed in terms of an Eley-Rideal or a Langmuir-Hinshelwood approach.

3. Results and discussion

Figures 1 left and middle show the validation of the models from Aguayo *et al.* [5] and Huang *et al.* [6], respectively. The application of the latter model to own kinetic measurements reveals high agreement except for butenes (Figure 1 right). This could be seen as a hint that some of Huang *et al.*'s [6] assumptions pertain, e.g., the missing equilibration between methanol and DME and the negligible formation of aromatics.

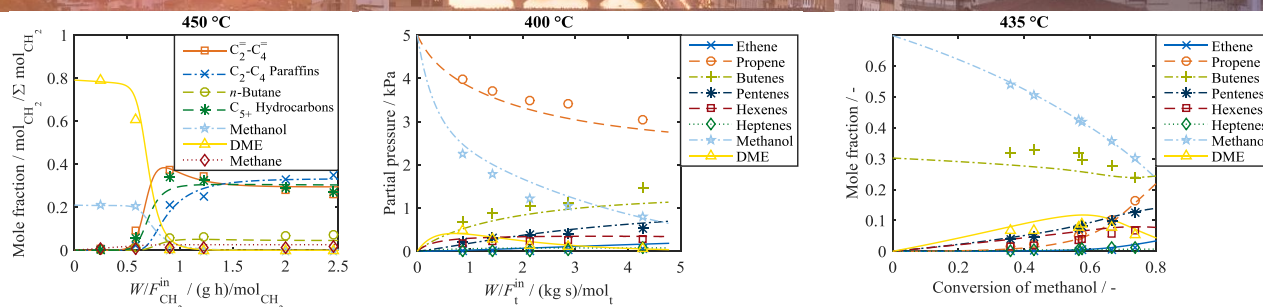


Figure 1. Validation of Aguayo *et al.*'s (left) [5] and Huang *et al.*'s (middle) [6] MTO models (lines: own implementation, symbols: original data points); simulation of own kinetic data with Huang *et al.*'s [6] model (right).

It was shown recently that the single-event kinetic model for 1-pentene cracking can be also applied to different catalysts, feed olefins and olefin mixtures (Figure 2 left) [8] by strictly separating kinetic and catalyst descriptors [4]. The analysis of different adsorption models leads to an improved description especially for the higher olefins (Figure 2 middle); the best agreement is achieved by assuming alkoxides with different stabilities as protonated intermediates. The inclusion of paraffin formation (Figure 2 right) via hydride transfer reactions [3] is the final step in preparing the transfer of this model to MTO.

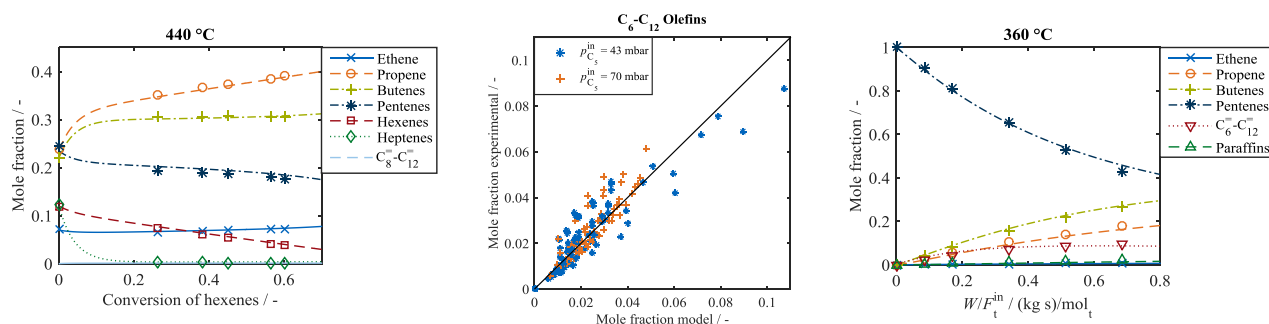


Figure 2. Simulation of an olefins mixture as feed with the single-event kinetic model (left) [8]; parity plot for higher olefins in 1-pentene cracking with improved adsorption model (middle); description of paraffins as side products in 1-pentene cracking (right).

4. Conclusions

Macrokinetic modeling of MTO yields a first assessment of the underlying reactivity. This knowledge is used in order to extend a single-event kinetic model for 1-pentene cracking. Further preparation steps are an optimization of adsorption correlations and an implementation of paraffin formation. Different sets of assumptions in the final MTO model should help to understand the ongoing reactions on a microkinetic level which allows a profound optimization of process parameters and catalyst properties in future work.

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Keywords

Olefins cracking; Methanol-to-olefins; Kinetic model; Single-event.