

## Selectivity and stability of zeolite catalysts in methanol-to-hydrocarbons reaction

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Zeolites (microporous crystalline aluminosilicates) represent one of the most prominent types of heterogeneous catalysts. Zeolites are characterized by regular pores, channels, and cages of molecular dimensions (0.3 - 1 nm). The microporous structure of zeolites allows for the stabilization of various active sites, intermediates, and products that would otherwise be unstable. A unique feature of zeolites is fascinating hydrocarbon pool chemistry, in which confined co-catalytic intermediates actively participate in the catalytic cycle. Methanol-to-hydrocarbons (MTH) is the prime example of a reaction following the hydrocarbon pool mechanism.[1] In addition to being a chemically intriguing reaction, MTH is an industrially relevant method to produce valuable light olefin and aromatic building blocks from virtually any carbon source (gas, coal, CO<sub>2</sub>, biomass) via the methanol intermediate.

With all these opportunities also come challenges, because the chemistry in confinement differs from the conventional chemistry. The processes, taking place inside the zeolite pores during conversion of a relatively simple methanol molecule to olefins and aromatics, are extremely complex. Entangled dynamic effects of co-catalytic intermediates, active sites, spectating and deactivating species, and diffusion limitations, define the MTH reactivity. Our understanding of these processes is deficient and the control that we can exert over them to tune the selectivity and stability of MTH catalysts is limited.

In this lecture, selected aspects of the reactivity of zeolite catalysts in the MTH reaction will be discussed. More specifically, I will focus on two strategies to control the reaction selectivity and catalyst stability: co-feeding of furanics to produce more aromatics [2] and modification of zeolites with alkaline earth cations to produce more propylene and decrease the deactivation rate [3]. These cases will also illustrate an effective toolbox of characterization techniques (operando FTIR, operando XRD, operando TG-MS, <sup>13</sup>C/<sup>1</sup>H NMR, pulse reaction technique, and isotopic labelling) for investigating the chemistry of MTH catalysts.

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[3] A. Liutkova, H. Zhang, J. F. M. Simons, B. Mezari, M. Mirolo, G. A. Garcia, E. J. M. Hensen, N. Kosinov, *ACS Catal.* **2023**, 3471.