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Kinetic study on the effects of zeolite topology on methylation reactions in the methanol-to-olefins process

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Catalytic conversion of methanol to light olefins (MTO) on acidic zeolites is currently one of the most prominent alternatives to traditional cracking processes for the production of bulk chemicals such as ethene and propene. Additional improvements of industrial process depend on further optimization of the catalyst to offer maximal conversion and light-olefin selectivity. This requires a thorough understanding of the underlying reaction mechanisms, which has proven a persistent challenge, despite considerable research efforts throughout the last decades.[1] Currently there is a consensus on an indirect mechanism in which olefin formation occurs through repeated methylation and/or cracking reactions of a pool of hydrocarbons present inside the zeolite pores. The predominant hydrocarbon pool species vary from small alkenes to bulky polymethylbenzenes, depending on the zeolite topology.[2]

While most studies originally focused on the archetypal MTO-catalysts H-ZSM-5 (MFI) and H-SAPO-34 (CHA), other zeolites such as H-ZSM-58 (DDR) and H-ZSM-22 (TON) are now also being investigated for their ability to convert methanol to olefins.[3,4] Since earlier theoretical research has confirmed methylation reactions as the rate-determining steps in most olefin-producing routes, these reaction steps are the focus of the current study.[5-7] Quantum chemical calculations which take the local environment of the active sites into account are employed to predict methylation kinetics in the cage-like framework of H-ZSM-58 (Fig. 1a) and the narrow channel structure of H-ZSM-22 (Fig. 1b). Kinetic parameters are subsequently compared with available data for H-ZSM-5 (Fig. 1c) to attain a better understanding of the relation between topological features of the catalyst and the activity of different species in the hydrocarbon pool.

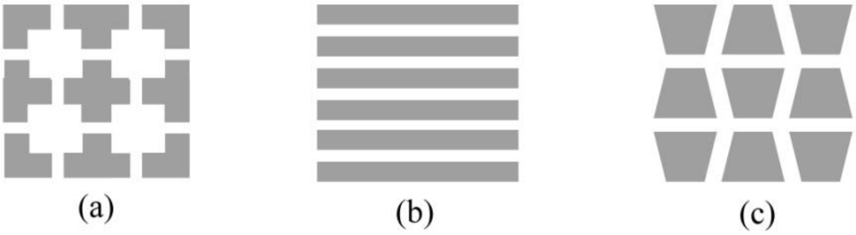

Figure 1. *Schematic representation of the differences in catalyst topology; (a) H-ZSM-58 (DDR), (b) H-ZSM-22 (TON), (c) H-ZSM-5 (MFI)*

Methodology

The zeolite catalysts are represented by extended cluster models, previously shown to provide reliable and computationally efficient predictions of rate coefficients and reaction barriers for methylation reactions in H-ZSM-5.[7] Stationary points are localized using a two-level ONIOM-method and their nature is verified by a normal mode analysis. Energies are further refined by single point calculations at the ωB97X-D level of theory, which includes dispersion. Rate constants are calculated in the temperature range 250 - 400 °C using conventional transition state theory (TST). Arrhenius parameters are obtained from a standard fitting procedure in the aforementioned temperature interval.

Results and discussion

Methylation rates are found to increase in the order ethene – propene – t-2-butene, in agreement with the relative stability of the carbenium ions formed as intermediates in the transition states. Comparing across the different catalysts, all alkenes follow roughly the same trend: methylation rates are similar in H-ZSM-58 and H-ZSM-22, and lower than in H-ZSM-5. However, closer inspection of the individual Arrhenius parameters, reveals different underlying effects in H-ZSM-58 and H-ZSM-22. For H-ZSM-58, activation energies are higher compared to H-ZSM-5, indicating that the reaction is energetically less favorable, while pre-exponential factors are only slightly larger, reflecting that similar entropy losses are incurred upon reaction. Final methylation rates are lower in H-ZSM-58 compared to H-ZSM-5 because the energetic contribution prevails over the entropic one. In contrast, activation energies in H-ZSM-22 are comparable to those in H-ZSM-5, but final methylation rates are lower due to much smaller pre-exponential factors. In H-ZSM-22, the greater loss of entropy outweighs the energetic stabilization of the intermediates. These results show that differences in catalyst topology may influence the rate of elementary reactions through both energetic and entropic effects, and both need to be considered to assess the activity of various species in the hydrocarbon pool.

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