A combined theoretical and in-situ spectroscopy study to obtain mechanistic insight into active MTO routes in chabazite derived topologies

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The methanol-to-olefins (MTO) process is currently one of the most prominent technologies to bypass crude oil as a fundamental feedstock. Methanol can be made from synthesis gas, which in turn can be formed from almost any gasifiable carbonaceous species, such as natural gas, coal, biomass and waste.[1] The reaction is catalyzed by protonated zeolites or zeotype materials: after a kinetic induction period hydrocarbons are formed. There is currently consensus that the active site consists of the Brønsted acid site together with organic reaction centers present in the zeolite pores as co-catalysts.[2-4] Catalyst and hydrocarbon pool (HP) species must find an optimal fit in order to generate an active material which is also selective towards the desired products such as ethene or propene.[5-7] To further progress in molecular optimization of the catalyst, it is essential to achieve insight into kinetics of individual reactions and to understand how the kinetics and selectivity depend on the specific HP species. Experimental kinetic studies on individual reactions taking place in the supramolecular catalyst are very scarce due to the occurrence of various side reactions.

Within this contribution, the activity of various structurally different HP species which are confined in chabazite type topologies (H-SAPO-34 and H-SSZ-13) is assessed by means of a combined experimental and theoretical approach. State of the art molecular modelling techniques have now matured to a point where it is possible to predict reaction rates within chemical accuracy. [8, 9] This approach is applied to derive first principle reaction rates of key reactions operating in active routes of the MTO process. The active HP species within H-SAPO-34 and H-SSZ-13 are established to be methylated aromatics, with a varying number of methyl groups and with one or two aromatic rings. In all investigated reactions, such polyaromatic HP species with a benzenic, naphthalenic or phenanthrenic core play a key role. These polyaromatics are ideally suited to study by means of in-situ UV-Vis micro-spectroscopy as they adsorb at different characteristic wavelengths.[10, 11] In contrast, direct kinetic measurements on such (poly)aromatic species are not possible as they cannot be pulsed on CHA-type catalysts beds due to diffusion limitations. The time evolution of the various absorption bands allows deducing invaluable information on the formation rate of various structurally different HP species.

On basis of the combined theoretical and experimental efforts, we are able to unambiguously show the interplay between the structure of the HP species and the effects of zeolite cage. The results show that methylation reactions are key reaction steps for the activity of HP species. When steric constraints are less important as in the benzene series, the largest effect on the rate is induced by the number of the methyl groups on the aromatic core, leading to five orders of magnitude acceleration in the reaction rate. For polyaromatic species these trends cannot straightforwardly be extrapolated as the medium-pore chabazite cage puts severe constraints on the transition state, slowing the reaction down. The effects of acidity of the zeolite crystals are very pronounced giving overall reaction rates which are about three orders faster in H-SSZ-13 compared to H-SAPO-34, although the specific acceleration is dependent on the structure of the HP species.

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