COMPUTATION OF CHEMICAL KINETICS: OLEFIN PRODUCING REACTION ROUTES DURING METHANOL CONVERSION AS A CASE STUDY

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The methanol-to-olefin (MTO) process is a very promising alternative for olefin production as waning oil reserves and an increasing demand for base chemicals arouse the use of alternative feedstocks. Methanol conversion occurs in acidic zeotype catalyst materials such as H-ZSM-5 and H-SAPO-34. The latter exhibits a particularly high selectivity towards light olefins due to its chabazite topology.[1] The generally accepted reaction mechanism for the MTO process is based on a hydrocarbon pool (HP) in which organic molecules (predominantly polymethylbenzenes) trapped within the anorganic zeolite framework co-catalyze the reactions.[2] To date, no decisive and detailed information exists on the dominant reaction mechanisms responsible for olefin production during methanol conversion in H-SAPO-34.

In a first part of this contribution the activity of various polymethylbenzenes in H-SAPO-34 is assessed by means of ab initio simulations. The methylation rate of the aromatic compounds serves hereby as an activity indicator. Heavy methylated benzenes such as hexamethylbenzene appear to be the most active HP species.[3]
In a second part multiple active olefin producing reaction cycles, starting from hexamethylbenzene, are investigated. The focus lies on the computation of accurate chemical kinetics of all individual reactions at actual working temperatures of the real catalyst.[4] The kinetic data are used to elucidate the dominant olefin producing reaction cycle(s). Calculations are performed on a large finite 44T cluster representative for the H-SAPO-34 material, making use of a two-layered approach.
A third aspect relates to the influence of the flexible zeolite environment on the chemical kinetics of reactions occurring within the nanoporous host. In order to assess this influence, molecular dynamics simulations are performed to determine the free energy profile along the reaction coordinate of the reactions under study. The knowledge of this free energy profile enables the determination of kinetic coefficients.[5]

References

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