Insight into the formation and reactivity of framework-bound methoxide species in H-ZSM-5 from static and dynamic molecular simulations

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Methylation reactions catalyzed by Brønsted acid zeolites are essential to many industrially important processes, e.g., the conversion of methanol to olefins such as ethene and propene.[1] Methylation can occur through either a concerted or stepwise mechanism. In the latter, framework-bound methoxide species are formed prior to the actual methylation.[2] In spite of ample research dedicated to this reaction, it is still unclear which mechanism prevails under realistic operating conditions, i.e., high temperature and high methanol partial pressure. Under these conditions, a mixture of methanol, dimethyl ether and water molecules is present in the zeolite pores, and the protic molecules can interact with each other and the framework, forming clusters in which protons can be shuttled along the hydrogen bonds.[3] In this study, the formation of methoxide species from methanol and dimethyl ether in H-ZSM-5 is studied at higher loadings, with particular regard for the effects of additional methanol and water molecules on the reaction mechanism and kinetics. Additionally, the reactivity of methoxides toward methylation of alkenes is assessed. A complementary set of molecular modeling methods are used. Static dispersion-corrected DFT calculations on large cluster models are supplemented with ab initio molecular dynamics simulations on periodic unit cells for a more rigorous sampling of the free energy surface at elevated temperatures. The metadynamics approach is employed to simulate rare events.[4]

References

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