Theoretical study of adsorption complexes in H-ZSM-5

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Catalytic conversions in acidic zeolites such as H-ZSM-5 find applications in a whole range of industrial production processes. Unraveling the actual network of reactions taking place inside the zeolite pores, however, can be a very challenging task. In recent years, theoretical modeling has proven to be a highly useful tool to complement experimental studies in gaining a deeper understanding of complex reaction mechanisms. Theoretical methods allow to establish if suggested reaction cycles can really occur in the zeolite pores, through the calculation of intrinsic barriers and rate coefficients for the elementary steps [1,2].

Although, before any reactions can take place, the reactants have to adsorb onto specific active centers inside the pores. With this preceding adsorption step, an additional enthalpy difference is associated, which is inevitably included in experimentally measured reaction barriers. Accordingly, to compare results from theoretical studies with experimental values, the heat of adsorption should be accounted for, and an accurate representation of the pre-reaction complexes is indispensable [3].

In this work, a series of adsorption complexes of alcohols and nitriles in H-ZSM-5, for which experimentally determined adsorption enthalpies are available in literature [4], is modeled using DFT-based quantum chemical techniques. We aim to verify whether these computational models (which have been successfully used to study elementary reaction steps at a reasonable computational cost) can qualitatively represent trends in adsorption enthalpies across a series of compounds, and if recently suggested additions to include long range dispersion interactions [5], succeed in improving accuracy of the theoretical results to the extent that prediction of experimentally observed values comes within reach.

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