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DISSERTATION TITLE: *Computational Investigations of the Zeolite Framework in Zeolite Catalysis – From Crystal Growth to Deactivation*

Avhandlingens enme er kvantekjemiske beregninger for å studere zeolittkatalysatorer og deres gitterstruktur. Arbeidet søker å forbedre de nåværende beregningsteknikkene som er tilgjengelige for å undersøke forskjellige aspekter knyttet til stabiliteten av zeolittkatalysatorer.

Zeolite catalysts for the Methanol to Hydrocarbons (MTH) process are of growing industrial interest, as well as being a viable mean to a potential fossil free future. This thesis aims to heighten the understanding of the zeolite catalyst framework from synthesis to deactivation. This is achieved through computational methods, always closely linked to experimental work carried out by other members in the project group or as found in the literature.

Starting at the creation of a zeolite catalyst, the surfaces of a zeolite will be discussed during synthesis in order to estimate the resulting morphology. It is shown that the very simple approximation of using only the number of OH-terminations per area, gives some insight into the resulting morphology of zeolites, however, for a complete picture, much more complicated calculations are needed, beyond what is feasible here.

Going from synthesis to deactivation behaviour, the reversible deactivation of a zeolite is discussed. Specifically addressing the deactivation behaviour of ZSM-5 during coking, and the effect on the unit cell parameters. Using DFT calculations, it is shown that coke molecules inside the zeolite cause the zeolite to expand, and the unit cell to appear tetragonal. This is also seen in experiments. This can be used for assessing the deactivation level of a ZSM-5 catalyst, by performing a simple X-Ray Diffraction (XRD) experiment. Furthermore, it is shown that coke in the form of methylated aromatics are likely to cause the expansion.

Zeolites are not only subject to reversible deactivation, but also a more permanent deactivation called dealumination. Understanding key elements of the dealumination, such as reaction path, kinetics and influence of surrounding molecules is of interest. The dealumination reaction is first modeled using DFT, and a special water reference state is introduced, in order to be able to model the kinetics of the reaction. Ab initio molecular dynamics (AIMD) is applied to address the role of surrounding water molecules during the dealumination reaction. The surrounding water is shown to have a small indirect effect on the reaction energy barrier. In the effort of improving zeolite catalysts, the synthesis of zeolites with specific active sites that are more resistant to deactivation or have specific selectivity, is of interest. A prerequisite to this, is being able to distinguish the different T-sites in zeolite catalysts. Hence, the last topic concerns the identification of specific Al sites in zeolite. The identification is done using ^{27}Al NMR and DFT calculations. The most robust method for performing the calculations is found, and used to identify the T-sites seen in the ^{27}Al NMR spectra in ZSM-23.