

## Surface Heterogeneity in Zeolite Catalysis

### Investigation of the Influence of Zeolites Surface Heterogeneity on Their Catalytic Activity in Alkane Cracking Process

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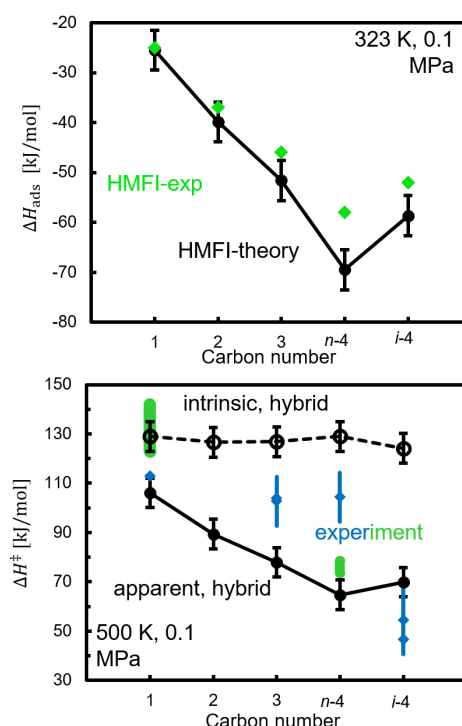
#### In Short

- A novel *ab-initio* computational scheme which enables calculation of enthalpies and free energies with chemical accuracy will be used to investigate the influence of the Brønsted site heterogeneity on the activity of the catalyst H-MFI
- The accurate reaction pathways of selected processes of the catalytic cracking of alkanes over H-MFI zeolite will be determined with high precision
- The hybrid dynamic approach will be applied to accurately predict the adsorption enthalpies of alkanes over zeolites
- Catalytical activity of surface active sites of zeolites will be investigated

Zeolites are porous aluminosilicates, which are widely used across many industrial applications. The Brønsted acidic groups, Al-O(H)-Si, which are present in the protonated forms of zeolites, are the source of the catalytic activity of these materials. One of the most important applications of acidic zeolites is the catalytic cracking of crude oil, which is a crucial process in the petrochemical industry. Cracking involves 3 basic reactions, namely (i) C-C bond cleavage, (ii) dehydrogenation and (iii) proton exchange. Optimization of the cracking process and design of better catalysts requires atomistic understanding of the active sites and elementary reaction steps. *Ab-initio* quantum chemistry can provide this information, but is useful only when energy barriers are predicted with chemical accuracy ( $\pm 4$  kJ/mol). This has recently been achieved for the methylation of ethene, propene and butene in H-ZSM-5 [1] and for the proton exchange barriers in the presence of methane in different zeolites [2]. In these studies we applied a computational scheme developed during our previous HLRN project (bec00083). In this approach, which we call QMQM-Anharm, chemical precision can be achieved by (i) the use of hybrid high level - low level calculations (QMQM) combining accurate wave-function methods at the reaction site with less accurate, but computationally more robust DFT calculations on the full system,[2] and (ii) calculating anharmonic vibrational energies (Anharm)

in an affordable way to improve the sampling of the potential energy surface.[3–5].

A prerequisite for the successful application of the QMQM-Anharm computational scheme is the selection of an appropriate model of the catalytic active site which is not always an easy task. Exemplified in our recent QMQM studies of the direct mechanism of the proton exchange between simple alkanes and the Brønsted acidic groups of H-MFI zeolite [6]. Results of these accurate hybrid calculations cannot perfectly explain all experimental findings. In Figure



**Figure 1:** Enthalpies of adsorption (top) and intrinsic and apparent activation enthalpies of the direct proton exchange reaction (bottom) of small alkanes over Al7-O(H)-Si7 Brønsted site of H-MFI zeolite, as a function of the number of carbon atoms. Results of the hybrid MP2:PBE+D2+ $\Delta$ CCSD(T) calculations - black points, experimental determined data - green and blue points. [6]

1 we present enthalpies of adsorption and activation enthalpies of the proton exchange of simple alkanes over Al7-O(H)-Si7 Brønsted site of the H-MFI zeolite. The calculated adsorption enthalpies agree well with experimental results up to the propane molecule, however for *n*- and *i*-butane the values are significantly underestimated. In the case of activation enthalpies, only results determined for methane molecule give good agreement with experimental values, whereas barriers of all other molecules are

underestimated. These discrepancies suggest that the Brønsted site model applied in these calculations may not be the appropriate one.

H-MFI zeolite is the most popular catalyst in petrochemical industry. However, it has very complex morphology, which consist of straight and zig-zag channels, those posses 12 unique T-atom positions in which Al can be loaded. This leads to the possibility of 48 different Brønsted sites. Most of the authors use in their calculations either “regular” or “channel intersection” sites, labeled “T7” or “T12” respectively (which we also used in our calculations). Several experimental and computational studies indicate that differences in relative stability across different Al sites are small. Some experimental studies conclude that the exchange of selected T sites by Al atom depends very strongly on the conditions of zeolite preparation, and represents a kinetically driven process. This suggests that the internal surface of H-MFI is heterogeneous. It also explains the variety of experimental reaction barriers reported in different experiments, which is clearly seen in Figure 1. Despite the importance of H-MFI zeolite in industry, until now no extensive *ab-initio* studies of the influence of Brønsted site heterogeneity on the reactivity of zeolites have been done. It is a demanding system due to the large primitive unit cell (about 300 atoms) which is accompanied by large computational costs. Since the calculations for all 48 Brønsted sites may be automated and performed in parallel, the investigation is an ideal task for high performance computational centers such as HLRN.

The aim of this project is to investigate the influence of the Brønsted site heterogeneity of the internal surface of H-MFI zeolite on the catalytic performance of this material towards catalytic cracking of alkanes. We will study adsorption, C-C bond cleavage, dehydrogenation, and proton exchange of alkanes (methane, ethane, propane, *n*-butane, *i*-butane, *n*-pentane and *n*-hexane) over different Brønsted sites of H-MFI zeolite.

The results of these studies will shed light not only on the types of Brønsted sites present in H-MFI zeolite but also provide accurate reaction pathways of the mono-molecular cracking process. This may also explain the symmetric distribution of cracking products observed experimentally, which previous theoretical calculations could not confirm. The activation barriers of the cracking reaction determined in this project will also be compared with different descriptors of Brønsted site activity (deprotonation energy, enthalpy of ammonia adsorption and shift of O-H stretching frequency upon adsorption of CO molecule) and on this basis we will try to determine the factors affecting the activity of the catalytic site. This may help to design better catalysts which is our overarching goal. During this project we also plan

to develop a simplified method for thermodynamic calculations within the anharmonic oscillator approximation. In this approach we will use subspaces of the normal modes, which should make these calculations much faster and stable. The estimated time for the realization of this project is 3 years.

In the first year of the project we studied (i) energetic ordering of all (48) possible Brønsted sites present in H-MFI, (ii) acidic properties of these sites measured by deprotonation energy [7] (iii) adsorption of alkanes on accessible acidic sites, (iv) monomolecular cracking of alkanes over selected active sites of H-MFI and (v) direct proton exchange mechanism of alkane molecules.

The results obtained in the first year of the project show that the intrinsic enthalpy barriers of the monomolecular cracking and the proton exchange of alkanes does not depend strongly on the heterogeneity of the active site. Only adsorption enthalpies of alkanes and, therefore, also apparent reaction barriers depend strongly on the Brønsted site model. The static approach routinely used in the molecular simulations ignores the less stable adsorbed-complex structures and underestimate the adsorption enthalpies. Therefore, in the second year of the project we will use recently developed hybrid dynamic approach to perform MD simulations of alkanes accurate adsorption enthalpies over the various acidic site models. We will also investigate the catalytic dehydrogenation of alkanes over selected acidic site models of MFI, and analyse monomolecular cracking process over the surface Brønsted sites of the nano-sheet MFI zeolite.

### More Information

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