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In Short

- A chemically accurate *ab-initio* computational scheme will be used to investigate the interactions of water molecules with different active sites in the acidic zeolite H-MFI
- The subtle interactions between up to three water molecules with the zeolite and with each other will be determined within chemical accuracy limits
- This investigation might explain the unusual experimental observation that the second water molecule adsorbs on H-MFI more strongly than the first one
- Our study will shed light on the interaction of ubiquitous water with the industrially very important zeolite H-MFI, helping to understand the initial structure of the active site in the wet catalyst

Zeolites, as acidic and porous aluminosilicates, are widely used across many industrial applications. Especially H-MFI is one of the most important heterogenous catalysts, e.g. for cracking, or the methanol to olefine (MTO) process. For acidic zeolites, the Brønsted acidic sites (BAS), Al-O(H)-Si, are the origin of the catalytic activity of these materials. Their structure and properties, however, can be significantly altered by adsorption of water, which is ubiquitous in most feed stocks. The adsorption of water becomes, typically, less exothermic the more water molecules per BAS are adsorbed. H-MFI, however, exhibits a contrary behavior: the first water molecule adsorbs less strongly than the second one (See Figure 1).[**??**] Accurate atomistic understanding of this behavior is still missing. Significant structural changes of the BAS could be the origin of it and would require a description that goes beyond the ideal structure model. The finding that incorporation of traces of water changes the nature of the active site would have drastic consequences on future investigations of reactions where water is involved.

Ab-initio quantum chemistry can provide such insights, but is only useful when adsorption enthalpies are predicted with chemical accuracy (±4 kJ/mol). This has recently been achieved for the methylation of ethene, propene and butene in H-ZSM-5 [**??**] and for the proton exchange barriers in the presence of methane in different zeolites [**??**]. In these studies a computational scheme developed during a previous HLRN project (bec00083) was applied. In this approach, which we call QM:QM, chemical accuracy can be achieved by (i) the use of hybrid high level - low level calculations (QM:QM) combining accurate wave-function methods at the active site with less accurate, but also computationally less demanding DFT calculations on the full system,[**??**] and (ii) calculating anharmonic vibrational energies in an affordable way to improve the sampling of the potential energy surface.[**??????**].

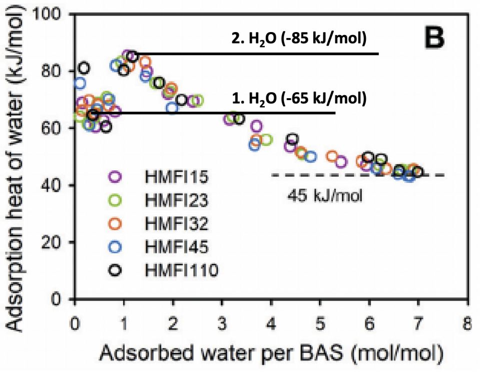

Figure 1: *Experimental enthalpies of adsorption of one to seven water molecules per BAS on H-MFI zeolite measured by Lercher and co-workers. Adapted from ref. [**??**]*

Figure **??** shows the experimental adsorption enthalpies of one to seven water molecules on H-MFI. While the already mentioned exception of an increased heat of adsorption going from the first to the second water molecule is significant, loading with more than two water molecules leads to the expected weakening of adsorption strength, eventually approaching the heat of condensation of water. The framework type MFI has a complex morphology (straight and zig-zag channels as well as intersections). It possesses 12 unique T-atom positions in which, in principle, an Al can substitute a Si atom. Based on previous experimental and computational studies on H-MFI, we will focus on 6 T-sites, which are promising candidates and allow for a comparative analysis. While experimental and computational studies suggest only small differences in thermodynamic stability across different T-sites, some experimental studies conclude that the BAS formation is kinetically driven and, therefore, strongly dependent on the preparation conditions. Hence, heterogeneity of the internal zeolite surface has to be expected. Little is known about the interaction of water with BAS but even less is known about differences in interactions of water with different T-sites. The protonation of water aggregates by a BAS, is claimed to strongly depend on the number of water molecules. While the adsorption of one water molecule does not lead to the deprotonation of the BAS, the adsorption of a second water molecule could already lead to the formation of a zundel cation, or a combination of a water attached to the BAS and a water attached to the aluminium atom. Adsorption of three water molecules is claimed to form protonated water clusters.[**??**] Especially the 'degree of protonation' could strongly depend on the method used to optimize the structure. Since the PBE density functional is known to underbind (bond strengths are too weak), a subsequent optimization with our MP2:PBE+D2 scheme will provide evidence for the protonation state of one, two, and three water molecules attachted to the aluminum site. Structural rearrangements and, therefore, adsorption strengths could also strongly depend on the investigated framework position rendering a comprehensive T-site sampling an integral and crucial part of the project. Since this zeolite has a large primitive unit cell (about 300 atoms) and calculations at six different T-sites with one, two, and three water molecules will be performed, the investigation is an ideal task for the high performance computational center HLRN.

The aim of this project is to investigate the adsorption process of water molecules on different active sites of H-MFI and to explain the unusual experimental trends in adsorption enthalpies in this zeolite type. Due to the potential gain in mechanistic understanding, these findings will provide more realistic models of active sites for catalytic reactions that involve or produce water, e.g. methylation reactions with methanol as used in the methanol to gasoline (MTG) process. Going beyond the ideal active site model may, in turn, lead to a better undestanding of reactivity and selectivity in a broad range of reactions. First, we will investigate the adsorption of one, two, and three water molecules on six different BAS in H-MFI, using educated guesses and simulated annealing to obtain the most stable adsorption complexes at the DFT level. Subsequently, we will use QM:QM optimizations, e.g. MP2:PBE+D2, to accuratly describe the protonation state of the BAS for the most stable water-BAS complexes, and to find a rational for the less exothermic adsorption enthlapy of the first water molecule compared to the second one. An anharmonic description of entropies using only an important subspace of the system will be used for thermodynamic calculations within the anharmonic oscillator approximation.

The estimated time for the realization of this project is one year. Our tests with VASP at HLRN-IV with selected VASP setting (PBE+D2 functional, 400 eV cutoff, Γ point) show that the total procedure planned for the project will consume $\sim$ 286 kNPL.

More Information

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