

## Probing the acidity of porous solids

Towards an atomic-level understanding of the interaction of probe molecules with acid sites in zeolites

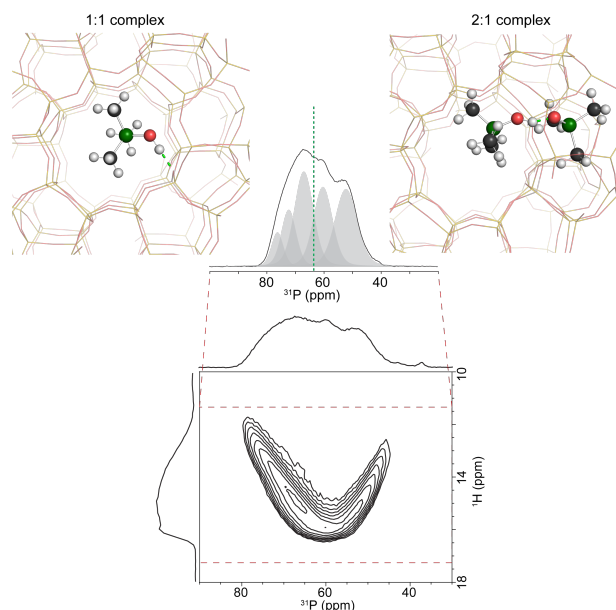
**M. Fischer**, Faculty of Geosciences, University of Bremen

### In Short

- Periodic first-principles simulations are used to study the interaction of probe molecules with Brønsted acid sites in zeolites.
- Mechanistic investigations focus on high-order complexes that involve more than one probe molecule per acid site.
- Computational findings will aid the interpretation of multinuclear solid-state NMR measurements and vibrational spectroscopy experiments.

Zeolites present a wide range of applications as solid acid catalysts in several industrial processes.[1] Highly siliceous zeolites, the most important zeolite catalysts, contain relatively small amounts of tetrahedrally coordinated aluminum atoms, the remainder of the tetrahedral sites being occupied by silicon. The charge of the framework aluminum atoms is balanced through protons, which are bonded to one of the surrounding oxygen atoms. The overall catalytic activity of these zeolites strongly depends on the location, amount, and acid strength of the framework protons (= Brønsted acid sites). To develop increasingly active and selective catalysts, it is essential to achieve a complete characterization of the acid site properties.[2,3] Surprisingly, although zeolite molecular sieves have been around for many decades, acid sites and siting of framework aluminum atoms are still poorly understood.

Probe molecules, such as ammonia, pyridine, and trimethylphosphine oxide (TMPO), have been widely used to study the acid properties of zeolites, as they can provide information about the acid-base interaction and the accessibility of the acid sites. Studies employing probe molecules typically identify several vibration modes (in vibrational spectroscopy) or distinct chemical shifts (in nuclear magnetic resonance [NMR] spectroscopy), which are commonly assigned to probe molecules interacting with Brønsted acid sites having different acid strength.[4] However, computational studies have shown consistently that the deprotonation energy, often considered as the true measurement of acid strength, of zeolites is homogeneous, independent of the acid site location and the zeolite framework.[5] We have recently shown

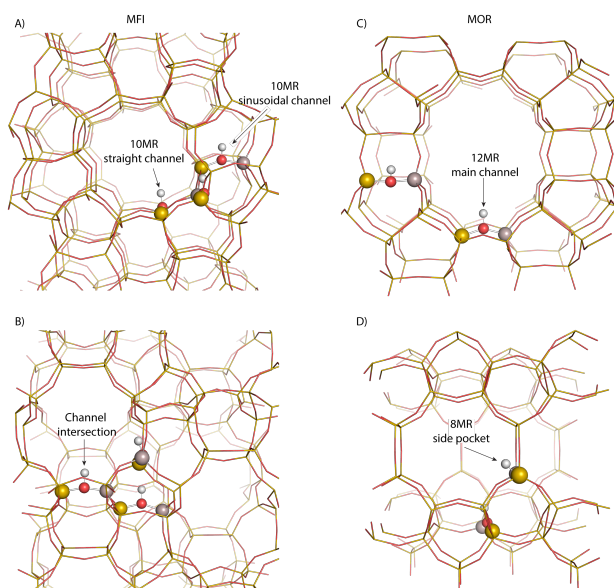


**Figure 1:**  $^1\text{H}$ - $^{31}\text{P}$  NMR spectrum of a TMPO-loaded MFI zeolite showing the spectral region assigned to 1:1 and 2:1 TMPO...Brønsted acid site complexes.

that high-order complexes, *i.e.*, complexes involving more than one probe molecule per acid site, can form in systems probed by TMPO.[6,7] Two-dimensional  $^1\text{H}$ - $^{31}\text{P}$  heteronuclear correlation NMR spectra of a TMPO-loaded MFI zeolite show that high-order complexes form at high TMPO loadings, as only 2:1 complexes can explain the U-shaped correlation peak observed experimentally (Figure 1).

The formation of such complexes is concerning because the quantification of acid sites is compromised if one does not properly account for the extent of dimerization. While there are some previous works suggesting the formation of high-order complexes in ammonia- and pyridine-loaded systems,[8,9] the large majority of studies ignore the formation of such species. In particular, no mechanism has been suggested to explain their formation.

Computational methods present a unique opportunity to better understand these systems. Ammonia, pyridine, and TMPO are strong bases that can easily capture the acidic proton from zeolite Brønsted acid sites. Upon protonation, these probe molecules form an acid conjugate that needs to be stabilized by the surrounding framework. Zeolites contain a wide range of molecular-sized voids, such as 8-, 10-, and 12-membered-ring (MR) channels, which offer distinct confinement effects and thus different stabilization environments. These might be reflected



**Figure 2:** A and B: Views of the MFI structure showing the three distinct Brønsted acid site locations in 10MR straight (i) and 10MR sinusoidal channels (ii) and at channel intersections (iii). C and D: Views of the MOR structure showing the two Brønsted acid site locations in the 12MR channels (iv) and the 8MR side pockets (v). The Brønsted acid sites (Si-OH-Al group) are depicted as balls and sticks. Silicon (yellow), oxygen (red), hydrogen (white) and aluminum (grey).

in distinct vibrational modes and/or NMR chemical shifts. This project aims at a comprehensive study of the interactions of ammonia, pyridine, and TMPO with their surroundings in two different zeolite frameworks, MFI and MOR. The MFI structure contains 10MR straight (i) and 10MR sinusoidal channels (ii), as well as more spacious channel intersections (iii), whereas the MOR structure contains main 12MR channels (iv) and 8MR side pockets (v). Figure 2 visualizes the pore structure of MFI and MOR, and shows representative distinct locations of framework Al atoms and Brønsted acid sites. Only channel intersections of MFI and 12MR channels of MOR offer enough space to allow the formation of high-order complexes (dimerization).

In the first project phase, a combination of density functional theory (DFT) structure optimizations and DFT-based *ab-initio* molecular dynamics (MD) simulations was used to investigate low (1:1 complexes) and high (2:1 complexes) probe molecule loadings. It could be shown that for low loadings, 1:1 complexes are formed where the probe molecule removes the Brønsted acid site proton, forming an ion pair of protonated probe molecule and negatively charged framework. At high loadings, the probe molecules tend to form dimeric species, where the proton is shared by the two probe molecules. Differences in the adsorption energies of the probe molecules at the distinct acid sites were also identified. The second project phase is aimed at a computation

of spectroscopic properties, namely NMR chemical shifts and vibrational modes of probe molecules interacting with zeolites' acid sites in different local environments. These results will facilitate the interpretation of experimental data acquired at CICECO, Aveiro Institute of Materials, Portugal, and at Diamond Light Source, UK. By combining state-of-the-art computational and experimental methods, this project hopes to contribute to a deeper understanding of the interaction of probe molecules with zeolites under experimentally relevant conditions.

## WWW

<http://www.miff.de>

## More Information

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## Project Partners

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