NMR-based Catalytic Center Elucidation for Hydrated Zeolites: Periodic DFT and Molecular Dynamics Investigations

Melissa J. Lucero and Štěpán Sklenák

Department of Theoretical Chemistry, J. Heyrovský Institute of Physical Chemistry,
The Czech Academy of Sciences, CZ-18223 Prague 8, Czech Republic

Standardization and improvement of zeolite catalytic properties rely heavily upon detailed knowledge of framework structure, the positions and properties of both extra-framework and active site counter-ions and the extent of hydration. Nevertheless, elucidating the nature of zeolite catalytic centers to this level of detail by purely experimental methods is often difficult. Computationally, this is fortunate, given the interest in the development of Kohn-Sham density functional theory (DFT) methods for the calculation of magnetic properties. Using the Quickstep[1] module in the CP2K[2] package, we perform rapid periodic DFT calculations (geometry and cell optimizations) of Chabazite, Ferrierite and ZSM-5 in a dual-basis of atom-centered Gaussian orbitals and plane waves. We then calculate NMR spectra using non-periodic clusters and compare to experiment. Our work demonstrates that large-scale electronic structure calculations of several systems, some including counter-ions, water and other extra-framework species are particularly helpful in determining NMR shieldings of catalytically-relevant tetrahedral (T) sites containing Al. We also probe effects of the extent of hydration, and the nature of the attendant counter-ions using large QM sections within QM/MM calculations and smaller, but efficient *ab initio* molecular dynamics calculations.

---

[1] Forschungszentrum Jülich, NIC Series, Vol. 25, 29 (2004).
[2] Comp. Phys. Comm. 167, 103 (2005).