

Modeling Acid/Base Chemistry in Zeolites: Structure and Dynamics Calculations for Comparison with NMR

Justin T. Fermann,¹ Usha Viswanathan,¹ Leanna Toy,¹ Karl Hammond,² Scott M. Auerbach,^{1,2,*} Thom Vreven³ and Michael Frisch³

¹Department of Chemistry, University of Massachusetts, Amherst, MA 01003 USA

²Department of Chemical Engineering University of Massachusetts, Amherst, MA 01003 USA

³Gaussian, Inc., 340 Quinpiac Street, Wallingford, CT 06492 USA

*auerbach@chem.umass.edu

Introduction

Zeolites are known as shape-selective acid catalysts [1], and may offer shape selectivity in base catalysis as well [2]. We are pursuing atomistic modeling of both acidic and basic zeolites, in an effort to shed light on how *acidic* zeolites function as catalysts, and to understand the behavior of functionalized zeolites with strong *basic* sites.

Regarding acidic zeolites, despite the many outstanding computational and experimental studies of proton siting and motion, we still lack the kind of quantitative agreement between experiment and theory that comes with complete understanding of the problem. This lack of agreement is remarkable given the relatively well-defined structures offered by zeolites. In this paper we offer an example of such quantitative agreement for internal proton transfer in acidic HY zeolite.

Regarding basic zeolites, recent studies of amine-substituted zeolites (i.e., zeolites with some bridging oxygens replaced by –NH– groups) suggest that these may provide basic sites as strong as those in calcined hydrothermalcites (standard solid base catalysts) [2]. Such basic zeolites would provide both strong active sites and shape selectivity, a useful combination for controlling addition reactions such as those in biofuel production [3]. Despite these promising results, it remains unclear whether active amine sites are truly incorporated into zeolite frameworks, or represent defects with varying structures. We address this by computing NMR chemical shifts and IR vibrational frequencies for amine groups substituted into various known zeolitic structures, for comparison with NMR and IR experiments.

Materials and Methods

We applied the Gaussian03 quantum chemistry package to perform ONIOM (embedded cluster) calculations of proton transfer energies for all allowed proton jumps in bare HY zeolite. The high-level calculations involved the B3LYP exchange-correlation functional with the 6-311G(d,p) basis set [4]. We used semiclassical transition state theory to compute rate constants for the 10 allowed jumps in HY. We then averaged over all these jumps, to yield an overall rate for comparison with NMR [5].

We applied Gaussian03 to compute chemical shifts and vibrational frequencies in amine-substituted zeolite clusters. The chemical shift calculations employed the GIAO theory. These computational results were then compared to NMR and IR experiments performed on zeolites with various levels of amine substitution.

Results and Discussion

We extracted an apparent activation energy for proton motion in HY zeolite, averaging over all 10 possible jumps. We obtained a value of 78.6 kJ/mol, in remarkable agreement with the NMR spin-lattice relaxation value of 78 kJ/mol [5]. These NMR data seem quite reliable, having been measured at high temperatures near 700 K [5]. As such, it is unlikely that water contamination or quantum tunneling plays any role in changing the mechanism of proton transfer from activated site-to-site jumping. Moreover, our calculations are likely reliable given our previous study of cluster convergence for this system [4].

For amine-substituted zeolites, our preliminary results show that –NH– bridging groups likely exist in real, amine-substituted zeolites, but that other amine sites also exist.

Significance

Our present study of proton transfer in bare zeolites represents a leap forward in the science of understanding proton dynamics in acidic zeolites. Never before has this level of agreement been obtained between such detailed experiments and computations for proton transfer in zeolites.

Our computational study of amine-substituted zeolites provides crucial support for characterization experiments on these novel materials, helping to shed light on the variety of active sites that may exist in these functionalized zeolites.

References

1. “*Handbook of Zeolite Science and Technology*,” Eds. S.M. Auerbach, K.A. Carrado and P.K. Dutta, Marcel-Dekker: New York, 2003.
2. Han, A.J., He, H. Y., Guo, J., Yu, H., *Micro. Meso. Mat.* **2005**, 79, 177.
3. Huber, G.W., Iborra, S., and Corma, A., *Chemical Reviews* **2006**, 106, 4044.
4. Fermann, J.T., Moniz, T., Kiowski, O., McIntire, T.J., Auerbach, S.M., Vreven, T., and Frisch, M.J., *J. Chem. Theory Comput.* **2005**, 1, 1232.
5. Ernst, H., Freude, D., Mildner, T., and Pfeifer, H., *Proceedings of 12th IZC*, Eds. M. Treacy, B. Marcus and M. Bisher, MRS: Warrendale, PA, 1999, 2955.