

Defect Centers in Microporous Aluminum Silicate Materials

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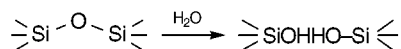
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An ab initio (DFT PW91) periodic model based on silica sodalite is applied to investigate the structure and energetics of formation and interconversion of defect centers in zeolites and related microporous materials. We calculate low energies of formation for a new range of defects including peroxy species which should be important Lewis and redox centers. The formation of such defects is shown to be facilitated by the presence of vicinal disilanol and Brønsted acid sites in these materials.

It is widely accepted that point defect structures play a crucial role in controlling the reactivity of zeolite catalysts. Indeed, the traditional model for the Brønsted acid site, which is generally considered to be the active site for much acid catalysis in these systems, comprises a simple point defect complex in which a protonated bridging oxygen is located on a site adjacent to an aluminum substituting for a silicon ion, as shown in Figure 1. The “proton nest” (or hydrogarnet) defect, illustrated in Figure 2, which is essentially a hydrolyzed silicon vacancy, is also known to be present in zeolites (and many other silicate systems) in significant concentrations. Indeed, the synthesis and postsynthetic processing conditions employed in preparing zeolite catalysts would be expected to lead to a wide range of complex defect structures. In this letter, we propose that a range of peroxy-based defect structures, generated by a combination of hydrolysis and oxidative calcination, will be widespread in zeolitic materials and could play a crucial role in key catalytic processes.

The starting point of our analysis is the reaction of water with the siloxane bridge, which has been discussed extensively in the context of other silica systems, notably quartz,¹ and which could be expected to generate two adjacent hydroxyl groups (or vicinal silanol defects) by the reaction:



To investigate the structures and energetics of these (and other) defects, we undertook density functional theory (DFT) electronic structure calculations employing periodic boundary conditions as implemented in the DSOLID code.² The exchange and correlation functionals used include the local density (LD) and generalized gradient (GG) terms of Perdew and Wang.³ In fact, the code applies the GG correction only to the energy and forces, while the charge density is calculated using the LD approximation.

Use of numerical atomic basis functions allows one to obtain an accurate and realistic representation of the charge density and the binding energies which are close to the DFT limit using the current functionals.⁴ In particular, we used (i) the double numerical basis set (two functions for each occupied valence orbital in a free atom) with polarization functions, (ii) the

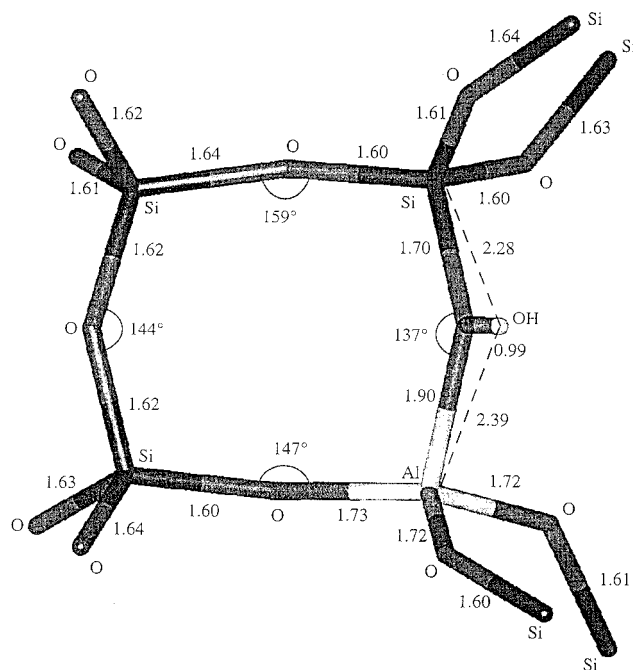
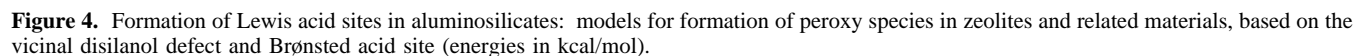


Figure 1. Structural model of a Brønsted acid site (bond lengths in Å, angles in deg).

medium-quality integration grid (a default option which provides a convergence of about 0.01 Å in the bond distances and usually better than 1 kcal/mol in the binding energies), and (iii) the frozen-core approximation.

In the present case, our calculations were based on a pure silica sodalite structure which has a cubic lattice with 36 atoms in its unit cell. Defects are introduced into the unit cell of the all silica sodalite system and repeated periodically. We note that the interactions between the periodic images are small as the overlap between the defect states is negligible and the strongest dipole–dipole electrostatic interactions sum to zero due to the lattice symmetry.

The crystal structure of the siliceous sodalite was fully optimized, and the resulting lattice parameter *a* (calculated as 8.878 Å, compared with 8.830 Å from experiment⁵ on single



In summary, our calculations suggest a new range of defect centers in microporous aluminium silicates, whose presence is supported by a range of experimental studies, and which almost certainly play a significant role in the catalytic activity of these materials.

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- (1) Casey, W. H.; Lasaga, A. C.; Gibbs, G. V. *Geochim. Cosmochim. Acta*. **1990**, *54*, 3369.
- (2) *EOM DSolid User Guide*; Molecular Simulations: San Diego, CA, 1996.
- (3) Perdew, J. P.; Wang, Y. *Phys. Rev. B* **1992**, *45*, 13244. Perdew, J. P.; Chevary, J. A.; Vosko, S. H.; Jackson, K. A.; Pederson, M. R.; Singh, D. J.; Fiolhais, C. *Phys. Rev. B* **1992**, *46*, 6671.
- (4) Delley, B. *J. Chem. Phys.* **1990**, *92*, 508.
- (5) Richardson, J. W.; Pluth, J. J., Jr.; Smith, J. V.; Dytrych, W. J.; Bibby, D. M. *J. Phys. Chem.* **1988**, *92*, 243.
- (6) *CRC Handbook of Chemistry and Physics*, 74th ed.; Lide, D. R., Ed.; CRC Press: Boca Raton, FL, 1993–1994.
- (7) Davis, L. P.; Burggraf, L. W. In *Ultrastructure Processing of Advanced Ceramics*; Mackenzie, J. D., Ulrich, D. R., Eds.; Wiley & Sons: New York, 1988; p 367.
- (8) Yamagishi, K.; Namba, S.; Yashima, T. *J. Phys. Chem.* **1991**, *95*, 872. Wu, P.; Komatsu, T.; Yashima, T. *J. Phys. Chem.* **1995**, *99*, 10923.
- (9) Hunger, M.; Käger, J.; Pfeifer, H.; Caro, J.; Zibrowius, B.; Bülow, M.; Mostowicz, R. *J. Chem. Soc., Faraday Trans. 1* **1987**, *83*, 3459.
- (10) Leheny, A. R.; Turro, N. J.; Drake, J. M. *J. Chem. Phys.* **1992**, *97*, 3736.
- (11) Slinkin, A. A.; Kucherov, A. v. *Russ. Chem. Rev.* **1985**, *54*, 61.
- (12) Barthomeuf, D. *Mater. Phys. Chem.* **1987**, *17*, 49.
- (13) Corma, A.; Fornés, V.; García, H.; Martí, M. A. *Chem. Mater.* **1995**, *7*, 2136. Blumenfeld, A. L.; Fripiat, J. J. *Top. Catal.* **1997**, *4*, 119.