Defect Centers in Microporous Aluminum Silicate Materials

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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 disilanols 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 siloxone bridge, which has been discussed extensively in the context of other silica systems, notably quartz, and which could be expected to generate two adjacent hydroxyl groups (or vicinal silanol defects) by the reaction:

$$-si^{O} si = \frac{H_2O}{-si}$$
 $siOHHO-si = \frac{1}{2}$

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

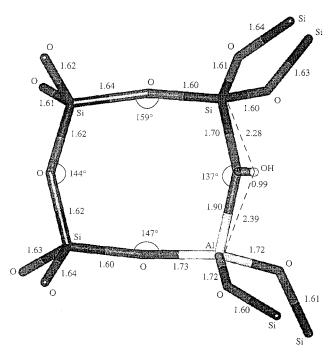


Figure 1. Structural model of a Brønsted acid site (bond lengths in Å, angles in deg).

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

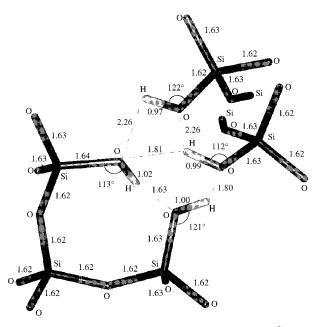


Figure 2. Structural model of a proton nest (bond lengths in Å, angles in deg).

crystals templated with ethylene glycol) was kept fixed in all following defect calculations, while we undertook full geometry optimization with respect to all atomic coordinates. (Relaxation of the lattice parameters in the supercell calculations, in our opinion, is a doubtful procedure for this study of dilute species.)

Our calculations of the defect formation energies were based on (i) the binding energy of 448.28 kcal/mol per SiO₂ formula unit obtained here for a pure silica sodalite, (ii) the physisorption energy of one water molecule adsorbed in the sodalite cage, of ca. 13.6 kcal/mol (we chose to use a physisorbed instead of free water as a more realistic model for the defect formation process and to avoid basis-set superposition errors introduced when comparing the molecular and bulk energies), and (iii) an experimental value of 118.2 kcal/mol for the atomization energy of the O₂ molecule⁶ (the theoretical value being far too inferior at the current level of theory. Since molecular oxygen is present in zeolite pores as a guest species introduced upon calcination, the O₂ physisorption energy is not accounted for in the energetics of defect formation).

Our calculations found a relatively low energy of 34 kcal/mol for the above hydrolysis reaction. Moreover, the geometry optimization revealed the fascinating symmetrical structure shown in Figure 3. This four-ring structure contains a relatively short O···O separation of 2.13 Å, indicative of a partial covalent bonding between the atoms. We note that a similar conformation has been considered in semiempirical and ab initio molecular studies of silanol polymerization.⁷

With this relatively low formation energy, we can therefore be confident that zeolites will contain appreciable concentrations of silanol defects of the type shown in Figure 3, which will be created during their synthesis or during post-synthetic treatments such as steaming. Let us now consider what the fate of such species might be in an oxidizing environment such as might occur during calcination.

Figure 4 charts a series of reactions which we have investigated using our electronic structure techniques. In the first, the hydrogen atoms are stripped of the vicinal disilanol by an oxygen atom to form initially a triplet peroxy species, which can convert exothermically to a symmetric singlet peroxy bridge species which has a short calculated bond length of ~ 1.58

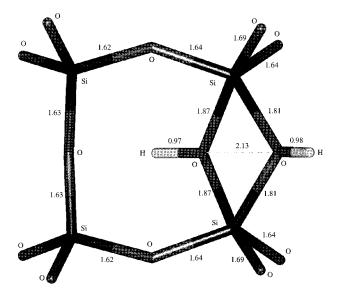


Figure 3. Structural model of a vicinal disilanol defect (bond lengths in Å, angles in deg).

Å. The low calculated energies for the reaction suggest that in an oxidizing atmosphere, such species would readily form. We also explored how these species would interact with Brønsted acid sites (Figure 1). As displayed in Figure 4, our results find, first, that the peroxy bridge will be trapped by the acid sites and, second, that it could migrate to form the Al hydroperoxide defect—essentially an oxidized Brønsted acid site. Again, the favorable calculated energetics indicate that such defects will be prevalent in oxidatively calcined systems.

These calculations thus define possible pathways for zeolite structural modifications by various synthesis procedures and subsequent treatments. They also serve to interpret experimental data documented in the zeolite literature. Indeed, it was shown unambiguously in $^{18}\mathrm{O}$ ion exchange, IR, and NMR experiments that the hydroxyl nest defects arise from the dealumination treatment and disappear upon alumination in zeolites HZSM-5 and mordenite.8 The high concentration of the defect sites with two adjacent silanol groups (disilanols) was also demonstrated in Na and proton exchange and in NMR experiments on TPAtemplated zeolite ZSM-5.9 A direct energy transfer from the excited adsorbates to the structural defects was reported in optical experiments on silicalites (thermal deflection spectroscopy), 10 which allowed the authors to estimate the defect concentration as one defect per unit cell; the optical absorption of the defect sites was thus identified at 293 and 283 nm, which in comparison with previously reported data suggested that the defect sites are either peroxy bridges or peroxy radicals. The role of dioxygen species formed at or next to Brønsted sites was also discussed in the context of Lewis and redox activity of zeolites based on the EPR data.11 However, no structural hypotheses were advanced.

By various estimations¹² it also appears that only a fraction of all available acid sites are catalytically active. In highly siliceous zeolites, this fraction could be very small, on the order of the defect concentration. Since most acid-catalyzed reactions with zeolites are conducted at high temperatures, the equilibrium between peroxy bridge species and the Al hydroperoxide defect could be responsible for the enhanced Brønsted and Lewis acidity by withdrawing the electron density from the Al through the oxygen ions. This model does not require the presence of any extraframework species for acidity enhancement and points toward a direct link between Brønsted and Lewis acidity in

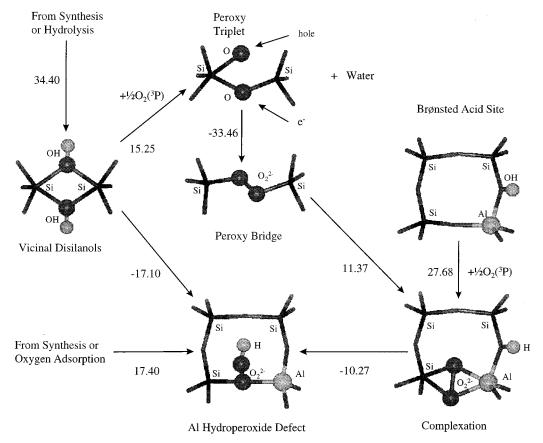


Figure 4. Formation of Lewis acid sites in aluminosilicates: models for formation of peroxy species in zeolites and related materials, based on the vicinal disilanol defect and Brønsted acid site (energies in kcal/mol).

zeolites (compare with e.g., ref 13). In this context, we should also emphasize the importance of organic reagents in the formation of the catalytically active sites by interactions with the zeolite framework. The Al hydroperoxide defect could easily be responsible for the formation of either radical ions or charge-transfer complexes in carbonium-ion-type catalysis or in radical-type cracking. Similar defects are expected to exist in metal-substituted zeolites, such as TS-1, thus defining their unique oxidation chemistry. The presence of the peroxy bridge and hydroperoxide defects can also play an important role in the stabilization of organic reaction intermediates and transition states.

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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