

Influence of short- and long-range factors in the Brønsted acidity of MCM-22 zeolite

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The acidity of the Brønsted sites of MCM-22 zeolite is calculated by atomistic simulation techniques and the effects of long- and short-range contributions in acidity are analysed; the two IR bands detected experimentally are reproduced in the calculations.

Since their introduction in fluid catalytic cracking, zeolites have been widely used as solid acid catalysts in a growing number of industrial chemical processes such as reforming, isomerisation, hydrocracking, oligomerisation, and others. Much attention has been devoted to the acid function in zeolites, and in particular Brønsted acidity has been characterised mainly by IR and NMR spectroscopies, as well as by computational chemistry methods.

The first simulations of Brønsted acidity in zeolites, employed the cluster model and the quantum chemistry methodology. Clusters of the size of the disiloxane molecule with a Si atom substituted by a trivalent atom T^{III} , mainly Al, and a proton bound to the oxygen atom in the $SiOT^{III}$ bridge are able to give reasonable OH stretching frequencies compared to IR experiments.¹ Among other results from quantum chemistry studies, a linear correlation was found between OH stretching frequency and $SiO(H)Al$ angle,² and this has been used to explain acidity differences between different zeolites or between different acid centres in a given zeolite. The question whether the long range factors—not accounted by the cluster model—do influence the acidity and to what extent, has led to calculations both with larger clusters and with periodic boundary conditions. The latter, require a considerable amount of computational resources, and thus less demanding methodologies to treat periodic solids such as those based on force fields are a reasonable alternative.

In spite of their lower accuracy, owing to the interactions neglected or averaged, force field methods have been successfully used to characterise different properties of zeolites such as cell parameters, geometry, framework stability, Al distribution, and Brønsted acidity.³ This methodology allows us to assess the short- and long-range contributions to acidity, and this makes it possible to span the number of calculations necessary to explore the different locations of the acid centres in a zeolite. It is the aim of this work to carry out a characterisation of the Brønsted acidity of the MCM-22 zeolite, and compare the results with IR data.

The calculations have been performed using the GULP code,⁴ employing the Ewald method for summation of the long-range Coulombic interactions, and direct summation of the short-range interactions with a cutoff distance of 12 Å. The RFO technique was used as the cell minimisation scheme with a convergence criterion of a gradient norm below 0.001 eV Å⁻¹. An empirical shell model forcefield⁵ (denoted empirical ff), and an *ab initio* shell model forcefield⁶ (denoted *ab initio* ff), have been used throughout. Electric fields, and OH stretching frequencies have been calculated with the GULP code. OH frequencies have been corrected for the empirical forcefield by subtracting an anharmonicity constant of 150 cm⁻¹,⁷ and for the *ab initio* forcefield by multiplying by a factor of 0.90.⁸

The hexagonal $P6/mmm$ structure of pure silica MCM-22⁹ has been used as a starting point and then has been minimised

without symmetry constraints. Then, a single Al atom has been introduced in the unit cell to create a Brønsted site and the resulting cell has been again minimised. The Al atom has been introduced in all the eight different T positions of the MCM-22 structure (Fig. 1), and the proton has been placed in all the four non-equivalent oxygen atoms linked to the corresponding Al in each case. Only the protons located on $SiOSi$ angles of 180° have been excluded, which correspond to the $Si(1)-O-Si(1)$, and the $Si(4)-O-Si(5)$ sites (Fig. 1). 29 different possibilities were considered, and this comes from the possible locations of a proton on each of the four oxygens linked to eight different T sites (32 possibilities), from which the $T(1)-O-T(1)$, $T(4)-O-T(5)$ and $T(5)-O-T(4)$ linkages have been subtracted. We distinguish between $T(x)-T(y)$ and $T(y) - T(x)$ ($1 \leq x, y \leq 8$) because in the first case the Al is on $T(x)$, whereas in the second case the Al is on $T(y)$.

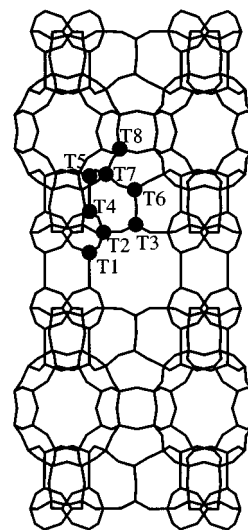


Fig. 1 Structure of MCM-22 showing the eight different T sites. Two independent void systems are present: a sinusoidal 10 MR, and a system of large (12 MR in size) cavities interconnected by short 10 MR conduits.

We have calculated the stretching OH frequency, $\nu(OH)$, for all the cases and the results are shown in Fig. 2, where they are plotted against the modulus of the electric field at the proton site, $|E_H|$. Two conclusions are drawn from this plot. First, the calculated values of $\nu(OH)$ (with the empirical ff) cover a wide range of 3530–3640 cm⁻¹ (Fig. 2), and they can be grouped in two bands: one around 3550 cm⁻¹, and the other around 3610 cm⁻¹. This result can be compared with experimental measurements of $\nu(OH)$ by IR spectroscopy performed on calcined MCM-22 of $Si/Al \approx 15$, where two bands appear at 3575 and 3620 cm⁻¹.¹⁰ Similarly, bands at 3550 and 3650 cm⁻¹ appear when using the *ab initio* forcefield (Fig. 2). The agreement with experiment is very reasonable, with the advantage that the simulations give a more detailed information about the origin of each OH frequency. The protons of MCM-22 can vibrate into four different environments: ‘unaccessible’ (for those which can not be reached by sorbate molecules), ‘cross’ (in the

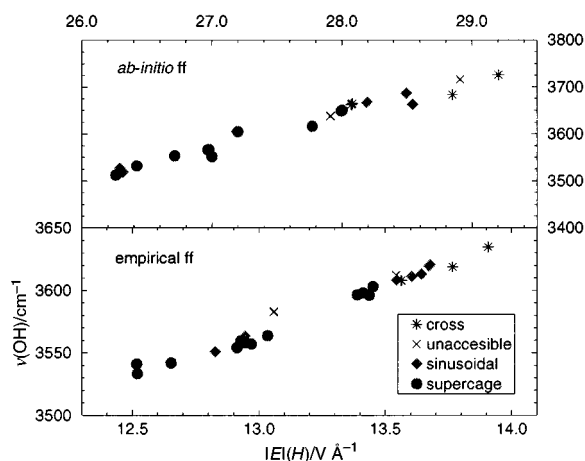


Fig. 2 Correlation between the modulus of the electric field at the proton ($|E_H|$) and the calculated OH stretching frequency, $\nu(\text{O-H})$ in the Brønsted sites of MCM-22. The location of the protons is indicated in the figure, showing no relation between environment and OH frequency. Two forcefields have been used as described in the text.

intersection between supercages), 'sinusoidal' (in the 10 MR sinusoidal system), and 'supercage' (inside the 12 MR supercage). Fig. 2 shows that some Brønsted sites located in the supercage belong to the low frequency band whereas others in the supercage belong to the high frequency band, and the same can be said about sites located in the sinusoidal system. A relation between cavity size and OH stretching frequency has not been found, in agreement with previous results.¹¹ The second conclusion we draw refers to the relationship between $\nu(\text{OH})$ and the modulus of the electric field at the proton site, $|E_H|$, which is a straight line regardless of the forcefield employed (Fig. 2), thus showing the direct correlation between the two properties. This shows the influence of the long range factors on acidity, as the electric field is caused by all the atoms of the zeolite framework.

In order to further explore the role of the short- and long-range factors in the Brønsted acidity we have plotted the OH stretching frequency against the Si-O(H)-Al angle, the latter being a geometric property that has been related to acidity as noted above. The results in Fig. 3 show a much poorer correlation than in the previous case. We find cases for which increasing angles give increasing frequencies and also cases with the opposite behaviour. Although the points are scattered (Fig. 3), a somewhat loose correlation shows decreasing OH frequencies as the Si-O(H)-Al angles increase, as noted in the literature.² The present calculations show that short range factors such as Si-O(H)-Al angles are not sufficient to fully explain the Brønsted acidity, and that a better correlation is found with a long range property, the modulus of the electric field at the proton site.

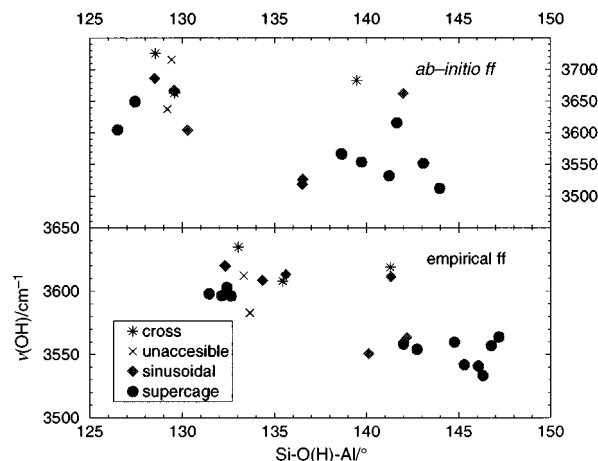


Fig. 3 Relation between the Si-O(H)-Al angle and the calculated OH stretching frequency, $\nu(\text{OH})$ in the Brønsted sites of MCM-22. The location of the protons is indicated in the figure, showing no relation between environment and Si-O(H)-Al angle. The lack of correlation between Si-O(H)-Al angle and $\nu(\text{OH})$ shows that the long-range factors (as well as the short-range) are important to determine the acidity. Two forcefields have been used as described in the text.

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