Supporting Information

Inelastic Neutron Scattering Study on the Location of Brønsted Acid Sites in High Silica LTA Zeolite

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1. Details of the periodic DFT calculations

The DMol3 module of MaterialsStudio 6.1 from Accelrys[1] [2] was used in order to carry out periodic DFT calculations. The double numerical plus-d-function basis set (DND) (all-electrons basis set) was used for all the calculations. The DND basis set includes one numerical function for each occupied atomic orbital and a second set of functions for valence atomic orbitals, plus a polarization d-function on all atoms. Double numeric-polarized basis sets (DNP), supplemented with polarization functions, are used for all the atoms[3]. The size of the DNP basis set is comparable to a Gaussian 6-31G**, but has a great deal more accuracy for a similar basis set size[4] [5]. In the self-consistent field calculations, the electronic-density convergence was set to 10^{-5} e/$Å^3$. The convergence criteria during geometry optimization without any symmetry constraints were 2×10^{-5} Hartree for the energy, 4×10^{-3} Hartree/Å for the force (energy gradient), and 5×10^{-3} Å for the atomic displacements.

Perdew-Burke-Ernzerhof parametrization of the generalized gradient approximation (PBE-GGA)[6] was used in all the calculations. The corresponding DFT quantum chemical calculations provide information on the frequencies of normal modes of the given systems and the amplitudes of the atomic displacements from the equilibrium positions.

The calculated neutron scattering spectra was obtained from the normal modes with a-Climax software[7].

The results (Figure S1) show that only using the spectrum including the first overtones (n=2), and not only the fundamental vibrations, it is possible to reproduce the broad band that appears at ca. 775 cm^{-1} in the experimental spectrum, and at ca. 700 cm^{-1} in the calculated spectrum. This band is due to the first overtone of the out-of-plane SiOH bending, whose fundamental frequencies are at 325 and 341 cm^{-1}. The origin of the discrepancy between the experimental (775 cm^{-1}) and calculated (700 cm^{-1}) frequency of this band, ca. 75 cm^{-1}, is due to the error in some fundamental frequencies in the low energy range (between 300 and 500 cm^{-1}).

In the case of this band, the discrepancy is less important than the fact that we can justify its origin, as a first overtone of bands related to the out-of-plane SiOH bending.

[1] B. Delley; "From molecules to solids with the DMol3 approach"; J. Chem. Phys. **2000**, 113, 7756–7764.

[2] Materials Studio 6.1 http://accelrys.com/products/datasheets/dmol3.pdf

[3] W. Kohn, L. J. Sham; Self-consistent equations including exchange and correlation effects. Phys. Rev. A **1965**, 140, 1133-1138.

[4] B. Delley; A scattering theoretic approach to scalar relativistic corrections on bonding. Int J Quantum Chem **1998**, 69, 423-433.

[5] B. Delley; Density functional crystal vs. cluster models as applied to zeolites. Int J Quantum Chem **1998**, 68, 135-144.

[6] J. P. Perdew, K. Burke, M. Ernzerhof. Generalized Gradient Approximation Made Simple. Physical Review Letters, **1996**, 77, 3865.

[7] A. J. Ramirez-Cuesta; aCLIMAX 4.0.1, The new version of software for analyzing and interpreting INS spectra; Comp. Phys. Comm. **2004**, 157, 226.

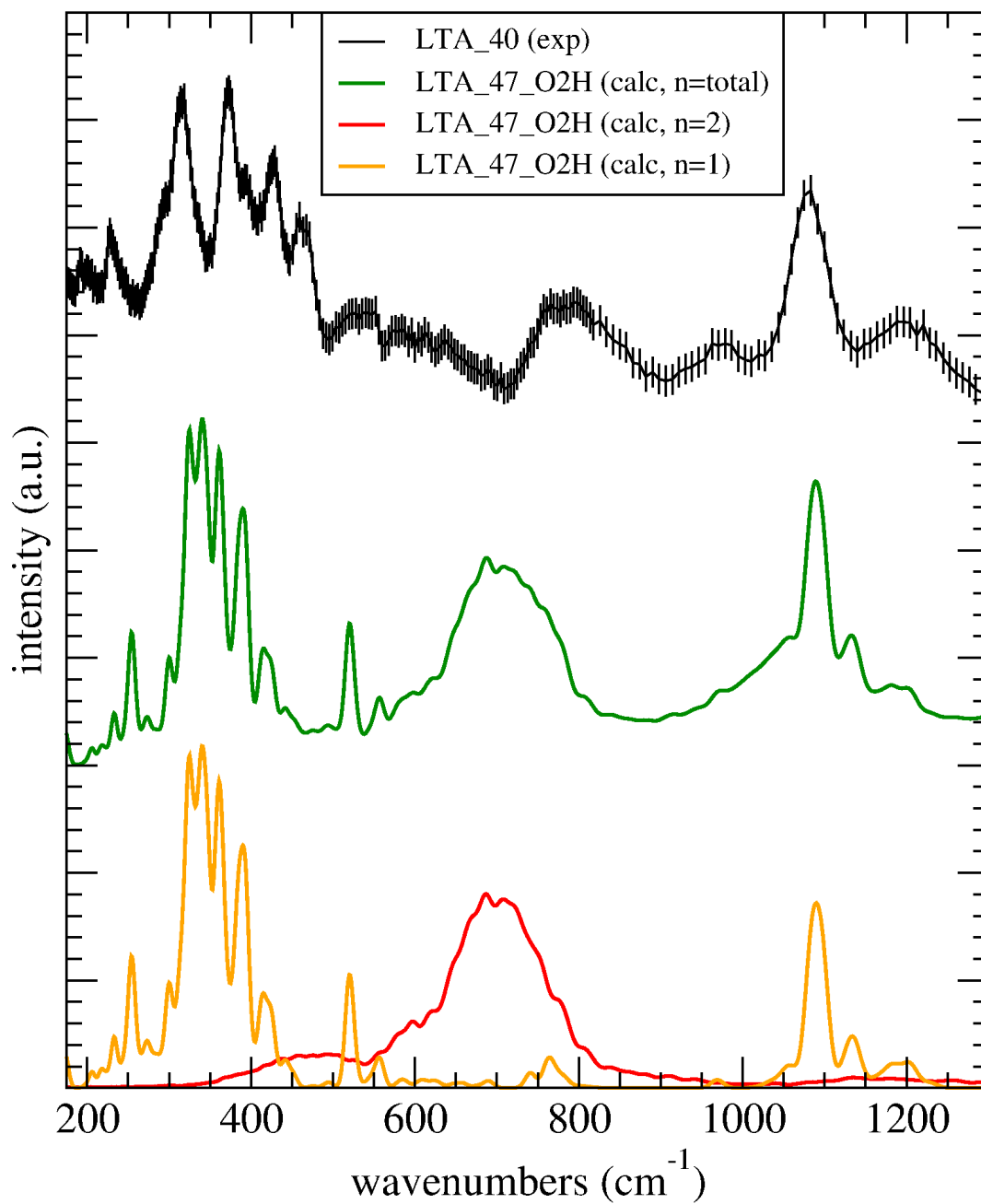**Figure S1**. Calculated neutron spectra calculated including different overtones: fundamental vibrations (n=1) and first overtone (n=2) of the LTA_47_O2H model, and total calculated neutron spectrum (n=total). Comparison with the experimental INS spectrum (LTA_40) is also shown.

A selection of the normal mode vibrational analysis for the LTA_47_O2H system is shown in Table S1, containing the frequencies and the components of the vibrations. There are movies for each vibration also included as separate files of this Supporting Information.

Table S1. Vibrational modes of LTA_47_O2H as calculated from periodic DFT.

Frequency (cm^{-1})	Vibrational modes	Peak in the experimental INS spectrum (cm^{-1}) (see Figure 6)
255	Zeolite framework	228
300	Zeolite framework + SiOH out-of-plane bending	296
325	SiOH out-of-plane bending	315
341	SiOH out-of-plane bending	
360	Zeolite framework + SiOH out-of-plane bending	373
390	Zeolite framework + SiOH out-of-plane bending	393
415	Zeolite framework + SiOH out-of-plane bending	429
441	SiOH out-of-plane bending	459
520	Al-O stretching	552
557	Zeolite framework	
675	Zeolite framework	
687	Zeolite framework	775
735	Zeolite framework	
969	SiOH in-plane bending + Si-O stretching	963
1058	SiOH in-plane bending + Si-O stretching	1083
1084	SiOH in-plane bending	
1132	SiOH in-plane bending + Si-O stretching	--
1183	SiOH in-plane bending + Si-O stretching	1188
1199	SiOH in-plane bending + Si-O stretching	

Periodic DFT energies. The periodic DFT calculations also allow to obtain the relative energies of the three unit cells LTA_47_OxH (x=1-3) with the following results: 13.5 (O1H), 0.0 (O2H), and 27.3 (O3H) kJ/mol. If we add the corresponding corrections from zero point vibrational energies: 1430.7 (O1H), 1428.3 (O2H), and 1429.7 (O3H) kJ/mol, the corrected values (1444.2 O1H, 1428.3 O2H, and 1457.0 O3H kJ/mol) do not change qualitatively the results, and O2H continues to be the most stable location. Hence, LTA_47_O2H is the one with lowest energy and this could be rationalised taking into account that O2H is the proton vibrating inside the smallest ring (6-ring), while the others (O1H and O3H) vibrate inside 8-rings. Vibration in a smaller ring leads to smaller O---H distances and hence stronger H-bond stabilising interactions, which justifies the lower energy of LTA_47_O2H.

It is likely that the major presence of O2H protons in the LTA_40 sample is related to this being the most stable position. In many occasions the proton location depends on how the organic template employed in the synthesis located in the zeolite cavity, but given the symmetry of the LTA cavity (α-cage) it is likely that any oxygen location (O1, O2, O3) can be accessible to the proton of the charged template, and we can assume that, a priori, any of the three proton sites (O1H, O2H, O3H) could be a possible outcome of the zeolite calcination process, where the charged template is removed from the micropore, leaving the proton as a zeolite Brønsted site. Under this condition, that all proton sites seem equally probable, it may hold the energetic argument, so that the energetically preferred proton location (O2H) is the most populated in the LTA_40 sample.

Discussion on the O-H stretching frequencies. The periodic DFT normal mode vibrational analysis also gives the O-H stretching frequency of each calculation (LTA_47_OxH, x = 1-3) although throughout this study only the range up to 1300 cm^{-1} is displayed (Figures 5, 6 and S1). The three calculations give the following as O-H stretching frequencies: 3600 (LTA_47_O1H), 3533 (LTA_47_O2H) and 3587 cm^{-1} (LTA_47_O3H). The infrared spectrum (Figure 4) gives two bands at 3560 cm^{-1} (strong) and 3618 cm^{-1} (weak). The comparison of the computational and the experimental values is not easy, but it is likely that the band at 3560 cm^{-1} (strong) is due to the O2H proton (LTA_47_O2H), whose calculated value is 3533 cm^{-1}, displaced only -27 cm^{-1} from the experimental value. It is also interesting to note that this band is strong, as it corresponds to our conclusion that all (or most) of the acid centres correspond to the O2H sites.

Then, the weak band that appears at 3618 cm^{-1} could be due to O1H protons, whose calculated value is 3600 cm^{-1}, displaced only -18 cm^{-1} from the experimental value, and in agreement with a similar underestimation of the other O-H stretching frequency at O2H. According to this, the infrared experiment would indicate a small number of O1H centres in addition to the large majority of centres at the O2H position. O3H centres, vibrating at 3587 cm^{-1} could also be responsible of the IR band observed at 3618 cm^{-1}. It is not possible to quantify the relative abundance from the infrared spectrum since it is not a quantitative technique for this task. From the comparison between the INS results and the calculated neutron spectra (Figure 5), the calculated peaks of O1H and O3H at 1033 cm^{-1}, and the doublet at 1060 and 1140 cm^{-1} respectively, do not appear in the experimental INS spectrum, suggesting that the O1H or O3H centres, if present, are a small number.

2. Discussion on the Brønsted sites and surface silanol groups.

A simple 'back-of-the-envelope' calculation is included below regarding an estimation on the relative number of Brønsted sites and surface silanols in a crystal of LTA zeolite.

We assume that we have a crystal of orthorhombic shape, with dimensions x,y,z. Then, the surface of the crystal will be, S_{crys} :

$$S_{crys} = 2 \cdot x \cdot y + 2 \cdot y \cdot z + 2 \cdot x \cdot z \qquad (1)$$

And, taking into account a unit cell of LTA with 24 T-atoms in a cubic unit cell of a $\cong$ 11.9 Å, the number of T-atoms in the crystal volume will be:

$$Num.\,T\text{-}atoms = \frac{24}{a^3} \cdot x \cdot y \cdot z \qquad (2)$$

The equation above assumes that all atoms are in the volume. To this amount, the atoms in the surface would need to be substracted, but neglecting this is a valid approximation and simplifies the calculation.

The corresponding number of Brønsted sites, assuming that this is equal to the number of Al atoms, will be:

$$Num.\ Br.\ sites = \frac{24}{a^3} \cdot x \cdot y \cdot z \cdot \frac{1}{Si/Al} \qquad (3)$$

The equation above assumes that all Al is in tetrahedral positions, and this is a valid approximation in view of the ^{27}Al NMR results in Figure 2 (right).

Now, the number of silanols per crystal surface (S_{crys}) can be calculated by taking the data of 8 silanol groups in each external face of the LTA unit cell, whose surface is a², as can be seen in the figure below.
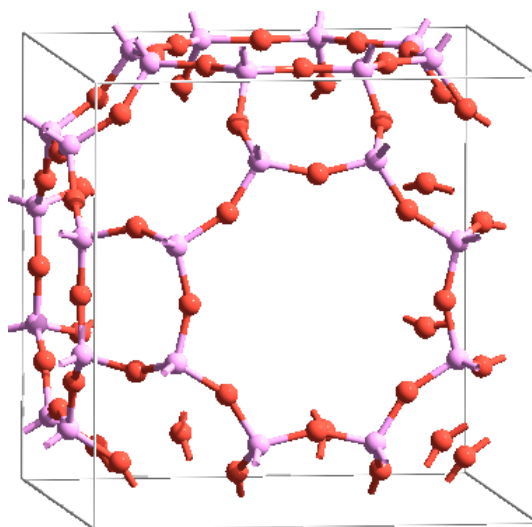
Of course other terminations of the crystal could be considered but they would gtive a lower number of silanols. By considering the case with more silanols we will be obtaining an underestimated value for the ration Br./silanol. Our aim is to demonstrate that even in that case, the ratio Br./silanol will be large enough so as to conclude that the number of silanols is sufficiently low so as to neglect its contribution to the INS spectrum.

$$Num.\ silanols = \frac{8}{a^2} \cdot 2 \cdot (x \cdot y + y \cdot z + x \cdot z) \qquad (4)$$

And the relative number of Brønsted and surface silanols can be found just by dividing equations 3 and 4, giving:

$$\frac{Num.\ Br.sites}{Num.\ silanols} = \frac{3}{2} \cdot \frac{x \cdot y \cdot z}{a \cdot (x \cdot y + y \cdot z + x \cdot z)} \cdot \frac{1}{Si/Al} \qquad (5)$$

Now, as a particular case, assuming that: the crystal is cubic (x = y = z), of size 10 µm (x = 10 µm), and using Si/Al = 40, we obtain a relative number of Brønsted sites per silanols of ca. 100.

This is similar to our experimental conditions and this indicates a much larger number of Brønsted sites than silanols, and therefore making valid our assumption that the peaks in the INS spectra are mainly due to the Brønsted sites and not to the surface silanols.