

Supporting Information

Water Interaction in Faujasite Probed by *In Situ* X-ray Powder Diffraction

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Electron densities from X-ray powder diffraction

Electron densities within a solid will determine its X-ray scattering pattern. In a nanoporous material that can sorb molecules within its pores and channels, one can identify a ‘clean state’, when its pores are free from sorbate molecules. For this state, the corresponding electron densities would be exclusively atomic in character, due to the framework atoms and/or charge compensating cations and could be reasonably modeled by a sum of atomic contributions. Once a starting model for the framework structure is known, one can refine its x-ray scattering pattern by conventional structural methods, i.e. by using the Rietveld method, for example. This procedure will provide a set of atomic coordinates representing the void or desorbed nanoporous solid.

When the nanoporous solid adsorbs molecules its electron density shows also contributions from the sorbate in addition to those from the framework. As sorption can be experimentally made in arbitrarily ‘small’ quantities, the sorbate contribution will affect the X-ray scattering in an almost continuous way. This fact points to the possibility to treat the sorbate contribution as a perturbative effect, at least in the initial stages of sorption.

Let us suppose that we know a model for a desorbed 3D ordered nanoporous solid. Its electron density can be described as a sum of atomic contributions:

$$\rho_f(\vec{r}) = \sum_{j=atoms} \rho_{at j} (\vec{r} - \vec{r}_j) \quad (1)$$

Where the summation runs over the framework atoms and extra-framework cations inside crystal unit cell:

$$\vec{r}_j = x_j \vec{a} + y_j \vec{b} + z_j \vec{c} \quad (2)$$

The corresponding structure factors $F_f(hkl)$ are related to the electron density by a Fourier transform:

$$F_f(hkl) = \int_{cell} \langle \rho_f(x, y, z) \rangle e^{-2\pi i(hx+ky+lz)} dx dy dz \quad (3)$$

The (hkl) are the Miller indices and the bracket around $\rho_f(x, y, z)$ means a ‘site- time-and multiple-unit-cell average of the atomic densities, including thermal motions and/or first type ‘disorder’, those that can be described by displacement of atoms from their equilibrium position. Once we know the set of atomic positions, ‘thermal’ and cell parameters for the structure from published crystal data or refined the desorbed material X-ray or neutron pattern, we can calculate the set of complex quantities $F_f(hkl)$.

From an X-ray diffraction experiment, one can obtain from a peak area the module of a structure factor $|F(hkl)|$, if that peak doesn’t overlap with one another. The information about the structure factor’s phase angle is lost. This is referred in crystallography as ‘the phase problem’. In the frequent case of dealing with centrosymmetric structures, their electron density are even function of coordinates, and according to the formula (3), the structure factors will be real and their phase angles will be 0 (+ sign) or 180 degrees (- sign). Even in the case of dealing with a structure with inversion symmetry, one cannot retrieve their structure factors signs from diffraction data alone.

A powder X-ray pattern from a known nanoporous structure (assuming it is a centrosymmetric one) can be obtained experimentally after interacting it with an arbitrary ‘small’ amount of sorbate molecules. From an isolated peak $I(hkl)$, measured after sorption, we can calculate the corresponding structure factor $|F(hkl)|$. If it changes its sign upon sorption, then at some sorbent dose, the corresponding peak intensity would vanish, because $F(hkl)$ will be close to zero. With this hint in mind, we propose a recursive way to guess the modules and signs of $\{F(hkl)\}$ as a function of dose, starting from the desorbed structure and its set $\{F_i(hkl)\}$, letting the solid sorb a known dose and looking at the peak intensities. If some structure factor changes sign upon sorption, its corresponding peak intensity will decrease until zero value. Otherwise, it will retain the sign of the clean structure. This procedure may be applied sequentially for analyzing diffraction data from subsequent sorbate doses.

In some cases, the low angle side of the X-ray diffraction pattern contains a set of well-resolved peaks. In these favorable cases, one can try to recover an electron density ‘representation’ of the structure by Fourier transform of the $F(hkl)$. Thus, we could also estimate an approximation for the excess electron density $\rho_s(x, y, z)$ due to the sorbate, as the transform of the difference between structure factors of the sorbed and framework material:

$$\rho_s(x, y, z) \cong \frac{1}{V} \sum_{hkl} (F(hkl) - F_f(hkl)) e^{2\pi i(hx+ky+lz)} \quad (4)$$

In order to obtain a faithful representation of the sorbate densities, the sum (4) does not need to go to high h, k, l numbers, i.e., it does not need to include high terms in reciprocal space, because sorbate species densities have a broad distribution in real space. Some drawbacks of the proposed method may arise due to incompleteness of the set $\{F(hkl)\}$, because powder diffraction peaks eventually overlap. But in favorable cases, powder diffraction provides a set of isolated peaks at low angle side of the pattern. In that case, it is possible to perform the Fourier transformation of eq. (4).

The Maximum Entropy Method (MEM), that is based on information theory, can also be used to invert equation (4), once some independent phased structure factors $\{F(hkl)-F_f(hkl)\}$, their respective uncertainties $\{\sigma_{hkl}\}$ and the number of excess electrons $N=(F(000)-F_f(000))$ are known. Basically, the maximum entropy algorithm searches for a distribution $\rho_s(x,y,z)$ that maximizes the information entropy contained in the m unit cell pixels, labeled by i :

$$S[\rho s'_i] = -N \sum_{i=1}^m \rho s'_i \ln \rho s'_i \quad (5)$$

$\rho s'_i = \frac{n_i}{N}$ being the normalized pixel density in the sense that $\sum_{i=1}^m \rho s'_i = 1$. Observed phased structure factors impose constraints on the maximization of the functional $S[\rho s'_i]$. They can be included by the technique of Lagrange multipliers as a kind of constraint upon a statistical knowledge of F-values within uncertainties, defining:

$$S'[\rho s'_i] = S[\rho s'_i] - \lambda (|F_{hkl}obs - F_{hkl}calc| - \sigma_{hkl}obs) \quad (6)$$

In this work, the 0th order single-pixel approximation¹ was employed. We performed a test of the feasibility of the maximum entropy method, trying to recover the faujasite framework electron density from 29 non-overlapped peaks obtained from experimental powder diffraction of the clean NaY support, limiting the resolution to 2Å, i.e., using X-ray powder data below $2\theta = 45$ deg. As shown in figure S1a, the recovered 3-D electron density map shows an X-ray ‘image’ of the framework (figure S1b), although the resolution is not enough to provide details about the T-O bond electronic distribution. It is possible to see where the charge compensation cations sit, as they are evidenced by sites where excess electron are found at I, I' and II in figure S1a. For dehydrated NaY, the excess electron distribution is atomic and its X-ray scattering can be easily modeled by a sum of atomic or ionic form factors. Since the 2Å resolution is enough to reveal some of the framework features, it will be

enough to ‘image’ the extra-framework electron distribution, since this contribution is less sharp defined in real space.

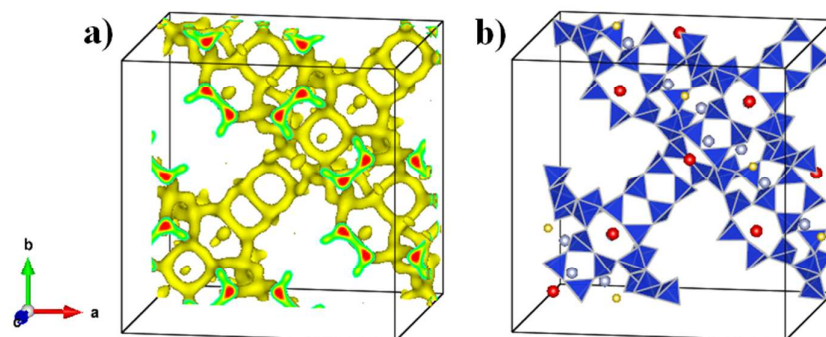


Figure S1. a) Limited resolution electron density of dehydrated NaY; b) Model as a sum of atomic/ionic contributions.

(1) Kumazawa, S.; Takata, M.; Sakata, M. On the single-pixel approximation in maximum-entropy analysis. *Acta Crystallogr.* **1995**, A51, 47–53.