Supporting Information

Structural analysis of IPC zeolites and related materials using positron annihilation spectroscopy and high-resolution argon adsorption

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Adsorption isotherms and pore size distribution

Measured isotherm $a(p)$ can be expressed in terms of the adsorption integral equation:

$$a(p) = \int_{w_{\min}}^{w_{\max}} q(p,w) f(w) dw \qquad (1)$$

In this equation $q(p, w)$ is the model kernel isotherm representing the amount adsorbed as a function of the pressure (p) and the pore size (w), ($w_{\min}$, $w_{\max}$) is the range of existing pore sizes and $f(w)$ is the PSD to be evaluated. The PSD describes the differential pore volume as a function of pore size. This method assumes a single pore model, *i.e.*, that each pore acts independently and there is no interaction between molecules adsorbed in different pores. Such assumption allows development of kernels for specific pore geometries such as slit, cylinder or sphere by calculating a series of theoretical model isotherms for a sequence of pore sizes covering the expected range of pore sizes ($w_{\min}$, $w_{\max}$).

The evaluation of the PSD from the experimental adsorption isotherm and equation (1) requires an assumption of the pore model which is used to calculate the kernel $q(p, w)$ of model isotherms. In this work, the cylindrical pore model was assumed and the kernel of model argon adsorption isotherms was calculated using the Tarazona version of the nonlocal density functional theory (NLDFT).[1-3] The fluid density profile ρ(**r**) in a pore at a given chemical potential (μ) and temperature (T) is found in this approach by minimization of the grand thermodynamic potential (Ω):

$$\Omega[\rho(\mathbf{r})] = F[\rho(\mathbf{r})] - \int d\mathbf{r}\rho(\mathbf{r})[\mu - V_{ext}(\mathbf{r})], \tag{2}$$

where F[ρ(r)] is the Helmholtz free energy functional and $V_{ext}(\mathbf{r})$ is the external potential of interaction of a fluid molecule with the pore walls. The free energy F[ρ(r)] is a sum of the energy of repulsive hard sphere (HS) interactions and attractive fluid-fluid interactions:

$$F[\rho(\mathbf{r})] = F_{HS} + \frac{1}{2}\iint \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r'}\,\rho(\mathbf{r})\rho(\mathbf{r'})\Phi_{atttr}(|\mathbf{r} - \mathbf{r'}|), \tag{3}$$

where Φ_{atrr} is the fluid-fluid interactions potential derived from the Lennard-Jones potential according to the Weeks-Chandler-Anderson prescription[4].

The external potential $V_{ext}(\mathbf{r})$ is modeled here as the interaction energy of a fluid molecule with the smooth cylindrical surface of the pore[5]:

$$V_{ext}(r,R) = E_{sf}\pi^2\sigma_{sf}^{\ 2}\left[\frac{63}{32}\left[\frac{1-(r/R)^2}{\sigma_{sf}}\right]^{-10} F\left[-4.5,-4.5;1;(r/R)^2\right] - 3\left[\frac{1-(r/R)^2}{\sigma_{sf}}\right]^{-4} F\left[-1.5,-1.5;1;(r/R)^2\right]\right] \tag{4}$$

where r is the radial distance from the pore center, R is the radius of the pore, F[α,β,χ,δ] is the hypergeometric function. The composite parameter E_{sf} is given by

$$E_{sf} = \varepsilon_{sf}\rho_s\,, \tag{5}$$

In the above equations σ_{sf} and ε_{sf} are the Lennard-Jones (LJ) solid-fluid interaction parameters; ρ_s is the surface number density of oxygen atoms in the pore wall. The specific parameter values used in the PSD calculations are included in Table S1.

Table S1. Parameters used to calculate the NLDFT kernel of argon isotherms for IPC family of samples.

E_{sf}/k (K/ Å)	σ_{sf} (Å)	ε_{ff}/k (K)	σ_{ff} (Å)
20	3.0	109.66	3.38

The fluid–fluid interaction parameters were obtained by fitting the mean-field DFT equation of state[6] to the bulk densities of the co-existing vapor and liquid phases assuming that the hard sphere and the LJ molecular diameters are equal, σ_{sf} was taken from reference[6].

The composite E_{sf} parameter depends on the potential of interaction between argon and the surface oxygen atoms and is specific to the density of oxygen atoms in the solid pore wall. The value of this parameter is essential for the calculated PSD as its position of on the pore diameter scale depends mostly on this parameter. In this work we evaluated the E_{sf} parameter specifically for the IPC type of materials. We calculated the PSDs for all studied samples using several values of E_{sf} and we chose the value that gave the PSD most consistent with XRD results for all samples.

To fit the kernel to the experimental data we apply numerical algorithm SAIEUS,[7] which solves the adsorption integral equation utilizing non-negativity constraints[8] and an L-curve[9] based regularization procedure. The SAIEUS program has been successfully utilized for the characterization of various surface properties of solids including the surface energy heterogeneity of alumina samples,[10] the distribution of acidity constants,[11] and the pore size distribution of carbon materials using NLDFT models.[12]

The calculated PSDs (Fig. 7) represent the optimal, conservative solutions of equation (1). To explain this issue, we note that this equation is a Fredholm integral equation of the first kind usually applied to solve inverse problems.[13] Our PSD analysis belongs to this category of mathematical problems that are typically ill posed or unstable in a sense that small changes in the data can cause huge changes in the solution.[14] Because of that, in order to obtain a stable solution for the PSD, in our calculations [7] we apply the regularization procedure based on the so-called L-curve [9]. The principle of this procedure is to add a regularizing (smoothing) term to the right hand side of equation (1)

$$a(p) = \int_{w_{\min}}^{w_{\max}} q(p,w) f(w) dw + \lambda \int_{w_{\min}}^{w_{\max}} \left[f''(w) \right]^2 dw \tag{1a}$$

and fit its modified form to the experimental data. The integral in the second term of equation (1a) is a measure of roughness of the solution *f* and λ is the regularization parameter that controls how much weight is given to the smoothing term. The calculated PSD is a function of λ that controls the balance between the roughness (noise) of the solution and the goodness of fit. To better understand the principle of the regularization procedure, in Figure S1A we plot the roughness of the calculated PSD versus the RMS error of fit the isotherm data with equation (1a) for a sequence of λ values using adsorption data of IPC-2 sample as an example. This is a very characteristic plot having a distinct L-shaped corner corresponding to the optimal balance between the roughness of the solution and the goodness of fit. In our example the L-curve corner corresponds to λ = 2.0. The effect of λ on the calculated PSD for this example is shown in Figure S1B where the PSD calculated with optimal value of λ is unimodal and more conservative compared to the more complex PSD calculated with lower value of λ = -2.5 and only slightly lower RMS error of fit, but dramatically higher roughness. Visually, the PSD related to the lower λ has three main peaks from which two apparently agree with structural data (XRD results) shown by the horizontal bars; however the third peak in the middle is completely random and unjustified.

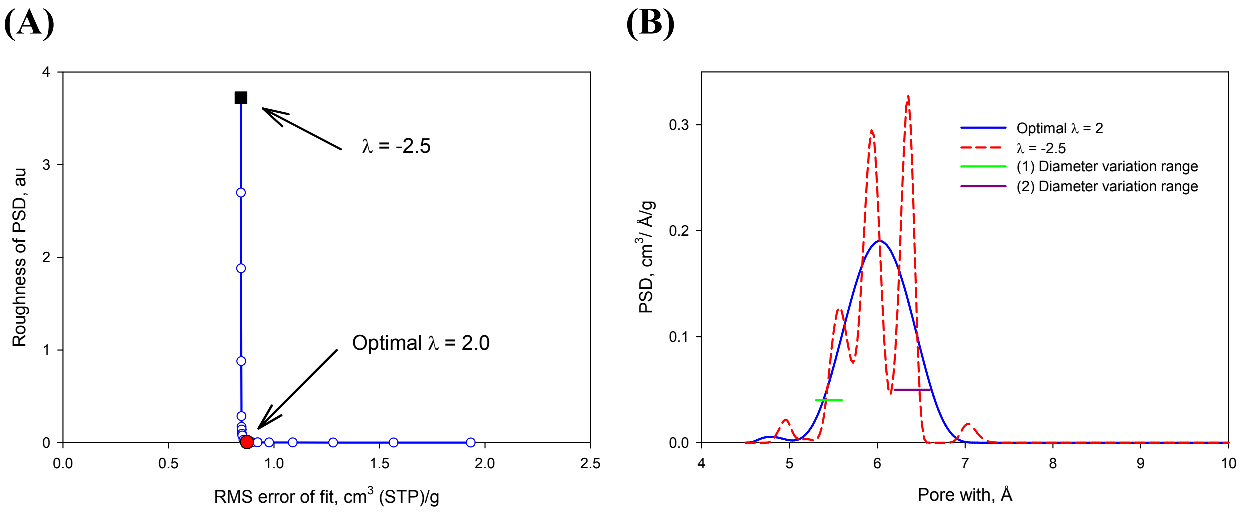

Figure S1. **(A)** The L-curve: Roughness of the calculated PSD versus the RMS error of fit the isotherm with equation (1a) for a sequence of λ values using adsorption data of IPC-2. **(B)** Effect of λ parameter on the PSD calculated for IPC-2 sample. Horizontal bars have the same meaning as in Figure 6.

PALS Analysis

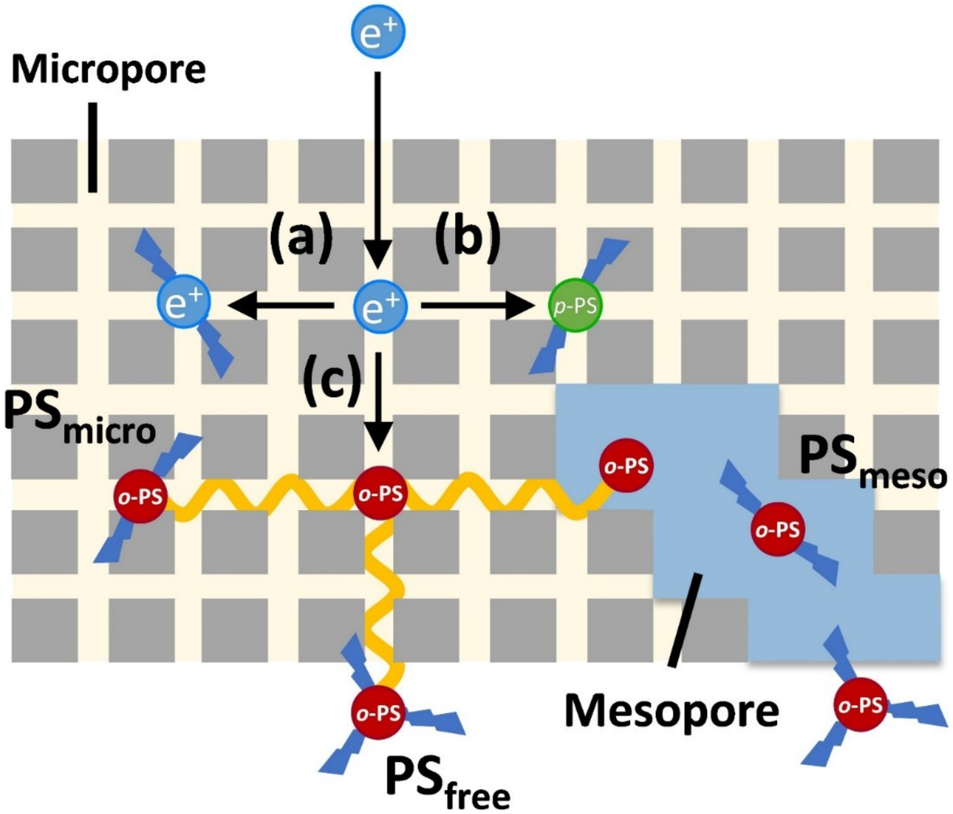

Figure S2. A schematic representation of the possible interactions of positrons (a-c) when implanted into a porous material. Metastable *ortho*-positronium (*o*-PS) atoms form throughout the zeolite crystals and are sufficiently long-lived to diffuse through the pore network. Since the lifetime of *o*-PS depends on the pore size, the PALS response provides direct information on the pore connectivity. Large pores connected to the external surface of the material act as shortcuts out of the crystal, leading to a greater contribution of *o*-PS annihilating in vacuum.

Table S2. The PALS data for UTL, IPC-1A, 1B, 2 and 4. The values in parentheses correspond to the error of the last significant figure.

Zeolite	Total *o*-PS intensity	Lifetime (ns)	Intensity (%)	Normalized (%)	Comment to annihilation
UTL	16.8(3) %	0.127(3)	20.3(5)	**-**	*p*-PS
		0.811(7)	62.9(3)	**-**	e^+
		3.06(7)	13.6(3)	**80.8(18)**	*o*-PS in micropores
		7.90(13)	1.8(2)	**10.8(18)**	*o*-PS in micropores
		110.4(7)	1.4(0)	**8.4(0)**	*o*-PS in vacuum
IPC-1A	26.8(8) %	0.618(3)	63(5)	**-**	*p*-PS + e^+
		1.59(5)	7(1)	**27.8(19)**	*o*-PS in micropores
		5.16(15)	0.02(2)	**14.7(4)**	*o*-PS in micropores
		74.6(56)	3.0(6)	**9.0(15)**	*o*-PS in mesopores
		138.5(15)	14(2)	**48.5(15)**	*o*-PS in vacuum
IPC-1B	34.7(10) %	0.558(13)	62.9(43)	**-**	e^+
		1.60(9)	11.0(8)	**31.7(23)**	*o*-PS in micropores
		4.06(11)	5.7(3)	**16.4(9)**	*o*-PS in micropores
		70.7(70)	2.0(4)	**5.8(12)**	*o*-PS in mesopores
		136.5(12)	16.0(4)	**46.1(12)**	*o*-PS in vacuum
IPC-2	33.5(6) %	0.708(7)	66.5(8)	**-**	*p*-PS + e^+
		2.42(6)	29.1(4)	**85.9**	*o*-PS in micropores
		5.92(2)	1.5(5)	**5.3**	*o*-PS in micropores
		124.0(15)	2.9(0)	**8.3**	*o*-PS in vacuum
IPC-4	31.6(3) %	0.135(10)	7.1(7)	**-**	*p*-PS
		0.689(6)	61.2(5)	**-**	e^+
		2.85(4)	25.7(2)	**81.3(6)**	*o*-PS in micropores
		6.85(14)	2.6(2)	**8.3(6)**	*o*-PS in micropores
		124.6(38)	3.3(1)	**10.5(3)**	*o*-PS in vacuum

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