Electronic supplementary information

Pore connectivity in hierarchical zeolites by positron annihilation lifetime spectroscopy: Instrumental and morphological aspects

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Method S1

The out-diffusion of Ps from zeolite crystals of different size has been modelled using the one dimensional diffusion equation integrating a term that accounts for the pick-off annihilation of Ps inside the host (W. Brandt, R. Paulin, *Phys. Rev. B*, 1972, **5**, 2430):

$$\frac{\partial}{\partial \mathrm{x}}\left(D(x)\frac{\partial n(x,t)}{\partial x}\right) - \lambda(x)n(x,t) = \frac{\partial n(x,t)}{\partial t} \quad \text{(S1)}$$

where the diffusivity, $D(x)$, and the annihilation rate, $\lambda(x)$, take different values depending on the pore architecture (purely microporous or hierarchical) and x is the coordinate along the length of the model, L_{model}. The initial conditions correspond to the probability of Ps formation, $n(x,0) = P(x)$, which has been assumed to be equivalent to the positron implantation profile. Dirichlent boundary conditions have been set in the limits of the crystal $n(0,t) = n(L_{\mathrm{model}},t) = 0$. In cases where the initial conditions were conflicting with the boundary conditions, $n(0,0)$ and $n(L_{\mathrm{model}},0)$ were set to decay rapidly to zero. The differential equation has been solved using finite element methods.

The fraction of Ps escaping from the zeolite crystal before annihilation (Ps_{vac}) is calculated as the time integrated flux across the particle boundaries:

$$Ps_{\mathrm{vac}} = -\int_0^T \left(\left[D(x) \frac{\partial n(x,t)}{\partial x} \right]_{x=L\mathrm{model}} - \left[D(x) \frac{\partial n(x,t)}{\partial x} \right]_{x=0} \right) \mathrm{d}t \tag{S2}$$

An integration time (T = 400 ns) longer than the lifetime of Ps in vacuum (142 ns) was chosen to ensure that all Ps had out-diffused from the particle. The diffusivity, $D(x) = L_{\mathrm{dif}} \cdot v_{\mathrm{dif}}$, is related to the positron diffusion length, L_{dif}. A diffusion rate (v_{dif}) of 1000 cm s^{-1} was selected to attain a value of Ps_{vac} comparable with the value measured in the beam setup for Z50C. The corresponding diffusivity of 0.03 cm^2 s^{-1} in the micropore is slightly lower than the diffusivity measured for crystalline ice (0.17 cm^2 s^{-1}, M. Eldrup, *et al. Phys. Rev. Lett.*, 1983, **51**, 2007).

Models of varying length (0.35-5 μm) have been calculated for Z50A and Z50C, while two models of 0.35 μm in length including an inner core and an outer shell were used to represent Z50A-H1 and Z50A-H2. The characteristics of the models are described in Table S7. The implantation range, z_0, of moderated positrons in Eq. (S2) has been set to 0.2 μm in all cases. For fast positrons, the Ps formation probability has been approximated by a constant distribution.

Table S1 Lifetimes and intensities derived from the conventional PALS measurements using PAScual. The numbers in brackets correspond to the error in the last significant digit.

Z50C, Total Ps intensity = 15.6(2)%						
Lifetime (ns)	0.54(2)	1(3)	3.0(7)	9.7(5)	33(3)	125(2)
Intensity (%)	52.5(4)	32(5)	8.3(4)	2.7(9)	0.9(7)	3.7(4)
Z50A, Total Ps intensity = 16.1(5)%						
Lifetime (ns)	0.49(4)	0.8(3)		5.2(3)	22(3)	133(3)
Intensity (%)	40(4)	44(4)		5.5(2)	3.5(3)	7.0(2)
Z50A-H1, Total Ps intensity = 18.8(1)%						
Lifetime (ns)	0.45(3)	0.8(2)	5.4(8)	22(1)	73(2)	113(3)
Intensity (%)	32(3)	49(3)	1.3(2)	2.7(2)	5.2(4)	9.6(4)
Z50A-H2, Total Ps intensity = 16.9(1)%						
Lifetime (ns)	0.48(2)	0.8(2)	6.6(7)	32(1)	73(3)	126(4)
Intensity (%)	49(4)	34(4)	0.9(2)	1.3(3)	5.1(6)	9.6(4)

Table S2 Lifetimes and intensities derived from the conventional PALS measurements using a combination of POSFIT and CONTIN. The numbers in brackets correspond to the error in the last significant digit.

Z50C, Total Ps intensity = 19.5(3)%						
Lifetime (ns)	0.43(3)	0.82(2)	2.3(10)	6.7(3)	26(1)	125(1)
Intensity (%)	39(2)	44(2)	10.1(2)	4.0(1)	1.4(1)	4.0(2)
Z50A, Total Ps intensity = 16.5(4)%						
Lifetime (ns)	0.45(5)	0.78(6)	3.1(4)	8.1(5)	29(2)	135(2)
Intensity (%)	48(9)	35(9)	2.3(2)	4.2(2)	2.8(1)	7.2(2)
Z50A-H1, Total Ps intensity = 19.0(3)%						
Lifetime (ns)	0.43(2)	0.77(2)	7.0(4)	25(3)	65(8)	122(5)
Intensity (%)	31(2)	50(5)	1.5(1)	2.2(3)	5.7(1)	9.6(1)
Z50A-H2, Total Ps intensity = 17.1(9)%						
Lifetime (ns)	0.42(2)	0.72(2)	6.9(3)	34(7)	76(20)	128(10)
Intensity (%)	33(2)	50(4)	0.8(2)	1.5(9)	5.3(3)	9.5(3)

Table S3 Lifetimes and intensities derived from the conventional PALS measurements using MELT.

Z50C, Total Ps intensity = 19.3(1)%							
Lifetime (ns)[a]	0.38(0)	0.80(0)	2.3(0)	6.4(0)	23(1)		120(2)
Intensity (%)	32(35)	49(32)	10.0(1)	4.0(2)	1.4(2)		3.9(1)
Z50A, Total Ps intensity = 11.6(10)%							
Lifetime (ns)[a]	0.41(0)	0.76(0)	3.4(0)	7.4 (1)	13(0)	30(2)	133(2)
Intensity (%)	45(132)	44(71)	1.5(2)	2.4(7)	0.9(7)	1.7(1)	5.1(0)
Z50A-H1, Total Ps intensity = 19.7(6)%							
Lifetime (ns)	0.29(0)	0.73(0)	2.5(0)	7.3(1)	21(1)	48(1)	112(13)
Intensity (%)	22(13)	58.8(4)	0.6(3)	1.4(1)	1.4(3)	4.1(2)	12.2(3)
Z50A-H2, Total Ps intensity = 14.3(5)%							
Lifetime (ns)	0.29(0)	0.67(0)	1.8(0)	7.3(0)	-	44(1)	113(8)
Intensity (%)	30(37)	55(8)	0.7(5)	0.7(1)	-	2.4(1)	10.5(1)

[a] The error of the lifetime is the full width half maximum of the fitted peak.

Table S4 Lifetimes and intensities derived from the beam PALS measurements (5 keV) using PAScual. The numbers in brackets correspond to the error in the last significant digit.

Z50C, Total Ps intensity = 15.3(5)%						
Lifetime (ns)	0.125(0)	0.99(6)	4.0(8)	8.9(5)	41(3)	139(4)
Intensity (%)	33.3(2)	51.3(2)	6.0(4)	4.9(2)	1.2(2)	3.1(7)
Z50C-C, Total Ps intensity = 34.8(3)%						
Lifetime (ns)	0.16(6)	1.00(2)	2.8(3)	14(1)	61(7)	135(6)
Intensity (%)	1(2)	64(2)	31(3)	2.4(6)	0.5(2)	0.9(1)
Z50A, Total Ps intensity = 18.2(4)%						
Lifetime (ns)	0.5(0)	0.81(2)	6.0(3)	16.0(20)	69(5)	141(2)
Intensity (%)	0.0(0)	81.7(1)	5.2(2)	1.7(2)	3.1(3)	8.2(3)
Z50A-H1, Total Ps intensity = 29.6(2)%						
Lifetime (ns)	0.125(0)	0.78(3)	4.8(2)	20(3)	70(20)	130(4)
Intensity (%)	20.9(2)	49.1(2)	1.8(1)	3.8(8)	4(2)	20(2)
Z50A-H2, Total Ps intensity = 24.8(7)%						
Lifetime (ns)	0.125(0)	0.74(5)	3.5(8)	16(1)	57(3)	136(3)
Intensity (%)	20.2(3)	55(3)	2.6(5)	7.2(3)	6.6(3)	8.4(3)

Table S5 Characterisation data of the coffin-shaped ZSM-5 zeolite crystals (Si/Al = 80).

Sample	Si/Al[a] (-)	V_{micro}[b] ($cm^3\ g^{-1}$)	S_{meso}[b] ($m^2\ g^{-1}$)	V_{meso}[c] ($cm^3\ g^{-1}$)	$c_{Brønsted}$[d] ($\mu mol\ g^{-1}$)	c_{Lewis}[d] ($\mu mol\ g^{-1}$)
Z80C-1	80	0.18	14	0.01	72	3
Z80C-2	87	0.17	8	0.01	74	6
Z80C-3	90	0.17	6	0.01	78	0

[a] ICP-OES; [b] *t*-plot method; [c] $V_{meso} = V_{pore} - V_{micro}$; [d] Pyridine-IR.

Table S7 Lifetimes and intensities derived from the beam PALS measurements (5 keV) using PAScual. The numbers in brackets correspond to the error in the last significant digit.

Z80C-1, Total Ps intensity = 34.5(3)%					
Lifetime (ns)	-	0.774(2)	3.67(7)	-	130(13)
Intensity (%)	-	65.9(2)	5.5(1)	-	29(2)
Z80C-2, Total Ps intensity = 28.9(3)%					
Lifetime (ns)	0.125(5)	0.87(2)	2.0(2)	5.0(3)	124(16)
Intensity (%)	6.8(3)	64(2)	7(2)	2.9(2)	19(2)
Z80C-3, Total Ps intensity = 33.5(2)%					
Lifetime (ns)	0.125(5)	0.94(1)	2.2(1)	6.0(4)	125(9)
Intensity (%)	10.5(3)	56(1)	14.5(9)	3.9(4)	15(1)

Table S6 Dimensions of the coffin-shaped ZSM-5 zeolite crystals (Si/Al = 80) determined by the analysis of at least 20 crystals in scanning electron micrographs. The numbers in brackets correspond to the error in the last significant digit.

Sample	l[a] (μm)	w[b] (μm)	t[c] (μm)	V:S (μm)
Z80C-1	2.33(50)	0.56(38))	0.22(14)	0.07
Z80C-2	16.48(105)	3.70(53)	0.60(14)	0.25
Z80C-3	54.51(110)	9.55(70)	6.60(82)	1.82

[a] length corresponds to the longest dimension of the crystal, along the *c*-axis; [b] width corresponds to the longest dimension in the direction of the *a*-axis; [c] thickness correspond to the longest dimension along the *b*-axis.

Table S8 Parameters used for the diffusion models to describe the measured samples.

Sample	L_{Model} (μm)	L_{shell} (μm)	L_{dif} (μm)	τ_{shell} (ns)	L_{core} (μm)	L_{dif} (μm)	τ_{core} (ns)
Z50C	0.5-5.0	-	5	20	0.5-5.0	0.3	3
Z50A	0.35	-	5	20	0.35	0.3	3
Z50A-H1	0.35	0.1	5	20	0.15	0.3	3
Z50A-H2	0.35	0.08	5	20	0.19	0.0	3

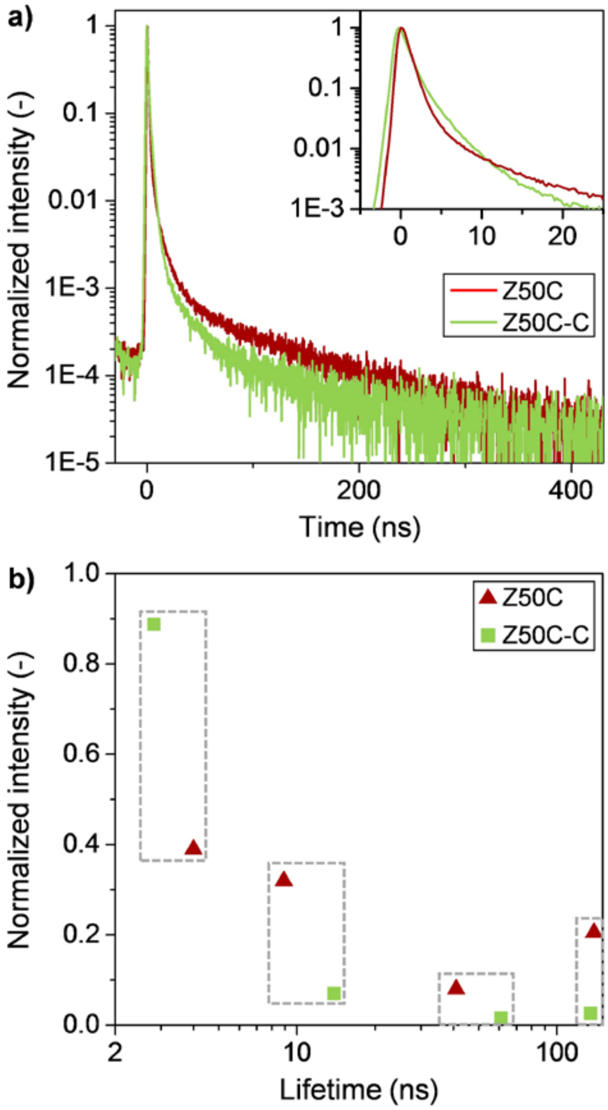

Fig. S1 a) Normalised PALS spectra of Z50C and Z50C-C collected with the BaF_2 detector in the beam set-up at 5 keV and b) lifetime components and relative fractions derived using PAScual.

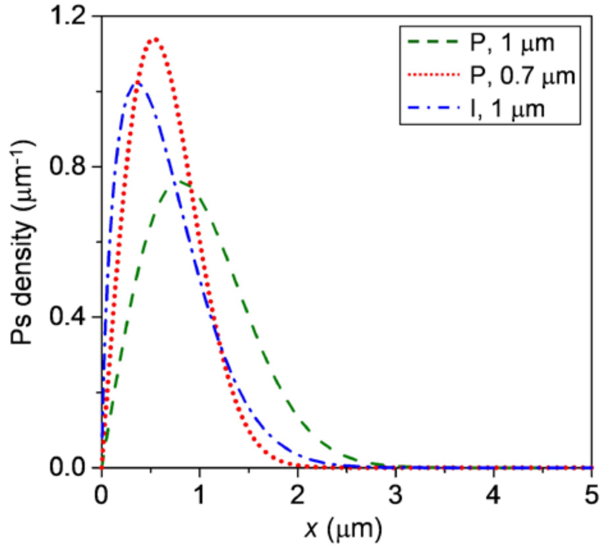

Fig. S2 Initial distributions of Ps calculated upon implantation of moderated positrons assuming a perpendicular (P) or isotropic (I) angle of incidence with different average implantation depths (0.7 or 1 μm).

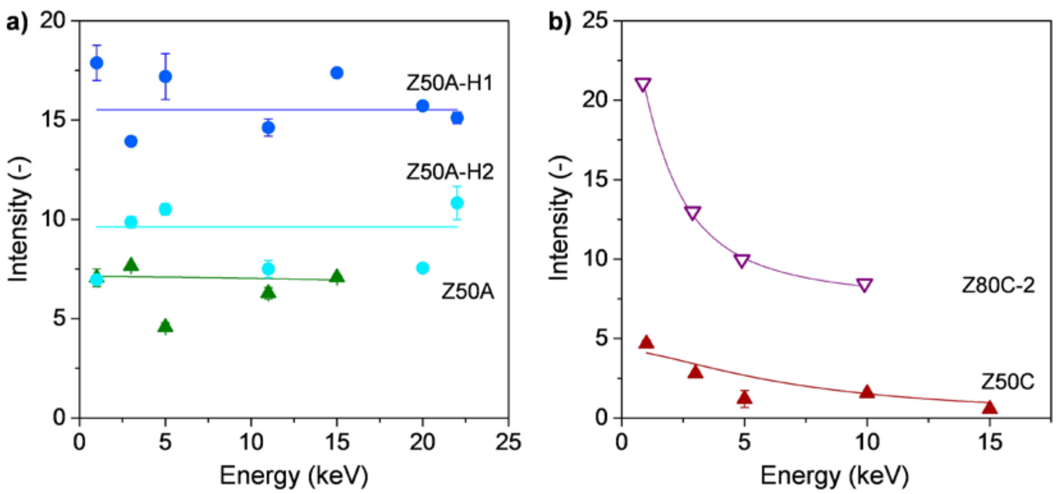

Fig. S3 Energy dependence of the total Ps intensity in vacuum for a) the purely microporous and hierarchical crystal aggregates (Z50A, Z50A-H1, and Z50A-H2) and b) the single crystal (Z50C, Z80C-2) zeolite samples measured with the beam setup (BGO detector). Intensity values were derived using PAScual.