POSITRON ANNIHILATION CHARACTERISTICS OF SOME LOW-SILICA ZEOLITES

Sanja Bosnar[1], Damir Bosnar[2]

[1]Division of Materials Chemistry, Ruđer Bošković Institute, Zagreb, Croatia
[2]Department of Physics, Faculty of Science, University of Zagreb, Zagreb, Croatia
E-mail: sbosnar@irb.hr

ABSTRACT

In order to test its applicability for zeolite structural characterizations, positron annihilation lifetime spectroscopy (PALS) was applied for characterizations of three low-silica zeolites, zeolite A, zeolite X and zeolite Y. Results show very good correlation of voids radii approximated from long-lived positron components to the sizes of building units characteristic for investigated zeolites.

Keywords: positron annihilation, low-silica zeolite

INTRODUCTION

Zeolites, with their specific and uniform porous structure, make excellent materials for different applications in industry and every-day life. Low-silica zeolites are often used as adsorbents, ion exchangers or catalysts. The most explored representatives are zeolite A, as well as zeolites X and Y. Basic building units of these zeolites are sodalite cages which, connected through cubic octamer (LTA structural type) or hexagonal prism (FAU structural type), form large α-cages [1,2]. In the case of LTA structural type α-cages have diameter of about 1.2 nm, and in FAU structural type α-cages have diameter of about 1.4 nm [1,2]. To advance zeolite application capability, there is a need to develop properties of known structures as well as to prepare new materials. As a part of that goal achievement, reliable characterization techniques are needed. One of them, not usually applied, but capable and informative, is positron annihilation lifetime spectroscopy (PALS). PALS is a non-destructive technique and it is used for structural characterization of different materials, metals, semiconductors, polymers, as well as zeolites among other porous materials [3,4]. Technique is based on the measurement of the lifetime of positron injected in investigated material. In non-porous materials, positrons will live much shorter than in porous materials. Different voids and pores in porous materials provide zones with lower electron density, in which positron, expelled from dense bulk, will live longer. Positron can also form bounded forms with an electron (positronium, Ps), which can be short-lived *para*-Ps, *p*-Ps, and long-lived *ortho*-positronium, *o*-Ps [4,5]. From the structural investigation point of view, *o*-Ps is the feature that provides information about size of free voids. Its lifetime can be correlated to the radius of the free void in which it has annihilated, by using simple Tao-Eldrup model [6,7]:

$$\frac{1}{\tau} = \lambda_b \left[1 - \frac{R}{R+\Delta R} + \frac{1}{2\pi} \sin\left(2\pi \frac{R}{R+\Delta R}\right) \right] \qquad (1)$$

where τ is positronium lifetime in ns, R is void radius in nm, $\Delta R = 0.166$ nm, and $\lambda_b = 2$ ns^{-1}. In this work, some results from PALS investigations of free voids in low-silica zeolites A, X and Y will be shown.

EXPERIMENTAL

Chemicals used for zeolite syntheses were: sodium silicate (Na_2SiO_3, Sigma-Aldrich, 51% Na_2O and 48% SiO_2), sodium aluminate ($NaAlO_2$, Riedel de Haen, 41% Na_2O and 54% Al_2O_3), NaOH (98%, Kemika), 30 % silica sol (Ludox HS-30, Sigma-Aldrich) and distilled water. Oxide molar composition of the obtained reaction mixtures were: $4Na_2O \cdot Al_2O_3 \cdot 10SiO_2 \cdot 158H_2O$, for zeolite Y; $3.17\ Na_2O \cdot Al_2O_3 \cdot 1.93\ SiO_2 \cdot 127.96\ H_2O$, for zeolite A; and $4.47\ Na_2O \cdot Al_2O_3 \cdot 2.03\ SiO_2 \cdot 132\ H_2O$, for zeolite X. The reaction mixtures were hydrothermally treated at preset temperature for determined time.

The powder X-ray diffraction spectra of samples have been taken by a Philips PW 1820 diffractometer with a vertical goniometer, using CuK_{α} radiation in the corresponding region of Bragg's angles ($2\theta = 5 - 100^{\circ}$).

Particles (crystals) size distribution curves of the crystalline products in the previously prepared water dispersion have been determined with a Malvern Mastersizer 2000 laser light-scattering particle size analyser.

PALS measuring system, with ^{22}Na as positron source sandwiched between tablets, is constructed based on the measurements of the time difference between 1.274 MeV γ-ray (emitted from the daughter ^{22}Ne nucleus almost immediately after positron emission from the ^{22}Na) and one of the annihilated 0.511 MeV γ-rays (emitted in annihilation of the positron in the sample). The measurements have been conducted with modified version of digitized positron annihilation lifetime spectrometer[8], which comprises conical BaF_2 scintillators coupled to XP2020 URQ photomultiplier tubes, analog CFDDs (Ortec 583B and FastComTec7029) and digital data acquisition chain with CAMAC TDC (CAEN C414) and ADC (CAEN C205A) units. The source activity was approx. 1 MBq and achieved time resolution in these measurements was about 205 ps.

RESULTS AND DISCUSSION

Experimental spectra obtained by positron annihilation lifetime spectroscopy for all three zeolite samples are shown in Figure1.
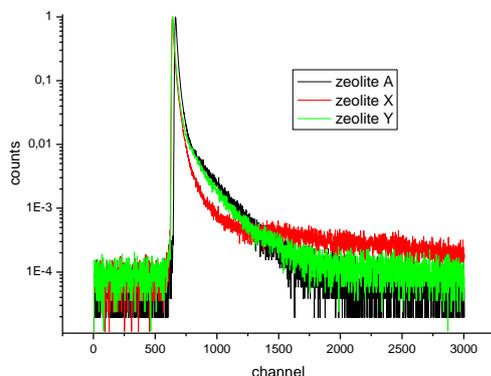

Figure 1. Experimentally obtained positron annihilation spectra for zeolite A (black), zeolite X (red) and zeolite Y (green)

Experimental data were processed by the LT v.9 fitting program[9] and four positron components, τ_1- τ_4, were obtained. Their averaged lifetime and intensity values are shown in Table 1.

Table 1. The lifetime and intensity values of positron components obtained by LT v.9 [9] from the experimental spectra

zeolite	τ_1(ns)	I_1(%)	τ_2 (ns)	I_2(%)	τ_3(ns)	I_3(%)	τ_4(ns)	I_4(%)
A	0.16	36.2	0.43	49.8	1.67	5.9	4.51	7.6
X	0.18	27.7	0.50	55.9	2.45	11.8	6.65	4.6
Y	0.17	41.0	0.57	47.3	1.97	8.2	33.3	3.5

The first, τ_1, and the second, τ_2, lifetime component are usually connected to the annihilation of short-lived *p*-Ps and free positrons in a bulk of the sample. The third, τ_3, and the fourth, τ_4, components are long-lived and are connected to the presence of the voids in the material, in this investigated case at least two types of free voids [3–5]. By using Tao-Eldrup model (Esq. 1) lifetime of long-lived components was correlated to the sizes of voids in which they annihilated. Voids radii R_3 approximated from τ_3 and voids radii R_4 approximated from τ_4 are shown in Table 2.

Table 2. Radii of voids detected in investigated zeolites approximated from long-lived positron components by Tao-Eldrup model (Esq. 1)

zeolite	R_3 (nm)	R_4 (nm)
A	0.254	0.451
X	0.323	0.544
Y	0.283	1.079

Radii approximated by Tao-Eldrup model from the third lifetime component, τ_3, for all three zeolites could be correlated to the sizes of sodalite cage, which is 0.66 nm. Furthermore, radii approximated from the fourth lifetime component, τ_4, could be, for zeolites A and X, correlated to the sizes of α-cages, which are 1.2 nm and 1.4 nm, respectively. In the case of zeolite Y, very large voids suggested by τ_4 value could not belong to structural voids of zeolite, but are the most probably connected to the large voids between zeolite crystals. Twice smaller crystals of zeolite Y as compared to crystals of zeolites A and X, which were established as 1μm and 2 μm, respectively, by particle size analysis, could partially explain this finding. It was found for small particles that a large part of positrons reaches the particle surface and annihilates in voids between particles [10]. Furthermore, the amount and kind of counter ions as well as their position inside zeolite structure can also influence positron characteristics[11], therefore this presumption is under current investigation.

CONCLUSION

Two long-lived positron components were obtained for investigated zeolite samples. This suggests that in zeolites A, X and Y voids with different sizes are present. The sizes of those voids could be connected to the sizes of sodalite cage and alpha cage, which are characteristic structural forms of investigated zeolites.

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REFERENCES

[1] R. Szostak, *Molecular Sieves Principles of Synthesis and Identification*, Blackie Academic & Professional, London, **1998**.

[2] S. M. Auerbach, K. A. Carrado, P. K. Dutta, *Handbook of Zeolite Science and Technology*, CRC Press, New York, **2003**.

[3] R. Krause-Rehberg, H. S. Leipner, *Positron Annihilation in Semiconductors: Defect Studies*, Springer Science & Business Media, Berlin, **1999**.

[4] Y. Kobayashi, K. Ito, T. Oka, K. Hirata, *Radiat. Phys. Chem.* **2007**, *76*, 224–230.

[5] V. P. Shantarovich, *J. Nucl. Radiochem. Sci.* **2006**, *7*, R37–R52.

[6] S. J. Tao, *J. Chem. Phys.* **1972**, *56*, 5499–5510.

[7] M. Eldrup, D. Lightbody, J. N. Sherwood, *Chem. Phys.* **1981**, *63*, 51–58.

[8] D. Bosnar, Z. Kajcsos, L. Liszkay, L. Lohonyai, P. Major, S. Bosnar, C. Kosanović, B. Subotić, *Nucl. Instruments Methods Phys. Res. Sect. A Accel. Spectrometers, Detect. Assoc. Equip.* **2007**, *581*, 91–93.

[9] J. Kansy, *Nucl. Instruments Methods Phys. Res. Sect. A Accel. Spectrometers, Detect. Assoc. Equip.* **1996**, *374*, 235–244.

[10] C. Hubner, T. Staab, R. Krause-Rehberg, *Appl. Phys. A Mater. Sci. Process.* **1995**, *61*, 203–206.

[11] A. Cabral-Prieto, *Micropor. Mesopor. Mater.* **2004**, *69*, 109–118.

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