

Gas filling of SBA-15 silica micropores probed by positron annihilation lifetime spectroscopy (PALS)

Marek Gorgol,
Radosław Zaleski,
Agnieszka Kierys

Abstract. Positron annihilation lifetime measurements were conducted *in situ* while two gasses (nitrogen and oxygen, respectively) were introduced into the SBA-15 porous silica sample. Slow changes in lifetime spectra were observed during a long lasting gas interaction with the sample. Introduced gases slowly filled the free volumes, starting from the smallest ones, especially small micropores. In the presence of a gas, the rate of change of *ortho*-positronium (*o*-Ps) and unbound positron intensity was larger than the rate of change of lifetime. This suggests the existence of an additional process, which reduces the number of *ortho*-positronium atoms due to the interaction with the gas. Moreover, the process of filling pores with gas was slower than the process of emptying them while the gas was pumped out.

Key words: SBA-15 porous silica • positron annihilation

M. Gorgol[✉], R. Zaleski
Maria Curie-Skłodowska University,
Institute of Physics,
Department of Nuclear Methods,
1 M. Curie-Skłodowskiej Sq., 20-031 Lublin, Poland,
Tel.: +48 81 537 6225, Fax: +48 81 537 6191,
E-mail: marek.gorgol@gmail.com

A. Kierys
Maria Curie-Skłodowska University,
Faculty of Chemistry,
Department of Adsorption,
3 M. Curie-Skłodowskiej Sq., 20-031 Lublin, Poland

Received: 31 July 2012
Accepted: 15 October 2012

Introduction

Porous materials are commonly used in many areas of contemporary industry. Therefore, it is important to characterize the structure of such materials and the way, how different processes change it. Application of positron annihilation lifetime spectroscopy (PALS) in porosimetry investigations has been studied for only a few years. This technique has some exceptional advantages such as the ability to characterize closed porosity [9, 12, 14], which is unworkable in methods such as liquid nitrogen sorption. Another advantage of PALS is the ability to perform measurements *in situ* (at various temperatures [2, 6, 11, 17], mechanical pressures [16] or in the presence of a pore filling gas [3, 13, 15]). This last factor will be studied more broadly in this paper.

In the PALS technique the probe used for pore size characterization is positronium (a bound state of a positron and an electron, which can be considered as a hydrogen-like pseudo-atom, where both particles, positron and electron, orbit a common centre of mass). A positron injected into the sample can catch an electron from it and create a positronium. Then this particle can be trapped in a free volume in the material. Positronium is unstable due to the annihilation process and can occur in two states, which have different mutual spin orientations of positron and electron. The singlet state called *para*-positronium (*p*-Ps) annihilates with an average lifetime of 125 ps which does not substantially depend on conditions of the material. A suitable

probe for pore size characterization is a triplet state of positronium called *ortho*-positronium (*o*-Ps). It annihilates with an average lifetime of 142 ns in vacuum. However, a positron bound in *o*-Ps can annihilate with an electron from the surrounding medium, instead of the electron bound in *o*-Ps. This process (called pick-off) decreases the average lifetime of *o*-Ps and relates it to the local electron density of the material, and hence the free volume size. This relation is described by the extended Tao-Eldrup (ETE) model [1]. However, there are some processes, which can disrupt the PALS results and should be taken into consideration during interpretation. One of such processes, which is the most significant one, is an *ortho-para* conversion [3]; *o*-Ps can be converted into *p*-Ps as a result of interaction with paramagnetic molecules.

Materials

Mesoporous silica SBA-15 was prepared according to the reported procedure using the amphiphilic triblock copolymer (Pluronic P123, BASF) as a structure-directing agent and tetraethyl orthosilicate (TEOS, Sigma-Aldrich) as the silica source [4, 18]. The following synthesis was performed: 4 g of Pluronic P123 were dissolved in 30 g of deionized water and 120 g of 2 M HCl solution (POCh, Poland) while stirring. Thereafter, 9.5 g of TEOS was added to the homogeneous solution, also while stirring. The resulting mixture was aged at 40°C for 24 h under stirring conditions and finally heated up to 100°C for 24 h. The final silica gel was filtered, rinsed with ion-free water, and dried at 80°C for 12 h. SBA-15 gel without an organic template was prepared by calcination in flowing air at 550°C for 12 h.

Experimental

In the PALS measurements two 2 mm layers of the powdered SBA-15 sample surrounded the 0.5 MBq ^{22}Na positron source enclosed in an 8 μm thick Kapton envelope. The sample was placed in a vacuum chamber, equipped with a gas dosing system. The sample was initially annealed for a couple of hours at 200°C and then kept in room temperature at a pressure of about 5×10^{-4} Pa for 260 h assuring it becomes degassed. Next, nitrogen at a pressure of 1×10^5 Pa was introduced into the sample and kept for 184 h. The positron annihilation lifetime spectra were collected continuously during the long-lasting gas interaction with the sample. Then, the nitrogen was pumped out, and the PALS measurements were performed over the next 68 h. After the following preparations of the sample (annealing at 200°C for 100 h and re-cooling to room temperature) the same procedure was performed using oxygen at a pressure of 1×10^5 Pa. The measurements lasted for 120 h after the gas introduction, and for 64 h after pumping it out.

A standard “fast-slow” delayed coincidence spectrometer was used to collect the positron annihilation lifetime spectra. The spectrometer was equipped with two cylindrical BaF_2 scintillators ($\varnothing 1 \times 1.5''$ in the start signal branch and $\varnothing 1 \times 1''$ in the stop signal branch). The stop energy window was wide opened to collect

the low energy quanta from three gamma annihilations of *o*-Ps. It resulted in a relatively wide time resolution function full width at half maximum (FWHM ~ 350 ps). The time range of the time-to-amplitude converter was 2 μs , while the time width of the single channel of the multichannel analyzer was 116.3 ps. The rate of coincidence registration was about 5×10^6 per hour.

The PALS spectra (where the total number of counts per each spectrum was about 4×10^7) were initially analyzed using the MELT program [10]. Such a large number of counts improved the accuracy of the analysis. The results provided information about the number of lifetime components. Then, analyses of *o*-Ps lifetimes were made using the LT 9.2 program [5]. For the LT analysis, the total number in each spectrum was about 2×10^7 , and the resolution curve was approximated by two Gaussians (with contribution of 74% and 26%, respectively).

Results and discussion

MELT analysis of the lifetime spectra measured for SBA-15 silica in the presence of nitrogen revealed the existence of five discrete lifetime components (Fig. 1a). The origins of the components are *p*-Ps, unbound e^+ and

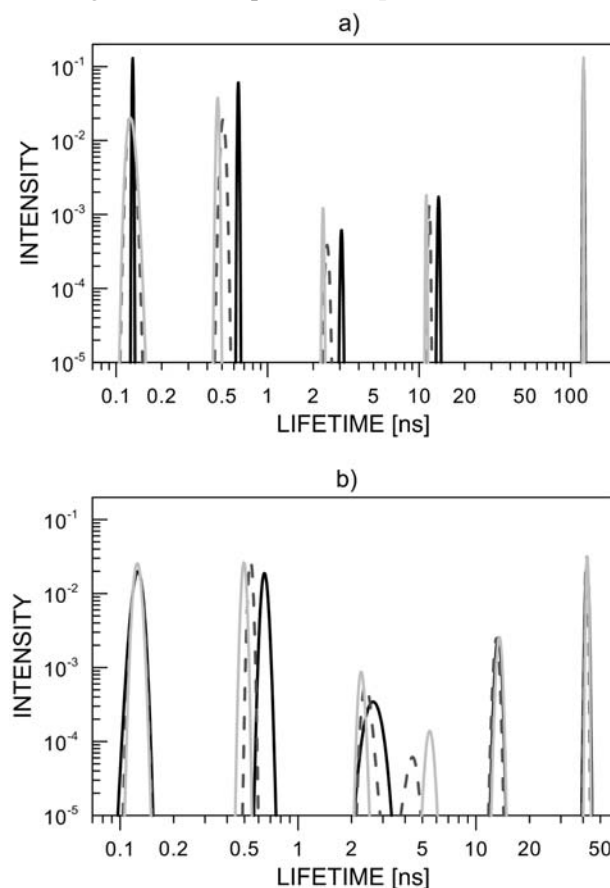


Fig. 1. The MELT results for the SBA-15 lifetime spectra after introducing nitrogen (a) and oxygen (b) to the sample. Continuous black curves correspond to the free volume size distribution for the spectra collected during the first 8 h after the gas was applied. The dark grey dashed curves show the distribution for the spectra collected after 82 h (a) and 56 h (b) after the gas was applied. The light grey curves indicate the free volume distribution for the spectra collected after 176 h (a) and 114 h (b) after the gas was applied.

3 fractions of *o*-Ps. The third component corresponds to the annihilation of *o*-Ps inside micropores, while the fourth and fifth correspond to the *o*-Ps trapped in free volumes of larger size. While five components are found in all spectra collected in the presence of nitrogen, MELT results for filling the free volumes with oxygen suggest a change in the number of lifetime components from five (directly after oxygen application) to six (after several dozens of hours in the presence of the gas) (Fig. 1b). Nevertheless, the LT analysis with the assumption of 6 discrete lifetime components did not give reasonable results corresponding to the MELT results. Therefore, an assumption of five components was chosen for analysis of the lifetime spectra obtained in the presence of both nitrogen and oxygen. In order to reduce any uncertainties in the results of the LT analyses τ_{p-Ps} was fixed at 125 ps. The absolute values of the particular components lifetime obtained from MELT and LT analyses did not correspond with each other, due to the different numerical procedures implemented in both programs. However, the behavioural tendencies of the corresponding lifetime components (except τ_3), and the dynamics of changes are retained, which allows us to interpret the processes which occur inside the material in the presence of a gas. For components, which have small intensity (e.g., I_3 or $I_4 \sim 1\%$ for most of analyzed spectra), results of lifetime determination by MELT are highly dispersed and probably affected by changes of lifetimes of neighbouring higher intensity components (Fig. 1). Therefore, such components are hardly reliable. This is mostly result of many degrees of freedom, characteristic for MELT calculation procedure. This is the reason of choosing approximate, but less dispersed LT analysis for further discussion.

Time dependencies of intensities and lifetimes of short-lived lifetime components (i.e., unbound e^+

(I_2, τ_2) and shortest-lived *o*-Ps component (I_3, τ_3) are presented in Fig. 2. Lifetime τ_{e^+} ranges from ~ 0.45 to 0.57 ns which is higher than for the crystalline silica [7], probably due to a more loose structure of the material. The τ_{e^+} values are averaged over two regions, i.e. pore walls and nearby free spaces. Therefore, while the adsorbed gas fills the free volumes, the averaged electron density increases and the decrease of τ_{e^+} can be observed. At the same time, an increase of τ_3 is also observed. This might be explained by the fact that the τ_3 value is an average of *o*-Ps annihilation lifetimes inside the micropores of different sizes. Applied gases probably adsorb on the pore walls and slowly fill the micropores, starting from the smallest ones, which indicates an increase of the resultant τ_3 value. With the exception of the initial changes, τ_4 and τ_5 do not show any changes during or after the application of gas, which means that changes in the sizes of the larger free volumes are negligible. Moreover, the lifetime of the longest-lived component in the presence of oxygen is shortened due to the *ortho-para* conversion. While the nitrogen fills the free volumes, the intensities of all *o*-Ps components decrease which means the decrease of a positronium formation probability. This change also causes an increase of I_{e^+} as a relative value. In order to quantitatively examine the dynamics of the processes performed inside the material during gas filling, the exponential functions ($X = Ae^{-\lambda t - B} + C$) were fitted to the experimental data, where A, λ, B and C are fitting parameters, X is a parameter (i.e., lifetime or intensity) of the chosen components. In order to estimate total influence of the observed processes on parameters of positron lifetime spectra, intensities and lifetimes of particular components at the early stage of gas filling and after long lasting gas exposure in nitrogen or oxygen are presented in Table 1, while the absolute values of

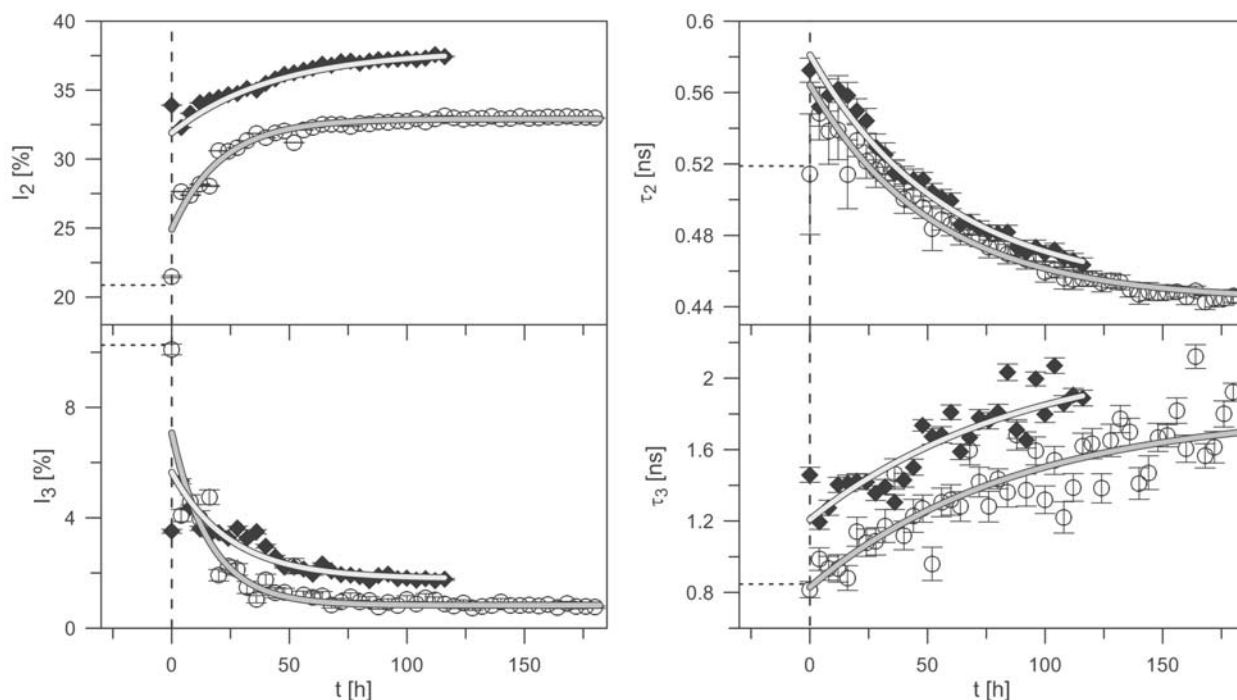


Fig. 2. Time dependence of intensities and lifetimes of the second and third component obtained for the SBA-15 silica after nitrogen (empty circles) and oxygen (full diamonds) were applied. Dashed vertical lines indicate the moment of gas application, and dashed horizontal lines show the initial values for particular components before the gas was applied. The exponential functions were fitted to the experimental data.

Table 1. Intensities and lifetimes of particular lifetime components calculated with LT 9.2 for SBA-15 with the presence of nitrogen and oxygen after 8 and 114 h since the gases were applied. Value of τ_1 was fixed at 125 ps

Parameters of lifetime components	N ₂ (after 8 h)	N ₂ (after 114 h)	O ₂ (after 8 h)	O ₂ (after 114 h)
I_1 (%)	38.6(8)	38.5(4)	40.7(5)	39.7(4)
I_2 (%)	27.4(9)	33.1(3)	33.3(5)	37.4(4)
τ_2 (ns)	0.54(1)	0.46(4)	0.56(7)	0.46(4)
I_3 (%)	4.6(11)	0.9(3)	4.4(6)	1.8(2)
τ_3 (ns)	0.9(3)	1.6(3)	1.3(2)	1.9(3)
I_4 (%)	1.0(2)	0.8(1)	3.4(2)	3.5(3)
τ_4 (ns)	11.7(6)	11.7(7)	11.5(5)	12.9(6)
I_5 (%)	28.5(7)	26.7(3)	18.2(3)	17.6(3)
τ_5 (ns)	122.6(4)	122.7(4)	42.0(3)	42.5(4)

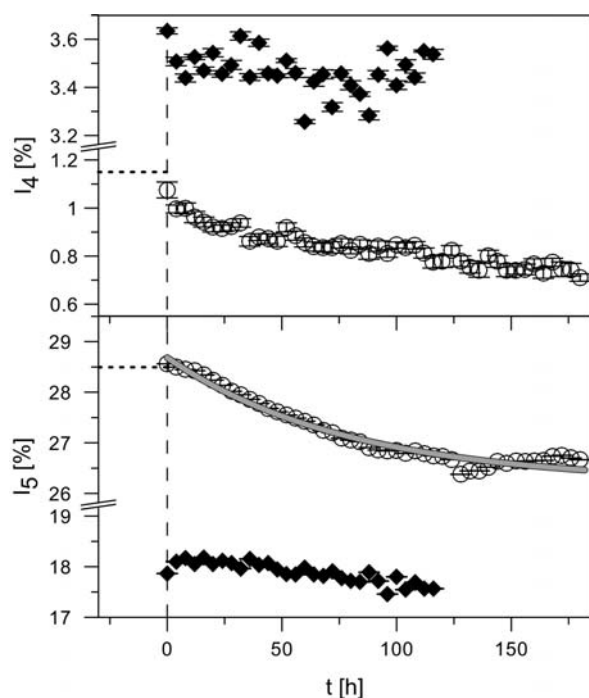
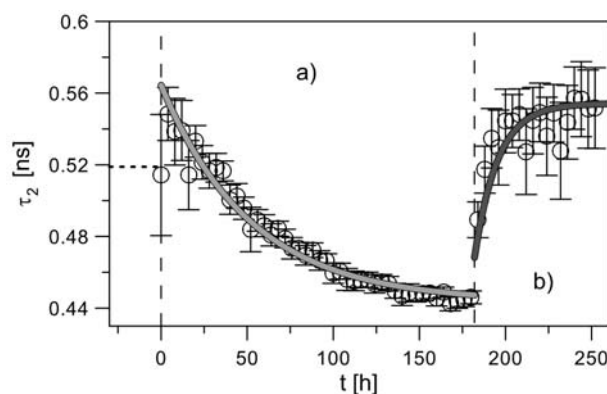
Table 2. Absolute values of time constant λ for intensities and lifetimes of particular components for the SBA-15 silica filled with nitrogen and oxygen. The τ_2 represents the τ_2 while the gas was being pumped out

Gas	$ \lambda_{I_2} $ (1/h)	$ \lambda_{I_3} $ (1/h)	$ \lambda_{I_5} $ (1/h)	$ \lambda_{\tau_2} $ (1/h)	$ \lambda_{\tau_3} $ (1/h) τ_3	$ \lambda_{\tau_2^*} $ (1/h)
Nitrogen	0.048(5)	0.062(11)	0.013(6)	0.019(4)	0.011(2)	0.074 (7)
Oxygen	0.023(4)	0.041(1)	–	0.017(6)	0.11(3)	–

the time constant ($|\lambda|$) are presented in Table 2. The $|\lambda_{\tau_2}|$ and $|\lambda_{\tau_3}|$ values are close to each other and do not show any dependence on the kind of gas introduced. This supports the idea of the micropores slowly filling with the gas. The changes in the intensities of the corresponding components are much faster than in the case of lifetimes, and do show a dependence on the type of gas. This supports the existence of both *o*-Ps quenching and inhibition responsible for the changes of lifetime and intensity, respectively. This simple description developed for polymers [8], is almost certainly

oversimplification in porous materials, where several *o*-Ps components are observed, but can serve as a first approximation of the observed phenomena. According to such simple assignment of the sources of component parameter changes, both quenching and inhibition are present in the sample at the same time, but their yields have various rate of change with time (i.e., inhibition saturates and becomes constant several times faster than quenching). In nitrogen the $|\lambda_{I_5}|$ value (which is connected to the longest-lived component change) corresponds to the $|\lambda_{\tau_3}|$, but does not correspond to $|\lambda_{I_2}|$ or $|\lambda_{I_3}|$ (Fig. 3), (Table 2). This means that in the proposed interpretation the process of *o*-Ps decomposition would be more visible in the vicinity of small free volumes (micropores). It can be explained by assuming that the probability of *o*-Ps creation is proportional to the specific surface of the sample, where micropores make a large contribution. Therefore, if the majority of *o*-Ps atoms are created on micropore walls, the change in their count is also primarily visible in the shortest-lived *o*-Ps component.

Because of their kinetic energy, *o*-Ps atoms created inside the small free volumes can probably diffuse to the larger free volumes and annihilate there. In the presence of oxygen, where the *ortho-para* conversion is observed,

**Fig. 3.** Time dependence of the intensities of the two longest-lived components obtained for the SBA-15 silica after nitrogen (empty circles) and oxygen (full diamonds) were applied. Dashed vertical lines indicate the moment of gas application, and dashed horizontal lines show the initial values for particular components before gas application. The exponential function was fitted to the experimental data.**Fig. 4.** A comparison of the time dependences of τ_2 instability after nitrogen application (a) and while the nitrogen was being pumped out (b).

the lifetime of all *o*-Ps atoms is shortened. This can result in a decrease of the probability of *o*-Ps diffusion to the larger free volumes, which can be observed as the decrease of I_5 immediately after oxygen introduction, with the increase of I_4 at the same time. This effect was not observed in the presence of nitrogen, where intensities of all *o*-Ps components decreased (Fig. 3).

Comparison of the e^+ lifetime alteration rates after gas introduction and removal is presented in (Fig. 4) and (Table 2). The time constants of the fitted exponential functions show that the process of filling the pores with gas ($|\lambda_{\tau_2}|$) is significantly slower than the process of emptying them ($|\lambda_{\tau_3}|$). This can be a result of different dynamics of the gas transport in both parts of the experiment. The sample was in a static nitrogen atmosphere when the gas was applied, while the gas molecules were dynamically removed by a turbomolecular pump when the gas was being pumped out.

Summary

Slow changes are observed in positron annihilation lifetime spectra after introducing a gas, at atmospheric pressure, into the SBA-15 sample. These changes arise mainly from the filling of micropores, which causes the τ_3 and I_2 to increase and τ_2 and I_3 to decrease. Intensity changes are faster than the changes of the corresponding components lifetime. This suggests the existence of *o*-Ps inhibition and quenching, respectively. Each of these processes is probably a result of various gas reactions with the silica surface. Appearance rate of different products (free radicals) is reflected in the rate of lifetime and intensity change with time. This idea is supported by the fact that the rate of the I_5 change in the presence of nitrogen corresponds to the rate of the τ_3 change. Moreover, lifetime changes do not exhibit any dependence on the type of gas (except that resulting from the *ortho-para* conversion), while the intensity changes do. Additionally, micropore emptying is significantly faster than the filling with gas.

References

- Ciesielski K, Dawidowicz AL, Goworek T, Jasińska B, Wawryszczuk J (1998) Positronium lifetimes in porous Vycor glass. *Chem Phys Lett* 289;1/2:41–45
- Fischer CG, Weber MH, Wang CL, McNeil SP, Lynn KG (2005) Positronium in low temperature mesoporous films. *Phys Rev B* 71;18:180102
- Goldanskii V, Mokrushin A, Tatur A, Shantarovich V (1975) Positronium interactions with gases in pores of silicagels. *Appl Phys A: Mater Sci Process* 5;4:379–382
- Hartmann M, Vinu A (2002) Mechanical stability and porosity analysis of large-pore SBA-15 mesoporous molecular sieves by mercury porosimetry and organics adsorption. *Langmuir* 18;21:8010–8016
- Kansy J (1996) Microcomputer program for analysis of positron annihilation lifetime spectra. *Nucl Instrum Methods Phys Res A* 374;2:235–244
- Kunishige S, Koshimizu M, Asai K (2009) Temperature dependence of positron lifetime in ordered porous silica (SBA-3). *Radiat Phys Chem* 78;12:1088–1091
- Kuriplach J, Anwand W, Brauer G, Skorupa W (2002) Positron characteristics of various SiO₂ polymorphs. *Appl Surf Sci* 194;1/4:84–88
- Mallon PE (2003) Application to polymers. In: Jean YC, Mallon PE, Schrader DM (eds) *Principles and applications of positron and positronium chemistry*. World Scientific, Singapore, pp 253–280
- Petkov MP, Wang CL, Weber MH, Lynn KG, Rodbell KP (2003) Positron annihilation techniques suited for porosity characterization of thin films. *J Phys Chem B* 107;12:2725–2734
- Shukla A, Peter M, Hoffmann L (1993) Analysis of positron lifetime spectra using quantified maximum entropy and a general linear filter. *Nucl Instrum Methods Phys Res A* 335;1/2:310–317
- Thraenert S, Hassan EM, Enke D, Fuerst D, Krause-Rehberg R (2007) Verifying the RTE model: *ortho*-positronium lifetime measurement on controlled pore glasses. *Phys Status Solidi C* 4;10:3819–3822
- Wang CL, Weber MH, Lynn KG, Rodbell KP (2002) Nanometer-scale pores in low-k dielectric films probed by positron annihilation lifetime spectroscopy. *Appl Phys Lett* 81;23:4413–4415
- Wilkinson NJ, Alam MA, Clayton JM, Evans R, Fretwell HM, Usmar SG (1992) Positron annihilation study of capillary condensation of nitrogen gas in a mesoporous solid. *Phys Rev Lett* 69;24:3535–3538
- Xi-Jie D, Yi-Fan H, Yu-Ying W (2010) Positronium diffusion in porous methylsilsequioxane thin films. *Chin Phys B* 19;1:013601
- Zaleski R, Dolecki W, Kierys A, Goworek J (2012) n-Heptane adsorption and desorption on porous silica observed by positron annihilation lifetime spectroscopy. *Microporous Mesoporous Mater* 154:142–147
- Zaleski R, Goworek J, Borówka A, Kierys A, Wiśniewski M (2009) Positron porosimetry study of mechanical stability of ordered mesoporous materials. In: Seaton N, Reinoso FR, Llewellyn P, Kaskel S (eds) *Characterisation of porous solids VIII*. RSC Publishing, Cambridge, pp 400–407
- Zaleski R, Wawryszczuk J, Goworek J, Borówka A, Goworek T (2003) Vacuum removal of the template in MCM-41 silica studied by the positron annihilation method. *J Colloid Interface Sci* 262;2:466–473
- Zhao D, Feng J, Huo Q *et al.* (1998) Triblock copolymer syntheses of mesoporous silica with periodic 50 to 300 Angstrom pores. *Science* 279;5350:548–552