

Porosity of silica monoliths with tailored mesopores of ink-bottle shape determined by nitrogen adsorption and positron annihilation lifetime spectroscopy

Andrzej Sienkiewicz^b, Agnieszka Kierys^b, Marek Gorgol^a, Radosław Zaleski^{a*}

^aMaria Curie-Skłodowska University, Institute of Physics, Department of Nuclear Methods, Pl. M. Curie-Skłodowskiej 1, 20-031 Lublin, Poland

^bMaria Curie-Skłodowska University, Faculty of Chemistry, Department of Adsorption, Pl. M. Curie-Skłodowskiej 3, 20-031 Lublin, Poland

*Corresponding author: radek@zaleski.umcs.pl

Aim of the research

The goal of the presented research was to test the agreement between the results of the two very different porosimetric methods based on: low temperature nitrogen adsorption-desorption and annihilation lifetimes of ortho-positronium (o-Ps) in silica monoliths obtained with different nanoscale pore directing agents (methanol, β -cyclodextrins and polystyrene nanobeads).

Introduction

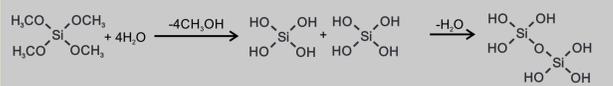
The silica gel is a well-known and widely studied material. It occurs in various natural and artificial shapes and forms. Due to its adsorptive properties, heat resistance and environmental friendly character the most interesting silica species are the porous one. During synthesis of silica gel, silica precursor e.g. tetramethyl orthosilicate, hydrolyzes and condenses to form the network of strong covalent silica-oxygen bonds. The condensation process spontaneously results in creation of porous structure. The shape and arrangement of pores can be successfully tailored by introduction of certain chemical compounds i.e. surfactants or more complexed matrices into silica precursor transformation environment. Silica species surround chemical entities present in their vicinity, and after their removal in the process of extraction or calcination, SiO₂ with voids is obtained.

Materials and methods

Tetramethyl orthosilicate (TMOS, Sigma-Aldrich)
Sodium hydroxide, NaOH (POCH, Poland)
 β -cyclodextrin (Sigma-Aldrich)
Methanol (POCH, Poland)
1% Polystyrene spheres solution (Nanosphere™ size standard, Thermo Scientific)

1) LN2, nitrogen adsorption-desorption experiment at 77K, ASAP 2405 Micromeritics,
2) PALS, the pore sizes; ETE model implemented in EELVIS routine ($\Delta = 0.18$ nm), pores = infinite cylinders.

TMOS hydrolysis and condensation

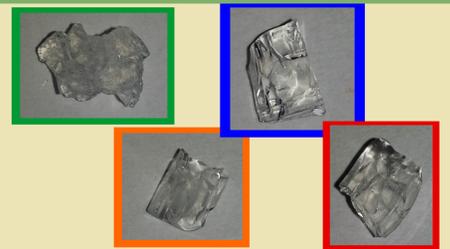


Monolith synthesis

TMOS+NaOH +
nothing
 β -cyclodextrin
methanol*
methanol+polystyrene spheres*

→ 1) annealing (3 days)
 *reactant solution changed form methanol to water during annealing
 → 2) drying (80°C, 8h)
 → 3) calcination (550°C, 6h)

→ SG
 → SG-CD
 → SG-M
 → SG-ML



Results

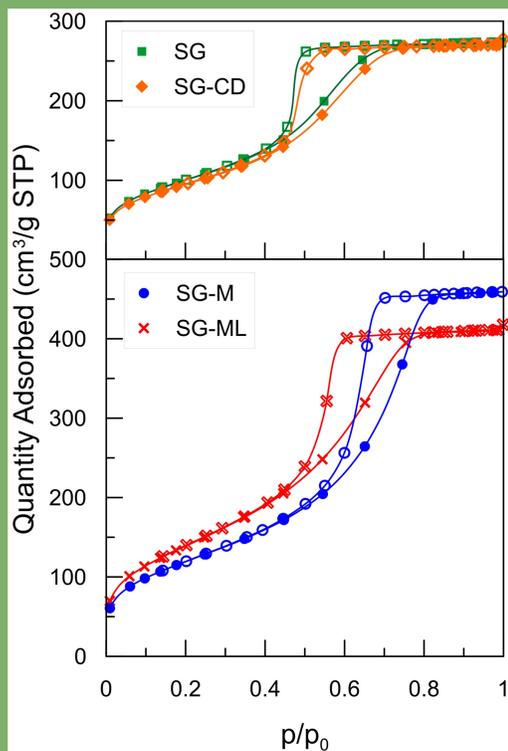


Fig.1 Nitrogen adsorption/desorption isotherms at 77 K for the samples under study. Adsorption – full symbols, desorption – empty symbols.

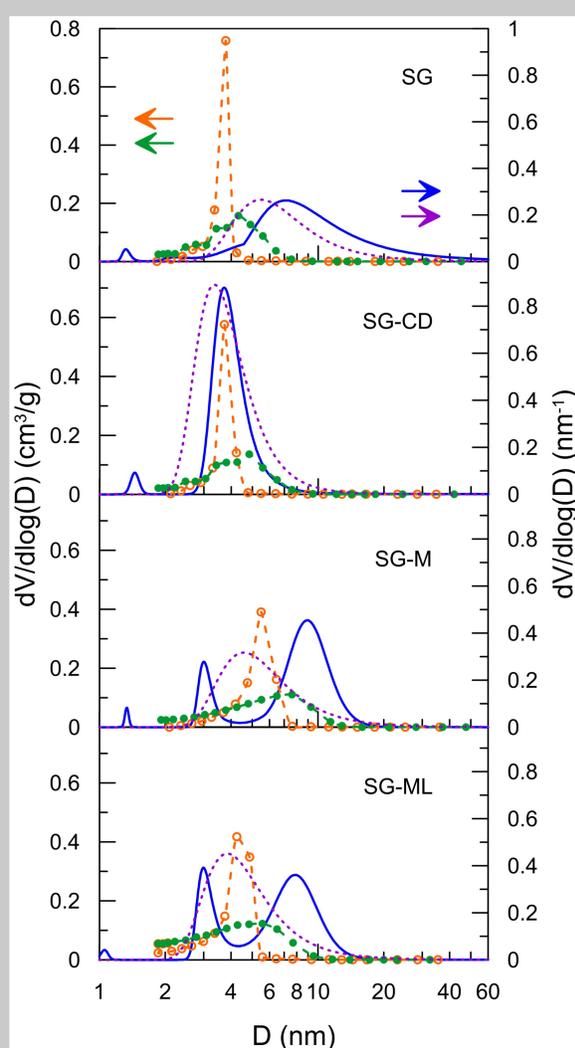


Fig.2 Pore size distributions calculated from the o-Ps lifetime distributions obtained by LT (dotted line) and MELT (solid line) compared to PSDs from the nitrogen adsorption (dashed line, full symbols) and desorption (dashed line, empty symbols) isotherm using the BJH method.

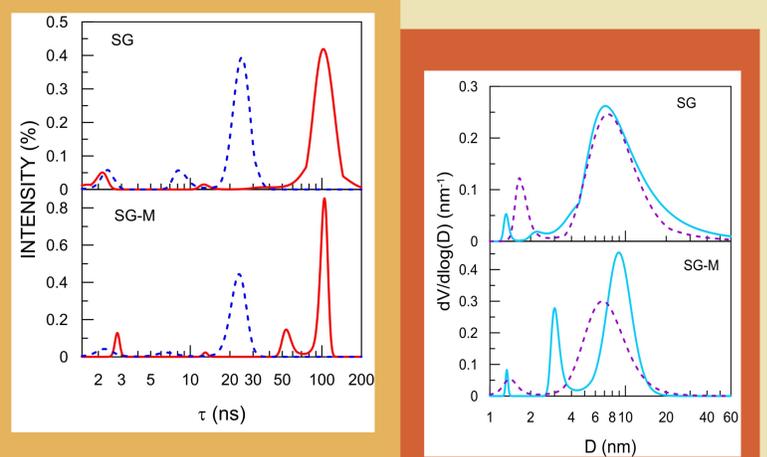


Fig.3 Lifetime distributions and PSDs derived from spectra measured in high vacuum (solid line) and oxygen atmosphere (dashed line).

Table 1 Parameters characterizing porosity of the samples obtained from nitrogen isotherms: the specific surface area (S_{BET}), the total pore volume (V_{LN_2}) and the pore diameter at the peak of PSD derived from the desorption ($D_{\text{BJH}}^{\text{des}}$) and adsorption ($D_{\text{BJH}}^{\text{ads}}$) branch of N₂ isotherm.

Sample	S_{BET} [m ² /g]	V_{LN_2} [cm ³ /g]	$D_{\text{BJH}}^{\text{des}}$ [nm]	$D_{\text{BJH}}^{\text{ads}}$ [nm]
SG	368	0.42	3.7	4.2
SG-CD	348	0.43	3.8	4.5
SG-M	439	0.71	5.3	6.0
SG-ML	516	0.65	4.2	4.7

Table 2 Intensities, lifetimes and dispersion of o-Ps components (LT programme)

Sample	I_3 [%]	τ_3 [ns]	I_4 [%]	τ_4 [ns]	I_5 [%]	τ_5 [ns]	σ_5 [ns]
SG	3.6(2)	1.8(2)	0.8(2)	14(1)	32.6(2)	104(2)	23(7)
SG-CD	2.9(3)	1.6(2)	0.9(2)	6(1)	36.9(3)	72(1)	19(4)
SG-M	2.8(2)	2.4(2)	0.7(1)	15(1)	29.8(2)	97(2)	24(6)
SG-ML	2.0(2)	2.6(3)	0.5(2)	12(1)	31.1(3)	87(2)	25(7)

Conclusions

- 1) The low temperature adsorption-desorption nitrogen measurements indicate that the addition of organic additives (i.e. β -cyclodextrin or polystyrene spheres) does not significantly influence the porosity of the final silica gels.
- 2) It is clear that transformation of silica precursor (under basic condition) in the presence of methanol, favours the silica gel production of larger specific surface area and the total pore volume. Thus, it may be concluded that methanol act as the pore forming agent.
- 3) The PALS measurements show a satisfactory agreement with the LN2 results for the SG-CD sample only. In the case of SG-M and SG-ML the problem lies most likely in the shape of PSDs. They are different from lognormal, which is inherited from the methods of PALS data analysis.
- 4) Both LT and MELT methods show tendency to represent their results in the form of one or more lognormal distributions. The greater number of degrees of freedom in MELT causes that it splits PSDs to bimodal distributions.
- 5) The origin of the discrepancy between the LN2 and PALS characterization of the porosity of SG is difficult to find. It cannot be explained by the presence of the closed pores since contribution from closed pores is negligibly small as indicated by the measurements in the O₂. Thus, the further studies on the molecular structure of these silica gel monoliths are required to understand the origin of the differences in the results. Also, it seems to be profitable to obtain information concerning the density and microporosity of the studied silica.