

## **Investigations of physicochemical processes in porous materials with the use of Positron annihilation lifetime spectroscopy.**

The aim of this PHD thesis was an examination of properties of host-guest materials with the use of Positron annihilation lifetime spectroscopy (PALS). Additionally, the physicochemical processes occurred within such materials were analyzed. Filling the borosilicate glass mesopores with organic red dye ROT-305 and silver nanoparticles was analyzed and the PALS results were compared to other porosimetric techniques such as SAXS and LN. In spite of matching sizes of the mesopores and admixture molecules, the incorporation process was not effective. The red dye molecules did not deposit on mesopore walls, but only blocked entries of the pores. On the other hand, silver nanoparticles caused the slight narrowing of pore diameters. In further investigations, the stability of the obtained composite materials as a function of time and temperature was examined. At room temperature, no instabilities in time were observed for all the samples. Otherwise, the long-term changes of PALS parameters were observed at other temperatures, especially at low ones. The average lifetime of these changes reached even a few tens of hours. In the temperature range of  $-180\text{ }^{\circ}\text{C} \div 0\text{ }^{\circ}\text{C}$ , a significant discrepancy between experimental results and the predictions of the Extended Tao-Eldrup (ETE) model were observed for all the samples. It was probably caused by an interaction of orthopositronium with the surface of open mesopores inside a silica matrix. The presence of both kinds of admixtures caused the slight inhibition of these effects and the hysteresis loops observed at low temperatures decreased. In the glass incorporated with dye molecules, no temperature instabilities were observed in the temperature range of  $0\text{ }^{\circ}\text{C} \div 100\text{ }^{\circ}\text{C}$ . Therefore, it promotes the use of such materials in production of optoelectronic devices. Heating the material incorporated with silver nanoparticles over  $130\text{ }^{\circ}\text{C}$  caused the reorganisation of the material structure. It was probably the result of deoxygenation of silver oxide and re-obtaining of the metallic nanoparticles.

The sol-gel materials, where incorporated molecules were added during the preparation of the porous glass, were also investigated. In such materials, obtained mesopores are mostly closed, and the admixture molecules are homogeneously spread inside the sample. PALS investigations of reference material and the one incorporated with Rot-305 molecules did not show any significant discrepancies between experimental results and theoretical predictions. The hysteresis, visible at low temperatures, was much smaller in comparison to vycor glass. It supports the hypothesis of the influence of open pores on the shortening of orthopositronium lifetime. A homogeneous spread of the metallic nanoparticles inside a sol-gel glass caused a significant o-Ps quenching. Additionally the total disagreement between experimental results and ETE model prediction was observed. Heating up the sample over  $130\text{ }^{\circ}\text{C}$  caused the stabilization of material structure and properties. It was confirmed by disappearance of

hysteresis of PALS parametres during the second cycle of temperature measurement. This stabilization was probably caused by grouping of the nanoparticles in larger clusters, which resulted in a decrease of a spread of the metallic particles inside the investigated material.

In order to examine the dynamics of open pore filling, the adsorption of nitrogen and oxygen inside SBA-15 ordered silica was investigated. The mesopores were filled immediately, while the micropore filling was a long-term process and did not depend on the type of the gas. The rate of change of particular components intensiteies as a function of time was not the same and did depend on the type of the gas. However, the rate of change of total o-Ps intensity was the same for both, nitrogen and oxygen. The change of the intensities of two longest-lived components because of o-Ps quenching due to interaction with oxygen particles was observed. it let us to examine the migration of o-Ps from smaller free volumes to larger ones.

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