

CONTROLLED POROSITY OF MCM-41 OBTAINED BY PARTIAL BLOCKING OF PORES BY SILICONE OIL



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MOTIVATION The Extended Tao-Eldrup (ETE) model describes the relation between the lifetime of ortho-positronium (*o*-Ps) and the pore size. It is applicable in the approximate range of 0.2-50 nm. This model is widely used for characterization of porous materials by means of positron annihilation spectroscopy (PALS). Development of the ETE model progresses in various ways. One of them is a search for a comprehensive relation between PALS parameters (i.e. the lifetime and intensity of pore related *o*-Ps components) and a pore size distribution to obtain universal porosimetric method.

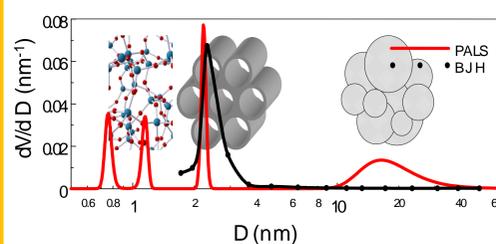
The main inconvenience of positron porosimetry is lack of the absolute calibration of the *o*-Ps intensity (I_{o-Ps}). To achieve this, a series of model materials with precisely controlled porosity is required. This is not easy to prepare series of the same material differentiated in respect to precise pore dimensions control. The popular model material is MCM-41, which pores are long, unconnected cylinders of uniform size. However, tailoring the pore size and specific surface of MCM-41 in the wide range, which is required for the calibration, is impossible at the synthesis stage.

The method of controlling the porosity of MCM-41 by partial blocking of pores with silicon oil is proposed. The silicon oil cannot be removed by pumping at room temperature due to its large molecular mass. This allows to carry out PALS measurements in high vacuum, which is required to apply the ETE model.

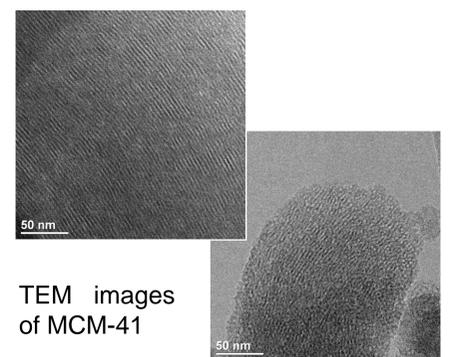
EXPERIMENTAL

- MCM-41 silica material was soaked with acetone/silicone DC550 oil mixture with different concentration of DC550 oil (5%, 10%, 20% v/v%). Wet samples were left for conditioning for 5 h at room temperature, next all samples were dried at 60 °C for 5h to evaporate the acetone. MCM-41 samples reached 23%, 41% and 58% (w/w%) DC550 oil content, respectively.
- Low temperature nitrogen adsorption/desorption measurements were carried out with a volumetric adsorption analyzer ASAP 2405 (Micromeritics, Norcross, USA). The specific surface area, S_{BET} , was calculated from the BET equation in the relative pressure range from 0.05 to 0.25. The pore size distributions (PSDs) were obtained using the Barrett–Joyner–Halenda (BJH) procedure, whereas the total pore volume, V_p , was estimated from a single adsorption point at the relative pressure of 0.985.
- PALS measurements: BaF₂ scintillators were used in standard fast-slow delayed coincidence spectrometer. The time range of time-to-amplitude converter was 2μs. FWHM of the resolution curve was about 290 ps (+5% of 440ps). Each sample was kept in vacuum ($p < 10^{-4}$ Pa), obtained with the use of turbomolecular pump. The total count number for each sample was about 1.7×10^7 . The spectra were analyzed with the use of the PALSfit3.

MCM-41

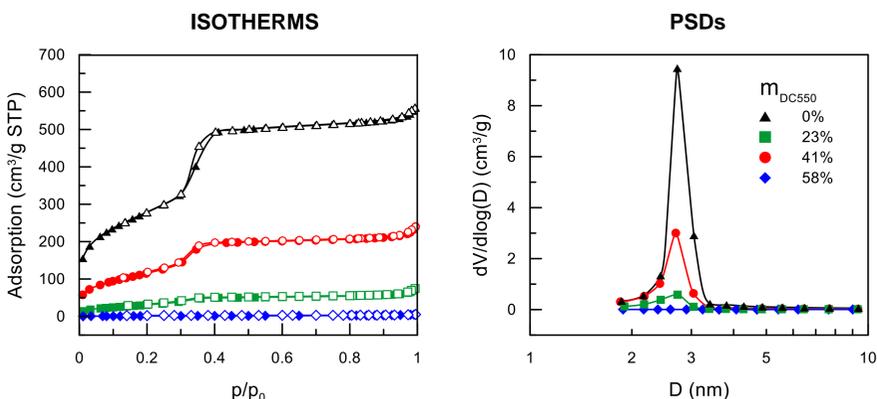


Pore size distribution obtained from PALS and N₂ sorption (BJH method) vs MCM-41 structure



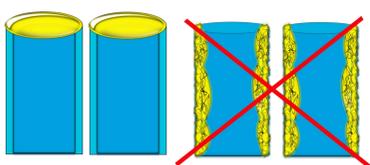
TEM images of MCM-41

N₂ SORPTION

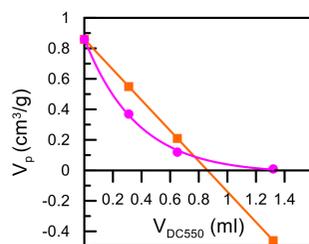


m_{DC550} (%)	S_{BET} [m ² /g]	V_p [cm ³ /g]	D_{BJH} [nm]
0	1008	0.86	2.7
23	433	0.37	2.7
41	119	0.12	2.7
58	4	0.01	n. a.

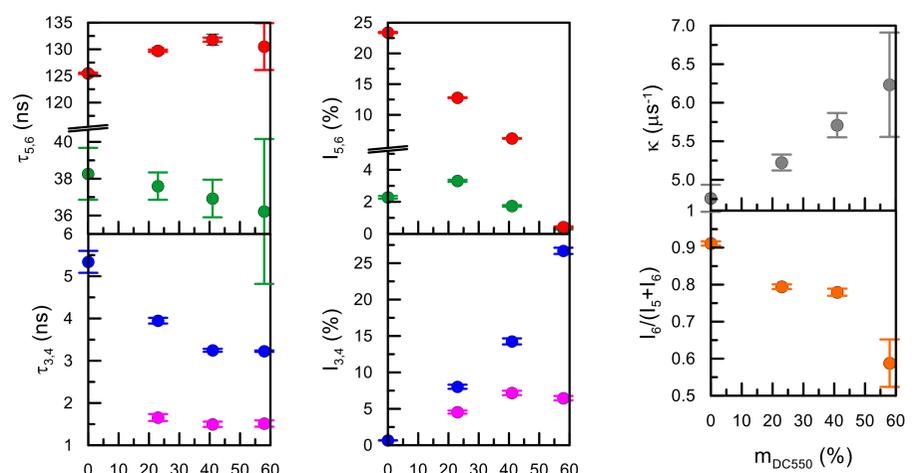
MCM41 + DC550



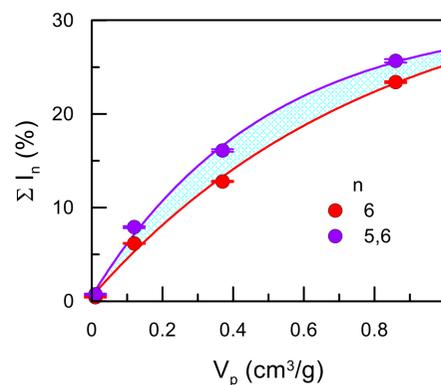
Total pore volume
 • from N₂ sorption
 • predicted basing on DC550 volume vs adsorbed DC550 volume



PALS



The lifetimes (τ_i) and intensities (I_i) of the *o*-Ps components ($i = 3-6$) as a function of the mass of DC550 introduced to MCM-41.



Intensity of particular PALS components as a function of total pore volume (from N₂ sorption data). Fitted curves represent calibration under assumption that all primary pores are closed, or open.

The rate of *o*-Ps migration from the primary mesopores to interparticle spaces (κ) and the intensity ratio of *o*-Ps in interparticle spaces to the total *o*-Ps in pores ($I_6/(I_5+I_6)$) as a function of the mass of DC550 introduced to MCM-41.

SUMMARY



- The porosity parameters S_{BET} and V_p are decreasing with increasing content of DC550, what indicates that the silicone oil is a good wetting agent for MCM-41 silica.
- The position of the peak in PSD remains unchanged despite the increasing DC550 content. It testifies that DC550 forms plugs in the pores, i.e. it completely fills whole clearance of pore at certain length instead of making it narrower.
- DC550 mostly blocks the primary pores (preferably their entrances), but part of it can locate also in the interparticle spaces.
- The calibration curve, linking *o*-Ps intensity (corresponding to annihilation in the primary pores) and pore volume, was proposed.
- Comparison of *o*-Ps migration rate the intensity ratio of *o*-Ps in interparticle spaces to the total *o*-Ps in pores, confirms the presence of both: closed and open pores in MCM-41 modified by DC550 oil. This requires the correction in the calibration curve.

