Characterization of nanoporous monoliths using nitrogen adsorption and positronium annihilation lifetime spectroscopy

J. Kullmann [a], D. Enke [a,*], S. Thraenert [b], R. Krause-Rehberg [b], A. Inayat [c]

[a] Institute of Chemistry, University of Halle, von Danckelmann-Platz 4, D-06120 Halle/Saale, Germany
[b] Institute of Physics, University of Halle, von Danckelmann-Platz 3, D-06120 Halle/Saale, Germany
[c] Department of Chemical Engineering, University of Erlangen-Nuremberg, Egerlandstraße 3, D-91058 Erlangen, Germany

ABSTRACT

The characterization of nanoporous materials is essential for their application as model systems. In this study, nanoporous glass monoliths with a pore diameter below 10 nm were used as model system to compare the pore size analysis performed via nitrogen adsorption and positronium annihilation lifetime spectroscopy (PALS). For determination of pore size distribution via nitrogen sorption, B.J.H. method and DFT method were used. By applying positronium annihilation lifetime spectroscopy as independent characterization technique, DFT method was validated to provide more realistic results for the pore size distribution of the model material.

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1. Introduction

The characterization of amorphous materials with pore sizes below 5 nm causes various difficulties since standard techniques for texture determination, such as nitrogen adsorption, mercury intrusion and electron microscopy, reach their limits in this pore size range [1].

In the case of low temperature nitrogen adsorption it is often very difficult to characterize amorphous micro- and mesoporous materials and to obtain a "real" pore size distribution. Furthermore, pore blocking or bubbling effects may occur [2,3]. Until now the Barrett–Joyner–Hallenda (B.J.H.) model has been a common tool to obtain pore size distribution curves from nitrogen sorption isotherms. But the B.J.H. evaluation method is only valid for pore diameters above 2 nm and does not give a completely realistic pore size distribution especially in the pore size range below 5 nm. Furthermore, the question arises whether adsorption or desorption branch of the isotherm should be used with the B.J.H. model, because the respective pore size distribution curves usually differ from each other.

Mercury intrusion can be used for pore size determination in the range of about 4–10,000 nm. But for pore sizes below 10 nm very

high pressures (up to 4000 bar) are needed, which causes the instrumental limitation that pores below 4 nm size cannot be detected by this method. Moreover, such high pressures can lead to changes of pore structure or even to destruction of the pore system according to the sample material (silica-gels).

In contrast to adsorption and intrusion techniques, electron microscopy offers the possibility to obtain pore sizes directly from the measurement without any model for pore size distribution. But whereas scanning electron microscopy suffers from the resolution limitation (around 10 nm for good instruments), transmission electron microscopy requires a very time-consuming sample preparation.

Since many users need nanostructured materials with tailor-made properties within the supermicropore (0.7–2 nm) and lower mesopore (2–10 nm) size range, e.g., for diffusion measurements [4], gas separation and sensor technology, the search for alternative characterization techniques and methods is very important. There are already different approaches to reach this objective.

Firstly, new characterization techniques are available, such as small-angle X-ray scattering (SAXS) [5,6] and positron lifetime spectroscopy (PALS) [7,8]. Secondly, advanced evaluation methods for the standard techniques have been introduced, such as density functional theory (DFT) for nitrogen sorption measurements [9,10].

The development and evaluation of new characterization techniques and methods requires model systems, which – in the case of pore size analysis – should have the following properties: narrow

* Corresponding author. Tel.: +49 345 5525912; fax: +49 345 5527163.
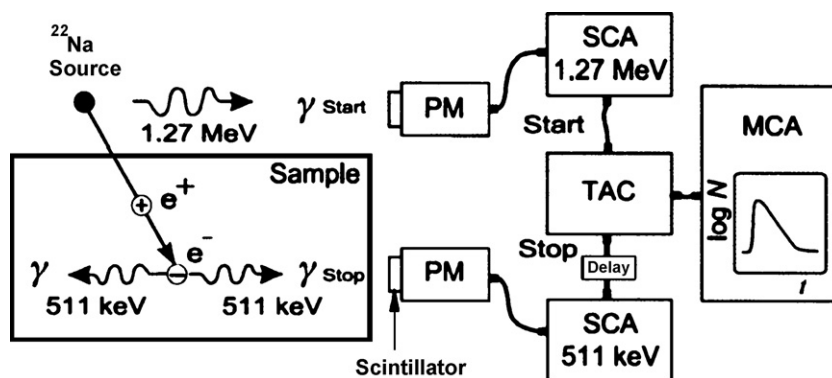*E-mail address:* dirk.enke@chemie.uni-halle.de (D. Enke).

Fig. 1. The positronium lifetime is measured as time difference between the appearance of the 1.27 MeV start γ-quantum and the registration of one of the 511 keV stop γ-quantums originating from annihilation of the positronium at the pore walls. The γ-quantums are converted into an electric signal by scintillator and photomultipler (PM). The amplitude of this signal is proportional to the respective energy. The differentiation of start and stop signal is accomplished by a single-channel-analyzer (SCA). The time-to-amplitude-converter (TAC) changes the time difference into a tension pulse and the impulse height is proportional to time. These pulses are stored in a multi-channel-analyzer (MCA) in form of the lifetime spectrum $N(t)$.

pore size distribution, tunable pore size in a broad range, stable pore system, variable macroscopic geometry and reproducible preparation of the samples.

Porous glasses as leaching products of phase-separated alkali borosilicate glasses are characterized by some special characteristics. These are the very flexible macroscopic shape (i.e., as beads, rods, fibres, hollow fibres, membranes), the controlled pores in the broad pore size range between 0.3 and 1000 nm and the very reactive surface [11–13]. The special properties distinguish porous glasses from other porous silicates. Porous glasses are commercially available as porous VYCOR glass or as controlled pore glasses [13]. Recently, porous glass membranes were prepared in shape of thin plates from a sodium borosilicate initial glass by phase-separation and combined acid and alkaline leaching treatment [12]. The thickness of the membranes varied between 100 and 1000 μm. The pore structure of the membranes can be tailored in the range between 1 and 120 nm. As a result of the special properties nanoporous monoliths based on porous glasses meet all these requirements defined above [11]. Recently, the microstructure of porous glasses with pore sizes in the range between 1.8 and 64 nm was investigated using a combination of nitrogen sorption, mercury intrusion and PALS [7,8].

In this study, nanoporous glass monoliths with a pore diameter below 5 nm were prepared and characterized using nitrogen sorption and PALS. The nitrogen sorption isotherm of this model material was analyzed with the B.J.H. model and the DFT method.

2. Experimental

A sodium borosilicate initial glass with the composition 70 wt.% SiO_2, 23 wt.% B_2O_3 and 7 wt.% Na_2O was used for the generation of the nanoporous monoliths. The initial glass blocks with dimensions of approximately 100 mm × 100 mm × 15 mm were cut with a diamond circular saw (SAW 15, Logitech) into smaller glass blocks. Since nanoporous monoliths with pore diameters smaller than 5 nm should be produced, an additional thermal treatment for phase-separation was not necessary. Next, the smaller glass blocks were cut into ultra thin flat plates with dimensions of 10 mm × 10 mm × 0.2 mm using an annular precision (Annular 55, Logitech) and a diamond band saw (SAW 15, Logitech). Finally, the ultra thin plates were leached with 1N hydrochloric acid at 90 °C for 1 h, washed and dried at room temperature. The general preparation procedure of these nanoporous glass monoliths was described in previous papers [12,13].

Nitrogen sorption measurements were carried out in an Autosorb-1-MP instrument from Quantachrome. Prior to the mea-

surements, samples were activated at 473 K for at least 3 h in vacuum. Adsorption and desorption isotherms were measured in a relative pressure range (p/p_0) from 0 to 1.0. Surface area was determined from the linear part of the Brunauer–Emmett–Teller (B.E.T.) plot in a relative pressure range (p/p_0) between 0.05 and 0.25. A value of $0.162 \ nm^2$ was used for the cross-sectional area per nitrogen molecule. The total pore volume was estimated from the amount of gas adsorbed at the relative pressure $p/p_0 = 0.99$ assuming that pores were filled subsequently with condensed adsorptive in the normal liquid state. The B.J.H. pore size distribution was determined from the adsorption branch of the isotherm. For the evaluation of DFT pore size distribution the following DFT kernel was used: N_2 at 77 K on silica (cylindrical pore, NLDFT equilibrium model).

The PALS measurements were done using a fast–fast coincidence system [14–16] (for experimental construction see Fig. 1) with a time resolution of 250 ps (FWHM, ^{22}Na source), an analyzer channel width of 121.5 ps, and a number of 8000 channels corresponding to a maximum delay time of 972 ns. The activity of the used positron source was 1.2×10^5 Bq (3.2 μCi). To avoid cryo-condensation effects the sample chamber was evacuated to 10^{-8} mbar. The calibration curve was recorded at a temperature of 300 K. By default the statistics were collected with 4 million counts. For analysis of the lifetime spectrum the routine LifeTime [17] in its
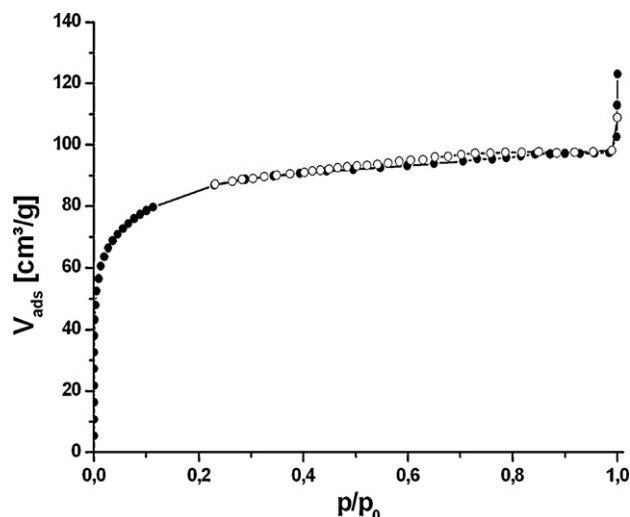

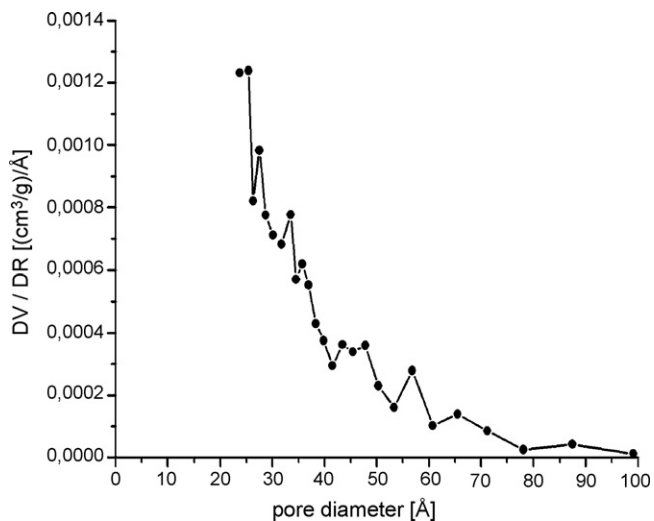**Fig. 2.** Nitrogen adsorption–desorption isotherm.

Fig. 3. Pore size distribution obtained from the B.J.H. method and the adsorption branch of the isotherm.

Fig. 4. Overlay of DFT and PALS pore size distributions (distribution curves were normalized for the same maximum).

version 9.0 was used [18]. The dependence of the positronium lifetime on the pore size was described by the Extended-Tao-Eldrup model [19,20]. Most of the lifetime spectra consist of four components, except when the pore size distribution is bimodal then there are five components. The two shorter lifetimes are due to positron annihilation which shows single exponential behavior. The third component is caused by positronium annihilation inside the glass volume. The experience shows that also this component can be satisfactorily fitted by a single exponential lifetime component. This has been confirmed by measurements of glass samples before they were processed to become a porous system. Only the longest component must often be fitted as an exponential component having a distribution of the lifetimes. This distribution is caused by the distribution of the pore size, which shows a broad variety around the mean pore size. This distribution can be fitted by the analysis program LifeTime 9.0. In this program, the probability density function of this distribution is a logarithmic Gaussian. Detailed information on spectra and measurements can also be obtained from [8].

3. Results and discussion

The nitrogen adsorption and desorption isotherm of the prepared nanoporous glass monoliths is shown in Fig. 2.

According to IUPAC nomenclature it can be classified as type I which is characteristic for microporous materials. The adsorption branch is characterized by a late transition into the plateau region around p/p_0 values of 0.4. This is an indication for the existence of so-called "supermicropores" (d_P approx. 0.7–2 nm). B.E.T. method gives a specific surface area of 318 m^2/g. The specific pore volume of the prepared nanoporous glass monolith is 0.15 cm^3/g. The pore size distributions obtained with B.J.H. method (using the adsorption branch of the isotherm) and DFT analysis are shown in Figs. 3 and 4, respectively.

It is obvious that there is a big difference between these two pore size distribution curves. Using DFT method, two pore size maxima can be found, one around 1.4 nm and the other around 2.5 nm. In contrast to that, the B.J.H. model does not lead to a distribution curve with a clearly visible pore size maximum. Furthermore, the pore size maximum between 1 and 2 nm (supermicropores) cannot be noticed by means of the B.J.H. model since it is only valid for pore sizes bigger than 2 nm.

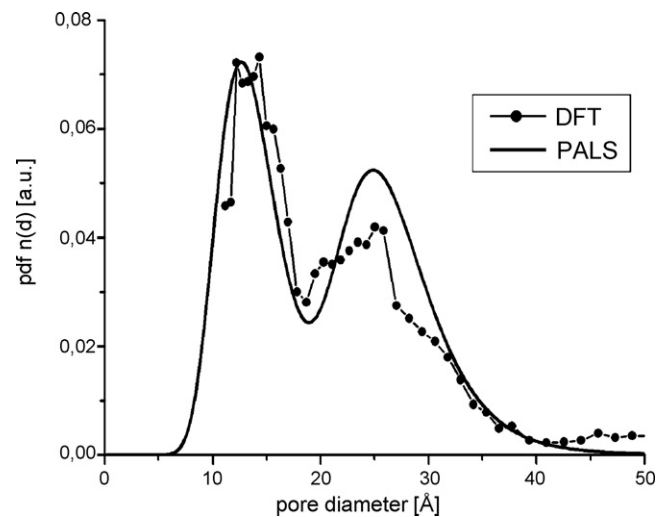In general, models and techniques for the analysis of supermicropores are still very rare. At present, DFT method seems to be the only valid tool to obtain pore size distributions from gas sorption measurements in this pore size range.

To prove the validity of a method, it is necessary to obtain comparable results with a second, independent method. For this purpose, we applied positronium annihilation lifetime spectroscopy (PALS) to the porous glass model system. The resulting pore size distribution curve can be found in Fig. 4. It shows two pore size maxima, the first one around 1.3 nm and the second around 2.5 nm.

In contrast to B.J.H. method, the DFT pore size distribution curve shows an almost ideal agreement with the results of the PALS measurement. Thus, DFT method is not only more sensitive than B.J.H. method for changes in the microstructure of the materials but also a valid tool to obtain realistic pore size distributions for materials with supermicropores.

The bimodal pore size distribution obtained for the model material by means of nitrogen sorption/DFT and PALS seems to be realistic because it can be explained as a result of the preparation procedure of the nanoporous glass monoliths in two ways.

Such a pore size distribution could result from the long leaching time. It is necessary to prepare completely porous monoliths. In this way not only the sodium rich borate phase is removed (generation of the supermicropores, first maximum in the pore size distribution curve) but also funnel-shaped pores at the surface of the sample are generated through the long contact time with hydrochloric acid (second maximum in the pore size distribution curve). This results from the dissolution of small amounts of silica of the pore walls in the leaching solution.

The formation of a small amount of finely dispersed silica-gel remaining in the cavities of the main silica framework after the acidic leaching procedure is another possible explanation [11]. It affects the pore structure of the resulting porous glass. The finely dispersed silica-gel is washed out during the leaching treatment. The process starts from the outer surface of the monolith and also leads to a bimodal pore size distribution.

An unambiguous clarification of this result requires the detailed knowledge of the cooling procedure of the initial glass. Currently, such information is not available. Regardless of, the obtained results show the potential of nitrogen sorption/DFT and PALS (alone or in combination) for the characterization of materials with pore sizes below 5 nm and for the detection of specialties in the microstructure.

4. Conclusions and outlook

In this study it was shown that the DFT method is suitable to determine the pore size distribution of porous glasses with pore sizes in the range below 5 nm. These results could be confirmed by positronium annihilation lifetime spectroscopy. Both techniques are very sensitive for changes in the microstructure of the material.

Additionally, the obtained results show the potential of nanoporous glass monoliths as model system for different applications, like pore size analysis, diffusion measurements, optics, sensor technology, gas separation, etc. This results from the combination of their very specific properties (e.g., controlled pore diameter between 1 and 100 nm, variable geometrical shape, good mechanical and thermal stability).

Currently, a comparative study of pore size distributions obtained by DFT, PALS, SAXS and diffusion measurements is being done for nanoporous glass monoliths with gradated pore diameters between 1 and 50 nm.

Furthermore, PALS is shown to be a new alternative technique for pore size determination. The technique is very sensitive in the range below 10 nm. PALS allows the recording of closed pores. Recently, Thraenert et al. [8] published a study regarding PALS on controlled pore glasses. It was found that an analytic function fitted to the theoretical ETE model curve can be used for the calculation of the pore size directly form the *o*-Ps lifetime. This analytic calibration curve makes the application of PALS as routine porosimetry tool easier. However, the technique is time-consuming and requires a high experimental effort. Further developments and optimizations are necessary.

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