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Fluid Behavior in Porous Silicon Channels with Complex Pore Structure

Muslim Dvoyashkin[1], *Alexey Khokhlov*[1], *Rustem Valiullin*[1], *Jörg Kärger*[1], *Matthias Thommes*[2]

[1]Universität Leipzig, Fakultät für Physik und Geowissenschaften, Germany
[2]Quantachrome Instruments, USA
E-Mail: dvoyashkin@physik.uni-leipzig.de

1. Introduction

Molecular dynamics under confinement is a subject of extensive scientific research. Besides fundamental interest, the understanding of the very intrinsic mechanisms of how confinements alter the fluid transport properties has an immense impact on application-oriented sciences, including life sciences in particular.

Having the possibility of preparing mesoporous materials with well-defined structural properties, one may thus study structure-related aspects of the fluid phase behaviour and of molecular propagation. Among such host systems, mesoporous silicon (PSi) which, by a proper tuning of the fabrication conditions, can be prepared to consist of macroscopically long, linear pores with a uniform pore diameter, allows a most straightforward quantification of the experimental results. Moreover, the fabrication procedure permits variation of the pore diameter along the pore axis, providing the option to study complex network effects in a simplified pore system [1].

2. Experimental Method and Sample Preparation

The PSi samples have been prepared using *p*-type Si wafers with a resistivity of 2-5 mΩ cm. The electrolyte contained HF (48%) and C_2H_5OH in a ratio of 1:1. PSi samples with pores of uniform diameter were obtained by etching with constant current densities, while the samples with modulated pores were prepared by alternating the current density between two values [2]. The etching time scheme was chosen to yield pore sections with the desired lengths. As an example, Fig. 1 shows one of the particular realizations of the used pore structure.

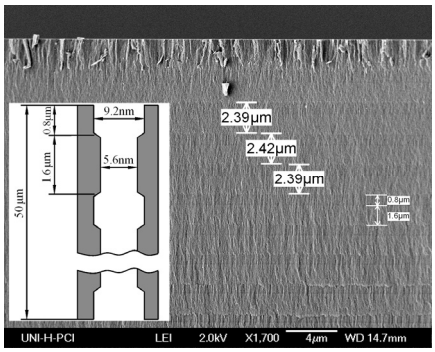

Fig. 1. SEM image of the cross section of one of the used PSi samples with a modulated structure revealing layers with different porosities (pore sizes). The inset shows the expected pore structure.

The thus prepared PSi samples have been characterized by NMR cryoporometry, diffusometry and gas adsorption methods. These studies have proven that the resulting materials possess linear pores, isolated from each other, with the pore diameters determined by the value of the applied current density.

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3. Results

In this contribution we report on two different types of studies which have become possible owing to the possibility to vary the pore diameter along the pore axis in a controlled way.

A first series of experiments refers to the experimental verification of how the structural characteristics of an ink-bottle pore affect the phase equilibrium of a fluid in the pore [3]. In particular, the effect of the length of the narrow necks separating the pore body from the external gas phase has been studied by nitrogen and krypton adsorption. Importantly, these data also provide additional information on the intrinsic, mesoscalic disorder inherent to mesoporous silicon, which may be of importance for the analysis of the diffusion process in this material.

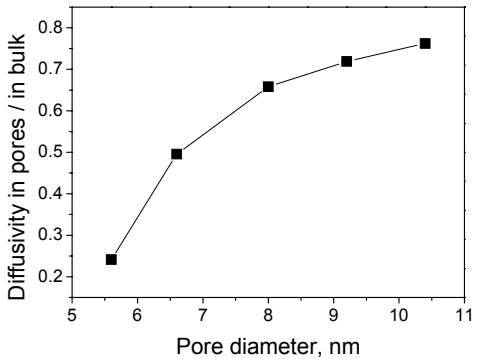

Fig. 2.: Normalized diffusivities of nitrobenzene in PSi with linear pores as a function of the average pore diameter.

The second type of experiments concerned diffusion of fluids in pores with an alternating pore diameter. From the observed dependency of the self-diffusivities on the pore diameter in the materials with uniform pores (Fig. 2) [4], the variation of the pore diameter may be considered as an alternation of transport resistances. Thus, by measuring the self-diffusivities of the fluids as a function of the structure parameters (section lengths, pore diameters) one may directly compare the obtained results to theoretical predictions. In particular, for structures similar to that shown in Fig. 1 one may expect that the effective (long-range) diffusivity can be obtained by summing the transport resistivities in each pore section. However, we found that the latter model underestimates the diffusivities as compared to the experimental data obtained using pulsed field gradient NMR. It is worth noting that the alternative model, considering a parallel connection of the transport resistivities, overestimates the overall diffusivities. Thus, the measurements are found to reveal quite complex patterns of molecular propagation which require further (both theoretical and experimental) investigations.

References

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