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In-situ-SANS Investigations of C_5F_{12} Condensation in Mesoporous Silicas with a Hierarchical Pore Structure

S. Mascotto[1], B.M. Smarsly[1], D. Wallacher[2], A. Brandt[2]

[1]Physikalisch-Chemisches Institut, Justus Liebig Universität, Heinrich Buff Ring 58,
35392 Giessen, Germany;

[2]Helmholtz Zentrum Berlin, Glienicker Strasse 100, 14109 Berlin, Germany;

E-mail: simone.mascotto@phys.chemie.uni-giessen.de;

1. Introduction

The condensation of liquids from the gas phase and the pore emptying mechanism in mesoporous frameworks (pore size 2 – 50 nm) represents an important scientific issue owing both to the significant industrial relevance (catalysis, separation process, etc.), but also to its importance for the fundamental understanding of the behavior of fluids in confined space. In general, the field of physisorption suffers from the lack of suitable independent techniques to verify theoretical models, which themselves are the basis for the determination of exact pore sizes. Furthermore, the basic phenomenon of filling and emptying large mesopores (> ca. 5 nm) from the filled state through smaller pores is still a matter of intense discussion and has to be regarded as one of the most fundamental topics in the field of physisorption [1].

In our previous work successful results were obtained performing in-situ small-angle neutron scattering (SANS) study during N_2 sorption at 77 K taking advantage of contrast matching between amorphous SiO_2 and liquid N_2. In essence, liquid N_2 has practically the same scattering length density as amorphous silica regarding neutrons. Since the small-angle scattering intensity $I(s)$ is related to the difference in scattering length densities (SLD) of void and silica/ N_2, $I(s) \sim (\delta_{\mathrm{void}} - \delta_{\mathrm{silica/nitrogen}})^2$, only unfilled pores contribute to SANS. If performed at various relative pressures p/p_0 during adsorption/desorption, the SANS curves therefore comprise information of the sorption mechanism [2].

2. Perfluoropentane Adsorption in Hierarchical Mesoporous Silica

Following the same principle in this work will be presented in-situ-sorption-SANS experiments using perfluoropentane (C_5F_{12}) which in liquid form posses almost the same SLD ($3.6\ 10^{-6}$ Ang^{-1}) as amorphous silica ($3.5\ 10^{-6}$ Ang^{-1}). This use of this gas is highly important to study sorption processes at ambient temperatures of organic molecules, because most technological processes are performed with hydrocarbons. Besides that C_5F_{12} has a bigger molecular size than N_2 so the connectivity of the pores can be compared.

The materials used in this study are two samples of mesoporous SiO_2 containing spherical mesopores of 14 and 20 nm in diameter, connected through smaller mesopores (3 nm), termed “KLE-IL” and “PIB-IL” silica respectively. Furthermore, these model materials possess a few additional, non-defined micropores of ~ 1nm in size in the SiO_2

matrix. Thus, this mesoporous silica can be regarded as a “hierarchical” architecture, in that the 3 nm pores are located between the larger spherical mesopores [3].

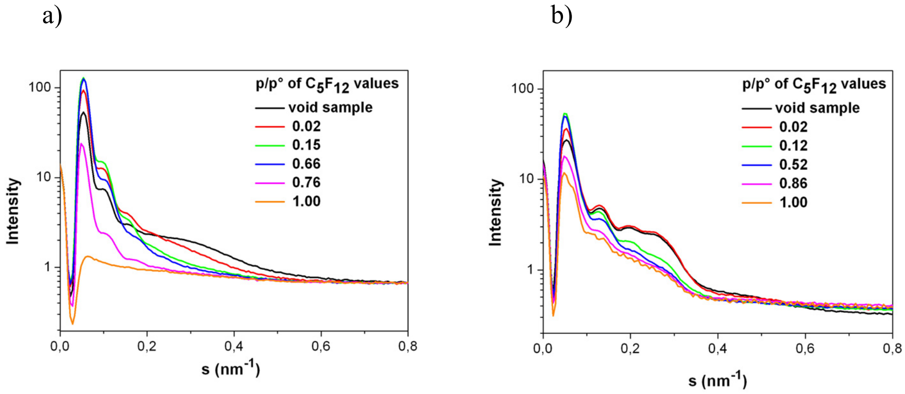

Fig.1: SANS pattern at different relative pressure of C_5F_{12} for PIB-IL (a) and KLE-IL (b) silica

The SANS patterns reveal a substantially different behavior of the materials with respect to C_5F_{12} adsorption, evidencing fine structure diversity regarding the connection of the larger mesopores through the smaller meso- and micropores. In the case of PIB-IL silica the filling of the micropores and the small mesopores takes place at small p/p° values. Enhancing the pressure of C_5F_{12} the larger mesopores get also filled, which evident from the decrease in scattering intensity at small q values. At $p/p° = 1$ the whole silica matrix is filled with the gas and no meaningful signals can be seen, proving ideal pore connectivity. The KLE-IL silica shows a completely different behavior. At large *p*/*p*° values the intensity of the signal corresponding to the larger 14 nm mesopores is still visible, indicating that they are not accessible for the relatively larger C_5F_{12} molecules through the smaller connecting pores (small meso- and micropores).

3. Conclusion

Thus, the combination of physisorption of perfluoropentane with SANS provides a unique methodology to directly investigate the pore connectivity in hierarchical porous architectures, evidencing structural differences which inhibit the diffusion of relatively large molecules.

References

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