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Experiment Report Form

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DUBBLE	Experiment title: **SAXS-assisted development of hydrothermally stable hybrid membranes for molecular separation**	**Experiment number**: **26-02-404**
Beamline: BM-26B 'Dubble'	**Date(s) of experiment**: From: 15-12-2007 To: 17-12-2007	**Date of report**: 28-01-2008
Shifts: 6	**Local contact(s)**: dr. K. Kvashnina	

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Report: (max. 2 pages)

The high energy efficiency of molecular separations using membrane technology is of great interest to industrial end-users. As an example, by the application of pervaporation in separation processes, the yearly energy saving potential amounts to hundreds of millions of barrels of oil. A typical membrane consists of a thin film of selective porous material on a support, allowing molecular size-based sieving. The development of a material that combines a high selectivity with a narrow nanopore (< 1 nm) size distribution and a high stability is a major challenge.

We have recently reported the development of an amorphous silica-based membrane with high hydrothermal stability [1,2]. The material was prepared with the sol-gel technique, and additionally has high chemical, thermal and mechanical resistance. The improved hydrothermal stability may result in effective and economic industrial application. The porous membrane layer was reported to be stable in water at 150^{o}C for over one year, close to the conditions required in industry. The organically linked silsesquioxane precursors are now considered to have the best prospects by far of all investigated materials. Full applicability requires further improvement of both stability and selectivity (*i.e.* pore size distribution). This is attempted by adapting the nature of the organic links. In order to obtain a better understanding of the polymerization reactions and network formation, these steps need close investigation. The same holds for the stages towards the formation of a porous selective layer, *i.e.* during drying and calcination, which are currently poorly understood.

We can use SAXS to study the condensation mechanism that underlies network formation. The random structure of the silica sol can be described by a mass fractal dimension (D_f) that relates the mass m to the radius r of the sol particles: $m \propto r^{D_f}$. Thus far, it was taken as a rule of the thumb that nanoporous selective networks only result from sols with fractal dimension $D_f < 1.5$. While this estimate works out fairly well for pure silica materials prepared from the simplest silane (tetraethylorthosilicate), there are indications that the network formation mechanism is different for materials from precursors with a more complex molecular structure, such as silanes with multiple organic links. At the same time, particle agglomerates should be slightly larger than the pores of the supporting mesoporous layer in order to achieve sufficiently high permeation. SAXS is a unique technique that allows quantitative determination of both the fractal dimension D_f and the gyration radius R_g of the agglomerates suspended in a solvent, and is thus essential for defining a sol structure for the required applications. By assessing a relation between the preparation parameters and the

sol structure, suitable recipes can be selected, leading to optimization of the microstructure towards an industrially applicable membrane with designed pore structure.

We have carried out Small-angle X-ray scattering (SAXS) measurements at the DUBBLE beamline BM-26B on silica sols with various stages of development. The fractal dimension of the primary particles (measured at high *q*) was of highest interest. We obtained data at short detector distance and studied samples with different bridging groups and also various monofunctionalised silanes (alkyltrialkoxysilanes). The latter are of interest to modify the pore structure, and thus the selectivity of the nanoporous membrane. By combining SAXS with other techniques, such as DLS (which determines the hydrodynamic radius of the sol particles), we can study the effect of the organic group on the development of the structure. We varied independently the catalyst concentration, hydrolysis ratio and silane concentration. Sols of pure tetraethylorthosilicate (TEOS) served as a reference. Beside sols, some powders were investigated that were prepared under the same conditions as the sols, followed by controlled drying and calcination. Finally, we studied in-situ the drying behaviour of sols and tried different set-ups for this purpose.

Sols were introduced in thin-walled glass capillaries. Two dedicated sample holders were used to enable measurement of up to 10 samples plus one background sample in one run and simultaneous filling of the other sample holder. Solid samples were applied onto kapton foil. The applied beam energy was 16 keV, and the sample-detector distance 2.7 m. These were the optimal conditions considering the fact that we also needed the WAXS detector and that the entry window allowed measurement of only a part of the scattering signal. Due to the fact that we had a weekend-experiment, it was not possible to change these towards better settings.

With the applied settings, analysis is greatly challenged by the background subtraction procedure, but the trends could be well observed. Higher catalyst and/or water concentrations as well as more concentrated sols give more scattering and higher fractal dimensions. We found excellent reproducibility of the scattering patterns, even considering the small variations in sample thickness and background intensity associated with the use of capillaries. We observed an increase of the scattering intensity during drying, and a subsequent decrease. Unfortunately, the data acquisition system crashed too often to carry out a real in-situ experiment. However, the tests were useful to assess the conditions under which future in-situ experiments on drying sols can be carried out. These will help to assess the desired parameters for membrane synthesis.

Sharp reflection lines were observed by WAXS for a number of monofunctionalised samples, indicating the existence of ordered crystalline structures. This suggests that we may use a self-organising phenomenon to further adapt the porous structure of these nanostructured materials.

References

[1] H.L. Castricum, A. Sah, R. Kreiter, D.H.A. Blank, J.F. Vente and J.E. ten Elshof: *Hybrid ceramic nanosieves: stabilizing nanopores with organic links*, Chem. Commun. (2008), DOI: 10.1039/b718082a.
[2] A. Sah, H.L. Castricum, J.F. Vente, D.H.A. Blank, and J.E. ten Elshof, *Microporous molecular separation membrane with high hydrothermal stability*, European Patent application EP 06100388.5 (16-1-2006).