



**DUTCH-BELGIAN BEAMLINE
AT ESRF**

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Experiment Report Form

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
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- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

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	Experiment title: SAXS-assisted development of hydrothermally stable inorganic membranes for molecular separation	Experiment number: 26-02-423
Beamline: BM-26B 'Dubble'	Date(s) of experiment: From: 24-7-2008 To: 28-7-2008	Date of report: 8-8-2008
Shifts: 12	Local contact(s): dr. K. Kvashnina	
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Report: (max. 2 pages)

The energy saving potential of membrane technology in industrial separation processes is very substantial. Full replacement of energy-inefficient processes as distillation and cryo-distillation by molecular separation with membranes amounts to yearly energy reductions of hundreds of millions of barrels of oil. Typically, membranes consist 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.

Amorphous silica-based membranes, prepared with the sol-gel technique, are known for their high chemical, thermal and mechanical resistance, but low hydrothermal stability hampers effective and economic industrial application [1]. Currently, the most promising class of nanoporous materials is that prepared from alkyl-bridged silsesquioxanes, of which the colloidal sols are dipcoated onto a porous support to serve as a selective layer. We have thus been successful in the preparation of a membrane that was stable in water at 150°C for over one year [2], close to the conditions required in industry. This class of organically linked precursors is now considered to provide the best prospects by far of all investigated materials. Further improvement of both stability and selectivity (i.e. pore size distribution) is envisaged by the introduction of metal oxides in the organosilica matrix, making use of the higher intrinsic hydrothermal stability of the M-O-Si bonds as compared to Si-O-Si. A second strategy involves a selectivity increase of the nanoporous layer by adaptation of the bridged silsesquioxane precursor. Careful control over all stages of the sol-gel preparation procedure, from the initial hydrolysis reactions to drying and calcination of the dipcoated solid layer, is vital to engineer an optimum structure. In recent runs, we have already been able to relate the synthesis conditions to the sol structure for various (organo)silanes and metal alkoxydes. We could thus observe higher fractal dimensions for a given agglomerate size for silanes and metal alkoxydes with a larger network-forming ability. We used the results to develop membranes with improved performance [3-5].

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 $D_f < 1.5$. 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. At the same time, with the high intensity of synchrotron radiation, drying can be studied, which is a very important but yet insufficiently studied stage in the preparation of a solid material. While further development of the network structure is allowed by slow solvent evaporation, it can be postulated that for very thin layers the sol network structure will rather be 'frozen in' as caused by rapid drying. At the same time, the colloids undergo crosslink condensation reactions with each other to form a continuous network layer, but there are insufficient data and very little insight in the timescale and the factors that determine the structure of the thin solid layer.

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. We obtained data at both short and long detector distance and studied samples with different bridging groups, a few monofunctionalised silanes (alkyltrialkoxysilanes) and mixed metal oxide sols. 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 groups on the development of the structure. We varied independently the catalyst concentration, hydrolysis ratio and silane concentration, and worked in different solvents. 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 using a home-built setup.

Sols were introduced in thin-walled glass capillaries, which were stored at low temperature between the two settings to prevent them from structural evolution. Solid samples were applied onto kapton foil. The applied beam energy was 16 keV, and the sample-detector distance 1.6 and 7.6 m. The CCD detector was used to monitor Wide Angle X-ray Scattering during long-distance SAXS.

While we found good resolution at short distance, optimal focusing for long distance or the application of lower beam energies to allow measurement of scattering at very low q was not well possible due to (probably) a leaking cooling system. Still, we were able to measure all samples, and found reactant- and catalyst-dependent development of colloidal sols. The time-resolved measurements suffered from a few disruptions of the beam delivery. 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. Further drying experiments are being planned in a dedicated setup, for which we expect to be able to acquire improved scattering patterns that allow for better quantitative analysis.

References

- [1] J. Campaniello, C.W.R. Engelen, W.G.Haije, P.P.A.C. Pex and J.F. Vente, *Long term pervaporation performance of microporous methylated silica membranes*, Chem. Commun. (2004) 834-835.
- [2] A. Sah, PhD thesis (2006) Universiteit Twente
- [3] 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*, International Patent PCT/NL2007/050017, 19-07-2007
- [4] H.L. Castricum, A. Sah, R. Kreiter, D.H.A. Blank, J.F. Vente, J.E. ten Elshof, Hybrid ceramic nanosieves: stabilizing nanopores with organic links, Chem. Commun. (2008) 1103–1105.
- [5] H.L. Castricum, A. Sah, R. Kreiter, D.H.A. Blank, J.F. Vente, J.E. ten Elshof, Hydrothermally stable molecular separation membranes from organically linked silica, J. Mater. Chem. 18 (2008) 2150–2158.