



**DUTCH-BELGIAN BEAMLINE  
AT ESRF**

**EUROPEAN  
SYNCHROTRON  
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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.
- make sure that the text, tables and figures fit into the space available.
- 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: <b>SAXS-assisted development of hydrothermally stable inorganic membranes for energy-efficient molecular separation</b>	<b>Experiment number:</b> <b>26-02-451</b>
<b>Beamline:</b> BM-26B 'Dubble'	<b>Date(s) of experiment:</b> From: 9-2-2009 To: 13-2-2009	<b>Date of report:</b> 20-2-2008
<b>Shifts: 9</b>	<b>Local contact(s):</b> dr. G. Portale	
<b>Names and affiliations of applicants</b> (* indicates experimentalists): <b>H.L. Castricum*, J.E. ten Elshof*, S.A. Veldhuis*, T. Stawski*, S. Khan* (Inorganic Materials Science, Universiteit Twente); J.F. Vente (ECN)</b>		

### **Report: (max. 2 pages)**

The implementation of membrane technology in molecular separation processes is expected to lead to very substantial energy savings by replacing notoriously energy-inefficient processes such as distillation and cryo-distillation. Yearly energy reductions could be effected of several hundreds of millions of barrels of oil. Among the various candidate-materials, a hybrid organic-inorganic microporous material now exhibits the most promising prospects for actual industrial application. The membrane consists of a thin film of sol-gel organosilica material with a narrow nanopore (< 1 nm) size distribution on a support. It combines high molecular separation selectivity with high structural stability. We have shown that this membrane is stable in water at 150°C for at least two years [1,2] and it can effectively be applied in dewatering processes. As these conditions are close to the ones that are required in industry, this class of materials is now considered to provide the best prospects by far of all existing materials.

We succeeded in greatly improving membrane stability, as compared to purely inorganic silica, by using an ethane-bridged silsesquioxane precursor. In order to further improve membrane stability and selectivity (i.e. pore size distribution), we have adopted three strategies. The first one involves variation of the precursor morphology. In order to engineer an optimum membrane structure, this involves careful control over all stages of the sol-gel preparation procedure, *i.e.* from the initial hydrolysis reactions to drying and calcination of the dipcoated solid layer. In recent runs, we have already been able to relate the synthesis conditions to the sol structure for various (organo)silanes. We used the results to develop membranes with improved performance [3]. A second strategy involves 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 final improvement is envisaged by changing a mesoporous  $\gamma$ -alumina support layer by templated mesoporous organosilica. Organosilica is better resistant to acid conditions. Replacement of  $\gamma$ -alumina by organosilica could lead to an overall improvement of membrane performance, *e.g.* in acid-catalyzed esterification reactions.

Not all recipes from bridged organosilanes lead to a nanoporous solid structure with molecular separation selectivity. Conditions in the later stages of synthesis substantially influence the final structure. Better understanding of the polymerization reactions in these stages is thus required to tune the preparation parameters in order to allow the selection of precursors that will give the highest hydrothermal stability. A

very important but yet insufficiently studied stage in the preparation of a solid material is that of drying. 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. As a consequence, there is a great need of making a comprehensive connection between the sol structure, which can easily and rapidly be studied for a great number of recipes, and the structure of the solid material that determines the separation properties when applied as a membrane. The high intensity of a synchrotron beam is ideal for studying the rapid structural evolution during dipcoating, using SAXS to study the drying process of a thin layer. In this way, a deeper understanding of network formation during rapid drying can be acquired, which has a broader applicability than in membrane production alone. Other examples are e.g. the formation of thin ordered mesoporous materials by 'evaporation-induced self-assembly', which is now under very extensive study for a wealth of applications. We also intend to study this process for the development of templated organosilica support layers. Better understanding of these processes will allow a more rational membrane design by recognition of the parameters that can be tuned to optimize the structure, and thus the separation selectivity. This will allow the development of applicable membranes to be greatly speeded up.

We have carried out Small-angle X-ray scattering (SAXS) measurements at the DUBBLE beamline BM-26B on (organo)silica sols with various stages of development. We obtained data at short detector distance and studied samples with different bridging groups, a silica sol in combination with an ionic surfactant template, 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 obtain a full description of 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. We successfully attempted in-situ drying experiments of sols using a specially developed 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 1.5 m.

Thanks to optimised slit settings and focusing on the beamstop, a high resolution was obtained, also for capillaries. We experienced a stable beam delivery throughout the experiment. Excellent reproducibility of the scattering patterns was found, enabling observation of reactant- and catalyst-dependent development of colloidal sols. The drying of colloidal sols with an ionic template showed how the mixture develops into a mesoporous structure. This gives very good prospects for further study of the introduction of self-organising templates into organosilica matrices. Another drying experiment provided us with an explanation for why a colloidal sol forms either a microporous or a mesoporous network. This is highly relevant for the further development of molecular separation membranes.

## References

- [1] H. L. Castricum, A. Sah, R. Kreiter, D. H. A. Blank, J. F. Vente and J. E. ten Elshof, *Chem. Commun.* (2008) 1103; H. L. Castricum, A. Sah, R. Kreiter, D. H. A. Blank, J. F. Vente and J. E. ten Elshof, *J. Mater. Chem.* 18 (2008) 2150–2158
- [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*, International Patent PCT/NL2007/050017, 19-07-2007
- [3] H.L. Castricum, R. Kreiter, H.M. van Veen, D.H.A. Blank, J.F. Vente and J.E. ten Elshof, *J. Membr. Sci.* 324 (2008) 111