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Experiment Report Form

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- fill in a separate form for each project or series of measurements.
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DUBBLE	Experiment title: **SAXS-assisted development of hydrothermally stable inorganic membranes for pervaporation**	**Experiment number**: **26-02-372**
Beamline: BM-26B 'Dubble'	**Date(s) of experiment**: From: 25-06-2007 To: 29-06-2007	**Date of report**: 28-07-2007
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Report: (max. 2 pages)

Chemically, thermally and mechanically resistant pervaporation membranes can be prepared from amorphous microporous silica with the sol-gel technique. Industrial application of such membranes could lead to large energy savings, but effective and economic application is hampered by low hydrothermal stability. While the use of organofunctionalized silanes has resulted in longer lifetimes [1], a major step has been achieved by applying alkyl-bridged silsesquioxanes that have recently become available. By careful engineering of the sol-gel recipe, we were successful in the preparation of a membrane that was stable in water at 150^{o}C for over one year [2], close to the conditions required in industry. However, full applicability requires further improvement of both stability and selectivity (i.e. pore size distribution).

Two distinct strategies are being employed. Firstly, the current highly promising class of membrane materials is optimized by using new types of bridged silsesquioxanes. With SAXS, we can quickly assess the effect of the recipe and the bridging groups on the sol structure, which is predictive for the structure of the porous solid material. A second strategy involves the development of a hybrid organic-inorganic membrane from metal alkoxydes and functionalized silanes. Pure metal oxides suffer from crystallization, which leads to extensive defect formation, but this can be avoided by homogenous mixing with a silane precursor. This strategy thus combines the higher intrinsic hydrothermal stability of the M-O-Si bonds as compared to Si-O-Si, and the flexibility of the functional groups of the silanes that are vital in the formation of a stable and defect-free thin porous film. The main challenge is the orders of magnitude faster reaction rate of metal alkoxydes, which prevents homogeneous mixing. With SAXS, we can investigate whether the degree of mixing can be improved by changing the sol-gel recipe.

The polymeric systems grow by random processes and can be represented by a mass fractal dimension (D_f) that relates the mass m to the radius r of the sol particles via $m \propto r^{D_f}$. 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.

Small-angle X-ray scattering (SAXS) measurements at the DUBBLE beamline BM-26B have been carried out on silica sols with various stages of development. Both the fractal dimension of the primary particles (high q) and the size of the secondary particles (low q) were of interest, and we obtained data at both short

and large detector distance. We were able to scan samples with 10 different bridging groups as well as monofunctionalised silanes (alkyltrialkoxysilanes) with 6 different side groups. 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 spacer on the development of the structure. The parameters that were independently varied were acid concentration, hydrolysis ratio and silane concentration. In addition, the effect of metal alkoxyde doping was closely investigated. 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.

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 12 keV, which was in the linear range of detection with the gas-filled 2D SAXS detector of DUBBLE. A total of more than 200 samples were measured at both settings, which was beyond expectations. For a small number of silanes, we were also able to measure the development of the initial sol stage in-situ at 60^{o}C by means of the Linkam.

Although analysis is challenged by the development of a good background subtraction procedure, the trends can be observed very well. For pure silane-based sols, higher acid and/or water concentrations as well as more concentrated sols give more scattering, higher fractal dimensions and larger secondary particles. Moreover, much more developed sols were found for silanes with higher weight and greater connectivity of the bridging groups. 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. The data will help to greatly speed up assessing the desired parameters for membrane synthesis. Remarkably, all metaloxide-doped samples showed a constant fractal dimension of 1.7. This is quite high as compared to pure silica-based materials, and indicates the development of dense structures. The pore structure of the membranes prepared from these sols was indeed found to be quite dense. The constancy of this value for all different metaloxide-doped silica recipes indicates that the development of more open structures requires other strategies than purely sol-gel technology.

The WAXS detector was used to verify the existence of ordered crystalline structures. For a few monofunctionalised samples, diffraction lines were observed. This is of interest and calls for further investigation, as some self-organising phenomenon is clearly at work.

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, *and* 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).