DUBBLE	**Experiment title: SAXS-assisted development of hydrothermally stable nanostructured silica-based membranes**	**Experiment number**: **26-02-284**
Beamline: BM-26B 'Dubble'	**Date(s) of experiment**: From: 02-12-2005 To: 06-12-2005	**Date of report**: 25-01-2006
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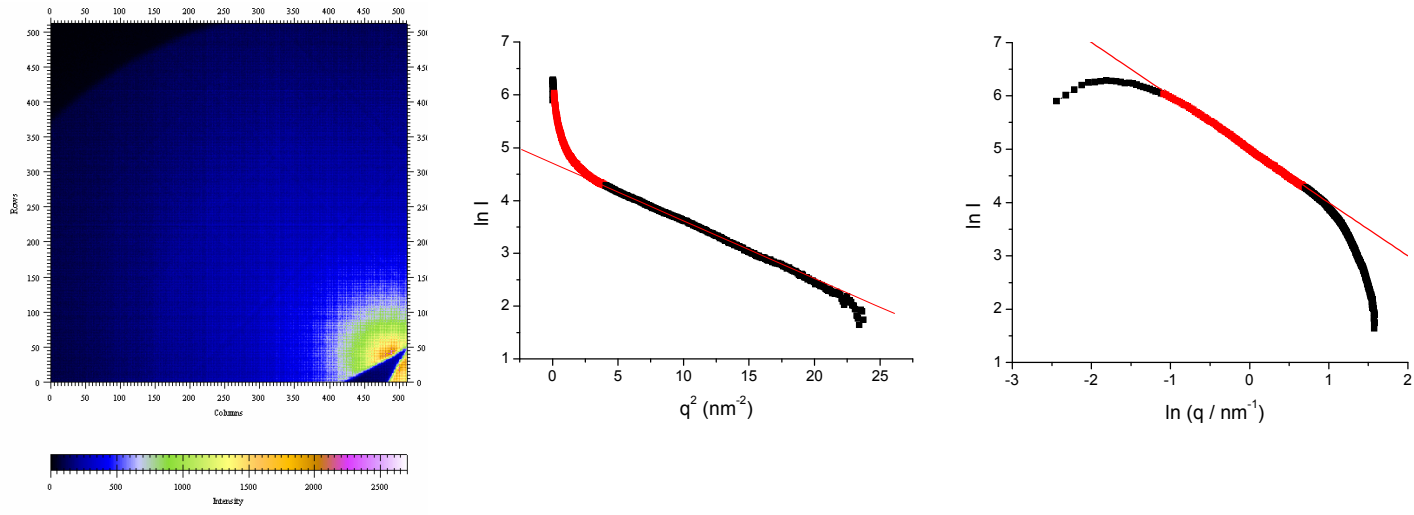
Report: (max. 2 pages)

Hybrid organic-inorganic SiO_2-based materials suffer less from degradation phenomena in wet atmospheres than standard hydrophilic silica. The forthcoming generation of membranes should therefore be based on this type of material, with its enhanced hydrophobicity and stability allowing application in a multitude of chemical separations in which water is involved. For this new generation of inorganic membranes, development of a suitable structure is much more complex than for classical membranes based on tetraethyl-orthosilicate (TEOS). This is associated with the differences in connectivity of the organomodified silane precursors, colloid formation and aggregation in the sol. As a consequence, only very specific recipes have the potential to give rise to a suitable membrane structure. We showed that certain recipes can result in a suitable membrane [1,2], but selectivity and flux may be improved greatly by optimization of the microstructure. The latter is strongly dependent on the sol structure that is formed in an early stage by acid-catalysed hydrolysis and condensation, which, after drying and calcination, gives rise to a microporous structure [3,4]. Both the fractal dimension and the size of size of the primary particles in the various stages of sol preparation and gel formation are relevant here. 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 recipe and the sol structure, a scientific basis will be provided for selection of suitable recipes and thus 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 from various stages in the reaction. As we were mainly interested in the size and fractal dimension of the primary particles, data were obtained with q-values > 10^{-1} nm^{-1} and thus at a short detector distance. It was considered most relevant to scan as many samples as possible in order to closely investigate the relation between the recipe and the scattering pattern in this q-range. The parameters that were independently varied were acid concentration, hydrolysis ratio, silane concentration, synthesis temperature and extent of metal alkoxyde doping. Various silanes, including organomodified silanes, as well as mixtures, e.g. of TEOS and methyltriethoxysilane (MTES), were used, with sols of pure TEOS serving as a reference material. 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. A sample holder was designed and built on the spot to enable measurement of up to 10 samples plus one background sample in one run. Solid samples were enclosed in 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. The scattering patterns of as many as 250 samples could be measured, which was beyond expectations. A new acute-angle beamstop was designed to enable measurement at the smallest angles possible and thus to obtain an as wide as possible range..

Figure 1a presents a typical scattering pattern. The new beamstop can be observed at the lower right corner. At the top left corner the edge of the scattering range can be observed, which is determined by the dimensions of the experimental setup. We found excellent reproducibility of the patterns, even considering the small variations in sample thickness and background intensity associated with the use of capillaries. Subtraction of the background and subsequent plotting and fitting of the data results in values for the radius of gyration of the primary particles and the mass fractal dimension, as illustrated in Figures 1b and c. At $q<2$ nm^{-1} scattering mostly originates from polymeric agglomerates of primary particles. Here the SAXS intensity closely follows an algebraic decay $I(q) \propto q^{-n}$ with the exponent $n = -1$ (panel c). For $q<2$ nm^{-1} the "straightness" of the data in the Guinier plot (panel b) suggests that here scattering is mostly related to scattering objects of one type, which were interpreted as primary units. The value of the radius of gyration $R_g = 0.4$ nm obtained from the Guinier plot agrees with the expected value for the primary particles.



a b c

Figure 1: Scattering pattern (a) of silica sol. Corresponding Guinier plot (b) and log-log plot (c) for determination of radius of gyration R_g and fractal dimension, respectively. The red points in both graphs correspond to the same data range, which was used to obtain the fractal dimension of the agglomerates.

For a number of samples, the WAXS detector was used to verify the existence of ordered crystalline structures. No diffraction lines were observed, confirming the absence of long range order for all of our samples, as it was intended.

References

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