



Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office using the **Electronic Report Submission Application:**

<http://193.49.43.2:8080/smis/servlet/UserUtils?start>

Reports supporting requests for additional beam time

Reports can now be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

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.

**Experiment title:**

Study of colloidal aggregation of zeolite building units and its role during zeolite formation

Experiment number:

26-02/339

Beamline: BM26B	Date of experiment: from: 18-SEP-06 to: 22-SEP-06	Date of report: 7-sep-07
Shifts: 3	Local contact(s): Nicolas Vilayphiou	<i>Received at ESRF:</i>

Names and affiliations of applicants (* indicates experimentalists):**C. Kirschhock¹** (main proposer)**B. Loppinet^{2*}****B. Goderis^{3*}****L. Follens^{1*}****A. Aerts^{1*}****T. Caremans^{1*}**

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Report:

In order to study the influence of chemical composition on the zeolite precursors several clear solutions were prepared and measured with SAXS. The amount of the structure directing agent, tetrapropylammonium-hydroxide, was varied in 20 sample. The water amount was altered in 10 clear solutions as was the ethanol contents in 4 solutions. The scattering patterns were recorded at room temperature with a gas-filled detector, at a distance of 1.50 m from the sample. The accumulation time per SAXS pattern was 60 s. The intensity I as a function of scattering vector (q) was obtained by radially averaging the 2D patterns, after applying the corrections for transmission and empty cell background. The q -axis was calibrated using Ag Behenate crystals.

The results of altering the amount of TPAOH were used in a paper recently published by Chem. Mat.

Reference: Aerts, A.; Follens, L. R. A.; Haouas, M.; Caremans, T. P.; Delsuc, M. A.; Loppinet, B.; Vermant, J.; Goderis, B.; Taulelle, F.; Martens, J. A.; Kirschhock, C. E. A., Combined NMR, SAXS, and DLS Study of Concentrated Clear Solutions Used in Silicalite-1 Zeolite Synthesis. *Chem. Mater.* **2007**, *19* (14), 3448-3454.

Abstract: Concentrated clear solutions, as used for the preparation of Silicalite-1 zeolite, were synthesized from tetrapropylammonium hydroxide, tetraethylorthosilicate, and water. The solutions were analyzed using three techniques: quantitative ²⁹Si NMR, synchrotron small-angle X-ray scattering (SAXS), and dynamic light scattering (DLS). ²⁹Si NMR showed the coexistence of silicate oligomers and particles. For the first time, both fractions were analyzed simultaneously, providing a global, quantitative description of the clear solution microstructure. The SAXS patterns, typical of interacting particles, could be used together with the ²⁹Si NMR deduced particle volume fraction to estimate a particle size. A careful analysis of DLS data of the

dynamics of the suspensions revealed the occurrence of two diffusive processes. The faster process is a collective particle diffusion. The slower process corresponds to the particle selfdiffusion and is present because of the presence of polydispersity in size, shape, and/or surface charge. The self-diffusion coefficient provides a means to estimate the equivalent hydrodynamic radius. The observations hence reveal a complex, polydisperse mixture of particles present at the onset of the Silicalite-1 zeolite formation. Implications on the proposed zeolite formation mechanisms are briefly discussed.

An other paper containing the results of the alteration of the water amount is in preparation for publishing in Microporous and Mesoporous Materials.

Reference: Follens L.R.A., Aerts A., Haouas M., Caremans T.P., Loppinet B., Goderis B., Vermant J., Kirschhock C.E.A., Taulelle F., Martens J.A., Influence of water on clear solution suspensions for the synthesis of Silicalite-1 studied with NMR, SAXS and DLS, *in preparation*.

Next to these studies on static samples, a dynamic study was done on the influence in a change of the template contents at different stages of the crystallization. Clear solutions quenched after different heating times were diluted with TPAOH and followed in time with SAXS at room temperature. The results of this study will be described in a paper.

The crystallization process of a clear solution was also followed *in-situ* during heating in a sealed cell. For this work a regular clear solution was heated at 95°C during 5h. Every minute a SAXS measurement was performed. Since ²⁹Si NMR measurements cannot be performed at high temperature, measurements with this diagnostic are performed at room temperature on quenched samples. To verify if these quenched samples can be compared to *in-situ* measurements, several quenched samples were prepared from the same clear solution and measured in capillary mode at room temperature. It was found that the quenched samples show the same SAXS pattern as the heated sample after similar heating time. The results of the *in-situ* study has been written in a paper and shall be submitted to ChemPhysChem.

Reference: Aerts A., Follens L.R.A., Haouas M., Caremans T.P., Goderis B., Vermant J., Loppinet B., Delsuc M.-A., Taulelle F., Martens J.A. and Kirschhock C.E.A., Nanoparticle assembly during the early stages of Silicalite-1 zeolite crystallization from clear solution, *in preparation*.

As can be seen, SAXS was a very powerful tool to study our system. In our original proposal we asked to use a combined SAXS/WAXS setup on our samples so we could also detect the first Bragg reflections. Unfortunately the WAXS detector was broken on our arrival so only SAXS measurements could be performed. We are still hoping to perform these WAXS measurements in a future synchrotron session, as study other alterations and crystallization in systems with other chemical composition.