



## 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:** Experiment title: In situ SAXS/USAXS investigations towards the role of Aluminum and structure directing agents in zeolite synthesis

**Experiment number:**  
SC-735

|                           |   |  |
|---------------------------|---|--|
| <b>Beamline:</b><br>ID02A | <b>Date of experiment:</b><br>from: 08/02/2001 to: 13/02/01 | <b>Date of report:</b><br><br><i>Received at ESRF:</i> |
| <b>Shifts:</b><br>15      | <b>Local contact(s):</b><br>T. Narayanan, P. Panine.        |  |

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**Report:**

Zeolites are industrially viable since they are selective ion exchangers and very efficient solid catalysts. Aluminium containing zeolites are of interest as they display unique catalytic properties. In fact aluminium introduces a negative charge in the framework, thus giving rise to acidity which provides the catalytic activity. Recently nanoscopic species<sup>1,2</sup> (2-4 nm) have been observed using SAXS and TEM in the reaction mixture of the pure silica ZSM-5 organic mediated synthesis and have been proposed to play a key role in the nucleation and crystal growth. Those nanoparticles appeared to be tablet like. Therefore, a series of *in situ* experiments was performed to investigate the effects of varying the Si/Al ratio in the synthesis solution. A combined SAXS/USAXS study allowed us to probe the influence of aluminium in both nucleation and crystal growth. Those measurements were performed at the ID02A beamline using high brilliance synchrotron radiation.

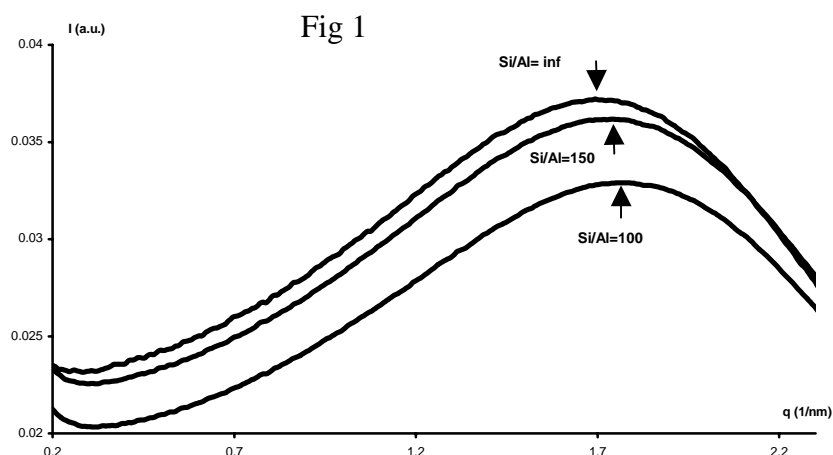
**Results:**

SAXS/USAXS involved the synthesis mixtures described in Table 1.

|           | Silica source | Template     | Si/Al mole ratio |
|-----------|---------------|--------------|------------------|
| <b>S1</b> | <b>TEOS</b>   | <b>TPAOH</b> | $\infty$         |
| <b>S2</b> | <b>TEOS</b>   | <b>TPAOH</b> | <b>150</b>       |
| <b>S3</b> | <b>TEOS</b>   | <b>TPAOH</b> | <b>100</b>       |
| <b>S4</b> | <b>TEOS</b>   | <b>TPAOH</b> | <b>50</b>        |

These starting solutions all lead to MFI formation upon heating and catalytic tests proved that aluminum is incorporated in the zeolite framework.

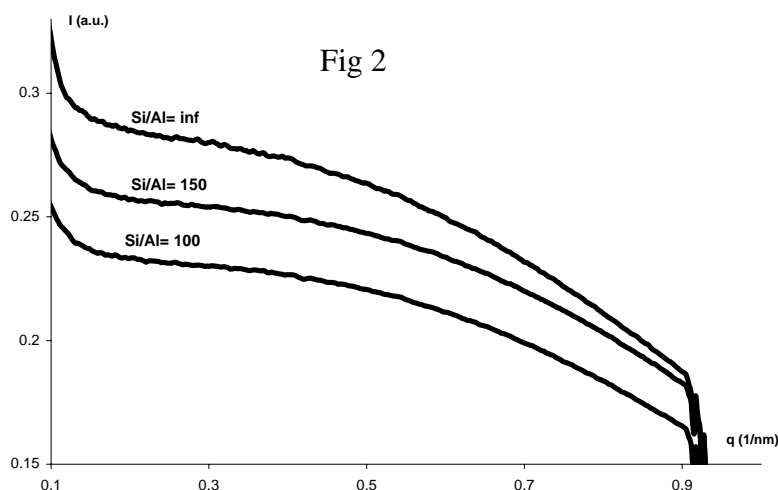
Figure 1 shows the SAXS patterns of the starting solutions S1, S2 and S3. At room temperature and after the silica dissolution, several peak maxima can be observed. They contain a well defined particle population with a different size depending on the alumina concentration.



Surprisingly, the use of aluminum leads to slightly smaller particles at RT. Indeed the characteristic lengths are 3.7, 3.61 and 3.53 nm for S1, S2 and S3 respectively.

This can be a direct proof for the incorporation of aluminum inside the particles. In that case, aluminum changes the ionic strength (incorporation of a negative charge) of the nanoparticles and the colloidal chemistry is greatly influenced.

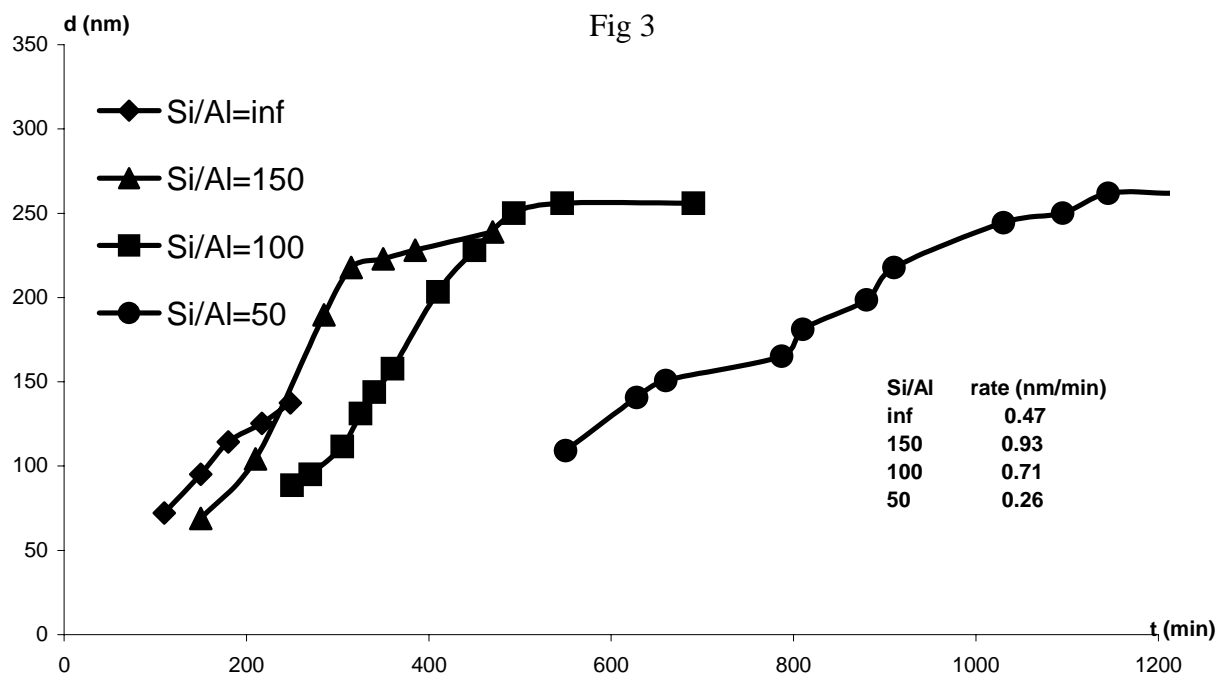
Upon heating it has been observed that these small particles disappear in favor of the formation of larger entities, not yet exhibiting Bragg reflections, and designated as intermediates. Figure 2 shows SAXS patterns of S1, S2 and S3 after 25 min. heating at 125°C.



Those intermediates have characteristic lengths of 11.41, 10.47 and 9.97 nm for S1, S2 and S3 respectively. Increasing the aluminum content leads to a decrease of the size of those intermediates. A previous study<sup>1</sup> on the all silica system suggested that these intermediates result in the aggregation of the smaller particles. Consequently these results strengthen our confidence that energetically favorable aggregation of the RT formed nanoparticles occurs.

Those intermediates are present throughout the nucleation and their size slightly increases (not shown). Nevertheless, we observed their consumption at the beginning of the crystallisation and the scattering is mainly due to the appearance of the first crystals. The notable fact is that no other particle population was observed in the 2-50 nm range (50 nm is the size of the first crystals). Only a small fraction of them transforms into viable nuclei and the rest is used for the crystal growth.

USAXS results showed the crystal growth rate and particle size at different aluminium content. Increasing the aluminium concentration in the synthesis solution affects the crystal growth rate to an appreciable extent as seen in Fig 3. The increase of the aluminium concentration in the starting solution reduces the crystal growth rate but increases the size of the final crystals. However, S1 (no aluminium) was found to have a crystal growth rate lower than the ones with a Si/Al equal to 150 and 100. We still are doubtful on this since we lack of numerous data points for this synthesis.



The results presented here show that combined SAXS/USAXS experiments are a powerful tool to study *in situ* the crystallisation of colloidal zeolites. The mechanism appears unchanged with the incorporation of aluminium. Based on these results we suggest that ZSM-5 crystals form in an organic mediated synthesis as follows: very well defined nanoslab are formed at RT due to the interactions between the organic template and silicates species. Upon heating, energetically favorable aggregation occurs and crystal growth is then accomplished by eliminating water molecules at the interface and oriented attachment. This attachment is most probably influenced by the aluminium content since negative charges have been introduced in the nanoparticles.

NB : Other results involving ZSM-5 formed from silicic acid as silica source have been performed. A publication on those experiment combined with other techniques is being written.

References :

<sup>1</sup> C.J.Y. Houssin, B.L. Mojet, C.E.A Kirschhock, V. Buschmann, P. A Jacobs, J.A. Martens, R.A. van Santen; Small angle X-ray scattering on TPA-Silicalite-1 precursors in clear solutions: influence of silica source and cations; *Proceedings of the 13<sup>th</sup> International Zeolite Conference, 2001*, O2-O-O1.

<sup>2</sup> C. E.A. Kirschhock, V. Buschmann, S. Kremer, R. Ravishankar, C. J.Y. Houssin, B. L. Mojet, P. J. Grobet, R. A. van Santen, P. A. Jacobs and J. A.Martens ; Zeosil Nanoslabs: Building Blocks in  $n\text{Pr}_4\text{N}^+$ -Mediated Synthesis of MFI Zeolite; *Angew. Chem. Int. Ed.* **2001**, Vol 40, 14, 2637-2640.