EUROPEAN SYNCHROTRON RADIATION FACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

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 via the User Portal:

https://wwws.esrf.fr/misapps/SMISWebClient/protected/welcome.do

Reports supporting requests for additional beam time

Reports can 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.

ESRF	**Experiment title:** In situ SAXS/WAXS study of Silicalite formation	**Experiment number**: CH-4557
Beamline: BM26b	**Date of experiment**: from: 05/10/15 to: 09/10/15	**Date of report**: 28/02/15
Shifts: 9	**Local contact(s)**: Daniel Hermida	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Glen Smales*

Andy Smith

Gopinathan Sankar

Report:

We were successful in completing our aim to investigate the effect of silica source on the morphology and size of silicalite zeolite material prepared using different silica source, *in-situ*. We were successful in preforming experiments using three different silica sources in the formation of Silicalite-1 (TEOS, Ludox AS-40 and Silica Nanospheres). We were able to preform these experiments at 150°C and at a further two different temperatures for experiments using the silica nanospheres as a silica source. The data obtained from this application has been analysed using both McSAS and SASView software packages to obtain models of particle size and their distrubitions in the systesms.

TEOS

From SAXS data analysis of the formation of Silicalite- 1 from TEOS it is possible to see that there is a large population of nanoparticles with a 2 nm diameter present in the starting reactant solution. This population remains visible over the first 45 minutes of the experiment; however, some of these particles grow/aggregate gradually to a size of c.a. 5nm in diameter. After roughly 30 minutes of being subjected to hydrothermal conditions a very small population of

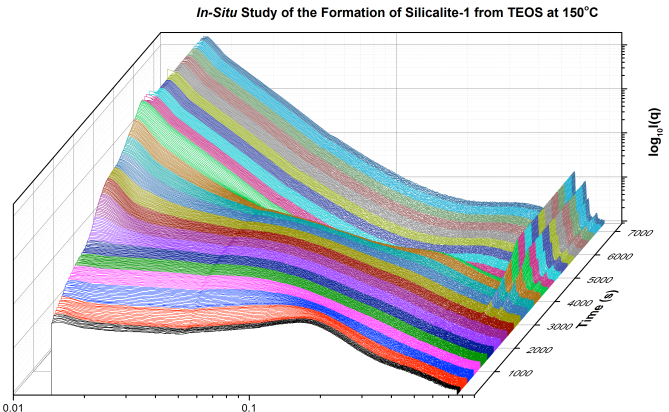

Figure 1: In-situ SAXS data for the formation of silicalite-1 from TEOS at 150°C.

nanoparticles between 10 – 20 nm in diameter can be seen. This appears to correlate with the decrease in number of the initial 2 – 5 nm population observed. However, during the next 15 minutes of the experiment (45 – 60 minutes) a population of particles larger that those initially observed begin to appear with diameters of c.a. > 30 nm, whilst the initial population of nanoparticles under 5 nm in diameter begins to decrease steadily in number. It is at this time that the low angle Bragg peaks are first observed in the data indicating the presence of crystalline material. After the first hour of the experiment the population of very small nanoparticles begins to drop in number dramatically to a point where there are very few particles left, however, the four distinct populations of larger particles begins to grow in number, however, there is very little observed change in their overall size. It is also at this point where the intensity of the Bragg peaks begin to level off giving some indication that the < 5 nm particles are perhaps amorphous in nature.

Ludox AS-40

From looking at the *in situ* SAXS data for the formation of Silicalite-1 from Ludox AS-40, it can be seen that there is a small population of particles c.a. 2nm in diameter alongside a population of particles roughly 25 nm in diameter (the primary Ludox particles). It can be seen that the Ludox particles are polydispersed as also observed with microscopy. The 2nm population looks to remain for the majority of the experiment with only minor changes in population size occur, however, the Ludox particles decrease in size until the majority of particles are c.a. 18 - 22 nm in diameter. This change in particle size takes roughly 5 minutes and after this time there is a slight increase in the number of 2 nm particles observed indicating that there maybe some dissolution nucleation occurring at these early stages of the reaction. It can be seen at this time that the number Ludox particles drops dramatically, however, it looks like this drop is compensated for by a broadening of the size range of the Ludox particles within the system. The smaller Ludox particles are present through to the end of the experiment, keeping an average size of c.a. 20 nm. Bragg peaks are first appear after 50 minutes of hydrothermal synthesis and grows steadily in intensity as the experiment goes on.

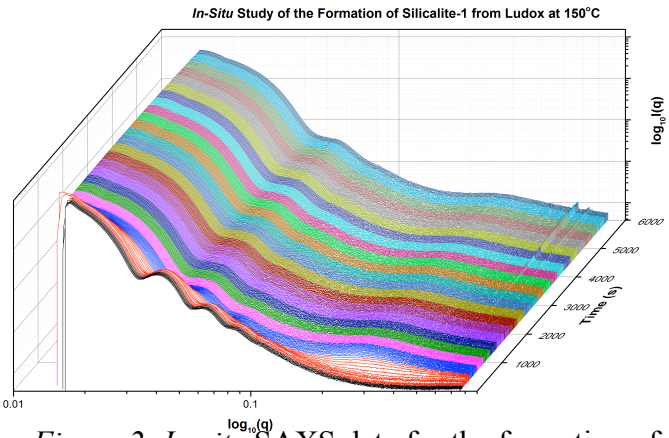

Figure 2: In-situ SAXS data for the formation of silicalite-1 from Ludox AS-40 at 150°C.

SNS500

At the start of the experiment there are again very few sub 5 nm particles present within the system, however a population begins to grow in numbers until a peak population size is met after roughly 75 minutes. A population of larger particles can also be seen, however, after 20 – 25 minutes the largest of these particles are no longer observed in the data, leaving particles in the region of 20 – 50 nm in diameter. This population is present until the end of the experiment, and looks to be

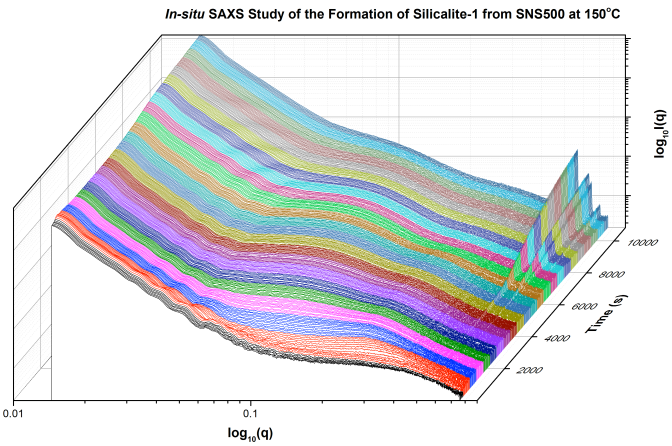

Figure 3: In-situ SAXS data for the formation of silicalite-1 from SNS500 at 150°C.

growing in population size over the course of the experiment. After 100 minutes and 150 minutes two distinct populations of larger are observed and seem to grow in number until the experiment ends. Bragg peaks are first observed in this data after 60 minutes and can only be seen to correlate with the increase in population size of the sub 5 nm particles and the population growth of the larger 20 – 50 nm particles.

Conclusion

The crystallization process of silicalite-1 from three different silica sources was investigated using an *in situ* SAXS/WAXS study. The findings indicate the existence of two different nucleation/crystallization mechanisms present within these systems. The first mechanism of the initial formation of sub 5 nm particles and subsequent aggregation larger species that eventually densify/crystallize through the creation of an interconnected network of silica. This is then followed by the secondary growth of larger more crystalline particles. This mechanism was seen clearly when using TEOS as a silica source, but evidence was also seen with Ludox and SNS500. The second mechanistic feature in the system is the coalescence of solid silica nanoparticles through what is most likely a dissolution-recrystallization mechanism. This is observed most prominently in the SNS500 system but is also seems to be present within the Ludox systems to some extent. With the proposed mechanism for the formation of macroporous Silicalite-1 could be first modified to other MFI systems such as ZSM-5 or TS-1 and then potential into other zeolitic frameworks there could be many advantages to industry. However, to make this happen the formation of crystals *via* the liquid phase path observed prominently in the TEOS synthesis would need to be suppressed to make sure that the majority of crystal synthesized possess the macroporous morphology.