ESRF	**Experiment title:** Time resolved *in-situ* studies of nucleation and crystallization in zeolite synthesis from clear solutions using combined small angle/wide angle powther diffraction and Dynamic Light Scattering	**Experiment number**: CH1070
Beamline: BM26	**Date of experiment**: from: 13/07/01 to: 17/07/01	**Date of report**: 15/07/02
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Report:

The present study is part of a larger project aimed to understand and control the parameters affecting zeolite nucleation and growth kinetics. Time resolved *in situ* studies of the crystallization processes of these microporous materials by combined techniques are important tools in the understanding of the mechanisms involved. Investigations on the nucleation and crystal growth of Lynde Type A zeolite (LTA) from clear solutions were performed *in situ* using combined synchrotron Small Angle/Wide Angle X-Ray Scattering (SAXS/WAXS) and Dynamic Light Scattering (DLS). The difficulty to univocally interpret the role of the amorphous forerunner to the crystallization, which may act differently in different systems, has brought to select two synthesis systems, one of which including organic additives as template directing agents (TDA).

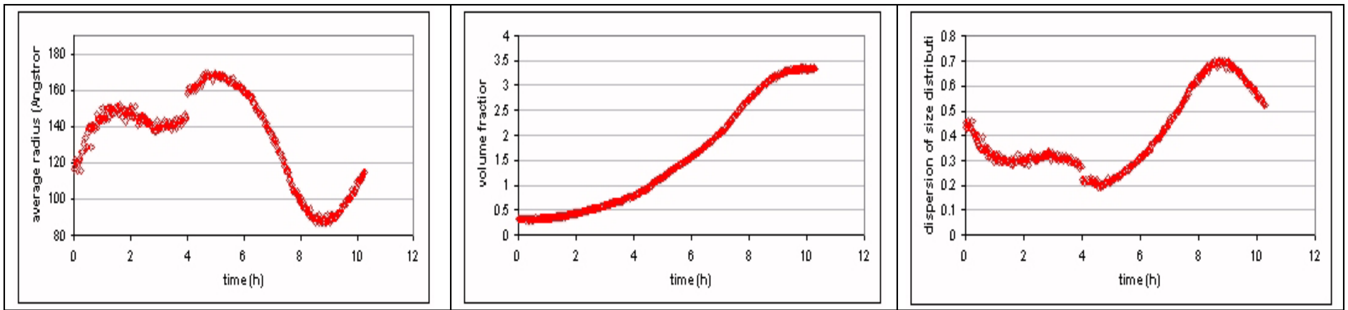
The simultaneous Small and Wide Angle Scattering data have been collected using the SAXS/WAXS equipment present at BM26 beam line. The DLS apparatus, integrated on the beam line, was based on a polarized He-Ne laser (22 mW) and an ALV 5000 correlator. The heater was designed *ad hoc* and consists of an aluminium cylinder re-covered by heater coils, in which the cell is accommodated. The cell was designed in order to satisfy the experimental requirements: the inner width was reduced at a value of 4 mm to avoid the absorption of the X-rays inside the cell and mica sheets have been chosen as the proper material for the cell windows. On the whole the cell consists of a multilayer of aluminium-mica-plastic layer-mica-aluminium.

Two synthesis systems have been chosen for the experiments. The first was $8.6Na_2O-0.18Al_2O_3-SiO_2-150H_2O$, the second $0.05Na_2O-1.2(TMA)_2O-0.165Al_2O_3-1SiO_2-70H_2O$. The synthesis temperature were 70, 80, 90, 100 °C for the first system; 90, 100, 110, 120, 130 °C for the fresh second system; 100, 110, 120 °C for the aged second system. SAXS data were processed with a modified version of the program FLAC [1], created *ad hoc* for systems analysis with two particle size distributions. The processing consists of the experimental data fit from consistent input parameters, that had to be chosen in a careful way as starting point for the fit, and from the selection of the size distribution function. In this report are shown the results obtained for the fresh second system at the isotherm temperature of 90 °C. At 90 °C the analysis of the SAXS data from fresh solution has shown the presence of two groups of particles: the first group is constituted by particles having a narrow distribution around 8 Å, they are interpreted as the TMAOH organic molecules in various states of hydration; the second group is formed by aggregates of size of the order of 300 Å, which could be interpreted as crystal blocks with side corresponding to 12 or 13 LTA elementary cells. The volume fraction of larger particles increases linearly after 3 h of heating up to 9 h, and during the same period the amount of TMAOH organic molecules within the sampled volume of solution seems to fluctuate (**fig. 1**).

During the first hour of heating an apparent increase in the average radius of larger particles is observed. They reach a mean size of 280-290 Å, whereas the total amount of particles seems to be constant. Subsequently, in the time range 1-4 h both the particles size and the volume fraction of TMAOH paticles in the solution seems to stabilize. During this stage the main observable process is the increase in the total amount of larger aggregates. After 5 h of heating the trends observed are totally different, and a marked increases in the size dispersion of both particle types is visible. The sudden apparent decrease in the average radius of the large particles starting from 5 h could be explained by the indirect size effect induced by the precipitation of the larger crystalline seeds to the cell bottom, by the occurrence of dissolution processes at the particle surface or even by the increase in the number of smaller critical nuclei within the sampled volume of solution. The marked increase in the dispersion of the larger particles may be an indication that a new generation of crystalline nuclei is indeed forming. No useable WAXS data were obtained, probably due to rapid sedimentation of the LTA crystals.

At 90 °C the first detectable particles with DLS appear right at the start of the experiment (**fig. 2**). At this stage the dispersion of DLS data is large and prevents the observation of any small increase in the decay time (i.e. in the scattering particle size). Such dispersion decreases drastically in the first hour and shows a further decrease during the second and third hours of the experiment. This behavior is in agreement with the results of the SAXS data, which analogously show a decrease in the distribution of the larger particles. At longer times, that is in the time range 4-8 hours, the decay time remains almost constant whereas the counting rate exhibits a continuous rise. This could be related to an increase in the scattering particles concentration, in agreement with the increase in the particle volume fraction observed by SAXS.

[1] F. Carsughi, A. Giacometti, D. Gazzillo, *Computer Physics Communication* **133** (2000) 66-75



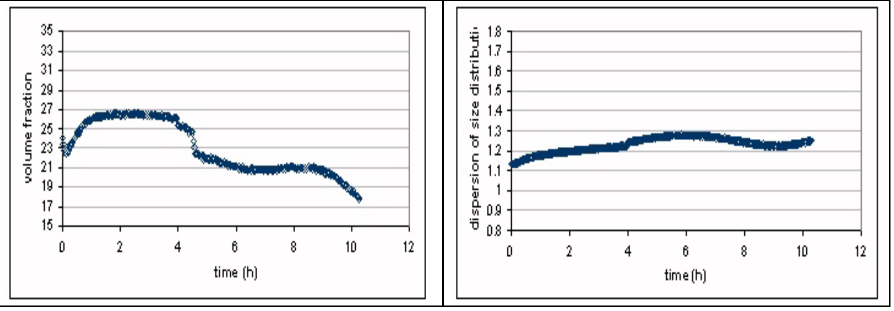


Fig. 1

Plot of the physical parameters (volume fraction, average radius, dispersion of the size distribution) as function of time for the small (blu) and the larger (red) particles present inside the solution at the synthesis temperature of 90 °C. During the data processing the average radius of small particles has been kept constant at the value of 8 Å.

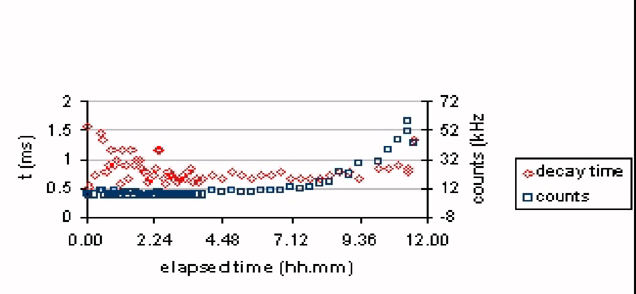


Fig. 2

DLS data results collected at 90 °C. The plot shows the characteristic decay time t of the auto-correlation function and the corresponding counting rate measured with DLS.