ESRF	**Experiment title:** Zeolite formation from clear solution Combined time resolved in-situ X-Ray powder diffraction (XRPD) and dynamic light scattering (DLS)	**Experiment number**: 08-02-248
Beamline: BM8-GILDA	**Date of experiment**: from: 28/02/01 to: 04/03/01	**Date of report**: 05/09/01
Shifts: 12	**Local contact(s)**: Carlo Meneghini	*Received at ESRF:*

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Report:

Zeolites are alumino-silicate compounds with a number of relevant industrial applications, due to their microporous structure. The detailed knowledge of the synthesis process is necessary to optimise products and/or production techniques, and it is still not completely elucidated despite substantial research efforts. Zeolite synthesis may take place in heterogeneous systems, involving the formation of precursor amorphous phases. In the case of clear solutions the synthesis occurs from homogeneous liquid phases. The development and validity of synthesis models require informations on the very early stages of the process, and specifically on the formation and dissolution of the amorphous phases and on the formation and growth of crystalline nuclei (scattering techniques are particularly suitable for such aims).

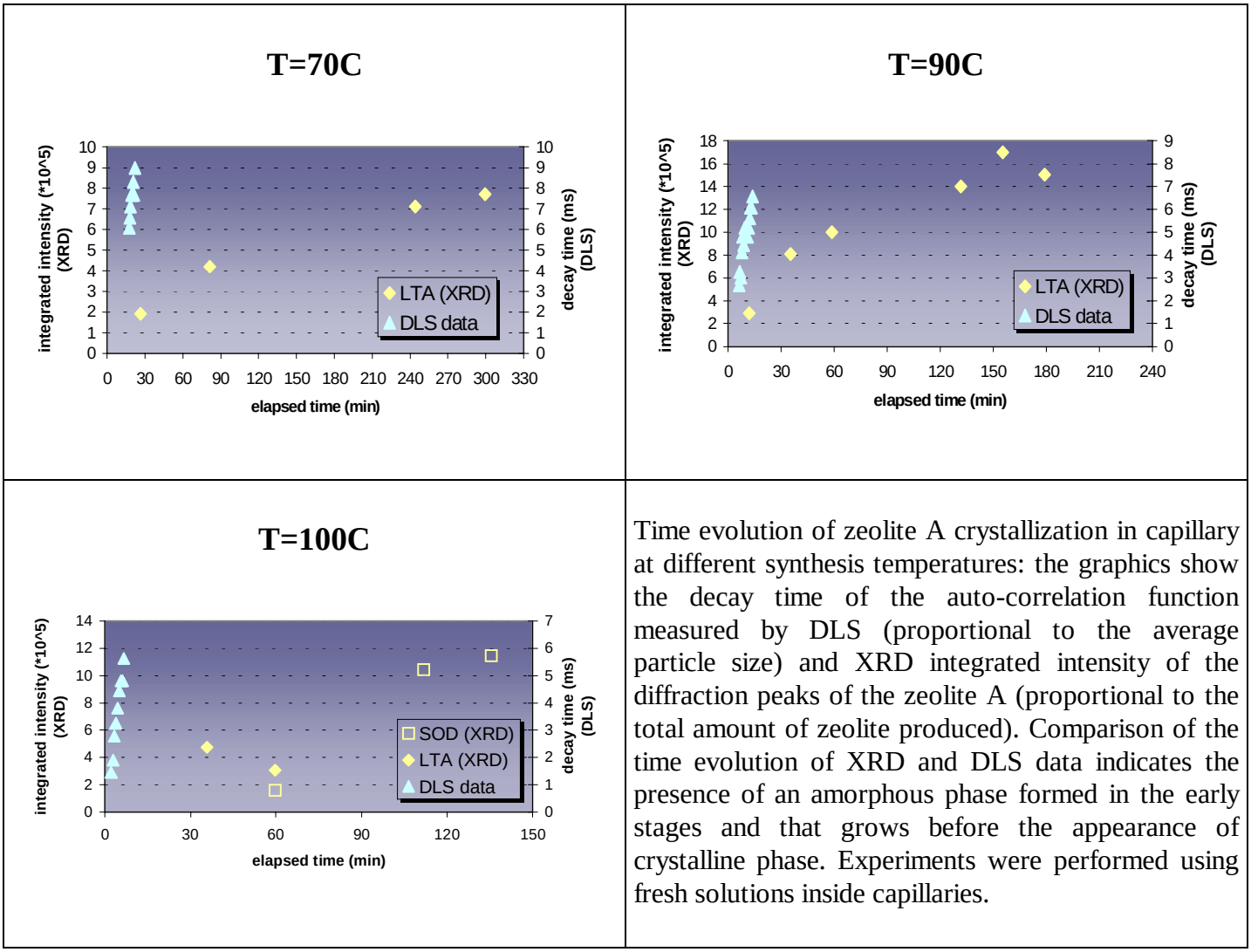
Investigations on nucleation and crystal growth of Lynde Type A zeolite (LTA) from clear solution were performed in situ using simultaneous synchrotron X-Ray Diffraction (XRD) and Dynamic Light Scattering (DLS). Combined XRD-DLS experiments in capillaries on fresh solutions were repeated at different isothermal temperatures on the BM8 line at ESRF. The DLS apparatus, based on a polarised He-Ne laser (22 mW) and an ALV 5000 correlator, was integrated on the beamline to perform simultaneous DLS and XRD data acquisitions. The synthesis system selected was $8.6Na_2O$-$0.18Al_2O_3$-SiO_2-$150H_2O$. The qualitative analysis of phases has shown only the presence of LTA zeolite. The quantitative analysis of LTA crystallization was performed through a profile fitting method.

The data analysis was performed following a kinetic model valid for crystallization in solution and allowed a kinetic interpretation of process. The modelling suggests that the crystallization mechanism in capillary from clear solution is the same taking place in large-volume synthesis (ex situ measurements): reactions have the same order and are controlled by the same process, having similar apparent activation energies and pre-exponential factors (in situ data: E_a = 70.9 kJmol^{-1}, A = 1.76 10^{10}; ex situ data: E_a = 75.9 kJmol^{-1}, A = 4.29 10^{10}). The nucleation occurs heterogeneously, possibly at the liquid/amorphous interface, and the effect of increasing temperature is to promote the kinetic of process.

The results obtained from XRD-DLS measurements indicate the amorphous nature of the aggregates present at the beginning of the experiments. The amorphous phase initially aggregates and grows at every temperatures, then it dissolves successively, when the crystalline nuclei of zeolite appear (fig.1). The aggregate growth starts immediately. The effect of ageing is the reduction of the induction time and the increase of the growth rate. These results, in agreement with other studies [1], indicate that nuclei form and agglomerate during the ageing period. The large decay times of data collected on fresh (i.e. not aged) solutions are compatible with the formation of large structures. After a certain growth period, the decay time decreases systematically, together with the scattered intensity; this could be due to settling or to dissolution of the aggregates.

[1] D. Caputo et al., A preliminary investigation on kinetics of zeolite crystallisation using optical diagnostics, Materials Chemistry and Physics, 66 (2000) 120

Figure 1



Time evolution of zeolite A crystallization in capillary at different synthesis temperatures: the graphics show the decay time of the auto-correlation function measured by DLS (proportional to the average particle size) and XRD integrated intensity of the diffraction peaks of the zeolite A (proportional to the total amount of zeolite produced). Comparison of the time evolution of XRD and DLS data indicates the presence of an amorphous phase formed in the early stages and that grows before the appearance of crystalline phase. Experiments were performed using fresh solutions inside capillaries.