ESRF	**Experiment title:** Time-resolved in situ studies of template-directed nucleation and crystallization in zeolite synthesis from clear solution	**Experiment number**: 08-02-323
Beamline: BM8-GILDA	**Date of experiment**: from: 24/04/02 to: 27/04/02	**Date of report**: 4/06/03
Shifts:	**Local contact(s)**: Carlo Meneghini	*Received at ESRF:*

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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 [1,2]. It's well known that the zeolite synthesis, as other microporous materials, can be directed by means of organic additives as template directing agents (TDA), that act as inhibitor of gel formation optimizing the zeolite production. Investigations on the nucleation and crystal growth of Lynde Type A zeolite (LTA) from clear solutions were performed in situ using synchrotron x-ray powder diffraction (XRPD). The composition of the clear starting solution was 0.05Na2O-1.2(TMA)2O-0.165Al2O3-1SiO2-70H2O. Isothermal runs were performed at 100, 110, 120, 130, 140 °C using the instrumental apparatus present on the beam line BM8 at ESRF. The powder patterns were integrated and analyzed by single peak profile fitting. Fig.1 shows the time evolution of the integrated intensity.
The kinetic analysis was performed following the same kinetic modelling used in the LTA synthesis without organic additives [1]. Table 1 shows the values resulting from the fitting procedure: *n* and *q* are the orders of reaction, *k* and *K* the rate constants calculed respectively from the Avrami model and the semplified equation of the population balance model. In fig. 2 is shown the Avrami plot of the collected data. The apparent activation energy obtained from the kinetic analysis is 117.73 kJ/mol, the pre-exponential factor $3.37 \cdot 10^{11}$. Fig. 3 shows the Arrhenius plot. The XRPD kinetic data are comparable with the data for the inorganic synthesis collected in the same experimental conditions, even if the *n* and *q* values extracted don't fully correspond with the theoretical values for homogeneous nucleation. The reaction orders are almost doubled suggesting a different crystallization mechanism.

[1] R. Grizzetti, G. Artioli, *Microp. Mesop. Mater.* **54** (2002) 105

[2] G. Artioli, R. Grizzetti, L. Carotenuto, C. Piccolo, C. Colella, B. Liguori, R. Aiello, P. Frontera, *Stud. Surf. Sci. Catal.* **142A** (2002) 45

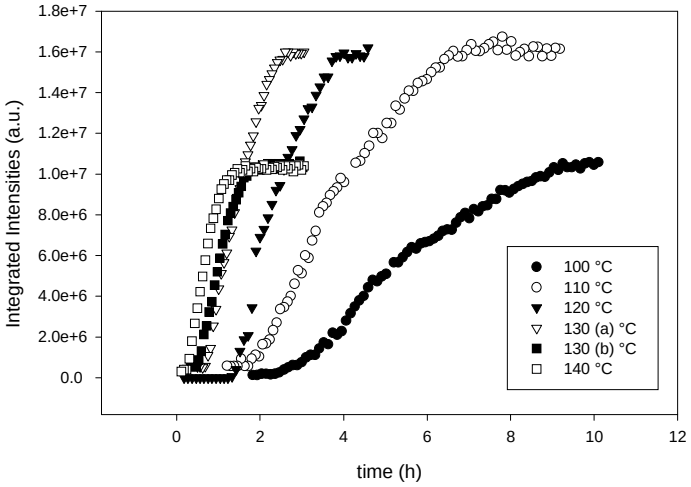

Fig. 1

Plot of the integrated intensity of zeolite LTA vs. time for each *in situ* experimental temperature (°C).

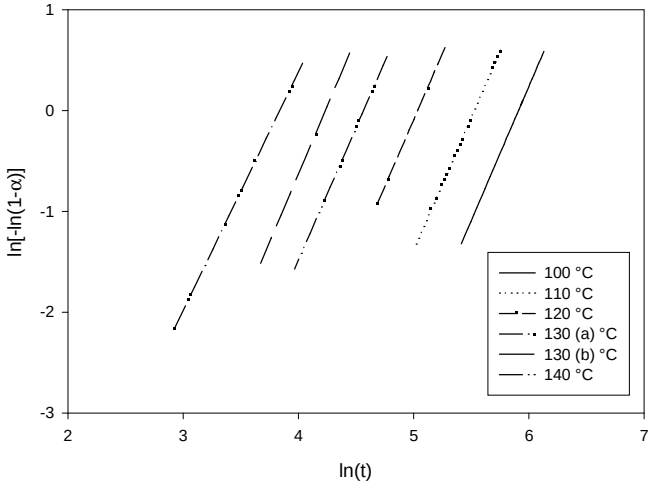

Fig. 2

Avrami plot of the *in situ* data collected at different temperature (°C).

Table 1

Parameters resulting from the kinetic analysis

isotherm temperature (°C)	$K*10^{-5}$	*q*	*n*	*k*
100	1.3	1.82	2.66	0.0027
110	2.7	1.81	2.63	0.0040
120	7.1	1.80	2.64	0.0065
130 (a)	13.0	1.85	2.62	0.0105
130 (b)	21.7	1.85	2.69	0.0145
140	55.1	1.87	2.36	0.0215

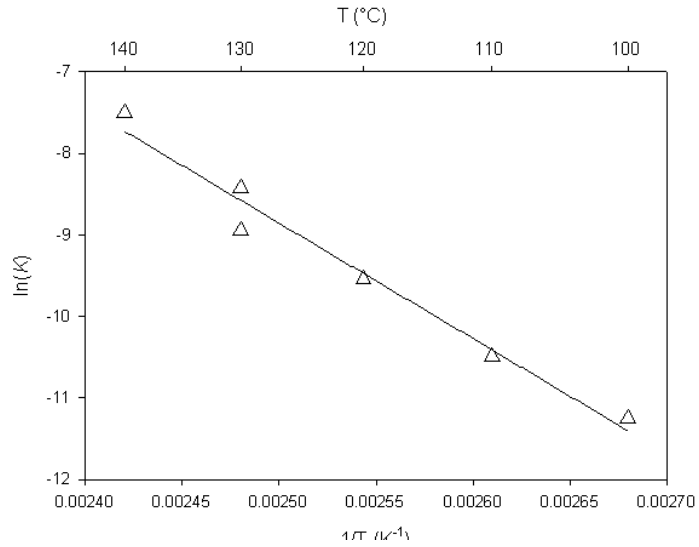

Fig. 3

Arrhenius plot of the kinetic data.