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Report:

In situ investigations on the synthesis of zeolite A were performed using synchrotron X-ray diffraction (XRD) and dynamic light scattering (DLS). Preliminary results showed the formation of an amorphous phase at the beginning; this phase dissolves successively, when crystalline nuclei appear.

Zeolite crystals are alumino-silicate compounds that have a number of relevant industrial applications. Due to their microporous structure zeolites are used in many fields, as molecular sieving, catalysis, and ion exchange. The detailed knowledge of the synthesis process could be very useful to optimise products and/or production techniques, but it is still not completely elucidated, despite of the large effort of a number of research groups.

Zeolite synthesis generally takes place in heterogeneous systems, and it involves the formation of precursor amorphous phases; in case of clear solutions, nucleation is assumed to take place directly from the liquid phase, with no amorphous phase present. In both cases, the development and validation of synthesis models require information on the very early stages of the process, and specifically on the formation and dissolution of amorphous phases and on the formation and growth of crystalline nuclei. Scattering techniques are particularly suitable for such studies.

The present paper presents preliminary results obtained on the nucleation and growth of zeolite A from clear solutions. The synthesis system $8.6Na_2O$-$0.18Al_2O_3$-SiO_2-$150H_2O$ was selected [1].

In situ investigation of reaction kinetics were performed using synchrotron X-ray powder diffraction (XRPD) and dynamic light scattering (DLS). The DLS apparatus is based on a polarised He-Ne laser (22 mW) and an ALV 5000 correlator. The DLS apparatus has been integrated on the BM8 line at ESRF (Grenoble, France) to perform simultaneous DLS and XRPD data acquisitions. The XRPD system is based on a parallel-beam capillary geometry, with a flat image plate detector that translates during the experiment to obtain time resolution [2].

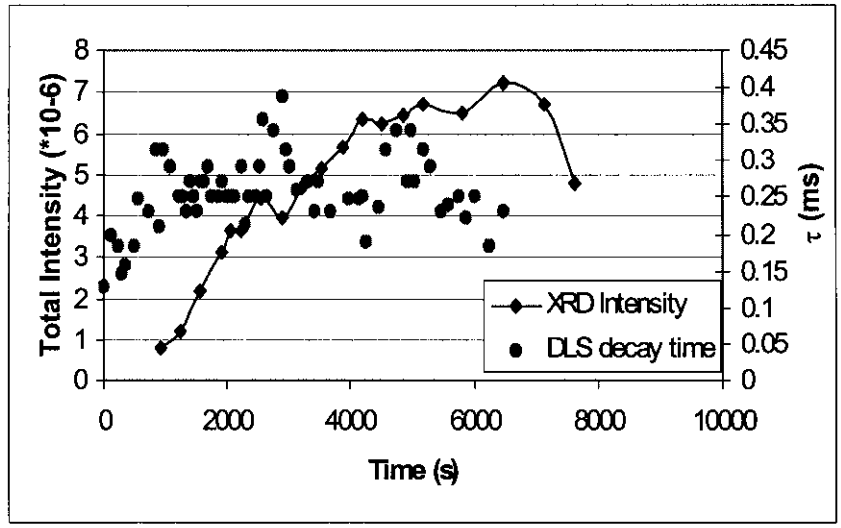

Fig. 1: Time evolution of zeolite A crystallisation in capillary at 80°C: τ is the decay time of the auto-correlation function measured by DLS, and it is proportional to the average particle size. XRD intensity refers to the integrated intensity of the diffraction peaks of the zeolite A, proportional to the total amount of zeolite produced.

Experiments performed using combined DLS and synchrotron XRPD indicate that aggregates were already present at the beginning of the experiments. DLS data recorded during an isothermal synthesis at 80°C are shown in Fig. 1. The aggregate growth starts immediately (0-900 s). Then the aggregate apparent size remains almost constant (900-2200 s) and successively it increases further (2200-2800 s).
The XRPD data allow quantitative evaluation of the kinetic parameters of the zeolite-A nucleation and growth. The results of experiments performed at 60-70-80-90 °C clearly indicate that the heterogeneous nucleation of the zeolite has a constant nucleation (q in the range 0.8-1.2) and a linear volume growth in time. Synchronization of the DLS and XRPD experiments indicate that the aggregates present in the early stages of the process are not crystalline, and that the amorphous phase initially aggregates and grows, then it dissolves successively, when the crystalline nuclei of the zeolite appear. It is quite clear from the extracted kinetic parameters (Fig. 2) that the liquid-amorphous interface do not supply additional nucleation sites, as it is the general case in autocatalytic processes.

The obtained results from the combined DLS and XRPD experiments are very interesting and allow a detailed intepretation of the early stages of the nucleation processes. The amorphous phase that is undetected by diffraction may play a role in the depletion and succesive release of nutrients from the solution, and thus control the nucleation process in the induction stage.
More experiments, using solutions with different aging times will be performed to clarify the role of the amorphous phase. It the future experiments a different heating technique will be used to keep the capillary in isothermal conditions, to avoid all possible sources of artifacts due to the gas blower. A static heating device based on a resistance heater has been designed and it will be soon tested.

1. R. Aiello, F. Testa, L. Maiorino, J.B. Nagy, Influence of the aging on the crystallization of zeolite A from clear solutions, submitted to Microgravity Quarterly.
2. C. Meneghini, G. Artioli, P. Norby, A. Balerna, A. Gualtieri, S. Mobilio, A new Translating Image Plate camera for in situ studies at the ESRF GILDA beamline, submitted to Journal of Synchrotron Radiation.

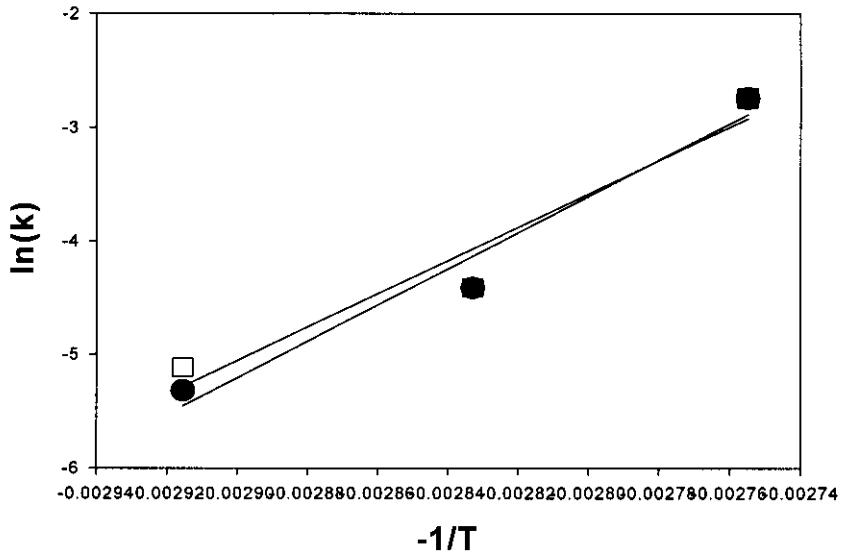

Fig. 2. Arrhenius plot derived from the isothermal synchrotron XRPD data. Preliminary values for the apparent nucleation energy are 29-32 kcal/mole.