



Experiment title: Determination of particle size distribution and crystallisation rates in hydrothermal synthesis of microporous and layered materials using combined high and medium resolved *in-situ* powder diffraction.

Experiment number:
CH-610

Beamline:

BM16

Date of experiment:

from: 28-4 1999 to: 2-5 1999

Date of report:

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Shifts: 12

Local contact(s): Andy Fitch

Received at ESRF:

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Report:

In-situ time- and temperature-resolved experiments have in the last years proven to be a powerful method for investigation of chemical reactions involving crystalline materials such as cation migration in zeolites¹, intercalation reactions², phase transitions and thermal transformations³⁻⁴, and hydrothermal synthesis of microporous materials⁵⁻⁷. When taking advantage of high intensity X-ray synchrotron radiation, combined with fast 1- or 2-dimensional detectors even quite fast chemical reactions can be studied.

The aim of the present experiment was to follow the crystallisation kinetics and determine the crystallite size distribution as a function of time during hydrothermal synthesis, using combined high and medium resolution data. Preliminary results for the kinetics of the crystallisation of the layered phosphate, α -Ti(HPO₄)₂·H₂O, are presented in the following.

A capillary based micro reaction cell developed for *in-situ* studies of hydrothermal crystallisation and chemical reactions⁸ was used. The reaction cell consists of a quartz capillary (0.7-1 mm with wall-thickness of 0.01 mm) mounted using a ferrule in a Swagelok T-piece. The T-piece is mounted on a goniometer head. For hydrothermal synthesis a closed capillary is used and a nitrogen pressure is applied from a cylinder to create hydrothermal conditions. With quartz capillaries pressures up to 45 atm. can be applied, allowing for synthesis temperatures up to 260°C. The reaction mixture consisted of amorphous titanium phosphate mixed with phosphoric acid (85 %). The samples were heated using a hot air blower. The heated area was kept larger than the size of the X-ray beam to avoid problems

with thermal gradients across the sample. Data were collected at 7 temperatures in the range 80-200°C.

The crystallisation curves were obtained by integrating 3-5 selected diffraction peaks using the program PeakFit. The integrated areas of the selected reflections were added and normalised to represent the percentage of crystallisation. The crystallisation curves were fitted using a first order rate equation, $\alpha=100(1-\exp(-k(t-t_0)))$, where k is a rate constant and t_0 is the starting time of the crystallisation. Fig. 1 shows a crystallisation curve for a synthesis performed at 110°C.

The rate constants obtained at different synthesis temperatures were then plotted in an Arrhenius-type plot which is shown in Fig. 2. The apparent activation energy (E_A) for the crystallisation of $\alpha\text{-Ti}(\text{HPO}_4)_2\cdot\text{H}_2\text{O}$ was then determined from the slope of the regression lines ($-E_A/R$).

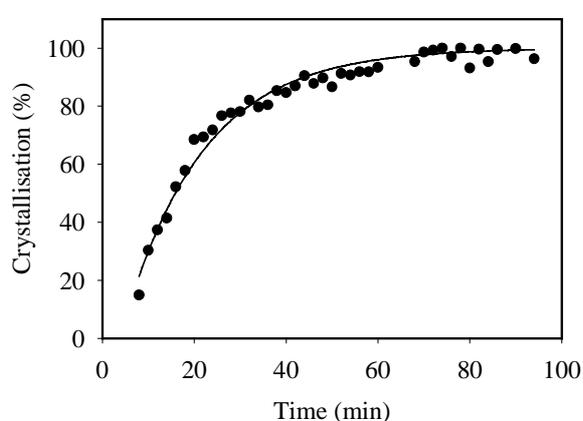


Fig. 1 Crystallisation curve for synthesis at 110°C

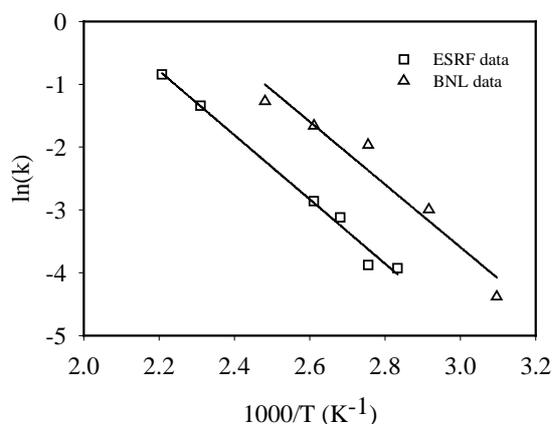


Fig. 2 Arrhenius plot

The data recorded at BM16 gives an activation energy of 42.6 KJ/mol. Preliminary data obtained at NSLS, BNL (see Fig. 2) give a similar activation energy (41.6KJ/mol), indicating that the crystallisation mechanism is the same in the two experiments. However, as can be seen from Fig. 2, the crystallisation rate is different. Further experiments are necessary to clarify the reason for this difference. The reason might be differences in preparation of the reaction mixture.

Counting statistics on the high resolution data did not allow a detailed analysis of the crystallite size distribution. However, a narrowing of the diffraction peaks was observed as a function of time. Further analysis of the data is in progress

References:

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