



	Experiment title: <b>In situ EXAFS and XANES investigation of the hydrothermal crystallisation of two AFI-type metalloaluminophosphates CoAPO-5 and CrAPO-5</b>	<b>Experiment number:</b> <b>26-01-707</b>
<b>Beamline: BM26A</b>	<b>Date(s) of experiment:</b> From: 07-07-2004  To: 10-07-2004	<b>Date of report:</b> 06-09-2004
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### Report:

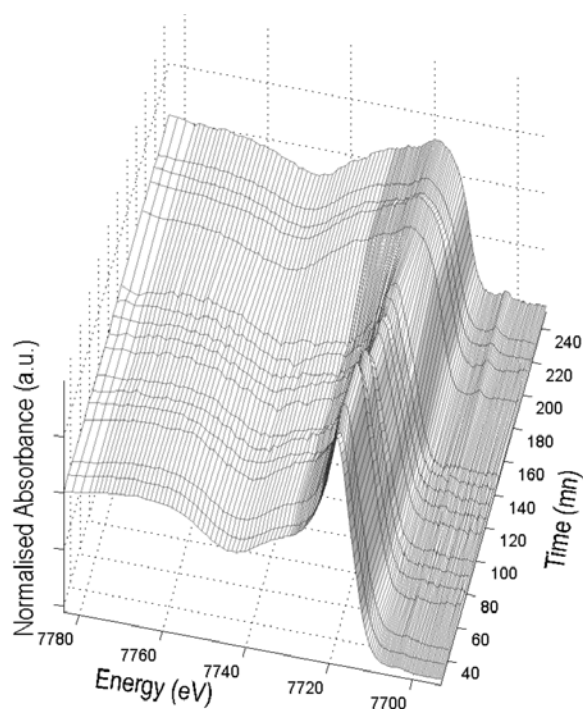
The understanding of the principles that determine how porous crystalline materials such as zeolites or aluminophosphates are formed starting from a precursor gel, under hydrothermal conditions (i.e. high temperatures and pressures), is of considerable fundamental interest because it could lead to a more rational approach towards molecular sieves. In the class of microporous materials, metalloaluminophosphates CoAPO-5 and CrAPO-5 (AFI crystalline structure) prepared with the classical triethylamine (TEA) templated gel have been extensively investigated and all studies agree that  $\text{Co}^{2+}$  is incorporated in place of  $\text{Al}^{3+}$  inside the aluminophosphate framework adopting a tetrahedral geometry whilst Cr is only anchored at the surface of the pore. CrAPO-5 with  $\text{Cr}^{3+}$  substituted into the framework has been prepared only recently by adding co-template molecules (acetate) into the starting TEA templated gel.

The objective of this experiment was to use for the first time time-resolved XANES/EXAFS to follow *in situ* the crystallisation of CoAPO-5 and CrAPO-5 metalloaluminophosphates at the Co or Cr K-edge. In order to perform a full comparison two CrAPO-5, one prepared with a classical TEA templated gel and the other with a co-templated gel have been investigated. This experiment have been complemented by an SAXS/WAXS experiment carried out at Dubble [**exp 26-02-230**] on the same systems and in the same conditions, to focus more specifically on the possible formation and arrangement of particles and/or primary units blocks in the colloidal mixture together with the onset of crystallisation.

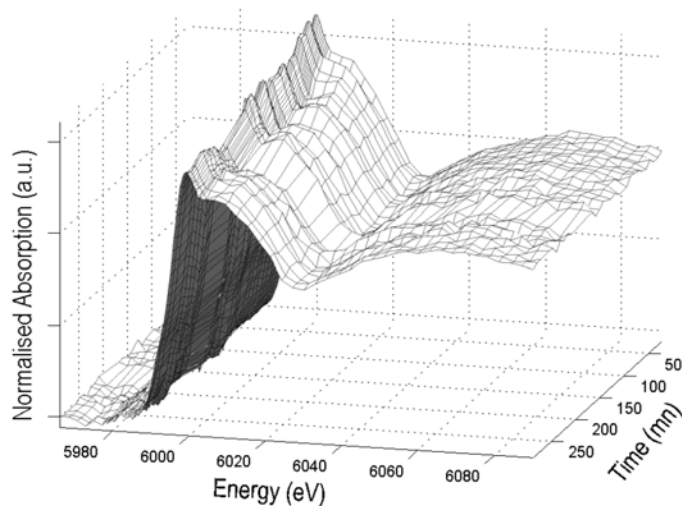
XANES/EXAFS measurements were carried out in a cell made by assembling 2 circular pieces of stainless steel (45mm diameter) each one fitted with a circular mica window (5mm diameter) and separated by one Teflon spacers (0.75mm thick). The cell was heated in an aluminium thermo-regulated block at a rate of one degree per minute up to 180°C and remained at this temperature for up to 4h under autogeneous pressure and static conditions. All crystallisations could be measure successfully using XANES short scans of 7-8 mn. However longer EXAFS measurements (30-40mn) turned out to be much more difficult to achieve due to the fast macroscopic changes (density and homogeneity) occurring in the sample during the hydrothermal process. Quick-EXAFS mode that will be soon available at Dubble and allow to acquire a full EXAFS scan in less than 2-3mn will certainly be much more suited to measuring EXAFS in these *in situ* processes. In addition we were unable to identify with precision the onset of crystallisation as

originally planned because the combination of time-resolved XAS and diffraction measurement was not available. Samples were however checked with diffraction after crystallisation using an INEL detector to verify that the AFI structure was formed.

Time-resolved normalised XANES spectra obtained during the crystallisation of CoAPO-5 and CrAPO-5 (co-templated gel) are respectively presented in Figure 1 and 2. Figure 1 clearly shows the large transformations that are affecting the XANES spectra at Co K-edge during the crystallisation. With increasing reaction times the sharp whiteline is clearly transformed into a more rounded shape pattern whilst at the same time a pre-edge feature is building up. These two changes demonstrate the transformation of the 6-fold coordination of Co in the gel into a 4-fold coordination in the CoAPO5 crystalline phase. This transformation seems to occur concomitantly to the onset of crystallisation.



**Fig 1:** Normalised time-resolved *in situ* XANES spectra recorded during CoAPO-5 crystallisation.



**Fig2:** Normalised time-resolved *in situ* XANES spectra recorded during CrAPO-5 (co-templated gel) crystallisation.

Figure 2 presents the time-resolved XANES spectra at Cr K-edge during the crystallisation process of CrAPO5 prepared with a co-templated gel. The changes affecting the XANES pattern are in this case not as dramatic as in the case of CoAPO5 whilst no extra features are appearing in the pre-edge region. These observations indicate that Cr keeps a 6-fold coordination during all the process of the crystallisation. However, changes in the resonance peak located at 20-30eV after the edge indicate that fine structural changes in Cr environment are certainly occurring in the process.

These preliminary results already show that very valuable information on the crystallisation mechanism of metalloaluminophosphates will be gained from these measurements when the full analysis of the data will be completed.