DUBBLE	Experiment title: **In situ SAXS and WAXS investigation of the hydrothermal crystallisation of two AFI-type Metalloaluminophosphates CoAPO-5 and CrAPO-5**	**Experiment number**: **26-02-230**
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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 Co^{2+} is incorporated in place of Al^{3+} inside the aluminophosphate framework adopting a tetrahedral geometry whilst Cr is only anchored at the surface of the pore. CrAPO-5 with 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 SAXS/WAXS to follow *in situ* the formation and the arrangement of gel particles and/or primary unit blocks in the colloidal mixture together with the onset of crystallisation during the hydrothermal synthesis of CoAPO-5 and CrAPO-5 metalloaluminophosphates. In order to perform a full comparison, a pure $AlPO_4$-5 as well as 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 XANES/EXAFS experiment carried out at Dubble [**exp 26-01-707**] on the same systems and in the same conditions at the Co or Cr K-edge, to focus more specifically on the evolution of the coordination and oxidation state of the transition metals during the crystallisation process.

SAXS/WAXS 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 (5 mm diameter) and separated by a Teflon spacer (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. SAXS patterns were collected in two separate runs at two different sample-detector distance of 1 and 8m corresponding respectively to k ranges of $0.1<k<10nm^{-1}$ (smaller particles <15nm) and $0.01<k<1nm^{-1}$ (larger particles <600nm). In addition, the WAXS detector was used to record the high-order Bragg reflections of the AFI crystalline structure. All crystallisations could be measured successfully

using the sample-detector distance of 1m and the data obtained were in general of good quality. However, difficulties appeared when a longer sample-detector distance of 8m was used, due to focusing problems of the beam on the sample.

SAXS /WAXS data are being currently analysed in order to identify the possible presence of precursors in the gel before crystallisation occurs as well as the type of kinetics involved in the process. However, raw SAXS and WAXS patterns plotted as a function of the reaction time can already show that measurements have been successful in showing the onset of crystallisation that is occurring at a temperature varying from 151ºC in the pure $AlPO_4$-5 to 180ºC in CrAPO-5 prepared with the classical gel method. It is also clear that no intermediate crystalline phase is formed before the Bragg reflections of the AFI crystalline structure appear both in the SAXS and in the WAXS patterns.

Figure 1 and 2 respectively present the raw time-resolved SAXS and WAXS pattern obtained during the crystallisation of CrAPO-5 with a co-templated gel.

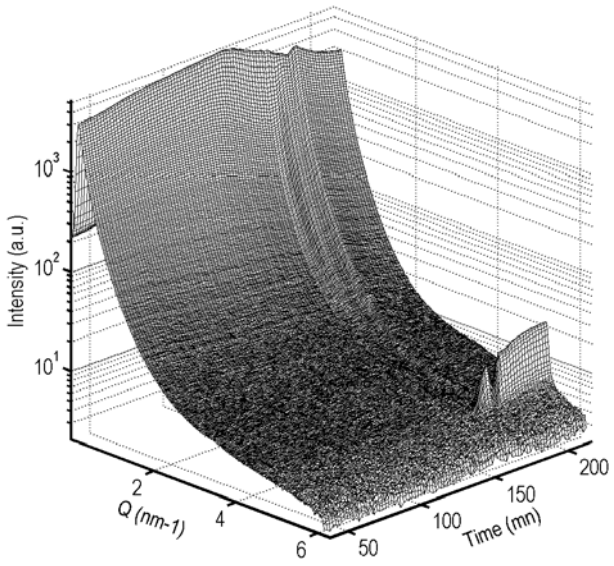

Fig 1: Time resolved SAXS pattern of CrAPO-5 crystallisation with a co-templated gel.

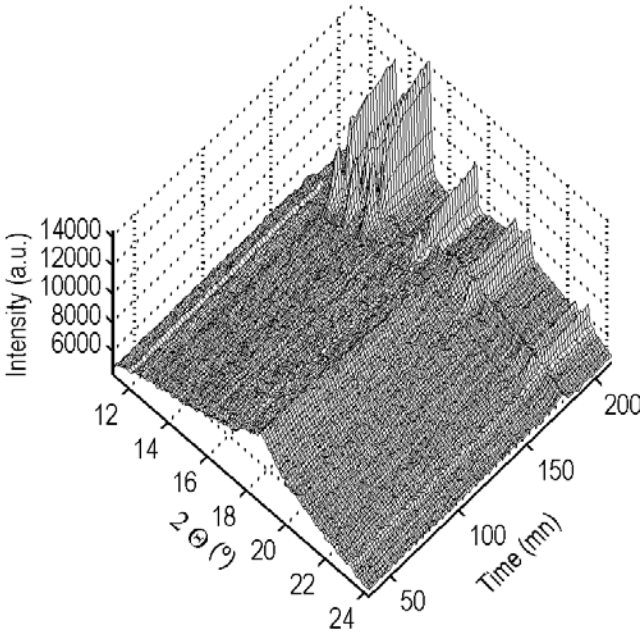

Fig 2: Time resolved WAXS pattern of CrAPO-5 crystallisation with a co-templated gel.

Figure 1 clearly shows the transformations affecting the SAXS pattern before and during the crystallisation process. The occurrence of the first Bragg reflection (100) corresponding to the largest d-spacing (11.94 Å) of the AFI structure is an accurate indication of the onset of crystallisation. In Figure 2 all Bragg reflections at wide angles correspond to the AFI crystalline phase. No reflections belonging to any other crystalline phase can be seen in the diffraction pattern proving the successful crystallisation of the AFI structure.

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.