Formation of an intermediate during the hydrothermal synthesis of ULM-5 studied using time-resolved, *in situ* X-ray powder diffraction†

Robin J. Francis,[a] Stephen J. Price,[a] Stephen O'Brien,[a] Andrew M. Fogg,[a] Dermot O'Hare,*[a]‡ Thierry Loiseau[b] and Gerard Férey[b]

[a] *Inorganic Chemistry Laboratory, University of Oxford, South Parks Road, Oxford, UK OX1 3QR*
[b] *Institut Lavoisier, IREM UMR C 173, Université de Versailles, 45 Avenue des Etat-Unis, 78035 Versailles, France*

***In situ* energy dispersive X-ray diffraction studies on the hydrothermal synthesis of the oxyfluorinated gallophosphate, ULM-5, show that when orthophosphoric acid is used as a starting material ULM-5 forms rapidly after an initial induction period, whereas when phosphorus pentoxide is used as a starting material a previously unobserved crystalline intermediate is formed, which subsequently reacts to form ULM-5; conditions have been identified in which this intermediate is relatively long lived and this has allowed the subsequent isolation of a pure sample of this intermediate.**

Microporous materials are an academically and industrially important class of materials due to their great utility as catalysts and absorbents.[1,2] These properties arise from their unique three-dimensional open-framework structures which consist of a regular array of uniform pores and channels. ULM-5 is a microporous oxyfluorinated gallophosphate $\{Ga_{16}(HPO_4)_{14}(PO_4)_2(OH)_2F_7\cdot 4NH_3CH_2CH_2NH_3\cdot 6H_2O\}$ containing large 16-membered rings and interconnecting 8-membered rings.[3] The 16-membered rings form oval channels with a free aperture of 12.20 × 8.34 Å. ULM-5 is synthesised hydrothermally; gallium oxide, a phosphorus source and hydrofluoric acid are reacted in water at 180 °C in the presence of the templating agent 1,6-diaminohexane.

Over the past few years much interest has focused on the synthesis of new open-framework materials with particular catalytic and ion-exchange properties. Unfortunately, although some mechanistic theories have been proposed,[4,5] the synthesis of new structure types is hampered by the fact that the fundamental processes occurring during hydrothermal syntheses are not well understood, and there is very little knowledge of the transformations occurring during the formation of the product phase. In an effort to gain a greater understanding of these reactions we have recently developed an apparatus capable of studying hydrothermal reactions *in situ*, using time-resolved energy dispersive synchrotron X-ray diffraction (EDXRD).[6,7] As has been pointed out by ourselves and others previously,[6–9] such non-invasive *in situ* measurements offer many advantages over other *ex-situ* techniques, since they allow the direct observation of crystalline intermediate and product phases, which avoids the possibly complicating effects of sample work-up.

As part of our on-going program of studying hydrothermal syntheses of microporous materials *in situ*, we have undertaken a study of the formation of ULM-5 under a variety of synthetic conditions in order to gain a greater understanding of the dynamics of crystal growth and nucleation. Here we report the importance of the phosphorus source on the reaction pathway, and the observation of the formation of a crystalline intermediate phase when phosphorus pentoxide is used as the source.

All reactions were performed using a reaction mixture of initial composition $Ga_2O_3:P_2O_5:2HF:1,6DAH:80H_2O$. Using orthophosphoric acid as the phosphorus source there is a short induction period, which presumably is partially due to reactant dissolution and partially due to a build up in pressure, after which pure ULM-5 is observed to rapidly and smoothly crystallise. No crystalline intermediates are observed to form at any stage. A plot of the integrated intensity of the 002 reflection is shown in Fig. 1. The main feature of note is the extremely rapid nature of the crystallisation after the induction period. The half-life of crystallisation at this temperature is under 1 min, and the reaction is essentially over 40 min after the onset of crystallisation. Initial analysis of the kinetic data suggests that the formation of ULM-5 under these conditions is an essentially diffusion limited process. We have also performed this reaction at other temperatures down to 130 °C, and whilst there is a general trend to longer induction times at lower temperatures the crystallisation kinetics after induction are essentially identical over this temperature range.

However, dramatically different behaviour was observed when the reaction was performed under identical conditions except for the replacement of orthophosphoric acid with phosphorus pentoxide as the phosphorus source. Under these conditions a highly crystalline intermediate phase is observed to form which then subsequently reacts to form ULM-5. The course of the reaction at 180 °C is shown as a three-dimensional plot in Fig. 2, and a plot of the integrated intensity of the 13.1 Å reflection and the ULM-5 final product 002 reflection is shown in Fig. 3. As can be seen from Fig. 3 after an induction time of approximately 5 min, the intermediate forms rapidly, the intensity of the diffraction peaks reaching a maximum intensity after just 15 min. The intensity of these peaks then immediately begins to decrease together with concomitant growth of peaks belonging to the product (ULM-5). Although not conclusive, the high degree of correlation between the decay of the intermediate and growth of the product peaks is good evidence for the two phases being related, and the intermediate phase directly converting into the final product. The transformation is much slower than both the initial formation of the intermediate

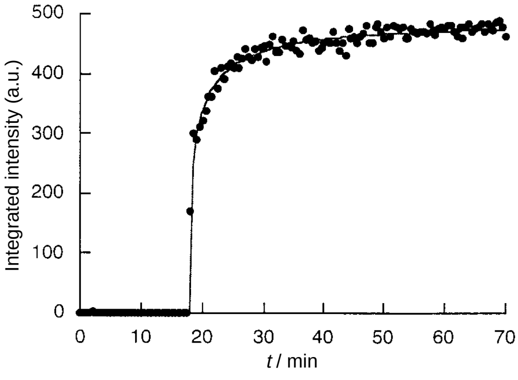

Fig. 1 Plot of intensity of the (002) Bragg reflection of ULM-5 as a function of time using orthophosphoric acid as a starting material. The solid line is a fit to the Avrami equation $I = A\exp[-k(t - t_0)]^{0.4}$, where t_0 is the induction time.

and the formation of ULM-5 when orthophosphoric acid is used as a starting material, taking over 2 h to go to completion.

The same reaction was also performed at lower temperatures. Broadly similar behaviour was observed; an intermediate being formed which converts to the final product. However, although the initial growth occurs at virtually the same rate, the transformation to product was much slower at lower temperatures. At 150 °C the beginnings of a 'plateau' in the intensity of the intermediate peak could be seen, and by 130 °C this plateau in intensity is pronounced, with the intermediate being stable for approximately 30 min. Conversion into the final product does not occur until after 40 min into the reaction at this temperature.

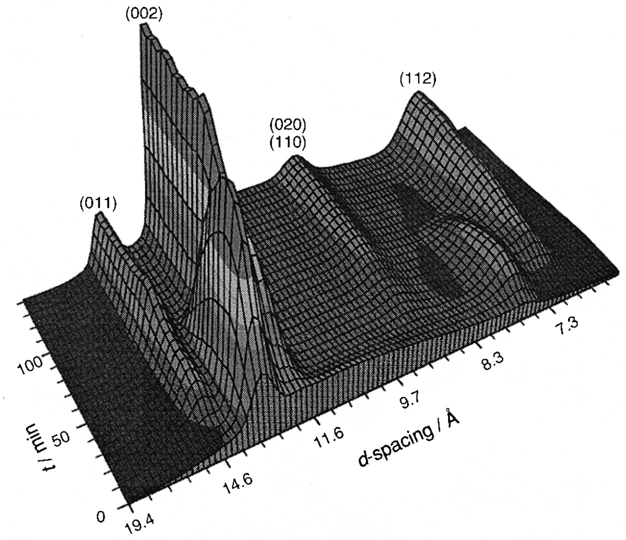

Fig. 2 Three-dimensional plot showing the EDXRD spectra as a function of time during the synthesis of ULM-5 using phosphorus pentoxide as a starting material. The peak labels correspond to the indices of the Bragg reflections of ULM-5. The experiments were performed on station 16.4 of the UK SRS at Daresbury Laboratory, Warrington. Each spectrum was acquired in 60 s at a diffraction angle of $2\theta = 1.22°$. Details of the experimental apparatus and station design have been published previously.[6,10]

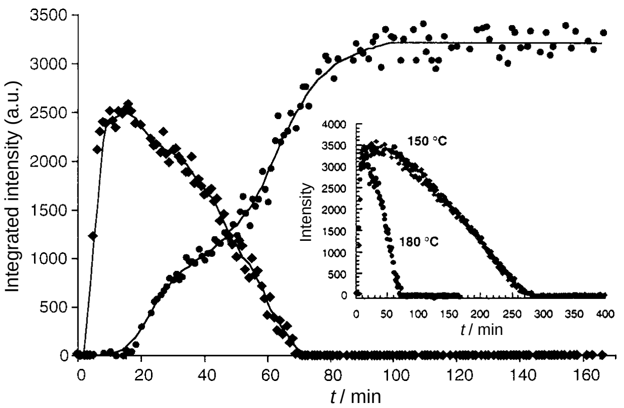

Fig. 3 Plot of the intensity of the (100) Bragg reflection of the intermediate (◆) and the (002) Bragg reflection (●) of ULM-5 as a function of temperature at 180 °C. Solid lines are for guidance only and have no physical significance. Inset: Plot of intensity of the (100) reflection of the intermediate at 180 and 150 °C.

The determination of conditions in which the intermediate is relatively stable opened up the possibility of isolation of this material by quenching of the reaction during the early stages before the conversion to the final product has begun, assuming that the material does not transform during the quenching procedure. In an attempt to do this another reaction was performed at 150 °C in which the reaction cell was removed from the heating block when the diffraction peaks due to the intermediate were observed to reach the maximum intensity, and the cell was then quenched with cold water. Powder X-ray diffraction of the material obtained from the quenched autoclave showed that the intermediate phase had indeed been successfully isolated. The X-ray diffraction pattern of this isolated phase could be tentatively indexed on the orthorhombic cell with lattice parameters $a = 20.274$, $b = 13.125$, $c = 24.550$ Å. Interestingly, two of these parameters are closely related to two of the cell parameters in ULM-5 which is also orthorhombic with $a = 10.252$, $b = 18.409$ and $c = 24.639$ Å (*i.e.* $a' \approx 2a$ and $c' \approx c$). This suggests that the two materials may be closely structurally related. Structural studies on this material are being carried out in order to determine the relationship between this material and ULM-5, but these have been hampered by the fact that the isolated product is metastable and transforms to another unknown material on standing for a few days at room temperature.

In conclusion, these *in situ* experiments are a dramatic illustration of the complexity of hydrothermal syntheses, and how subtle changes in the reaction conditions, such as the use of slightly different starting materials, can greatly affect the course of these reactions. It also demonstrates the unique ability of *in situ* experiments to gain information not available using other techniques.

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Footnotes

† This ChemComm is also available in enhanced multi-media format *via* the World Wide Web: http://chemistry.rsc.org/rsc/cccenha.htm

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