Direct \textit{in situ} observation of increasing structural dimensionality during the hydrothermal formation of open-framework zinc phosphates

Richard I. Walton,* Alexander J. Norquist,† S. Neeraj,‡ Srinivasan Natarajan,§ C. N. R. Rao∥ and Dermot O’Hare‡

\textsuperscript{a} School of Chemistry, Stocker Road, University of Exeter, Exeter, UK EX4 4QD
\textsuperscript{b} Inorganic Chemistry Laboratory, South Parks Road, Oxford, UK OX1 3QR
E-mail: dermot.o hare@chem.ox.ac.uk
\textsuperscript{c} Chemistry and Physics of Materials Unit, Jawaharlal Nehru Centre for Advanced Scientific Research, Jakkur PO, Bangalore, 560 064, India

Received (in Cambridge, UK) 27th June 2001, Accepted 10th August 2001

First published as an Advance Article on the web 18th September 2001

The first time-resolved \textit{in situ} X-ray diffraction studies of the hydrothermal crystallisation of open-framework zinc phosphates reveal a pathway of sequential crystallisation involving formation of a metastable low dimensional chain phase before the growth of three-dimensional zeolitic architectures.

A great deal of effort is currently focussed on understanding the crystallisation mechanism of microporous solids which can have applications in shape-selective catalysis, separation science, and ion-exchange. It is hoped that an understanding of mechanisms leading to the formation of these zeolite-like solids at the atomic-scale will allow the rational synthesis of new materials.\textsuperscript{1,2} The common use of hydrothermal synthesis conditions in the preparation of such open-framework solids requires sealed thick-walled reaction vessels and it is only in recent years that \textit{in situ} probes of hydrothermal crystallisation have been developed to follow reactions under these experimentally-challenging conditions.\textsuperscript{3} For example, in a study of the phosphates of gallium using energy-dispersive X-ray diffraction (EDXRD) some of us have observed previously-unknown, transient phases prior to the onset of crystallisation of open-framework phases,\textsuperscript{4,5} and Taulelle \textit{et al.} have identified oligomeric ‘building blocks’ in hydrothermal reaction solutions using NMR spectroscopy.\textsuperscript{6} The results of such studies provide a foundation on which to build descriptions of reaction mechanisms.

The first results of an \textit{in situ} EDXRD study of the hydrothermal synthesis of zinc phosphates are described here. This large family of solids has recently been the focus of study by some of us, and an Aufbau principle for the building up of three-dimensional structures from structures of lower dimensionalities proposed.\textsuperscript{7} With an aim of gaining further information about crystallisation mechanisms it is crucial to study systems such as these using \textit{in situ} measurements of crystallisation, since it has been established that on arresting a hydrothermal reaction by cooling to room temperature the material recovered is not necessarily representative of the material present under reaction conditions.\textsuperscript{8,5} The EDXRD method uses intense synchrotron X-rays which allows the use of a laboratory-sized hydrothermal reaction vessel, mimicking the conditions employed in the synthetic laboratory and permitting rapid data collection (<1 min) for kinetic studies. An apparatus developed over the past few years by O’Hare and co-workers\textsuperscript{8} was used in the current work.

In the first zinc phosphate system studied we focussed on the reaction between piperazine phosphate ([C\textsubscript{4}N\textsubscript{2}H\textsubscript{12}][HPO\textsubscript{4}]·H\textsubscript{2}O, PIP-P) and zinc oxide in dilute hydrochloric acid solution. Fig. 1 shows a stack plot of the time-resolved EDXRD data measured during the sequential crystallisation of zinc phosphates from the reaction mixture ZnO:1.5 HCl:1.75 PIP-P:100 H\textsubscript{2}O which was heated to 180 °C in an autoclave at ca. 5 °C min\textsuperscript{-1} (detector angle 0.9325°). The use of a three-element energy discriminating detector system\textsuperscript{9} allows unambiguous identification of known crystalline phases, owing to the large amount of diffraction data that can be simultaneously recorded.\textsuperscript{10} Characteristic Bragg reflections of the phosphite and amine source, PIP-P, are observed only during the first minute before disappearing; presumably this is due to dissolution of this rather soluble species. Remarkably, we observe that characteristic Bragg reflections of a known zinc phosphate, [C\textsubscript{4}N\textsubscript{2}H\textsubscript{12}][Zn(HPO\textsubscript{4})\textsubscript{2}(H\textsubscript{2}O)] (ZnPO–PIP-I),\textsuperscript{11} are present in the first spectrum recorded (31 °C), suggesting that this material forms on mixing the chemicals at room temperature. The compound has a 1-D ladder structure (see Table 1 for descriptions of the phases discussed in this paper). After heating to 163 °C new strong Bragg reflections (of a phase not yet identified) are apparent, and these diffraction features, along with those of ZnPO–PIP-I, have constant intensity for 30 min during which time a temperature of 180 °C is reached. Over a period of 10 min, these two phases and the starting material ZnO are replaced by two known zinc phosphates, [C\textsubscript{4}N\textsubscript{2}H\textsubscript{12}][Zn\textsubscript{1.5}(PO\textsubscript{4})\textsubscript{3}(H\textsubscript{2}O)] (ZnPO–PIP-II)\textsuperscript{11,12} and [C\textsubscript{4}N\textsubscript{2}H\textsubscript{12}][Zn\textsubscript{3.5}(PO\textsubscript{4})\textsubscript{3}(H\textsubscript{2}O)\textsubscript{2}] (ZnPO–PIP-III),\textsuperscript{11} which are the sole two products after 145 min of heating. ZnPO–PIP-II and ZnPO–PIP-III both have three-dimensional framework structures.

On changing the amount of PIP-P we observed rather different behaviour. For a mixture of composition ZnO:1.5 HCl:1.75 PIP-P:100 H\textsubscript{2}O, held at a constant temperature of 180 °C, the ladder phase ZnPO–PIP-I is present in the first spectrum
observed of these crystallisation studies is that for the first time we have unexpected to discover new metastable phases. The importance unknown structures form during the reactions. Given the huge observed. In certain cases, crystalline materials with as-yet

tion of a number of open-framework solids was directly

The dissolution of starting materials and sequential crystallisa-

tion of materials with increasing dimensionality. Recently it

studies to survey other ZnPO/amine systems in order to understand more fully the nature of the structural transforma-

tions taking place.

We thank the EPRSC for funding and provision of beam-time at SRS, Daresbury Laboratory.

Notes and references
†EDXR D experiments were performed on Station 16.4 of the Daresbury Synchrotron Radiation Source (I ~ 200 mA, ~2 GeV synchrotron). Station 16.4 was illuminated with X-rays in the energy range 5–120 keV from a 6 T superconducting wiggler insertion device. Diffacted X-rays were measured using a three-element germanium solid-state detector; this allowed access to three d-spacing ranges, dependent on the angle to which the detector was set. The delay between mixing reagents, sealing in the hydrothermal autoclave and beginning data collection was of the order of 5 min.


<table>
<thead>
<tr>
<th>Compound (dimensionality)</th>
<th>Formula</th>
<th>Miller index, observed d (expected)/Å</th>
<th>Lowest EDXRD detector at 0.9325(^{a})</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnPO–PIP–I(^{a}) (1-D)</td>
<td>([\text{C}_6\text{N}<em>2\text{H}</em>{12}][\text{Zn}(\text{HPO}_4)\text{Zn}(\text{H}_2\text{O})])</td>
<td>011, 7.77 (7.333)</td>
<td>200, 7.05 (7.012)</td>
</tr>
<tr>
<td>ZnPO–PIP–II(^{a}) (3-D)</td>
<td>([\text{C}_6\text{N}<em>2\text{H}</em>{12}][\text{Zn}(\text{HPO}_4)\text{Zn}(\text{H}_2\text{O})])</td>
<td>020, 7.05 (7.813)</td>
<td>200, 7.05 (7.012)</td>
</tr>
<tr>
<td>ZnPO–PIP–III(^{a}) (3-D)</td>
<td>([\text{C}_6\text{N}<em>2\text{H}</em>{12}][\text{Zn}(\text{HPO}_4)\text{Zn}(\text{H}_2\text{O})])</td>
<td>110, 7.30 (7.300)</td>
<td>200, 7.05 (7.012)</td>
</tr>
<tr>
<td>ZnPO–PIP–IV(^{a}) (3-D)</td>
<td>([\text{C}_6\text{N}<em>2\text{H}</em>{12}][\text{Zn}(\text{HPO}_4)\text{Zn}(\text{H}_2\text{O})])</td>
<td>111, 6.74 (6.717)</td>
<td>200, 7.05 (7.012)</td>
</tr>
</tbody>
</table>

\(^{a}\) Ref. 11 \(^{a}\) Ref. 12. \(^{c}\) Bottom EDXRD detection.