

***In Situ* Single-Crystal X-ray Diffraction Study of Crystallization Kinetics in Clathrasil Dodecasil-3C**

Russell E. Morris,^a Scott J. Weigel,^b Poul Norby,^c Jonathan C. Hanson^c and Anthony K. Cheetham^b

^aSchool of Chemistry, Purdie Building, University of St Andrews, St Andrews KY16 9ST, UK, ^bMaterials Research Laboratory, University of California, Santa Barbara, CA 93106, USA, and ^cDepartment of Chemistry, Brookhaven National Laboratory, Upton, NY 11973, USA. E-mail: rem1@st-and.ac.uk

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The formation of single crystals of the clathrasil dodecasil-3C from a solvothermal synthesis has been followed by *in situ* diffraction techniques using synchrotron radiation and an image-plate area detector. The high intensity of the X-ray beam, coupled with the ability to record time-resolved two-dimensional data using the image plates, allowed the crystallization kinetics to be studied and rate expressions to be fitted to the crystallization curves.

Keywords: *in situ* X-ray diffraction; zeolite synthesis; crystallization kinetics.

1. Introduction

The study of zeolite formation is important in order both to optimize the synthetic conditions for industrial production and to gain mechanistic information that may facilitate the design of new zeolitic materials. The kinetic study of crystallization processes using diffraction techniques has often been carried out on quenched samples. This approach is less than ideal for a number of reasons, not least because the quenched samples may not accurately represent the high-temperature situation. Recently, with the advent of more intense radiation sources, *in situ* diffraction experiments on the crystallization of polycrystalline samples using both rotating-anode and synchrotron sources have been accomplished, including two early studies using energy dispersive X-ray diffraction on the synthesis and phase transformations of a number of zeolites (Munn, Barnes, Hauserman, Axon & Klinowski, 1992; He, Barnes, Munn, Turrillis & Klinowski, 1992). More recently, Wilkinson, Speck, Cheetham, Natarajan & Thomas (1994) have studied the formation of $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_5$ materials from alkoxide precursors, while Norby, Christensen & Hanson (1994) and Rey *et al.* (1995) have studied the crystallization of zeolite-A and Co-AIPO-5 from hydrothermal preparations. However, studies of the formation of single crystals, as opposed to powders, from hydrothermal syntheses have, as far as the authors are aware, not been performed prior to this study.

Image-plate area detectors, although not inherently suited to time-resolved studies, can be utilized for such experiments by mechanically (or manually) moving them between or during X-ray exposures. Their high count-rate capability, together with high quantum efficiency and wide dynamic

range, makes them particularly suited for use at synchrotron X-ray sources, especially for the collection of single-crystal data.

This communication reports the use of synchrotron X-ray diffraction with image-plate area detectors to study the formation of large single crystals of the clathrasil dodecasil-3C (MTN). The synthesis, first reported by Kuperman *et al.* (1993), involves the competitive formation of a purely siliceous zeolite, ferrierite (FER), and MTN, both of which form large single crystals. We have recently undertaken an extensive study of the synthesis in order to elucidate the mechanism of the reaction, especially the effect of the organic templating molecules on the final crystal structure (Weigel *et al.*, 1996).

2. Experimental

All experiments were performed on instrument X7B at NLSL. The beamline has focused beam optics with a spherical pre-mirror, a double-crystal Si monochromator and a cylindrical focusing mirror (Hastings, Suortti, Thomlinson, Kvik & Koetzle, 1983). The wavelength used in the experiment was 1.1056 Å.

The synthesis gel, of composition $\text{SiO}_2\text{-HF/pyridine-H}_2\text{O-propylamine-pyridine}$ (1.5:2:4:8:16), was prepared as described by Morris *et al.* (1994), aged at room temperature for 1 week, and then poured into a 0.5 mm quartz glass capillary using a fine syringe. The capillary was mounted in a Swagelock fitting using a Vespel ferrule. The fitting was mounted on a goniometer head as illustrated in Fig. 1, and a pressure of 500 psi was applied through the connecting tube

using nitrogen gas. The capillary was heated using a hot-air blower positioned ~ 3 mm below the sample (Norby, 1996). A thermocouple was mounted between the air blower and the capillary and the temperature was calibrated using the thermal expansion of a silver powder sample. The hot zone was ~ 5 mm long. A narrow beam (size 0.5×2 mm) was used in order to minimize the thermal gradient over the illuminated part of the sample.

The detector was a flat 200×400 mm flexible Fuji imaging plate mounted perpendicular to the incoming beam at a distance of 200 mm from the sample. The sample-detector distance, the tilt angle and the zero point were determined from a powder pattern of LaB_6 (Norby, Hanson, Derovsky & Meshkovsky, 1996).

The temperature of the mixture was ramped quickly to 453 K (~ 5 min), and once at this level diffraction data were collected every 15 min. The capillary was rotated by $\sim 10^\circ$ to ensure the largest possible number of reflections observed during exposure. Each exposure to the X-rays lasted approximately 6 min. An isothermal data-collection method was chosen to be as close as possible to the normal laboratory synthesis of the materials.

3. Results and discussion

The first image ($t = 5$ min) showed an intense amorphous ring from the reaction gel plus two diffraction peaks; the latter could be identified as reflections of the intermediate

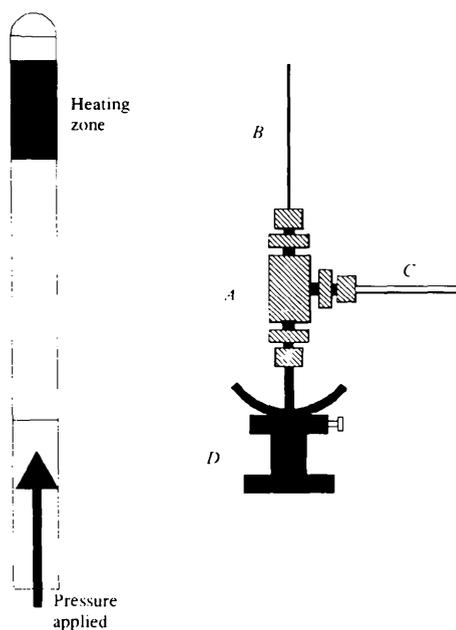


Figure 1

Schematic illustration of the sample mounting showing the Swage-lock T-fitting (A), the quartz capillary (B; an enlarged view illustrating the heating zone is shown on the left), the connecting tube used to apply pressure using N_2 gas (C), and the goniometer head (D).

phase $(\text{PrNH}_3)_2\text{SiF}_6$, described by Weigel *et al.* (1996) at d -spacings of ~ 3.31 and 1.81 Å, respectively. The intensity of these peaks remained invariant throughout the experiment. Data collection during a slower ramping of the temperature showed that crystallization of $(\text{PrNH}_3)_2\text{SiF}_6$ begins at ~ 403 K and is essentially complete by 443 K. After 45 min other diffraction maxima could be observed, and these increased in intensity with time. These peaks could be identified, by comparison with previously collected powder X-ray patterns, as reflections from single crystals of MTN. The number of reflections visible in the diffraction patterns indicate that several single crystals of MTN were formed during the experiment, and that they grew with different orientations. The full-width at half-maximum of the reflections does not change through the course of the experiment, indicating that the resolution of the instrument in this mode of operation is insufficient for coherence-length measurements to be made. The intensity of the amorphous ring decreased during the course of the experiment, indicating the transformation of amorphous to crystalline material. The percentage decrease is small however, because of the large contribution to the amorphous scattering by the quartz glass capillary (Fig. 2). The positions of the diffraction peaks and their intensities were measured using software written in-house.

The intensities of three well-shaped single diffraction spots were fitted to JMAK kinetics using the Avrami equation (Brown, Dollimore & Galeway, 1980), which applies to a constant linear rate of crystal growth assuming random nucleation. A number of the stronger MTN peaks could not be used for kinetic studies as they saturated the image-plate reader because of the high intensity of the X-ray flux. Other peaks were present as overlapping pairs. Only nicely shaped, single reflections were used in the data analysis.

The Avrami equation is written

$$Z = 1 - \exp[-k(t - t_0)^n],$$

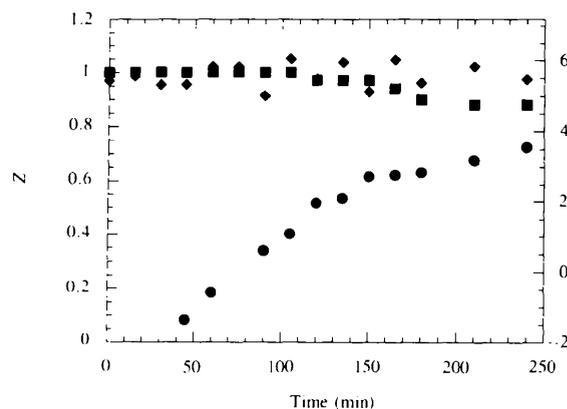


Figure 2

Variation of the diffraction intensities, expressed in terms of the fraction of material crystallized, of the MTN (008) reflection (●), the amorphous ring (■), and the hexafluorosilicate intermediate phase (◆) against time.

Table 1

Reaction orders (n) and rate constants (k) calculated for the growth of MTN crystals.

Diffraction peak	d	n	k (s ⁻¹)
(008)	2.43	1.03 (4)	0.006 (1)
(242)	2.87	1.02 (4)	0.007 (1)
(622)	2.10	1.04 (6)	0.013 (3)

where Z is the fraction of material crystallized, k is a rate constant and t_0 expresses the time when crystallization started. The fraction of material crystallized and the induction period, t_0 , were estimated using simple extrapolation and regression analysis.

The results of the fits to the Avrami equation are shown in Table 1, and the growth of intensity and Avrami fit for the (008) reflection are shown in Figs. 2 and 3, respectively. Note that the crystallization of the MTN phase is preceded by an induction period of 30–40 min. As expected for the growth of individual single crystals, the order of the crystallization is ~ 1 (Table 1). In the larger-scale synthesis using Teflon-lined steel autoclaves as the reaction vessels under otherwise identical conditions, it appears that the propylamine leads to the nucleation and growth of the FER crystals; it is unnecessary for MTN growth (Weigel *et al.*, 1996). In the present experiment, however, MTN rather than FER is formed, possibly due to heterogeneous nucleation by the walls of the quartz capillary. The difficulty of reproducing the synthesis conditions used in the laboratory exactly in the X-ray diffraction experiment will produce different temperature gradients, and thus different mass transport properties in the gels, and so it is not surprising that the results reported in the two methods are not entirely in agreement, especially in a complicated, competing synthesis such as the one reported here. However, the invariance of the hexafluorosilicate intermediate reflection intensities throughout the course of the reaction indicates that, at least initially, it is not likely that the MTN forms by recrystallization of this phase.

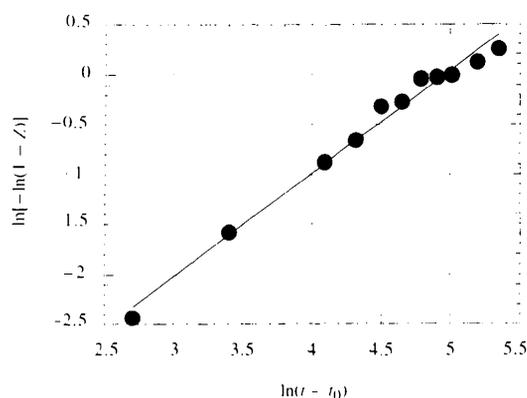


Figure 3
Representative fit of the integrated intensity data for the MTN (008) reflection to the Avrami equation at 453 K

4. Conclusions

It is clear from this experiment that *in situ* single-crystal diffraction experiments hold great promise for the elucidation of crystallization kinetics, and possibly crystallization mechanisms. The experimental set-up allows both temperature and pressure to be varied between experiments, and from such data more information on the energetics of the crystallization processes can be obtained.

In experiments such as the one reported here, where relatively large single crystals are formed, it is unlikely that *in situ* powder X-ray diffraction will be possible since the small number of crystals present will lead to incomplete powder diffraction rings. Single-crystal Laue experiments, on the other hand, may be possible, although the difficulty in accurately extracting single reflection intensities might be a limiting factor when multiple crystals are formed. The relatively large size of the single crystals formed in this experiment lead us to believe that experiments of this kind may be possible using a rotating-anode source since the high intensity of the beam at the synchrotron source caused problems with saturation of the image plates for a number of the most intense reflections, which could be avoided using a less intense beam. This will, however, be sample dependent, and the use of synchrotron radiation will be necessary when the crystals produced are relatively small or when the crystallization rates are relatively fast. Further experiments of this kind will be especially enlightening with respect to the MTN–FER synthesis, where variations in the chemical compositions of the gel are also expected to alter the nucleation and crystallization processes.

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