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Hydrothermal synthesis of the microporous aluminophosphate CoAPO-5; in situ time-resolved synchrotron X-ray powder diffraction studies

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Abstract

Time-resolved powder diffraction using synchrotron X-ray radiation has been used for real-time studies of syntheses and chemical reactions. Recent studies from the NSLS beam line X7B are summarized. In situ cells for hydrothermal synthesis and gas flow using quartz glass capillaries are described. A new translating imaging plate (TIP) camera for time-resolved powder diffraction experiments is also described. Measurement of full powder patterns in times as short as 30 s is essential to these studies. New results from in situ studies of hydrothermal synthesis of cobalt-substituted microporous aluminophosphates are presented. © 1998 Elsevier Science B.V.

Keywords: Aluminophosphate; Kinetics of crystallization; Synchrotron radiation; Zeolite synthesis

1. Introduction

In order to extend the knowledge of structure-properties relationships, in situ characterization methods have become increasingly important in studies of catalysis and catalysts. Although knowledge of the room temperature structural properties is valuable, it cannot immediately be extrapolated into the realm of working catalysts. Only by probing the catalyst at actual working conditions it is possible to get a clear picture of the structural and chemical changes involved in the catalytic reactivity.

In situ time-resolved studies of the formation of catalysts are likewise very important in order to understand the synthesis mechanisms. In situ observation also enables detection of intermediate phases, helps in establishing optimal synthesis conditions and makes it possible to investigate the kinetics of formation and to determine crystallite size as a function of time and reaction conditions. Targeted hydrothermal synthesis of zeolites and zeolite-like materials with specific catalytic properties, such as shape selectivity, is an intriguing possibility. However, this requires intimate knowledge not only about catalytic reaction mechanisms, but also about the role of nucleation and templates during hydrothermal synthesis.

We have developed a facility for in situ time-resolved powder diffraction using X-ray synchrotron radiation at the Chemistry beam line, X7B, at the National Synchrotron Light Source (NSLS) at Broo-

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khaven National Laboratory (BNL). The main objective of the facility is real-time in situ studies of syntheses and chemical reactions. High intensity, tunable wavelength and low divergence are features that make synchrotron X-ray radiation a unique probe for in situ and time-resolved studies.

In situ diffraction facilities have also been established at the Daresbury Synchrotron [1–3] and at HASYLAB [4].

Information obtainable from in situ powder diffraction experiments include:

- Kinetics of crystallization, transformation and degradation.
- Detection of crystalline or amorphous intermediate phases.
- Crystallite size as a function of time/temperature.
- Observation of induction periods.
- Optimization of synthesis conditions.
- Real-time crystal structure refinement.
- Phase identification and composition.

Diffraction methods can primarily be used for studies of reactions involving microcrystalline materials. However, also amorphous intermediates can be detected, either as an absence of diffraction peaks, or by the presence of very broad peaks. Crystallinity as well as progress of crystallization can be monitored by using the peak width and intensity of diffraction peaks.

We have performed numerous in situ time-resolved experiments at X7B including:

- Hydrothermal synthesis of zeolites [5–7] and aluminophosphates [8].
- Hydrothermal conversion of zeolites [9,10].
- Oxidation/reduction of $Sr_xLa_{1-x}MnO_{3+\delta}$ at high temperatures [11,12].
- Formation and transformation of mesoporous silicates [13].
- Adsorption/desorption and structure of HFC in zeolites [14].
- Organic synthesis; carboxylation of phenolates with CO_2 [15].
- Kinetics of crystallization of zeolite single crystals [16].
- Formation of layered Ti- and Zr-phosphates [9,17].
- Ion exchange of natural zeolites using molten salts [18].
- Ion exchange of zeolites from aqueous solutions (25–180°C) [19].
- Formation of microporous sulfides [20,21].
- Reactions in the MgO–$MgCl_2$–H_2O system, Sorel Cements [22,23].
- Dehydration of zeolites [24–26] phosphates and germanates.
- Thermal transformations [27].

As an example of a time-resolved in situ study of hydrothermal synthesis, the formation of cobalt containing microporous aluminophosphates is described. The aim of the experiments was to follow the crystallization of Co-substituted $AlPO_4$-5(CoAPO-5). The ideal structure of $AlPO_4$-5 is hexagonal with one-dimensional 12-ring channels running along the *c*-axis (IUPAC framework nomenclature: AFI). A few percent cobalt substitution on framework positions is possible [28,29]. The present work is part of a study investigating the influence of transition metal cations on the crystallization behavior of microporous aluminophosphates [8].

2. Experimental

2.1. The reaction cell

A simple but very versatile reaction chamber was developed for the in situ studies [4,5]. All reactions and syntheses are performed in 0.5–1 mm quartz glass capillaries mounted using a ferrule in a Swagelock T-piece. This is mounted on a goniometer head as shown in Fig. 1. For in situ studies of hydrothermal syntheses the capillary is closed in one end, and a pressure of nitrogen is applied using the connected tube. This allows hydrothermal conditions to be obtained in the hot zone. Pressures up to 45 atm can be used, which allows hydrothermal syntheses up to ca. 260°C to be studied. The sample is heated using a hot air blower. To avoid problems with thermal gradients across the sample the size of the X-ray beam is kept smaller than the hot zone. Typically the hot air stream is 7 mm wide while the X-ray beam is 2–3 mm wide.

The setup with a closed capillary has also been used for studies of reactions between solids and gases under static conditions, as for instance carboxylation of

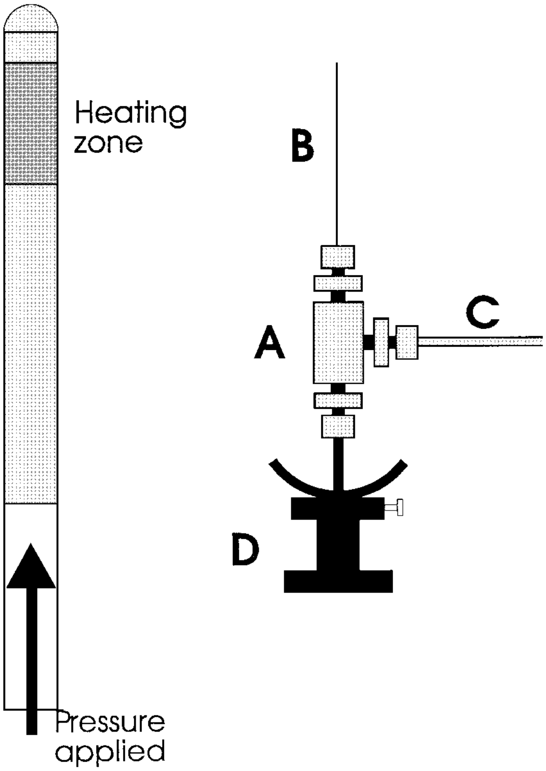

Fig. 1. The reaction cell is made from a 0.5–1 mm quartz glass capillary (B) mounted using a ferrule in a Swagelock T-piece (A) on a goniometer head (D). Using an "external" pressure (C) on the surface of the reaction mixture makes it possible to obtain hydrothermal conditions. In situ powder diffraction studies have been performed at temperatures as high as 260°C using pressures up to 45 atm.

phenolates using CO_2 [15], and for in situ studies of adsorption of gases on zeolites [14].

Using an open capillary, reactions between solids and gases can be studied under flow conditions. Fig. 2 shows a sketch of a two-stringed flow system, where computer controlled valves allow shifting between gases. This makes kinetic studies of a solid–gas reaction possible, and we have used it for studies of oxidation/reduction behavior of high temperature solid oxide fuel cell (SOFC) cathode materials at realistic working conditions, i.e. at temperatures of 700–950°C. Profile refinement was used to determine the unit cell parameters as function of time after changing from high to low oxygen partial pressures. Kinetic parameters were extracted by fitting the unit cell volume as a function of time [11].

2.2. *Detectors*

It is very important to be able to extract structural information from powder diffraction data obtained using very short exposures. We have used two types of detectors for the time-resolved powder diffraction studies. An INEL CPS120 curved position sensitive detector was used initially. We have demonstrated that it is possible to refine crystal structures during dehydration of natural zeolites using a position sensitive detector. Using 5 min exposures it was possible to obtain detailed information concerning the hydration state and cation positions [24].

We have recently constructed a translating imaging plate (TIP) camera designed especially for time-, temperature- and wavelength-dependent powder diffraction experiments [30].

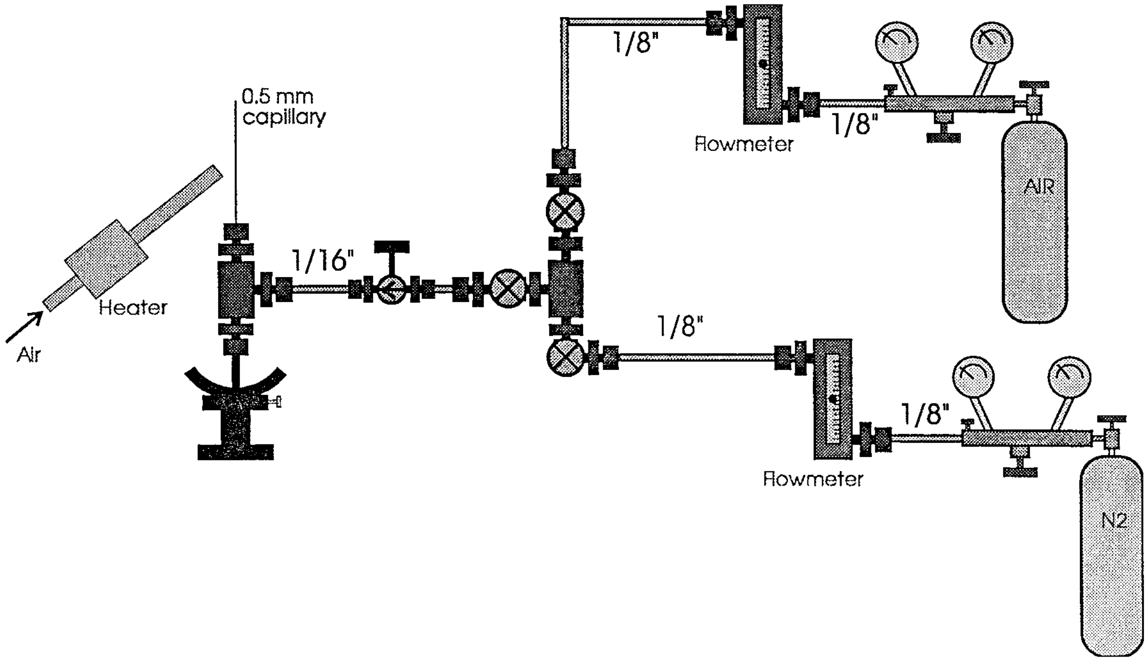

Fig. 2. Sketch of a two-stringed flow system, where computer controlled valves allow shifting between gases.

The principle of the TIP camera is similar to that of high temperature Guinier–Simon or Guinier–Lenne cameras except that the imaging plate technique is used, and the camera has a flat plate geometry. Fig. 3 shows a sketch describing the principle behind the TIP camera. The imaging plate (200×400 mm Fuji) is placed behind a steel screen with a vertical slit typically 3 mm wide. The imaging plate is mounted on an aluminum support, and is kept in place and flat using vacuum. The metal support is mounted on a slide, which allows the imaging plate to be translated behind the steel screen. The diffraction cones from the capillary sample are intercepted by the steel slit in front of the imaging plate, and when the plate is translated a continuous series of time-resolved powder patterns are recorded.

Using the imaging plate technique we were able to solve the crystal structure of $Zr(HPO_4)_2$ and refine it, using the Rietveld method, from a 30 s powder diffraction pattern [31]. Rietveld refinement of standard ZrO_2 and α-quartz demonstrated that imaging plate powder diffraction data yields reliable structural parameters [31,32].

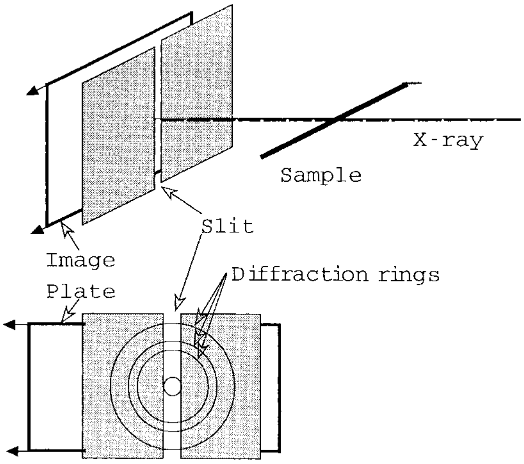

Fig. 3. A sketch that describes the principle behind the translating image plate (TIP) camera.

Combining the TIP camera with the in situ reaction cell results in a unique setup, where even fast chemical reactions can be followed as a function of time.

2.3. Hydrothermal synthesis

The gel for the synthesis of aluminophosphate $AlPO_4$-5 with partial Co-substitution (CoAPO-5) was prepared using a slight variation of the method of Shiralkar et al. [28]. The template used in the synthesis was triethylamine $N(C_2H_5)_3$ (TEA). Hydrolyzed and washed aluminumpropoxide was used as the aluminum source. This was stirred together with water and cobalt sulfate, and then 85% phosphoric acid was added. While cooling on an ice bath TEA was slowly added, and the resulting gel was stirred for 1 h. The composition of the amorphous starting gel for the in situ hydrothermal synthesis was

$$0.8Al_2O_3 : 0.4CoO : P_2O_5 : 1.5TEA : 32H_2O$$

The pink gel was filled into 0.7 mm quartz glass capillaries using a 0.5 mm capillary mounted on a syringe. After the in situ crystallization experiments the crystallization of CoAPO-5 is immediately visible, as the material in the heated section of the capillary turns bright blue.

3. Results and discussion

Fig. 4 shows an example of time-resolved in situ powder diffraction data collected using the TIP camera. The figure is a three-dimensional representa-

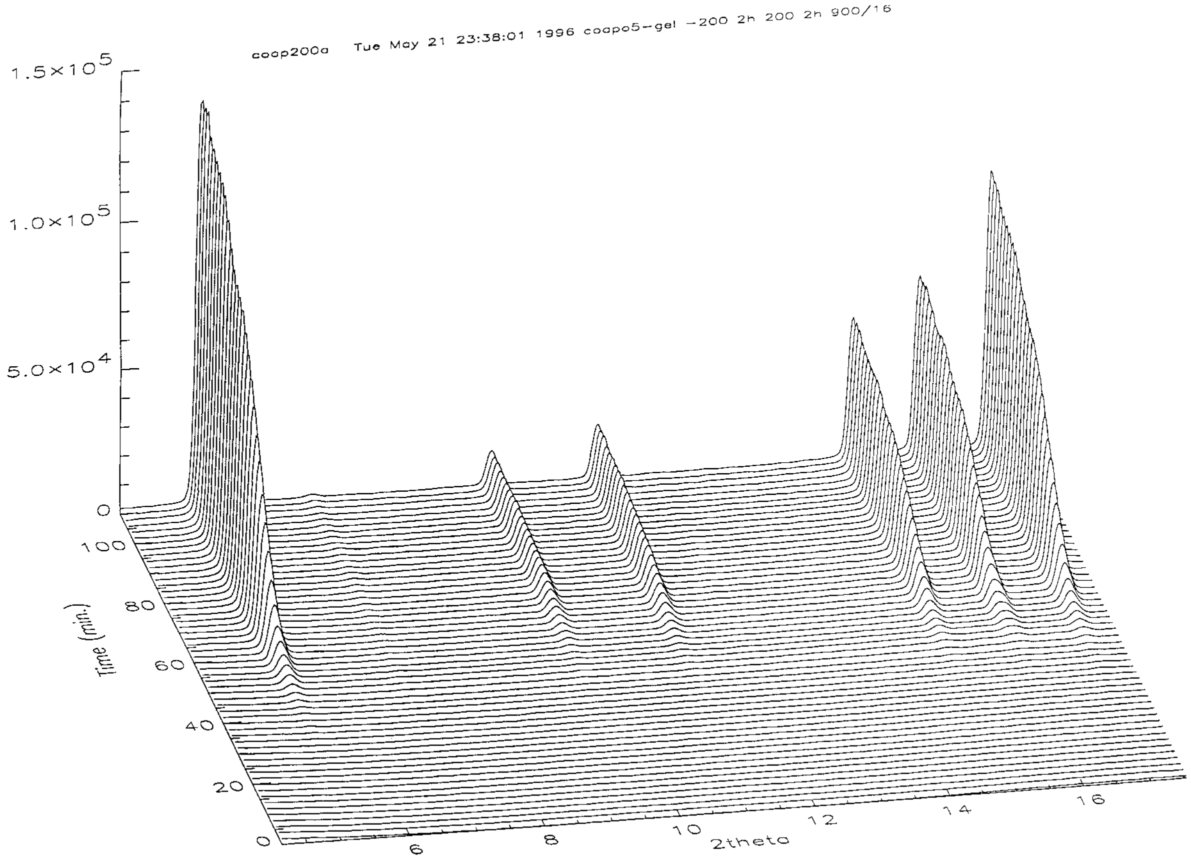

Fig. 4. A three-dimensional representation of a small part of the diffraction patterns obtained during hydrothermal formation of zeolite CoAPO-5. The diffraction angle 2θ is displayed along the x-axis, time along the y-axis and diffraction intensity along the z-axis. The low angle reflections 100, 110, 200, 210, 002, (211/102/003) are visible. The temperature was ramped to 200°C in 2 h, and kept at that temperature for additional 2 h.

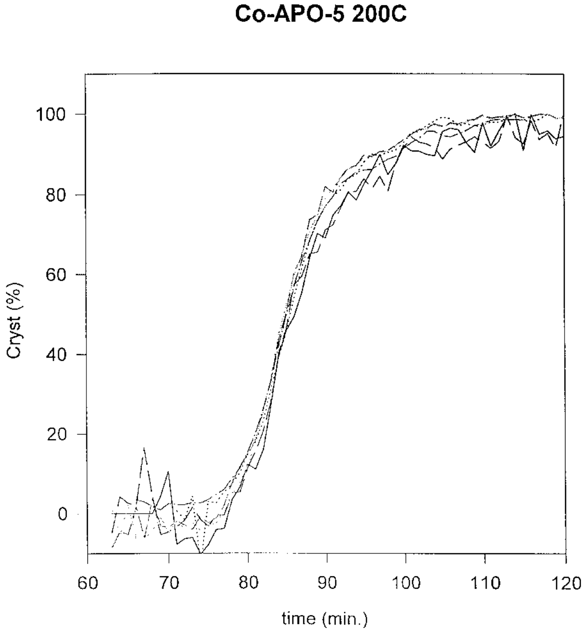

Fig. 5. The crystallization curve obtained using integrated intensities of the three different reflections (100, 210, (211/102/003)).

tion of a small part of the diffraction patterns obtained during hydrothermal formation of CoAPO-5. The temperature was ramped to 200°C in 2 h, and kept at that temperature for an additional 2 h. From the amorphous starting material CoAPO-5 starts crystallizing after ca. 70 min, when the temperature has reached ca. 130°C. The crystallization progresses, and close to the final temperature crystallization is complete. Fig. 5 shows the crystallization curve obtained using integrated intensities of the three different reflections. In order to study the long-time hydrothermal stability of the aluminophosphate under high temperature synthesis conditions, an experiment at 225°C was performed. The temperature was ramped up in 30 min, and held at 225°C for 6.5 h. Fig. 6 shows the time-resolved powder diffraction pattern of the 210, 0 0 2 and (211/102/003) reflections during this run. The formation of CoAPO-5 is clearly visible, but after ca. 2 h a second phase starts to form. The additional diffraction lines were similar to those reported for a dense cubic aluminophosphate (PDF 31-0028).

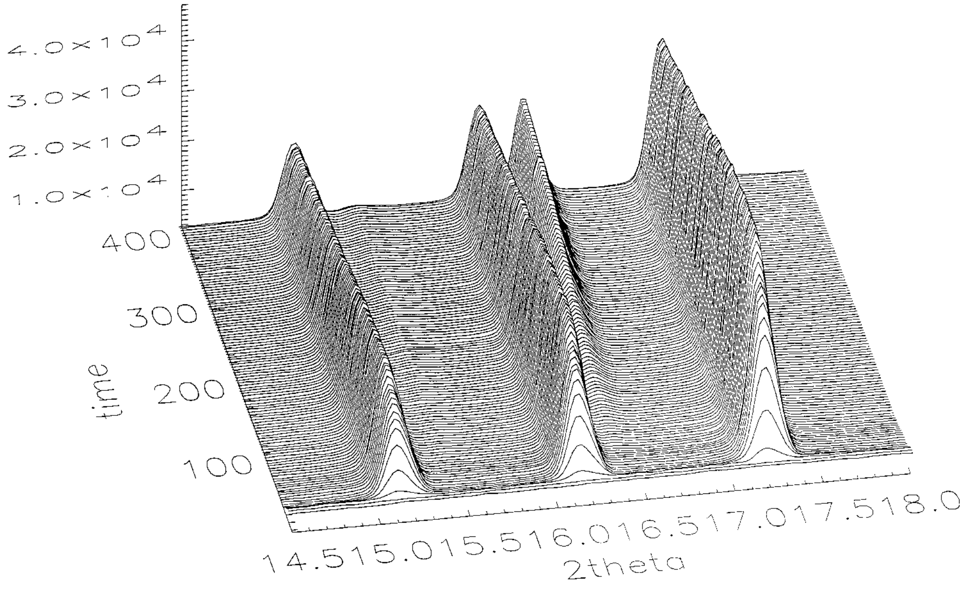

Fig. 6. The time-resolved powder diffraction pattern of the 210, 002 and (211/102/003) and 1 2 1 reflections during a run where the temperature was ramped to 225°C and held at that temperature. The formation of CoAPO-5 is clearly visible, but after ca. 2 h a second phase starts to form. This phase was identified as $AlPO_4$, a dense cubic aluminophosphate.

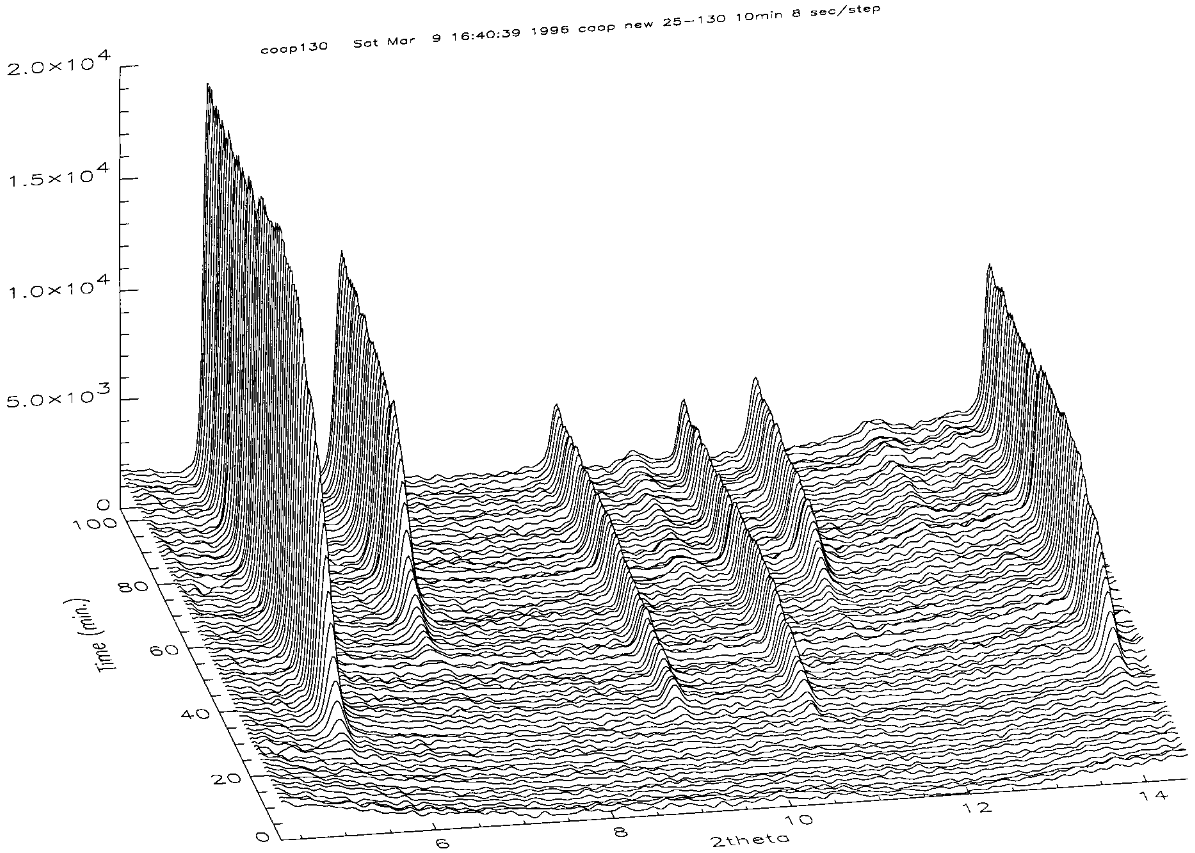

Fig. 7. Results from an in situ study of a hydrothermal synthesis where two microporous aluminophosphate phases are formed, namely CoAPO-5 and CoAPO-47. The temperature was ramped from 25°C to 130°C in 10 min and kept at 130°C for 2 h. The crystallization of CoAPO-5 occurs first, as seen by the appearance of the 100, 110, 200 and 210 reflections (lines 1, 3, 4 and 6). Shortly thereafter CoAPO-47 (Chabazite type structure CHA) starts to form (lines 2 and 5).

Fig. 7 shows results from an in situ study of a hydrothermal synthesis where two microporous aluminophosphate phases are formed, namely CoAPO-5 and CoAPO-47. The temperature was ramped from 25°C to 130°C in 10 min and kept at 130°C for 2 h. The crystallization of CoAPO-5 occurs first, as seen by the appearance of the 100, 110, 200 and 210 reflections. Shortly thereafter CoAPO-47 (Chabazite type structure, CHA) starts to form. Fig. 8 shows the corresponding crystallization curves at 150°C, and it can be seen that not only the induction times, but also the crystallization rates are different for the two materials. No appreciable change in amount of CoAPO-5 is observed when the second phase starts to form. Fig. 9 shows crystallization curves extracted from two experiments at 130°C and 150°C, respectively. The temperature dependence of the crystallization rate is clearly visible.

4. Conclusion

The above results demonstrate that kinetic parameters and intermediate phases can be determined from the in situ time-resolved method described above. Future studies include in situ time-resolved synchrotron powder diffraction from active catalyst.

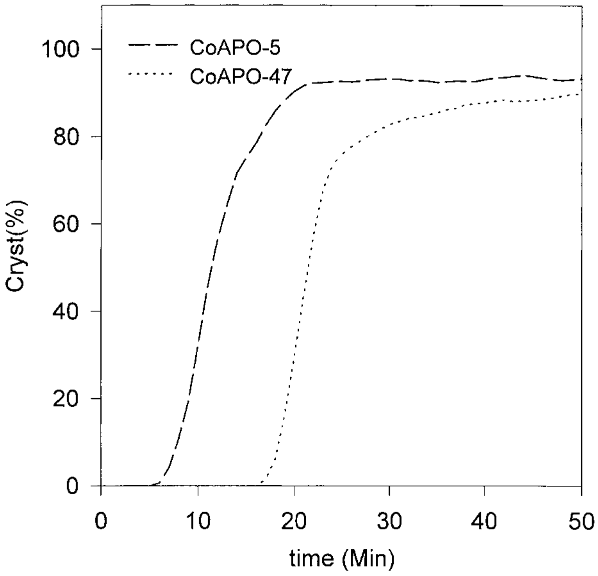

Fig. 8. The crystallization curves for the two phases shown in Fig. 7 at 150°C, and it can be seen that not only the induction times, but also the crystallization rates are different for the two materials. No appreciable change in the amount of CoAPO-5 is observed when the second phase starts to form.

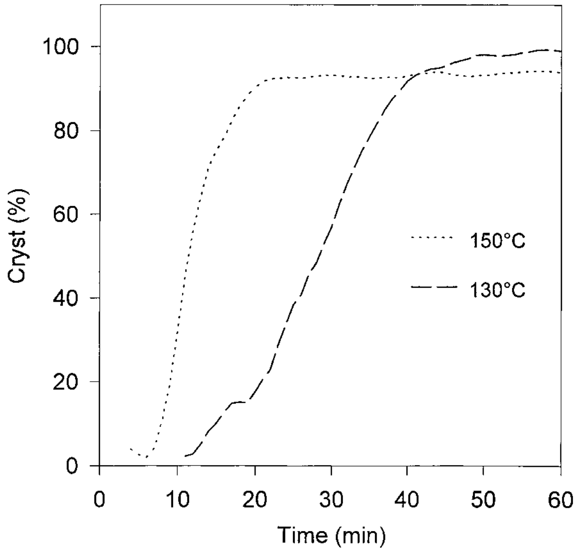

Fig. 9. Crystallization curves extracted from two experiments at 130°C and 150°C. The temperature dependence of the crystallization rate is clearly visible.

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