IN-SITU TIME RESOLVED SYNCHROTRON POWDER DIFFRACTION
STUDIES OF SYNTHESSES AND CHEMICAL REACTIONS.

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ABSTRACT

Equipment for time and temperature dependent powder diffraction has been developed, especially in order to be able to study hydrothermal syntheses of zeolites. The system is very versatile and has so far been used to study e.g. hydrothermal syntheses of zeolites and aluminophosphates, syntheses of layered phosphates, formation of Sorel cements, dehydration and phase transformations of zeolites, solid state synthesis of lanthanum manganites, ion exchange of zeolites using molten salt, and oxidation/reduction of lanthanum manganites at high temperatures. The sample is contained in quartz capillaries and is heated using a stream of hot air. External pressure can be applied allowing hydrothermal syntheses at temperatures up to 200°C to be performed. Controlled atmosphere is obtained by flowing gas or a mixture of gases through the capillary.

INTRODUCTION

In-situ studies are of considerable interest in many areas of research including solid state chemistry. When crystalline materials are involved, powder diffraction is a powerful tool in obtaining information ranging from identification of the phases involved to determination of crystallite size to estimating the degree of crystallization to determination of the structure of the involved crystalline phases. Classically thermal transformations have been studied using powder diffraction, but due to slow data collection when using conventional X-ray sources little emphasis has so far been given to studies of chemical reactions and synthesis. A few examples exists where hydration reactions of cements have been studied using neutron powder diffraction. Usually studies of e.g. crystallization reactions have been performed ex-situ, i.e. samples are extracted from the synthesis mixture after different periods of reaction, and the amount of crystalline material is determined. However, the availability of synchrotron sources, with its very intense X-ray beam, have made real in-situ studies of even quite fast chemical reactions and syntheses feasible. The present work describes a versatile equipment developed for in-situ X-ray powder diffraction experiments enabling studies of e.g. hydrothermal syntheses, reactions between solids and gas phase at elevated temperatures, and solid state syntheses.

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SCOPE OF THE EXPERIMENTS:

The scope of the experiments are real time structural studies of syntheses and chemical reactions involving crystalline materials. Solid-solid, solid-gas and solid-liquid phase reactions can be investigated using the equipment developed. Areas where this type of time resolved experiments are of particular interest include:

- Catalysis
- Fuel cells
- Batteries
- Ion exchange
- Syntheses

The information obtainable from the experiments are e.g.:

- Kinetics of crystallization, transformation and degradation.
- Existence 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

The information available is depending on the rate of the reaction and speed with which measurements can be done. Using synchrotron radiation and a position sensitive detector enables even fast reactions and syntheses to be followed[1].

Examples of in-situ experiments performed[1-4]:

- Hydrothermal synthesis of zeolites/aluminophosphates
- Ion exchange of natural zeolites in molten salts
- Reactions in the MgO-MgCl₂-H₂O system, formation of Sorel Cements
- Solid state syntheses
- Dehydration of zeolites, phosphates and germanates
- Thermal transformations
- Phase diagrams (temperature/oxygen partial pressure)
- Oxidation of high-TC superconductors
- Wavelength-dependent diffraction (DAFS-experiments)
- Kinetics of crystallization of zeolite single crystals
- Formation of layered Ti- and Zr-phosphates
- Oxidation/reduction of SrₓLa₁₋ₓMnO₂₋ₓ at high temperatures
- Hydrothermal conversion of zeolites
- Crystal Structure determination/refinement using IP-data
- Organic synthesis; carboxylation of phenolates with CO₂

DESCRIPTION OF THE EQUIPMENT.

The sample is contained in a 0.5-0.7 mm quartz capillaries, which is mounted using a ferrule in a T-piece which is again mounted on a goniometer head, as shown in Figure 1. Using the slides and arcs on the goniometer head the capillary can be aligned in the usual way before the tubes are connected. The tubing used are Teflon or steel depending on the applied pressure. The Teflon tubing can be used up to a pressure of approx. 25 atm., but if higher pressures is used, or if e.g. oxygen diffusion through the tubing is a problem, steel tubing is used.

Depending on the type of experiment conducted the capillary can be open or closed. For hydrothermal syntheses the capillary is closed, and the applied pressure allows hydrothermal conditions to be obtained.
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This setup is used also for solid-gas reactions at elevated pressure if a gas flow is not necessary. Pressures up to 45 atm. have been successfully applied, usually using nitrogen.

For studies of reactions between gases and solid materials the capillary is open, and gas is flowed through the capillary. A two stringed flow system makes it possible to change gas composition during an experiment, making time resolved studies of solid-gas reactions possible. A sketch of the flow system is given in Fig. 2. This setup has been used e.g. in a series of experiments where the kinetics of oxidation/reduction reactions of cathode materials for Solid Oxide Fuel Cells were studied at high temperatures (600-800°C).

The sample is heated by a flow of hot air using two different heater guns. One used for temperatures up to 250°C consisted of a heating spiral in an insulated glass tube. The other heater gun used for obtaining temperatures up to 900°C is an Enraf Nonius heater gun.

All experiments were performed at the National Synchrotron Light Source (NSLS), at Brookhaven National Laboratory (BNL), USA, at the Chemistry Beamline, X7B. A horizontally and vertically focused beam is used, resulting in a high intensity beam at the sample position.
Two types of position sensitive detectors were used:

- Two curved position sensitive detectors covering 120 and 90° in 2θ respectively (INEL CPS120 and CPS90). For most experiments the limit in time resolution obtained was 30s.
- A Translating Image Plate System was developed especially for time- temperature- and wavelength-dependent powder diffraction experiments. An Image plate is mounted on a computer controlled slide and moves behind a steel slit of 1-3 mm. in a way very similar to the high-temperature Guinier cameras. Thus, a continuous series of powder patterns is obtained, where the time resolution is determined by the speed of the slide combined with the width of the slit. For well diffraction samples powder patterns suitable for Rietveld refinements can be obtained using exposure times of less than 10 s. The equipment will be described in greater detail in a separate communication.

EXAMPLES

Formation of layered titanium phosphates.
The formation of layered titanium phosphates was studied in-situ using an autoclave synthesis with amorphous titanium phosphate and phosphoric acid as starting materials[5]. The products are: α-TiP: Ti(HPO₄)₂, H₂O, γ-TiP: Ti(H₂PO₄)(PO₄) 2H₂O and β-TiP: Ti(H₂PO₄)(PO₄)

α-TiP is formed at lower temperatures; the crystallization starts at 50°C. Above 200°C, with the present conditions, β-TiP, which is the anhydrous form of γ-TiP, starts to form.
The rate of crystallization of α-TiP was determined from experiments at different temperatures. Figure 3 shows the derived crystallization curves at 70 and 110°C fitted using a first order rate expression.

Figure 3. Crystallization curves of α-TiP at 70 and 110°C

At higher temperatures β-TiP is formed. Hydration of β-TiP gives the γ-phase with preserved layer structure. The formation of α-TiP from amorphous titanium phosphate and the subsequent transformation into β-TiP was followed in-situ using the moving Imaging Plate system. Figure 5 shows a 3-D representation of the diffraction profiles as a function of time. Figure 6 shows the derived crystallization curves for α- and β-TiP. The starting material is amorphous and after a short induction period a rapid crystallization of α-TiP is observed. The subsequent transformation from α- to β-TiP is slower. The intersection of the crystallinity curves for α- and β-TiP is close to 50%, indicating that no intermediate amorphous phase is involved.
Hydrothermal conversion of zeolite LTA.

A series of time resolved powder diffraction experiments following hydrothermal conversion of zeolite Na-LTA into other zeolites or aluminosilicates have been initiated. Preliminary results on reaction with aqueous LiCl are reported. Hydrothermal conversion of zeolite LTA at temperatures below 350°C results in formation of zeolite Li-ABW, LiAlSiO₄. H₂O[6].

In-situ syntheses were performed at temperatures from 240-260°C. To obtain hydrothermal conditions a pressure of 45 atm. was applied using compressed nitrogen as described above. The concentration of LiCl and the ratio between zeolite LTA and water was varied.

The sample was heated to the target temperature in 1/2-1h, and the temperature was maintained for 2-4h. When a high concentration of LiCl is used, formation of Li/Cl-sodalite is observed. At more dilute systems a mixture of zeolite Li-ABW and a phase, which is probably a Li/Na-cancrinite is formed.

Figure 7 shows the resulting powder diffraction patterns obtained using the moving imaging plate system of the conversion of zeolite LTA to a mixture of zeolite Li-ABW and cancrinite. Figure 8 shows crystallization curves for the hydrothermal conversion of zeolite LTA into Li/Cl-sodalite. The degree of crystallization is estimated from integrated intensities of a number of diffraction peaks.
Figure 7. Powder diffraction profiles during hydrothermal conversion of zeolite LTA with aqueous LiCl at 240°C.

Figure 8. Crystallization curves for the hydrothermal conversion of zeolite LTA into LiCl-sodalite.

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