

Hydrothermal Transformation of Microporous Lithium Zinc Phosphates; A Kinetic Study using *in situ* Synchrotron Radiation Powder Diffraction.

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Abstract

The solution mediated phase transformation of a lithium zinc phosphate has been investigated. The zeolite type ABW phase, $\text{LiZnPO}_4 \cdot \text{H}_2\text{O}$, suspended in an aqueous solution of LiNO_3 , transforms to the more dense phase, $\delta\text{-LiZnPO}_4$ (cristobalite type structure). *In situ* time resolved powder diffraction using synchrotron radiation, has been utilised to obtain isothermal crystallisation curves in the temperature range 179 °C to 210 °C. A power law was used for the kinetic analysis, giving an apparent activation energy for the reaction, $E_a = 93.1$ kJ/mole. The order of the power law varies from 2.80 to 4.41 in the observed temperature range. This indicates a continuous change in the mechanism of the nucleation.

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Introduction

Microporous materials have received considerable interest due to potential applications, as catalysts, adsorbents, ion conductors *etc.* A variety of microporous phosphates have been prepared *e.g.* Aluminium Phosphates (AlPO). Recently *in situ* time resolved powder diffraction using synchrotron radiation, has proven valuable for kinetic studies [1-4]. Detailed knowledge of a reaction mechanism can be gained from crystallisation curves, $\alpha(t)$, extracted from *in situ* powder diffraction data. Kinetic informations are invaluable for industrial applications.

In this study a zeolite type ABW lithium zinc phosphate, $\text{LiZnPO}_4 \cdot \text{H}_2\text{O}$ [5, 6], has been chosen for further investigation. The ABW structure has 8-ring channels in one crystallographic direction. Upon heating solid $\text{LiZnPO}_4 \cdot \text{H}_2\text{O}$ dry or suspended in water at temperatures $> 130^\circ\text{C}$, it transforms to the more dense phase, $\delta\text{-LiZnPO}_4$. The product $\delta\text{-LiZnPO}_4$ has a cristobalite type structure with 6-ring channels running in 3 directions in the crystal structure [6, 7]. Both structures can be described as framework structures built from corner sharing tetrahedra of ZnO_4 and PO_4 with Li ions molecules placed in the channels. A kinetic study of the hydrothermal conversion is reported here.

Experimental

The material, $\text{LiZnPO}_4 \cdot \text{H}_2\text{O}$, was prepared as described elsewhere [5, 6], using LiOH , $\text{Zn}(\text{NO}_3)_2$ and H_3PO_4 heated to 69°C , 75 hours, pH = 6.0.

Solid lithium zinc phosphate, $\text{LiZnPO}_4 \cdot \text{H}_2\text{O}$, was suspended in an aqueous solution of LiNO_3 to insure that the chemical conditions were within the stability field of the product, $\delta\text{-LiZnPO}_4$. The samples were placed in 0.7 mm quartz capillaries, and mounted in a special developed goniometer head [8]. Fig. 1.

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Fig. 1. shows that this set up allows a pressure of N_2 gas to be applied to prevent the suspension from boiling. The samples were heated to a fixed temperature within minutes using hot air.

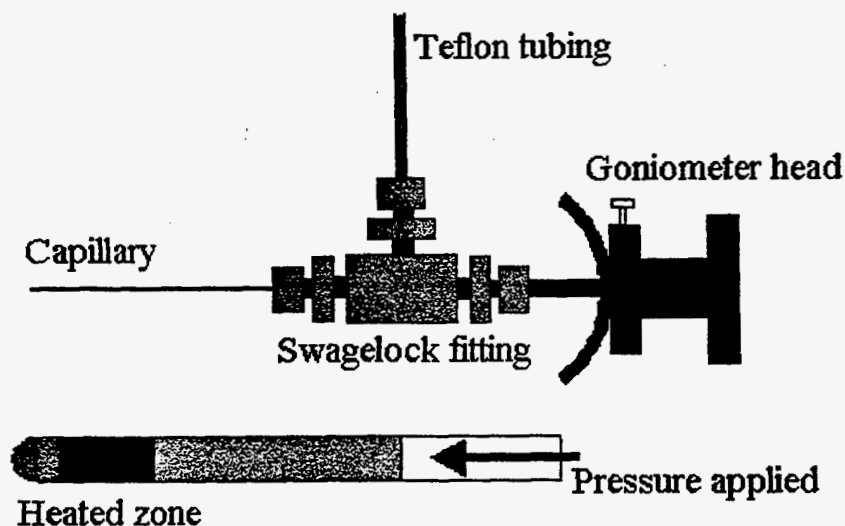


Fig. 1. Reaction cell for the hydrothermal conversion of $LiZnPO_4 \cdot H_2O$.

The diffraction data were recorded using a position sensitive detector (INEL CPS 120) covering 120° in 2θ . The high flux of the synchrotron radiation enabled fast sampling of the data (30 s or 60 s exposure for each powder pattern) to give good time resolution. The data collection was carried out at beamline X7B, NSLS, Brookhaven National Laboratory, USA, using a wavelength of $\lambda = 1.3080 \text{ \AA}$.

Results

Selected well separated Bragg reflections were integrated using a semi automatic routine and a Gaussian peak shape. Integrated intensities from each powder pattern were added and the data sets were normalised, $\alpha(t) = I(t)/I_0$. The crystallisation isotherms, $\alpha(t)$, of $\delta_T\text{-LiZnPO}_4$ versus time are shown in Fig. 2.

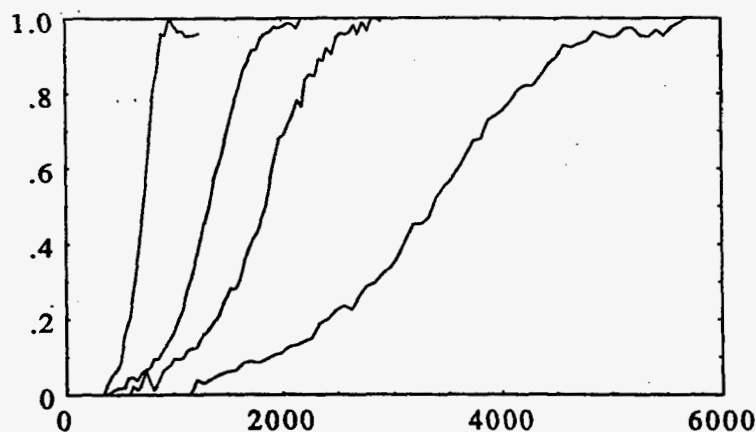


Fig. 2. Degree of formation of $\delta_T\text{-LiZnPO}_4$, $\alpha(t)$ versus time (s), at 179, 190, 200 and 210°C.

A power law (Eq. 1), was used for the data analysis. This expression applies for solution mediated reactions, *e.g.* zeolite synthesis [2, 3]. The constant, K , can be implemented as a combined rate constant for the nucleation and crystal growth. The exponent, q , is dependent on the mechanism [9].

$$\alpha(t) = K \cdot t^q \quad \text{Eq. 1.}$$

This kinetic expression (Eq. 1.) does not include the deceleratory part of the crystallisation curves, for that reason it was fitted to, $0 < \alpha(t) < 0.5$.

Table 1. lists the results. The exponent, q , is varying with the temperature giving the rate constant, K , a variable dimension (time^{-q}). Upon calculating the apparent activation energy from an Arrhenius plot it is essential to transform the rate constants to a common dimension, e.g. $\ln k = \ln K/q$, (time^{-1}).

Table 1. The reduced power law, with rate constants defined as $\ln k = \ln K/q$.

T ($^{\circ}\text{C}$)	q	K ($\cdot 10^{-11} \text{ s}^{-q}$)	$\ln(k)$
210	4.41	0.0127	-6.729
200	3.67	0.169	-7.386
190	3.14	2.72	-7.748
179	2.80	6.84	-8.373

E_a (kJ/mole)	93.1
$\ln A$	16.4

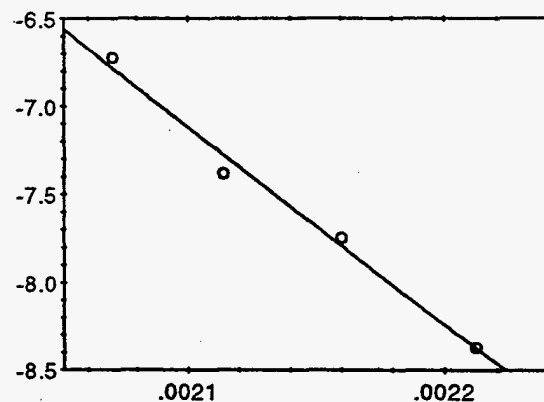


Fig. 3. Arrhenius plot, $\ln(k)$ versus T^{-1} (K^{-1}).

Discussion

The sigmoidal shape of the crystallisation curves of formation of $\delta\text{-LiZnPO}_4$ suggests a process with 2 steps. Before crystal growth nucleation takes place, during the induction period, t_0 . Inclusion of the induction period, t_0 , in the kinetic model, $\alpha(t) = K \cdot (t - t_0)^q$, gave $t_0 \approx 0$. This means that the initial nucleation is a fast process and crystal growth starts immediately after the first nuclei has formed.

Information about the nucleation process can be extracted from the value of the exponent, q . The nucleation process is homogenous if all nuclei are present at the beginning of the reaction ($q \approx 3$). The nucleation rate is constant for heterogeneous nucleation ($q \approx 4$), and the rate is increasing if the nucleation process is autocatalytic ($q > 4$) [9]. In-situ studies of the synthesis of zeolite Na-A [LTA] and hydroxysodalite from natural kaolinites gave q values which were generally higher than 4 suggesting autocatalytic nucleation[2,3]. Table 1. shows that q varies from 2.80 to 4.41 in the observed temperature range, with an average of 3.51. This suggests that the mechanism of the nucleation is changing continuously as a function of the temperature.

The Arrhenius plot, Fig. 3., of $\ln k$ versus $1/T$ can be approximated by a 1. order polynomial. This gives a pre-exponential frequency factor of, $\ln A = 16.4$. The apparent activation energy, E_a , can be calculated from the slope, $E_a = 93.1 \text{ kJ/mole}$. This apparent activation energy for the nucleation and crystal growth contains little physical meaning, but it can be of importance in comparison with other similar reactions. The apparent activation energy is also useful in optimising a chemical reaction by comparing values obtained under different conditions.

Future work

The phase transition of $\text{LiZnPO}_4 \cdot \text{H}_2\text{O}$ to $\delta\text{-LiZnPO}_4$ can be performed under 2 different chemical conditions, either dry heating or hydrothermal heating. The aim of this and the following work is to investigate how much kinetic knowledge about these possibly very different mechanisms of this phase transition can be extracted from high resolution powder diffraction data.

To obtain a more complete description of the mechanism the combined use several techniques will be investigated. Valuable information about the nucleation mechanism of hydrothermal conversion of $\text{LiZnPO}_4 \cdot \text{H}_2\text{O}$ can be extracted from Scanning Electron Microscopy. Comparing pictures of partially converted $\text{LiZnPO}_4 \cdot \text{H}_2\text{O}$ at different temperatures might give indications of the nucleation mechanism. Data from *in situ* ^{31}P MAS NMR spectroscopy at elevated temperatures will also be included.

The dry heating phase transition will be investigated using *in situ* ^{31}P MAS NMR at elevated temperatures, static solid state ^1H NMR, Thermo Gravimetric Analysis, Scanning Electron Microscopy as well as *in situ* time resolved powder diffraction (the work is in progress). Especially the combination of solid state NMR spectroscopy and *in situ* time resolved powder diffraction might prove fruitful for the detailed kinetic analysis.

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