

SYNTHESIS AND KINETIC STUDY OF ZEOLITE FROM LOPBURI PERLITE

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Abstract

This work was an intensive study on synthesis and crystallization kinetics of zeolite from an economically viable Lopburi perlite. Hydrothermal process was carried out to survey the zeolite crystallization under various conditions. At 100°C and atmospheric pressure the product was zeolite Na-P1. At 100-140°C and 20-50 psi the major product obtained was analcime. Under the influence of 3 M NaOH and 1:5 solid/liquid ratio at 140°C for 24 h, perlite was mainly converted to analcime. When the solid/liquid ratio was changed to 1:20 cancrinite was formed. Kinetics of analcime crystallization were determined at different temperatures. It was found that the activation energy was 11.2 kcal/mol. The Avrami exponent (n) obtained was in the range of 3.4 to 6.4 indicating that crystallization of an amorphous phase took place in the autocatalytic stage of the crystallization process.

Keywords: Perlite, synthesis, kinetic, analcimes, Arrhenius, Avrami

Introduction

Zeolites are crystalline, hydrated aluminosilicate compounds that have three-dimensional structures arising from a framework of tetrahedral units of SiO₄ and AlO₄, each tetrahedral unit linked by an oxygen atom (Breck, 1974). Zeolites have been used in numerous applications including water treatment, radioactive waste storage, gas separation and purification, liquid phase separation, molecular sieves, detergency, fertilizer, ion exchange, catalyst, desiccation, soil improvers and animal feed supplements (Dyer, 1984).

At present, synthetic zeolites are used commercially more often than natural zeolites due to the purity of crystalline products and the uniformity of particle sizes (Breck, 1974). Moreover, syntheses can be carried out using rather inexpensive starting materials. A very wide range of silica sources have been used in zeolite synthesis, for example natural materials such as kaolinite, volcanic glasses (perlite and pumice), rice husks, diatomite and chemical materials such as silicate (King, 1994). Perlite is a volcanic glassy rock with a characteristic texture and an

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amorphous structure, which is one of the attractive raw materials for synthesis of zeolite.

An understanding on the formation mechanism of zeolites is important because of their huge in industrial and commercial value. Walton *et al.* (2001) suggested that determination of reaction kinetics is often the first step in determining the mechanism of any reaction.

The aim of this study was to carry out an inspection of the synthesis of zeolite from a low-cost silica-alumina source, such as perlite, under various NaOH concentrations, and solid to liquid ratios; temperatures and times, expected to obtain zeolite with the highest percent crystallinity. Kinetic parameters were also investigated.

Materials and Methods

Synthesis

Perlite was prepared by grinding with a SpectroMill Ball Pestle Impact grinder and sieved with sieving size 230 mesh before using as a starting material. The starting material reacted with NaOH solution at various concentrations between 1 M and 3 M and with the solid to liquid ratio (g/ml) of 1:5 to 1:20. The temperature and pressure used was in the range of 100°C to 140°C for various times and at a pressure of 20 psi to 50 psi. A 500 ml high pressure/high temperature stirred reactor (Parr Instrument) was used. After hydrothermal treatment, the reactor was cooled to room temperature. Synthesized products were filtered, washed with distilled water and dried at 120°C for 6 h. The solid products were identified by XRD and SEM was used to investigate the morphology of the analcime product.

Kinetic Study

Since the analcime was the major product under the studied conditions, therefore it was selected for further study on the crystallization kinetics. The kinetics of analcime were extensively studied under a constant NaOH concentration and solid/liquid ratio at various

temperatures. The perlite used as a starting material was reacted with 3 M NaOH solution and a 1:5 ratio (g/ml) of solid to liquid ratio at the reaction temperatures range from 130°C to 145°C for different periods of reaction time and at a pressure of 20 psi to 50 psi, in a 500 ml high pressure/high temperature stirred reactor (Parr Instrument). The percentage of zeolite crystallinity was determined by XRD as following equation (Ghosh *et al.*, 1994):

$$\% \text{ Crystallinity} = \frac{\text{total area of 12 strong peaks of sample}}{\text{total area of 12 strong peaks of standa}} \times 100\%$$

Identification and Characterization

The chemical composition of raw perlite was determined by the wavelength dispersive X-ray fluorescence spectrophotometer (XRF), Model Negative Magix Pro, Phillips. Perlite consists mainly of the following oxides expressed as percent by weight; SiO₂, 70.63%; Al₂O₃, 32.36%; Na₂O, 2.36% and 4.71% of K₂O. Synthesized samples were identified by powder X-ray diffractometer (XRD), Model D5005, Bruker and they were characterized by FT-IR. Infrared spectra were obtained from 5 mg of samples in 300 mg KBr. The samples were scanned in the range of 4,000 cm⁻¹ to 370 cm⁻¹ using Fourier transform infrared spectrophotometer (FT-IR), Model Spectrum GX, Perkin-Elmer. Scanning electron microscope (SEM), Model JSM6400, JEOL, was used to investigate the morphology of the analcime product. Silicon-aluminum ordering was 1.97, characterized by ²⁹Si MAS NMR with a Varian Unity Inova spectrometer, at a frequency of 59.58 MHz. The spectra were recorded with a spinning rate of 6 kHz in a Varian 5 mm MAS probe, at ambient temperature.

Results and Discussion

Synthesis of Zeolite

Conversion of the inexpensive raw perlite to zeolites under various conditions is shown in Table 1. It can be seen that zeolite Na-P₁, analcime and cancrinite could be synthesized

Table 1. Products from perlite under various conditions

Concentration (M)	Temperature (°C)	Solid/Liquid (g/ml)	Time (h)	Product	
1	100*	1:5	24	Zeolite Na-P ₁	
			48	Zeolite Na-P ₁	
			72	Zeolite Na-P ₁	
			96	Zeolite Na-P ₁	
		1:20	24	Zeolite Na-P ₁	
			48	Zeolite Na-P ₁	
			72	Zeolite Na-P ₁	
			96	Zeolite Na-P ₁	
		100	1:5	168	Analcime
				168	Analcime
			1:20	120	Analcime
				24	Analcime
	140		1:5	48	Analcime
				72	Analcime
	3	100*	1:5	24	Zeolite Na-P ₁
				48	Zeolite Na-P ₁
				72	Zeolite Na-P ₁
				96	Zeolite Na-P ₁
				120	Zeolite Na-P ₁
				144	Zeolite Na-P ₁
			1:20	24	Zeolite Na-P ₁
				48	Zeolite Na-P ₁
				72	Zeolite Na-P ₁
				96	Zeolite Na-P ₁
120				Zeolite Na-P ₁	
144				Zeolite Na-P ₁	
100	1:5	168	Analcime		
		168	Analcime		
		1:20	24	Analcime	
			48	Analcime	
	120	1:5	72	Analcime	
			96	Analcime	
		1:20	24	Analcime	
			48	Analcime	
	140	1:5	72	Analcime	
			96	Analcime	
			120	Analcime	
			144	Analcime	
1:20		168	Analcime		
		96	Cancrinite		
		120	Cancrinite		
		144	Cancrinite		
		168	Cancrinite		

* = atmosphere pressure

from perlite under the conditions studied. At 100°C and atmospheric pressure, the results revealed that the product was only zeolite Na-P₁ at a concentrations of 1 to 3 M NaOH and transformation took place over a period of 1 to 4 days. This result corresponds to Khodabandeh and Davis (1997). Yang *et al.* (1997) reported that, at a crystallization temperature of 100°C, the most stable structure is gismondine (Na-P₁). Zeolite Na-P₁ typically crystallizes under milder conditions. It was suggested that, at higher temperatures (140°C and 150°C), zeolite Na-P₁ is unstable and transforms into analcime (Gualtieri, 2001). At 20-50 psi with alkalinity concentration of 1 M to 3 M NaOH, solid/liquid ratios of 1:5 and 1:20, and reaction temperatures of 100°C to 140°C, the zeolite product was found to be only analcime with the percentage of crystallinity depending on reaction time. When the reaction was carried out under the influence of 3 M NaOH and a 1:5 solid/liquid ratio at 140°C, perlite is tentatively converted to a single phase of analcime with the highest percentage of crystallinity. Formation of cancrinite was favored with 3 M NaOH and a 1:20 solid/liquid ratio at 140°C.

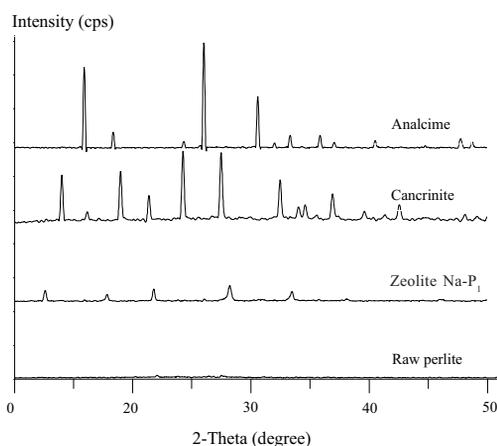


Figure 1. X-ray diffraction patterns of raw perlite and synthesized zeolites obtained under the best condition for each zeolite

Figure 1 represents the XRD patterns of raw perlite, and synthesized zeolites obtained under the best condition for each zeolite. Zeolite Na-P₁ showed 5 strong main peaks at $2\theta = 5^\circ$ to 33.5° , while cancrinite as well as analcime showed strong XRD patterns matched with those reported in literature (Treacy and Higgins, 2001). However, the intensity of XRD peaks for analcime is very strong compared with the other zeolites. This was also confirmed by SEM image (Figure 2).

A comparison of IR spectra of raw perlite, zeolite Na-P₁, cancrinite and analcime is shown in Figure 3. Their IR spectra are also matched with a fingerprints of wave number values (Flanigen *et al.*, 1971). In the region of OH stretching vibration, all samples showed absorption bands around $3,440\text{ cm}^{-1}$. Analcime showed a band at $3,622\text{ cm}^{-1}$, which is attributed to free OH stretching vibration. An absorption band at $1,640\text{ cm}^{-1}$ is due to the bending vibration of adsorbed water molecule. Vibration bands in a region of TO₄ tetrahedral (T = Si or Al) units of zeolite at about $1,020\text{ cm}^{-1}$, 737 cm^{-1} , 619 cm^{-1} and $444 - 460\text{ cm}^{-1}$ are asymmetric stretching, symmetric stretching, double ring and T-O bending vibrations, respectively (Breck, 1974). However, the assignments of vibrational framework of the three different zeolite products are given in Table 2. In the case of analcime, it was found that the absorption bands are slightly

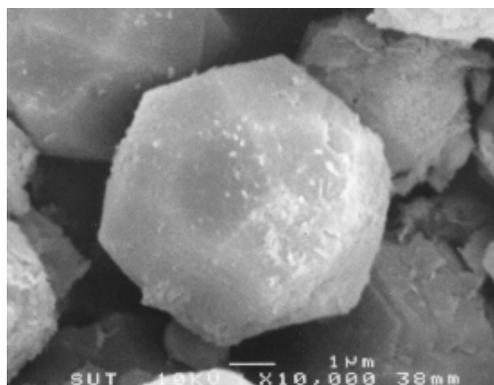


Figure 2. SEM micrograph of analcime crystals prepared from perlite

different from those reported by Flanigen *et al.* (1971). This may be due to the different ratio of Si/Al presented in analcime framework, i.e. 1.97 compared to 4.

Kinetics of Crystallization of Analcime

The effect of reaction time and temperature on the crystallization of analcime synthesized from perlite was examined under the fixed condition at 3 M NaOH and a 1:5 solid/liquid ratio with a temperature range from 130°C to 145°C. XRD patterns of solid phases obtained from the synthesis during different crystallization periods at 135°C are shown in Figure 4. These patterns reflected that raw perlite is amorphous. After 4 h, some peaks of zeolite Na-P₁ appeared and all peaks of analcime appeared after 9 h. The peak intensities slightly increased as the crystallization period increased.

Figure 5 shows the percentage crystallinity of analcime as a function of time at different temperatures. The optimum condition to obtain the highest percent crystallinity was found to be 3 M NaOH, a 1:5 solid/liquid ratio, 140°C and reaction time of 24 h. A product obtained at this condition was used as a standard to calculate the percentage of crystallinity.

The mechanism of zeolite crystallization referring to kinetics, such as autocatalysis of crystallization, has been sufficiently studied. Therefore, in this part, we attempted to calculate the activation energy of crystallization from the Arrhenius equation and to fit the data with the nucleation and growth model by Avrami plot. The activation energy (E_a) of the process was extracted from the slope of the plot $\ln(k)$ against $(1/T)(K^{-1})$, derived from a general Arrhenius equation, $k = Ae^{-E_a/RT}$ as shown in Figure 6. The pre-exponential factor (A) was extracted from the intercept of the line. The resulting value was shown in Table 3. The E_a value was found to be 11.2 kcal/mol, which is in good agreement with those of other zeolites reported by Breck and Flanigen (1968). It was suggested that the activation energy is not related to diffusion of the crystal building unit in solution, but to the condensation reaction between the crystal surface and crystal building unit (Van Bekkum *et al.*, 1991). The Avrami equation can provide a good empirical fit of the kinetic curves. However, the Avrami equation essentially describes solid-state reactions, but not solution-mediated processes. Therefore, it does not refer to any particular mechanism (Gualtieti *et al.*, 1997). According to the Avrami equation,

Table 2. Infrared assignment of vibrational framework of the three different zeolite product

Zeolite	Asymmetric stretching	Symmetric stretching	Double ring	T-O bending
Analcime	1,021, 925	740, 686	615	442
Cancrinite	1,000, 965	680	624, 567	458
Zeolite Na-P ₁	995-1,000	722, 670	600	435

Table 3. Activation energy of analcime crystallization under a reaction condition of 3 M NaOH at various temperatures between 130-140°C and 1:5 solid/liquid ratio

Temperature (°C)	k	R factor (A)	Pre-exponential kcal/mol	E_a
130	14.50			
135	16.92	0.99	16.59	11.2
140	24.50			
145	22.65			

$[-\ln(1-\alpha)] = (kt)^n$, the reaction order (n) was extracted from a plot of $\ln[-\ln(1-\alpha)]$ against $\ln(t)$ as shown in Figure 7. α is the conversion factor ranging from 0 to 1. The rate constant k is derived from the intercept. These parameters have been evaluated for each reaction temperature; the results are shown in Table 4.

Based on the Avrami model, the n value is expected to vary between 1 and 4 depending on the dimensionality of the growth process and on the kinetic order of nucleation. The n values of 3 and 4 can be interpreted as follows. With $n = 3$, the growth process in three dimension is combined with zero order nucleation and, with

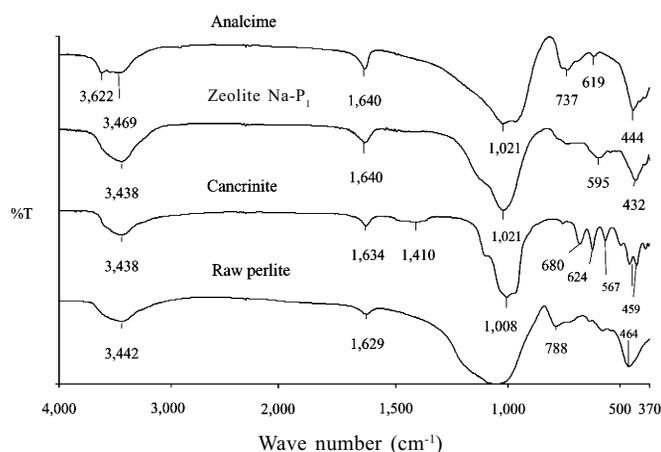


Figure 3. FT-IR spectra of raw perlite and zeolite products of zeolite Na-P₁, cancrinite and analcime

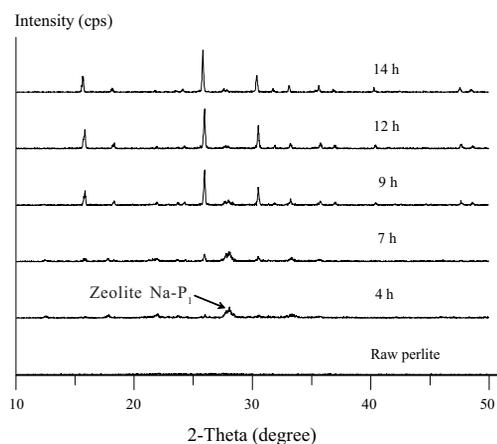


Figure 4. X-ray diffraction patterns of raw perlite and analcime samples obtained with different crystallization periods at 135°C

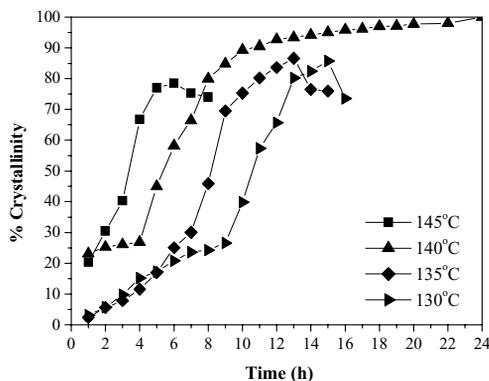


Figure 5. Kinetics of analcime crystallization at different temperatures

n = 4, the similar process of crystal growth appears, but nucleation is the first order. However, the n value found in this work varies from 3.4 to 6.4 a decreasing with temperature from 145°C to 130°C, except at 140°C. The same trend of the n value was observed also in the synthesis of zeolite Na-A (Wongwiwattana and Rangsiwatananon, 2002) and zeolite Na-X (Thammavong and Rangsiwatananon, 2003). It was suggested that, when n exceeds 4, crystal-

lization of an amorphous phase should take place in the autocatalytic stage of the crystallization process under conditions where either the rate of nucleation or the rate of crystal growth increases (Zhdanov *et al.*, 1990). At 140°C, the n value is the highest; it is assumed that the nucleation of analcime is more favored than the other conditions as indicated by the percentage of analcime crystallinity shown in Table 5.

Table 4. The Avrami exponent for analcime crystallization

Temperature (°C)	130	135	140	145
n	5.3	4.2	6.4	3.4
k	1.52×10^{-6}	1.01×10^{-4}	2.71×10^{-6}	3.70×10^{-3}
R	0.98	0.99	0.99	0.99

Table 5. Kinetics of analcime formation from perlite under 3 M NaOH and 1:5 solid/liquid ratio at various reaction temperatures for 24 h

Temperature (°C)	130	135	140	145
% Crystallinity	85.8	89.7	100	95.7

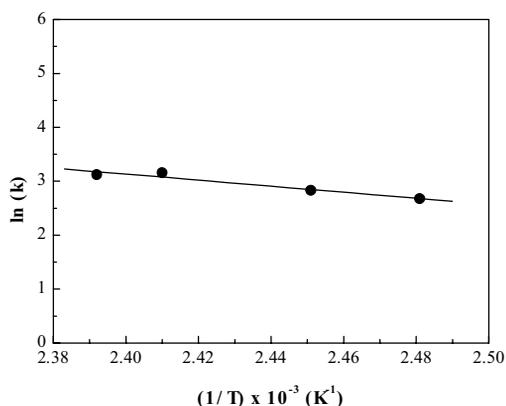


Figure 6. The Arrhenius plot for analcime crystallization

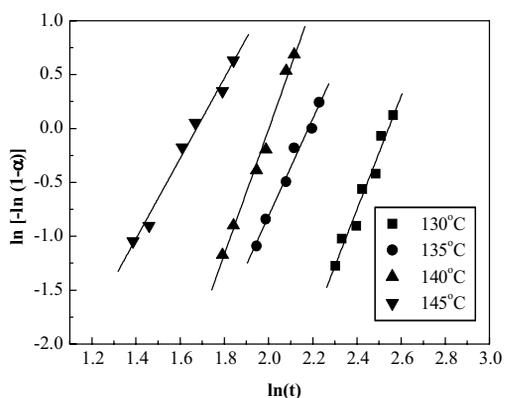


Figure 7. The Avrami plot for $\ln [-\ln(1-\theta)]$ against $\ln(t)$ of analcime crystallization

Conclusions

An inspection of zeolite crystallization from perlite under various conditions was studied. The results indicated that analcime was obtained with the highest percent crystallinity under the condition of 3 M NaOH with a 1:5 solid/liquid ratio at 140°C, for 24 h. The rate of crystallization increased with increasing reaction temperature. The activation energy was found to be 11.2 kcal/mol. This value can be connected with dehydration of silicate and aluminate ion in solution to form crystal building and condensation reaction between the crystal surfaces. The Avrami exponent (n) reflected that reaction is governed by autocatalytic nucleation.

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