Hydrothermal transformation of clinoptilolite

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Abstract. Procedure for hydrothermal transformation of natural clinoptilolite at 160°C is described. The synthesis is carried out in the system $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$. Products of 24–168 hr runs are characterized by x-ray diffraction, IR spectroscopy, energy dispersive analysis of x-rays (EDAX), and electron microscopy. Presence of analcime-type and faujasite-type zeolites in the final products is established. Si/Al ratio of the final mixed phase is estimated as 2.91. Spheroid crystals of analcime, fibrous crystals of mordenite (on analcime), and well developed polyhedral crystals of analcime-faujasite mixed phase are illustrated and described. It is shown that crystals grow by two-dimensional nucleation mechanism.

Keywords. Zeolite; analcime; faujasite; mordenite; polyhedral.

1. Introduction

There are several minerals which are not directly usable in their native form. However, there is ample scope for converting them to more useful materials. Synthesis of more useful forms of zeolites, having scientific and industrial applications, has drawn the attention of several research workers all over the world. The hydrothermal method is principally used for zeolite synthesis and several successful attempts have been made in this laboratory. Choudhari (1983) has effected transformation of (i) calcined scolecite into synthetic analogues of analcime crystals of spheroid and cubic morphologies and (ii) calcined stilbite into synthetic analcime type crystals of habits like needles, spheroids and prisms. Choudhari (1983) also transformed mineral clay into polyhedral (euhe-dral) analcime-type, mordenite-type acicular needle and erionite-type bunched needle crystals. These two investigations were carried out at 180° and 160°C respectively, and at autogenous pressure. Similar experiments have also been successfully carried out on the transformation of mesolite. In this laboratory Joshi *et al* (1982a, b, 1983) have grown vzs-1, 2, 3 and 4 zeolites by the hydrothermal method. Recently, we have also succeeded in synthesizing zsm-5 and zsm-8 type zeolites. Robson and Riley (1977) have reported that hec-ter clinoptilolite, when treated with sodium hydroxide, forms faujasite. Sudo and Matsuoka (1959) treated volcanic glass with sodium hydroxide and obtained sodalite and faujasite. Conversions of clinoptilolite and mordenite to faujasite-type and *p*-type zeolites have been reported by Miyata and Okazaki (1970). Negishi and Nakamura (1970) treated clinoptilolite with NaOH-NaCl solution at 100°C and observed the conversion sequence clinoptilolite → amorphous material → x-type zeolite → sodalite. The present paper reports observations and results of our attempts to transform natural clinoptilolite by the hydrothermal method.

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2. Experimental details

Clinoptilolite used in the present investigation was rich in calcium and had a Si/Al ratio of 3.6. Powdered clinoptilolite was calcined at 700°C for twelve hours. Structural collapse thus effected was ascertained with the help of x-ray diffraction. Chemical composition was determined by energy dispersive analysis of x-rays (EDAX). Calcined clinoptilolite, sodium hydroxide and aluminium hydroxide were taken in the ratio 4:2:1 by weight with excess of double distilled water. Tetrapropylammonium hydroxide was used as a base during crystallization. The resulting gelling mixture had a pH of 11.5. This mixture was transferred to the Berghof autoclave, which is made up of special stainless steel (type DIN 1.4571) having poly tetra fluoro ethylene (PTFE) interchangeable liners. It can be used upto a maximum working temperature of 250°C, for an indefinite period of time. The temperature can be measured with the help of the Ni-Cr-Ni thermosensor which is fixed at the centre of the autoclave. The temperature is regulated by a thermostatically controlled heating circuit with an accuracy of $\pm 5^\circ\text{C}$. Temperature regulation operates only when the thermosensor is connected. There is a hollow cylindrical shaft with stirrer wings which can be rotated electrically at the desired speed. Stirring ensures homogeneity of the gelling mixture. Pressure is measured by a manometer pressure gauge fixed in the lid. The pressure in our experiments was 1000 psi, with a rupture disc to ensure that the pressure does not exceed the limit of the autoclave. In the present investigation crystallization was carried out at 160°C. Runs of duration ranging from 24 to 168 hrs were tried. The product obtained at the end of each run was repeatedly washed with double distilled water, and then dried in an electrical oven at 110°C. Each product was then characterized with the help of x-ray diffraction, IR spectroscopy and EDAX were done. Morphology of the crystals grown was examined by a scanning electron microscope.

2.1 X-ray powder analysis

Observed d values for the final product, with the relative intensities, are given in table 1. X-ray analysis shows that the synthetic product contains analcime and faujasite as the main phases.

2.2 Infrared spectral analysis

Infrared spectra of the synthesized products were recorded with the help of a Perkin Elmer 180 model using KBr pellets. In these spectra characteristic sorption bands of the zeolite family were detected. Assignment of the infrared bands as per Flanigen *et al* (1971) for the final product is given in table 2.

2.3 Chemical analysis

Results of chemical analysis by EDAX, for the product obtained at the end of a 168 hr run, are shown in table 3. The Si/Al ratio for this product, which is the mixed phase of sodium analcime and sodium faujasite, is found to be 2.91.

2.4 Study of morphology by SEM

Each sample (at the end of each growth run) was examined under a scanning electron

Table 1. X-ray powder data for clinoptilolite transformation; 168 hr run

d Å	I/I_0	Phase
5.5912	94	<i>a, f</i>
4.8216	28	<i>a, f</i>
3.6479	14	<i>f</i>
3.4076	100	<i>a, f</i>
2.9214	79	<i>a, f</i>
2.7968	13	<i>a, f</i>
2.6827	28	<i>a, f</i>
2.498	24	<i>a, f</i>
2.420	13	<i>a</i>
2.3559	32	—
2.222	15	<i>a</i>
2.1659	5	<i>a</i>
2.0403	13	<i>a</i>
2.0230	7	<i>a</i>
1.9028	20	<i>a</i>
1.8661	13	<i>a</i>
1.7399	25	<i>a</i>
1.7142	10	<i>a</i>
1.7098	10	—
1.6865	10	<i>a</i>
1.6639	10	<i>a</i>
1.6156	10	<i>a</i>
1.5951	10	<i>a</i>
1.4796	7	<i>a</i>
1.4447	9	—
1.4135	10	<i>a</i>
1.3576	13	—

a — analcime; *f* — faujasite

microscope. Crystals obtained at the end of a 48 hr run are shown in figure 1. Mostly spheroid analcime crystals are obtained. Fibrous crystals of mordenite, grown over analcime spheroid crystals, are also seen in this SEM. Figure 2 shows crystals obtained at the end of a 72 hr run. Well developed polyhedral and platy crystals are obtained. The latter exhibit growth layers. From these observations it is suggested that crystals grow by two dimensional spreading and piling of growth layers. Well developed crystals of a mixed phase of sodium analcime and sodium faujasite are illustrated in figure 3, also an SEM (growth run 144 hr). Two polyhedral, well developed, analcime-type crystals are shown in figure 4 (growth run 168 hr).

3. Discussion

Transformation of clinoptilolite has been effected to more important phases, sodium analcime and sodium faujasite zeolites. The reacting gel mixture contains sodium and

Table 2. Infrared spectral assignment—clinoptilolite transformation; 168 hr

Vibrational mode	Frequency cm^{-1}
A. Structure sensitive (external linkages)	
Double ring (sbu)	
650–500	520 <i>sh</i>
Pore opening	360 <i>wsh</i>
420–300	390 <i>wsh</i>
Symmetric stretch	
750–820	790 <i>w</i>
Asymmetric stretch	
1150–1050	1130 <i>sh</i>
B. Structure insensitive (internal tetrahedron)	
Asymmetric stretch	
1250–950	1100 <i>b</i>
Symmetric stretch	
750–650	700 <i>b</i>
T-O bend	
500–420	470 <i>b</i>
H ₂ O bend	1650 <i>s</i>
OH stretch	3480 <i>sb</i>

sh—shoulder; *wsh*—weak shoulder; *w*—weak; *b*—broad; *sb*—strong broad; *s*—strong

Table 3. Chemical analysis of clinoptilolite transformation; 168 hr run (EDAX)

Element	Weight % (element)	Weight % (oxide)	Atomic % (element)	Atomic % (oxide)
Na	6.025	8.122	5.282	7.923
Al	10.971	20.730	8.195	20.486
Si	33.257	71.148	23.864	71.591

Si/Al = 2.91 (mixed phase of sodium analcime and sodium faujasite)

calcium ions with tetrapropylammonium hydroxide as an organic base. Synthesis was carried out in the system $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$. Calcium ions are also present in the reacting gel. Crystallization of the reaction mixture could be in the system $\text{Ca}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$ or in the mixed system of calcium and sodium. Crystallization of calcium aluminosilicate gels requires a temperature of 275°C and about four weeks time. In the present investigation the temperature was 160°C and, the maximum time of growth was 168 hr. Under these conditions crystallization in calcium system is not possible. Barrer and Denny (1961) have synthesized Ca-*D*, Ca-*I*, Ca-*J* zeolites and, found that no significant crystallization of a zeolite phase in calcium system can occur below 225°C . It is inferred that calcium ions have not taken part in the crystallization, since the temperature was low. In the present case, sodium aluminosilicate gel alone has crystallized. Crystallinity was poor for growth runs below 72 hr. The induction period for crystallization was 24 hr. Crystallinity was better for crystals obtained from a 144 hr run, while good crystals were secured from growth runs of 168 hr.

Figures 1-2. 1. SEM: spheroid (analcime) and fibrous (mordenite) crystals (48 hr run); $\times 3000$. 2. SEM: polyhedral crystals of mixed phase - sodium analcime and faujasite (72 hr run); $\times 2500$.

Figures 3–4. 3. SEM: sodium analcime and sodium faujasite phase well-developed crystals (144 hr run); $\times 4500$.
4. SEM: two well-developed crystals of analcime (168 hr run); $\times 4500$.

4. Conclusions

The presence of tetrapropylammonium hydroxide influences the morphology of crystals grown, more useful phases being produced. Crystals grow by a two dimensional growth mechanism.

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References

- Barrer R M and Denny D J 1961 *J. Chem. Soc.* 983
Choudhari A L 1983 *Studies on physico-chemical properties of natural scolecite and stilbite, and synthesis of some zeolites by hydrothermal method* Ph.D. thesis, Sardar Patel University, Vallabh Vidyanagar
Flanigen E M, Khatami H and Szymansky H A 1971 *Molecular Sieve Zeolites* (Washington D.C.: American Chemical Society) 1 201
Joshi M S, Choudhari A L and Kanitkar R G 1983 *Cryst. Res. Technol.* **18** 1347
Joshi M S, Rao Mohan P, Choudhari A L and Kanitkar R G 1982a *Cryst. Res. Technol.* **17** 925
Joshi M S, Rao Mohan P, Choudhari A L and Kanitkar R G 1982b *J. Mater. Sci. Lett.* **1** 195
Miyata Y and Okazaki S 1970 *Kogyo Koyaku Zasshi* **73** 1940
Negishi T and Nakamura H 1970 *Kobustugaku Zasshi* **10** 72
Robson H E and Riley L K 1977 *Molecular Sieves II. Amer. Chem. Soc. Symp. Ser.* **40** 233
Sudo T and Matsuoka M 1959 *Geochim. Cosmochim. Acta* **17** 1