

Research Article

Synthesis of Analcime Crystals and Simultaneous Potassium Extraction from Natrolite Syenite

Jian Chen,^{1,2,3} Hongwen Ma,^{1,2} Changjiang Liu,^{1,2,3} and Jiangyan Yuan^{1,2,3}

¹School of Materials Science and Technology, China University of Geosciences, Beijing 100083, China

²Beijing Key Laboratory of Materials Utilization of Nonmetallic Minerals and Solid Wastes, China University of Geosciences, Beijing 100083, China

³Blue Sky Technology Corporation, Beijing 100083, China

Correspondence should be addressed to Hongwen Ma; mahw@cugb.edu.cn

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Analcime single crystals were successfully synthesized from natrolite syenite powder (K_2O 10.89%) and 92.6% of potassium was extracted simultaneously by means of soda roasting followed by alkali-hydrothermal method. Effects of NaOH concentration, reaction temperature, and holding period on the analcime formation and potassium extraction were investigated systematically. The results indicated that NaOH concentration plays an important role in determining the chemical composition of zeolites and size distribution; by turning the NaOH concentrations, three different pure zeolites (i.e., the phillipsite-Na, the analcime, and the sodalite) were prepared. Besides, a higher temperature could accelerate the dissolution of K^+ ions and enhance the crystallinity degree of zeolite. The reactions involved in the analcime synthesis can be summarized as follows: sodium aluminum silicate dissolution \rightarrow precipitation and dissolution of metastable zeolite-P \rightarrow analcime nucleation \rightarrow analcime growth. The extraction ratio of K^+ is associated with the types of synthesized zeolites, among which analcime is the most effective to promote potassium leaching out from zeolite lattice position. The optimal condition for analcime crystallization and K^+ leaching is found to be as follows: 175°C for 4 h in 0.5 mol/L NaOH solution.

1. Introduction

Analcime ($NaAlSi_2O_6 \cdot H_2O$) is a hydrated aluminosilicate mineral, the complex framework of which builds by corner-sharing $[SiO_4]$ and $[AlO_4]$ tetrahedron resulting irregular channels and some cavities occupied by the exchangeable Na ions in the crystal lattice [1, 2]. Such unit cell structure and chemical properties permit the analcime to have wide utilization in a number of fields, such as catalysts in petroleum industry [3, 4], fertilizers in agriculture [5], adsorbents in waste water treatment [6–9], and membranes in surfactants and gas separation [10].

Natural analcime can be found in cavities of altered mafic and some undersaturated volcanic rocks [11]; however, the commercial usage of natural analcime is quite limited due to the uneven distribution as well as the low purity [12]. Therefore, many efforts have been devoted to the synthesis

of high purity analcime. Generally, analcime is prepared starting from pure chemical reagents using a hydrothermal crystallization method within the temperature range of 100–200°C. For example, Yokomori and Idaka [13] took tetraethylorthosilicate and aluminum isopropoxide as silica and alumina source, respectively, with tetramethylammonium bromide as organic template for the synthesis of analcime. Liu et al. [14] used aluminum hydroxide, sodium hydroxide, and water glass as starting materials for synthesizing analcime. In addition to such an approach, there is also an emerging trend to use natural minerals, clays, rocks, industrial and agricultural wastes, such as perlite [6, 7], kaolin [15], potassium-rich rocks [16, 17], coal fly ash [18], and rice husk ash [19], as raw materials for analcime synthesis, due to their advantages of wide distribution and lower cost. For example, Sandoval et al. [20] investigated the synthesis of analcime from natural clinker, and Atta et al. [15] obtained analcime after 72 h aging

and 24 h reaction at 180°C by a hydrothermal reaction using rice husk ash and metakaolin as the sources of silica and alumina, respectively.

The two approaches have their advantages and disadvantages. The main disadvantages lie in the complex synthesis process (i.e., long aging and reaction time) and the use of expensive template which make it costly and difficult to industrialization; besides, those raw materials can solely provide the aluminum and/or silicon sources for zeolites. Therefore, finding alternative cheap raw material with all the necessary components for zeolite by a simple and economic method is of great significance.

Recently, Ma et al. [16] firstly proposed an idea to utilize quartz syenite (one kind of potassium-rich rocks) as raw material to synthesize analcime via an alkali-hydrothermal reaction (treated at 240°C for 4 h). This approach takes full use of the aluminosilicate and alkali metal source for analcime preparation; at the same time, it can also extract potassium ions (K^+) which can be used to prepare potassium fertilizer, the most rare fertilizers in China and India [21–24]. Lately, Yuan et al. [17] investigated the analcime synthesis as well as the simultaneous extraction of K^+ from K-feldspar in Na_2SiO_3 solution, which could be realized by hydrothermal dissolution process at 250°C for 5 h. These attempts not only explore the feasibility of preparing analcime zeolite from abundantly available resources, but also provide a new idea for K^+ extraction from insoluble potassium resources.

We notice that in the above mentioned reports the potassium extraction (~75%) is not ideally high and there exist impurities in analcime (microcline and biotite) caused by the incomplete decomposition of microcline and indissolubility of biotite in alkaline aqueous, which will hinder the practical industrial application. In this study, we report a simple and economic method (i.e., the soda roasting followed by alkali-hydrothermal approach) to convert natrolite syenite (an important potassium-rich rock in China) into pure analcime and potassium salts. In this reaction, the effects of the NaOH concentration, crystallization temperature, and time on the formation of analcime zeolite and the extraction of K^+ were studied in detail. The reaction mechanism of analcime synthesis and dissolution of K^+ ions was also discussed.

2. Experimental

2.1. Materials. The natrolite syenite sample was collected from Fengcheng City of Liaoning Province (China) and natrolite syenite powder (particle size < 74 μm) for this research was prepared by crushing and grinding. The main chemical composition of natrolite syenite powder is SiO_2 54.72 wt%, Al_2O_3 19.54 wt%, K_2O 10.89 wt%, and a small quantity of Fe_2O_3 , Na_2O , MgO , and CaO (Table 1). According to the results of X-ray diffraction of the natrolite syenite powder (Figure 1(a)), the predominated mineral is microcline, natrolite, and biotite. Based on the principle of material balance [25], mineral composition of the powder is the following (wt%): microcline 60.8, natrolite 19.0, biotite 6.4, muscovite 6.4, chlorite 4.1, calcite 1.3, sphene 1.6, and apatite 0.4. Both soda and NaOH used were of analytical reagent

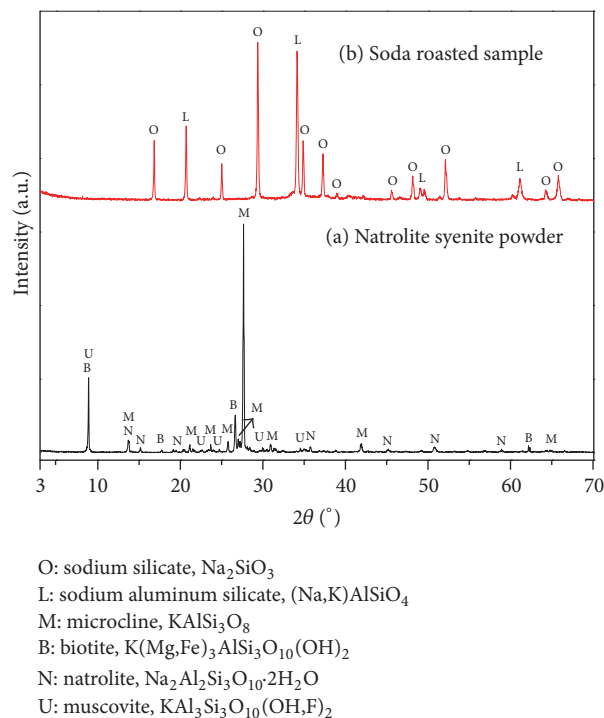


FIGURE 1: XRD patterns of natrolite syenite powder (a) and soda roasted sample (b).

grade (Beijing Chemical Reagent Ltd.) and all the solutions were diluted using deionized water.

2.2. Synthesis Experiments. In order to break the stable structure of microcline, natrolite, biotite, and muscovite for forming the active aluminosilicate to synthesize zeolite, and leaching out K^+ ions from hydrothermal product, the whole experiment was designed into two parts: soda roasting and hydrothermal crystallization. Firstly, roasting was conducted by placing the mixture of natrolite syenite powder and soda with 1:1 (mass ratio) in an electrically heated furnace at 830°C for 2 h. XRD patterns of the natrolite syenite powder and soda roasted sample are shown in Figure 1, indicating that the main minerals in natrolite syenite were completely transformed into sodium silicate (Na_2SiO_3) and sodium aluminum silicate ($(Na, K)AlSiO_4$) after roasting with soda; the same results were obtained in our previous study by soda roasting with coal fly ash [26]. According to the principle of material balance, the chemical composition of roasted sample can be expressed as $0.8K_2O \cdot 6.2Na_2O \cdot 1.3Al_2O_3 \cdot 6.0SiO_2$, the mole ratio of silica to alumina is about 2.4 within the range of synthesis of analcime, and no additional silicon and alumina sources are required. Secondly, hydrothermal reactions were performed in a stainless steel autoclave. 10 g of roasted sample was mixed with 100 mL of different concentration of NaOH solutions and then added into autoclave and heated at 125~225°C for different times, respectively. After reaction, the solid products were filtered, washed with distilled water repeatedly, and dried at 105°C for 12 h. The filtrates and washing solutions were collected and diluted to 500 mL to measure potassium content. The schematic diagram of

TABLE 1: Chemical composition of natrolite syenite powder (wt%).

Samples	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	Loss	Total
NS-1	54.72	0.78	19.54	4.11	0.01	1.15	1.93	3.26	10.89	0.16	3.32	99.87

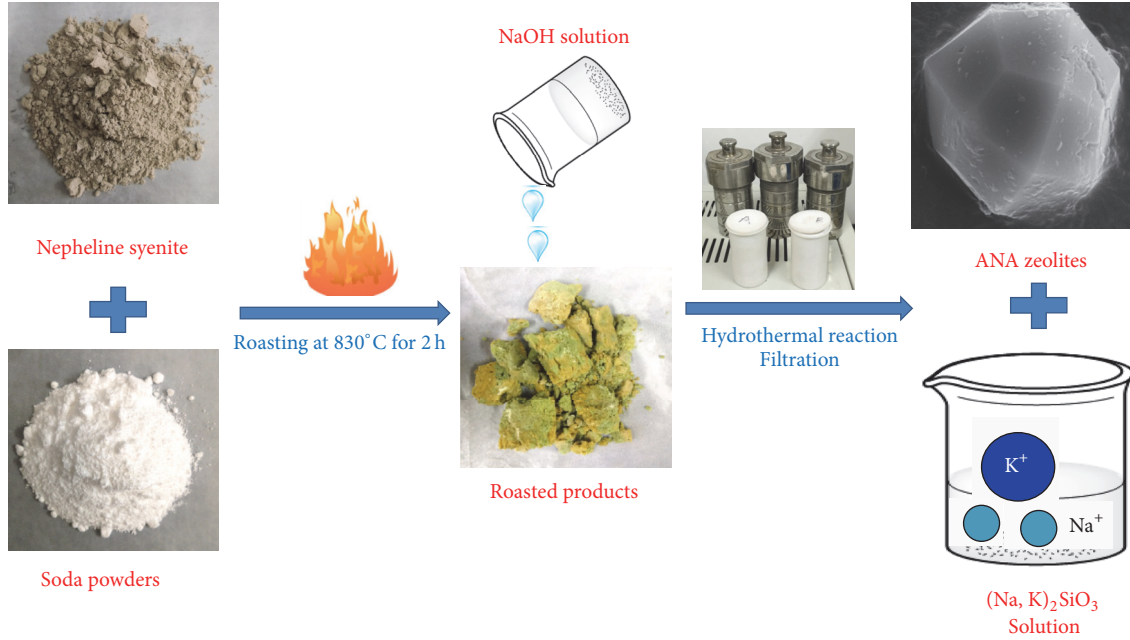


FIGURE 2: The schematic diagram of analcime synthesis with potassium extraction from natrolite syenite.

analcime synthesis with potassium extraction from natrolite syenite is shown in Figure 2.

2.3. Characterization. The chemical compositions of natrolite syenite powder were determined by wet chemical analysis. The contents of SiO₂ and Al₂O₃ were determined by polyethylene oxide dehydration method and EDTA complexometric method, respectively. The X-ray diffraction (XRD) analysis was performed on a Rigaku D/Max 2500 X-ray diffractometer with Cu K α radiation. Data were collected over a 2θ range of 3–70° with a step size of 0.02° and scanning rate of 8°·min⁻¹. The microstructures of the solid samples were observed by field emission scanning electron microscopy with energy dispersive X-ray (SEM-EDX, Hitachi S-4800, Japan). FT-IR spectra of synthesized analcime were collected by Perkin Elmer 2000 FI-IR spectrometer in the 4000–400 cm⁻¹ region using potassium bromide as the diluent and binder. The contents of potassium in the resulting filtrates were measured by flame photometric method and the extraction ratio of potassium (η_{K_2O}) was calculated by the following formula:

$$\begin{aligned} \eta_{K_2O} &= \frac{C_K \times 0.5}{((m_1 \times \gamma \times 10.89\%) / m_2) \times 10} \times 100\% \\ &= \frac{0.459 \times C_K \times m_2}{m_1 \times \gamma} \times 100\%. \end{aligned} \quad (1)$$

m_1 denotes the weight of the mixture powder of natrolite syenite and soda before roasting (g), m_2 represents the weight of the mixture powder after roasting (g), γ is the mass fraction of natrolite syenite in mixture powder before roasting, and C_K is the contents of K₂O in the diluted solution (g/L).

3. Results and Discussion

3.1. Effect of NaOH Concentration. Phase diagram in Na₂O-Al₂O₃-SiO₂-H₂O system is the basis used to synthesize zeolites [27]. Due to the presence of K₂O in raw material, the hydrothermal crystallization of analcime zeolite in this research can be extended to the phase equilibrium of K₂O-Na₂O-Al₂O₃-SiO₂-H₂O. To investigate the effect of NaOH concentration on the formation of analcime and the dissolution of K⁺ ions, the hydrothermal experiment was performed in 0.0, 0.5, 1.0, 1.5, 2.0, and 2.5 mol/L NaOH solutions at 175°C for 4 h, respectively. The XRD patterns of the synthesized products are shown in Figure 3. It is apparent that three different zeolites, phillipsite-Na (Na₄KAl₅Si₁₁O₃₂·10H₂O, ICDD 73-1419), analcime (Na₆Al₆Si₁₂O₃₆·6H₂O, ICDD 76-0906), and sodalite (Na₈Al₆Si₆O₂₄(OH)₂·2H₂O, ICDD 76-1639), can be obtained in the K₂O-Na₂O-Al₂O₃-SiO₂-H₂O system. The lower NaOH concentration (0.0 mol/L) is in favor of phillipsite-Na formation, and higher concentration of NaOH (1.0–2.5 mol/L) accelerated the formation of sodalite. The results are in good agreement with the report of previous

TABLE 2: The phase composition of as-prepared product and the extraction rates of potassium under different concentrations of NaOH solution.

Samples	Experiment conditions			Results		Si/Al ratio	η_{K_2O} (%)
	C_{NaOH} (mol/L)	T ($^{\circ}C$)	t (h)	Solid product phase composition			
SM-0	Soda roasting at 830 $^{\circ}C$ for 2 h			Sodium silicate	Na_2SiO_3	2.4	—
				Sodium alumina silicate (Na, K) $_4Al_2Si_2O_9$			
SM-1	0.0	175	4	Phillipsite-Na	$Na_4KAl_5Si_{11}O_{32} \cdot 10H_2O$	2.1	54.6
SM-2	0.5	175	4	Analcime	$NaAlSi_2O_6 \cdot H_2O$	2.0	92.6
SM-3	1.0	175	4	Sodalite	$Na_8Al_6Si_6O_{24}(OH)_2 \cdot 2H_2O$	1.0	86.5
SM-4	1.5	175	4	Sodalite	$Na_8Al_6Si_6O_{24}(OH)_2 \cdot 2H_2O$	1.0	86.4
SM-5	2.0	175	4	Sodalite	$Na_8Al_6Si_6O_{24}(OH)_2 \cdot 2H_2O$	1.0	86.0
SM-6	2.5	175	4	Sodalite	$Na_8Al_6Si_6O_{24}(OH)_2 \cdot 2H_2O$	1.0	85.9

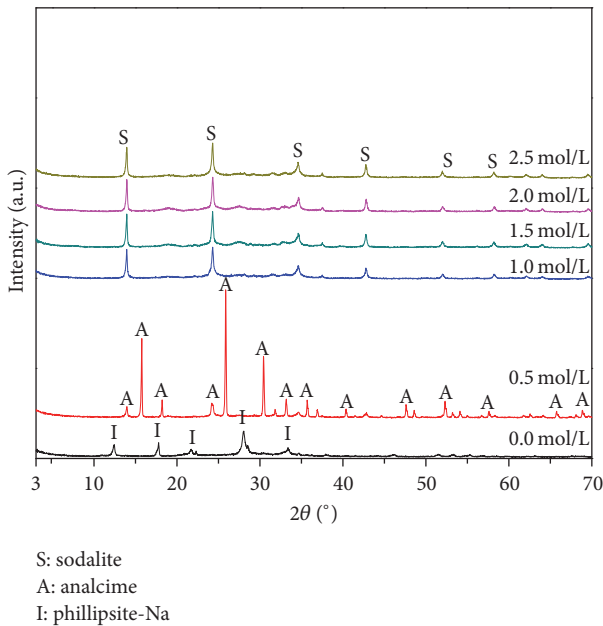


FIGURE 3: XRD patterns of products prepared under different NaOH concentrations.

study [28, 29]. It was also shown that pure analcime could only be synthesized at 0.5 mol/L NaOH solutions, and the diffraction peaks at $2\theta = 15.8^{\circ}$, 25.9° , and 30.6° are in accordance with the high crystallinity analcime crystals synthesized from chemical-grade reagents [3, 13, 19]. The results indicated that NaOH concentration plays an important role in determining the chemical composition of synthesized zeolite.

Figure 4 shows the SEM images of the samples prepared at different NaOH concentrations. The SEM results are in good consistence with XRD analysis. The phillipsite-Na zeolite with poor crystallinity and cotton-like morphology is shown in Figure 4(a). The icositetrahedra crystal with average size of $10 \mu m$ was identified as analcime in Figure 4(b), which is similar to the morphology of analcime obtained by using clinker [20], rice husk ash [15], and quartz syenite [16] as raw

materials. It was also shown that most of analcime crystals are clean faceted, and some fractures exhibited may be associated with the presence of metallic impurities of Fe and Ti in natrolite syenite. According to previous study [30, 31], the additions of Fe and/or Ti into a synthesis mixture in preparation of zeolite led to structural defects in the analcime produced. As the NaOH concentration was higher than 0.5 mol/L, the spherical sodalite with surface covered by short columnar crystals appeared (Figure 4(c) and Figure 4(d)). Analcime and sodalite crystals with uniform size distribution are shown in Figure 4, indicating that the presence of metallic impurities and the increase of NaOH concentration help to narrow the size distribution of particles. The results proved that, with hydrothermal crystallization treated at 0.5 mol/L NaOH solution, the pure, single-phase analcime crystals with diameter of $10 \mu m$ could be obtained.

Table 2 shows the phase composition of as-prepared product and extraction ratio of potassium under different concentrations of NaOH solution. It was found that the Si/Al mole ratio of synthesized zeolites decreased from 2.1 to 2.0 and down to 1.0 finally with NaOH concentration increasing. This can be explained by the behavior of Si and Al in alkali aqueous, and higher alkalinity leads to higher solubility of the Si and Al sources, decreases the degree of silicate anion polymerization, and speeds up the polymerization of the polysilicate and aluminate anions [32, 33]. It was also observed that the extraction ratio of K^+ is associated with the types of synthetic zeolite. After phillipsite-Na zeolite was synthesized in water, only 54.6% of K^+ ions were leaching, which may be caused by the remaining K^+ ions required to balance the resulting net negative charge of the aluminosilicate framework structure in zeolite. However, synthesis of sodalite is corresponding to about 86.0% of K^+ extracted, and 92.6% of K^+ was recovered from the solution after analcime synthesis. The results reveal that analcime and sodalite formation would promote the K^+ ions leaching from zeolite lattice position, which could mainly be attributed to the limited ions exchange capacity with K^+ in both zeolites. According to the report by Barrer and Hinds [34, 35], analcime ($NaAlSi_2O_6$) shows limited solid solubility of leucite ($KAlSi_2O_6$) at both higher temperatures

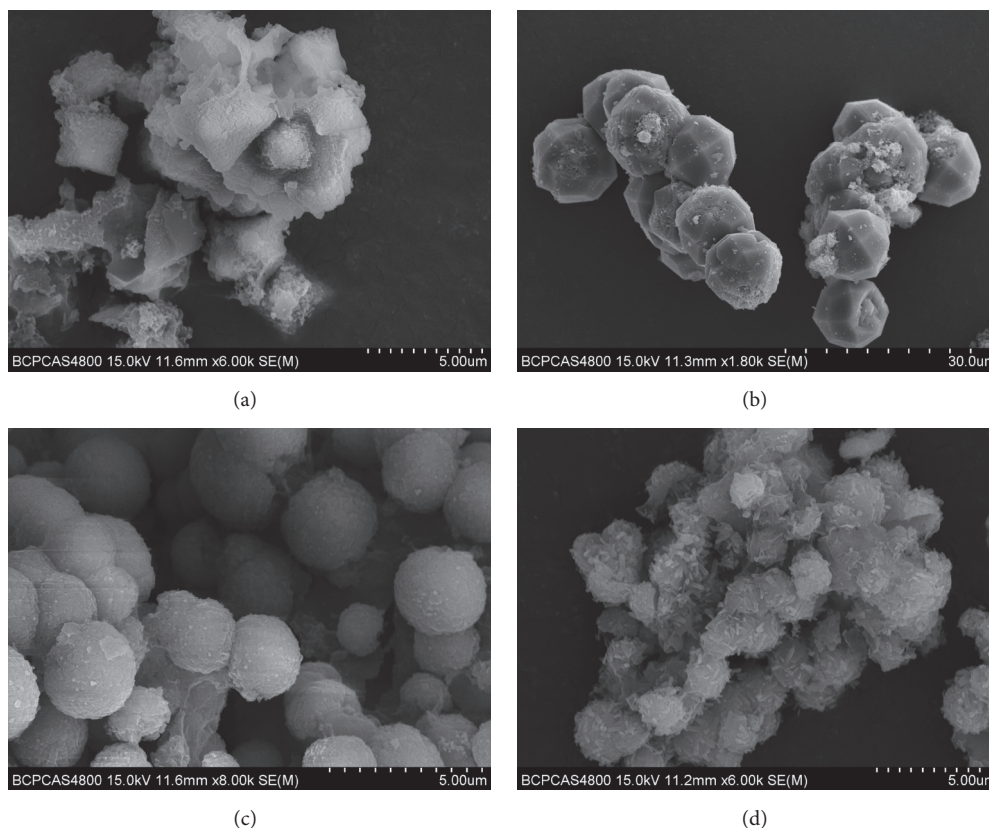


FIGURE 4: SEM images of samples prepared at different NaOH concentrations: (a) 0.0 mol/L, (b) 0.5 mol/L, (c) 1.0 mol/L, and (d) 1.5 mol/L.

and very low temperatures under hydrothermal conditions. Similarity results were obtained by Balgord and Roy [36]; in the case of K^+ exchange, no more than 10% of K^+ is tolerated in the analcime crystalline at equilibrium. The content of potassium component substituting in sodalite is in the ranges of 0.1%–5.3% according to the report by Taylor [37]. Thus, the optimal NaOH concentration for analcime preparation and K^+ leaching should be chosen as 0.5 mol/L.

3.2. Effect of Temperature. The effects of crystallization temperature on synthesis of analcime and leaching of K^+ were investigated under 0.5 mol/L of NaOH solution at 125°C~225°C for 4 h. The XRD patterns of the solid samples and the results of potassium extraction ratio at different temperatures are shown in Figure 5. It can be seen that pure phase of zeolite-P obtained in solid products is corresponding to 63.7% of K^+ dissolved into mother liquor at 125°C. When the temperature increased to 150°C, the diffraction peaks corresponding to zeolite-P were enhanced and potassium extraction efficiency was also increased, indicating that a higher temperature could enhance the degree of crystallinity of zeolite [38] and accelerate the dissolution of K^+ . By increasing temperature from 150°C up to 175°C, the zeolite-P disappeared completely and the pure analcime zeolite phase formed with the maximum of potassium extraction efficiency (92.6%). However, when the temperature was above 175°C, the phase of sodalite appeared in solid products, and the dissolution ratio of K^+ was reduced

with the increase of temperature. These results indicated that both zeolite-P and analcime are metastable zeolites and have a tendency to convert into a more thermodynamically stable zeolite-sodalite with the temperature increasing [39–41]. On the other hand, it seems that analcime synthesized is more advantageous than sodalite to K^+ dissolution. In a word, a suitable temperature of 175°C is the most beneficial to the maximization of K^+ dissolution, which can reach 92.6%.

FT-IR spectrum of analcime synthesized at 175°C is illustrated in Figure 6. The obtained peaks are similar to those of analcime single crystals reported in a previous study [42, 43]. The peaks at 1003 cm^{-1} , 690 cm^{-1} , and 576 cm^{-1} were assigned to T-O (T=Si, Al) asymmetric stretch vibration, T-O symmetric stretch vibration, and T-O-T bending vibration, respectively. The broad bands at 3420 cm^{-1} and 1654 cm^{-1} are attributed to zeolite water, and the bands at about 470 cm^{-1} are due to vibrations related to internal of the TO4. The lattice parameters of analcime zeolite synthesized at 175°C are shown in Table 3, and the results are in good agreement with that of cubic analcime (ICDD 76-0976). The results indicated that the analcime with pure, single-phase, and high crystallinity was successfully synthesized at the crystallization temperature of 175°C.

3.3. Effect of Crystallization Time. In order to explore the effects of crystallization time on the as-prepared products, the hydrothermal process was conducted at 175°C for different

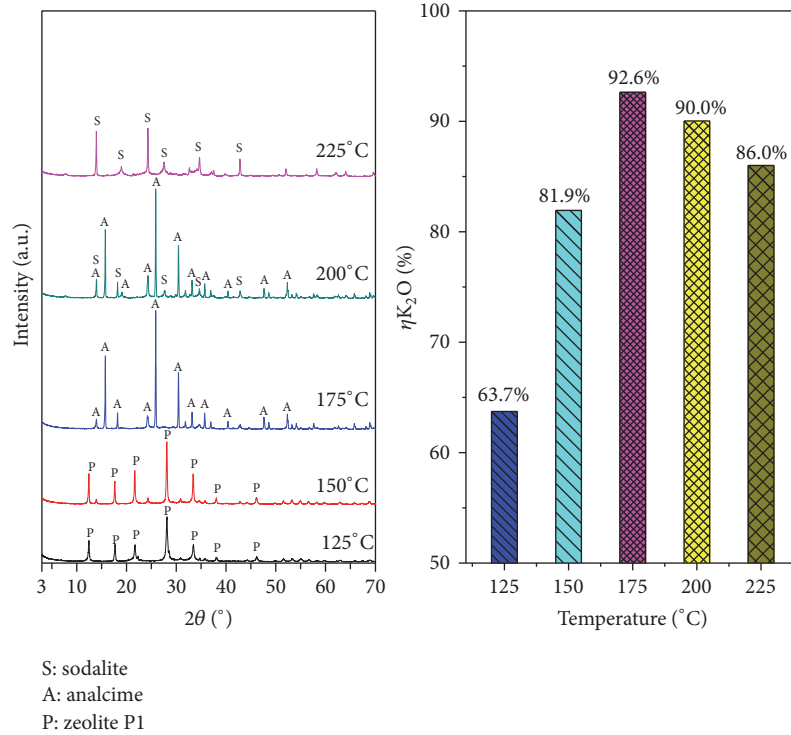


FIGURE 5: XRD patterns of the solid samples and the results of potassium extraction ratio at different temperatures.

TABLE 3: The calculated lattice parameters of prepared analcime obtained at optimal conditions.

Sample	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)	Cell volume (Å ³)	Cell density (g·cm ⁻³)
Analcime	13.7568	13.7568	13.7597	90	90	90	2604.04	2.2462
ICDD 76-0907	13.7210	13.7210	13.7350	90	90	90	2585.83	2.2620

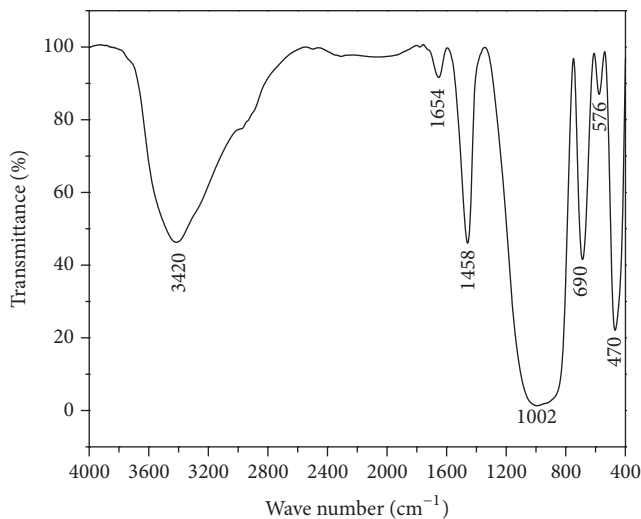


FIGURE 6: FT-IR spectrum of ANA zeolite synthesized in 0.5 mol/L NaOH solutions at the crystallization temperature of 175°C for 4 h.

crystallization times (1 h to 5 h) in 0.5 mol/L NaOH solution. The XRD patterns of the products obtained at different

crystallization time are presented in Figure 7. It is shown that the diffraction peaks of sodium aluminum silicate phase still existed after reaction for 1 h, indicating that the dissolution rate of the precursor materials in the NaOH solution is slower than those using pure chemical agents as raw material. Therefore, it is clear that there is enough time to generate zeolite-P nucleations in a supersaturated solution [44]. After two-hour treatment, the zeolite-P product was detected. With the prolongation of the hydrothermal crystallization time to 3 h, the metastable zeolite-P dissolved gradually and transformed into analcime zeolite. There is no crystalline phase of zeolite-P that appeared after 4 h treatment, and the products were pure analcime crystals; the analcime crystals were still stabilized after reaction for 5 h. The results indicated that zeolite-P appears to be a metastable intermediate phase in the formation of analcime, and analcime zeolites could be obtained as the ultimate equilibrium phase in the initial batch of composition $8.0\text{K}_2\text{O}\cdot 115.9\text{Na}_2\text{O}\cdot 13.3\text{Al}_2\text{O}_3\cdot 63.3\text{SiO}_2\cdot 5550.0\text{H}_2\text{O}$ at least for 4 h.

The results of potassium extraction ratio at different crystallization time are shown in Figure 8, indicating that a significant increase in potassium extraction ratio was obtained by extending reaction time from 1 h to 4 h. The K^+ ion dissolution reached equilibrium after hydrothermal treatment

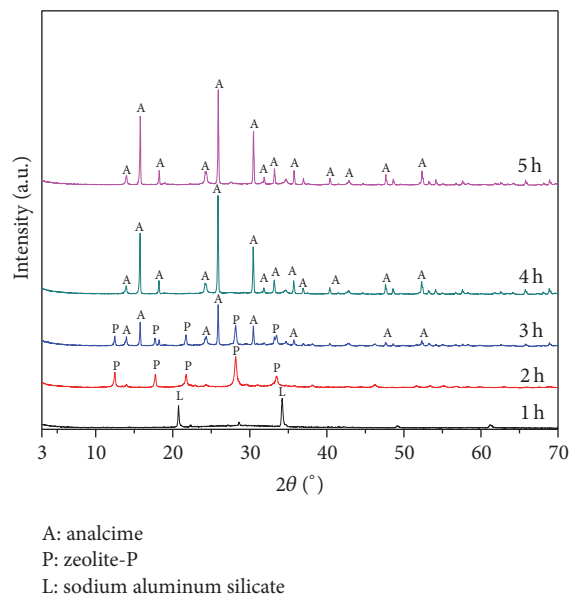


FIGURE 7: XRD patterns of the products obtained at different crystallization time.

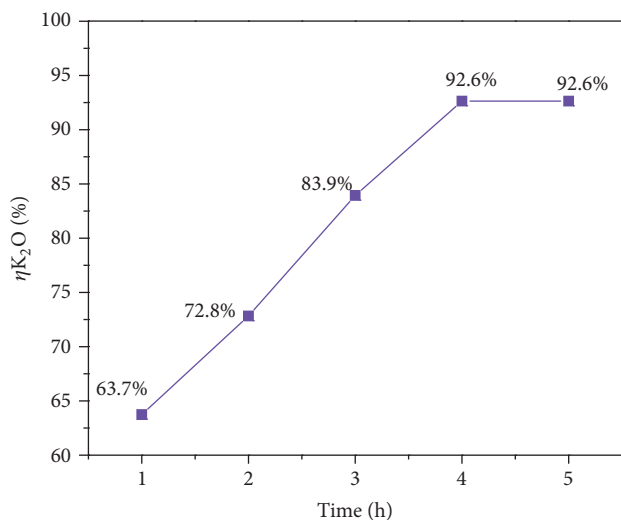


FIGURE 8: The results of potassium extraction rates at 175°C for different crystallization times (1 h to 5 h) in 0.5 mol/L NaOH solution.

was prolonged to 4 h, and the maximum of potassium extraction ratio reached was 92.6%. Thus, the crystallization time for 4 h is appropriate for potassium extraction.

SEM images of the samples collected at different crystallization time are presented in Figure 9. The half-moon-shaped particle with the size of about 4–6 μm and smooth surface was identified as sodium aluminum silicate precursor (Figure 9(a)). The irregular octahedrons with surface accumulated by plate-like crystals were identified as zeolite-P (Figure 9(b)), consistent with the previously reported in the literature [45]. With the reaction time extended, the irregular hollow octahedron structure of zeolite-P

cracked (Figure 9(c)) and the icositetrahedra analcime crystals started crystallizing (Figure 9(d)). After 4 h crystallizing, the perfect icositetrahedra analcime single crystals with the uniform size of 10 μm were obtained (Figures 9(e) and 9(f)). We can see that some small crystals emerged on the surface of intergrowths analcime crystals. According to the report by Ge et al. [46], when two particles with different sizes attach to each other, energetic factors drive the larger particle to grow, drawing from the smaller particle, which shrinks. In addition, the coincident results illustrated by SEM and XRD revealed that the reaction mechanism of the analcime synthesis could be summarized as follows: sodium aluminum silicate dissolution \rightarrow precipitation and dissolution of metastable zeolite-P \rightarrow analcime crystal nucleation \rightarrow analcime crystal growth.

4. Conclusions

In this work, we successfully converted natrolite syenite into pure, single-phase, and high crystalline analcime zeolites with the average particle size of about 10 μm via the soda roasting followed by alkali-hydrothermal method. In the process of hydrothermal crystallization, 92.6% of K^+ ions could simultaneously be dissolved. The optimal condition for analcime crystallization and K^+ leaching is found to be as follows: 175°C for 4 h in 0.5 mol/L NaOH solution. It was also concluded that (1) the NaOH concentration plays an important role in determining the chemical composition of zeolites and size distribution, (2) higher temperature could enhance the degree of crystallinity of zeolite and accelerate the dissolution of K^+ , (3) the mechanism of the analcime synthesis was summarized as sodium aluminum silicate dissolution \rightarrow precipitation and dissolution of metastable zeolite-P \rightarrow analcime nucleation \rightarrow analcime growth, and (4) the extraction ratio of K^+ is associated with the types of synthesized zeolites, among which analcime is the most

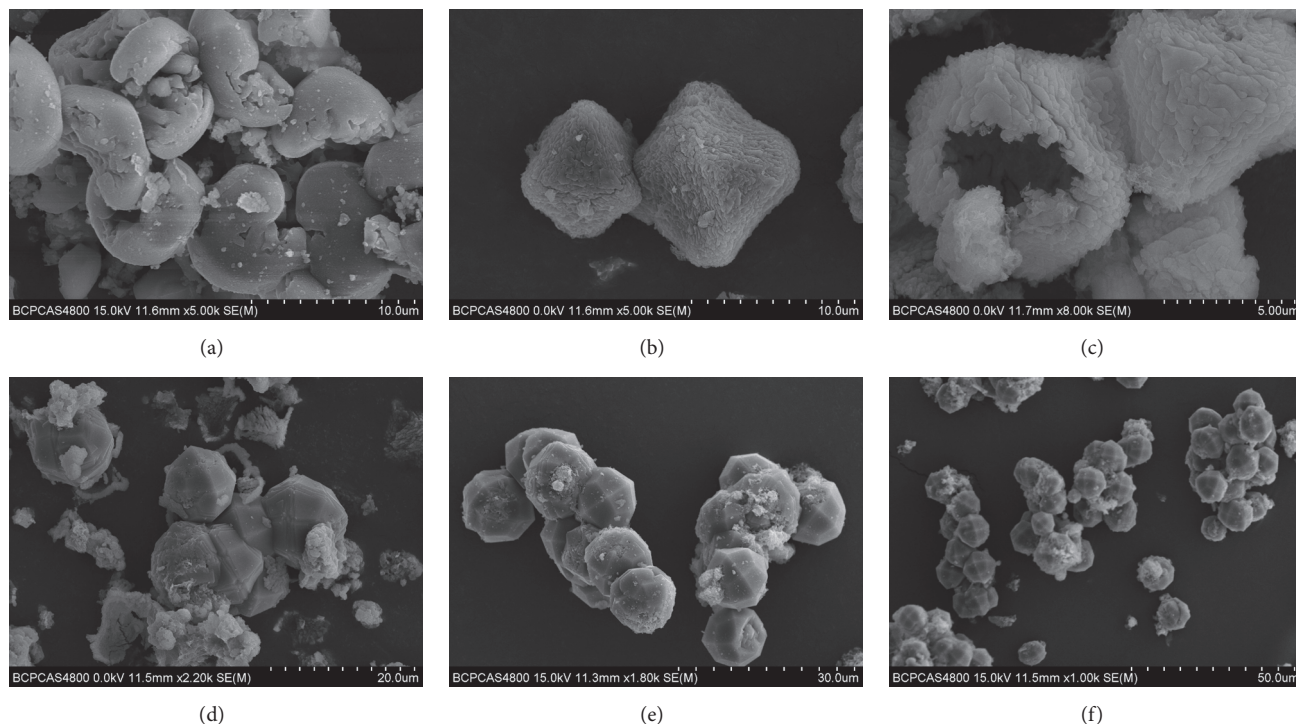


FIGURE 9: SEM images of samples collected at different crystallization time: (a) 1 h, (b) 2 h, (c) 3 h, (d) 3 h, (e) 4 h, and (f) 5 h.

effective to promote potassium leaching out from zeolite lattice position. As a result, this work successfully proved that the soda roasting and subsequent alkali-hydrothermal method were an economically available technique for the extraction of potassium and the synthesis of analcime from natrolite syenite, due to the comprehensive utilization of silicon, alumina, and potassium resources without additional expensive reagents needed.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

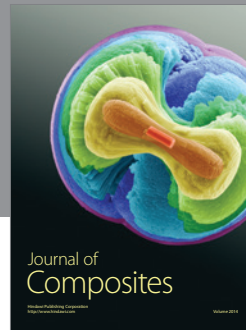
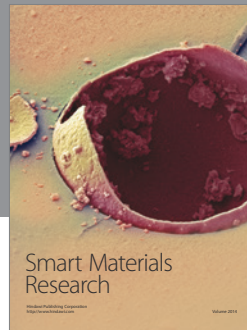
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