Analcime single crystals were successfully synthesized from natrolite syenite powder (K₂O 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 systemically. 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.
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 Na₂SiO₃ 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 SiO₂ 54.72 wt%, Al₂O₃ 19.54 wt%, K₂O 10.89 wt%, and a small quantity of Fe₂O₃, Na₂O, 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 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 (Na₂SiO₃) and sodium aluminum silicate ((Na, K)Al₅O₈) 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 0.8K₂O·6.2Na₂O·1.3Al₂O₃·6.0SiO₂, 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%).

<table>
<thead>
<tr>
<th>Samples</th>
<th>SiO$_2$</th>
<th>TiO$_2$</th>
<th>Al$_2$O$_3$</th>
<th>Fe$_2$O$_3$</th>
<th>MnO</th>
<th>MgO</th>
<th>CaO</th>
<th>Na$_2$O</th>
<th>K$_2$O</th>
<th>P$_2$O$_5$</th>
<th>Loss</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>NS-1</td>
<td>54.72</td>
<td>0.78</td>
<td>19.54</td>
<td>4.11</td>
<td>0.01</td>
<td>1.15</td>
<td>1.93</td>
<td>3.26</td>
<td>10.89</td>
<td>0.16</td>
<td>3.32</td>
<td>99.87</td>
</tr>
</tbody>
</table>

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

2.3. Characterization. The chemical compositions of natrolite syenite powder were determined by wet chemical analysis. The contents of SiO$_2$ and Al$_2$O$_3$ 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 Kα 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 FT-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 ($\eta$K$_2$O%) was calculated by the following formula:

$$\eta K_2O = \frac{C_K \times 0.5}{(m_1 \times y \times 10.89%)/m_2} \times 100\%$$

where $C_K$ is the content of K$_2$O in the diluted solution (g/L), $m_1$ 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), $y$ is the mass fraction of natrolite syenite in mixture powder before roasting, and $C_K$ is the contents of K$_2$O in the diluted solution (g/L).

3. Results and Discussion

3.1. Effect of NaOH Concentration. Phase diagram in Na$_2$O-Al$_2$O$_3$-SiO$_2$-H$_2$O system is the basis used to synthesize zeolites [27]. Due to the presence of K$_2$O in raw material, the hydrothermal crystallization of analcime zeolite in this research can be extended to the phase equilibrium of K$_2$O-Na$_2$O-Al$_2$O$_3$-SiO$_2$-H$_2$O. 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 (Na$_8$KAl$_2$Si$_{11}$O$_{33}$·10H$_2$O, ICDD 73-1419), analcime (Na$_8$Al$_6$Si$_{2}$O$_{23}$·6H$_2$O, ICDD 76-0906), and sodalite (Na$_8$Al$_6$Si$_6$O$_{24}$·(OH)$_2$·2H$_2$O, ICDD 76-1639), can be obtained in the K$_2$O-Na$_2$O-Al$_2$O$_3$-SiO$_2$-H$_2$O 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...
Clinker, rice husk ash, and quartz syenite 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 μm 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⁺ ions required to balance the resulting net negative charge of the analcime. 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 alumino-silicate 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 (NaAlSi₂O₆) shows limited solid solubility of leucite (KAlSi₂O₆) at both higher temperatures.
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$^+$ leachingshould 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
crystallization times (1h to 5h) 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 1h, 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 3h, the metastable zeolite-P dissolved gradually and transformed into analcime zeolite. There is no crystalline phase of zeolite-P that appeared after 4h treatment, and the products were pure analcime crystals; the analcime crystals were still stabilized after reaction for 5h. 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 $8.0K_2O\cdot115.9Na_2O\cdot13.3Al_2O_3\cdot63.3SiO_2\cdot5550.0H_2O$ at least for 4h.

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 1h to 4h. The $K^+$ ion dissolution reached equilibrium after hydrothermal treatment

$$\text{Table 3: The calculated lattice parameters of prepared analcime obtained at optimal conditions.}$$

<table>
<thead>
<tr>
<th>Sample</th>
<th>$a$ (Å)</th>
<th>$b$ (Å)</th>
<th>$c$ (Å)</th>
<th>$\alpha$ (°)</th>
<th>$\beta$ (°)</th>
<th>$\gamma$ (°)</th>
<th>Cell volume (Å$^3$)</th>
<th>Cell density (g cm$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Analcime</td>
<td>13.7568</td>
<td>13.7568</td>
<td>13.7597</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>2604.04</td>
<td>2.2462</td>
</tr>
<tr>
<td>ICDD 76-0907</td>
<td>13.7210</td>
<td>13.7210</td>
<td>13.7350</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>2585.83</td>
<td>2.2620</td>
</tr>
</tbody>
</table>

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

Figure 6: FT-IR spectrum of ANA zeolite synthesized in 0.5 mol/L NaOH solutions at the crystallization temperature of 175°C for 4h.
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 icositetrahedral analcime crystals started crystallizing (Figure 9(d)). After 4 h crystallizing, the perfect icositetrahedral 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
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.

Acknowledgments

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References


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.


