Microwave-assisted and conventional hydrothermal synthesis of potassium merlinoite from K-feldspar

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A B S T R A C T

Potassium merlinoite was successfully synthesized from K-feldspar powder by microwave-assisted as well as conventional hydrothermal methods. Effects of aging, H2O/Al2O3 molar ratio, crystallization temperature, crystallization time, and mixed heating strategy on potassium merlinoite formation were systematically studied. It was observed that aging was not a necessary factor to the formation of merlinoite, and merlinoite was the unique crystalline product at a wide range of H2O/Al2O3 molar ratio, crystallization temperature and time. The reaction rate of microwave-assisted hydrothermal synthesis was 2–3 times as much as conventional method. The acceleration effect of microwave was proved to work only at the initial period of irradiation, and a mixed heating method was considered as an appropriate strategy to prepare merlinoite. A simple and economical chemical process has been proposed to convert the natural K-feldspar powder into merlinoite-type eco-fertilizer in this paper.

1. Introduction

Zeolite materials, with specific adsorption and ion exchange properties, are able to maintain water in soil, improve the availability of nutrient elements, and remediate the heavy metal-polluted farmland if applied in agriculture [1,2]. The agricultural use of natural Na-zeolites (such as clinoptilolite and stilbite) has been reported in literatures [3,4]. Some nutrient-loaded (N- and K-) zeolites have also been used as slow-release fertilizers to improve the low efficiency situation of traditional chemical soluble fertilizers [5]. Nutrients-loaded zeolites, with both soil remediation and fertilizer effects, are excellent eco-fertilizers in modern agriculture.

Potassium merlinoite, which is also called zeolite W in some literatures [6], together with other two types of K-zeolites, zeolite L and zeolite T, is a common product in K2O-Al2O3-SiO2-H2O hydrothermal system [7]. Merlinoite synthesized from coal fly ash has been proved to be an efficient slow-release K-fertilizer for plant growth [8]. It has also been studied as a molecular sieve for the extraction of potassium from seawater [9,10].

Conventional zeolite synthesis method requires aluminosilicate gels prepared from synthetic chemical agents. Besides, the utilization of natural rocks and minerals, industrial and agricultural wastes, including kaolin [11], coal fly ash [12], and rice husk ash [13,14] etc., as starting materials for zeolites has attracted much of attention. However, those raw materials only provide the aluminum and/or silicon sources for zeolites. Expensive alkaline chemical agents, NaOH and KOH, are still required. Finding alternative cheap raw materials with all the necessary components for zeolite is of great significance for zeolite preparation.

As a widely abundant rock-forming mineral, K-feldspar (KAlSi3-O8) is an important insoluble potassium source [15]. Recently, extraction of potassium from K-feldspar to meet the agricultural potash needs has become an international topic [16,17]. Conversion of K-feldspar into slow-release K-fertilizer (merlinoite) can not only supply potassium element for plants, but also take full advantage of the aluminum and silicon components in the insoluble mineral, which satisfies the principle of green chemistry [18]. K-feldspar has a stable tectosilicate framework. Direct hydrothermal treatment on K-feldspar with KOH solution resulted in the formation of kalsilite (KAlSiO4) phase, instead of K-zeolites [19]. In order to obtain high reactive amorphous intermediates,
pre-activation on raw materials is a necessary step, such as calcination of kaolinite before zeolitization, which requires a thermal activation temperature of 500–900 °C [20]. Besides, alkaline fusion is another activation method, needing a relative low temperature of 400–600 °C [21].

In addition to conventional hydrothermal (CH) synthesis, microwave-assisted hydrothermal (MH) heating can always increase reaction kinetics by several orders of magnitudes, which has been considered as an effective method for the preparation of zeolites. Though lots of papers reported the microwave-assisted hydrothermal synthesis of zeolite [22], the effects of microwave working strategies on zeolite formation are seldom reported. The microwave-assisted hydrothermal synthesis of potassium merlinoite from K-feldspar has not been reported, as well.

The aim of present work is to systematically study the formation of potassium merlinoite from K-feldspar by microwave heating. As a comparison, conventional hydrothermal synthesis under same experimental conditions are investigated. To explore the effects of heating strategies on merlinoite formation, the mixed methods of CH and MH heating are studied.

2. Experimental

2.1. Materials

The raw K-feldspar powder (particle size <74 μm, Sample ID: SK15-2) was obtained from crushed and grinded syenite, a kind of potassic rock collected from Shangdu county of Inner Mongolia autonomous region, China. Its chemical composition determined by wet chemical analysis is listed in Table 1. Based on the principle of material balance [23], considering the three feldspar end-members (KAlSi3O8, NaAlSi3O8, CaAl2Si2O8) and other common minerals in igneous rocks (micas, apatite, magnetite, etc.), mineral composition of the powder is (wt%): K-feldspar 91.35, quartz 6.91, and minor other minerals (mica, apatite, magnetite, etc.) 1.74. Potassium hydroxide (G.R. 85% KOH, Beijing Chemical Works) and deionized water were used in the following experiments.

2.2. Methods

5 g K-feldspar powder was firstly mixed with potassium hydroxide at mass ratio of 1:1.2 in a nickel crucible, and then fused at 400 °C for 90 min. The mixtures after fusion were dissolved into different volume of deionized water, 30, 40, 50, and 60 mL, to obtain aluminosilicate gels. The gels were heated immediately, or after 15 h of aging at room temperature.

MH synthesis was conducted in 100 mL Teflon-reactors placed in a microwave digestion oven (HG08Z-4, HuaGangTong Technology Co., Ltd). A microwave generator (Panasonic 2M261-M32) was equipped on the oven to generate microwave irradiation with a working frequency of 2.45 GHz. Temperature-rising period was set for 4 min, with 0–100% of 1000 W output power, and the temperature-holding period was operated at 0–100% of 600 W output power. CH synthesis under the same conditions was conducted in a Teflon-lined stainless steel autoclave. To examine the effects of heating strategy on potassium merlinoite synthesis, mixed heating methods between microwave field and conventional heating oven at different heating period were carried out (see part 3.4, Fig. 5).

After experiments, the products were filtered, washed repeatedly, and dried at 105 °C for 12 h.

2.3. Characterization

X-ray diffraction (XRD) analysis was done by a X-ray diffractometer (SmartLab, Rigaku) using Cu Kα radiation in steps of 0.02° over 2θ range of 3–50° (scanning speed: 0.10 s/step). Relative crystallinity (RC) was calculated by comparing of the diffraction intensities of three strong peaks (I(111), I(114), I(311)) with the maximum-intensity-sample among all the synthesized products. Morphology was observed by scanning electron microscopy (JSM-IT300, JEOL). CECs of the synthesized potassium merlinoite samples were determined by measuring the exchanged NH4+ in 2 M KCl solution from NH4+-saturated samples, prepared by equilibrating with 2 M ammonium chloride solution. NH4+ concentration was determined using colorimetric method.

3. Results and discussion

3.1. Effects of aging

All the diffraction peaks in Fig. 1 confirm the crystallization of potassium merlinoite phase (PDF card No. 30-0902). The RC of direct-crystallized samples (Fig. 1b, 30.32% for 2 h, 100% for 4 h) show much higher than the aged samples (Fig. 1a, 15.51% for 2 h, 64.28% for 4 h), even when increase crystallization time from 2 h to 4 h. For MH method, the difference becomes more obvious. Poorly crystalline products were obtained after aging (Fig. 1c), whereas, high X-ray intensity merlinoite pattern was identified after 45 min of microwave heating in the direct-crystallized sample (Fig. 1d).

It is well known that aging before zeolite crystallization is an essential step for the nucleation of zeolite from the starting gels. For example, the synthesis of zeolite A can be finished in 1 min after prolonged aging using MH heating [24]. A ten-hour aging period was suitable for merlinoite formation in other report [9]. However, what was found in this work illustrates that aging has a retardation effect on potassium merlinoite zeolitization. Directly hydrothermal synthesis is superior to long time aging in this study. This phenomenon may be caused by the raw material that is different from traditional aluminosilicate gels. The K-feldspar after fusion may provide some sub-units that were beneficial to directly zeolitization, but easy to be destroyed by prolonged aging time.

As a consequence, we conclude that the synthesis process of potassium merlinoite from potassium aluminosilicate procedures using K-feldspar as starting material can be simplified by neglecting the unnecessary aging period.

3.2. Effects of H2O/Al2O3 molar ratio

According to the report of Ref. [6], potassium merlinoite has a K:Al:Si ratio of 1:1:(1.78–2.37). Theoretically, K-feldspar (K:Al:Si = 1:1:3) can provide sufficient and necessary potassium, aluminum, and silicon sources for merlinoite. The raw K-feldspar powder has a M2O/Al2O3 ratio of 1.05, where M2O belongs to the alkalai metal oxides (K2O with minor Na2O) and trace amount of divalent metal oxides (CaO, MgO). Therefore, no extra potassium, aluminum, and silicon sources are needed in the synthetic process.

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Chemical composition of the K-feldspar powder (SK15-2) (wt%):</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO2</td>
<td>66.27</td>
</tr>
<tr>
<td>TiO2</td>
<td>0.03</td>
</tr>
<tr>
<td>Al2O3</td>
<td>17.50</td>
</tr>
<tr>
<td>Fe2O3</td>
<td>0.04</td>
</tr>
<tr>
<td>FeO</td>
<td>0.24</td>
</tr>
<tr>
<td>MnO</td>
<td>0.01</td>
</tr>
<tr>
<td>MgO</td>
<td>0.23</td>
</tr>
<tr>
<td>CaO</td>
<td>0.70</td>
</tr>
<tr>
<td>Na2O</td>
<td>0.89</td>
</tr>
<tr>
<td>K2O</td>
<td>13.83</td>
</tr>
<tr>
<td>P2O5</td>
<td>0.04</td>
</tr>
<tr>
<td>LOI</td>
<td>0.44</td>
</tr>
<tr>
<td>SUM</td>
<td>100.23</td>
</tr>
</tbody>
</table>
The excess potassium hydroxide in pre-activation stage can be reused by further causticization. The only varied factor that might affect merlinoite crystallization was $\text{H}_2\text{O}/\text{Al}_2\text{O}_3$ ratio. The gel composition was $6.4\text{SiO}_2:1.0\text{Al}_2\text{O}_3:6.3\text{M}_2\text{O}:x\text{H}_2\text{O}$ in this study, where $x$ stands for $\text{H}_2\text{O}/\text{Al}_2\text{O}_3$ molar ratio values, varying as 197.3, 261.2, 325.2, 389.2, depending on the amount of water introduced into the system after fusion.

Fig. 2 shows the XRD patterns and RC of potassium merlinoite synthesized by CH and MC methods from different $\text{H}_2\text{O}/\text{Al}_2\text{O}_3$ molar ratios. It was found that potassium merlinoite was the only crystalline phase with different RC in various $\text{H}_2\text{O}/\text{Al}_2\text{O}_3$ molar ratios by both CH and MH methods. The optimal gel composition of $(5–10)\text{SiO}_2:\text{Al}_2\text{O}_3:(0.05–0.31)\text{Na}_2\text{O}:(0.7–7.7)\text{K}_2\text{O}:(27–72)\text{H}_2\text{O}$ for merlinoite (zeolite W) crystallization at temperature range of 100–150°C for 24–240 h was summarized in reference literature [7]. The synthesis conditions in this study are in the range of above composition, but beyond the scope of the given time and temperatures limits, indicating there is a more broad crystallization zone of potassium merlinoite in the $\text{K}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$ hydrothermal system.

It can be observed that $\text{H}_2\text{O}/\text{Al}_2\text{O}_3$ molar ratio of 325.2 was more appropriate for the synthesis of highly crystalline potassium merlinoite by both CH and MH heating methods.

3.3. Effects of synthesis temperature and time

Zeolites are thermodynamically metastable materials, and their formation are generally controlled by kinetics factors such as synthesis temperature and time. In $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$ system, three different zeolites, Y-type, P-type and analcime can be acquired from the same gel composition by only changing the temperature and time during synthesis processes [25]. Therefore, temperature and time are important factors that may affect the formation of potassium merlinoite. In this work, crystallization
from 140 to 180 °C, and heating time of 0–6 h for CH, 0–90 min for MH, were investigated. Systematically experimental results analyzed by XRD (patterns not shown) identify the unique crystalline phase of merlinoite under above temperature and time ranges, which proves that merlinoite is thermodynamically stable within the above conditions. Therefore, kinetic study of merlinoite formation under CH and MH methods is necessary.

Fig. 3 plots the RC values vs. crystallization time under different temperatures. Generally, the crystallization of zeolite from starting gels mainly includes three steps: an induction period, an accelerated crystal growth period, and deceleration of the growing process [26]. For MH method, at 180 °C, the induction period can be neglected, and accelerated crystal growth was lasted from 0 to 45 min. As a comparison, it took approximate 1 h for induction by CH heating at 180 °C, after which merlinoite phase began to generate. The fast crystallization period was from 1 h to 4 h, and the best crystalline merlinoite was obtained after 4 h by CH heating. It was found that decreasing temperature to 160 °C and 140 °C sharply reduced the RC of merlinoite products for both CH and MH methods. At 140 °C, merlinoite began to crystallize after 30 min using MH synthesis, or 3 h using CH heating. Even prolonged synthesis only resulted in the RC of 7.25% for CH and 14.45% for MH methods. As a result, MH for 60–90 min at 180 °C is suitable for merlinoite synthesis from the K-feldspar.

Fig. 3. Relations of relative crystallinity (RC) vs. crystallization time for CH and MH methods under different temperatures.

Fig. 4. Morphology of the products after 6 h of CH heating, and 90 min of MH heating under different temperatures.
It is observed obviously that merlinoite crystallization was enhanced by MH method. The rapid crystallization of zeolites by MH method has been compared with CH in other reports. The suitable time that is needed for zeolite synthesis depends largely on the types of targeting zeolites. As a summary, the reaction rate increased by 3–4 times for zeolite Y at 100 °C [27], about 4 times for zeolite T at 120 °C [28], and over 20 times for zeolite X at 90 °C [29]. This work demonstrates that the formation rate of merlinoite by MH method is 2–3 times faster than by CH method, similar to the formation of zeolite A synthesized from metakaolinite at 70–80 °C [20].

SEM images of the products obtained by CH and MH methods under different temperatures is shown in Fig. 4. At 140 °C, irregular aggregates probably belonging to the X-ray amorphous products were observed for both CH- and MH- samples. Merlinoite obtained from CH heating exhibits as dumbbell-like pillars at length of approximate 10 μm. The shape of both ends is in the form of single pillar similar to that of cauliflower. The MH-sample obtained at 160 °C shows slender stick-like morphology, with length of about 5 μm. When temperature increased to 180 °C, small clusters with column-like morphology are observed. It is a common results that zeolite morphology is affected by microwave irradiation [30,31]. The merlinoite grains synthesized using MH method were relative small and narrow compared with those using CH method. This may be attributed to the homogeneous heating by microwave irradiation inside the reaction mixture. An “effective temperature [32]” at the reaction interface was more promotive to the nucleation of merlinoite, and resulted in the small but uniformed-size crystal grains. In CH method, as heat was from outside, the temperature distribution was heterogeneous in the mixture, by which the nucleation and crystal growth was affected. Consequently, grain morphology became different.

3.4. Effects of heating strategy

The reaction mixtures were microwave-heated for an interval of time, then transferred to a conventional heating oven; or firstly conventional-heated for 45 min before MH heating (see Fig. 5). For all experiments total heating time was maintained for 90 min. The CECs and RC of the synthesized potassium merlinoite samples are shown in Fig. 6. CECs have a slight change within 54.84–57.23 mgNH₄+/g, along with a variation of RC at different heating strategies. This is probably caused by the special material. Some sub-units or structures may existed in the fused K-feldspar with similar ion-exchange properties to merlinoite. Thus, even the sample with poor RC (68.18%) had a CEC close to the maximum value.

It was found that 4 min of MH heating during temperature-rising period followed by 90 min of CH heating for the next 90 min caused the RC of 68.18% (CM-A). In contrast, RC of the sample synthesized by CH method for 90 min is below 20% (Fig. 3, curve of CH 180 °C). This finding particularly indicates that even short-time microwave irradiation can greatly promote zeolite formation. However, the strategies of CM-B (MH for 15 min then CH for 75 min, RC = 83.90%), and CM-C (MH for 30 min then CH for 60 min, RC = 86.90%) illustrated in Fig. 5 had almost the same effect as direct MH heating for 90 min (89.73%), which means prelonged irradiation time after 15 min has un conspicuous effect on zeolitization. In the case of strategy CM-D, 45 min of MH heating followed by 45 min of CH heating even generated a poor RC of 68.56%, equaling to that of 45 min-MH product (RC = 68.61%), indicating that CH at the following 45 min had no effect on crystallization.

From above results, two aspects findings are summarized: (i) the reaction rate can be accelerated only at the initial period of microwave heating, (ii) the effect of CH heating after microwave irradiating for 45 min was insignificant. Similar consequence was also reported by Inada et al. in their synthesis of NaP zeolite from coal fly ash. Their results showed that the yield of NaP increased at early stage, decreased at middle stage, and was not influenced by microwave heating at last stage [33]. However, in this work the best crystalline merlinoite (RC = 99.25%) can be obtained by 45 min irradiation after 45 min CH heating (CM-E). It turned out that pre-heating by CH method followed by MH heating was more appropriate for merlinoite formation. It is deduced that CH pre-heating stage in the induction period led to a supersaturation in the gel. The followed MH heating could promote nucleation of merlinoite from the supersaturated gel. Thus, highly crystalline merlinoite was synthesized via strategy CM-E. Additionally, both the CH and MH time was shortened to 45min by using the mixed
heating method, which also reduces energy cost. Despite that microwave working mechanism is complex and need further investigation, its acceleration effect on the formation of merlinoite was obvious.

Table 2 lists a series of raw sources, synthesis methods and conditions of potassium merlinoite in other literatures. For most of the researches, pure chemical agents were the major sources for merlinoite. Though coal fly ash and diatomite were introduced in some reports, the additional potassic agent, KOH, was still required. It is unreasonable to convert the expensive potassic agents into K-fertilizers! In contrary, all the necessary sources for merlinoite were from the natural material of K-feldspar powder in this work, which could largely reduce the raw material costs. It is obvious that CH heating was the dominated synthesis method, and little research reported MH method for merlinoite. The mixed heating strategy by the combination of CH and MH methods has hitherto not been reported. This strategy shortened the synthesis time within 90 min, which is a considerable way to reduce the energy cost for merlinoite synthesis.

In conclusion, this work has proposed a simple and economical chemical process to convert the natural K-feldspar powder into merlinoite-type eco-fertilizer, which shed new light on the comprehensive utilization of potassium, aluminum, and silicon components.

4. Conclusion

Potassium merlinoite was synthesized by both microwave-assisted (MH) and conventional hydrothermal (CH) methods from raw K-feldspar after pre-activation by fusion with potassium hydroxide as additive.

It was found that aging was not a necessary step, even had a retardation effect on merlinoite crystallization. Merlinoite was the unique thermodynamically favored product at temperature range of 140–180 °C, and H2O/Al2O3 molar ratio of 197.3–389.2, within 90 min for MH and 6 h for CH. The optimum conditions for the synthesis of high crystallinity potassium merlinoite is H2O/Al2O3 of 325.2, temperature of 180 °C, time of 60–90 min for MH, and 6 h for CH methods. MH method can enhance the reaction rate by 2–3 times of CH method. The slender and uniformed stick-like morphology is affected by microwave irradiation. Microwave has been proved to promote zeolitization at the initial period of irradiation. The mixed heating strategy with CH pre-heating followed by MH has been considered appropriate for potassium merlinoite synthesis.

This work provide a new sight on the process of K-feldspar by converting it into merlinoite-type eco-fertilizer, with the comprehensive utilization of natural insoluble potassium sources.

Acknowledgements

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[3] M. Reháková, S. Cuvanová, M. Dzivák, J. Rimár, Z. Gaval’ová, Agricultural and chemical process to convert the natural K-feldspar powder into potassium merlinoite synthesis. Potassium merlinoite was synthesized by both microwave-assisted (MH) and conventional hydrothermal (CH) methods from raw K-feldspar after pre-activation by fusion with potassium hydroxide as additive.

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Table 2
Summary of raw sources, methods and conditions for the synthesis of potassium merlinoite (zeolite W).

<table>
<thead>
<tr>
<th>Silicon, Aluminum, and Potassium sources</th>
<th>Synthesis method</th>
<th>Temperature/°C</th>
<th>Time/h</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boehmite, Silica solution, Potassium hydroxide</td>
<td>CH</td>
<td>140</td>
<td>96</td>
</tr>
<tr>
<td>Coal fly ash, Amorphous SiO2 or quartz, Potassium hydroxide</td>
<td>CH</td>
<td>180–250</td>
<td>1–2</td>
</tr>
<tr>
<td>Tetramethyl orthosilicate, Aluminum tri-sec-butoxide, Potassium hydroxide</td>
<td>CH</td>
<td>165</td>
<td>48</td>
</tr>
<tr>
<td>Ludox, Aluminum hydroxide, Potassium hydroxide/Potassium nitrate</td>
<td>CH</td>
<td>165</td>
<td>24</td>
</tr>
<tr>
<td>Silica acid, Aluminum hydroxide, Potassium hydroxide</td>
<td>CH</td>
<td>165</td>
<td>72</td>
</tr>
<tr>
<td>Water glass, Sodium aluminate, Potassium hydroxide</td>
<td>CH</td>
<td>170</td>
<td>22</td>
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<tr>
<td>Coal fly ash, Potassium hydroxide</td>
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<td>150–200</td>
<td>8–24</td>
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<tr>
<td>Diatomite, Aluminum hydroxide, Potassium hydroxide</td>
<td>CH</td>
<td>150</td>
<td>20–120</td>
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<tr>
<td>TEOS, Aluminate solution, Potassium hydroxide</td>
<td>CH</td>
<td>170</td>
<td>48</td>
</tr>
<tr>
<td>Silica sol, Sodium aluminate, Potassium hydroxide</td>
<td>CH</td>
<td>165</td>
<td>72</td>
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<tr>
<td>Ludox, Aluminum hydroxide, Potassium hydroxide</td>
<td>CH</td>
<td>165</td>
<td>72</td>
</tr>
<tr>
<td>K-feldspar</td>
<td>CH + MH</td>
<td>180</td>
<td>1.5</td>
</tr>
</tbody>
</table>

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