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Synthesis of KAlSiO_4 by Hydrothermal Processing on Biotite Syenite and Dissolution Reaction Kinetics

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Abstract: To make potassium from K-bearing rocks accessible to agriculture, processing on biotite syenite powder under mild alkaline hydrothermal conditions was carried out, in which two types of KAlSiO_4 were obtained successfully. The dissolution-precipitation process of silicate rocks is a significant process in lithospheric evolution. Its effective utilization will be of importance for realizing the comprehensiveness of aluminosilicate minerals in nature. Two kinds of KAlSiO_4 were precipitated in sequence during the dissolution process of biotite syenite. The crystal structures of two kinds of KAlSiO_4 were compared by Rietveld structure refinements. The kinetics model derived from geochemical research was adopted to describe the dissolution behavior. The reaction order and apparent activation energy at the temperature range of 240–300 °C were 2.992 and 97.41 kJ/mol, respectively. The higher dissolution reaction rate of K-feldspar mainly relies on the alkaline solution, which gives rise to higher reaction order. During the dissolution-precipitation process of K-feldspar, two types of KAlSiO_4 with different crystal structure were precipitated. This study provides novel green chemical routes for the comprehensive utilization of potassium-rich silicates.

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Keywords: K-feldspar; kalsilite; kinetics; hydrothermal processing

1. Introduction

The continuous growth of the world population causes a lack of crops production. The global demand for potassium will appear as a rising tendency in the coming several decades [1]. At present, the potassium salt is obtained mainly from water-soluble potassium salt resources [2]. The imports of potash have increased in China year-by-year. The recovery of potassium from potassium-rich rocks has attracted more attention in recent years and will become a promising way to relieve the shortage of potassium from a green chemistry perspective. Therefore, the use of water-insoluble potassium resources, such as potassium feldspar, nepheline, and muscovite, is a guarantee for Chinese agriculture sustainable development [3]. Feldspars consisting of a group of minerals are fairly common in igneous rocks such as granites, gneisses and schists, as well as metamorphic and some sedimentary rocks, constituting 60% of both the continental and the oceanic crusts of our planet [2]. Thereby, K-feldspar was suggested as a source of potassium for agriculture in the beginning of the twentieth century [3,4].

The approach based on the use of ground K-feldspar is simple and involves minimum energy consumption, but it has not yet been successfully implemented in mainstream agriculture, mainly because of the extremely slow rate of potassium released from the minerals [5,6]. Recently, Ciceri and Allamore [7] measured the leaching rate of K^+ ions from syenite in a microfluidic environment and demonstrated that K^+ is available at a higher rate than that observed with conventional apparatuses. Therefore, they thought

that the research of potassium rock is important particularly for tropical soils and countries that cannot afford or access traditional potassium fertilizers. The stable structure of K-feldspar makes it difficult to release K^+ and, therefore, it cannot be used as a fertilizer in the soil directly [8]. The production of potassium salts from potassium-rich rocks should meet the following requirements: lower energy to destroy the structure of potassium feldspar, efficient decomposition process, comprehensive utilization of K_2O , Al_2O_3 , and SiO_2 resources, as well as clean production [9–11]. Therefore, the conversion of K_2O in potassic rocks (potassium feldspar) into the structure that is easy to be dissolved in the soil is the main goal. An additional goal is to convert the byproducts of Al_2O_3 and SiO_2 into useful substances leading to comprehensive and cost-effective utilization of potassic rocks.

The slow-release K^+ fertilizer in kalsilite-type attracts lots of attention among researchers, such as K_2MgSiO_4 , $K_2MgSi_3O_8$, $K_2MgSi_5O_{12}$, $K_4Mg_2Si_5O_{14}$, and $K_2MgSi_3O_8$ [12–17]. The solubility results suggest the release of K_2O of these compounds in 0.5 mol/L HCl (24–38%), citric acid 0.1 mol/L (17–24%), and water (3–8%), all of which reached the Chinese national standard of slow-release fertilizer and can function as slow-release fertilisers to supply K, Mg, and Si nutrients for crops [16,18]. Owing to the lower resources reserves of kalsilite, the application of kalsilite in agriculture is limited. There are many different methods to synthesize kalsilite, such as the sol-gel method, solid-phase reaction method, and the hydrothermal method. Bogdanovicieni synthesized $KAlSiO_4$ and $K_{0.5}Na_{0.5}AlSiO_4$ using analytical grade reagents (CH_3COOK , CH_3COONa , $Al(NO_3)_3 \cdot 9H_2O$ and $SiO_2 \cdot 0.3207 H_2O$) through the sol-gel method [19]. Kalsilite was obtained through the ion exchange of K^+ and LTA zeolite by Dimitrijevic et al. [20]. Compared with these synthesis methods, it is more economical and convenient for the synthesis of kalsilite to utilize the hydrothermal method. The synthesis and transformation mechanism of kalsilite from kaolinite in KOH solution were reported by Becerro et al. [21]. However, compared to those compounds, the synthesis of $KAlSiO_4$ is easier and of lower energy consumption for the green and clean production of K-feldspar ($KAlSi_3O_8$).

Dissolution and precipitation process of feldspars are of importance in the formation of zeolites and clay minerals as well as the hydrothermal transformation process of K-feldspar. There are many factors influencing the dissolution rates of feldspar both in nature and laboratory experiments, such as ionic strength, temperature, pH, fluid saturation state, and so on [22,23]. Here, we mainly use the coupled process to transform the potassium from K-feldspar into secondary mineral (kalsilite) in order to enhance potassium utilization efficiency in soil [24]. Our team has long-term research on the preparation of potassium salts and fertilizer from potassic rocks in order to realize the green utilization of potassic rocks [3–6,25–28], mainly including the soda sintering method and hydrothermal alkaline digestion. In our previous study, the dissolution products of potassic rocks were investigated in different solutions to prepare potassic salts. Most of them focus on optimizing hydrothermal treatment techniques of potassic rocks in order to realize the maximum utilization of resources and clean production [29,30]. The reaction rate plays a key role in influencing the efficiency of preparation techniques and dissolution process. The dissolution kinetics study will provide an important theoretical basis for the hydrothermal reaction and promote potassium preparation techniques development. Here, a potassium-rich biotite syenite powder mainly composed of K-feldspar was collected as the raw material in this study. Two types of $KAlSiO_4$ were prepared during the dissolution and precipitation process of K-feldspar, the reaction kinetics of which was analyzed using the geochemical models. It will provide a new insight for separating potassium from the minerals which were difficult to decompose.

2. Experiment

2.1. Materials

The biotite syenite bulk sample (XS-16) used in this study was collected from Xiyuanxia village in Rongcheng County of Shandong province, China. The biotite syenite powder (XS-16) was obtained by handpicking and then crushed, ground, ball-milled and passed

through a 200-mesh smaller than 75 μm in diameter. The chemical composition of XS-16 determined by wet chemical analysis and electron microprobe results were shown in Table 1 [4,25,26,31]. According to the principle of mass balance and MIFORM F90 software (Beijing Key Laboratory of Materials Utilization of Nonmetallic Minerals and Solid Wastes, Beijing, China) [32], the main phase of XS-16 was microcline with the chemical formula of $\text{K}_{1.000}\text{Na}_{0.045}\text{Ca}_{0.002}[\text{Fe}^{3+}_{0.005}\text{Ti}_{0.003}\text{Al}_{0.992}\text{Si}_{2.987}\text{O}_8]$ and its content was 88.1 wt.%, the accessory minerals were: biotite (4.6 wt.%), quartz (5.2 wt.%) and others (2.1 wt.%). Potassium hydroxide (85%, analytical reagent grade) was supplied by Beijing Modern Eastern Fine-chemical Co., Ltd., Beijing, China. The deionized water produced in the local laboratory was used in the experiments.

Table 1. The chemical compositions of biotite syenite and microprobe analysis of microcline (wt.%).

Sample	SiO ₂	TiO ₂	Al ₂ O ₃	TFe ₂ O ₃	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	LOI	Total
XS-16	64.84	0.29	17.95	0.83	0.01	0.65	0.36	0.63	14.15	0.08	0.47	100.24
microcline	63.84	0.08	17.99	0.14	0.04	0.02	0.03	0.50	16.76	-	-	99.39

Microcline composition is the average values of 17-point determinations by electron microprobe.

2.2. Experimental Procedure

The reaction device used in this experiment has been described in our previous report [33]. In hydrothermal experiments, 15 g biotite syenite powder was dissolved in KOH solution (5–7 mol/L) with the solid to liquid ratio of 1/3 in a 100 mL Teflon liner assembled in a steel hydrothermal autoclave installed in a temperature-controlled homogenous reactor at 240–300 °C for 0.5–8 h with a rotation speed of 6 r/s. The reaction pressure was the automatic pressure. After hydrothermal treatment, the separation of solid-liquid phase was realized by filtration and washing with deionized water. The solid precipitation was obtained by drying at 105 °C for 16 h.

2.3. Characterization

The X-ray diffractometer (XRD) patterns of K-feldspar powder and the solid products obtained under different conditions were recorded by a D8 Advance X-ray diffractometer with Cu K α radiation ($\lambda = 0.154$ nm, 40 kV/40 mA) (Bruker Scientific Instruments, Germany). The powder diffraction data were analyzed using a computer software General Structure Analysis System (GSAS) package (Los Alamos National Laboratory, University of California, Oakland, CA, USA) [34]. The chemical composition of samples was investigated by WD-X-ray fluorescence spectrometer (XRF, Malvern Panalytical, Almelo, The Netherlands). The morphology of samples was examined by using a Zeiss Gemini 450 scanning electron microscope (SEM) (Carl Zeiss, Germany). Fourier-transform infrared spectra (FTIR) of samples were collected by a Perkin Elmer 2000 in the 4000–400 cm^{-1} region using potassium bromide as the diluent and binder. Potassium, aluminum, sodium, and silicon ions' concentration in solutions were measured by Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) with a wavelength range at 166–847 nm (ICAP 7600, Thermo Fisher Scientific, Waltham, MA, USA).

3. Results and Discussion

3.1. Synthesis and Characterization of Two Kinds of KAlSiO_4

Two kinds of KAlSiO_4 were precipitated by utilizing the dissolution-precipitation process of biotite syenite. Figure 1 shows the XRD patterns of the products obtained after hydrothermal reaction at 260 °C for 0.5–8 h (named as XS-K-0.5h, XS-K-1h~XS-K-8h, respectively). In our study, we found that the intermediate phase was well-matched with the megakalsilite (ICDD-PDF No. 00-054-1123 (2020)) of $P6_3$ [35], which is similar to the crystal structure of MZnPO_4 ($M = \text{Na, K, Rb, Cs}$) as described in the report of Andratschke [36], so the intermediate product was abbreviated as MEK. The diffraction peaks of other product samples can be well indexed into microcline (ICDD-PDF No. 00-

019-0932 (2020)) with the space group of $P\bar{1}$, kalsilite (ICDD-PDF No. 00-011-0579 (2020)) of $P6_3$, suggesting that the increase of reaction time is caused the difference of products, but both have the same space group. The formation of precipitation phases occurs only when the bulk solution is oversaturated. In the report of Hellmann & Tisserand [37], only when $\Delta G \geq -25 \text{ kJ} \cdot \text{mol}^{-1}$, the formation of secondary phases was thermodynamically feasible. It is shown that K-feldspar powder presents slate-like morphology with layers of cleavage on the sides (Figure 2a). Visible corrosive pitting was generated at the originally smooth and plate-like surface of K-feldspar (Figure 2b,c) and after 0.5 h will increase the contact area between the KOH solution and K-feldspar as well as accelerate the dissolution of K-feldspar further [38]. Table 2 gives the chemical composition of reaction products and calculated phase composition results. $\eta(\text{SiO}_2)$ was calculated by Equation (1),

$$\eta(\text{SiO}_2) = [C(\text{SiO}_2) \times V(\text{filtrate})] / [\omega(\text{SiO}_2) \times M(\text{XS-16})] \times 100\% \quad (1)$$

where $\eta(\text{SiO}_2)$ represents the leaching ratio of SiO_2 from K-feldspar; $C(\text{SiO}_2)$ is the concentration of SiO_2 in the filtrate solution obtained from the hydrothermal reaction; $\omega(\text{SiO}_2)$ denotes the mass fraction of SiO_2 in XS-16. After reacting for 1 h, reaction products were composed of microcline (68%) and MEK (32%), consistent with SEM results in Figure 2d, in which there are some small particles of MEK around massive bulk K-feldspar with a lot of erosional pits in Figure 2d. With the extension of reaction time, the K-feldspar disappeared and MEK formed completely with uniform and regular hexagram shapes (Figure 2f). After reacting for 4 h, reaction products were composed of MEK (42%) and Kls (58%) as shown in Figure 2g, where the morphology consists of some hexagrams (MEK) and hexagonal flakes (Kls). Longer reaction time is beneficial to the crystallization of kalsilite, so the morphology of the product transformed into a hexagonal shape completely in Figure 2i.

Figure 1. The XRD patterns of K-feldspar and precipitation samples obtained after the hydrothermal treatment of K-feldspar for 0.5 h, 1, 2, 3, 4, 6 and 8 h. ◆—microcline, ▽—MEK, *—Kalsilite.

Figure 2. SEM images of K-feldspar (a) and the dissolution and precipitation products of K-feldspar in KOH solution for 0.5 (b,c), 1 (d), 2 (e), 3 (f), 4 (g), 6 (h) and 8 h (i).

Table 2. The chemical composition of precipitation samples obtained after hydrothermal treatment of K-feldspar (Mic—microcline, Kls—kalsilite).

Sample	Time/h	SiO ₂	K ₂ O	Al ₂ O ₃	C (SiO ₂)/mol·L ^{−1}	ηSiO ₂ (%)	Product Phase
XS-K-1	1	44.98	21.53	28.77	2.062	57.52	Mic (68%) + MEK (32%)
XS-K-2	2	38.60	28.83	30.66	2.278	63.54	Mic (31%) + MEK (69%)
XS-K-3	3	38.89	28.46	30.35	2.269	63.27	MEK
XS-K-4	4	37.81	29.66	30.04	2.305	64.29	MEK (42%) + Kls (58%)
XS-K-6	6	37.23	29.09	29.95	2.325	64.84	Kls
XS-K-8	8	37.69	29.12	30.47	2.310	64.41	Kls

In order to seek a better understanding about the difference between the crystal structure of kalsilite and MEK, Rietveld structure refinements for two types of KAlSiO_4 were carried out based on the GSAS program using the powder XRD data. Figure 3a,c displayed the Rietveld fit of the XRD pattern of kalsilite and MEK, and the final refined unit cell parameters are summarized in Tables 3 and 4. It is clear that all Bragg diffraction lines of kalsilite and MEK are assigned to the hexagonal system with space group $P6_3$. The unit cell of MEK: $a = b = 18.12930 \text{ \AA}$, $c = 8.48727 \text{ \AA}$, $V = 2415.809 \text{ \AA}^3$, is more than ten times as large as that of kalsilite ($a = b = 5.167334 \text{ \AA}$, $c = 8.712779 \text{ \AA}$, $V = 201.4744 \text{ \AA}^3$). The layers of $[\text{TO}_4]$ tetrahedra forming six-membered rings (S6R) are perpendicular to the c axis where the $[\text{SiO}_4]$ tetrahedron is surrounded by four $[\text{AlO}_4]$ tetrahedron and vice versa. It is obvious that all the rings in Figure 3d have tetrahedra pointing alternately up and down, which is expressed as UDUDUD, where U and D represent tetrahedral pointing up and down respectively. However, it is very different in Figure 3b, whose structure is based on two types of ring topologies, UDUDUD and UUUDDD [39]. Combining Figure 3

and Table 4, we can obtain that the K atoms have six sites in MEK but only one in kalsilite. The different K sites were shown in Figure 3b. The K atoms of kalsilite and K4 atoms of MEK are arranged in the cell edge along c axis. From the plane (0001), layers generated by interlaced S6R have several open tunnels, and K2 atoms are located in the center channel. The tunnels occupied by K6 and K5 next to the central channel and tunnels taken up by K1 and K3 off-center form the diagonal of metastable KAlSiO_4 unit cell. The distances of Al-O and Si-O in kalsilite structure are 1.71 and 1.64 Å, respectively, which is different from the values of 1.75 and 1.61 in the report of Smith & Bailey [40]. And the distances of Al-O and Si-O in MEK were summarized in Table 5. The average bond lengths of Al-O and Si-O are 1.93 and 1.54 Å, respectively, which indicate an ordered distribution of silicon and aluminum in neighboring tetrahedra [35].

Figure 3. (a,c) Experimental, calculated XRD patterns and their difference for the Rietveld fits of MEK and kalsilite using the GSAS program; (b,d) the crystal structure of MEK and kalsilite based on the refinement result.

Table 3. Fractional atomic coordinates, occupancies, and isotropic thermal parameters of kalsilite obtained from the GSAS Rietveld Refinement using X-ray powder diffraction data at room temperature.

Atom	x	y	z	Occupancy
K	0	0	0.2407	1.0
Al	1/3	2/3	0.0379	1.0
Si	1/3	2/3	0.4237	1.0
O1	0.3831	0.9875	0.4858	1.0
O2	0.3339	0.7155	1/4	1/3

space group: $P6_3$ —hexagonal; $a = b = 5.16733(4)$ Å, $c = 8.71277(9)$ Å, $V = 201.474(4)$ Å³; $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$; $R_{wp}(\%) = 7.32$, $R_p(\%) = 4.50$.

Table 4. The refined positions of all the atoms and the lattice parameters of MEK.

Atom	x	y	z	Occupancy
K1	0.1511	0.3310	0.9303	1.0
K2	0.5222	0.5196	0.9254	1.0
K3	0.3346	0.1392	0.9135	1.0
K4	0.0000	0.0000	0.4655	1.0
K5	0.3333	0.6667	0.4183	1.0
K6	0.3333	0.6667	0.9277	1.0
Al1	0.1673	0.1535	0.7300	1.0
Al2	0.6649	0.0019	0.1082	1.0
Al3	0.4989	0.3295	0.7370	1.0
Al4	0.3336	0.5023	0.7352	1.0
Si1	0.3287	0.3321	0.7182	1.0
Si2	0.3409	0.5067	0.1269	1.0
Si3	0.1726	0.1591	0.1204	1.0
Si4	0.4956	0.6689	0.6303	1.0
O1	0.1283	0.0795	0.2391	1.0
O2	0.0441	0.1803	0.4529	1.0
O3	0.3843	0.2958	0.6735	1.0
O4	0.3555	0.4147	0.6313	1.0
O5	0.1151	0.2009	0.1159	1.0
O6	-0.0755	0.5481	0.1801	1.0
O7	0.2847	0.5400	0.1858	1.0
O8	0.4059	0.6121	0.6790	1.0
O9	0.2576	0.2238	0.2024	1.0
O10	0.5291	0.7519	0.7230	1.0
O11	0.4130	0.1104	0.6923	1.0
O12	0.2747	0.0359	0.1714	1.0
O13	0.1950	0.4789	0.4575	1.0
O14	0.3310	0.3435	0.8875	1.0
O15	0.1381	0.5802	0.2328	1.0
O16	0.6184	0.4725	0.4636	1.0

space group: $P6_3$ —hexagonal; $a = b = 18.12930$ Å, $c = 8.48727$ Å, $V = 2415.80(9)$ Å³; $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$; $R_{wp}(\%) = 7.22$, $R_p(\%) = 5.23$.

Above all, two kinds of $KAlSiO_4$ were precipitated during the dissolution process of biotite syenite under mild hydrothermal conditions, which is beneficial to realize the industrial utilization of this process. Compared to microcline, two kinds of $KAlSiO_4$ obtained here are easier to be decomposed in the acid soil, which not only can supply potassium nutrition to plants but can ameliorate the soil with the porous structure. Although some large-pore potassium-rich zeolites such as L-types, A-types, and F-types can be prepared from the aluminosilicate residues or fusion products of K-feldspar, their treatment processings are complicated [27,29]. The synthesis of two types of $KAlSiO_4$ was simpler and just involved one step, which fits with the green chemical production. Moreover, kalsilite also can be used as a heterogeneous catalyst for biodiesel production [41,42] and as an ingredient in dental ceramic materials [43,44].

Table 5. The bond lengths of Si-O and Al-O in MEK.

Bond	Bond Length (Å)	Bonds	Bond Length (Å)	Bond	Bond Length (Å)	Bond	Bonds Length (Å)
Si1-O3	1.51	Si2-O7	1.51	Al1-O1	1.96	Al2-O6	1.93
Si1-O4	1.51	Si2-O11	1.58	Al1-O2	1.95	Al2-O9	1.97
Si1-O12	1.48	Si2-O15	1.55	Al1-O5	1.89	Al2-O11	1.94
Si1-O14	1.45	Si2-O16	1.53	Al1-O12	1.98	Al2-O14	1.89
Si3-O1	1.61	Si4-O6	1.48	Al3-O3	1.92	Al4-O4	2.02
Si3-O2	1.51	Si4-O8	1.59	Al3-O7	1.89	Al4-O8	1.82
Si3-O5	1.57	Si4-O10	1.53	Al3-O13	2.00	Al4-O10	1.80
Si3-O9	1.57	Si4-O13	1.64	Al3-O15	1.83	Al4-O16	2.08
Average bond length of Si-O: 1.54 Å				Average bond length of Al-O: 1.93 Å			

3.2. Reaction Kinetics

3.2.1. Kinetic Model

In a general sense, the dissolution reaction behavior of some minerals such as montmorillonite [45] and diaspore [46] in alkaline solution was described by the rate law reported by Lasaga et al. [47]:

$$r = k_0 \exp(-E_a / RT) a_{\text{H}^+, \text{OH}^-}^{n_{\text{H}^+}, n_{\text{OH}^-}} g(I) \prod_i a_i^{n_i} f(\Delta_r G) \quad (2)$$

where r represents the overall rate of reaction obtained directly from the quantity of SiO_2 concentration released from the feldspar to solution; k_0 is the rate constant; E_a represents the apparent activated energy of overall reaction; R is gas constant; T is the Kelvin temperature (K); $a_{\text{H}^+, \text{OH}^-}$ stands for the activity of hydronium or hydroxyl ions, which reveals the influence of pH on the reaction rate; $g(I)$ represents the rate that may be independent of ionic strength; $\prod_i a_i^{n_i}$ accounts for the effect of the catalyzation or inhibition of possible aqueous species on the overall reaction; $\Delta_r G$ incorporates the Gibbs free energy driving the advance of the overall reaction, the increasing negative value of which always can show the thermodynamic “distance” from chemical equilibrium; $f(\Delta_r G) = 0$ represents the chemical reaction is in the equilibrium state; $f(\Delta_r G) = 1$ as $\Delta_r G \rightarrow \infty$, stands for a chemical reaction that is in the highly undersaturation state that is far from equilibrium. In the transition state theory (TST) [48], to describe the linear relationship between r and $\Delta_r G$ in Equation (1), the following expression was introduced,

$$f(\Delta_r G) = [1 - \exp(\Delta_r G / RT)] \quad (3)$$

However, a large amount of experiments shows the relationship between r and $\Delta_r G$ is not fit with the linear TST rate law when the reaction is near equilibrium, especially in the dissolution process of feldspar [22,37]. Alekseyev [49] proposed a non-linear relationship,

$$f(\Delta_r G) = \{1 - [\exp(\Delta_r G / RT)]^p\}^q \quad (4)$$

where p, q are the fitting parameters. In general, the Gibbs free energy of reaction deviating from the equilibrium can be expressed as:

$$\Delta_r G = RT \ln(Q / K_{\text{eq}}) \quad (5)$$

where Q is the activity quotient of the forward dissolution reaction and K_{eq} is the equilibrium constant. $Q = K_{\text{eq}}$ at the chemical equilibrium means the forward reaction rate equals the reverse rate.

3.2.2. Kinetics Analysis

In the reaction system, the dissolution of K-feldspar controlled the reaction rate. Assuming kalsilite has an ideal crystal structure, the dissolution of K-feldspar and precipitation of kalsilite are expressed as follows:

In the reaction (R1), the release ratio of SiO_2 from K-feldspar can be used to provide a measurement for the dissolution rate of K-feldspar with the following equation:

$$X\% = [\text{C}(\text{SiO}_2) \times V(\text{filtrate})] / [2/3 \times w(\text{SiO}_2) \times M(\text{XS-16})] \times 100\% \quad (6)$$

where $\text{C}(\text{SiO}_2)$ represents the concentration of SiO_2 in filtrate (g/L); $V(\text{filtrate})$ represents the filtrate volume; $w(\text{SiO}_2)$ is the mass fraction of SiO_2 in XS-16; $M(\text{XS-16})$ represents the mass of XS-16 added into the reaction (R1). Thermodynamic parameters for mineral end-members were referred from Holland et al. [50]. Activities and Gibbs free energy were calculated by the mixed solvent electrolyte (MSE) model [51]. Detailed methods for DG are referred from the report of Liu et al. [27] from our team.

The dissolution ratio of K-feldspar shows an obvious upward trend during the initial 90 min and higher temperature indicates a greater dissolution rate (Figure 4a). After 270 min, the dissolution ratio of K-feldspar at 260 and 280 °C increases to 84.6% and 89.2% for 270 min, respectively, and then remains relatively stable. The reaction at 300 °C reach equilibrium (90.05%) at 90 min, indicating higher temperature will make the dissolution ratio of K-feldspar reaching equilibrium quicker (Figure 4a). For a different KOH concentration, a higher value makes greater dissolution ratio of K-feldspar at 260 °C, indicating more OH^- is beneficial to the dissolution and structure breakdown of K-feldspar [52]. The reaction rate of K-feldspar can be expressed in the following equation:

$$r = \frac{dX}{dT} \quad (7)$$

In the report of Hellmann & Tisserand [37], the curve of $r-\Delta G$ consists of three parts, $-150 \leq \Delta G \leq -70 \text{ kJ}\cdot\text{mol}^{-1}$ is far from equilibrium; $-70 \leq \Delta G \leq -25 \text{ kJ}\cdot\text{mol}^{-1}$ represents transition equilibrium regime; $\Delta G \geq -25 \text{ kJ}\cdot\text{mol}^{-1}$ is closer to equilibrium. In general, more negative the values of ΔG are, the further from equilibrium reactions are. In this study, all ΔG values are over $-25 \text{ kJ}\cdot\text{mol}^{-1}$, suggesting that high reaction temperature and basic environment can accelerate the reaction rate. The curve of $r-\Delta G$ reported by Hellmann and Tisserand [37] is highly non-linear and has a gentler slope at 150 °C and pH 9.2 than that in the report of Burch et al. [22] at 80 °C and pH 8.8, which can explain well why the tendency of all $r-\Delta G$ relationships in this study is non-linear and sigmoidal at temperature ≥ 240 °C and pH > 12. As shown in Figure 4c,d, the r is greater at a higher temperature and higher concentration of KOH when the reactions have the same values of ΔG .

The specific surface area (A) at different times is not able to be obtained synchronously, so the specific surface area A is assumed as a constant value. In Equation (R1), only OH^- ions influence the reaction activity in the reactant. At a given temperature, K_0 is a constant relevant to A and E_a . Equation (1) can be replaced by Equations (8) and (9) is the combination of Equations (4) and (9).

$$K_0 = k_0 A \exp(-E_a / RT) \quad (8)$$

$$r = K_0 a_{\text{OH}^-}^n f(\Delta_r G) \quad (9)$$

$$r = K_0 a_{\text{OH}^-}^n \{1 - [\exp(m\Delta_r G / RT)]^p\}^q \quad (10)$$

Figure 4. X-t relationship (a,b) and r- $\Delta_r G$ correlation (c,d) for reaction (R1) at different reaction temperatures and concentrations of KOH.

Considering the mutual relationship between r and $\Delta_r G$, the parameter of M related to K_0 and a_{OH^-} was set to build a function about reaction order (n) as shown in Equation (12), where the reaction order can be obtained by changing the concentration of OH^- . And the apparent activation energy is calculated at different temperatures, as shown in Equation (13) deriving from Equation (8).

$$M = K_0 a_{\text{OH}^-}^n \quad (11)$$

$$\ln M = \ln K_0 + n \ln a_{\text{OH}^-} \quad (12)$$

$$r = M \{1 - [\exp(m\Delta_r G/RT)]^p\}^q \quad (13)$$

$$\ln K_0 = \ln(k_0 A) - E_a/RT \quad (14)$$

As shown in Figure 5, the relationship between reaction Gibbs free energy ($\Delta_r G$) and reaction rate (r) was built by the experiments under various concentrations of OH^- and various reaction temperatures. The values of M listed in Table 6 at different KOH concentrations and various reaction temperatures can be obtained by the better fitting relationship between r and $\Delta_r G/RT$. In Equation (12), the activity values of OH^- are correlated with the reaction temperature, KOH concentration, and saturated vapor pressure. Based on Equation (12), the value of reaction order (n) obtained from the slope of the fitting straight line between $\ln M$ and $\ln a_{\text{OH}^-}$ is 2.992 (Figure 6a), and according to Equation (14), the apparent activation energy (E_a) calculated from the liner-fitting relationship of $\ln K_0 - 1/T$ is 97.41 kJ/mol (Figure 6b). Considering the apparent activation energy, the value of E_a (97.41 kJ/mol) reveals a chemical reaction controlling the dissolution of feldspar. Hellmann [37] reported that the dissolution reaction order of albite under acidic, neutral and alkaline solutions are 4.4, 3.3, and 3.8, respectively, as well as

the apparent activation energy, are 89, 69 and 85 kJ/mol, respectively. In conclusion, the concentrated alkaline solution under the hydrothermal condition was a major factor accelerating feldspar dissolution.

Figure 5. The relationship between dissolution reaction Gibbs free energy ($\Delta_r G$ and reaction rate (r), (a) concentration-time series experiments, (b) temperature-time series experiments.

Table 6. The fitting parameter (M) and activity of OH^- at different KOH concentration and reaction temperatures.

Parameters	KOH Concentration (mol/L)			Reaction Temperature (°C)		
	5.0	6.0	7.0	240	260	280
M	1.142	2.334	3.291	1.122	2.334	1.582
a_{OH^-}	0.422	0.551	0.593	0.638	0.551	0.466

Figure 6. The plot of $\ln M$ - $\ln a_{\text{OH}^-}$ (a) and $\ln K_0$ - $1/T$ (b).

4. Conclusions

In summary, two kinds of KAlSiO_4 were precipitated in the dissolution process of K-feldspar and the dissolution reaction dynamic was studied by adopting the aluminosilicate mineral geochemical dissolution model. The results indicate that the MEK, an intermediate product, was generated during the transformation process from K-feldspar to kalsilite. Two kinds of KAlSiO_4 obtained here are easier to be decomposed in the acid soil, which

not only can supply potassium nutrition to plants but can ameliorate soil via the porous structure. In addition, the reaction order and apparent activation energy at the temperature range of 240–300 °C were simulated to be 2.992 and 97.41 kJ/mol, respectively. Compared with geochemical weathering process of K-feldspar, the high reaction order was considered to be the major factor promoting the rapid reaction.

The hydrothermal approach proposed in this study provides an appropriate and simplified way for the comprehensive utilization and clean production of K-silicates.

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