Ceramics International xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Ceramics International

journal homepage: www.elsevier.com/locate/ceramint

Hydrothermal synthesis of nano-kaolinite from K-feldspar

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ARTICLE INFO

Keywords:
Nano-kaolinite
K-feldspar
Hydrothermal synthesis
Chemical weathering
Kaolinite of paper-coating grade

ABSTRACT

Development of sustainable routes for the synthesis of kaolinite in nano-scale (nano-kaolinite) is very significant for producing high quality kaolinite of paper-coating grade in kaolin industry. Duplicating chemical weathering processes in nature, two routes were developed and compared for the synthesis of nano-kaolinite from K-feldspar. Kaolinite of uniform plate-like morphology with thickness of around 14 nm was obtained in this study. Both synthesis routes may lead to the comprehensive utilization of K-feldspar for the synthesis of pure kaolinite for not only high quality paper-coatings but also medical and other uses.

1. Introduction

Materials circulation on the surface of the Earth largely depends on chemical weathering processes [27]. Natural kaolinite is the product of long-term chemical weathering of aluminosilicate rocks, the formation of which is closely correlated with the types of primary minerals, fluid concentration and washout time [7,12]. Initially, the synthesis of kaolinite was just aimed at studying the genesis and stability conditions of clay minerals owing to geological interest [15]. K-feldspar is one of the least reactive minerals and its conversion to kaolinite takes a long time by chemical weathering process [7]. The kaolinization reactions of feldspar play a significant role in deformation processes and this reaction needs the aid of acidic fluids. Understanding the weathering of minerals under natural environmental conditions can provide clues for the accelerated experimental synthesis of relevant mineral phases for industrial applications by a facile method.

Excellent chemical and thermal stability of kaolinite [19] makes it widely useful in ceramic technology [1], advanced inorganic glass, cosmetics [32], coatings [24] and binder [3]. Kaolinite occurs widely throughout the world and it can be mined for commercial applications from more than 60 locations in many countries such as the United States, Britain, Brazil and China. It was reported that global kaolin reserves reach to the extent of 22.2 billion tons, but kaolin of high-quality or paper coating grade is in short supply [3]. China has abundant and widely distributed kaolin resources of different purities including abundant ordinary kaolinitic soils of low quality with lot of impurities. But, more or less pure kaolin is distributed in Suzhou, Maoming, Longyan and Datong areas with better quality, the latter can be used to prepare catalysts for crude oil cracking, paper coatings, advanced ceramics and as raw materials for other applications [37]. However, kaolinite of high-quality for special applications of paper-coating grade, medicinal use etc. is extremely rare and has become an urgent necessity in kaolin industry. Therefore, how to produce cost-effective and high-quality kaolinite has become an important issue.

At the present time, several complex processing techniques, such as mechanical grinding, classification, stripping, intercalation and other treatments were used to achieve high quality kaolinite [4]. However, high energy consumption, low yield, high cost and minor impurities make the ultra-fine production of kaolinite impractical even for premium products. Chemical synthesis method may be the best route to obtain much purer kaolinite of nano-scale. Here, using the natural chemical weathering processes of feldspar to kaolinite as a model, we used K-feldspar for suppling SiO_2 and Al_2O_3 components for the synthesis of kaolinite by hydrothermal method. This process of using natural K-feldspar not only can solve the problem of expensive cost of inorganic potassium salts and organic compounds, but also lead to synthesis of purer kaolinite. Moreover, feldspars are one of the most abundant minerals in the Earth's crust [6], which constitute 60% of both the continental and the oceanic crusts of the Earth [33]. Adequate conversion of K_2O, SiO_2 and Al_2O_3 in K-feldspar into sustainable

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https://doi.org/10.1016/j.ceramint.2018.05.227
Received 5 May 2018; Received in revised form 21 May 2018; Accepted 26 May 2018

Table 1
Chemical compositions of K-feldspar (w_t/%).

Sample	SiO_2	TiO_2	Al_2O_3	TFe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	LOI	Total
XS-16	64.84	0.29	17.95	0.83	0.010	0.65	0.36	0.63	14.15	0.082	0.47	100.24

* TFe_2O_3 = Total iron oxides as FeO and Fe_2O_3.

resources will play a significant role in modern ceramic industry. Herein, we designed two different routes, mimicking chemical weathering processes in nature, to synthesize kaolinite from K-feldspar aiming to develop and find a cost-effective, most useful and sustainable method to synthesize nano-kaolinite.

2. Materials and methods

2.1. Materials

The bulk K-feldspar sample (XS-16) used in this study was collected from Xiyuanxia village in Rongcheng county of Shandong province, China. K-feldspar powder was obtained by crushing, grinding, ball-milling and passing through a 200-mesh sieve with most particles smaller than 74 μm in diameter and its chemical composition is shown in Table 1. Major chemical components are SiO_2 (64.84%), Al_2O_3 (17.95%) with a K_2O content of 14.15%. Potassium hydroxide (85%, analytical reagent grade) was supplied by Beijing Modern Eastern Fine Chemical Co., Ltd. HNO_3 solution (analytical purity, 65~68%) was supplied by Beijing chemical works and CH_3COOH solution (≥ 99.5%) by Sinopharm chemical reagent Co., Ltd. Hydrochloric acid (HCl) and sulfuric acid (H_2SO_4) were supplied by Beijing chemical factory. Deionized water was produced in the local laboratory.

3. Experimental methods

3.1. Pretreatment of K-feldspar

Firstly, K-feldspar powder was decomposed in KOH solution in a high pressure hydrothermal autoclave at 280 °C for 2 h [34]. The alkali hydrothermal treatment of K-feldspar was aimed at dissolving the stable structure of microcline and getting kalsilite [22,36]. Table 2 gives the chemical composition analyses of kalsilites, which were synthesized in different batches. Next, two routes to synthesize kaolinite from kalsilite were given and compared.

The first synthesis route (named M-1) was previously developed [20] but also used here for comparison: The kalsilite obtained in the pretreatment stage (Eq. (1)) was dissolved in H_2SO_4 solution to obtain aluminosilicate gel (AS) (Eq. (2)) with higher chemical reactivity and the filtrate was collected by filtering for further use. The filtrate can be used to prepare K_2SO_4 by evaporation [35,21]. The obtained aluminosilicate, AS was treated hydrothermally with HCl solution (pH = 2) (Eq. (3)) to obtain kaolinite [20]. The different steps are given as follows:

$$K-\text{feldspar}\,(KAlSi_3O_8) + 4KOH \rightarrow \text{Kalsilite}\,(KAlSiO_4)\,(S)\downarrow + 2K_2SiO_3 + 2H_2O \quad (1)$$

$$2KAlSiO_4 + H_2SO_4 + (n-1)\,H_2O \rightarrow 2K_2SO_4 + Al_2O_3{\cdot}2SiO_2{\cdot}nH_2O \quad (2)$$

$$Al_2O_3{\cdot}2SiO_2{\cdot}nH_2O + HCl \rightarrow Al_2[Si_2O_5]\,(OH)_4 + (n-2)\,H_2O + HCl \quad (3)$$

The second synthesis route (named M-2): The kalsilite obtained in the pretreatment stage (Eqs. 1, 4) was reacted with HNO_3 solution (Eq. (5)) by hydrothermal method directly to obtain kaolinite. After hydrothermal reaction, autoclaves were cooled quickly with cold water. The solids were separated from the solution by filtration, washed with deionized water, dried and then characterized. However, the obtained solution by filtration was used to prepare potassium nitrate. The second method developed here uses the following steps:

$$\text{K-feldspar}\,(KAlSi_3O_8) + 4KOH \rightarrow \text{Kalsilite}\,(KAlSiO_4)\,(S)\downarrow + 2K_2SiO_3 + 2H_2O \quad (4)$$

$$2KAlSiO_4 + 2HNO_3 + H_2O \rightarrow \text{Kaolinite}\,Al_2[Si_2O_5](OH)_4 + 2KNO_3 \quad (5)$$

3.2. Characterization

The chemical composition of K-feldspar sample and kalsilite were determined by wet chemical analysis. Powder X-ray diffraction patterns of raw materials and as-prepared samples were recorded by a SmartLab (Rigaku) X-ray diffractometer with Cu Kα radiation (40 kV/40 mA). Fourier-transform infrared (FTIR) spectra of samples were collected by a Perkin Elmer 2000 in the 4000–400 cm^{-1} region using potassium bromide as the diluent and binder. The morphologies of as-prepared samples were examined by Sirion 200 scanning electron microscope (SEM) under the analytical conditions of EHT = 5.00 kV and Signal A = SE. The thermal decomposition of product sample was studied by differential scanning calorimetric and thermal gravimetric analysis (DSC-TGA) using an SDT Q600 V20.9 Build 20 instrument in air atmosphere at a heating rate of 10 °C/min.

4. Results and discussion

As a highly stable and poorly reactive mineral, K-feldspar must be pretreated firstly according to Eq. (1) before being used as a precursor for the synthesis of kaolinite. In the pretreatment stage, K-feldspar was treated using KOH solution in order to transform K-feldspar, microcline into kalsilite ($KAlSiO_4$) completely, where 2/3 SiO_2 of microcline was released into solution and existed in the form of $[SiO_3]^{2-}$, which can be precipitated by adding lime milk to obtain $CaSiO_3{\cdot}nH_2O$ and KOH solution for recycling [22]. Here, synthesis of kaolinite (named method M-2) was accomplished by reactions based on Eqs. (4) and (5), which show that all K^+ can be collected by the evaporation of water as KNO_3, which is an important potassium resource for some crops sensitive to

Table 2
chemical composition of kalsilite in different batches.

Sample	SiO_2	TiO_2	Al_2O_3	TFe_2O_3[a]	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	LOI	Total
gl-1	37.82	0.10	28.74	2.32	0.16	0.61	0.38	0.60	27.18	0.03	1.63	99.57
sj-1	37.68	0.05	30.13	0.87	0.01	0.13	0.79	0.57	28.13	0.08	0.93	99.37
Avg	37.75	0.08	29.44	1.60	0.09	0.37	0.59	0.59	27.66	0.06	1.28	99.47

[a] TFe_2O_3 = Total iron oxide as FeO and Fe_2O_3. Avg represents the average values of above data.