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Research paper

# Preparation, morphology, and structure of kaolinites with various aspect ratios

Shilong Zhang[a,b], Qinfu Liu[c,*], Yongjie Yang[c], Ding Wang[c], Junkai He[d], Luyi Sun[b,*]

[a] School of Chemical and Environmental Engineering, China University of Mining and Technology, Beijing 100083, China
[b] Department of Chemical & Biomolecular Engineering and Polymer Program, Institute of Materials Science, University of Connecticut, Storrs, CT 06269, United States
[c] School of Geological Science and Survey Engineering, China University of Mining and Technology, Beijing 100083, China
[d] Department of Chemistry, University of Connecticut, Storrs, CT 06269, United States

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ABSTRACT

A series of four kaolinite (Kaol) samples with various aspect ratios were prepared via a multi-step treatment consisting of intercalating Kaol by potassium acetate, ball-milling, de-intercalation, and classification. The morphology and structure of the samples were characterized by particle size analysis, scanning electron microscopy (SEM), transmission electron microscopy (TEM), and X-Ray diffraction (XRD). Compared with intercalation by potassium acetate only or ball-milling only, intercalation followed by ball-milling was proved to be a much more effective method to delaminate Kaol to generate high aspect ratio samples. The results showed that the grade of structural order increased with an increase of Kaol aspect ratio, which was supported by an increase of Hinckley index calculated from their XRD patterns. This method offers a facile and scalable production of Kaol with various aspect ratios for different applications.

## 1. Introduction

Kaolinite (Kaol) has a wide range of applications. It can be used as a filler for paper and polymers, a pigment for coatings, an extender in paints and inks, and a major component of ceramics (Aras, 2004; Bundy and Ishley, 1991; McConnell and Garner, 1983; Ninness et al., 2003; Xia et al., 2010; Zhang et al., 2015a; Zhang et al., 2016). Some characteristics of Kaol, including morphology, crystallinity, structural defect and surface property, could directly affect its applications (Hu and Yang, 2013; Zhang et al., 2014). Layered silicate mineral particles geometrically approximate discs. The aspect ratio (ρ) of a particle is defined as the ratio of its major diameter to its thickness (Cheng et al., 2014). Aspect ratio is one of the key parameters that significantly impact its application. Therefore, a detailed study on the preparation method and characterization of Kaol with various aspect ratios is highly desirable.

Numerous researches on the preparation and characterization of Kaol products have been conducted in the past few decades (Bundy and Ishley, 1991; McConnell and Garner, 1983; Xia et al., 2010; Zhang et al., 2015a,b,c; Zhang et al., 2016) However, so far little research has been carried out to investigate the effect of Kaol aspect ratio on the properties of Kaol containing materials. This is mainly because of the challenge to control the aspect ratio of Kaol.

Natural Kaol samples exhibit a great variability of particle size distribution. Kaol samples with five different particle sizes from different locations were investigated by Cases et al. (1986). It was shown that the decrease in grade of structural order of the samples was accompanied by a reduction in grain size. Kaols from the same origin were also classified into four samples with various aspect ratios by Zhang et al. (2014). With an increase of Kaol aspect ratio, the structural order degree increased.

In order to obtain Kaol with a high aspect ratio, delamination of Kaol is usually involved. Because the layers are tightly linked together through hydrogen bonding (Castellano et al., 2010), delamination of Kaol is typically very difficult to achieve.

Ball milling is an efficient mechanical process and has been subjected for research for a long time (Hamzaoui et al., 2015; Soto et al., 2000). Slepetys and Cleland prepared two sets of Kaol: standard set and mechanically delaminated set (Slepetys and Cleland, 1993). The standard set of different sizes was obtained from a dispersion of the original crude clay by separating various size-fractions in a continuous centrifuge. The delaminated clay slurry was also separated into various size fractions in the same centrifuge. The experimental results revealed that shape factors of the delaminated samples were higher than those of non-delaminated ones. Franco et al. (2004) examined the effect of sonication on particle size. Their experiments showed that particle size reduction can be controlled through different variables such as power

* Corresponding authors at: Department of Chemical & Biomolecular Engineering and Polymer Program, Institute of Materials Science, University of Connecticut, Storrs, CT 06269, United States.
*E-mail addresses:* lqf@cumtb.edu.cn (Q. Liu), luyi.sun@uconn.edu (L. Sun).

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of ultra-sonicator, concentration of Kaol slurry, and duration of treatment. But delamination of Kaol into individual aluminosilicate layers via ball milling has not been reported, presumably because it is necessary to overcome the bonding energy that holds 1:1 layers together (Valášková et al., 2007).

Aiming at separating Kaol layers, there are several procedures that can be adopted to weaken the interlay bonding between the Kaol layers. One of the most straightforward approaches is to directly intercalate small molecules within Kaol, including dimethyl sulfoxide, urea, *N*-methyl formamide, acetamide, formamide, potassium acetate (Cheng et al., 2010; Deng et al., 2002; Kelleher et al., 2002; Makó et al., 2009; Mbey et al., 2013; Singh and Mackinnon, 1996; Song et al., 2013; Valášková et al., 2007; Zhang et al., 2015c, 2015d). Even though the basal spacing of Kaol can be extended from 0.71 to 1.41 nm after being intercalated by potassium acetate, which is one of the largest among Kaol intercalation compounds obtained via one-step intercalation (Bergaya et al., 2006), the delamination of Kaol into individual aluminosilicate layers has not been achieved yet.

Herein, we explored to delaminate Kaol through one-step intercalation of potassium acetate followed by ball-milling. Kaol samples with different aspect ratios were obtained via classification. The relationship among the Kaol particle size, aspect ratio, morphology, and grade of structural order were investigated.

## 2. Experimental

### 2.1. Materials

The Kaol used in this study is from Zhangjiakou, Hebei, China. This Kaol was formed by hydrothermal alteration (Zhang et al., 2014), contains a small amount of quartz as an impurity. The chemical composition of the obtained Kaol in wt% is $SiO_2$ 44.64%, $Al_2O_3$ 38.05%, $Fe_2O_3$ 0.22%, MgO 0.06%, CaO 0.11%, $Na_2O$ 0.27%, $K_2O$ 0.08%, $TiO_2$ 1.13%, $P_2O_5$ 0.13%, and MnO 0.002%, with a loss on ignition of 15.06%. The Kaol was ground to pass a 200-mesh sieve, labeled as Kaol-raw. Potassium acetate (KAc, > 99.5%) was used as received from Xilong Chemical Company, China.

### 2.2. Intercalation of potassium acetate

A sample of 100 g Kaol-raw was thoroughly mixed with 200 g of potassium acetate saturated aqueous solution. The mixture was stirred for 3 days at 60 °C. The progress of intercalation was monitored by X-ray diffraction (XRD) characterization.

### 2.3. Delamination via ball-milling

After intercalation, the delamination of Kaol via ball-milling was conducted using a GF-1100 Laboratory Multi-Functional Disperser (Shenzhen Shuangye Machinery Company, Shenzhen, China). A sample of 300 g potassium acetate intercalated Kaol (labeled as Kaol-KAc) was added into a 2 L milling steel jar filled with zirconium oxide spheres (1.2 mm in diameter and 300 g in mass). The slurry was milled at 2000 rpm for 2 h at room temperature, then separated from zirconium oxide spheres by a mesh. The resultant suspension was centrifuged and washed five times with distilled water until the potassium acetate was de-intercalated completely (labeled as Kaol-wash), which was confirmed by the XRD characterization.

### 2.4. Classification

The obtained Kaol-wash suspensions were re-dispersed in distilled water at a concentration of 25%, and 0.5% sodium polyacrylate was added as a dispersant. The pH of the suspension was adjusted to 10.0 using a sodium hydroxide solution to promote the dispersion of Kaol-wash in the aqueous system (Zhang et al., 2014). The suspension was stirred for half an hour at 2000 rpm. Then the upper suspension was extracted to another container with the siphon method after settling for 3 h. The impurities at the bottom were separated from the Kaol-wash suspension.

The new suspension was re-settled for 480 min, and then 2 cm height suspension was extracted from the upper suspension and labeled as Kaol-1. The rest of the suspension was stirred for 1 h again and re-settled for 184 min. Then, 1 cm height of the stable suspension at the top was collected through siphoning, and labeled as Kaol-2. According to the same procedures of collecting Kaol-2, Kaol-3 was also collected after being re-settled for 114 min. The residual suspension was labeled as Kaol-4.

### 2.5. Characterization

XRD patterns were recorded using an X-ray diffractometer (Rigaku D/max-2000, Japan) with Cu Kα radiation operated at 40 kV and 150 mA. The particle size distribution of the four Kaol samples was measured using a Mastersizer 2000 laser particle size analyzer of Malvern Company.

Scanning electron microscopy (SEM) micrographs were obtained using a Hitachi S4800 LV electron microscope under 3.0 kV. For SEM imaging, the samples were prepared as follows: after classification, four Kaol suspensions (i.e., Kaol-1, Kaol-2, Kaol-3, Kaol-4) were diluted to a concentration of ca. 1 wt%. The suspension drop was deposited on a silicon slide and air dried at room temperature. Then the silicon slides, as well as the four Kaol films attached on them, were fractured in liquid nitrogen. Both the surface and the cross-section were observed under SEM. Transmission electron microscopy (TEM) observations were conducted on a FEI Tecnai G2 F30 S-TWIN high resolution transmission electron microscope. For TEM experiments, the specimens were prepared as follows: the Kaol samples were ultrasonicated in ethanol for 10 min and then a drop of the dispersion was deposited onto a carbon-coated copper grid, which was left to dry completely before being transferred into the microscope.

## 3. Results and discussion

Fig. 1 shows the XRD patterns of Kaol-raw, Kaol-KAc, and Kaol-wash. After intercalation by KAc, the interlayer distance of Kaol-raw was expanded from 0.71 to 1.42 nm. After de-intercalation, the peak shifted back to ca. 0.72 nm, which is in good agreement with the literature (Franco et al., 2004; Frost et al., 1999, 2002). The above results confirmed a successful intercalation and de-intercalation, suggesting that deintercalated Kaol can be easily obtained after this series of treatments.

The particle size distributions of the classified Kaol samples

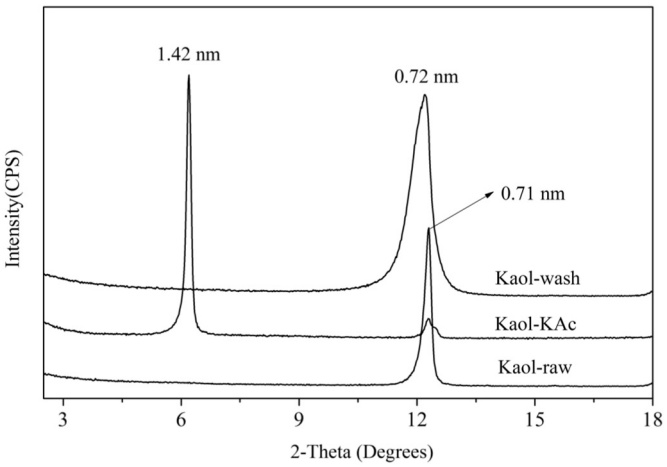


**Fig. 1.** XRD patterns of Kaol samples.