



Mechanism of kaolinite sheets curling via the intercalation and delamination process

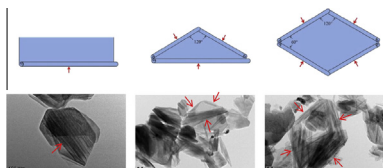


Xiaoguang Li^a, Qinfu Liu^{a,*}, Hongfei Cheng^{a,b}, Shuai Zhang^a, Ray L. Frost^{b,*}

^a School of Geoscience and Surveying Engineering, China University of Mining & Technology, Beijing 100083, PR China

^b School of Chemistry, Physics and Mechanical Engineering, Science and Engineering Faculty, Queensland University of Technology, 2 George Street, GPO Box 2434, Brisbane, Queensland 4001, Australia

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 22 October 2014

Accepted 8 December 2014

Available online 25 December 2014

Keywords:

Kaolinite
Intercalation
Delamination
Nanoscroll
Curling model

ABSTRACT

Kaolinite naturally occurs in the plate form for the interlayer hydrogen bond and the distortion and adaption of tetrahedron and octahedron. But kaolinite sheets can be exfoliated to nanoscrolls artificially in laboratory through multiple-step displacement intercalation. The driving force for kaolinite sheet to be curled nanoscroll originates from the size discrepancy of Si–O tetrahedron and Al–O octahedron. The displacement intercalation promoted the platy kaolinite sheets spontaneously to be scrolled by eliminating the interlayer hydrogen bond and atomic interaction. Kaolinite nanoscrolls are hollow tubes with outer face of tetrahedral sheet and inner face of octahedral sheet. Based on the theoretical calculation it is firstly reported that the minimum interior diameter for a single kaolinite sheet to be scrolled is about 9.08 nm, and the optimal 24.30 nm, the maximum 100 nm, which is verified by the observation of scanning electron microscope and transmission electron microscope. The different adaption types and discrepancy degree between tetrahedron and octahedron generate various curling forces in different directions. The nanoscroll axes prefer the directions as $[100]$, $[1\bar{1}0]$, $[110]$, $[3\bar{1}0]$, and the relative curling force are as follows, $[3\bar{1}0] > [100] = [1\bar{1}0] > [110]$.

© 2014 Elsevier Inc. All rights reserved.

1. Introduction

Kaolinite, an important industrial raw material, has a wide variety of applications in industry, particularly as paper filler and coating pigment [1–7]. It is used as an extender in aqueous based paints and inks, a functional additive in polymers and is the major

component in ceramics [8–10]. It is composed of Al–O octahedral sheets and Si–O tetrahedral sheets in a 1:1 relationship. The ideal formula of the pseudo-hexagonal unit cell is $\text{Si}_2\text{Al}_2\text{O}_5(\text{OH})_4$. The layers are bound to each other by hydrogen bonding between oxygens of the tetrahedral sheet and the hydroxyls of the adjacent octahedral sheet. The major minerals of kaolinite sub-group include kaolinite, halloysite, dickite and nacrite; the serpentine sub-group includes chrysotile, lizardite, antigorite and greenalite and other different structures and variants of magnesium ion, iron ion and aluminium ion.

Depending on the application, kaolinite is often modified from its natural state by physical or chemical treatment to enhance

* Corresponding authors. Fax: +86 10 62331248, +86 10 59714676 (Q. Liu). Fax: +61 7 3138 2407 (R.L. Frost).

E-mail addresses: lixiaoguang12345@126.com (X. Li), lqf@cumt.edu.cn (Q. Liu), h.cheng@cumt.edu.cn (H. Cheng), szhang870119@hotmail.com (S. Zhang), r.frost@qut.edu.au (R.L. Frost).

the properties of the material. Therefore, an important part of research in laboratory is focused on the preparation of kaolinite complexes intercalated by organic molecules. One of the most studied systems to date is the intercalation of synthetic polymers into layered aluminosilicates [11–15]. It was reported that after repeated water washing–intercalation delamination some kaolinite sheets can be curled and kaolinite nanoscrolls are formed with repeated intercalation and deintercalation of potassium acetate in kaolinite [16]. If alcohols are used to graft and modify the direct-intercalation kaolinite, bigger molecules are easy to intercalate into the interlayer of kaolinite, forming a kind of intercalation compound which has a interlayer spacing times of intercalation compound of original kaolinite. Komori et al. [17] proved that kaolinite has higher intercalation ability for a wider variety of guest species than previously accepted if kaolinite/methanol intercalation compound are used as an intermediate. The basal spacing increased up to 5.75 nm when octadecylamine was used. A sequence of interlayer-grafted derivatives of kaolinite was synthesized with a pre-intercalated kaolinite [18]. Furthermore, primary n-alkylamines intercalation compound were synthesized and were delaminated into halloysite-like nanoscrolls [19]. It was reported by Matusik et al. [20] that the number of rolled kaolinite layers depended heavily on the efficiency of the intercalation steps. Alkyl-trimethylammonium salts and 1-hexadecyl-3-methylimidazolium chloride were also intercalated into the interlayer space of methoxy-grafted kaolinite via one-step method, leading to the delamination of kaolinite sheets and formation of kaolinite nanoscrolls [21]. The reaction temperature, interaction mechanism and the thermal stability of the nanoscrolls were investigated by using one-step delamination of kaolinite-cetyltrimethylammonium chloride intercalation compound [22]. Despite previous research, the characterization of the morphology of the kaolinite nanoscrolls and explicit explanation on the curling mechanism remains largely unknown.

In the present study, the nanoscroll formation mechanism of kaolinite sheets via the intercalation–liquid phase exfoliation process was proposed. The curling deformation of kaolinite was detected by scanning electron microscope (SEM) and transmission electron microscope (TEM).

2. Mineral structure features of kaolinite

Kaolinite belongs to triclinic system, with lattice constants of $a_0 = 0.514$ nm, $b_0 = 0.893$ nm, $c_0 = 0.737$ nm, $\alpha = 91.8^\circ$, $\beta = 104.5^\circ$ and $\gamma = 90^\circ$. The structure and arrangement of kaolinite is constituted of 1:1 one-layer Si–O tetrahedral sheet and one-layer Al–O octahedral sheet. However, the actual structure of octahedral

sheet is $a_0 = 0.506$ nm and $b_0 = 0.862$ nm and the actual structure of tetrahedral sheet is $a_0 = 0.514$ nm and $b_0 = 0.893$ nm. The size of Al–O octahedron is smaller than that of Si–O tetrahedron.

The Si–O tetrahedron and Al–O octahedron share one oxygen atom, forming one indivisible entirety (Fig. 1A). Theoretically, six Si–O tetrahedrons shall bind on the plane to form a stable orthohexagonal ring structure (Fig. 1B.I). However, because the size of Al–O octahedral sheet is smaller than that of Si–O tetrahedral sheet, there is a structure adaptation process for both. In the actual crystal structure of kaolinite, Si–O tetrahedron can only turn from idealized hexagonal sheet into ditrigonal arrangement to shrink the spacing between the top oxygens (Fig. 1B.II) [23,24]. The adaption between the Si–O tetrahedron and the Al–O octahedron was realized in this kind of mild curling.

The yield morphology of naturally well crystallized kaolinite is a fake-hexagonal sheet parallel to (001) and the aggregation presents wormlike (Fig. 2c and g). The platy kaolinite can stably exist. This may attribute to the following [24,27]: (1) The mutual repulsion between the same electric charges of Si^{4+} and Al^{3+} leads to the overall morphology of the layered superposition. (2) There is hydrogen bond force between the tetrahedron bottom oxygen and hydroxide radical of the neighboring layer. (3) The wrinkling curling of tetrahedron bottom oxygen enables it to adapt to the hydroxide radical of the neighboring layer in the dimensional orientation. Fig. 1 shows the interlayer curling adaption effect of Si–O tetrahedron in the Si–O tetrahedral layer. It forms a shorter axial length. Multiple factors contribute to the macroscopic platy mineral morphology in the nature.

It was found that considerable amount of kaolinite nanoscrolls can be prepared via the liquid intercalation and delamination process [19,21,22,28,29]. The morphology features of this kind of product inherit the mineral structure properties of original kaolinite (Fig. 2 d, e, f, h and j).

3. Curling model of kaolinite

3.1. Curling driving force

The structure and arrangement of kaolinite contains 5-layer atomic planes. Even ten-layer superposition still can reach a considerable radius-thickness ratio and the internal structure dislocation forms a strong driving force. With the inherent instable morphology of two-dimensional nano-materials, it is difficult to maintain the stability for kaolinite in this two-dimensional scale. Only through certain curling and wrinkling (Fig. 3), even completely curling to form into tube shape on c axis can the stable structure be realized (Fig. 2d–f).

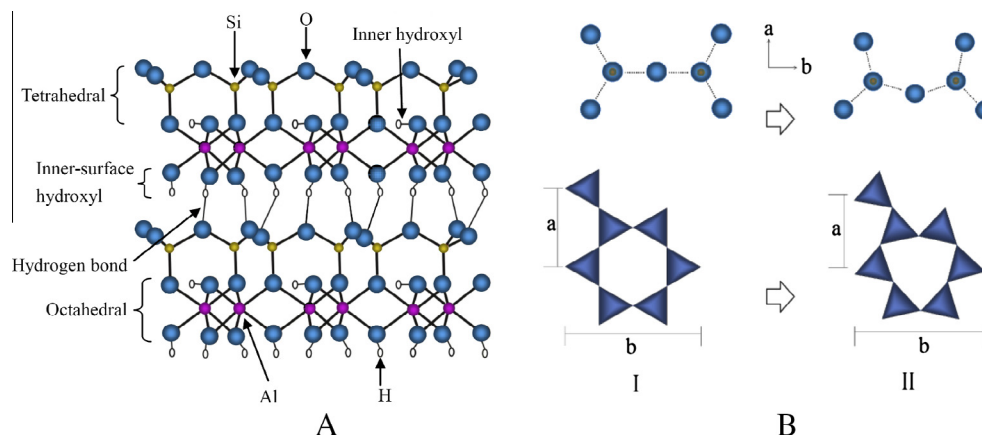


Fig. 1. Kaolinite structure and arrangement of Si–O tetrahedron in kaolinite [24–26]. (I) an idealized hexagonal sheet; (II) a ditrigonal arrangement.

Download English Version:

<https://daneshyari.com/en/article/606961>

Download Persian Version:

<https://daneshyari.com/article/606961>

[Daneshyari.com](https://daneshyari.com)