



Preparation of kaolinite nanotubes by a solvothermal method

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Abstract

Kaolinite nanotubes were prepared by intercalation and solvothermal reactions using pristine kaolin as a starting material. Firstly, an intercalation compound of kaolinite/dimethyl sulfoxide was prepared as a precursor. Then, kaolinite/methanol (KM) was achieved by replacing dimethyl sulfoxide with methanol through solvothermal reaction at 100 °C. Dimethyl sulfoxide molecules can be replaced mostly when the reaction time was 2 h, and the intercalation ratio of KM compound reached 97.9% for the reaction time of 24 h. Finally, the kaolinite nanotubes were achieved by the solvothermal reaction of the KM compound and methanol solution of CTAC (1 M) at 100 °C for 24 h. XRD, IR, SEM, and N₂ sorption measurements were used to characterize the as-prepared samples. It is found that the kaolinite nanotubes had a specific surface area of 45.44 m²/g. The length of the nanotubes is about 300–2000 nm and the internal diameter and external diameter is about 15–55 nm and 40–80 nm, respectively.

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1. Introduction

Kaolinite is a 1:1-type layered silicate mineral of which the layer consists of a SiO₄ tetrahedral sheet and an AlO₂(OH)₄ octahedral sheet. It is not easy to intercalate guest molecules into kaolinite due to the strong hydrogen bonds between the adjacent layers. Highly polar and small molecules such as dimethyl sulfoxide (DMSO), formamide, urea, etc. could be possible candidates to break the hydrogen bonds and insert into the adjacent layers. Therefore, some large-size molecules can be introduced through a so-called “displacement method” by replacing the small molecules [1].

Kaolinite nanotubes were formed spontaneously with a very limited yield by repeating intercalation and deintercalation of potassium acetate [2]. The mechanism is that kaolinite layers

curl to compensate the lateral misfit between the octahedral sheet and tetrahedral one when the interlayer hydrogen bonds are sufficiently weakened. In energy aspect, the curling mechanism is more favorable than the SiO₄ tetrahedral rotation mechanism in planar kaolinite particles. However, the former one can only occur in sufficiently thin particles with highly disordered structures and strongly weakened interlayer hydrogen bonds [3]. As a result, delaminating kaolinite to obtain thin lamellae and then intercalating large-size molecules into them is beneficial to the formation of kaolinite nanotubes.

To intercalate large-size guest molecules into kaolinite, the intercalation compound of kaolinite/methanol (KM) was confirmed as a highly efficient intermediate [1,4]. The intercalation ratio (I.R.) of KM is a key factor influencing the displacement intercalation. The reported methods to prepare KM have the disadvantages of long reaction times and low I.R., although some precursors, such as the intercalation compound of kaolinite/DMSO (KD), were used. For example, the (001) diffraction peak of kaolinite is detected clearly for the reaction time of 5–7 days [1,5–7]. From the I.R. point of view,

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the I.R. of KM is relative low even using the PTFE-lined autoclave and intercalating at high reaction temperature and long time of 200–270 °C and 89 h [8].

Using KM as an intermediate, Gardolinski and Lagaly achieved nanotubes with relative high yield by a cycle of intercalation and deintercalation of alkylamines [9]. Kaolinite nanotubes were fabricated by Kuroda et al. using N-Hexadecyl trimethyl ammonium chloride (CTAC) as a guest molecule [10]. Moreover, the structural order of kaolinite has an important effect on the formation of nanotubes [11,12]. The yield of nanotubes is significantly increased in high structural ordered kaolinite. The increasement of yield is mainly contributed by the grafting reaction with methanol and the subsequent reaction with long-chain octadecylamine [12]. However, all these processes mentioned above are extremely time-consuming in steps of stirring, intercalation/deintercalation and rolling.

Recently, hydrothermal [13,14] or solvothermal [15,16] reactions are widely used to synthesize materials. Although kaolinite and halloysite have been synthesized by using the oxides or hydroxides of silicon and aluminum under hydrothermal conditions [17–19], there are no public reports about the preparation of kaolinite nanotubes through hydrothermal or solvothermal methods by using kaolinite as raw material. In this paper, kaolinite nanotubes were prepared through a solvothermal method by using pristine kaolin with high yield and short time.

2. Material and methods

2.1. Materials

Natural white kaolin was come from Zhangjiakou (Hebei province, China), which mainly composed of kaolinite with a calculated Hinckley index of 1.31 [20], as well as a small amount of quartz and calcite (Fig. 1). Kaolinite crystals are pseudo-hexagonal with high crystallinity (Fig. 2a). The size and specific surface area of kaolin powder are ~2–4 μm and 8.08 m²/g, respectively.

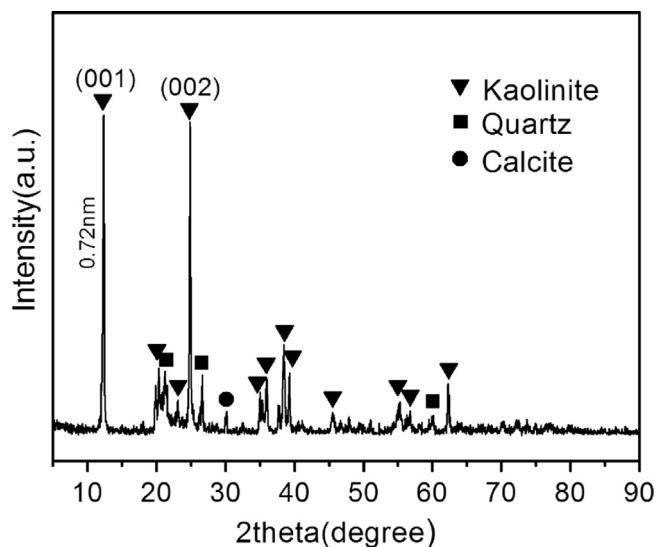


Fig. 1. XRD pattern of the raw kaolin.

The raw kaolin was treated by the intercalation/delamination method to achieve delaminated kaolinite (DK) powder with a specific surface area of 8.66 m²/g. The diameter and thickness of DK particles are smaller than those of raw kaolinite particles (Fig. 2b). The delaminated kaolinite presents a platy-like shape, which is beneficial for the formation of kaolinite nanotubes.

DMSO (analytically pure, ≥ 99%, Shuangshuang Chemical Co., Ltd., Yantan, China), methanol (analytically pure, ≥ 99.5%, the Regent Chemical Co., Ltd., Tianjin, China), CTAC (Sino-pharm Chemical Regent Co., Ltd., Shanghai, China) were used as guest reagents. Anhydrous ethanol used in this paper (analytically pure, ≥ 99.7%) was obtained from Yantai Shuangshuang Chemical Co., Ltd., China.

2.2. Experimental process

2.2.1. Preparation of the intercalation compound of kaolinite/DMSO

DMSO was dispersed well in distilled water with a volume ratio of 10:1. 10 g DK powder was added into the mixture of 77 ml, then mechanically stirred at 80 °C for 24 h. Subsequently, solid particles were separated by centrifugation and washed with anhydrous ethanol twice and dried at 60 °C for 12 h in order to obtain KD.

2.2.2. Preparation of the kaolinite/methanol compound by the solvothermal method

KD and methanol, with a solid/liquid ratio of 1 g:75 ml, were mixed and magnetically stirred at room temperature for 30 min. The suspension was poured into a 100 ml PTFE-lined autoclave, sealed and placed into an oven at 100 °C for 24 h. And the methanol was replaced by a fresh one with the same volume every 6 h. Finally, the KM samples were obtained by centrifuging and drying the above suspensions.

2.2.3. Preparation of kaolinite nanotubes by a solvothermal method

The wet KM obtained from 2.2.2 without drying was put into the methanol solution of CTAC (1 M) with a solid/liquid ratio of 1 g:75 ml and magnetically stirred at room temperature for 30 min. Then, the mixture was transferred into a 100 ml PTFE-lined autoclave, which was sealed and heated at 100 °C for 24 h in an electrical oven. During the solvothermal treatment, the used methanol solution of CTAC was replaced by a fresh one with the same volume every 6 h. Finally, kaolinite nanotubes were achieved by filtering, washing (twice using ethanol) and drying the suspension.

2.3. Characterization

X-ray powder diffraction (XRD) analysis was carried out on an XD-3 X-ray diffractometer (Beijing purkinje general instrument Co., Ltd., China), using a Cu K α radiation ($\lambda=1.5406 \text{ \AA}$) with the scanning rate of 4° min⁻¹ at 36 kV, 20 mA. I.R. of the intercalation compound was determined from the X-ray diffractograms by the following formula:

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