Research paper

Morphology and orientation of curling of kaolinite layer in hydrate

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ABSTRACT

In order to determine if there are curlings along other directions than [100] and [010] in kaolinite (Kaol) layer, 1 nm Kaol hydrate with 85% yield was synthesized by the fluorine-free method. Its structure and morphology were investigated by X-ray diffraction (XRD), field emission transmission electron microscopy (FETEM) and selected area electron diffraction (SAED). The results show that: (1) there are not only single curling and two opposite parallel curlings, but also two adjacent curlings with about 120° angle in one single layer; (2) there are four new orientations of curlings [$1\bar{1}0$], [110], [310] and [$3\bar{1}0$] in Kaol hydrate. The reasons that Kaol layers can curl along multiple directions may be that: first, two types of incompatible matchings between tetrahedrons and octahedrons; second, the hexagonal distribution and the zigzag distribution of two types of matchings.

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As one of the most important minerals in the kaolinite (Kaol) group, 1 nm halloysite (Hal) has a similar 1:1 layer structure to Kaol and an additional layer of water molecules. When Kaol structure was first proposed, Pauling (1930) pointed out that Kaol would have a small tendency to curve because of the mismatch between the dimensions of aluminum–oxygen octahedral sheet and silicon–oxygen tetrahedral sheet, which could be overcome by the forces between layers. Bates et al. (1950) pointed out that layers in Hal could not overcome the curving tendency only through the weak hydrogen bond with water molecule, and thus showed the tubular morphology. They also estimated the Hal diameter with the gibbsite size as a natural octahedral sheet size. Based on these results, Singh (1996) studied the effects of tetrahedral curving and tetrahedral rotation and then proposed a model to explain why tubular Hal rolled in preference to tetrahedral rotation to correct the misfit between octahedral and tetrahedral sheets.

In the abovementioned and other studies (Honjo and Mihama, 1954; Kohyama et al., 1978), curling orientations discussed by people are all along the a-axis or the b-axis of the Kaol layer, so, are there some curlings along other directions in practice? Unfortunately, over the years, although there are numerous studies on Hal morphology, no purely Hal morphology studies have concentrated on curling orientations.

1 nm Hal can be formed only under certain geological conditions, and is easy to dehydrate. This brings the considerable difficulties to compare the results between different researchers. To address this, Costanzo et al. (1980, 1982) proposed to synthesize 1 nm Kaol hydrate with reproducible crystallinity and even impurity, and expected it as the ideal structure of 1 nm Hal. After intercalating dimethylsulfoxide

(DMSO) into Georgia Kaol, they used fluoride ions to replace interlayer hydroxyl then used water for another replacement to gain 1 nm Kaol hydrate (Costanzo et al., 1984). Later, Costanzo et al. (1984) and Raythatha and Lipsicas (1985) found that the yield of Kaol hydrate could increase significantly without fluoride ions when adding the new methanol washing step after DMSO intercalation (called as fluorine-free method). Tunney and Detellier (1994) used ethylene glycol for the second intercalation to Kaol after being intercalated by DMSO, then methanol washing and water washing. Finally, 0.84 nm hydrate was gained. Ben Haj Amara (1997) intercalated potassium acetate into nacrite, after water washing, 0.84 nm hydrate was gained. So far, only Singh and Mackinnon (1996) have studied the morphology of Kaol hydrate. They repeated potassium acetate intercalation and water washing several times and then investigated the change in the morphology of Kaol. The results showed that this method could only prepare 0.73–0.97 nm Kaol hydrate, which was quite different from natural 1 nm Hal and might be inappropriate for morphology analogy. In this paper, 1 nm Kaol hydrate (85% yield) was synthesized following Raythatha and Lipsicas's fluorine-free method, and then multiple curling orientations other than [001] and [010] were first determined using FETEM and SAED. Furthermore, the forming reason of these curlings was also discussed in detail.

1. Experiments

1.1. Materials and synthesis

The <2 μm, raw Kaol from the Maoyingzi deposit (Xiaoxian, Anhui, China) was used in the present study. Major composition (mass%) of Kaol measured by X-ray fluorescence spectroscopy (XRF) (S8 TIGER,

Bruker) is shown in Table 1. DMSO and methanol were obtained from Shanghai Suyi Chemical Reagent Co. Ltd. All of these reagents were of analytical grade purity (>99.0%) and used as received.

The DMSO-intercalated Kaol (denoted as DMSO-Kaol) was prepared according to the method described by Olejnik et al. (1967). The synthesis of 1 nm hydrate followed the procedure described by Raythatha and Lipsicas (1985). In a typical synthesis, a dispersion of 3 g of Kaol in 100 ml of DMSO (containing 9% water by volume) was stirred at room temperature for 3 days. DMSO-Kaol was collected by centrifugation (4000 rpm) and excess DMSO was discarded. After washing with 100 ml methanol six times, 100 ml water washing was immediately performed three times and then 1 nm hydrate was obtained. Similar to the results in reference (Singh and Mackinnon, 1996), there was almost no layer curling to be observed. Thus the above-described procedure was repeated 20 times for the full relaxation of Kaol layer to obtain the final sample with the analyzable quantity of curlings.

1.2. Characterization

XRD patterns were collected on a Rigaku D/Max-3B diffractometer using Cu radiation, graphite monochromator, 35 kV operating voltage, 30 mA operating current, 0.02° step, and 3°/min scanning rate. When preparing XRD samples, wet hydrate was smeared on a glass slide with a shallow groove, then smoothed and scanned fast in order to ensure that interlayer water molecules were not lost in the scanning process.

A JEOL 2010 field emission transmission electron microscopy was used to determine sample morphology. The operating voltage was 200 kV. FETEM samples were prepared from ethanolic particle dispersions on amorphous carbon coated copper grids.

2. Results

2.1. XRD

XRD pattern of raw Kaol shows that there are no significant impurities (Fig. 1a); the Hinckley index (HI) (Hinckley, 1963) calculated in the 2θ range of 19–28° is 0.95 which indicates the high crystallinity of Kaol. After hydration (Fig. 1b), the 1.01 nm reflection with a high intensity at the 2θ value of 7.84° relative to the 0.713 nm reflection at the 2θ value of 12.24° indicates that most Kaol transforms into 1 nm hydrate. No other products are found. The proportion of Hal to Kaol is 85:15, which can be estimated using the areas of 1.01 nm and 0.713 nm reflection peaks from Fig. 1b.

2.2. TEM

The TEM morphologies show that raw Kaol is irregular angular and consists of plate-like particles (Fig. 2). Further examination indicates that these particles are assembled by the thinner layers and many corners are near 120°, that is a typical feature of Kaol with irregular shape (Ekosse, 2001). Several narrow dark areas in Fig. 2 are caused by the overlap or side standing of the small particles. Any curlings of Kaol layers cannot be found even through higher transmission voltages and greater multiples of amplification. This result combined with the XRD results and the formamide expansion test (Churchman, 1990, not given here) shows that the raw Kaol sample does not contain natural 1 nm Hal.

Relative to the original morphology, significant change occurs to Kaol layer after hydration treatment. Two similar curlings shown in Fig. 3 are obviously both in the initial stage of the curling process. The
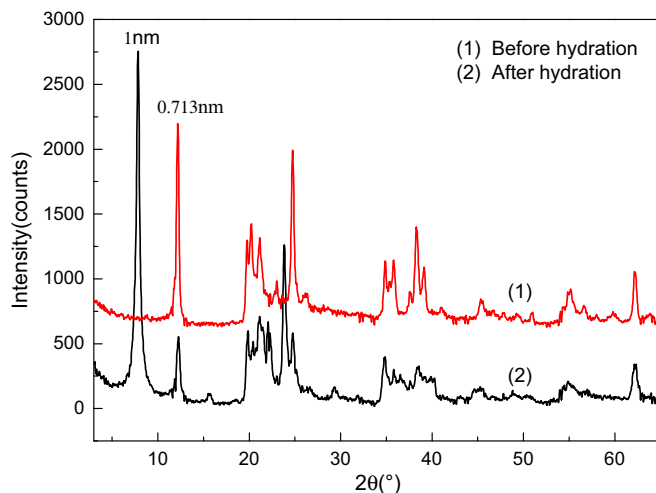

Fig. 1. X-ray diffraction patterns of Kaol before and after hydration.

curled layer in Fig. 3a is thinner than that in Fig. 3b, and exhibits a smoother curling appearance. Because of the unstable structure, the TEM morphology should be attributed to the dehydration product of 1 nm Hal, however, Kohyama et al. (1978) found that Hal morphologies before and after dehydration did not change significantly by using environmental electron microscopy (EEM). So in this work, the dehydrated product of 1 nm hydrate formed in the high vacuum can still reflect the corresponding 1 nm hydrate morphology.

In two curlings in the further stage (Fig. 3c and d), the leading edges of Kaol layers have been connected with the uncurled substrates. Only the middle part of the layer in Fig. 3c is rolled, not overall, and the fracture of layer occurs. The reason may be that: (1) before curling, the fracture has been formed and when curling only part of the layer participates; (2) in curling, the fracture is gradually produced by the stress concentrated on the gap of local irregular edge. If the Kaol has the regular quasi-hexagon shape, one edge of the layer may be rolled overall in the manner of reference (Singh and Mackinnon, 1996). In Fig. 3d the irregular edges can be clearly seen from the side, besides a crack occurs along an edge gap in the curling layer, as indicated by the arrow.

The curlings in Fig. 3a–d are both formed on one side of the Kaol layer. The reason may be that the other part of the layer is constrained by the surrounding particles. If the layer is small and/or the constraint is few, then the simultaneous curling of two opposite sides will occur. This curling type with two small layers is shown in Fig. 3e. The anti-color graph is given here in order to distinguish different particles more clearly, in which the solid arrow and the dotted arrow indicate two different curlings. Another curling of this type has developed further (Fig. 3f) and presents more obvious tube feature. The middle tube might be formed earlier and prevent two sides from rolling further, which results in the spectacle of three tubes coexisting. In fact the similar case also occurred in other experiments (Singh and Gilkes, 1992; Singh and Mackinnon, 1996), but had not been pointed out.

Besides the curlings formed on one side (Fig. 3a–d) and two opposite sides (Fig. 3e and f), two adjacent curlings in the Kaol layer (Fig. 3g and h) are also formed. This type of morphology has not been reported so far. The angles between the adjacent tubes measured from the graphs are about 117° and 115°. In addition, the obvious fracture is found on the intersection region of the tubes, which may be caused by the stress concentration in the intersection.

2.3. SAED

SAED technology was used to determine the curling direction. First, the deflection angle between the diffraction pattern and the TEM morphology was corrected. The superposition graph of the curling on the

Table 1
Chemical composition of Kaol sample (mass%).

Na$_2$O	MgO	Al$_2$O$_3$	SiO$_2$	K$_2$O	CaO	Fe$_2$O$_3$	TiO$_2$	P$_2$O$_5$
0.09	0.34	37.6	47.0	0.11	0.24	0.85	0.95	0.09