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### Arrangement models of alkylammonium cations in the interlayer of HDTMA<sup>+</sup> pillared montmorillonites

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**Abstract** The orientation of HDTMA<sup>+</sup> in the interlayer of organic pillared montmorillonites prepared at different concentrations of HDTMA<sup>+</sup> have been studied using X-ray powder diffraction (XRD) and theoretical calculation. A series of arrangement models of HDTMA<sup>+</sup> in the interlayer of montmorillonite have been proposed as lateral-monolayer (LM), lateral-bilayer (LB), pseudotrilinear (PT), paraffin-type-monolayer (PM), paraffin-type-bilayer (PB). With the increase of the concentration of HDTMA<sup>+</sup>, the arrangement model of HDTMA<sup>+</sup> in the interlayer of montmorillonites changes as lateral-monolayer→lateral-bilayer→paraffin-type monolayer→pseudotrilinear→paraffin-type-bilayer and the packing density of HDTMA<sup>+</sup> in the interlayer increases gradually. In the intermediate stages, different models may coexist.

**Keywords:** organic pillared montmorillonite, arrangement model, XRD, HDTMA<sup>+</sup>.

Organic pillared-clay is a kind of hybrid formed by exchange reaction between organic cations and the exchangeable interlayer cations in clay minerals. Organic pillared-clays were used in a wide range of practical applications. Examples include catalysts<sup>[1]</sup> or carrier<sup>[2]</sup>, rheological control agents in paints and greases<sup>[3]</sup>, adsorbents for the treatment of contaminated waste streams<sup>[4,5]</sup>, reinforcements in polymer matrix composites and plastics<sup>[6]</sup>, raw materials of nanocomposites<sup>[7]</sup> and pore materials<sup>[8]</sup>.

The behavior and properties of the organic pillared clays depend largely on the structure of the composites and the organic molecular/ion environment in the interlayer<sup>[3]</sup>. Recently, more attentions have been paid to the orientation and arrangement model of organic molecules/ions in the interlayer of clays and several arrangement models have been presumed<sup>[3,9-12]</sup>. Lagaly<sup>[10]</sup> proposed that the arrangement of alkylammonium ions in the interlayer of clay minerals depend on the interlayer cation density ( $\xi$ ) and the alkyl chain length, and the short-chain alkylammonium ions are arranged in lateral monolayers (LM) with a basal spacing of 1.36nm, long-chain alkyl ammoniums in lateral bilayers (LB) with the basal spacing of 1.77nm whereas pseudotrilinear (PT), paraffin-type monolayer (PM) or paraffin-type bilayer (PB) arrangements should be observed only in smectites with high charge density<sup>[3,9]</sup>. Beneke and Lagaly<sup>[9]</sup> suggested that there be a correlation between the the layer charge and the tilt angle ( $\alpha$ ), which is the angle between the alkyl chain and the basal plane (001) of layer silicates. Increasing the layer charge to the theoretic maximum, the tilt angle ( $\alpha$ ) would increase to a maximum of 90°. However, Tamura and Nakazawa<sup>[11]</sup> found that crystallinity and heterogeneity of charge distribution of host minerals were important factors affecting organic pillaring behaviors in clay minerals. Vaia et al.<sup>[3]</sup> investigated the structural states of alkylammonium cations in interlayer by means of Transmission Fourier transform infrared spectroscopy (FTIR) and found that the

alkylammonium cation arrangement is not an all-trans configuration assumed by most people but a gauche configuration, and the long chains adopted a disordered, liquid-like structure in interlayer when the packing density was low. So, the arrangements of organic molecular in the interlayer are very complicated and there are still many different opinions on arrangements of organic molecules or cations in organic pillared clays.

Most previous studies paid much attention to the effect of organic molecular/cations with different R-chain length or clay minerals with different properties. However, there are only a few reports concerning the arrangement models of alkylammonium cation with long alkyl chain in the interlayer of pillared clays prepared at different concentrations of pillaring solution<sup>[11]</sup>. In this paper, the arrangement models and their transformations of HDTMA<sup>+</sup> pillared montmorillonites prepared at different concentrations of pillaring solution are studied. It is helpful for us to reveal the structure of pillared clays.

## 1 Materials and experimental methods

The montmorillonite (HM) sample was taken from Hebei, China and purified by sedimentation. The  $\square 5\mu\text{m}$  size fraction was collected and dried at  $90\square$ . Then, the sample was ground and sieved to particle size of  $<200$  meshes and sealed in a glass tube for use. The structural formula of HM montmorillonite is  $(\text{Na}_{0.053}\text{Ca}_{0.176}\text{Mg}_{0.1}\cdot n\text{H}_2\text{O}) [\text{Al}_{1.58}\text{Fe}_{0.03}\text{Mg}_{0.39}] [\text{Si}_{3.77}\text{Al}_{0.23}]\text{O}_{10}(\text{OH})_2$ . The total charge of the interlayer cation is 0.62 and the cation exchange capacity is 57.9mmol/100g. Hexadecyltrimethylammonium bromide with a purity of 99%. was taken as pillaring reagent.

Preparation of Na exchangeable montmorillonite (Na-Mont): 10g of the mixture of montmorillonite and  $\text{Na}_2\text{CO}_3(\text{C.P.})$  which equals to 6% weight of montmorillonite was added into 100ml of deionized water and stirred at  $80\square$  for 3 h. Na-Mont was collected by centrifugation and washed with deionized water until the pH was neutral. The Na-Mont was dried at  $90\square$ , ground into 200 meshes and kept in a sealed bottle.

Preparation of organic pillared montmorillonite: 2.5 g of Na-Mont was dispersed in about 300 ml of deionized water and then a desired amount of Hexadecyltrimethylammonium bromide as solid salt was slowly added. The concentrations of HDTMA<sup>+</sup> varied from 0.2CEC to 4.0CEC, in which 0.2CEC meant that the added amount of HDTMA<sup>+</sup> was 0.2 times of CEC of montmorillonite in the suspension and the others were marked as the same way. The reaction mixtures were stirred for 10h at  $80\square$ . All products were washed free of bromide anions, dried at  $90\square$  and ground in an agate mortar to pass through 200 mesh sieve.

X-ray diffraction (XRD) patterns were recorded between  $1.5$  and  $20^\circ(2\theta)$  at a scanning speed of  $2^\circ/\text{min}$ . using Rigaku D/max-1200 diffractometer with  $\text{CuK}\alpha$  radiation. All samples were analyzed as oriented clay-aggregate specimens prepared by drying clay suspensions on glass slides.

## 2 Results

Fig. 1 shows the XRD patterns of the montmorillonite and the complexes. For convenient discussion, the XRD patterns are divided into four parts ( $\square$ ,  $\square$ ,  $\square$  and  $\square$ ) based on the basal spacing.

part  $\square$ : The  $d_{(001)}$  (1.54nm) of main peak indicates that the original sample is Ca-montmorillonite. In X-ray diffraction profile, there are weak peaks of impurity minerals (Illite and Kaolinite) at  $8.8^\circ$  and  $12.3^\circ$ , respectively. The value of V/P parameter, which is used

to evaluate the crystallinity of montmorillonite and can be got from XRD pattern of the oriented film saturated with glycol, is 0.96. This implies a high crystallinity for HM montmorillonite<sup>[13]</sup>. The  $d_{(001)}$  of Na-Mont decreases from 1.54nm to 1.28nm which is characteristic  $d_{(001)}$  of Na-montmorillonite.

part □: After intercalated by organic pillaring reagent at low concentration, the  $d$  values and intensities of diffraction peaks change obviously, and the  $d_{(001)}$  of main peak shifts from 1.28nm to 1.48nm.

part □: With the increase of pillaring reagent concentrations (0.7~2.0CEC), the location of main diffraction peaks shift to smaller angles. The values of  $d_{(001)}$  increase gradually (1.78nm→2.25nm→2.79nm→3.05nm).

part □: In the range of 2.2CEC and 4.0CEC,  $d_{(001)}$  reaches the maximum (4.03nm) and the profile of the peak becomes sharper with the increase of HDTMA<sup>+</sup> concentration. The peak of 1.98nm occurs in the range from 1.9CEC to 4.0CEC.

Figure 1. X-ray diffraction patterns of organic pillared montmorillonite prepared at different concentration

### 3 Discussion

The shape of perfect straight-chain quaternary ammonium cation, HDTMA<sup>+</sup>, like a nail while the long alkyl chain is 'body' of the nail and the chain end holding three methyls is the 'nailhead'. According to the data of van der Waals radius, covalent bond radius and bond angle, the steric configuration, size and shape of organic molecules or cations could be calculated<sup>[14]</sup>. When the HDTMA<sup>+</sup> is lying flat, the height of alkyl-chain is 0.4nm and the 'nailhead' is 0.51nm. In this case, adding the thickness of phyllosilicate's TOT layer (0.96nm), the thickness of HDTMA<sup>+</sup> pillared montmorillonite should be 1.47nm. This value is consistent with the  $d_{(001)}$  value (1.48nm) as shown by XRD. This suggests a lateral-monolayer arrangement of HDTMA<sup>+</sup> in the interlayer of montmorillonite (Fig. 2-a).

The peak of 1.78nm, which holds an interlayer space of 0.82nm, is the main reflection in the sample 0.7CEC, it is approximate to the height of lateral bilayer (0.81nm). The organic ion arrangement can be considered as lateral bilayer. The possible arrangement model of the lateral bilayer is that the protrudent methyl inserts into cavity between organic cations or into the hexagonal hole of basal oxygen plane<sup>[15]</sup>, consequently, the alkyl chains may come close together and arrange in LB model (Fig. 2-b). So, the height of LB model depends on the height of the double layers of alkyl chains rather than that of the cation end of HDTMA<sup>+</sup>.

When the concentration of HDTMA<sup>+</sup> increases to 1.9CEC, a basal reflection at 2.79nm occurs and this reflection shifts to 3.05nm while the concentration reaches 2.0CEC. This process reflects the evolution of paraffin-type monolayer arrangement. Tamura and Nakazawa<sup>[11]</sup> considered that the  $d_{(001)}$  of 2.0~3.0nm represent the products of the intermediate stage in the course of preparing HDTMA<sup>+</sup> intercalated hectorite. Taking the length of HDTMA<sup>+</sup> (2.5nm) and the height of TOT layer into account, it can be calculated that the angles,  $\alpha_{LM}$ , between the alkyl chain and basal surface are 31°, 47° and 56° for the hybrids prepared at 0.7CEC, 1.9CEC and 2.0CEC, respectively (Fig. 2-c). However, the basal reflection at 3.46nm does not occur in our experiment, which was reported by Beneke and Lagaly<sup>[9]</sup> and was attributed to alkyl chains being perpendicular to (001). We believe that it should be attributed to the low charge density of our montmorillonite. Furthermore, we believe that 3.05nm would be

the largest basal spacing value of paraffin-type monolayer pillared montmorillonite in our experiment. In this stage, the basal reflections are very broad, representing polyphase systems.

In our experiment, the peak at 1.98nm always exists when the concentration of HDTMA<sup>+</sup> is above 1.9 CEC. It indicates that there is an interlayer spacing of 1.02nm in height. The height of the two layer of HATMA<sup>+</sup> in a bilayer-mirror-image arrangement is just 1.02nm, which equals to the interlayer spacing corresponding to the peak at 1.98nm. But, considering the repulsive force between cations, the probability for this kind of arrangement is little. Pseudotrilyer arrangement may explain well the basal reflection at 1.98nm (Fig. 2□d). Brindley and Moll<sup>[16]</sup>, Beneke et al.<sup>[9]</sup> reported the arrangement model of alkyl chains with mutual interlocking, in which the parallelly packing of the chains were presumed that a -CH<sub>2</sub> group of one chain lay between two such groups of neighbouring chains. In this case, the height of the bilayer with interlocking chains should be smaller than that without interlocking chains. The decrease of the height is 0.1nm when adding one layer with interlocking, compared with that without interlocking. Therefore, the height of the alkyl chains with pseudotrilyer arrangement should be 1.0nm. This value is similar to our experimental results and that reported by Choy<sup>[17]</sup>.

The basal reflection shifts to 4.03nm and remains unchanged in the XRD patterns of the sample prepared in the range of 2.2 – 4.0CEC, indicating that this is the final structure of HTDMA<sup>+</sup>/montmorillonite hybrids. In the study of fluorohectorite pillared with quaternary phosphonium salt [C<sub>16</sub>H<sub>33</sub>P(C<sub>4</sub>H<sub>9</sub>)<sub>3</sub>]<sup>+</sup>Br at 0.5CEC, Ijdo<sup>[18]</sup> recorded three reflections at 4.0nm, 2.8nm and 1.24nm respectively. They proposed that the 4.0nm basal spacing should be the result of regular stacking of two types of galleries since this spacing agreed well with the sum of the basal spacing of C<sub>16</sub>H<sub>33</sub>P(C<sub>4</sub>H<sub>9</sub>)<sub>3</sub><sup>+</sup> fluorohectorite (2.8nm) and Na-fluorohectorite (1.24nm). In this case, a basal spacing at 4.33nm should occur in the XRD pattern of the hybrid prepared at 2.2CEC since the sum of the basal spacings at 1.28nm for Na-montmorillonite and 3.05nm for HDTMA<sup>+</sup>-montmorillonite is 4.33nm. However, the basal spacing of 4.33nm does not occur in our XRD patterns. In the study of alkylammonium intercalated mica, Tamura and Nakazawa<sup>[11]</sup> proposed that the basal spacing of 3.98nm should be attributed to PB model and the  $\alpha_{PB}$  was 30°. In the analogous study, Benke and Lagaly<sup>[9]</sup> pointed out that long alkyl chain (n>16) alkylammonium arranged in a PB model and the basal spacing reached 4.0nm. The occurrence of the basal spacing of 4.03nm in our study implies that HDTMA<sup>+</sup> should be arranged in PB model and the  $\alpha_{PB}$ =38°. This is supported by the results of the thermogravimetry analysis (TGA). In the case of the interlayer cations of montmorillonite completely replaced by HDTMA<sup>+</sup> in the ratio of 1:1, the weight loss of HDTMA<sup>+</sup>/montmorillonite hybrid should be 16%. However, the TGA result shows that the weigh loss of the sample prepared at 3.0CEC is about 26%, indicating that there are nearly twice HDTMA<sup>+</sup> entering into montmorillonite. This result is similar to that reported by Yui et al.<sup>[20]</sup> and suggests that interlayer cations in montmorillonite should be replaced by HDTMA<sup>+</sup> completely. Furthermore, there is no the basal spacing at ~1.28 nm corresponding to na-montmorillonite found in the XRD patterns of samples prepared in the range of 0.7- 2.0 CEC. Therefore, we presume that there is no Na-montmorillonite layer in the hybrids prepared in the range of 2.2-4.0 CEC and exclude the possibility of 1□1 heterostructure in the hybrids as proposed by Ijdo. We prefer that the final structural model for HDTMA<sup>+</sup>/montmorillonite hybrids in our study should be a paraffin-type bilayer and the reflections at 1.98 nm and 1.30 nm correspond to the (002) and (003) of the peak at 4.03 nm. Since the basal spacing of 1.98 nm for the hybrid with pseudotrilyer

arrangement begins to occur in the XRD pattern of the sample prepared at 1.9CEC and this  $d$  value is the same as the (002) of the peak at 4.03 nm, the possibility that the sample prepared in the range of 2.2-4.0 CEC consists of two phases with different arrangement models cannot be excluded.

In our study, with the increase of HDTMA<sup>+</sup> concentrations, five typical basal spacings are obtained: (1).~1.48nm, (2).~1.78nm, (3).~1.98nm, (4).~3.05nm (5).~4.03nm, corresponding to the arrangement models of LM (Fig. 2-a), LB (Fig. 2-b), PT (Fig. 2-d), PM (Fig. 2-c), PB (Fig. 2-e), respectively. Simultaneously, The obviously broadened peaks in the range of 0.7CEC - 2.0CEC may imply that there may be several phases coexisting. In the course of transformation of the arrangement models of HDTMA<sup>+</sup>, different models may coexist as followings LM(0.2 CEC)→LB+PM(0.7 CEC)→PM+PT(2.0 CEC)→PB+PT(2.2 CEC).

Figure 2. HDTMA<sup>+</sup> aggregation in montmorillonite:

- (a) lateral monolayer (b) lateral bilayer (c) paraffin-type monolayer (d) pseudotrillayer  
(e) paraffin-type bilayer

#### 4 Conclusions

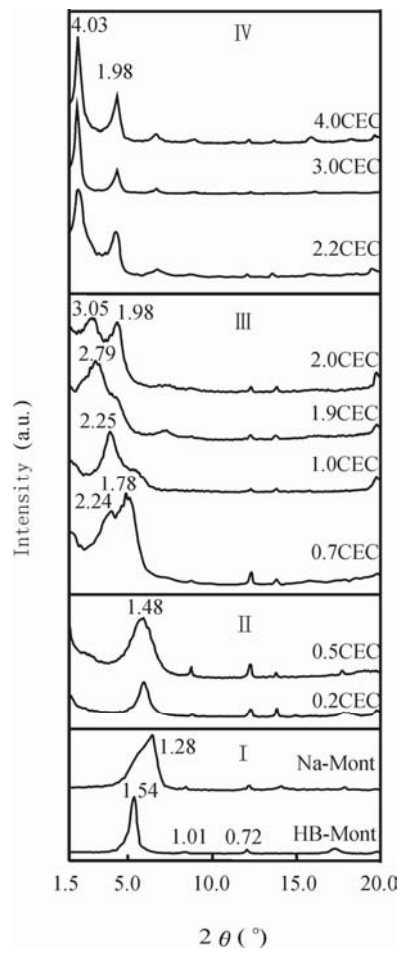
(1) The orientation of organic cations may be influenced significantly by the concentration of pillaring reagent. The PT and PB arrangements, which previously proposed to appear only in the interlayer space of montmorillonite with high charge density, can also occur in montmorillonite with low charge density; (2) In our study, the basal spacing of 3.05nm is the largest record in PM arrangement and the  $\alpha_{PM}=56^\circ$ ; The basal spacing of 4.03nm corresponds to the PB arrangement and the  $\alpha_{PB}=38^\circ$ ; (3) With the increase of the concentration of pillaring reagent, the stack density of organic cations in the interlayer space increases, resulting in the change of the arrangement of organic cations as followings LM→LB→PM→PT→PB. The heterogeneity of charge on various layers may be the crucial factor for different arrangements coexisting.

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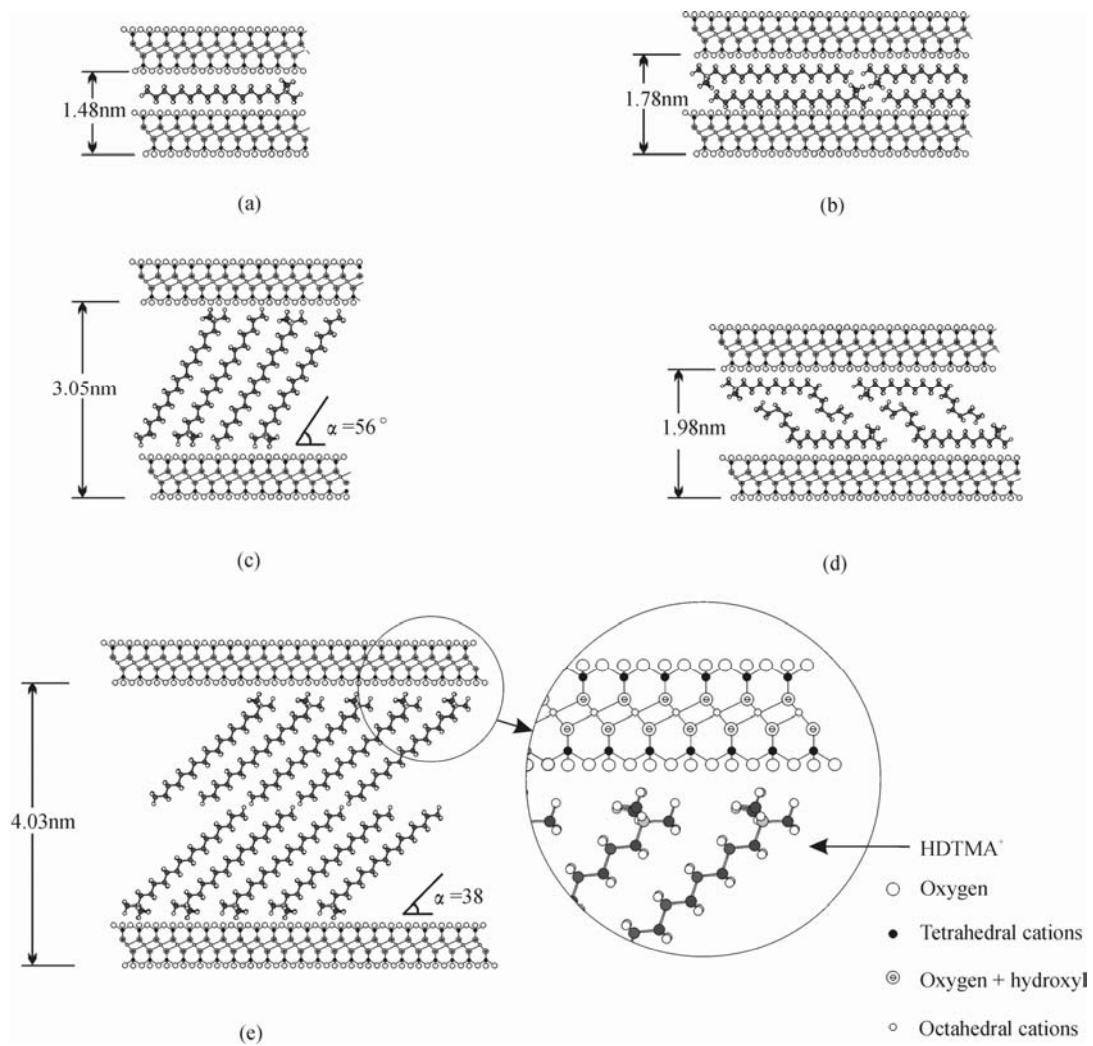
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**Figure 1**



**Figure 2**