Cleavage nature, electrokinetics, aggregation and dispersion of kaolinite①

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Abstract: Quantum chemical simulation calculation shows that kaolinite is cleaved to produce (001) and ($00\bar{1}$) basal planes. (001) plane is dominant by [SiO_4] tetrahedral, which interacted easily with hydrogen ion or other positive ions by electrostatic forces or hydrogen bonding. ($00\bar{1}$) plane is dominant by [$AlO_2(OH)_4$], which interacted easily with high negativity group such as − O− , − N− , F− etc. The apparent zeta potential and surface points of zero charge(PZC) are different for hard and soft kaolinites depending on their crystallinity index (HI) . The self-aggregation between edge and basal plane due to the electrostatic interactions may occur at acidic media. The dispersion of kaolinite particles at alkaline media may be attributed to the electrostatic repulsion between basal planes and/ or edges. The aggregation or dispersion behavior is revealed by scan electron microscope and the transmittance measurements for the suspension of kaolinite parti-cles.

Key words: kaolinite; cleavage planes; electrokinetics; self-aggregation; dispersion

CLC number: TD 929; TD 952   **Document code:** A

1 INTRODUCTION

Kaolinite is currently used in ceramics, paper manufacturing, medical applications, agricultural chemicals, chemical engineering, refractory material and defense industry because kaolinite has many high processing properties as an industrial mineral due to its surface properties[1, 2]. In reverse flotation of di-asporic bauxite, which is very important for the in-dustry of aluminum oxide production, kaolinite is needed to be removed. Therefore, It is useful to un-derstand the crystal structure, cleavage nature, sur-face electrokinetics, wettability and floatability of kaolinite.

Kaolinite is a layer structured mineral. Each kaolinite layer comprises one octahedral and one tetra-hedral sheet. Kaolinite layers are less tightly bound together in the c-direction by hydrogen bonding be-tween hydroxyl sites on the gibbsite basal plane and the oxygen of the silicon tetrahedral sheet. According to the crystal structure, kaolinite is divided into the structural order and the structural disorder. The structural order or disorder of kaolinite was deter-mined by XRD using a side-loading sample holder to minimize mineral orientation[3]. During grinding, kaolinite is cleaved mainly in the parallel layer direc-tions by overcoming the inter layer forces. The physicochemical properties of the resultant surfaces are determined by mineral crystal structures. Kaolin-ite has different surface structures between base planes and edge planes. The surface electric proper-ties of kaolinites have been investigated[4-8]. The basal surfaces of kaolinite are believed to carry a con-stant structural charge due to the isomorphous substi-tution of Si^{4+} by Al^{3+}, whereas the charge on the edges is due to the protonation or deprotonation of ex-posed hydroxyl groups and it depends on the solution pH. It has been reported that depending on the par-ticular kaolinite crystal structure an edge surface should carry a positive double layer in acid solution and a negative double layer in alkaline solution, with a PZC in the neighborhood of pH 7[9], pH(7. 3 ±0. 2)[10], pH 7. 3[11]. Because of high face area to edge area ratio, the kaolinite particles carry an overall net negative charge, though they maybe carry little net positive charge in low pH solution. Tari et al[12] re-ported a gradual increase of zeta potential when pass-ing from well-ordered kaolinite to the poorly ordered kaolinite. Hu et al[13, 14] reported the change of zeta potential of hard and soft kaolinite and revealed the nature of cleavage faces and wettability of kaolinites. On the other hand, the kaolinite suspensions are com-plicated by the fact that kaolinite particles are usually plate like and exposed two crystallographically differ-ent surfaces to the solution, i. e. the basal surfaces and edge surfaces. In these suspensions, the synthesis of electrical double layer interactions and van der Waal's-London attractions will be different for parti-cles associating edge to edge, edge to face or face to

face[9, 15-17].

In the present work, the cleavage nature, surface electrokinetics, aggregation and dispersion of kaolinite were investigated through zeta potential measurement, SEM analysis and settlement tests.

2   EXPERIMENTAL

2. 1   Materials

Kaolinite clays from four different deposits were collected for this study. Sample Ka-ML from Miluo, Hunan, China was a representative of the so-called "soft-kaolin" type. The other three samples Ka-JX, Ka-DYG, Ka-MC were from Jiaxian, Dayugou and Mianchi in Henan province, China, respectively. They were of the "hard-kaolin" type. The chemicals used in the experiments include HCl(AR) and NaOH (AR) used for pH adjustment and KNO₃(AR) for supporting electrolyte. The pure water used in the experiments was double-distilled water.

2. 2   X-ray diffraction

To determine mineralogical phases of the samples, a powder diffractometer (Shimadzu) in the reflection mode was used with graphite-filtered CuK$_\alpha$ as radiation(50 mV, 100 mA). The goniometer was run from 5° to 85° at a 2θ speed of 4°/min. This operation parameter resulted in a d-spacing measurement precision of 0.01°.

2. 3   Zeta potential measurement

The zeta potential of mineral suspension was measured on a Brookhaven Zeta Plus instrument. The ground kaolinite samples were dispersed in an electrolyte solution containing 0.02% solids in a 100 mL beaker. The suspension at a given pH was agitated for 15 min, and the suspension pH reported was measured at the end of agitation to an accuracy of ±0.01 with a REX Model PHS-3C pH meter. The agitated suspension was transferred to a square sample vessel, zeta potential was measured, and the measurement error was found to be within 5 mV after at least three measurements.

2. 4   SEM analysis

3 g mineral samples were added into 40 mL pure water. After sequential addition of modifiers, the suspension was agitated for 2 min. A suspension drop of 5 mm base diameter was created on the sheet glass using a micro dropper. The sample was then air-dried at ambient temperature. The samples were examined under a scanning electron microscope of Noran Jeol model JSM-5600LV fitted with energy dispersive X-ray analyzer.

2. 5   Settlement tests

Add 20 mg, < 5 μm kaolinite samples into a beaker with 40 mL pure water, adjust pH by HCl or NaOH and agitate for 2 min. After suspension pH was measured, 10 mL suspension was transferred to a quartz cell and equilibrated for 2 min. Then the transmittance of the suspension was measured on the 756 MC UV-VIS spectrometer.

3   RESULTS AND DISCUSSION

3. 1   Crystal structure and cleavage of kaolinite

Kaolinite [Al₄Si₄O₁₀(OH)₈] is a two-layer structured aluminosilicate, consisting of alternating layers of tetrahedral silicates and octahedral aluminum oxyhydroxides. Two layers are covalently bound together through common oxygen atoms, forming a layer-structured repeating unit. Hydrogen bonds between the hydroxyl ions of octahedral aluminum oxyhydroxides and the oxygen atoms of tetrahedral silicates hold the repeating units together, as can be seen from Fig. 1.
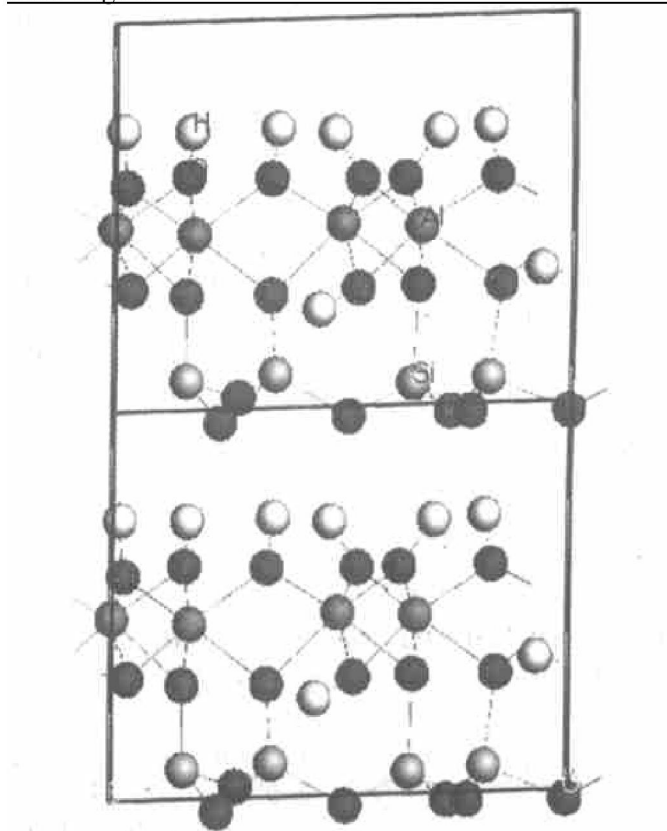

Fig. 1   Crystal structure of kaolinite

Fig. 2 shows that kaolin is cleaved along (001), (010) and (110) planes, in which the (001) plane is the basal, (010) and (110) planes are the edges. When being cleaved along (010) plane three unsaturated Al–O bonds and one Si–O bond per cell face will be produced (Fig. 2(a)). The cleavage of kaolin along (110) is anticipated to form four Al–O and two Si–O suspended bonds per cell face on the cleaved surface (Fig. 2(b)).
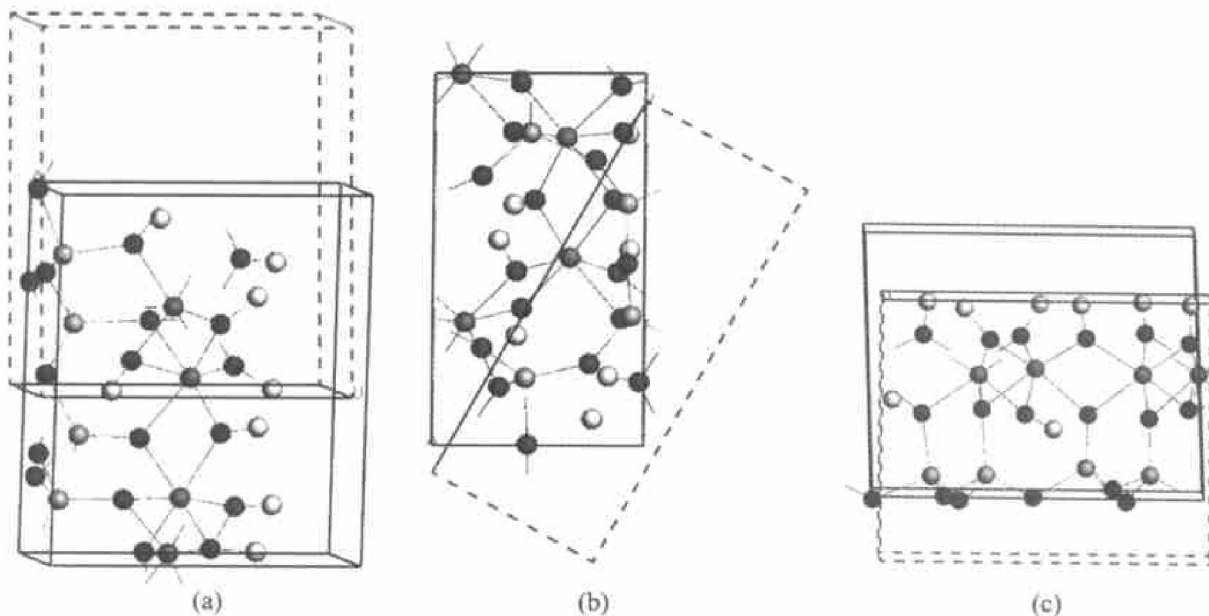
Fig. 2 Cleavage of kaolinite crystal along edges (010)(a), (110)(b), and basal plane (001)(c)

When kaolin cleaved along (001), the hydrogen bonds were broken between the repeating units. The surface Si−O and Al−OH are saturated and no residual bond can be seen from the middle solid line in Fig. 2(c). It follows that the crystal plane above the solid line is different from that below the solid line. The plane above is named as (00$\bar{1}$) face and the plane below is named as (001) face.

The atom arrangement on (001) and (00$\bar{1}$) planes are schematically shown in Fig. 3. It can be seen that the (001) face exhibited the characteristics of tetrahedral silicates, and it contains six high electronegativity oxygen atoms per cell face(Fig. 3(a)). The (00$\bar{1}$) face shows the characteristics of octahedral of aluminum oxyhydroxides, and it contains six low electronegativity hydrogen atoms per cell face.

3. 2 Crystal structure and electrokinetics

Kaolinite crystal structure is highly complex as a result of the large number of stacking faults that may appear during its formation and growth. The XRD method usually employed to study kaolinite order only provides an approximation of the real structure. There are lots of factors influencing kaolinite order such as stacking layer disorder, cation distribution disorder, non-plane layer structure, machine disorder etc. The Hinckley index (usually abbreviated as HI) is one of the most widely used crystallinity indexes to express kaolinite order[18, 19]. It is usually known to be well ordered kaolinite if its Hinckley index (HI) > 0. 9[3]. According to the scale proposed by Hinckley, the crystallinity index of kaolinite in kaolin clays are calculated from the XRD patterns of the four samples, as listed in Table 1. The detailed discussion
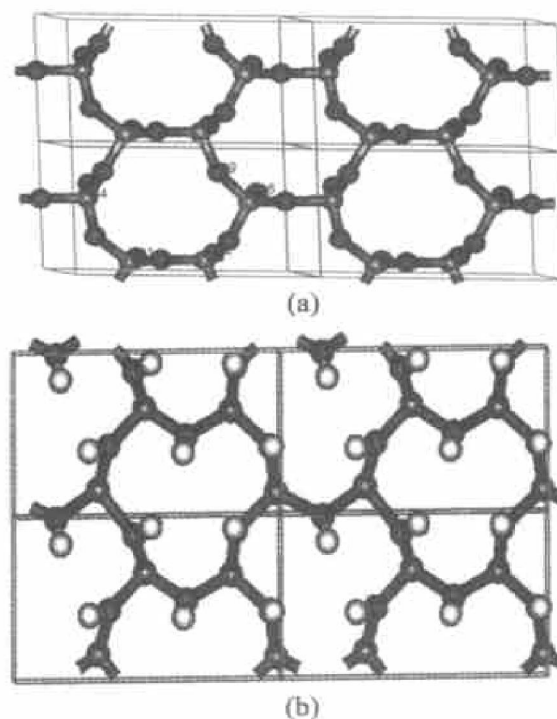

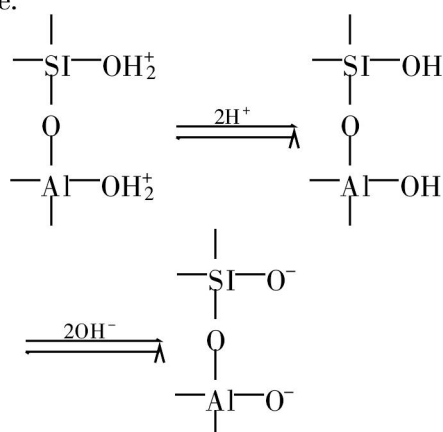**Fig. 3** Atom arrangement on (001)(a) and (00$\bar{1}$)(b) planes of kaolinite

Table 1 Crystallinity index(HI) of four kinds of kaolinite

Sample	Location	Sample	HI	Note
Ka-ML	Hunan Miluo	Soft kaolin	1. 00	Weather-eluviation type
Ka-JX	Henan Jiaxian	Hard kaolin	0. 77	In coal-bearing strata
Ka-DYG	Henan Dayugou	Hard kaolin	0. 74	In coal-bearing strata
Ka-MC	Henan Mianchi	Hard kaolin	0. 82	In bauxite horizon

about this index can be seen in Ref. [20].

We have studied the zeta potential for four kinds of kaolinite as a function of pH. The result shows that the higher the HI, the lower the negative zeta potential[20].

It has been reported that isomorphous substitution of Al^{3+} or Fe^{3+} for Si^{4+} in the tetrahedral sheet would give rise to a small permanent negative charge on the Si basal planes. The exposed Al and Si centers at kaolinite edges are terminated by hydroxyls. Positive edge charge is attributed most reasonably to gibbsite-like edge sites. Negative surface charge is culminated by the contribution of silanol groups. Therefore, following reaction develops surface charge of kaolinite.

(a)

(b)

Fig. 4 Schematic diagrams of edge-face self-aggregation(a) at acidic pH region and dispersion(b) at alkaline pH region of kaolin particles

The experimentally measured zeta potential and PZC values of kaolinite particles may call as apparent zeta potential and PZC due to the different charged nature on edges and basals. The results above indicated that the different charged natures on edges and basals might have different effect on the aggregation/dispersion and/or flotation of kaolinite.

3. 3   Interaction models between kaolinite particles at acidic and alkaline media

At acidic pH range, the edges of kaolinite are positively charged and basal planes are small permanent negatively charged. The self-aggregation between edges and basals may be possible through the electrostatic interactions. Due to the existence of a lot of suspended oxygen atoms on the edges, the H-bonding between the suspended oxygen on edges and the hydroxyl on (001) basal planes may play more important roles in the self-aggregation of kaolinite particles, which can be schematically shown in Fig. 4(a). The SEM image of kaolinite particle suspension in acidic media clearly showed the self-aggregation of edge to face(Fig. 5(a)).

At alkaline pH range, both edges and basals are negatively charged, and the kaolinite suspension may be dispersed well due to the electrostatic repulsion among various surfaces. The schematic diagram is plotted in Fig. 4 (b). The dispersed kaolinite particles are demonstrated by the SEM image
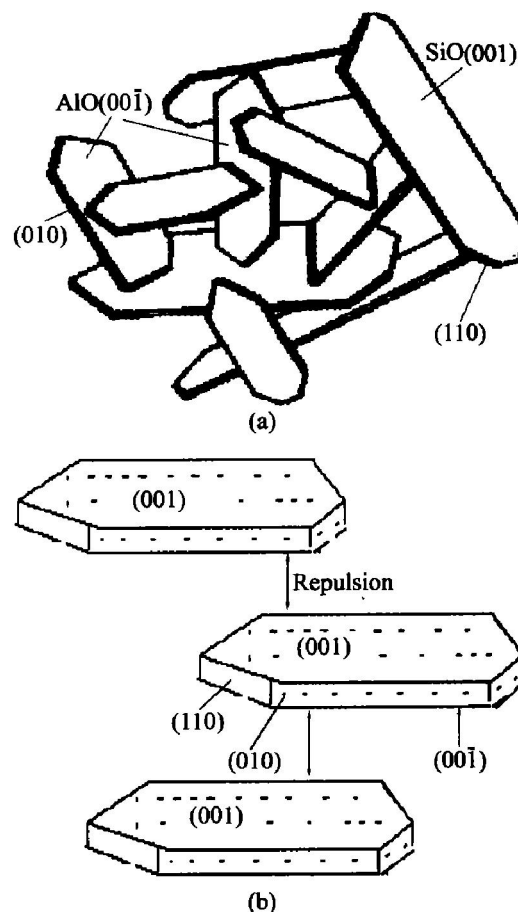
Fig. 5 SEM images of particle of kaolinite suspensions at different pH values
(a) —pH= 2; (b) —pH= 10

in Fig. 5(b) .

Fig. 6 shows the transmittance of the suspension of kaolinite particles as a function of pH. It can be seen that the transmittance of the suspension is high at acidic pH range indicating the occurrence of self-aggregation of kaolinite particles. With the increase of pH, the transmittance of the suspension is decreased indicating that the stability of the suspension is increased and the particles are dispersed. The electrostatic interactions and van der Waals' interactions between edge and edge, face and face, edge and face of kaolinite particles are further calculated to explain the aggregation of edge and face at acidic media and the dispersion of face and face at alkaline media.
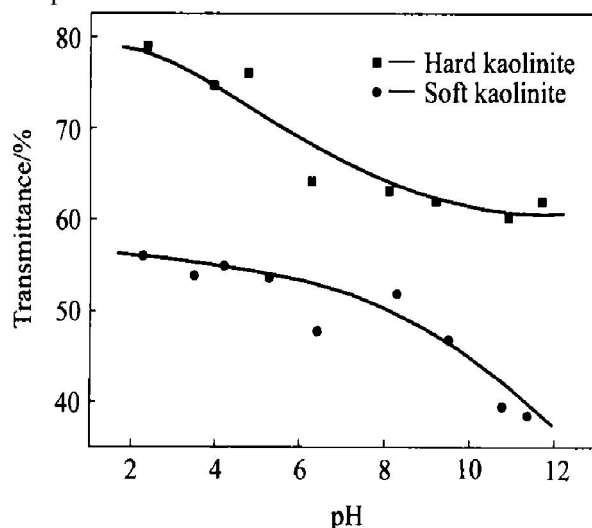

Fig. 6 Transmittance of kaolinite
suspension as function of pH

4 CONCLUSIONS

1) Kaolinite is cleaved to produce edges (010) , (110) and basal planes (001) and (001). (001) plane exhibits the characteristics of the oxygen of the silicon tetrahedral sheet and the (001) shows the nature of hydroxyl of aluminum oxyhydroxide octahedral.

2) Based on the value of the crystal index, the kaolinite can be either hard or soft.

3) In acidic media, the self-aggregation of kaolinite particles may occur possibly through the H-bonding between the hydroxyl on (001) planes and oxygen on edges or through the electrostatic interaction between the positively charged edges and negatively charged (001) planes.

4) In alkaline media, the suspensions of kaolinite particles are dispersed well due to the electrostatic repulsion between the similarly charged planes.

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(Edited by YANG You-ping)