# Preparation and characterization of mixed hydroxy-Fe-Al pillared montmorillonite with large basal spacing

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Abstract: Mixed hydroxy-Al-Fe pillared montmorillonites with large basal spacing were successfully prepared through cation-exchanging of Na$^+$ - montmorillonite with mixed hydroxy-Al and hydroxy-Fe pillaring solutions made from hydrolysis of corresponding metal salts, followed by calcination to convert hydroxy-Al and hydroxy-Fe into intercalated polycations. According to XRD analysis, the basal spacing d(001) of pillared products dramatically enlarged from 12.7 Å in the Na-montmorillonite to 81 Å in the hydroxy-Fe -montmorillonite and 77.5 Å in mixed hydroxy-Al-Fe-montmorillonite. The N$_2$ BET surface areas of the pillared montmorillonites also greatly increased to more than 200 m$^2$/g as compared to about 27 m$^2$/g for the Na-montmorillonite. IR analysis of hydroxy-Fe, and mixed hydroxy-Al-Fe pillared montmorillonites revealed a new absorption vibration at 1384 cm$^{-1}$ wavelength. XRF elemental analysis data also showed a high content of Fe$_2$O$_3$ in the hydroxy-Fe pillared montmorillonite.

Keywords: hydroxy-Al; hydroxy-Fe; montmorillonite; preparation; characterization

## Introduction

Montmorillonite is a clay mineral with substantial isomorphic substitution. Mesoporous pillared montmorillonite can be prepared by introducing gallery templates, such as quaternary ammonium cation and long chain amine. Thus formed organo-montmorillonites have improved capabilities to adsorb hydrophobic contaminants and are widely used as sorbents to treat industrial wastewaters(Steven, 1998; Srinivasan, 1990; Stephen, 1988; James, 1994; Wibulswas, 1999; Zhang, 1993; Dentel, 1998; Hermosin, 1992). However organo-montmorillonites have very small basal spacing, and therefore their cation exchanges capacities are limited.

Pillared montmorillonite with large basal spacing can be produced by the ion-exchange of large hydrated polymeric inorganic cations. Compared to those pillared with organic cations, the resulting materials have larger interlamellar distances, higher pore volumes and larger amount of micropores. Their applications as catalysts and adsorbents in the area of environmental pollution control have been widely reported in the past decade (Rodriguez-gonzalo, 1993; Srinivasan, 1990; Dubbin, 1995; 1994; Zhu, 1997; Rightor, 1991; Sannino, 1997).

Among them, hydroxy-Al or hydroxy-Fe pillared montmorillonites received most attentions from the researchers due to their higher stability under various application conditions. Rightor(Rightor, 1991) and Doff (Doff, 1988) prepared hydroxy-Fe montmorillonite with d(001) value of 21—29Å. Mandalia(Mandalia, 1998) achieved mixed hydroxy-Al-Fe montmorillonite with basal spacing of 56 Å. In this study, a new synthesis procedure to prepare mixed hydroxy-Fe-Al pillared montmorillonite with larger basal spacing (77.5 Å) was developed. The properties of these pillared montmorillonites were characterized and studied by various analysis techniques. Their large basal spacing and high surface areas showed the promise to be effective adsorbents for the removal of pollutants.

## 1   Materials and methods

### 1.1   Materials

The raw clay used in this study was a naturally occurred mineral located in Linan, Zhejiang Province, China. It contained about 60% montmorillonite with cation exchange capacity(CEC) of 62 meq/100 g. The composition of this clay was analyzed by XRF spectroscopy. The results are given in Table 1 on a dry basis.

Table 1   Chemical analysis data( wt.% ) of the raw montmorillonite

|       | SiO$_2$ | Al$_2$O$_3$ | CaO | Na$_2$O | Fe$_2$O$_3$ | MgO | K$_2$O | MnO | TiO$_2$ | P$_2$O$_5$ |
|-------|---------|-------------|-----|---------|-------------|-----|--------|-----|---------|------------|
| wt.%  | 59.8    | 14.3        | 4.0 | 2.1     | 1.7         | 1.7 | 1.4    | 0.4 | 0.3     | 0.03       |

The raw clay was first treated with 0.3 wt.% ( NaPO$_3$ )$_6$ solution for three times to purify, and the content of montmorillonite in above-treated clay increased to more than 98%. This montmorillonite was then fully converted into Na-form by further washing with 1.0 mol/L NaCl solution for five times. It was then again washed with deionized water to remove residual Cl$^-$ completely as indicated by AgNO$_3$ test. Thus obtained sample was then centrifuged, and dried at room temperature. The dried solid was ground and sieved into powder with particle size < 2 $\mu$m. The final sample was calcinated at 105℃ for 1 h.

### 1.2   Preparation of hydroxy-Al pillared montmorillonite

0.4 mol/L NaOH solution was added slowly while stirring to a 1.0 mol/L AlCl$_3$·6H$_2$O solution until it reached an OH:Al$^{3+}$ molar ratio of 2.4 in the mixture. After being aged for 2 d at 60 ± 0.5℃, a pillaring solution containing hydroxy-Al oligocations was formed. It had a pH value of 3.76.

3 g Na-montmorillonite powder was used to make a 1.0 wt.% aqueous suspension. The above hydroxy-Al pillaring oligocations solution was added slowly into the suspension while stirring until the ratio of Al$^{3+}$ cation to Na-montmorillonite reached 10 mmol/g. Thus obtained mixture was aged at 60 ± 0.5℃ for 2 d, followed by the separation of the solid from liquid through filtration. The resulting solid was washed with

deionized water until it was free of $Cl^-$ ions. The final sample was dried at room temperature and then ground and sieved into < 2 $\mu$m powder.

### 1.3  Preparation of hydroxy-Fe pillared montmorillonite

In order to prevent $Fe^{3+}$ cations from precipitating, anhydrous $Na_2CO_3$ powder was added slowly into a vigorously stirred $Fe(NO_3)_3$ solution at room temperature. Nitrogen was bubbled through the solution to facilitate the removal of $CO_2$ form the system and avoid the formation of $Fe(OH)_3$. The concentration of $Fe^{3+}$ in the final solutions was adjusted to 0.3 mol/L. Thus obtained solution was aged for 1 to 2 d at room temperature before being used. There were no visible precipitates in the solution. The pH value of this solution was about 1.56.

The rest was the same as 2.2, only the ratio of Fe cation to Na-montmorillonite was changed to 70 mmol/meq.

### 1.4  Preparation of mixed OH-Al-Fe-pillared montmorillonite

Above-made hydroxy-Fe and hydroxy-Al pillaring solutions were mixed together to form a mixed OH-Fe-Al-pillaring solution with a Fe/Al + Fe molar ratio of 0.5. The procedures for making a mixed OH-Al-Fe-pillared montmorillonite were the same as 1.2 and 1.3.

### 1.5  Characterizations

The above-made OH-Al-, OH-Fe- and mixed OH-Al-Fe-pillared montmorillonites were characterized with IR, XRD, BET and XRF analysis. Their IR spectra were recorded with a Shimadzu IR-408 spectrophotometer, using KBr powder. The XRD analysis was performed with a Philips X'Pert MPD instrument, using Cu-K$\alpha$ as radiation($\lambda$ = 0.15 nm). Samples for XRD analysis were prepared according to the following procedures: (1) make suspensions containing 1 wt.% pillared montmorillonites; (2) drop these suspensions on the top of sample glasses; (3) form the oriented thin films on the surfaces of the sample glasses after the samples were dried at ambient conditions. Porosity and surface areas of the samples were measured with the three-point BET method on a Coalter Omnisorp 100 surface analyzer. Prior to BET analysis, samples were outgassed at 300℃ under a flow of argon for 3 h. XRF data of samples were obtained on a Siemens SRS-3000 sequential X-ray fluorescence(XRF) spectroscopy. Samples were heated at 105℃ for 24 h before XRF analysis.

## 2  Results and discussion

Table 2 shows XRD data of raw and pillared montmorillonites. The raw clay was calcium-form montmorillonite, with the d(001) value of 15.2 Å. After being exchanged with $Na^+$, the basal spacing of the montmorillonite decreased to 12.6 Å, since $Na^+$ is smaller than $Ca^{2+}$.

**Table 2    XRD data of raw and pillared montmorillonite:d(001)(Å)**

|            | Raw clay | Na- Mt | OH-Al- Mt | OH-Fe- Mt | OH-Fe-Al- Mt |
|------------|----------|--------|-----------|-----------|--------------|
| d(001), Å  | 15.2     | 12.6   | 18.6      | 81.8      | 77.5         |

Note: Mt = montmorillonite

At $OH^-/Al^{3+}$ molar ratio of 2.4 and pH value of about 3.7, most cations are in the form of large inorganic Keggin ions, i.e., $[AlO_4 Al_{12}(OH)_{24}(OH_2)_{12}]^{7+}$ ($Al_{13}^{7+}$ ions). The Keggin ions, consisting of a central tetrahedron surrounded by four sets of three octahedral, are approximately 9 Å in size and can accommodate many different cations. The small peak at $2\theta$ = 4.7 (d(001) = 18.6 Å) of the OH – Al – montmorillonite sample in Table 2 indicated that $Al_{13}^{7+}$ Keggin ions had been exchanged between the layers. This d(001) value was close to that

reported by other researchers for OH-Al-montmorillonite (Dubbin, 1994), thus confirming the success of pillaring.

The mechanism of hydrolysis of $Fe^{3+}$ ions has been understood in recent years. Spiro(Spiro, 1966) tried to prove that the hydrolysis of ferric nitrate could lead to the formation of a large polymer of $[Fe(OH)_x (NO_3)_{3-x}]_n$, where $x$ lied between 2.3 to 2.5 and $n$ was in the order of 900. The hydrolysis of $Fe^{3+}$ can lead to the formation of discrete spherical as large as 30 Å in diameter. Therefore, the intercalation of these polycations into montmorillonite can dramatically increase basal spacing of pillaring montmorillonite. As shown in Table 2, the d(001) value of the pure OH-Fe-montmorillonite was 81.8 Å while that of mixed OH-Al-Fe-montmorillonite was 77.5 Å. Although OH-Fe pillaring montmorillonite with d(001) of 76 Å was obtained by Mandalia and Messa(Mandalia, 1998), mixed OH-Al-Fe-montmorillonite with such large basal spacing value has never been reported so far.

The IR spectra of Ca-, Na-, OH-Al-, OH-Fe-, and OH-Fe-Al-montmorillonite were compared in Fig. 1. The raw clay was Ca-montmorillonite, with IR spectrum almost identical to that of Na-form: OH-stretching area was divided into a non-hydrogen-bonded region comprising the 3624 $cm^{-1}$ band and a hydrogen-bonded water region comprising complex series bands maximizing at 3470 $cm^{-1}$; an adsorption band at 1630 $cm^{-1}$ was also due to interlamellar water. But adsorption bands near 1100 $cm^{-1}$ were because of Si-O vibration, the greatest adsorption of in-plane Si-O-Si stretching vibrations occurred in the 1040 $cm^{-1}$ range.
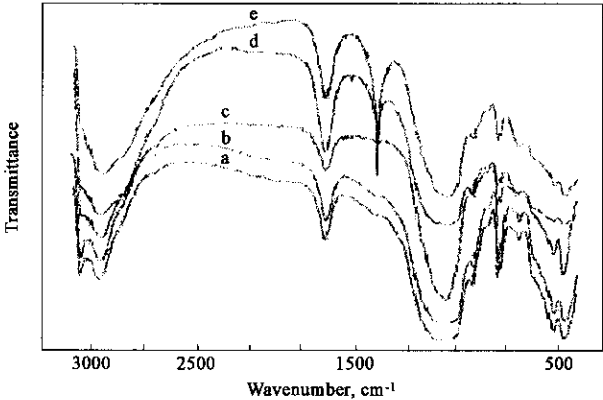


Fig.1    Infrared spectra of Ca- Na- and pillared montmorillonites
a. Ca-Mt; b. Na-Mt; c. OH-Al-Mt; d. OH-Fe-Mt; e. OH-Fe-Al-Mt;
(note: Mt = montmorillonite)

Compared to $Ca^{2+}$-, $Na^+$-montmorillonites, the IR spectra of OH-Al-montmorillonite revealed a small increase on the intensity of 1040 $cm^{-1}$, 469 $cm^{-1}$, and a small shift of frequency from 1040 $cm^{-1}$ to 1048 $cm^{-1}$. Fig.1 also shows that there was a new strong adsorption band at 1384 $cm^{-1}$ in the IR spectra of OH-Fe- and OH-Al-Fe-montmorillonites, indicating existence of hydroxy-Fe polymers in the interlayer space of montmorillonites. Montmorillonite possesses a 2:1 layered structure consisting of one octahedral sheet and two tetrahedral sheets. Exchangeable cations between 2:1 units balance the negative charges generated by isomorphic substitution within the montmorillonite structure.

Table 3 shows that the raw and $Na^+$ exchanged montmorillonites had very low surface areas, 24.8 and 26.9 $m^2/g$ respectively. Their

pore volumes were as low as 0.13 cm$^3$/g. As expected, the surface area of OH-Fe-montmorillonite was 201.0 m$^2$/g, nearly 9 times that of the raw clay. With addition of hydroxy-Al ions, the surface area of the mixed Al-Fe-pillared montmorilonite increased slightly while that for the pure OH-Al sample was 229.6 m$^2$/g. It was reported that some precipitated oxyhydroxide Fe species were retained outside the intermallar spaces of the clay. Therefore, it was hard to define the intrinsic surface area. This was also indicated by the fact that mixed OH-Al-Fe pillared montmorillonite possesses some mesopores between the clay particles. This partly explained the large basal spacing of mixed OH-Al-Fe pillared

montmorillonite. On the other hand, the pillars may hinder the access to the intermellar spaces and thus decrease the microporosity of the material. Therefore, OH-Fe-montmorillonite showed a slightly smaller surface area as compared to OH-Al montmorillonite.

**Table 3　The surface areas( $S.A.$ ), pore volumes( $V_p$ ) of raw and pillared montmorillonite**

| | Raw clay | Na-Mt | OH-Al- Mt | OH-Fe- Mt | OH-Fe-Al- Mt |
|---|---|---|---|---|---|
| $S.A.$, m$^2$/g | 24.8 | 26.9 | 229.6 | 201.0 | 213.4 |
| $V_p$, cm$^3$/g | 0.13 | 0.13 | 0.21 | 0.19 | 0.20 |

Note: Mt = montmorillonite

**Table 4　Chemical composition( % ) of raw and pillared montmorillonite**

| Sample | Al$_2$O$_3$ | CaO | SiO$_2$ | P$_2$O$_5$ | TiO$_2$ | MnO | Fe$_2$O$_3$ | K$_2$O | Na$_2$O | MgO |
|---|---|---|---|---|---|---|---|---|---|---|
| Crude clay | 14.3 | 4.0 | 59.8 | 0.03 | 0.3 | 0.4 | 1.7 | 1.4 | 2.0 | 1.7 |
| Na-Mt | 13.9 | 1.1 | 59.7 | 0.10 | 0.3 | 0.6 | 2.3 | 1.0 | 2.8 | 2.1 |
| Al-Mt | 16.6 | 0.6 | 60.4 | 0.03 | 0.3 | 0.5 | 2.1 | 0.9 | 0.6 | 2.0 |
| OH-Al Mt | 17.9 | 0.6 | 59.5 | 0.09 | 0.3 | 0.5 | 1.9 | 0.9 | 0.7 | 1.7 |
| Fe-Mt | 11.5 | 0.5 | 59.9 | 0.03 | 0.3 | 0.4 | 9.5 | 0.8 | 0.6 | 1.8 |
| OH-Fe-Mt | 7.8 | 0.4 | 40.5 | 0.04 | 0.3 | 0.3 | 35.4 | 0.8 | 0.5 | 0.9 |
| OH-Al-Fe-Mt | 8.1 | 0.4 | 41.8 | 0.06 | 0.3 | 0.3 | 33.1 | 0.8 | 0.5 | 1.0 |

Note: Mt = montmorillonite

The chemical compositions of raw clay, Na-, Al-, Fe-, OH-Al-, OH-Fe-, and OH-Al-Fe- montmorillonite are presented in Table 4. The raw clay contained large amount of Ca-montmorillonite with 14.3% Al$_2$O$_3$, 4.0% CaO and 1.7% Fe$_2$O$_3$. When Na-montmorillonite was transformed into Al-, or OH-Al-montmorillonite, Na$_2$O content decreased from 2.8% to about only 0.7% while Al$_2$O$_3$ content slightly increased from 13.9% to 16.6% and 17.9% respectively. Notably shown in Table 4, the content of Fe as Fe$_2$O$_3$ increased dramatically, from 2.3% to 35.4% in OH-Fe-montmorillonite, and to 33.1% in mixed OH-Al-Fe-montmorillonite, over 15 times higher than before. These results suggested: ( 1 ) Na$^+$ in montmorillonite could be easily exchanged by other cations, such as Al$^{3+}$, Fe$^{3+}$, hydroxy-Fe, and hydroxy-Al; ( 2 ) hydroxy-Fe polymer cations could get into the interlamellar layer more easily than hydroxy-Al cations.

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