Characteristics of organoclays modified with hexadecyltrimethylammonium chloride prepared by convention and microwave

ลักษณะของ ออร์แกโนเคลย์ ที่ถูกดัดแปรด้วย เฮกซะเดซิลไตรเมธิลแอมโมเนียม คลอไรด์ โดยเตรียม แบบทั่วไปและไมโครเวฟ

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Abstract

This work focused on modification of bentonite, kaolin and halloysite with cationic surfactant (hexadecyltrimethylammonium chloride, HDTMA). Two methods used for preparation of the organoclays were convention and microwave. The modification was done with concentrations of surfactant not only at critical micelle concentration (CMC) (1.3 mM) but also at higher (2.0, 4.0 and 6.0 mM) and at lower (0.3 and 0.6 mM) than its CMC. It found that the preparation reaction time for organoclays was decreased from 24 hours by convention to only 10 minutes by microwave, which confirms that microwave method is very effective for preparing organoclay. Chemical and physical properties of before and after treatment with surfactant were determined by XRD, FTIR and DTA/TGA. The existence of HDTMA in clay minerals was confirmed by FT-IR. It showed the bands around 3000 cm^{-1} and 2800 cm^{-1} attributed to asymmetric and symmetric stretching vibration of C-CH_2 of alkyl chain, respectively and the band at about 1450 cm^{-1} was assigned to vibration of trimethyl ammonium quaternary group C-$N(CH_3)_3^+$. The amount of HDTMA adsorbed on bentonite was much higher than that on kaoline and halloysite. It was related to the nature of the clays. In the microstructure of adsorption layer by X-ray diffraction techniques revealed that in the case of bentonite the interlayer spacing (d_{001}) increased significantly with increasing concentration of HDTMA, while d-spacing of kaolin and halloysite changed very slightly. The extended interlayer of bentonite kaolin and halloysite with 6.0 mM of HDTMA were 22.91, 7.29 and 7.38 Å, respectively. It indicated that HDTMA was mainly adsorbed on external surfaces of kaolin and halloysite, whereas HDTMA was mainly adsorbed in the interlayer of bentonite. In DTA curve of organobentonite at concentrations of higher than CMC it reached three overlapping endothermic peaks indicating that there are three different arrangements of HDTMA on bentonite. But in organokaolin and organohalloysite there was only one endothermic broad band. It implied that the arrangement of adsorbed HDTMA on both of mineral is different from that on bentonite.

บทคัดย่อ

งานนี้มุ่งที่ การดัดแปร เบนโทไนต์ เกาลิน และฮาล์ลอยไซต์ กับ สารลดแรงตึงผิวจำพวกไอออนบวก (เฮกซะเดซิลไตรเมธิลแอมโมเนียม คลอไรด์, HDTMA) สองวิธีที่ใช้เตรียมออร์แกโนเคลย์ คือ แบบทั่วไป และแบบไมโครเวฟ การดัดแปรทำที่ความเข้มข้นของสารสารลดแรงตึงผิว ไม่เฉพาะที่ความเข้มข้น คริทิคอล ไมเซล (CMC) (1-3 mM) แต่ทำที่ความเข้มข้นสูงกว่า (2.0, 4.0 and 6.0 mM) และน้อยกว่า (0.3 and 0.6 mM) ค่า CMC

ของมัน ซึ่งพบว่า เวลาในการเตรียม ออร์แกโนเคลย์ลดลงจาก 24 ชั่วโมง ด้วยวิธีทั่วไป เป็น 10 นาทีด้วยวิธีไมโครเวฟ จึงเป็นการยืนยันว่าวิธีไมโครเวฟมีประสิทธิภาพในการเตรียมออร์แกโนเคลย์ คุณสมบัติทางเคมี และฟิสิกส์ ก่อนและหลังดัดแปรด้วยสารลดแรงตึงผิว ถูกพิสูจน์เอกลักษณ์ด้วย XRD, FTIR and DTA/TGA การมีอยู่ของ HDTMA บนออร์แกโนเคลย์ถูกยืนยันด้วย FT-IR ซึ่งแสดงแบนด์ที่ ประมาณ 3000 cm^{-1} และ 2800 cm^{-1} เป็นการสั่นแบบอสมมาตร และแบบสมมาตรของ $C\text{-}CH_2$ ของ โซ่อัลคิล ตามลำดับ และแบนด์ที่ประมาณ 1450 cm^{-1} เป็นการสั่น ของไตรเมธิล แอมโมเนียม คลอเทอนารี ของกลุ่ม $C\text{-}N(CH_3)_3^+$ จำนวนของ HDTMA ที่ดูดซับบนเบนโทไนต์ สูงกว่า เกาลิน และฮาล์ลอยไซต์ ซึ่งสัมพันธ์กับธรรมชาติของเคลย์ ในชั้นการดูดซับของโครงสร้างในระดับไมโคร ของชั้นการดูดซับ โดยเทคนิคการสะท้อนของ ของ รังสี X แสดงให้เห็นในกรณี เบนโทไนต์ ซึ่งช่องว่างระหว่างชั้น (d_{001}) เพิ่มขึ้นเมื่อความเข้มข้นของ HDTMA เพิ่มขึ้น ในขณะที่ เกาลิน และฮาล์ลอยไซต์ ช่องว่างระหว่างชั้นมีการเปลี่ยนแปลงเล็กน้อย ซึ่งช่องว่างระหว่างชั้น ของ เบนโทไนต์, เกาลิน และฮาล์ลอยไซต์ ที่ความเข้มข้นของ HDTMA 6.0 mM มีค่า 22.91, 7.29 และ 7.38 Å ตามลำดับ มันแสดงให้เห็นว่า HDTMA ส่วนใหญ่ถูกดูดซับบนพื้นผิวด้านนอกของ เกาลิน และฮาล์ลอยไซต์ ในขณะที่ HDTMA ส่วนใหญ่ดูดซับบนที่ระหว่างชั้นของเบนโทไนต์ ในกราฟ DTA ของออร์แกโนเบนโตไนต์ ที่ความเข้มข้นสูงกว่าค่า CMC มันมี พีคเอนโดเทอร์มิก 3 พีค ซึ่งซ้อนทับกันแสดงถึงมีการจัดเรียงตัวของ HDTMA ถึง 3 แบบ ที่แตกต่างกันบนเบนโทไนต์ แต่ในออร์แกโนเกาลิน และออร์แกโนฮาล์ลอยไซต์ มีเพียงเอนโดเทอร์มิกแบนด์ที่กว้าง แบนด์เดียว มันชี้ให้เห็นว่า HDTMA มีการจัดเรียงตัวบนแร่ทั้งสองแตกต่างจากบนเบนโทไนต์

Introduction

Organoclays have attracted great interest in a number of applications such as adsorbents for organic pollutants. The modification of surface properties of negatively charged clays and the control of hydrophobicity are possible by cation exchange of natural charge-balanced cations (Na^+, K^+, Ca^{2+} or Mg^{2+}) with high molecular weight quaternary ammonium ions. Bentonite is clay consisting predominantly of smectite minerals, usually montmorillonite. They consist of two tetrahedral layer and one octahedral layer. Kaolinite as well as halloysite is a clay mineral with the chemical composition $Al_2Si_2O_5(OH)_4$. It is a layered silicate mineral with one tetrahedral sheet linked through oxygen atoms to one octahedral sheet of alumino octahedral. However, amorphology of kaoline and halloysite like sheet and tubular, respectively.

Microwave heating technique has recently attracted increasing interest in chemical analysis and sample preparation. These studies have demonstrated that reaction velocity is increased and the activation energy of reaction is reduced by microwave.

This work was focused on preparation of organoclays by convention method and microwave method. The chemical modification of natural clays with hexadecyltrimethylammo-nium chloride (HDTMA) was done not only at the critical micelle concentration but also at lower and higher than that concentration.

Research objectives

1. To improve the properties of halloysite, kaoline and bentonite by modification with surfactant (hexadecyltrimethylammonium chloride; HDTMA).
2. To prepare the organoclays with microwave and conventional method.
3. To characterize the physical and chemical properties of the organoclays.
4. To compare the results from the different preparation methods.

Experimental

1. Preparation of organoclays by microwave

The organoclays were prepared by adding 50 ml of HDTMA (from Fluka Co.) with concentration of 0.3, 0.6 ,1.3, 2.0 4.0 and 6.0 mM to 0.2 g of clays. The mixtures were mixed and put into microwave oven with power 600 W and irradiated 10 min. Then, the treated clays were washed with deionized water at least three times until it was chloride free and dried by freeze dry.

2. Preparation of organoclays by convention

1.0 g of the natural clay was added by 250 ml of HDTMA with concentrations of 0.3, 0.6 ,1.3, 2.0 4.0 and 6.0 mM. The mixtures were subjected to stirr for 24 h, then the solid phase were separated by centrifugation. The treated clays were washed with deionized water at least three times until it was chloride free, then dried by freeze dry. After that the prepared samples were characterized by XRD, FTIR and TGA/DTA.

Results and discussion

XRD analysis

In Fig. 1 the XRD of the natural bentonite showed a reflection peak at about $2\theta = 6.02^{\circ}$ which corresponds to a basal spacing of d_{001} 14.68 Å. After modification the reflection peaks shifted to lower than that of $2\theta = 6.02^{\circ}$. In the case of organobentonites prepared by convention method (COB) the 2θ slightly shifted to lower angle with concentration of 0.3-0.6 mM HDTMA, whereas it dramatically shifted with concentration of 1.3 mM and again slightly shifted with higher concentration than 1.3 mM. For organobentonites prepared by microwave method (MOB) the great shift of 2θ started with 2.0 mM HDTMA.

The correlation between 2θ and d-spacing value depending on concentration of HDTMA of both preparation methods for organobentonite was shown in Fig. 2. It indicated that the expansion of interlayer spacing with both methods was similar. However, at low concentration (0.3 mM - 1.3 mM HDTMA) d_{001} of COB is slightly larger than that of MOB, but at concentration of 4.0 mM and 6.0 mM HDTMA interlayer spacing of MOB was lager than that of COB. It showed that preparation of organobentonite with microwave was able to increase interlayer spacing more than that with convention at quite high concentration of surfactant.

The XRD (see Fig. 3-4) of natural kaolin and halloysite showed the reflection peaks at about $2\theta = 12.33$ and 12.06° which correspond to a basal spacing 7.17 and 7.33 Å , respectively. After modification of kaolin its interlayer spacing was changed very

slightly from 7.17 to 7.29 Å with 6.0 mM HDTMA, whereas it seemed to be constant in the case of halloysite. This may result from the swelling property indicating that HDTMA sorption of HDTMA of kaolin and halloysite was adsorbed on external mineral surfaces.

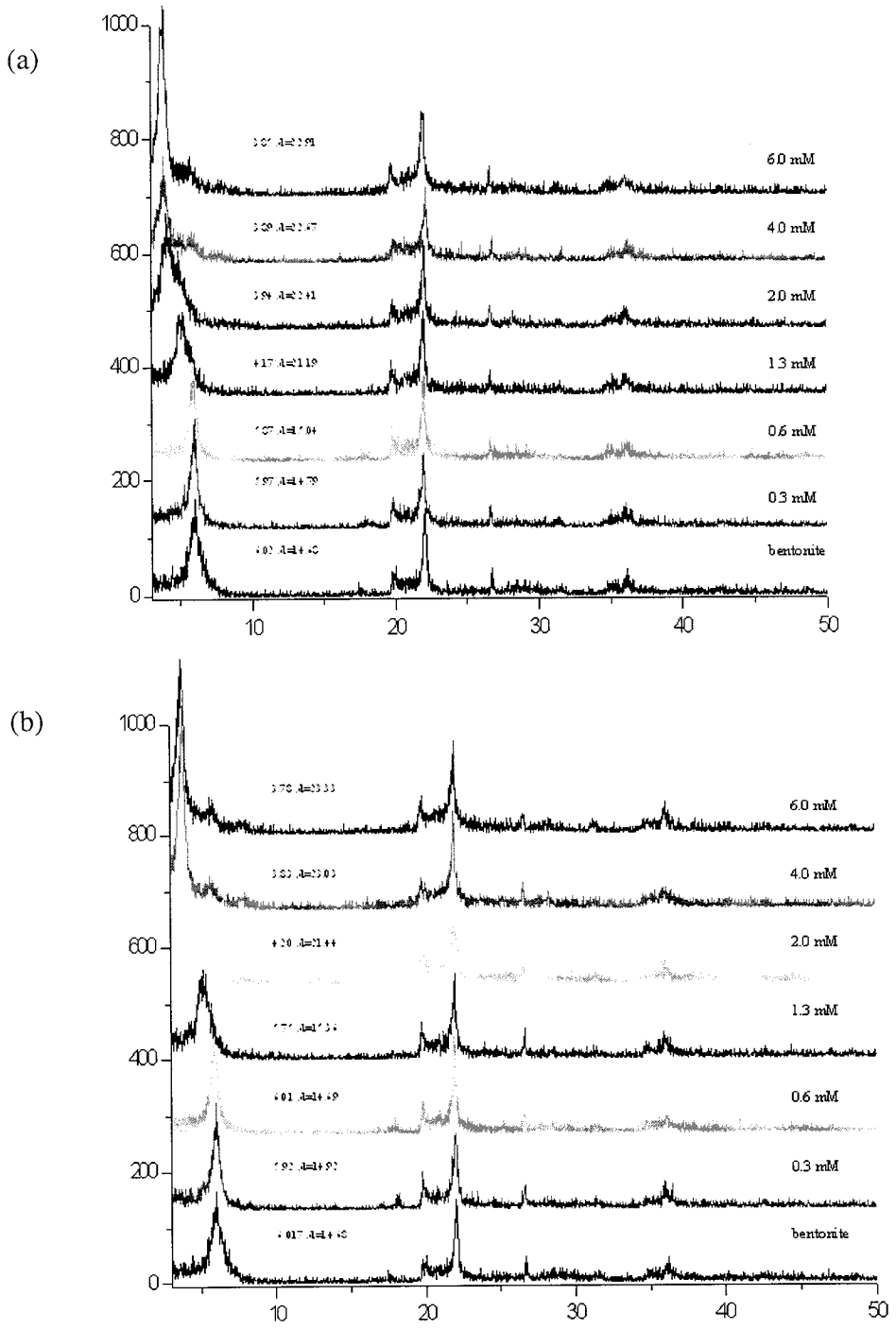

Fig. 1. The XRD patterns of the organobentonite with various concentrations of HDTMA (a) prepared by convention method (b) prepared by microwave method.

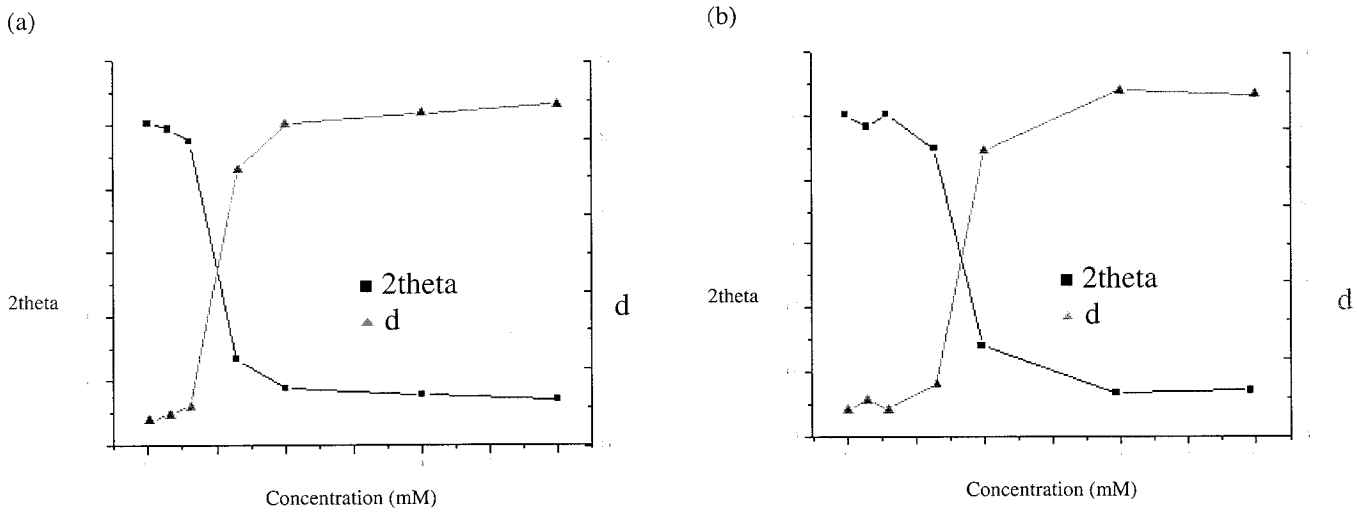

Fig. 2. Theta and d spacing of the organobentonite with various concentrations of HDTMA (a) prepared by convention method (b) prepared by microwave method.

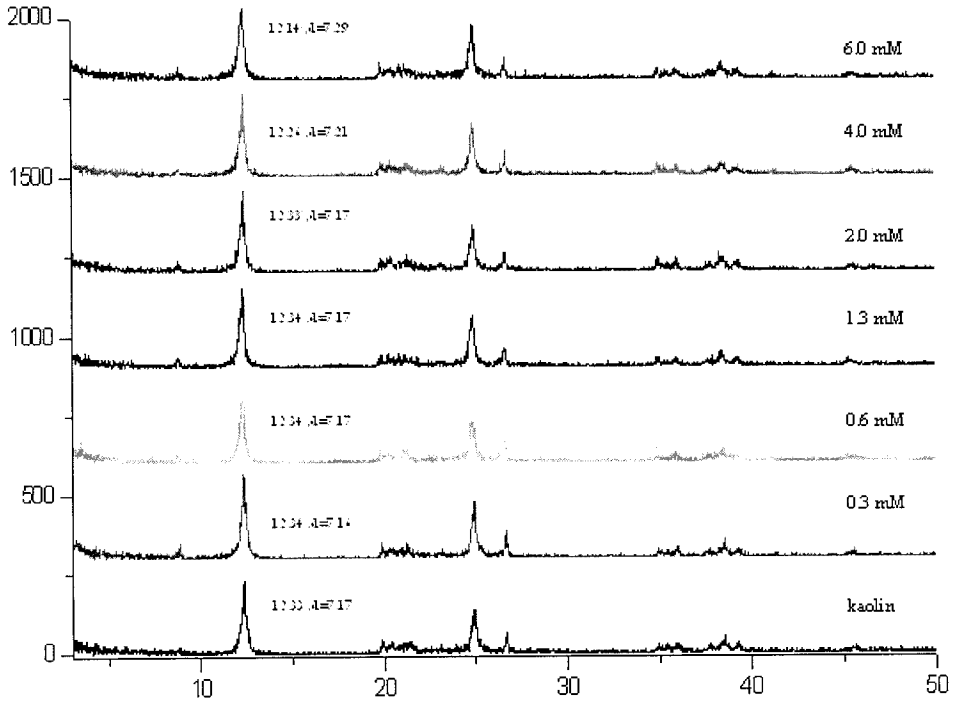

Fig. 3. The XRD patterns of the organokaolin with various concentrations of HDTMA prepared by convention method.

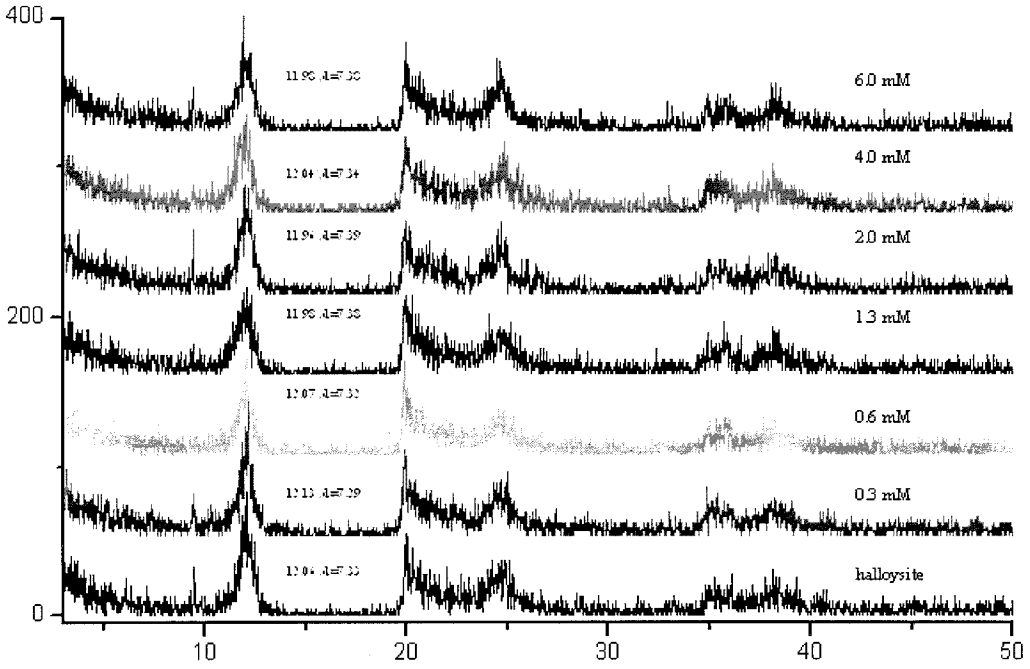

Fig. 4. The XRD patterns of the organohalloysite with various concentrations of HDTMA prepared by convention method.

FT-IR spectra

The FT-IR spectra of the modified clay minerals (see Fig. 5-7) with the different concentrations of HDTMA were recorded in the region of 4000-400 cm^{-1}. Two bands around 3000 and 2800 cm^{-1} appeared in the organoclay were assigned to asymmetric and symmetric stretching vibration of C-CH_2 of alkyl chain, respectively and the band at about 1450 cm^{-1} was assigned to vibration of trimethyl ammonium quaternary group C-$N(CH_3)_3^+$. In Fig 5, when increased concentration of HDTMA the intensity is increased, but the intensity of both modified kaolin and halloysite were not distinguished (Fig 6).

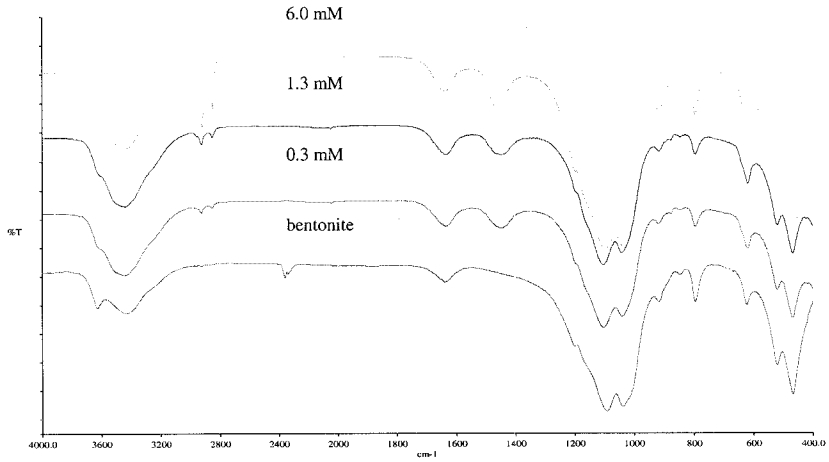

Fig. 5. FT-IR spectra of the organobentonite with various concentrations of HDTMA prepared by convention method.

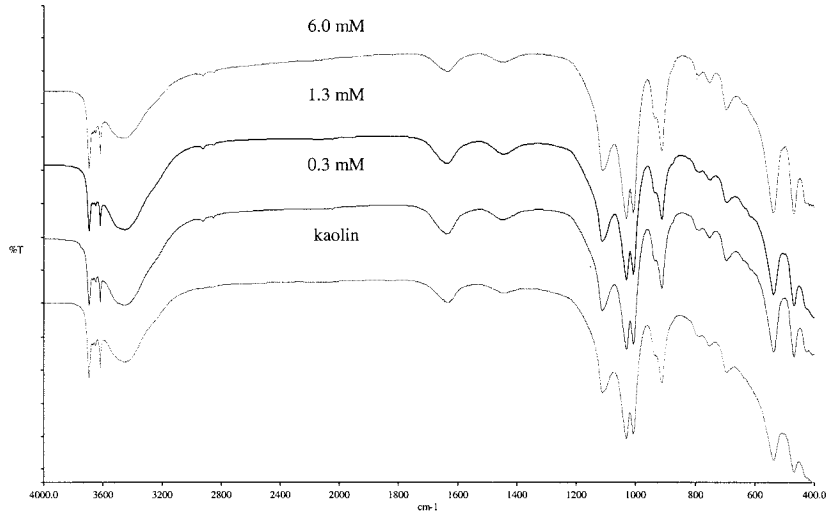

Fig. 6. FT-IR spectra of the organokaolin with various concentrations of HDTMA prepared by convention method.

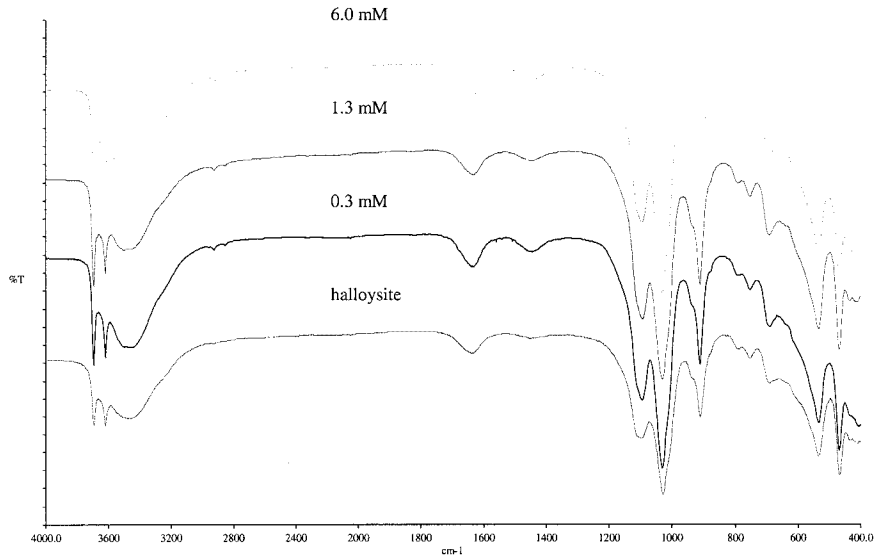

Fig. 7. FT-IR spectra of the organohalloysite with various concentrations of HDTMA prepared by convention method.

DTA/TGA curves

Fig. 8-10 showed DTA curves of organobentonite, organokaolin and organohalloysite. DTA curve of organobentonite at 0.6 mM HDTMA showed the broad band with maximum peak at about 361°C when increased concentration to 2.0 mM it appeared the endothermic band consisting of three overlapping peaks at 290, 320 and 360°C (confirmed with DDTA in Fig. 11). At 6.0 mM HDTMA it showed the additional band at 235°C. It implied that at high concentration (2.0 mM) there are three different arrangements of HDTMA adsorbed on bentonite. This may result from that most of HDTMA was adsorbed in different arrangement between the layer, which corresponded

to the result of XRD that interlayer spacing of bentonite was increased from 15.0 Å at 0.6 mM to 22.4 Å at 2.0 mM. At concentration of 6.0 mM HDTMA the additional band at 235°C may be due to the arrangement of HDTMA adsorbed on external surface of bentonite.

For DTA curves of kaolin it showed clearly the exothermic peak at 504°C (natural kaolin), 512°C (0.6 mM), 515°C (2.0 mM) and 505°C (6.0 mM). This peak resulted from the transformation of kaolin into metakaolin. In the rang of 200 – 400°C DTA curves of organokaolin at all of concentration of HDTMA were similar and they were very broad. Then it was very difficult to indicate the endothermic peak related to eliminate the adsorbed HDTMA. However, from DDTA curves of kaolin in Fig. 12 it showed the broad bands which was indicated to be the loss of HDTMA. According to the XRD results the interlayer spacing was very slightly increased from 7.13 Å for natural kaolin to 7.29 Å for organokaolin with 6.0 mM HDTMA. This indicated that most of HDTMA was adsorbed on external surface instead of interlayer spacing.

In the case of halloysite DTA curves and DDTA (see Fig. 13) were similar to that of kaolin. The interlayer spacing of halloysite seemed to be somewhat constant. It meaned that HDTMA could not penetrate into the interlayer of halloysite. Then HDTMA was adsorbed only on the external surface.

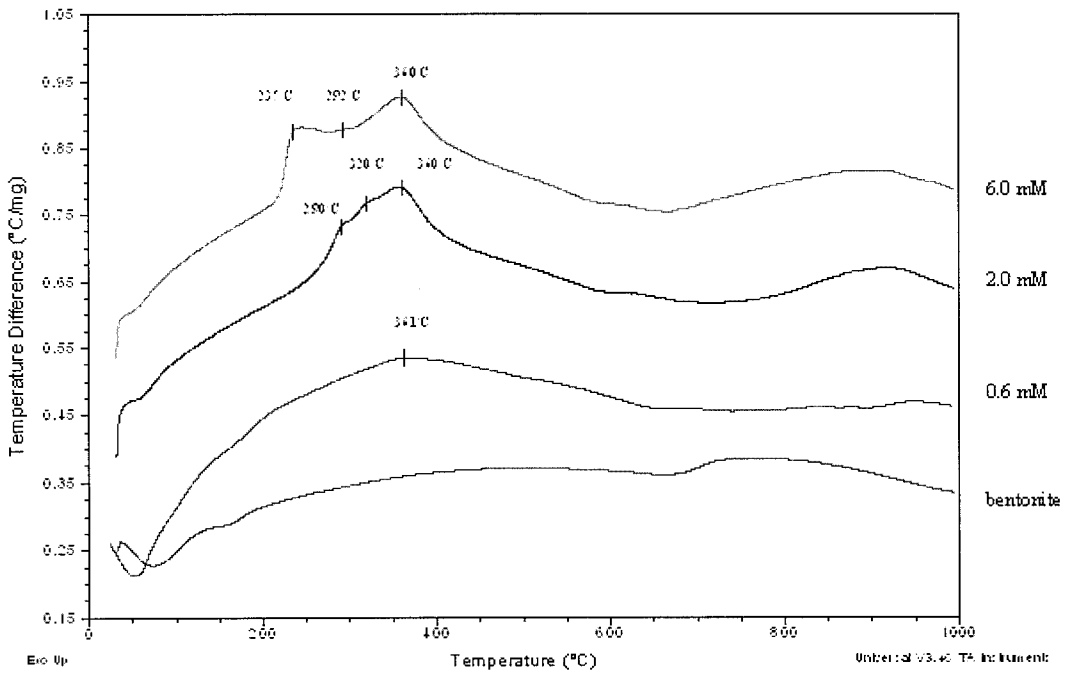

Fig. 8. DTA of the organobentonite with various concentrations of HDTMA prepared by convention method.

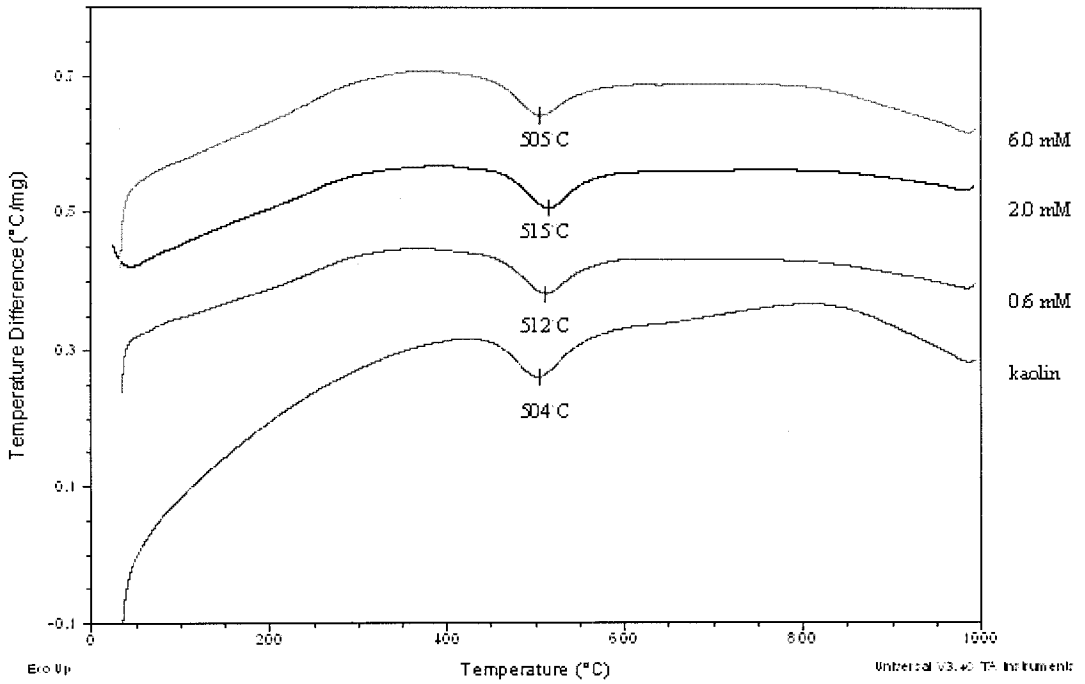

Fig. 9. DTA of the organokaolin with various concentrations of HDTMA prepared by convention method.

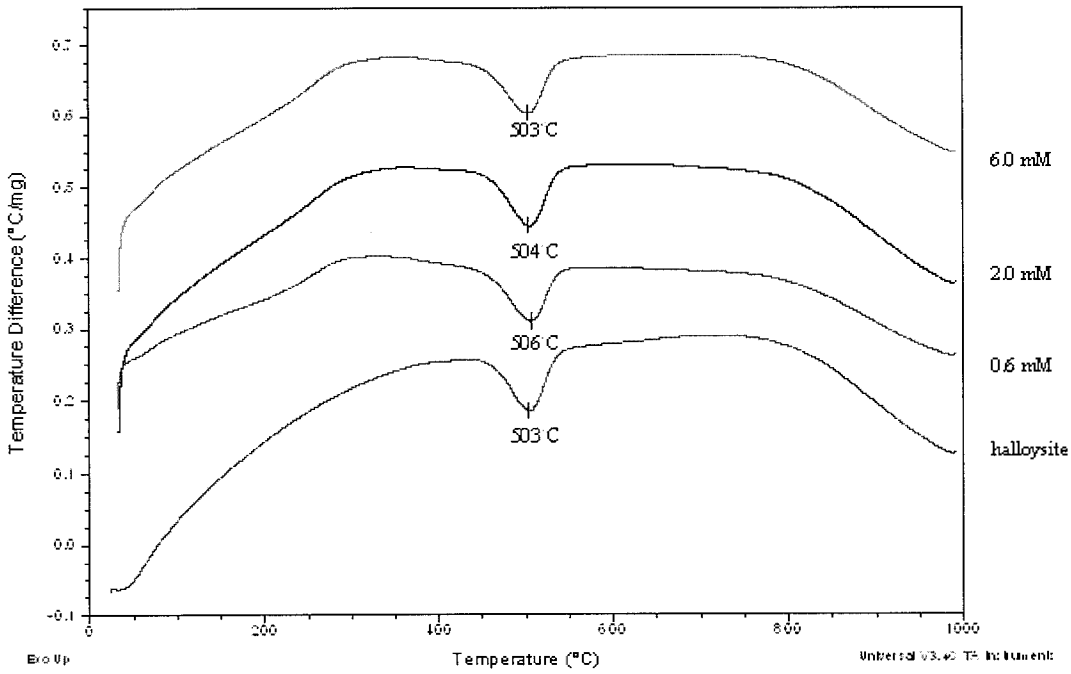

Fig. 10. DTA of the organohalloysite with various concentrations of HDTMA prepared by convention method.

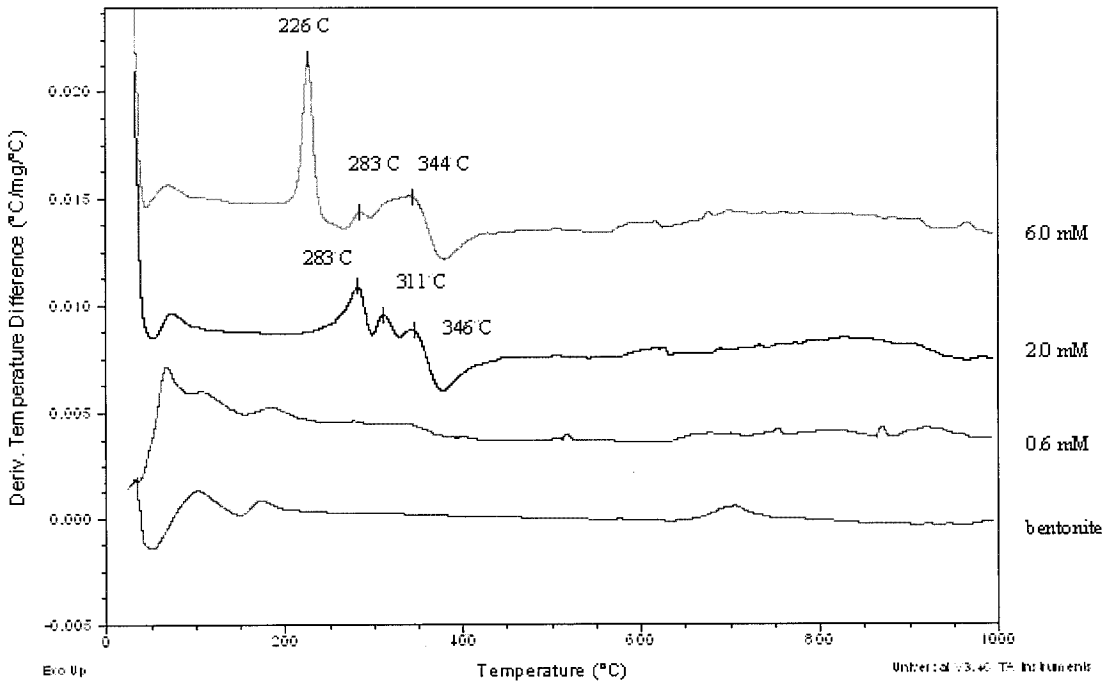

Fig. 11. DDTA of the organobentonite with various concentrations of HDTMA prepared by convention method.

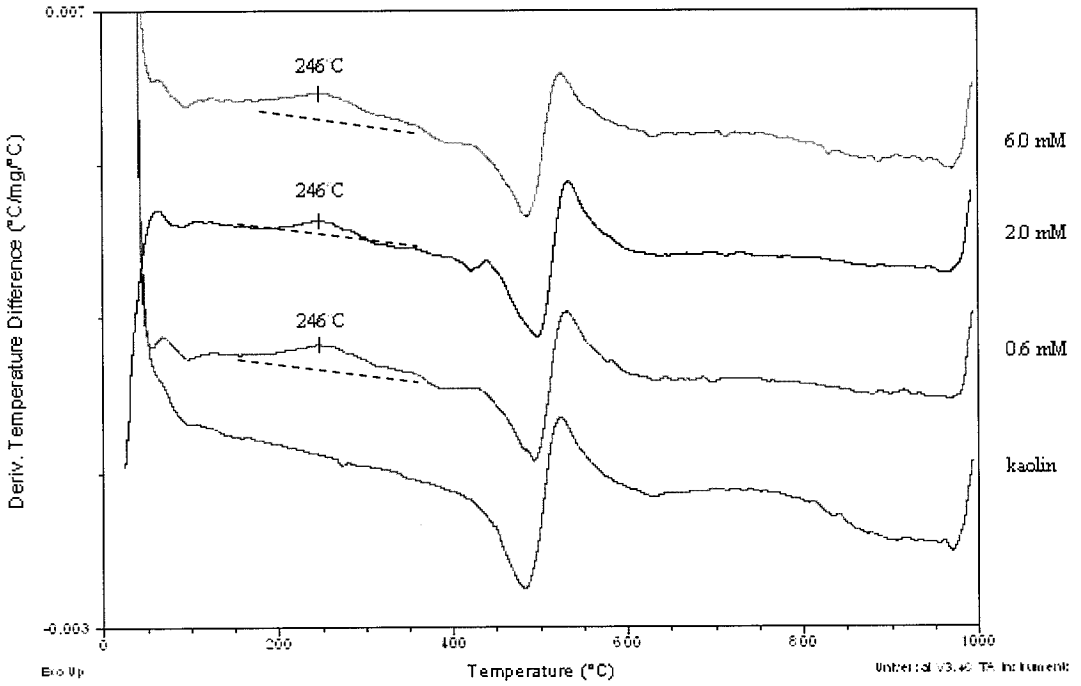

Fig. 12. DDTA of the organokaolin with various concentrations of HDTMA prepared by convention method.

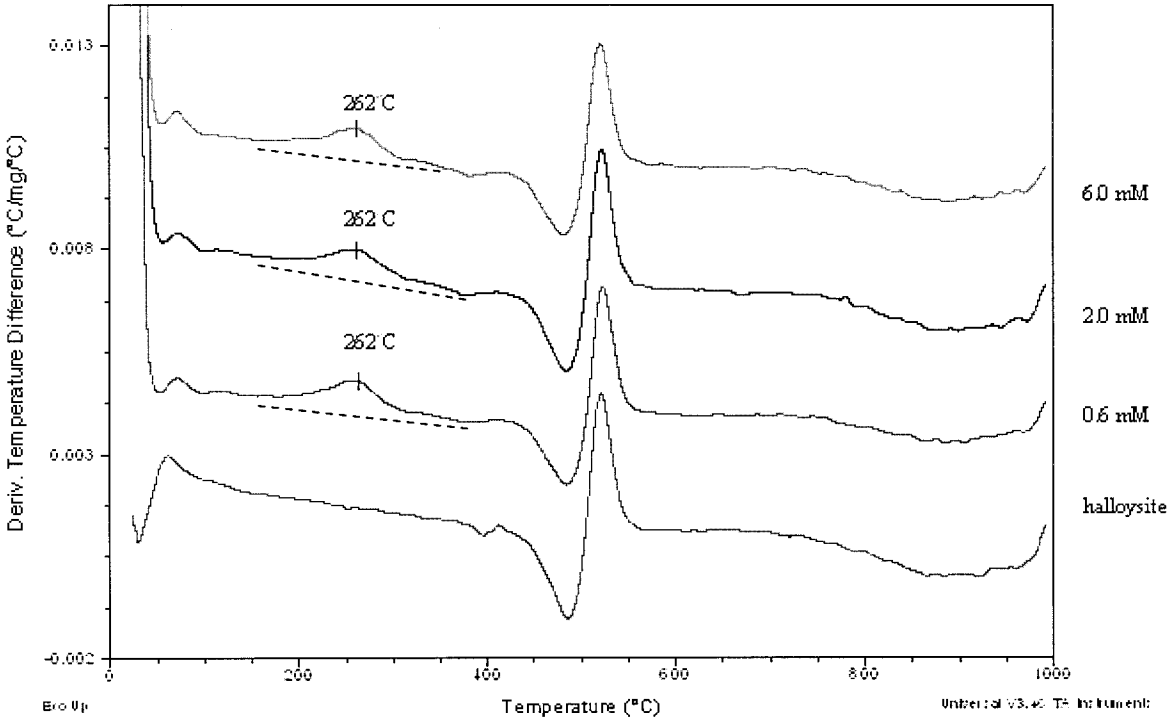

Fig. 13. DDTA of the organohalloysite with various concentrations of HDTMA prepared by convention method.

In the range of 0-200°C the percent mass loss of all natural clays was higher than that of organoclays except for organobentonite at 0.6 mM HDTMA. It indicated that most of the mass loss in this range was adsorbed water whose amount was very high in the natural clays. At 0.6 mM the percent mass loss was higher for organobentonite than that for bentonite due to some mass loss of HDTMA. For the range of 200-400°C it showed that the change of mass loss of organobentonite was significant with increasing HDTMA concentration. It indicated that in this temperature range most of the amount of adsorbed HDTMA was eliminated which is consistent with the result of DTA. For organokaolin and organohalloysite mass loss was slightly increased with increasing HDTMA concentration (except for organohalloysite at 6.0 mM). In the temperature range of 400-550°C the percent mass loss of natural kaolin and halloysite was very high compared to the other ranges. In the case of kaolin it found that the mass loss of the natural kaolin was higher than that of organokaolin. This implied that the mass loss was the result of dehydroxylation in the process of transformation of kaolin into metakaolin, which was easily occurred when without adsorbed HDTMA.

Table
The percent mass loss of the natural clays and organoclays at various concentration of HDTMA in different ranges of temperature

Rang of temperature(°C)	Bentonite				Kaolin				Halloysite			
	Concentration of HDTMA (mM)				Concentration of HDTMA (mM)				Concentration of HDTMA (mM			
	0.0	0.6	2.0	6.0	0.0	0.6	2.0	6.0	0.0	0.6	2.0	6.0
0-200	4.97	9.04	3.47	4.23	1.15	0.88	0.78	0.97	1.86	1.26	1.19	1.5
200-400	0.88	2.13	8.15	11.78	1.04	1.87	2.12	2.45	1.33	2.45	2.61	2.5
400-550	0.69	1.09	2.54	2.81	10.97	9.53	9.90	10.09	11.40	11.61	11.89	11.9
550-700	2.60	2.77	4.75	5.27	2.19	2.43	2.44	2.37	1.13	1.26	1.18	1.3
700-1000	0.38	0.95	1.93	2.24	0.47	0.55	0.62	0.61	0.25	0.31	0.47	0.4

Conclusions

The surface modification with HDTMA of organoclays can be prepared by microwave and convention method. It found that the preparation reaction time for organoclay was decreased from 24 hours by convention to only 10 minutes by microwave, which confirms that microwave method is very effectively for preparing organoclay. The amount of adsorbed HDTMA on bentonite was dramatically increased with increasing HDTMA concentration but it was slightly increased in the case of kaolin and halloysite. The adsorption of HDTMA on bentonite was different from kaolin and halloysite. Most of HDTMA was adsorbed between the layer of bentonite but it was adsorbed on external surface in the case of kaolin and halloysite. From DTA it indicated that there were at least three different arrangements of adsorbed HDTMA on bentonite at highest HDTMA concentration.

Acknowledgments

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