Modification of Montmorillonite with Cetyl Trimethylammonium Bromide and Tetra Ethyl Ortho Silicate

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Abstract. Modification of montmorillonite (MMt) with cetyltrimethylammonium bromide (CTAB) and tetraethyl ortosilicate (TEOS) has been done. The aim of the research is to study the effect of TEOS and CTAB into MMt. This research is a preliminary step to invent material that can be modified with other functional materials. The study was conducted by recting TEOS with MMt and varying CTAB concentration on MMt previously modified with TEOS. The TEOS concentration was 4.72 M while CTAB concentration was 0.25; 0.5; 2; 3.5; and 5 mmol/g in MMt which has been reacted with TEOS. Material characterization was done by X-Ray Diffraction (XRD), Fourier Transform Infra-Red Spectrophotometer (FTIR) and Scanning Electron Microscope (SEM). Cation exchange capacity (CEC) of materials was analyzed by titration method. The results show that TEOS and CTAB successfully modified. TEOS adsorbed onto MMt. It was identified from increased basal spacing, specific group and also by its elemental composition, originally having basal spacing 16 Å. After modification with CTAB, basal spacing increased to 28.45 Å or 77.64%. This indicates that CTAB is intercalated within the MMt layers. The CEC of new material is 0.93 meq/g, increase from 0.83 meq/g.

1. Introduction
Inorganic materials are often explored for interact with organic materials. One of the most commonly used inorganic materials is clay. Clay is a natural material easily found in minerals, particle size less than 0.002 mm which are generally dominated by secondary phillosilicate, has large surface area and a negative charge.

The commonly used phillosilicate clay is the smectite which composed of 2: 1 layer structure [1]. One example of smectite is montmorillonite which characterized with its high aspect ratios, large surface area, abundant inorganic compounds, large expansion ability, and easy to modify, abundant inorganic compounds, good expansion capacity, and easy to modify [2,3].

However, montmorillonite has limitation due to the presence of inorganic cations that are electropositive, which tends to attract water molecules to form hydrates, resulting in the surface being hydrophilic and the small cation size causing the intercellular spacing of aluminosilicates to be low. These properties cause montmorillonite rarely used directly to interact with hydrophobic organic molecules, so that surface modification is required [4]. One attempt to increase the value of montmorillonite is to modify montmorillonite with silanes. Therefore, MMt need to be modify to increase the efficiency of montmorillonite by increasing the surface area and increasing its organophilic properties.
Modification of MMt with Tetraethoxysilane (TEOS) (silanization technique) is not only used to enhance the interaction of the atar surface but also as a link between the chemical reactions between clays and functional groups in macromolecules. The effect of silane on clays is indicated by the reaction between the alkoxy group of the silane and the alkoxy group of the. In other words, silanization potentially modify the surface of the material by increasing the functional group interaction in the material [5].

On the other side, clay modification with surfactants, especially cationic surfactants, will change the nature of clay that was originally hydrophilic to organophilic. Modified Montmorillonite CTAB can be applied in various fields such as adsorbent, heterogeneous catalyst, nanocomposite synthesis, and drug delivery [6]. CTAB can act as a good intercalator agent, since it can insert into montmorillonite molecules that have inter-layered spacing while maintaining its layered structure [7]. However MMt modif with TEOS and Cetyl Trimethyl Ammonium Bromide (CTAB) simultaneously is one type of cationic surfactant [8,9]. Research on modification of montmorillonite with CTAB has not been developed.

Therefore, in this study focused on modification of montmorillonite with CTAB to know the chemical characteristics and the material physics of the modified results. The presence of a CTAB at a certain concentration may alter basal spacing (d), surface area, montmorillonite thermal properties, and montmorillonite cation exchange capacity (CEC). The larger the surface area of the modified material, the more efficient the montmorillonite is applied, the greater the cation exchange capacity, the more interchangeable ions it can be applied more widely.

2. Experimental

2.1. Reagent

The MMt nanoclay was K10 grade purchased from Sigma–Aldrich with a surface of 279.28 Å 0.846 m2/g. Cetyltrimethylammonium Bromide (CTAB) with chemical formula of C19H42BrN and molecular weight of 364.46 g/mol as the surfactant was purchased from Merck, Germany. Its critical micelle concentration (CMC) is 328 mg/L. All others chemicals and reagents were of analytical grade purchased from Merck, Germany.

2.2. MMt Sylanized TEOS

An amount of 10 g MMt was first dispersed in 8 mL TEOS and 100 mL ethanol for 12 hours using a magnetic stirrer to swell and to reach homogeneity. Then stirring was stopped and the product was filtered and washed with distilled water by several times until became free solvent and dried at 80°C in an oven. The product sylanization was ready to the next step.

2.3. Modification of MMT sylanized TEOS with CTAB

The synthesis of CTAB modified MMt was conducted by the following procedure. An amount of 2 g sylanization product was dispersed in 50 mL distilled water and stirrer to swell and to reach homogeneity. Then a desired amount of CTAB (0.364 g) which is 1.0 times CEC of MMt was slowly added. The reaction mixture was stirred for 6 hours, then stirring was stopped and the resultant organoclay was filtered and washed by distilled water for several times until it became free from excess salts and dried at 80°C in an oven. The product of CTAB intercalated MMt was ready.

2.4. Characterization Instrument

The X-Ray Diffraction (XRD) studies were XRD instrument (Rigaku Miniflex 600) using Cu Ka radiation (λ=1.5406 Å) at wide angle range (20 = 0-90°), the accelelerating voltage 40 kV and the emission current 15 mA. The functional groups were analyzed by using Fourier Transform Infra-Red (FTIR) spectrophotometer of Shimadzu 8201 PC under a dry air at room temperature by the KBr pellets method. The spectra were collected over the range from 4000 to 400 cm⁻¹. Surface area and pore size were observed by using Surface Area Analyzer (SAA) with BET (Brunauer-Emmet-Teller) method of NOVA. Morphology of surface particles and elemental composition were identified with Scanning Electron Microscope (SEM) of JEOL JED 2300.
3. Result and Discussions

3.1 Characterization of the MMt and Modified MMt

XRD patterns of MMt shown in Fig. 1. Montmorillonite clay sample has 2:1 layered structure of smectite class. As seen in Fig. 2, with an addition of surfactant, the basal spacing of the resultant organoclay increases indicating location of CTA\(^+\) ions between layers of clay and resulting in a decrease of the hydration water content. So, the surface property changes from hydrophillic to hydrophobic. As known, the amount of added surfactant has a direct effect on the interlayer expansion of smectite. The main peak of MMt in \(2\theta = 5.512^\circ\) (\(d=16.018\ \text{Å}\)). In CTAB intercalated MMt the peak of MMt experienced a shift at \(2\theta = 5.089^\circ\) (\(d=17.349\ \text{Å}\)), \(2\theta = 4.791^\circ\) (\(d=18.429\ \text{Å}\)), \(2\theta = 4.672^\circ\) (\(d=18.897\ \text{Å}\)), \(2\theta = 3.102^\circ\) (\(d=28.455\ \text{Å}\)), \(2\theta = 5.223^\circ\) (\(d=16.905\ \text{Å}\))

![Figure 1. Difractogram of MMt](image1)

![Figure 2. Difractogram (a) Intercalation 0.25 mmol/g. (b) Intercalation 0.5 mmol/g. (c) Intercalation 2.0 mmol/g. (d) Intercalation 3.5 mmol/g. (e) Intercalation 5.0 mmol/g.](image2)

The FT-IR spectra of pure MMt and MMt containing CTAB were shown in Fig 3. A relatively small band around 3626 cm\(^{-1}\) was attributed to Al2OH group of the octahedral layer from the IR spectra of MMt. A broad band around 3643 cm\(^{-1}\) was ascribed to the overlapping symmetric and asymmetric hydroxyl group stretching vibration of water molecules on the external layer. The band around 1053 cm\(^{-1}\) was attributed to asymmetric stretching vibration of Si–O–Si tetrahedra in the MMT. Comparison of FT–IR spectra of CTAB/MMT with that of pure MMT exhibits significant changes in some of the peaks (Fig. 1). In particular, the shift in the siloxan peak from 1053 cm\(^{-1}\) to 1037 cm\(^{-1}\)
after loading of CTAB highlights the role of siloxan group in the adsorption of surfactant onto the MMT surface. From the IR spectra of the organoclay (CTAB/MMT), the adsorption band observed around 3631 cm\(^{-1}\) corresponding to the stretching vibration of the hydroxyl group and the interlayer water molecules was observed. Bending vibration of water molecules causes peak 1629 cm\(^{-1}\). Also, the additional peaks at 3000 cm\(^{-1}\), appointed to \(-\text{CH}\)- stretching vibration, could be observed in CTAB/MMT. Additionally, the band at 3460 cm\(^{-1}\) was disappeared after the modification of MMT nanomaterial with CTAB, which indicates the removal of water molecules and the change in the hydrophobicity of MMT nanomaterial. It has been reported that the ordered conformation of the alkyl chains in the confined system has a strong dependence on amine concentration and orientation. In relatively high concentration range, the confined amine chains adopt an essentially all-trans conformation and the frequency of the asymmetric CH\(_2\) stretching absorption band locates at a relatively low frequency. However, in the relatively low amine concentration range, the frequency shifts significantly to high frequency and the confined amine chains adopt a large number of gauche conformations. Only when the chains are highly ordered (all-trans conformation), the narrow absorption bands appear around 2918 cm\(^{-1}\) asymmetric CH\(_2\) and 2850 cm\(^{-1}\) symmetric CH\(_2\) in the infrared spectrum. If conformational disorder is included in the 3460 cm\(^{-1}\) was disappeared after the modification of MMT with CTAB, which indicates the removal of water molecules and the change in the hydrophobicity of MMT nanomaterial. It has been reported that the ordered conformation of the alkyl chains in the confined system has a strong dependence on amine concentration and orientation. In relatively high concentration range, the confined amine chains adopt an essentially all-trans conformation and the frequency of the asymmetric CH\(_2\) stretching absorption band locates at a relatively low frequency. Only when the chains are highly ordered (all-trans conformation), the narrow absorption bands appear around 2918 cm\(^{-1}\) asymmetric CH\(_2\) and 2850 cm\(^{-1}\) symmetric CH\(_2\) in the infrared spectrum.

![Figure 3. FTIR spectra](image)

**Figure 3.** FTIR spectra (a) Modified MMT-TEOS. (b) Intercalation 0.25 mmol/g. (c) Intercalation 0.5 mmol/g. (d) Intercalation 2.0 mmol/g. (e) Intercalation 3.5 mmol/g. (f) Intercalation 5.0 mmol/g.

SEM analysis was carried out to evaluate surface morphology of the unmodified and modified MMT and the results are depicted in Fig. 4. As it is shown, the figure reveals that the surface morphologies of both MMT samples are different and both unmodified and modified MMT have uneven structure with non-uniform size distribution. The MMT shows massive, aggregated morphology, and some large flakes were observed in some instances. After modification with polymeric species, the clay surface was changed to a non-aggregated morphology and there are a large number of small flakes with severely
crumpled structures. Furthermore, the surface of modified MMt was expanded due to the chemical intercalation.

![Figure 4. Morphology (a) Pure MMt. (b) Intercalation 0.25 mmol/g. (c) Intercalation 0.5 mmol/g. (d) Intercalation 2.0 mmol/g. (e) Intercalation 3.5 mmol/g. (f) Intercalation 5.0 mmol/g.](image)

Surface area analysis using BET (Brunauer-Emmet-Teller) method for analysis surface area of MMt and CTAB intercalated MMt. As seen in Table 1, with an addition of surfactant, the surface area of the resultant organoclay decrease indicating that molecule of CTAB has succesfully logged into MMt, so the N\textsubscript{2} adsorption at organoclay decrease. Distribution pore of modified MMt with CTAB have uniform size distribution. As seen in Fig. 5, distribution pore size of modified MMt with CTAB is at about 1.8-1.9 nm. This shown that the dispersion of modified MMt with CTAB is in teh mesoporous region, which is 2-50 nm.

| Sample                      | Surface Area (m\textsuperscript{2}/g) |
|-----------------------------|--------------------------------------|
| MMt                         | 186.282                              |
| MMt-CTAB (0.25 mmol/g)       | 107.539                              |
| MMt-CTAB (0.5 mmol/g)        | 57.735                               |
| MMt-CTAB (2 mmol/gr)         | 50.629                               |
| MMt-CTAB (3.5 mmol/gr)       | 47.545                               |
| MMt-CTAB (5 mmol/gr)         | 40.589                               |
Cation exchange capacity (CEC) for physico-chemical analysis of MMT and modified MMT with CTAB increases indicating CTA+ could to replaced cations in interlayer of MMT. MMT had CEC amount 0.83 meq/g, modified MMT with CTAB at concentration (0.25 mmol/gr) had CEC amount 0.83 meq/g, modified MMT with CTAB at concentration (0.5 mmol/g) had CEC amount 0.84 meq/g, modified MMT with CTAB at concentration (2 mmol/g) had CEC amount 0.86 meq/g, modified MMT with CTAB at concentration (3.5 mmol/g) had CEC amount 0.91 meq/g, and modified MMT with CTAB at concentration (5 mmol/g) had CEC amount 0.93 meq/g.

4. Conclusion
Modification of MMT with TEOS and CTAB could to increase basal spacing, influenced of functional group, distribution pore, and cation exchange capacity.

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