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# PREPARATION AND CHARACTERIZATION OF TETRAMETHYLAMMONIUM- AND $Al_2O_3$ -MONTMORILLONITES USING NATURAL BENTONITE AS A BASE MATERIAL

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## ABSTRACT

The preparation of Tetramethylammonium (TMA)-montmorillonite was carried out by treating the natural Na-bentonite (Na-montmorillonite) with tetramethylammonium chloride aqueous solution for 24 hours three times at room temperature. The amounts of added TMACl was 2 times of the CEC of the bentonite. The obtained TMA-montmorillonite intercalation compound or pillared montmorillonite was washed with free ion water several times, dried and then characterized with x-ray diffractometer and infrared spectrophotometer. The intercalation compound was also heated at various temperatures to test the thermal stability of the structure. The  $Al_2O_3$ -montmorillonite was prepared by treating Na-bentonite with aluminium polyoxocations solution for 24 hours at room temperature. The obtained suspension was shaken for 24 hours at room temperature, filtered and the solid phase was calcined for 2 hours at  $250^\circ C$ . The physico-chemical properties of the calcined product was characterized with x-ray diffractometer, gas sorption analyser and infrared spectrophotometer.  $Al_2O_3$ -montmorillonite was heated at various temperatures to test the stability of the intercalation compound structure. The characterization results showed that the basal spacing of the TMA-montmorillonite was  $14.27 \text{ \AA}$ , showing the increase of the montmorillonite interlayer spacing of  $4.67 \text{ \AA}$  (the thickness of the silicate sheet is  $9.6 \text{ \AA}$ ). In the infrared spectrum of the TMA-montmorillonite, the absorption band due to C-N stretching vibration appeared at  $1488.9 \text{ cm}^{-1}$ . Moreover, the thermal stability test indicated that the intercalation compound structure was stable up to  $300^\circ C$ . At  $400^\circ C$  the intercalation compound was collapsed. In case of  $Al_2O_3$ -montmorillonite, x-ray diffractometry analysis result exhibited that the basal spacing of the intercalation compound was  $16.89 \text{ \AA}$ , indicating the increase of the montmorillonite interlayer of  $7.29 \text{ \AA}$ . The intercalation of the alumina into the interlayer of montmorillonite resulted in also the increase of the specific surface area of the montmorillonite of  $82.25 \text{ m}^2/\text{g}$ . Thermal stability test conducted on the compound exhibiting that the intercalation compound structure was still stable up to  $400^\circ C$ . Thus from the characterization results, the formation of TMA-and  $Al_2O_3$ -montmorillonites was confirmed.

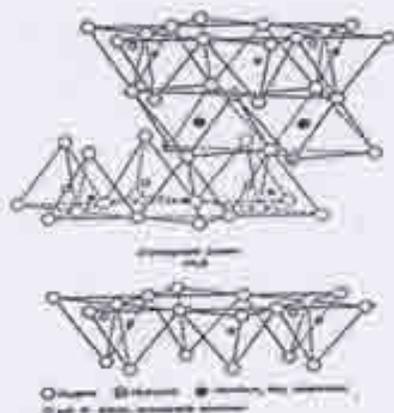
*Key words* : Tetramethylammonium-montmorillonite,  $Al_2O_3$ -montmorillonite, intercalation, pillared montmorillonite.

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## 1. Introduction

Montmorillonit is 2:1 type layered clay minerals consisting of negatively charged silicate layers and exchangeable interlayer cations, and possess attractive features such as swelling behavior, ion exchange property and large surface area. Montmorillonite is usually used as an adsorbent. A high ability of montmorillonite to adsorb water molecules makes its thermal stability decrease. Therefore, at the temperature higher than  $250^\circ C$ , the structure of the clay can

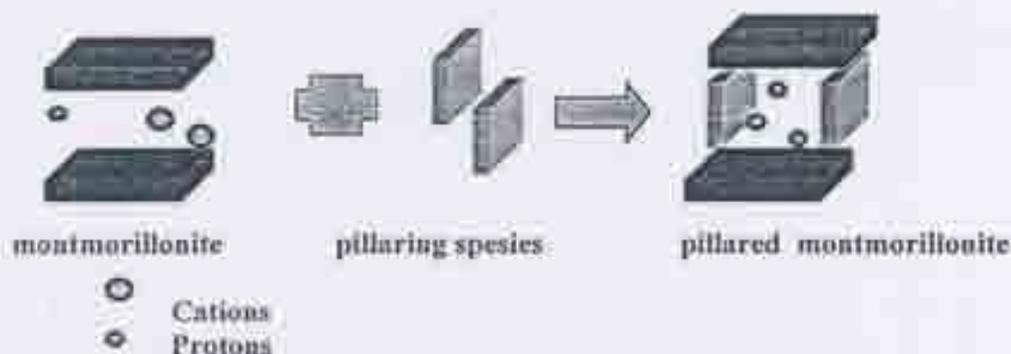
be collapsed. The another weakness of unmodified montmorillonite is its lack of permanent porosity.



**FIGURE 1:** Idealised structure of montmorillonite showing the (O) Oxygen atoms and (OH) hydroxyl groups. Silicon and sometimes aluminium occupy the tetrahedral positions in the oxygen framework. The thickness of the sheets is assumed to be ca. 9.6 Å)

To avoid this problem, the montmorillonite be modified by intercalating pillars in the interlayer region of the montmorillonite clay. Pillared montmorillonite is defined as montmorillonite which its interlayer cationics have been exchanged with large robust cations capable of acting as molecular or ionic props or pillars between the layer. Various type of cations have been used as pillaring agents, such as bicyclic amine cations, metal chelate complexes, polynuclear hydroxy metal cations, and alkylammonium ions. Fig. 2 shows schematic representative of pillared montmorillonite.

By pillaring the montmorillonite, its physico-chemical properties such as high pore volume, surface area and thermal stability were created. Thermal stability becomes important factor when applying pillared montmorillonite in high temperature experiment condition. In general pillared montmorillonite can be stable up to 400-500 °C



**FIGURE 2:** The formation scheme of pillared montmorillonite

In this study, we investigated intercalation of tetramethylammonium (TMA)-cations and alumina into the interlayer of montmorillonite. The obtained pillared montmorillonites were then characterized their physico-chemical properties. After pilarization the properties of the montmorillonite clay, such as surface area, basal spacing and thermal stability will be enhanced.

## 2. Experimental

### 2.1. Materials

Natural Bentonite (purchased from PT Tunas Inti Makmur, Semarang, Indonesia) in powder form (100 mesh) was used as the base (host) material. The reported elemental composition is as follows (%):  $\text{SiO}_2$ , 61.02;  $\text{Al}_2\text{O}_3$ , 15.21;  $\text{Fe}_2\text{O}_3$ , 4.89;  $\text{TiO}_2$ , 0.62;  $\text{CaO}$ , 2.08;  $\text{MgO}$ , 1.94;  $\text{K}_2\text{O}$ , 0.46;  $\text{Na}_2\text{O}$ , 3.45; LOI, 10.31. The majority of chemicals used in this study, i.e.: Tetramethylammonium (TMA) chloride (Tokyo Kasei) and  $\text{AlCl}_3$  (Merck) were used without further purification.

### 2.2 Synthesis of TMA-pillared montmorillonite.

Tetramethylammonium (abbreviated as TMA)-pillared montmorillonite intercalation compound was prepared by treating the montmorillonite (purchased from PT Tunas Inti Makmur, Semarang, Indonesia as Bentonite) with tetramethylammonium chloride (Tokyo Kasei Industries, Tokyo, Japan) aqueous solution for 24 hours three times. The amounts of added TMA-Cl was around two times of the cation exchange capacity of montmorillonite. The TMA-pillared montmorillonite was washed repeatedly with water in order to remove the excess of TMA ions which adsorbed on the surface of montmorillonite. The washing was ended until negative silver nitrate test was obtained for the supernatant, TMA-montmorillonite then was dried under vacuum pressure and ground with an agate mortar at room temperature under an open air atmosphere.

### 2.3 Synthesis of $\text{Al}_2\text{O}_3$ -pillared montmorillonite.

The  $\text{Al}_2\text{O}_3$ -pillared montmorillonite was prepared by treating montmorillonite (Bentonite) with aluminium polyoxocations solution at room temperature to form a suspension. The suspension was shaken for 24 hours at room temperature, filtered and the solid phase was calcined for 24 hours at  $250^\circ\text{C}$  and then ground with an agate mortar at room temperature. The physico-chemical properties of the calcined product was characterized with x-ray diffractometer, gas sorption analyser and infrared spectrophotometer. To study thermal stability of  $\text{Al}_2\text{O}_3$ -pillared montmorillonite, the compound was heated at various temperatures for 5 hours.

Polyoxocations of aluminium solution as pillaring solution was prepared by hydrolysing 0.2 M  $\text{AlCl}_3$  solution with 0.2 M NaOH, leading to an OH/Al ratio of 1 and pH of ca. 4. The solution was aged for ten days under reflux conditions before being used to prepare  $\text{Al}_2\text{O}_3$ -pillared montmorillonite.

### 2.4. Characterization

X-ray diffraction patterns were obtained on Shimadzu Diffractometer using Ni filtered  $\text{CuK}\alpha$  radiation. Infrared spectra were recorded on a Hitachi Fourier Transform Spectrophotometer by KBr-disk method, porosities of the montmorillonite and pillared montmorillonite were obtained on a gas sorption analyser, Quanta Chromé Corporation. The amounts of aluminium in  $\text{Al}_2\text{O}_3$ -pillared montmorillonite and montmorillonite were analysed by neutron activation method analysis conducted in Atomic Energy Agencies (BATAN), Jogjakarta, Indonesia.

## 3. Results and discussions

### 3.1. Synthesis of TMA-pillared montmorillonite

Fig. 3 shows the xrd patterns of the montmorillonite and TMA-pillared montmorillonite. By the intercalation with TMA-ions, the  $d(001)$  diffraction peak shifted toward lower  $2\theta$  region, suggesting the expansion of the interlayer space of montmorillonite. After calculation by Bragg's equation, the obtained basal spacing of the TMA-pillared montmorillonite was 14.27 Å, indicating the increase of the montmorillonite interlayer spacing of 4.67 Å (the thickness of the silicate sheet is assumed to be 9.6 Å).

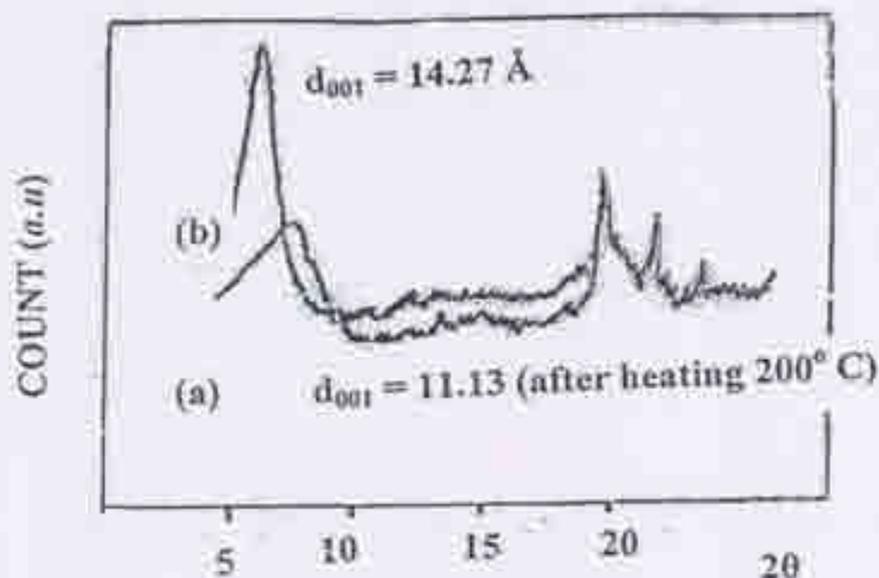


FIGURE 3: The xrd patterns of montmorillonite (a) and TMA-pillared montmorillonite (b)

The infrared spectra of montmorillonite and TMA-pillared montmorillonite were shown in Fig. 4. The absorption band due to TMA-ions such as C-N vibration appeared at  $1488.9 \text{ cm}^{-1}$ , confirming the intercalation or pillarization.

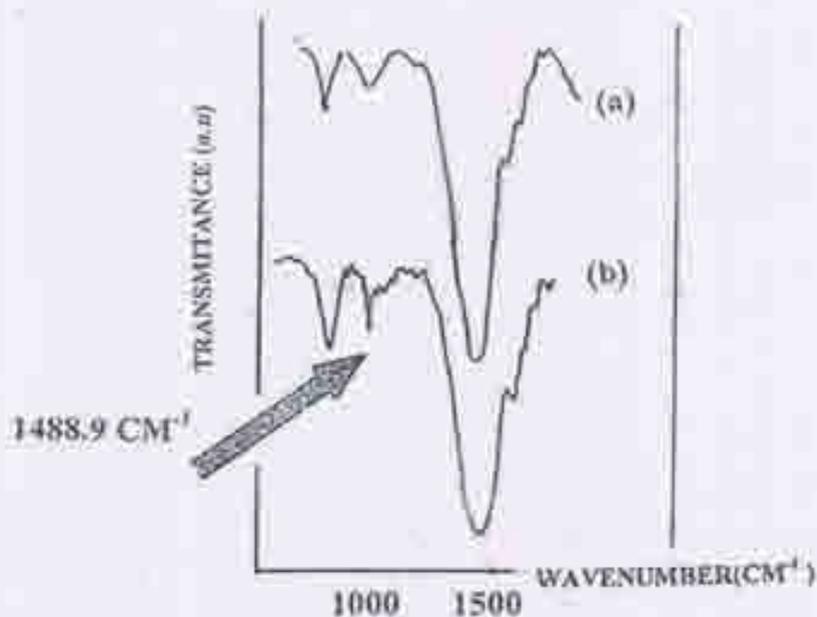


FIGURE 4 Infrared spectra of montmorillonite (a) and TMA-pillared montmorillonite (b)

Table 1 shows the basal spacings of the montmorillonite and TMA-montmorillonite prepared in this research. Judging from the observed basal spacings, thermal stability of TMA-pillared montmorillonite was relatively higher than unpillared montmorillonite, indicated that intercalated TMA was stable up to  $300^\circ\text{C}$ . Further increase of the heating temperature up to  $400^\circ\text{C}$

°C will lead to collapse of the montmorillonite layers due to the sintering of the pillars and the dehydroxylation of the clay sheets. The intercalation compound, therefore, was collapsed.

TREATMENT	BASAL SPACING OF MONTMORILLONITE	BASAL SPACING OF TMA-MONTMORILLONITE
Before heating	14.43	14.27
After heating at 200 °C	11.13	14.13
After heating at 300 °C	10.13	13.85
After heating at 400 °C	-	12.27

TABLE 1: The change of basal spacing of montmorillonite and TMA-montmorillonite due to the heat treatment.

From the above stated results it can be confirmed that tetramethylammonium cations were intercalated into montmorillonite through cation exchange process. The tetramethylammonium cations induced the interlayer space of montmorillonite to form TMA-pillared montmorillonite.



#### 4.2 Synthesis of Al<sub>2</sub>O<sub>3</sub>-pillared montmorillonite.

Fig. 5 shows the xrd patterns of the montmorillonite and Al<sub>2</sub>O<sub>3</sub>-pillared montmorillonite. The basal spacing of Al<sub>2</sub>O<sub>3</sub>-pillared montmorillonite was 16.89 Å, indicating the increase of the montmorillonite interlayer of 7.29 Å.

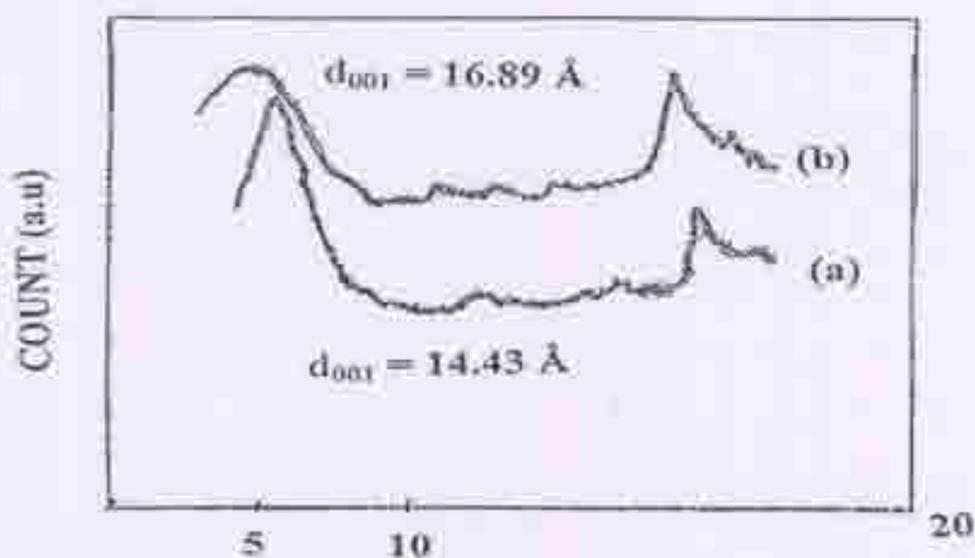


FIGURE 5: The xrd patterns of the montmorillonite (a) and Al<sub>2</sub>O<sub>3</sub>-pillared montmorillonite (b).

The porosimetry analysis results were showed in table 2. From that table it can be seen that the presence of alumina in the interlayer of montmorillonite resulted in the increase of the specific surface area of 82.25 m<sup>2</sup>/g.

PARAMETER	MONTMORILLONITE	Al <sub>2</sub> O <sub>3</sub> -PILLARED MONTMORILLONITE
Specific Surface Area (m <sup>2</sup> /g)	88.13	170.38

TABLE 2: Surface area of montmorillonite and Al<sub>2</sub>O<sub>3</sub>-pillared montmorillonite

The amount of intercalated aluminium was determined by using neutron activation analysis. Analysis result indicated that the concentration of aluminium in the montmorillonite was increased due to the pillarization.

SAMPLE NAME	CONCENTRATION (%W/W)
Montmorillonite	3.72
Al <sub>2</sub> O <sub>3</sub> -pillared montmorillonite	7.45

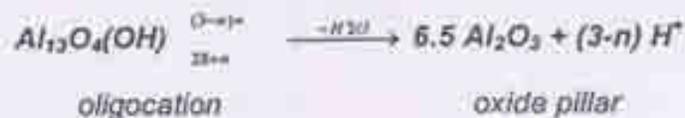
TABLE 3: Concentration of aluminium in montmorillonite and Al<sub>2</sub>O<sub>3</sub>-pillared montmorillonite

Heat treatment was conducted to observe the thermal stability of the montmorillonite before and after pillarization. Table 4 shows the basal spacings of the clays. When temperature was increased up to 400 °C, the basal spacing of Al<sub>2</sub>O<sub>3</sub>-pillared montmorillonite was decreased significantly and for unpillared montmorillonite the increase of temperature resulted in destruction of the layers.

TREATMENT	BASAL SPACING OF MONTMORILLONITE	BASAL SPACING OF Al <sub>2</sub> O <sub>3</sub> -MONTMORILLONITE
Before heating	14.43 Å	16.89 Å
After heating at 400 °C	-	11.71 Å

TABLE 4: The change of basal spacing of montmorillonite and Al<sub>2</sub>O<sub>3</sub>-pillared montmorillonite due to the heat treatment.

Judging from all above stated characterization, the pillarization of montmorillonite with alumina was observed. The mechanism of the pillarization probably occurred due to ion exchange and alumina formation in the interlayer of the montmorillonite. The alumina formation of the pillar was assumed occurred due to dehydroxylation of the oligocations.



#### 4. Conclusion

In general, from the characterization result, the formation of TMA- and  $Al_2O_3$ -pillared montmorillonites using Indonesia Bentonite as a base material was confirmed. The physicochemical properties of the pillared montmorillonite, such as basal spacings, and specific surface area were also improved and it had much better in quality than unpillared montmorillonite.

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