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Abstracts
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SYNTHESES OF PILLARED MONTMORILLONITE USING INDONESIAN BENTONITE AS A BASIC MATERIAL

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ABSTRACT

We have investigated pillarization of montmorillonite using Indonesia Bentonite as a basic material and inorganic oxides such as TiO_2, Fe_2O_3 and Cr_2O_3 as pillars. The pillarization of montmorillonite by means of those oxides was carried out via intercalation of the pillaring agents (in form of oligocation of metals) into suspensions of montmorillonite. The pillared montmorillonites were obtained after calcination of the intercalated compounds at certain temperature. All calcined products were then characterized using infra red spectrophotometry, gas sorption analysis and x-ray diffractometry.

The results showed that the basal spacing of montmorillonite increased after pillarization with TiO_2 (from 15.53 Å for Na-montmorillonite (hydrated) to ≥ 21.75 Å for TiO_2–pillared montmorillonite). The specific surface area of Na-montmorillonite and TiO_2–pillared montmorillonite were 88.13 and 249.36 cm^2/g, respectively. The total volume of Na-montmorillonite was found to be 0.0697 cm^3/g whereas that of TiO_2–pillared montmorillonite was 0.2061 cm^3/g. The content of titanium was 16.43%(w/w) in TiO_2–pillared montmorillonite and 0.047% (w/w) in Na-montmorillonite. In case of Fe_2O_3–pillared montmorillonite, the highest specific surface area and total pore volume was observed on Fe-PILC$_{200}$ (Fe_2O_3–pillared montmorillonite after being calcined at 200°C). The average content of iron in Fe_2O_3–pillared montmorillonite and in Na-montmorillonite were 23.36% (w/w) and 17.3%(w/w), respectively. This pillared clay showed the existance of house of cards structure. For the Cr_2O_3–pillared montmorillonite, the measured basal spacing (d_{001}) and specific surface area were 18.55 Å and 174.93 m^2/g, respectively and the average content of chromium in Cr_2O_3-pillared montmorillonite was 21.09%(w/w), while that found in Na-montmorillonite was only 0.18% (w/w).

Key words: Indonesian Bentonite, Pillared Montmorillonite, Pillaring Agents

I. INTRODUCTION

In chemistry pillarization means to put big ions, molecules and compounds in an interlayer of a layered structure such as montmorillonite clays. Pillarization of the clays having the physico-chemical properties become possible by the combination of host and guest. In this research montmorillonite having layered structure were used as host materials and various inorganic oxides were intercalated into the layer of the clays in order to obtain pillared clays.[1,2,3,4,5]

Montmorillonite (contained in Bentonite) is 2:1 type layered clay minerals consisting of negatively charged silicate layers and exchangeable interlayer cations, and posses various attractive features such as swelling behavior, ion exchange properties, large surface area etc. Therefore, application of that clay has attracted increasing interest from both scientific and practical interests.[6,7,8]

In this research, we investigated pillarisation of montmorillonite clay (contained in Indonesia Bentonite) using inorganic oxides such as TiO_2, Fe_2O_3, Cr_2O_3 as pillars. The obtained porous material will be used as host materials for various applications such as adsorbents and catalysts.[8,9,10]

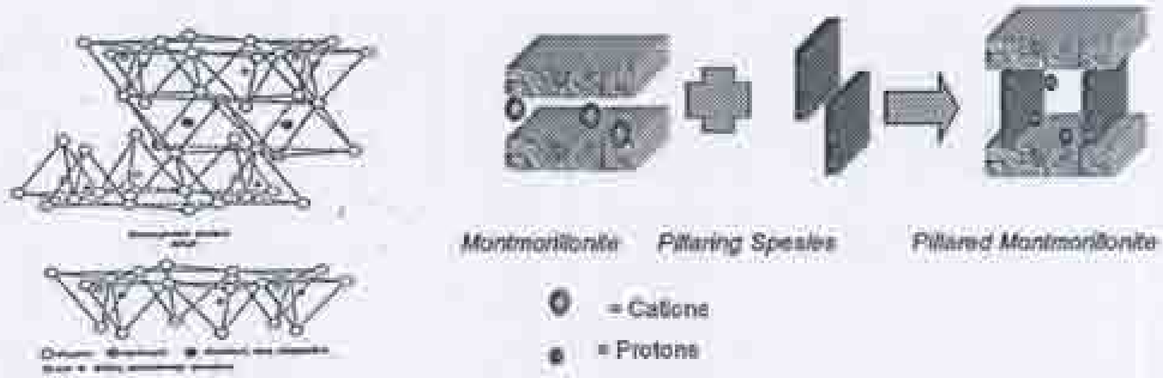

Fig. 1. Structure of montmorillonite and pillaring process scheme

II. METHODS

2.1 Preparation of Na-Montmorillonite

Before being used as host materials, the natural bentonite clay was saturated with sodium chloride in order to exchange the interlayer cations of montmorillonite with sodium cations.

2.2 Syntheses of TiO_2–Pillared Montmorillonite

The pillarization of montmorillonite using TiO_2 was carried out by dispersing the pillaring agent (in form of oligocation of titan) into suspension of non acid activated clay and acid activated clay (i.e clays which were treated with various concentrations of sulphuric acid, i.e 0.2 M, 0.6 M, 1 M, 1.5 M and 2.0 M). The pillaring agent was prepared by hydrolizing titanium-(IV)tetrachloride in hydrochloric acid.

The pillared clay was obtained after calcining the intercalation compounds at 350 °C for 24 hours. The calcined compounds then were characterized using x-ray diffractometry and gas sorption analysis method.

2.3 Syntheses of Fe_2O_3–Pillared Montmorillonite

An ionic pillaring species that was structurally analogous to the Al_{13} ion was suggested to be formed upon base hydrolysis of Iron(III) aqueous solutions. The obtained pillaring solution then used to prepare Fe_2O_3-pillared montmorillonite.

The pillaring spesies was intercalated into interlayer region of the Na-montmorillonite and the intercalation compound then was calcined at various temperatures (100, 150, 200, 250 and 300 °C for 5 hours) in order to convert intercalated pillaring spesies into Fe_2O_3. X-ray powder diffraction patterns were obtained by a Shimadzu diffractometer using Cu-filtered Cu K_α radiation. Surface area and total pores volume were obtained with a Nitrogen Gas Sorption Analyzer. Surface acidites of each sample were determined with a gravimetric analysis method and infra red analysis.

2.4 Syntheses of Cr_2O_3 –Pillared Montmorillonite

The Cr_2O_3-pillared montmorillonite was prepared by a direct ion exchange method. First, the polyhydroxychromium as pillaring spesies was intercalated into the interlayer region of the Na-montmorillonite, resulted in montmorillonite polyoxy-chromium intercalation compound. The pillaring spesies was prepared by hydrolizing of chromium (III) in aqueous solution.

These intercalated pillaring spesies were not stable, hence they were stabilized by calcination process, polyoxychromium were then transformed, via dehydration and dehydroxylation processes into Cr_2O_3, which constitute the so-called pillar that prop the clay layers apart to a relatively large distance. Information on basal spacings of the Na-montmorillonite and pillared montmorillonite obtained from its XRD diffarctogram. Their surface area and total pore volumes were also studied using nitrogen gas sorption analysis. Surface acidity was determined by a gravimetric analysis method and infra red analysis.

III. RESULTS

3.1 Syntheses of TiO_2 –Pillared Montmorillonite

The pillarization of TiO_2 into the interlayer of montmorillonite resulted in an expansion of basal spacings significantly.

The characterization result showed that the basal spacing of TiO_2–pillared without and with acid-acitvated montmorillonite clays were $\geq$ 21.75 Å, while hydrated Na-montmorillonite clays was 15.53 Å. The specific surface area of Na-montmorillonite, TiO_2–pillared montmorillonite, and TiO_2–pillared acid-activated montmorillonite have value of 88.13, 249.36 and 260.32 to 275.60 m^2/g respectively. The total volume of Na-montmorillonite was found to be 0.07 cm^3/g, meanwhile total volume of TiO_2–pillared montmorillonite, and TiO_2–pillared acid-activated montmorillonite were found to be 0.21 and vary from 0.21 to 0.21 cm^3/g.

The surface acidity of Na-montmorillonite measured by gravimetric after adsorbing ammonia was 0.51 mmol/g meanwhile that of TiO_2–pillared acid-activated montmorillonite clays were 5.70 to 6.00 mmol/g with Brǿnsted and Lewis acid sites.

The concentration of titan in the TiO_2–pillared acid-activated montmorillonite compound was ca.14.32 % (w/w) in average and ca. 0.05 % (w/w) for Na-montmorillonite.

These result suggest that pillarization of montmorillonite with TiO_2 was quite successful.

Table 1. Specific surface area and total pores volume of Na-montmorillonite, TiO_2-pillared montmorillonite and TiO_2-pillared acid activated montmorillonite.

SAMPLE NAME	SPECIFIC SURFACE AREA (M^2/g)	TOTAL PORES VOLUME (Cm^3/g)
Na-MONTMORILLONITE (Na-M)	88.13	0,07
TIO_2-PILLARED MONTMORILLONITE (TiO_2-PILC)	249.36	0.21
TIO_2-PILLARED ACID ACTIVATED MONTMORILLONITE (0.2 M sulphuric acid) (TiO_2-PILC-0.2)	260.32	0.20
TIO_2-PILLARED ACID ACTIVATED MONTMORILLONITE (0.6 M sulphuric acid) (TiO_2-PILC-0.6)	264.65	0.20
TIO_2- PILLARED ACID ACTIVATED MONTMORILLONITE (1 M sulphuric acid) (TiO_2-PILC-1.0)	267.73	0.21
TIO_2-PILLARED ACID ACTIVATED MONTMORILLONITE (1.5 M sulphuric acid) (TiO_2-PILC-1.5)	275.60	0.21
TIO_2-PILLARED ACID ACTIVATED MONTMORILLONITE (2.0 M sulphuric acid) (TiO_2-PILC-2.0)	270.16	0.20

Table 2. Surface acidity of Na-montmorillonite, TiO_2-pillared montmorillonite and TiO_2-pillared acid activated montmorillonite

SAMPLE NAME	SURFACE ACIDITY (MMOL/GRAM)
Na-MONTMORILLONITE (Na-M)	1.69
TiO_2-PILLARED MONTMORILLONITE (TiO_2-PILC)	5.83
TiO_2-PILLARED ACID ACTIVATED MONTMORILLONITE (0.2 M sulphuric acid) (TiO_2-PILC-0.2)	5.84
TiO_2-PILLARED ACID ACTIVATED MONTMORILLONITE (0.6 M sulphuric acid) (TiO_2-PILC-0.6)	5.87
TiO_2- PILLARED ACID ACTIVATED MONTMORILLONITE (1 M sulphuric acid) (TiO_2-PILC-1.0)	5.92
TiO_2-PILLARED ACID ACTIVATED MONTMORILLONITE (1.5 M sulphuric acid) (TiO_2-PILC-1.5)	6.00
TiO_2-PILLARED ACID ACTIVATED MONTMORILLONITE (2.0 M sulphuric acid) (TiO_2-PILC-2.0)	5.70

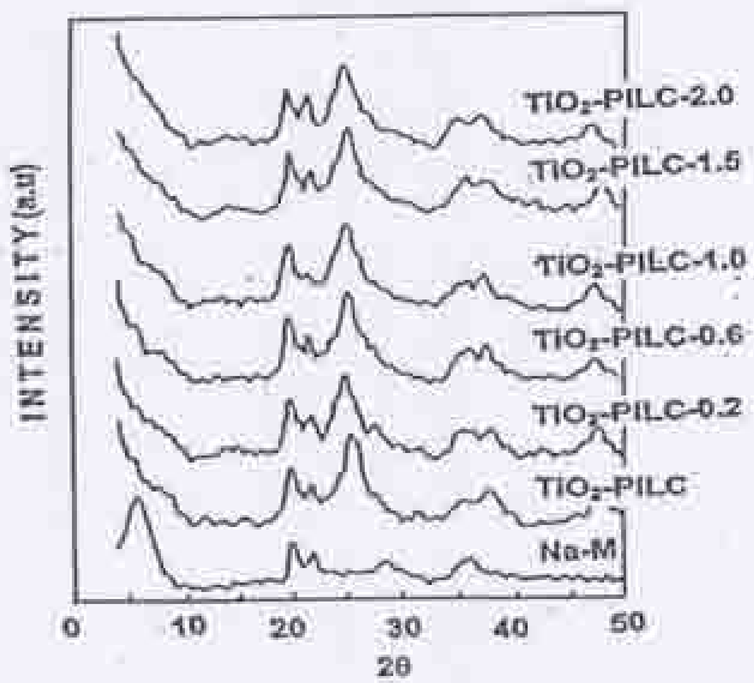

Fig.2. Xrd patterns of Na-montmorillonite (hydrated), TiO_2-pillared montmorillonite and TiO_2-pillared acid activated montmorillonite

3.2 Syntheses of Fe_2O_3–Pillared Montmorillonite

On the basis of the x-ray diffractometry characterization result, the Fe_2O_3 was intercalated into interlayer of the montmorillonite formed a house of card structure. The presence of the structure was indicated by the their broad, low intensity reflections of the pillared montmorillonites.

The higgest specific surface area and total pore volume of Fe_2O_3–pillared montmorillonite was found on Fe_2O_3–pillared montmorillonite after being calcined at 200°C for 5 hours (Fe_2O_3–$PILC_{200}$).

The concentration of iron in Fe_2O_3–pillared montmorillonite was 23.36% (w/w) in average and in Na-montmorillonite was 17.3% (w/w) in average.

The surface acidity of Na-montmorillonite determined by gravimetric analysis method after adsorbing ammonia was 0.51 mmol/g, whereas that of Fe_2O_3–pillared montmorillonite were 2.25 to 7.05 mmol/g.

Table 3. Specific surface area and total pores volume of Na-montmorillonite and Fe_2O_3-pillared montmorillonite.

SAMPLE NAME	SPECIFIC SURFACE AREA (M^2/GRAM)	TOTAL PORES VOLUME (CM^3/GRAM)
Na-MONTMORILLONITE (Na-M)	88.13	0.07
Fe_2O_3– PILLARED MONTMORILLONITE AFTER HEATING AT 100°C (Fe_2O_3–PILC-100)	155.08	0.13
Fe_2O_3 – PILLARED MONTMORILLONITE AFTER HEATING AT 150°C (Fe_2O_3–PILC-150)	164.09	0.13
Fe_2O_3- PILLARED MONTMORILLONITE AFTER HEATING AT 200°C (Fe_2O_3–PILC-200)	170.54	0.15
Fe_2O_3 – PILLARED MONTMORILLONITE AFTER HEATING AT 250°C (Fe_2O_3–PILC-250)	161.13	0.15
Fe_2O_3- PILLARED MONTMORILLONITE AFTER HEATING AT 300°C (Fe_2O_3–PILC-300)	144.35	0.15

Table 4. Surface acidity of Na-montmorillonite and Fe_2O_3-pillared montmorillonite

SAMPLE NAME	SURFACE ACIDITY (MMOL/GRAM)
Na-MONTMORILLONITE (Na-M)	0.51
Fe_2O_3– PILLARED MONTMORILLONITE AFTER HEATING AT 100°C (Fe_2O_3–PILC-100)	2.25
Fe_2O_3 – PILLARED MONTMORILLONITE AFTER HEATING AT 150°C (Fe_2O_3–PILC-150)	7.05
Fe_2O_3- PILLARED MONTMORILLONITE AFTER HEATING AT 200°C (Fe_2O_3–PILC-200)	3.67
Fe_2O_3 – PILLARED MONTMORILLONITE AFTER HEATING AT 250°C (Fe_2O_3–PILC-250)	6.19
Fe_2O_3- PILLARED MONTMORILLONITE AFTER HEATING AT 300°C (Fe_2O_3–PILC-300)	5.29

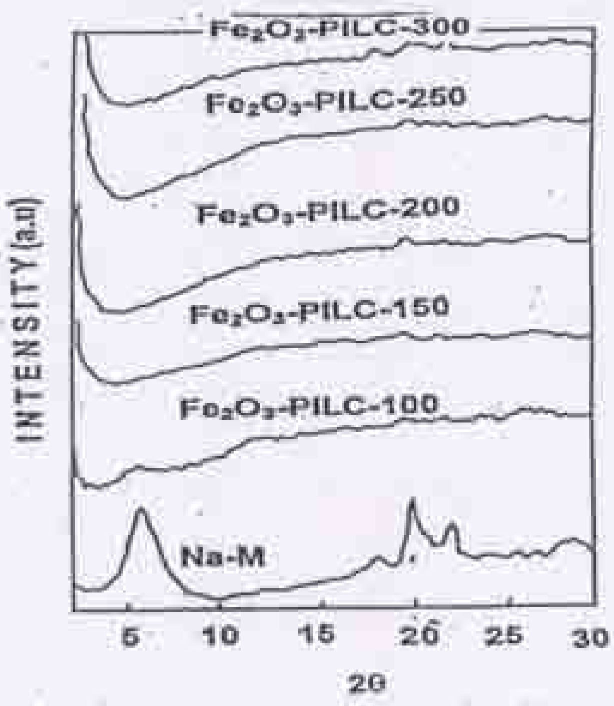

Fig.3. Xrd patterns of na-montmorillonite (hydrated), Fe_2O_3-pillared montmorillonite

3.3 Syntheses of Cr_2O_3 –Pillared Montmorillonite

The resulting Cr_2O_3-pillared montmorillonite showed a basal spacing (d_{001}) of 18.55 Å, meanwhile the basal spacing of the hydrated Na-montmorillonite was 14.43 Å. The height of the pillar was therefore 8.95 Å ($\Delta d_{001} = d_{001} - 9.60$ Å), with 9.6 Å is the alumina-silicate thickness. The founded specific surface area of the Cr_2O_3-pillared montmorillonite was 174.93 m^2/g and Na-montmorillonite was 81.34 m^2/g respectively. The concentration of chrom in Cr_2O_3–pillared montmorillonite was ca. 21.09% (w/w) in average and in Na-montmorillonite was ca. 0.18% (w/w).

The surface acidity of Na-montmorillonite determined by gravimetric analysis method after adsorbing ammonia was 0.51 mmol/g, whereas that of Cr_2O_3–pillared montmorillonite was found to be 2.70 mmol/g.

Table 5. Specific surface area and total pores volume of Na-montmorillonite and Cr_2O_3-pillared montmorillonite.

SAMPLE NAME	SPECIFIC SURFACE AREA (M^2/GRAM)	TOTAL PORES VOLUME (CM^3/GRAM)
Na-MONTMORILLONITE (Na-M)	86.13	0.07
Cr_2O_3-PILLARED MONTMORILLONITE (Cr_2O_3-PILC)	174.93	0.10

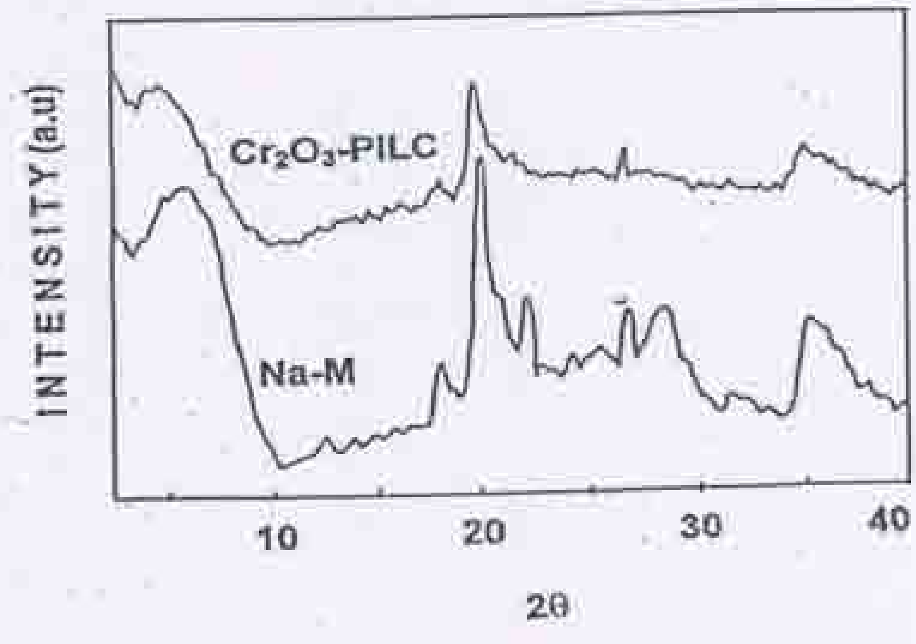

Fig.4. Xrd patterns of Na-montmorillonite (hydrated), Cr_2O_3-pillared montmorillonite

IV. CONCLUSIONS

The characterization results exhibited that the basal spacing of montmorillonite increased after being pillarized with TiO_2 as well as with Cr_2O_3. The existance of the pillar supported also by gas sorption analysis result.

In case of Fe_2O_3–pillared montmorillonite, this pillared clay possibly indicated the presence of house of cards structure, exhibited by broad, low intensity of its reflection. This results was in a good agreement with previous research results conducted by other researchers.

Pillarization resulted in increasing of the acidity of the montmorillonite clay significantly.

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Refrences

1. Baksh, M.S., Kikkides, E.S., dan Yang, R.T., 1992, Characterization by Physisorption of a New Class of Microporous Adsorbents : Pillared Clays, *Ind. Eng. Chem. Res.*, 31, 2181-2189

2. Breen, C., Clegg, F., Hughes, T. L. dan Yarwood, J., 2001, Distinguishing Interlayer Cations in Montmorillonite by Thermal Analysis of Dimethylformamide-Saturated Sampel, *J. Phys. Chem. B*, 105, 4872-4878

4. Brindley, G.W. dan Yamanaka, S., 1979, A Study of Hydroxy-Chromium Montmorillonites and The Form of The Hidroxy-Chromium Polymers, *American Mineralogist*, 64, 830-835

5. Cheng, L.S. dan Yang, R.T., 1995, A New Class of Non-Zeolite Sorbent for Air Separation: Pillared Clays, *Ind. Eng. Chem. Res.*, 31, 2021-2028

6. Derek, L.H., Briber, R.M. dan Glinka, J.C., 2001, Characterization of Organically Modified Clays Using Scaterring and Microscopy Techniques, *Chem. Mater.*, 13, 2154-2159

7. Drljaca, A., Spiccia, L., Anderson, J.R. dan Turney, T.W., 1997, Intercalation of Montmorillonite Clay with Individual Oligomeric Rhodium (III) Aqua Cations, *Inorganic Clinica Acta*, 254, 218-224

8. Gil, A., Vicente, M.A. dan Gandia, L.M., 2000, Main Factors Controlling The Texture of Zirconia and Alumina Pillared Clays, *Microporous and Mesoporous Material*, 34, 115-125

9. Hutson, N. D., Hoekstra, M. J. dan Yang, R.T., 1999, Control of Microporosity of Al_2O_3-Pillared Clays: Effect of pH, Calcination Temperature and Clay cation Exchange Capacity, *Microporous and Mesoporous Material*, 28, 447-459

10. Kumar, P., Jasra, R. V. dan Bhat, T. S., 1995, Evolution of Surface Acidity in Montmorillonite Clay on Acid Activation, *Ind. Eng. Chem. Res.*, 34, No. 4, 1441-1448