Modification of Three Types of Bentonite with Zirconium Oxide Chloride (ZOC) of Local Products Using Intercalation Process

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ABSTRACT

Three types of bentonite modified with ZOC local products of Center for Accelerator Science and Technology-National Nuclear Energy Agency using intercalation process have been done. The purpose of this research is to create new material as a catalyst or industrial raw materials. Existance of chloride anion on the intercalation process product was releasing with water and titration using silver nitrate. The release of alkali and alkaline earth cations and Fe^{3+}, Al^{3+} and Zn^{3+} into the water phase (WP) and the solids phase (SP) was detected by atomic absorption Spectrometry (AAS). While X-Ray Fluorescence (XRF) was to observe of Zr intercalated to bentonite layer. Modificated products were form of a porous material and their measured as micro, meso and macro pores using Surface Area Analysis (SAA) and the image of the porous material was observed by Transmission Electron Microscopy (TEM). Intercalation process products obtained were porous materials with a porous size of 1.50-1.55 nm at bentonite-3 with a pore area of 2250 ($m^2/Å/g$) and TEM image of the 50 nm was the most transparent among the others. As for the pores size of 1.60-1.97 nm to meso pores size of 2.0-50.0 nm were dominated by bentonite 2 with a maximum of pore 1250 ($m^2/Å/g$). While the results of the TEM image of bentonite 2, although their porous degree were small they have the pores size distribution of 5.7% micro-pore, 52.5% meso-pore and 41.7% macro-pore.

Keywords: intercalation; release; micro-pores; meso-pores; macro-pores

ABSTRAK

Telah dilakukan modifikasi tiga jenis bentonit dengan ZOC produk lokal PSTA-Batan Yogyakarta menggunakan proses interkalasi. Tujuan penelitian ini adalah untuk membuat bahan baru sebagai bahan katalis atau bahan baku industri. Keberadaan anion klorida hasil proses interkalasi dihilangkan dengan mengunakan air dan dilakukan titrasi memakai perak nitrat. Kation alkali dan alkali tanah serta Fe^{3+}, Al^{3+} dan Zn^{3+} dilepas ke dalam fase air (FA) dari fase padatan (FP) dan dianalisis dengan Spektrometri serapan atom (AAS). X-Ray Flourescence (XRF) digunakan untuk mengetahui terinterkalasinya Zr ke dalam lapisan bentonit. Diharapkan hasil berupa material porous yang ukuran mikro, meso dan makro pori menggunakan Surface Area Analysis (SAA) dan citra porous bahan diamati dengan transmission electron microscopy (TEM). Hasil proses interkalasi didapat bahan porous dengan ukuran porous 1,50-1,55 nm pada bentonit 3 dengan ukuran luas pori 2250 ($m^2/Å/g$) dan citra TEM pada 50 nm paling transparan dibandingkan yang lain. Sementara untuk ukuran pori 1,60-1,97 nm sampai ukuran meso pori 2,0-50,0 nm didominasi oleh bentonit 2 dengan maksimum ukuran luas pori 1250 ($m^2/Å/g$). Sementara hasil citra TEM bentonit 2 walaupun derajat porousnya kecil, mempunyai distribusi ukuran mikro pori 5,7%, meso pori 52,5% dan makro pori 41,7%.

Kata Kunci: interkalasi; pelepasan; mikro pori; meso pori; makro pori

INTRODUCTION

Bentonite is a major mineral in clay and its modification products has become an important raw material in industrial usage. Some of their usage in industries such as palletizing iron ore, ceramics, adhesives, dust absorbent, emulsion stabilizers, cosmetics, paints, pharmacy, pillarization on organoclay, nanocomposite polymers, catalysts and supporting catalyst. The number of modified bentonite applications are due to its superiority in chemical and physical properties such as strength, swelling, elasticity, cohesion/coherence, compressibility, particle size, cation exchanger, modifiable pore structure, high surface area, acidic and catalytically active surfaces. So today's research on organically and inorganically modified bentonite have been very interesting and widely developed [1].

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Bentonite can be modified by using several processes such as heating processes, activation by acidification, cation exchange and intercalation by using intercalant metal [1]. The modifications were also often done by using coprecipitation and anion exchange processes [2]. Heating and activation by acidifying processes are less favored because they led to the greater number of interlayer damaging of its silicate layers.

Cation exchange and intercalation processes in clay via the exchange of intercalant ionic polymer were so simple. Cation exchange and intercalation processes were characterized by the existence of cations encountered in the interlayer of bentonite such as (Na^+, Mg^{2+}, Zn^{2+}, Ca^{2+} Al^{3+}, Fe^{3+}) in the some clay minerals such as bentonite and intercalant cations such as Ti, Zr, Al and Cr [3]. The intercalation processes was easily done by mixing the dispersion of bentonite in water containing intercalant cations and by adding the polar organic such as glycerol or ethylene glycol [4]. Owing to that cation exchange process, more than 95% intercalant cations would replace in the interlayer of bentonite [1,5]. Even some anions such as chloride and nitrate would follow intercalant cations entering into the interlayer of bentonite [6-7].

Modification of natural bentonite in the form Na/Ca-bentonite has been widely carried out such as by reacting Na montmorillonite (Russia and Kazakhstan) with polyoxocation $ZrOCl_2$ for methanol and propylene oxide catalyst [8]. Synthesis of titanium-zirconium pillared montmorillonite ([Ti, Zr]-PILC) of Na-bentonite originated from Poland river with Ti and $ZrOCl_2 \cdot 8H_2O$ (Fluka Analytical Grade) and $TiCl_2$ (Aldrich, pure > 98%) had been conducted by using the intercalation process [9]. In the same research group ([Ti, Zr]-PILC) was used as a capturing chlorinated volatile organic compounds CVOCs [10].

The new material Zr/Al-pillared montmorillonite was made by intercalation process of Na-bentonnite originated from Minghui Mining Co., Anhui China, with zirconium(IV) oxychloride ($ZrOCl_2$ $8H_2O$) of Aladdin Chemistry Co., Ltd, China for adsorping phosphate [11], Then Fischer-Tropsch (FT) (Zr-pillared MMT (Zr-PILC) catalysts) was prepared by intercalation processes of materials provided by Sigma-Aldrich such as Sodium montmorillonite (Na-MMT), Zirconium Oxychloride ($ZrOCl_2 \cdot 8H_2O$) and cobalt nitrate ($Co(NO_3)_2 \cdot 6H_2O$) as Co-nanoparticle supported [12]. Furthermore, polymeric Fe/Zr pillared montmorillonite was synthesized through a intercalation process of calcium montmorillonite (Ca-MMT) from Nanhai, Guangdong Province, China with $FeCl_3$ $6H_2O$ and $ZrOCl_2 \cdot 8H_2O$ from Guangzhou chemical reagent factory, Guangdong Province, China for removing Cr(VI) liquid waste [13].

So in this research, three kinds of bentonite would be modified with zirconium oxichloride ($ZrOCl_2 \cdot 8H_2O$) (ZOC) as a local product made in the Center for Science and Accelerator Technology (PSTA) through cation exchange intercalation process. The intercalation process was done by using ethylene glycol as supporting agent [14]. Thus, the objective of this research was focused on (1) the exchange of alkaline and alkaline earth as well as Fe^{3+}, Al^{3+} and Zn^{3+} cation metals contained in the bentonite into the water phase, (2) The release of chloride ion as an intercalation product and (3) identification of the surface porosity by using surface area meter (SAA) and transmission electron microscopy (TEM) instruments.

EXPERIMENTAL SECTION

Materials

At this research bentonites used was Na-montmorillonite type consisted of Na-bentonite 1 originated from Thailand, bentonite 2 from Gunung Kidul and bentonite 3 provided by Aldrich (marked by K-10, no. 281 522), ethylene glycol pa, Na, Ca, Mg, Fe, Al, and Zn standard solutions respectively were provided by Merck. As Zr intercalant cation solution, a certain amount of $ZrOCl_2 \cdot 8H_2O$ (made by PSTA-Batan) was dissolved into 100 mL of deionized water as such that the concentration of which was 0, 01M Zr and then for which 50 mL of ethylene glycol was added and stirred for 3-4 h and left it overnight.
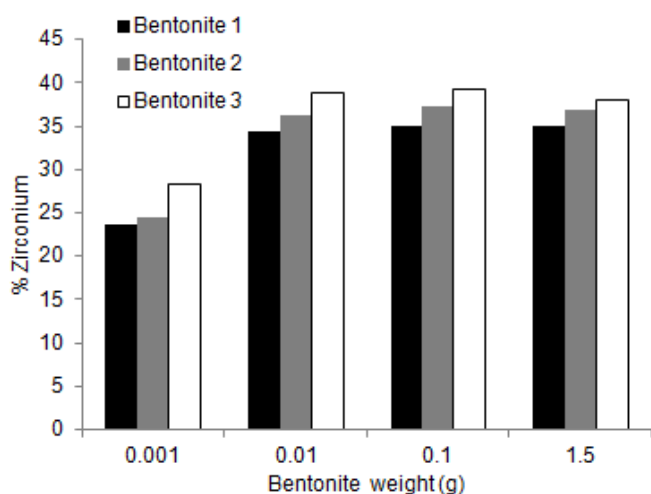
Instrumentation

The instruments used were in this research were Atomic Absorption Spectrometry (AAS) type 50 AA-made by Agilent Australia, Surface Area Analysis (SAA), X-Ray Fluorescence (XRF) and transmission electron microscopy (TEM) and a set up of bomb digester unit.

Procedure

Intercalation

Each of those three Na-montmorillonite types with the weight of 100 g (200 mesh in size) was put in a glass beaker. Each of which was added by 500 mL of intercalant solution, and was stirred and refluxed for 24 h. The washing product of which was filtered and rewashed with distilled water several times at each of 50 mL intercalation product. At the first washing product was taken 50 mL sample, in which the release of alkaline and alkaline earth as well as Fe^{3+}, Al^{3+} and Zn^{3+} cation metals was analyzed by using AAS which

Fig 1. Intercalation Zr from local ZOC with a variety of three types of bentonite minerals

Fig 2. Released of alkaline and alkaline earth metals from solids phase(SP) into the water phase (WP) of in three types of bentonite
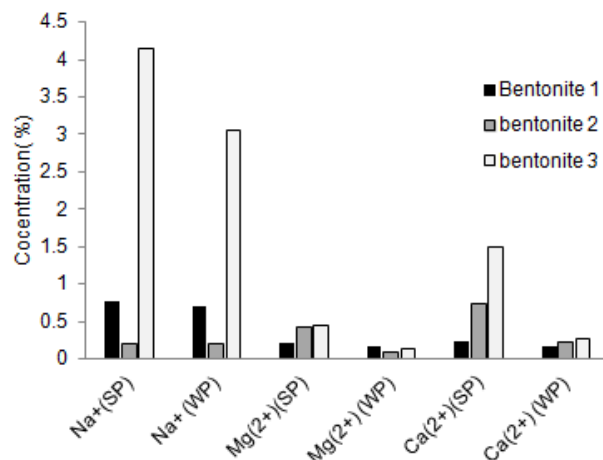
was then referred to water phase (WP), and the decrease of Zr concentration was analyzed using XRF with Am-241 as a source. The washing process was considered complete when the chloride ion disappeared after being titrated by using silver nitrate. Intercalant product was dried in an oven at a temperature of 110 °C for 24 h. Intercalant product was ground and its porosity degree was analyzed using SAA and TEM.

Solid Phase (SP)

Each Na-montmorillonite weight of 0.2 g, was put in the Teflon tube then added to which the mixture of 1.0 mL HNO_3 and 0.2 mL HF, and then it was put in the stainless-steel tube. All of which then put in the tightly closed oven at 150 °C temperature for 4 h. Bomb digesting product was then diluted and analyzed by using AAS and it was further named as solid phase (SP).

RESULT AND DISCUSSION

The cations exchange in solid-liquid system was the most intercalation mechanism frequently occurred in the clay. The ion exchange mechanism occurs in the lining of layered double hydroxides (LDHs) to form a porous material through the intercalation process of polyoxometal $[M^{2+}1{-}xM^{3+}x(OH)_2](A^{n-})x/n{\cdot}zH_2O$ in clay ((M^{2+} could be Na^+, Mg^{2+}, Zn^{2+}, Ca^{2+} whereas M^{3+} could be Al^{3+}, Fe^{3+}, Ga^{3+} ect.). Alkaline and alkaline earth as well as Al^{3+}, Fe^{3+} and Zn^{2+} metal cations in LDHs layer were weakly polar so that they were easily desorped and would simultaneously be replaced by intercalant cations such as Zr and Ti [15]. The following was zirconium intercalation processes products from local ZOC into three types of bentonite which was analyzed by using X-ray fluorescence with Am-241 as the radioactive source.

From Fig. 1, it can be shown that the intercalated zirconium at the lattice of interlayer bentonite lining obviously increased with the weight addition of bentonite and continuously at the weight of 0.1 gr. Through the absorption system was obviously that bentonite 1 < bentonite 2 < bentonite 3. This matter was in accordance with Olszewska [16] which stated that the intercalation of zirconium will be influenced by the type, the content of alkali and alkaline earth metals as well as the origin of the mineral montmorillonite area. These intercalation process was obviously not much different from the literatures [10-12], which had mixed up 0.001-0.01 g Na-bentonite, Na-montmorillonite from various regions with 0.01 to 0.1 M Zr concentration of $ZrOCl_2{\cdot}8H2O$. Furthermore, the detection of alkaline and alkaline earth metals as well as and Al^{3+}, Fe^{3+} and Zn^{2+} metals Layered double hydroxides (LDHs) released which were replaced by Zr was an indicator of the intercalation successful [17-18]. The following were observation results of alkali and alkaline earth metals released in the water phase (WP) compared to the solids phase (SP) during the intercalation process Zr with three types of bentonite, whereas the observation was made by using the atomic absorption methods.

In Fig. 2, it can be shown that during the intercalation the cationic transfer of Na^+ (SP) into (WP) had been occurred both in bentonite 1 and 2 as well as 3. The highest Na^+ (WP) cationic transfer was gained by bentonite 3 up to 3%. Then Mg^+ transfer into WP for those three of bentonites were insignificant, but for the most significant Ca^+ transfer was gained at bentonite 3 up to 0.45%. With the greater elements transfer of Na^+ and Ca^{2+} from SP into WP, this matter proved that both the two elements were the most role playing at the intercalation process in the lining of inter layer LDHs
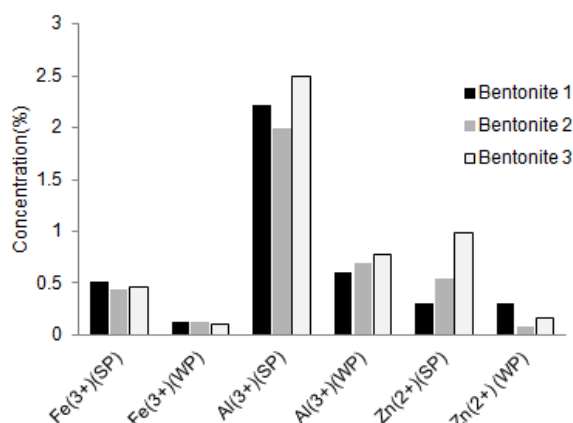
Fig 3. Release of Al^{3+}, Fe^{3+} and Zn^{2+} from solids phase(SP) into the water phase (WP) in three types of bentonite
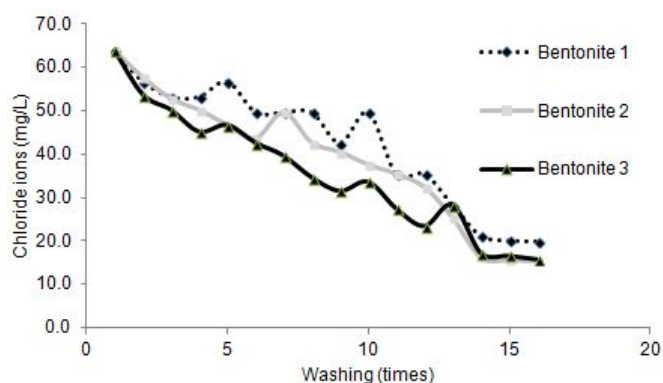
**Fig 4.** Release of chloride ions into the water phase (WP) in three types of bentonite
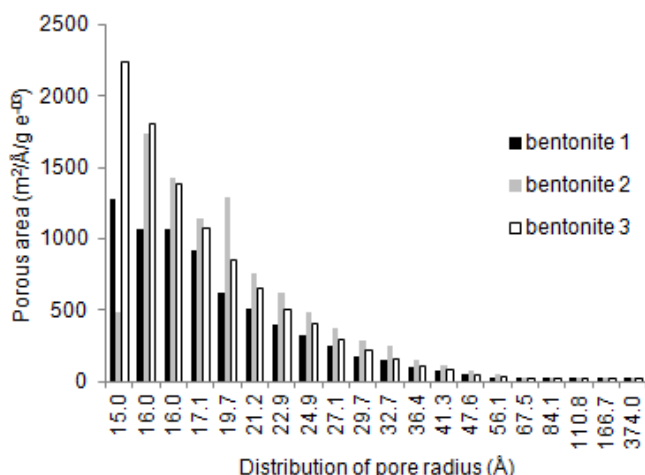
Fig 5. Distribution of pore radius by using DVR methods

bentonite [18].

From Fig. 3, it can be seen that during intercalation the release of Al^{3+} cation of SP to WP was the highest if compared with the others. Even for bentonite 3 the

release of Al^{3+} may reach 1.89%, so at the intercalation process had been a transfer of Al^{3+} cation with Zr^{4+} in the inter layer LDHs layer of bentonite. From Fig. 2 and 3, it can be shown that almost all alkaline and alkaline earth elements as well as Al^{3+}, Fe^{3+} and Zn^{2+} will experience the release from SP into WP. Furthermore, when compared to Fig. 1, concerning the zirconium concentration increase phenomenon indicated that the cations exchange in the intercalation process had been occurred. In this matter the writer agrees with Plamondon [6], which stated that the intercalation was strongly influenced by cationic and non-ionic surfactant supported by polypropylene glycol (PPG). Although in this study the maximum intercalated Zr on bentonite was only 40% (Fig. 1) the supporting of ethylene glycol surfactant was quite appropriate.

According to Duan [18] the intercalation process of ion exchange in the lining of inter layer LDHs of bentonite obvious of anion also participated in that process. LDHs layer as an inter layer and intra-layer which was undergoing the intercalation process could be expressed as $[M^{2+}_{1-x}M^{3+}_x(OH)_2](A^{n-})_{x/n}\cdot zH_2O$ and (A^{n-}) notation was an anion. So as M^{2+} and M^{3+} metals as well as anions also participated in the intercalation process [19]. Furthermore, as a bentonite modification material ZOC will be dissociated in the water by releasing chloride ions as the following reaction

$$4[ZrOCl_2\cdot 8H_2O]_{(s)} + H_2O \leftrightarrow [Zr_4(OH)_8]^{+8} + 8Cl^- + 29\,H_2O$$
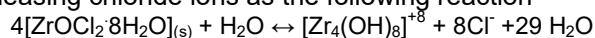
Owing to the further process (pillarization) needed calcination at temperature of 600 °C and with the chloride ion which is corrosive. Therefore, the chloride ion should be removed from intercalation process product. In Fig. 4, it was shown that the chloride ion removal by washing the intercalation product using water. It was obvious that the chloride ion removal for bentonite 1, 2 and 3 were relatively constant in the 15th washing of which was 50 mL, respectively. According to Sun [19], intercalation the existence of chloride ion in the hydroxide matrix would bound intercalant cation at the ionic binding based. The removal of which using water would be very effective due to the existence of very strong hydrogen binding between the water molecules for removing the chloride ions[18].

One of the intercalation main goals was formed a new porous material with a porosity degree of micro-meso pore. The degree of micro-meso pores was known from the relationship between the distributions of pore radius (Å) with pore area measured by using surface area meter. In Fig. 5 it can be shown that the pore distribution in bentonite 1, 2 and 3 were in the range of 15 Å to 56.1 Å and 56.1 Å to 166.7 Å, in this matter it was happened the pore degree of micro-macro porous pore (IUPAC states that micro pore size is < 2 nm, meso pore 2-50 nm and macro pores > 50 nm). In the porosity analysis with micro degree size of
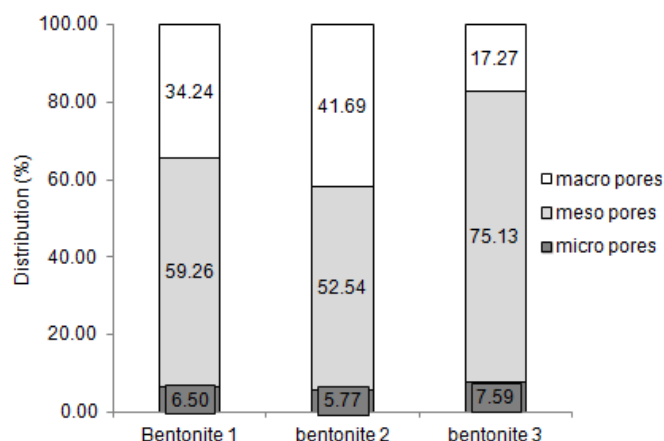
Fig 6. Pores distribution percentages of three types of bentonite modification
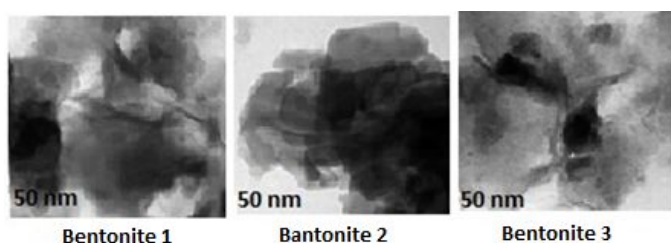
Fig 7. TEM image of modified bentonite with local ZOC using process intercalation

1.50-1.55 nm (1A = 0.1 nm) turned out to be dominated by bentonite 3 with the maximum pore size area of 2250 $(m^2/\text{Å}/g)$. As for the pore size of 1.60-1.97 nm to meso pore size 2.0-50 nm dominated by bentonite 2 with the maximum area size of 1250 $(m^2/\text{Å}/g)$. While for the macro pore size > 50 nm as the area larger the pore size decreased. At this research authors agree with Cecilia [20] who had made porous clay heterostructures (WFHs) by Zr intercalation with natural montmorillonite. The synthesis products of WFHs was also porous distributed in the micro, meso and macro pores sizes.

Furthermore, in Fig. 6, the ore distribution percentages of each bentonite. At bentonite 1, proved that at bentonite 1, there existed 6.5% micro pores, 59.26% meso pores and 34.24% macro pores. At bentonite 2, the percentages of micro pores was the same as that of bentonite 1, but the percentages of meso pores was higher than that of macro pores. Furthermore, on 3 bentonite, micro-pore percentages was slightly increased to 7.59%, but the meso pores increased up to 75.13% and the remaining macro pores was 17.27%. As the percentage of meso pore had exceeded 70.0%, according to Cecilia [20] the possibility of natural montmorillonite as a modified material had been used for 1-butene isomerization.

In Fig. 7, it can be shown TEM image of the three types of bentonite at 50 nm as representative types of porous meso pores. At the meso pores condition shown that the TEM image of bentonite 1 was more visible and slightly transparent by which illustrated more porous than that of bentonite 2. Furthermore, the bentonite 3 imaged was more transparent than others at 50 nm meso pores, thus having bentonite 3 has a higher degree porous than others.

CONCLUSION

Zirconium oxide chloride ($ZrOCl_2 \cdot 8H2O$) (ZOC) local products can be done to modify the properties of bentonite through the intercalation process. Intercalation process products showed that there has been an exchange of cations from the solid phase (SP) into the water phase (WP). Cation exchange occurred with the increasing concentration of Zr intercalant and the increasing cation concentration from FS into WP. Although the chloride anion of dissociated ZOC participated in the intercalation process of bentonite, but this can be overcome by removing with the aid of 750 mL of water. Intercalation generate new material with a pore size of 1.50-1.55 nm on bentonite 3 with a pore size area of 2250 $(m^2/\text{Å}/g)$ and 50 nm TEM image of the most transparent. As for the pore size of 1.60-1.97 nm up to meso pore size 2.0-50 nm dominated by bentonite 2 with a maximum size of 1250 area $(m^2/\text{Å}/g)$. While the results of the TEM image of bentonite 3 shown less porous than bentonite 1 or bentonite 2.

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