

Microwave Assisted Preparation of Zirconia-Pillared Bentonite

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Abstract: The development of zirconia-pillared bentonite has been carried out by intercalating the solution of cationic polyoxozirconium using $ZrOCl_2$ precursor into natural bentonite was continued through radiation process using microwave of 800 watt for 10 minutes to produce metal oxide formation. The synthetic product was then characterized using XRD, XRF, FTIR, TEM and analysis of N_2 adsorption/desorption. The success of pillarization process of zirconium into natural bentonite has been proved by the analysis result of XRD. The result showed that the basal spacing shifted (001) into left direction, and the reflections showed the structure of bentonite/pillared bentonite of $2\theta=4-6^\circ, 19^\circ$ and 25° . In addition, the result of XRD performed new reflections of $2\theta=31.24^\circ$ and 35° as the reflection of ZrO_2 . Meanwhile the analysis result of XRF showed that the amount of Zr metal in ZrO_2 -Bentonite was found at 8,38%. Moreover, the acidity was analyzed using FTIR in which it showed the increasing trend both in the acidity in ZrO_2 -Bentonite material compared to bentonite, and the volume of total pore of 0.061 into 0.063 $cm^3 g^{-1}$.

Keywords : Bentonite, Zirconium, Intercalation, Pillarization, Microwave radiation.

1. Introduction

Clay is a layered material that consists of one layer of octahedral and two tetrahedral layers or commonly known as composition of 2:1¹. The type of clay that is commonly used is bentonite since it has an ability to swelling, being more flexible and having bigger pore or interlayer space compared to natural zeolite, therefore the implementation of pore engineering to produce pillared microporous or mesoporous bentonite will be feasible to do.

To achieve high performance of a clay, the distribution process of metal into its structure to produce pillared clay material is one of the methods to develop. The process of metal distribution into bentonite is applied with intercalation of pillaring agents of metal hydroxy cation, into interlayer of silica or it is called as pillarization. Through heating process at high temperature, metal hydroxy cation onto interlayer will experience dehydration and dehydroxylation to produce metal oxide in its interlayer to obtain high thermal stability and interlayer space in molecular dimension⁸⁻⁹. In addition, calcination theoretically will produce uniforming of pore distribution, increasing material crystallinity, and increasing specific surface area⁵⁻⁷.

The pillarization of bentonite is influenced by synthesis variables such as pH of intercalation process, intercalating precursor, temperature of calcination, and the calcination method in which the stability of

polyoxocation within low pH range will cause destruction effect on bentonite structure^{4,10}. Zirconium-pillared clays with different physiochemistry properties have been produced using ultrasonic technic and microwave radiation¹¹⁻¹⁵. Intercalation with microwave radiation can inhibit the production of polimerization of zirconium species and can also be used in calcination process to produce homogenous pillar distribution while increasing primary space of 12,4Å to 19Å^{12,4}.

The use of zirconium-metaloxide as pillaring agent was caused by the thermal stability and acidity property of ZrO₂. The pillarization of clay with zirconium-metaloxyde is reported of producing pore distribution in mesoporous scale and increasing the specific surface area¹⁶⁻¹⁸. Next, it can be used as catalyst in acylation reaction of 1,4-butanediol, alkylation of phenol, benzene and catalyst for hydrocracking^{12,13,19,20,2}. The main objective of this research is to characterize the physical and chemical properties of zirconium-pillared bentonite that was prepared using ZrOCl₂•8H₂O precursor and microwave radiation for calcination process. The pillarization of bentonite clay with polycation zirconium oxide was started by intercalation through ion exchange process of Na⁺, K⁺ or Ca²⁺ inside of bentonite interlayer with highly charged polyoxocation zirconium of keggin ion [Zr(OH)₂•4H₂O]⁸⁺. Through calcination, pillaring species would be oxidized to produce stable ZrO₂, in purpose of being pole/pillar between interlayer of bentonite and opening layers in bentonite to produce larger new pores. The produced ZrO₂ would bind with tetrahedral SiO₄ of bentonite in which forming covalent bond of Zr-O-Si.

2. Experimental

2.1 Chemicals and Instruments

The reagents used in this research included natural bentonite, ZrOCl₂•8H₂O, AgNO₃ (E. Merck), distilled water, aquabides, and ammonium.

The apparatus used in this research included: one set of glassware, centrifuge (Kokusai H-107), oven (Memmert), porcelain cup, analytical balance, 200 mesh sieve, modified Electrolux microwave, porcelain mortar and pestle.

Diffraction patterns of the sample were recorded on a XRD-6000 Shimadzu, using CuKα powder irradiated by the λ = 0.5406Å. FTIR spectra were performed on PC 8201 infrared spectrophotometer (Shimadzu) using KBr pellet at room temperature. Surface acidity of solids are conducted by ammonia adsorption followed by FTIR measurements. and Zr content determination by X-ray Fluorescence (XRF, EG & G OTEG 7001). N₂ adsorption-desorption isotherms were measured at liquid nitrogen temperature with a gas sorption analyzer (Quantachrome, NOVA 11000). TEM measurements were done using a field emission transmission electron microscope (TEM- JEOL 1400).

2.2 Preparation of Bentonite

100 gram of bentonite was crushed to produce 200 mesh-fine bentonite. The fine bentonite was then dispersed in 200 mL of HF 1% and stirred within 2 hours. Afterwards, the bentonite was sieved and dried in oven at 120°C. Next, the dried bentonite was sifted and sieved using 200 mesh sieve and the result is called as Bentonite (Bent). The bentonite is characterized further using XRD, FTIR, Gas Sorption Analyzer and TEM.

2.3 Synthesis of ZrO₂- Bentonite

Polyhydroxy of salt precursor of 0.1M ZrOCl₂•8H₂O was refluxed at 70°C within 24 hours. Afterwards, the intercalation was carried out by adding pillaring solution into bentonite suspension and stirred in room temperature within 24 hours. The result was then sieved and washed with distilled water till being neutral. The obtained result was dried at 120°C and had microwave radiation of 800 watt within 10 minutes. The calcination result is called ZrO₂- Bent, was analyzed using XRD, Gas Sorption Analyzer, FTIR, TEM and XRF. The character of ZrO₂- Bent was compared with to the character of bentonite.

3. Results and Discussion

3.1. The characterization of structure

X-ray Diffraction

Cristallinity data of solid bentonite before and after pillarization is shown on Fig.1. The diffractogram of Bentonite measurement (Fig. 1b) was obtained the peak at $2\theta=5.68^\circ$ (001) reflection ($d=15.993\text{\AA}$), $2\theta=19.92^\circ$ (100) reflection ($d=4.45\text{\AA}$), $2\theta=20.74^\circ$ ($d=4.279\text{\AA}$) that are the characteristic of montmorillonite mineral with specific intensity. Few peaks at $2\theta=25.57^\circ$ ($d=3.480\text{\AA}$) and $2\theta=26.52^\circ$ ($d=3.358\text{\AA}$) showed quartz in high quantity in aquades-washed bentonite. The clay mineral showed (001) reflection space range of 30\AA and 3\AA that fulfilled with 2θ angle of 2° and 30° . The washing process with HF would increase the cristallinity where it was proved by the increasing trend of peak at $2\theta=5.68^\circ$ along with increasing intensity that indicating the montmorillonite mineral and cleaned impurities (feldspar and quartz) existed in clay (Fig. 1b).

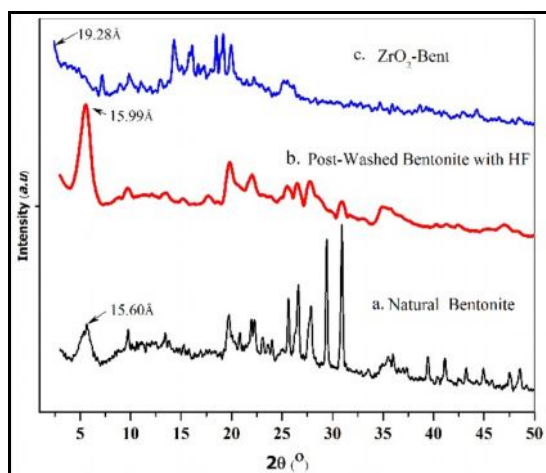


Figure 1. Diffractogram (a) Natural bentonite, (b) Bentonite, (c) ZrO_2 -Bentonite.

The synthesis of zirconia-pillared bentonite (ZrO_2 -Bent) was carried out using precursor of oxide chloride zirconium ($ZrOCl_2 \cdot 8H_2O$) that was intercalated in bentonite with reflux and calcination treatment with microwave radiation. Zirconium tetramer could polymerate to produce bonded layer to build a three dimensional polymer pillar. The diffractogram of ZrO_2 -Bentonite (Fig 1c) shows the visible montmorillonite reflection, however the main peak at $2\theta=5.68^\circ$ is not shown specifically. This phenomenon had caused by the peak shift into left direction (minor angle) or there occurs basal spacing structure shift (001) of montmorillonite due to the intercalation of Zr^{4+} polycation. Fig.1c shows a peak shift of bentonite prior to intercalation at angle of 5.68° into $2\theta=4.34^\circ$ on ZrO_2 -Bentonite material, and the increasing basal spacing d_{001} -value of $9,7\text{\AA}$. The success of ZrO_2 pillarization on bentonite is shown by the existing of new peak at $2\theta=31^\circ$; 31.24° and $2\theta=35^\circ$ that are ZrO_2 reflections as a results of calcination process using microwave radiation in which the microwave radiation could convert the imperfect pillar into oxide pillar^{11,3}. This phenomenon is shown through an analysis using XRF. It shows the quantity of Zr metal in ZrO_2 -Bent material of 8.38%.

Analysis of FT-IR

A characterization of functional groups was learned qualitatively with FTIR spectrophotometer, the results is shown on Fig. 2. The infrared spectra of clay mineral is observed at wave number of $400-4000\text{ cm}^{-1}$. The Fig. 2 has two graphs which are Bentonite (Fig. 2a) and ZrO_2 -Bentonite material (Fig. 2b). Bentonite that obtained an absorption band at the wave number of 3749.62 cm^{-1} and 3433.27 cm^{-1} that are the characteristic vibration peaks of octahedral $-OH$ and vibration stretching absorption of $-OH$ in water molecule. The absorption band at wave number of 1635.64 cm^{-1} shows the characteristic of stretching vibration and the deformation of $-OH$ in material. The absorption at wave number of 462.92 cm^{-1} shows bending vibration of $Si-O-Si$. The bending vibration of $O-Si-O$ is shown by the absorption of wave number of 768.96 cm^{-1} and the absorption of wave number of 918.12 cm^{-1} indicates an absorption of stretching vibration for $O-Al-O$ ²¹. On the other hand, the ZrO_2 -Bentonite material (Fig. 2b) showing the expanding absorption band at wave number of

3749.62 cm^{-1} and 1635.54 cm^{-1} are the characteristics of $-\text{OH}$ vibration. The expanding absorption band in the concerned wave number was caused by pillarization process¹⁷. The merging of Zr polycation with hydroxy in the bentonite layer was proved by both the missing absorption of Al_2OH at wave number of 918.12 cm^{-1} and its shift into smaller wave number. In addition, the absorption band at wave number of 1041 cm^{-1} shows an expanding symmetrical vibration of Si-O-Si on ZrO_2 -bentonite material.

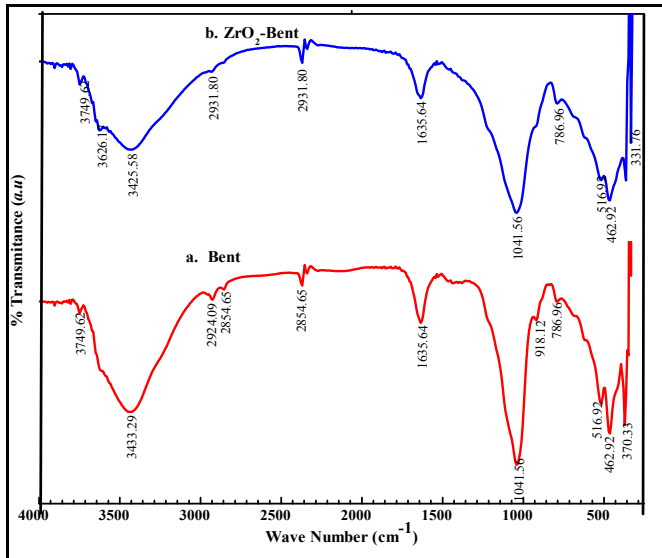


Figure 2. Analysis of FTIR (a). Bentonite, (b). ZrO_2 -Bentonite

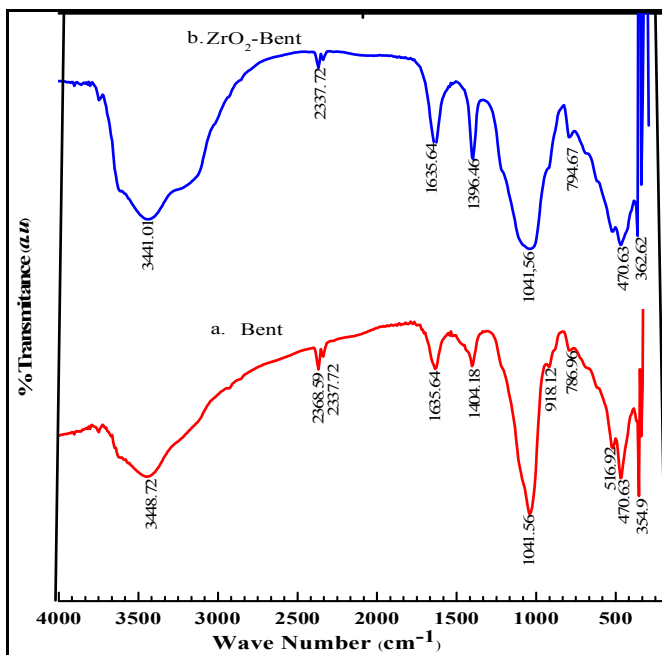


Figure 3. Spectra of FTIR (a). Bentonite, (b). After ammonia adsorption of ZrO_2 -Bentonite

3.2. Examining The Acidity of Catalyst

Examination of acidity on the surface of ZrO_2 -Bentonite was learned with ammonia adsorption (NH_3) and identified with the adsorption of existing ammonia species on the surface of material (Fig. 3). The surface acidity contribution was not only derived from proton (H^+) that was released in calcination process as the Bronsted acid site but also from the species type of pillaring agent used as Lewis acid. The acidity of Bronsted and Lewis was characterized by FTIR with the absorption at wave number of 1400–1635 cm^{-1} . When ammonia has been proceeded through adsorption process, ammonia molecule would experience protonation and bind in

coordination covalent bond with the acid site of Bronsted and Lewis [21]. The spectra of ZrO_2 -Bentonite (Fig. 3b), the absorption band at wave number of 1635.64 cm^{-1} shows sharply the increasing Bronsted acid as the result of hydroxyl functional group in hydrated zirconium [6]. The absorption band at wave number of 1404 cm^{-1} also shows the Lewis acid site, resulted by the pillared ZrO_2 . This phenomenon shows that the pillarization of bentonite with zirconium will increase the acidity of Bronsted and Lewis on the surface of bentonite²³.

3.3. The Characterization of Surface Morphology with TEM

The interlayer arrangement and silicate layer width change of Bentonite and ZrO_2 -Bentonite are shown on Fig. 4a and 4b. The production of new particle on interlayer of bentonite can be predicted as oxide zirconium pillar. The result shows that pillarization of bentonite was successfully carried out without any damage in bentonite structure despite there is an existing of oxide zirconium functioning as pillar in between of silicalayers.

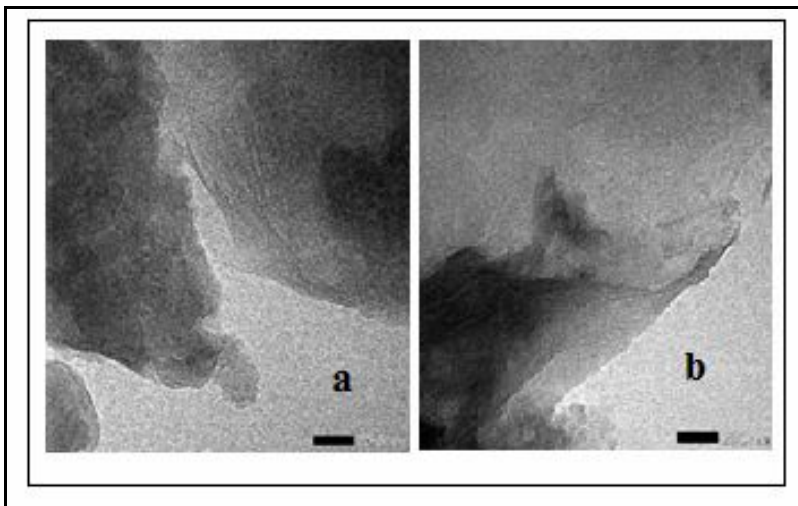


Figure 4. Analysis Profile of TEM of (a). Bentonite (b). ZrO_2 -Bentonite

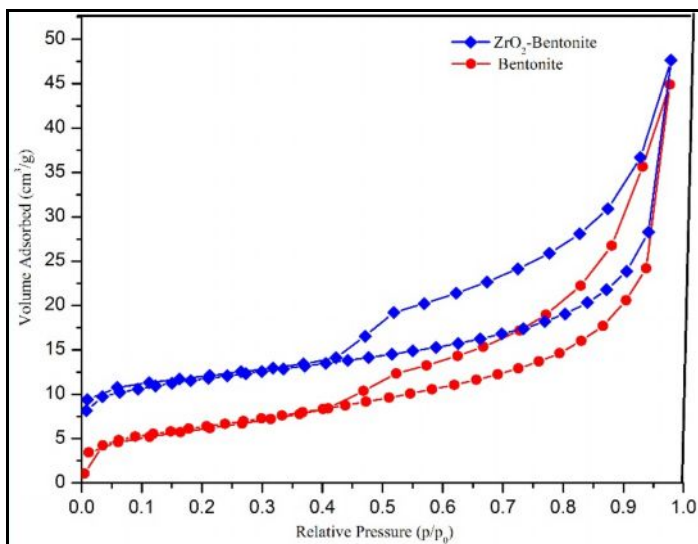


Figure 5. The Isotherm of Adsorption-Desorption Nitrogen of Bentonite and ZrO_2 -Bentonite material

3.4 Analysis of Surface Area and Porosity

The results of surface area analysis and total pore volume of ZrO_2 -Bent and bentonite are shown on table 1. The data on table 1 shows the specific surface area of Bentonite of $21.678\text{ m}^2/\text{g}$ and ZrO_2 -Bentonite of $18.524\text{ m}^2/\text{g}$. The decreasing surface areas of ZrO_2 -Bentonite has been occurred since the pore of surface area was partially covered with oxide metal or the aggregation of oxide metal on surface. This effect is commonly called as cards-house effect. The isotherm pattern of desorptions are shown on Fig. 5 that produces the isotherm

adsorption pattern change due to the pillarization of bentonite. The bentonite shows the type III of isotherm adsorption pattern based on the classification of BDDT that shows the occurring of solid adsorption on the material with larger diameter than the micropore. Whereas the ZrO_2 -Bentonite obeyed type IV of isotherm adsorption that indicated the formation of mesoporous.

The existing of this mesopore was supported with the existing hysteresis loop on ZrO_2 -Bentonite sample and based on the classification of IUPAC, this phenomenon was classified as type H4 that showed the formation layered material. The adsorption pattern of zirconium- bentonite showed the formation of more dominant mesopore. It was proved by the increasing trend of adsorption simultaneously on all relative pressures of p/p_0 . Based of the adsorptions pattern, there was obtained the distribution curve of pore size as shown on the Fig6.

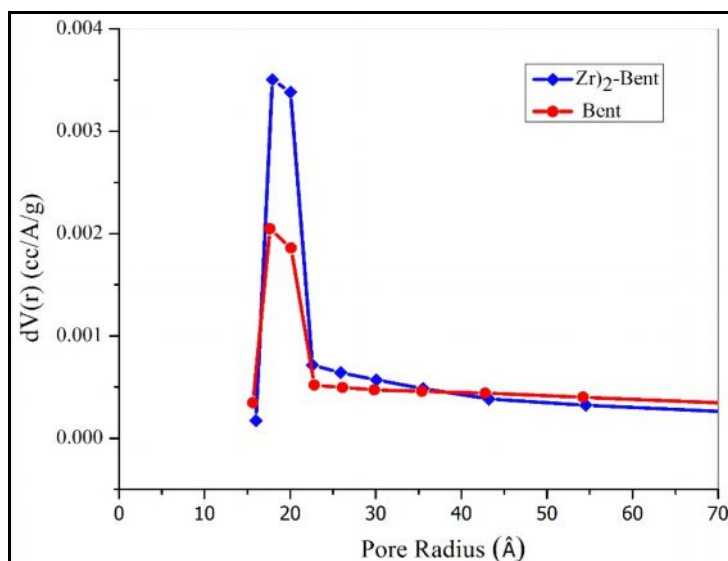


Figure 6. The distribution curve of pore size of bentonite and ZrO_2 -Bentonite.

The distribution curve of pore size (Fig. 6) gives the conclusion that the dispersion of ZrO_2 on bentonite occurred homogeneously. The pillaring also caused the increasing porosity of bentonite that is shown by the total volume pore data (Table 1). It describes that the total pore volume of after pillarization-bentonite would be increasing of 0.061 into 0.063 $cm^3.g^{-1}$. This phenomenon shows that the existing pore distribution in mezo size would dominate in bentonite after pillarization using zirconium metal oxide (ZrO_2).

Table.1 The Analysis Result of Nitrogen Gas Adsorption

Sample	Specific Surface Area (m^2/g)	Total Pore Volume ($cm^3.g^{-1}$)	Pore Radius (Å)
Bentonite	21.678	0.061	17.62
ZrO_2 -Bentonite	18.524	0.063	17.92

4. Conclusion

The intercalation of zirconium cationic polyoxo solution inside the bentonite interlayer and continued through a heating process using microwave radiation of 800 watt for 10 minutes would result the formation of ZrO_2 -Bentonite material with different characters towards the natural bentonite. The success of pillarization process was studied using XRD. The analysis showed the basal spacing shift (001) in left direction and the increasing of primary distance at 9.7 Å . While, infrared analysis showed the increasing acidity property of zirconia-pillared bentonite and its porosity. Additionally, the dispersion of ZrO_2 on bentonite occurred homogeneously.

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