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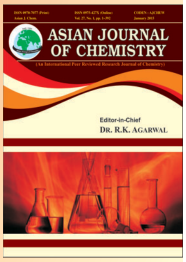

Synthesis and Characterization of ZrO_2-Pillared Bentonites

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Bentonite is a clay mineral that has layered structure, porous and having potential as a catalyst as well as an adsorbent. Pillarization process against bentonite aims to increase the surface area, pore volume, thermal stability and catalytic active sites of pillar metal oxide. Pillarization mechanism stages begin with pillar ion exchange in interlayer structure ions with the formation of oxide ions into the metal oxide through calcination. Characterization towards bentonite pillared synthesis result was performed using AAS, XRD, TEM and analysis of N_2 adsorption/ desorption. The analysis showed that the surface area and pore volume of ZrO_2 pillared bentonite increased from 52.830 m^2/g and 0.152 cc/g into 269.165 m^2/g and 0.204 cc/g. The XRD and TEM analysis also showed that the presence of metal oxide ZrO_2 was able to increase the basal spacing of 1.38 to 1.89 nm and raised no damage to the structure of bentonite.

Keywords: Bentonite, Pillarization, Basal spacing, Surface area.

INTRODUCTION

Bentonite is a phylo-silicate mineral group and being the most attention mineral. Besides these minerals also have the ability to swell, the interlayer space or having pores larger and more flexible structure rather than the natural zeolite pores so that it can be engineered as to form a pillared bentonite with micro size and/or mesoporous which can be used as selective catalysts, separation agents, supporting materials, adsorbents[1]. In addition to the negatively charged of surface layer bentonite, it occurs electrostatic force and van der Waals forces are so weak that the cation contained in bentonite interlayers easily replaced by other cations[2-5]. Related to its applications, it has limitations due to the use of bentonite surface area and low thermal stability. In general, the bentonite dehydrate and damage the structure at the high temperature reaction. Therefore, it is necessary to modify the structure of clays to increase the surface area and thermal stability with pillarization[6]. Bentonite can be pillared with a variety of organic compounds, compound and complex metal oxides into its interlayer. Pillared process can lead to clay porous getting bigger and homogeneous and inter-layered character becomes relatively more stable. Through the calcination was obtained metal oxide that will support bentonite interlayer space. Pillarizationis performed by cation exchange between clay layers and pillared metal. Then calcination is carried out for the formation of metal oxides as permanent pillar thus it is forming a pillared clays[6]. The main interest of pillarization bentonite is to produce structure that is created by controlling the size and population of it inter layer. Pillared material has potential as a catalyst for various hydrocracking hydrocarbon reactions and acid catalyst.

Among various metal oxides, zirconia is one of the few transition metal known as pillared with good thermal stability[7]. Zirconia pillared clay is a microporous solids with large surface area. The nature of zirconia itself was good as acid sites or as co-catalysts. It has proven to be the preferred catalyst in various reactions[8]. Pillarization process is highly dependent on synthesis method and pillaring solution concentration[9,10]. Intercalation time is also an important factor that is significantly related to the distribution of pillared agent. Zirconium hydroxide compound is formed by hydrolysis. Zirconyl chloride octahydrate solution ($ZrOCl_2 \cdot 8H_2O$) has been used to form a stable oxide pillars between layers in smectite clays[11,12]. Pillarization impact is able to increase the surface area, acidity and high selectivity. $ZrOCl_2 \cdot 8H_2O$ solution normally used in ion exchange[12], though hydroxy zirconia structure of intercalation process and the transformation into ZrO_2 is not easy to understand until present. In this study, it will be reviewed pillarization using zirconia into the interlayer of bentonite to get ZrO_2/bentonite material. Pillarization zirconia on clays has been studied previously that $ZrOCl_2 \cdot 8H_2O$ solution would be hydrolyzed into polycationic compounds $[Zr_4(OH)_8(H_2O)_{16}]^{8+}$ that are positively charged displacing cation in the interlayers of bentonite by ion exchange mechanism. Finally, the product was calcined to form ZrO_2 metal oxide served as pillars in the interlayer of bentonite. ZrO_2 pillarization on bentonite interlayer causes basal spacing d_{001} of bentonite will be increasing. The purpose of this study was to synthesize and determine ZrO_2/bentonite physico-chemical properties such as specific surface area, total pore volume, basal spacing and the image formation of defect structure after pillarization process.

EXPERIMENTAL

Materials used in this study are natural bentonite, zirconyl chloride octahydrate ($ZrOCl_2·8H_2O$), silver nitrate ($AgNO_3$) and deionized water from the Laboratory of Chemical Physics, UGM.

Glass tools, grinding tools, 150 mesh sieve, magnetic stirrer, heater, thermometer, oven, centrifuge, analytical balance, Buchner filter, furnaces, appliances instrument include: X-ray diffractometer (Shimadzu Model X-RD 6000), spectroscopy infrared (FTIR Shimadzu 8201 PC), atomic absorption spectrophotometer (AAS) (Perkin Elmer), transmission electron microscope (TEM) (JEOL Hitachi H-600) and sorption gas analyzer (Quantachrome NOVA instrument instruments 11:0 version 1994-2010).

Clay preparation: Bentonite clay with diluted using deionized water for 24 h, then it was separated by decantation. Furthermore, colloidal solution filtrate was centrifuged then obtained its precipitation and its filtrate. Moreover, the filtrate evaporated and resulted bentonite. Bentonite solid was dried at 110 ºC and sieved to 150 mesh size.

Preparation of zirconia solution oligo-cation: Pillared agent was made by hydrolysis. As much as 7.7g ($ZrOCl_2·8H_2O$) were dissolved in 240 mL of deionized water for 2 h as well as reflux it.

Synthesis of zirconia oxide pillared bentonite: This stage begins with the preparation of zirconia oligo-cation solution. Furthermore, 8 g of bentonite which has been suspended was added to a solution of oligomers slowly and then stirred for 24 h at room temperature. After stirring finished, zirconia oligo-cation bentonite obtained was centrifuged and its sediments were washed several times using deionized water until the filtrate was clear and free from chloride ions. The test was done using $AgNO_3$ solution dropped into centrifuge result. The sediments were dried in oven at 70 °C and crushed as well as sieved it using 150 mesh. Then, it was heated at 400 ºC for 2 h.

Characterization: Analysis of Na and Ca elements in bentonite were analyzed by AAS. Determination of basal spacing was analyzed by X-ray diffraction using a Shimadzu XRD 6000 diffractometer with CuK_α radiation. Infrared spectroscopy was used to identify the functional groups in bentonite. TEM was used to determine the morphology and the distance between layers of bentonite. BET NOVA 1994-2010 instrument version 11:0 was used to determine the specific surface area and porosity of bentonite.

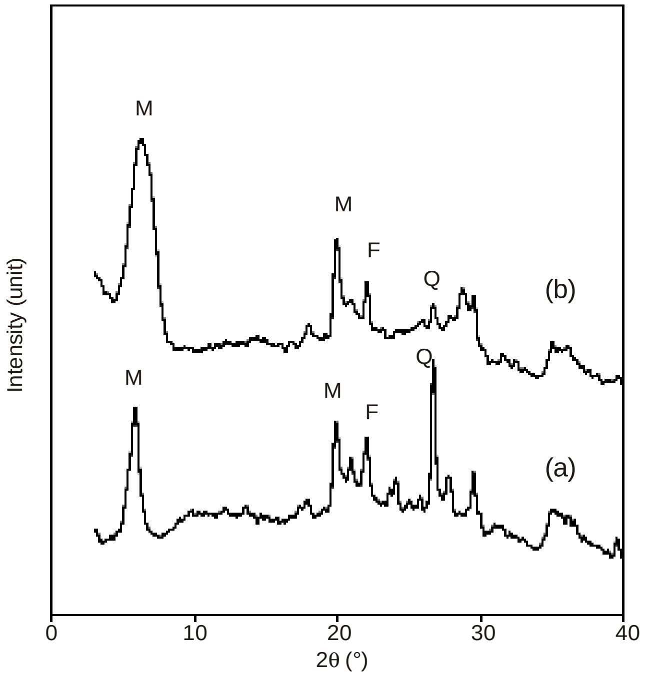
RESULTS AND DISCUSSION

Bentonite analysis: Natural bentonite used was soaked with deionized water overnight to remove impurities that can dissolve in water and attached to the surface of the bentonite. Then, the precipitate was separated from bentonite colloids filtrate and the colloid filtrate was centrifuged. The result was a solid bentonite (grade-2). The filtrate obtained was evaporated until solids bentonite (grade-1) was produced as a product being used. Bentonite characteristic sample as starting material was conducted using XRD, atomic absorption spectrophotometry (AAS) and infrared spectroscopic. Cation contained result in bentonite was performed using AAS as shown in Table-1 indicate that bentonite analysis was Na-bentonite.

TABLE-1
CATION ANALYSIS RESULT ON BENTONITE

Cation type	(%)
Na^+	0.60
Ca^{2+}	0.04

Diffraction result of bentonite using X-ray (Fig. 1) demonstrated that high intensity was in the region 2θ = 5.76° and 19.91° with a value of d = 15.31 Å and 4.45 Å for the sample (a) and 2θ = 6.39 ° and 19.96 ° with value of d = 13.81 Å and 4.44 Å for the sample (b) on which was a typical reflection of montmorillonite samples. These results can be concluded that natural bentonite minerals containing high purity especially in the sample (b) with the loss of impurity type quartz. Infrared spectral data of Na-bentonite samples provide information about the functional groups on the Na-bentonite. Infrared spectra result of Na-bentonite was presented in Fig. 2.



Note: M = monmorilonite, F = Feldspar, Q = Quartz

Fig. 1. XRD pattern from Na-bentonite (a) grade-2 (b) grade-1

Based on Fig. 2, absorption band 3626.17 and 3448.72 cm^{-1} that were identified as a strain -OH vibrational bands of octahedral and ribbon -OH stretch vibration of water molecules. Further it was strengthened by the appearance of absorption bands at wave numbers 1643.35 cm^{-1} which was a buckling -OH absorption bands of water molecules. Absorption band

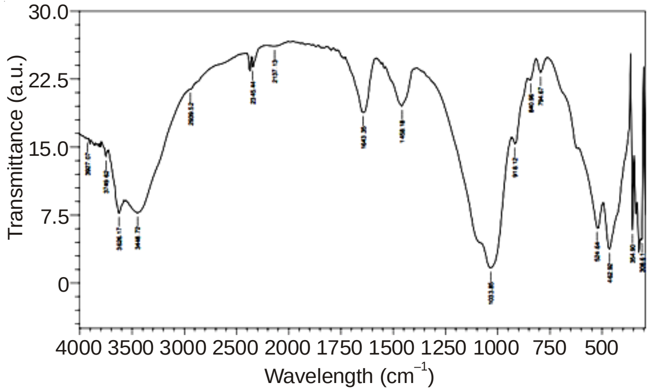


Fig. 2. Infrared spectra of Na-bentonite

at wavenumber 462.92 cm^{-1} showed the bending vibration of Si-O-Si. Absorption band at 794.67 cm^{-1} was characteristic of bending vibrations of O-Si-O, while the vibrational strain O-Al-O appears on local wave number[13] at 918.12 cm^{-1}. The emergence of absorption bands at wave numbers 1033.85 cm^{-1} showed a typical absorption vibrational strain of Si-O-Si in the tetrahedral layer. Besides the absorption at wave numbers around 3448.72 cm^{-1} was the strain -OH absorption band in the octahedral structure (Al-OH). These data also confirmed the results of previous studies[14,15] which showed absorption at wave numbers were almost the same so that the results of the characterization of bentonite with the infrared spectrum showed the presence of functional groups of the tetrahedral and octahedral sheets that was mineral montmorillonite type.

Synthesis of ZrO_2-bentonite composite: Zirconia-bentonite composite was synthesized through intercalation process pillared agent zirconyl chloride octahydrate ($ZrOCl_2 \cdot 8H_2O$) and through the process of hydrolysis produce poly-cation zirconia into inter-layer of Na-bentonite silicate. Polycation zirconia formation process was highly dependent on the degree of polymerization of the species on the zirconia chloride octahydrate solution. Most zirconyl chloride octahydrate species in solution at room temperature formed tetramer zirconia $[Zr_4(OH)_{8+x}(H_2O)_{16-x}]^{(8-x)+}$ that intercalation was able to widen the distance between silicate layers around 7 Å[16]. Nonetheless zirconia ions were known to form stable tetrameric species under acidic conditions and was also considered as the main species in pillared zirconia oligomers solution with structural formula[17]: $[Zr_4(OH)_8(H_2O)_{16}]^{8+}$. Based on the results of hydrolysis, the poly-cation would replace cation on bentonite inter- layer that were easily exchanged and through the calcination of zirconia poly-cation, it would turn into oxides supported between silicate layers of bentonite. Through the formation of the zirconia oxide would be obtained point changes on basal spacing d_{001}, specific surface area and porosity including pore volume, pore size distribution and its adsorption isotherm.

Structural analysis using X-ray diffraction: The results of X-ray diffraction analysis showed that in intercalation stage there has been peak shifting of Na-bentonite on angle $2\theta = 6.39°$ (a) shifting toward intercalation $2\theta = 4.26°$ (b), which means the process has been done. Characterization of zirconia poly-cation intercalation product into silicate Na-bentonite interlayer using X-ray diffraction was shown in Fig. 3(a) and (b). It was characterized by increased basal spacing Na-bentonite d_{001} = 13.81 Å into d_{001} = 20.72 Å for Na-bentonite intercalated.

The change of basal spacing point indicated that there has been poli-cation zirconia $[Zr_4(OH)_8(H_2O)_{16}]^{8+}$ intercalation process in bentonite interlayer. Basal spacing change was determined by calculating the difference between basal spacing d_{001} point of zirconia-bentonite intercalation product with the thickness of the silicate–bentonite interlayer anhydrated or usually written as $\Delta d = (d_{001} - 9.6)$ Å. Based on the calculation formula, there was an increasing interlayer distance in silicate as many as 7.96 Å which be in accordance with the above calculations that the tetramer zirconia intercalation was able to widen silicate interlayer distance to around 7 Å[16]. The results of the analysis for pillarization stage as shown in Fig. 3(c) also showed that there has been shifting peak of Na-bentonite before intercalation at angle $2\theta = 6.39°$ (3a) shifted towards conditions ZrO_2-bentonite $2\theta = 4.45$ ° (3c). The shifting peak was followed by a shifting in basal spacing Na-bentonit d_{001}= 13.81 Å or Δd_{001}= (13.81 – 9.6) Å = 3.21 Å basal spacing ZrO_2-bentonite into d_{001} = 18.9 Å or Δd_{001} = (18.9-9.6) Å = 9.3 Å. Changes in basal spacing showed that pillarization zirconia oxide in silicate interlayer of bentonite has been successfully carried out with silicate increasing in the interlayer distance of (9.3 to 3.21) Å = 6.09 Å.

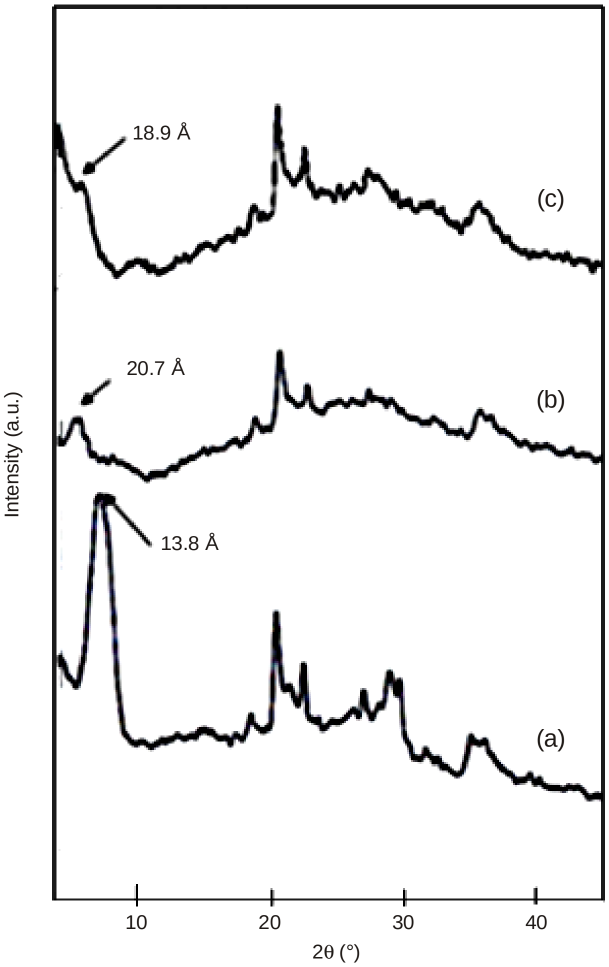


Fig. 3. XRD diffractogram (a) Na-bentonite (b) Zirconia-bentonite intercalation (c) ZrO_2-bentonite pillared

Surface area and porosity analysis: Based on Table-2 it can be seen that ZrO_2-clay composites have a specific surface area five times higher than Na-bentonite. Specific surface area inclining was due to the increased distance of the resulting silicate interlayer of zirconia oxide pillars on bentonite and delamination structure formed. It happened because the process pillarization has also forming card house structure. Process pillarization caused new pores forming into micro-porous, whereas the structure of the card caused the pore size becoming meso-porous. Thus, it was contributing to the increased specific surface area. It was also supported by porous total volume data showed that the total pore volume of the ZrO_2-bentonite was greater than the total pore volume of Na-bentonite. It means that the formation of iron oxide into zirconia silicate interlayer can improve the porosity of bentonite. Pillarization increased bentonite porosity as showed in Table-2. The table showed that the ZrO_2-bentonite was causing total pore volume increased.

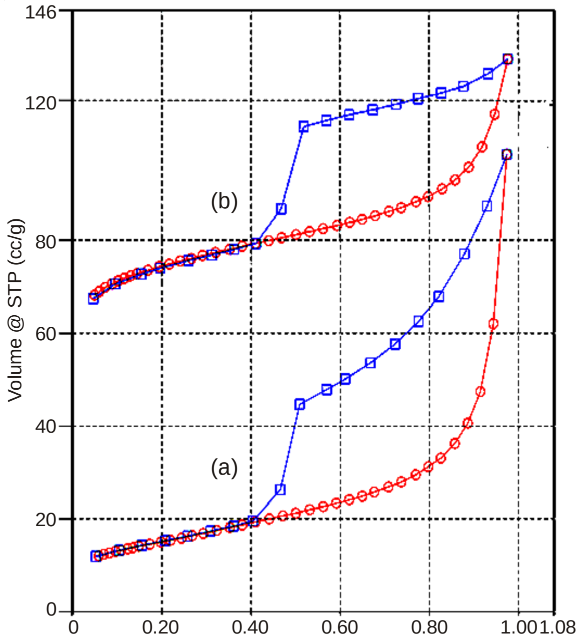


Fig. 4. Adsorption-desorption isotherms graph on (a) Na-bentonite (b) ZrO_2-bentonite

TABLE-2
ZrO_2-BENTONIT AND Na-BENTONITE POROSITY

	Na-Bentonite	ZrO_2-Bentonite
Surface area	52.830 (m^2/g)	269.165 (m^2/g)
Pore volume	0.152 (cc/g)	0.204 (cc/g)

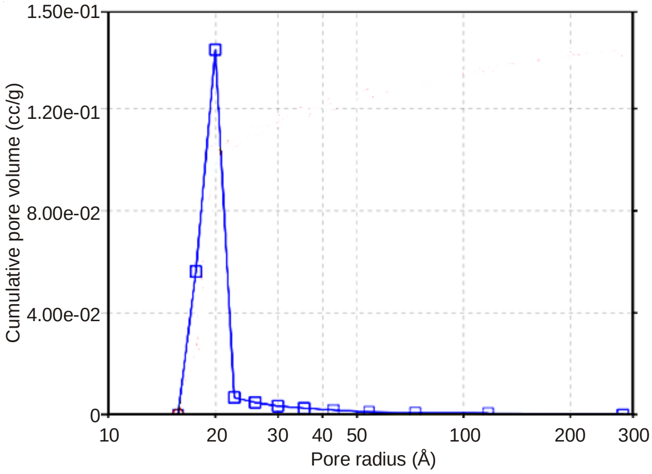


Fig. 5. Size pore distribution on ZrO_2-bentonite

The total of pore volume was combination of the volume of microporous with mesoporous volume indicated the pore size distribution in microporous and mesoporous bentonite shape. This phenomenon was supported by the results of research[15-17] on which stated that the pore size distribution in the pillared clays consists of two types of microporous pore size and mesoporous pore size. Pore size was caused by pillared layer and microporous pore size was caused by the formation of mesoporous delamination in the bentonite structure.

The results analysis of adsorption-desorption hysteresis graphs on Fig. 4 reinforced that zirconia oxide pillarization on bentonite was able to increase the porosity of natural bentonite characterized by the ability to absorb N_2 gas higher than in natural bentonite. It can be stated that ZrO_2-bentonite composite were bimodal pore size distribution as in Fig. 5 *i.e.* pore structure on microporous and mesoporous size. Total pore of ZrO_2-bentonite composites were relatively higher than the number of pores on Na-bentonite (indicated by the total pore volume of the composite is greater than the total pore volume of Na-bentonite). It result N_2 adsorption capability of the composite was relatively higher than in Na-bentonite.

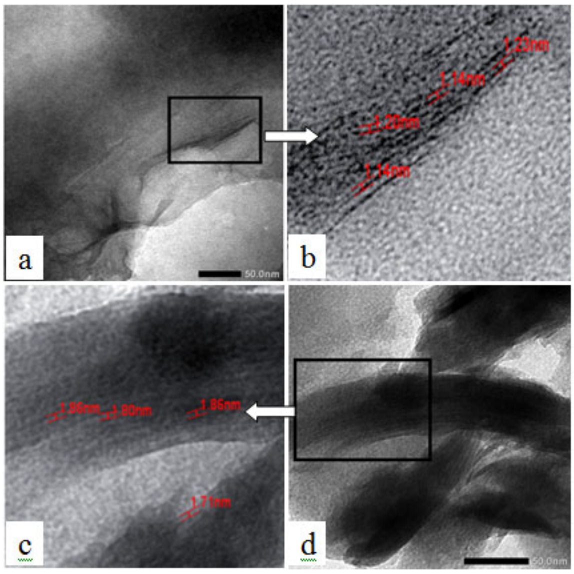


Fig. 6. TEM (a,b) Na-bentonite (c,d) ZrO_2-bentonite

Morphology analysis using TEM: TEM analysis was used to determine the morphology and size structure of Na-bentonite and bentonite-ZrO_2 composites. TEM characterization result was presented in Fig. 6(a,b). Those figures were the morphology of Na-bentonite in the amount of Na-bentonite interlayer distance varies 11.4-12.3 Å. While similar results were also obtained interlayer magnitude distance pillarization on ZrO_2-bentonite in Fig. 6(c,d) based on the TEM photograph varies between 17.1-18.6 Å.

The results obtained by measuring the interlayer distance of clay-ZrO_2 composites showed that most of the material has microporous size. Increasing the interlayer distance could be caused by metal oxides intercalation or pillarization as well as delaminated. Bentonite delaminated could be generated from the 3-dimensional structure of the cation aggregation or nanoparticles ZrO_2. Overlapping between bentonite silicate layers and metal cation aggregates in the outer layer of bentonite was causing delamination formation of mesoporous structure characterized by dilation of basal spacing d_{001}[15-17]. Another characterization results such as pore size distribution in the Fig. 5 explained that there were two types of pores that contribute to pore size *i.e.* microporous and mesoporous. Moreover, the pore size was more predominantly by microporous pore size as well as increasing of bentonite silicate inter layer distance was still in the range of microporous (18.9-11.4 Å). Thus it can be seen that the increasing of surface area and pore volume was due to new formation of microporous. It was due to the zirconia oxide rather than the effect of delamination. The result was also reinforced by TEM diffraction data in Fig. 7 on which showed that pillarization process could increase bentonite crystallization structure. The occurrence of new particle on bentonite inter layer could be predicted as pillared zirconia oxide. The result proved that natural bentonite pillarization was successfully performed without any damage to the structure of bentonite by the presence of zirconia oxide which serves as pillared on natural bentonite between silicate layers.

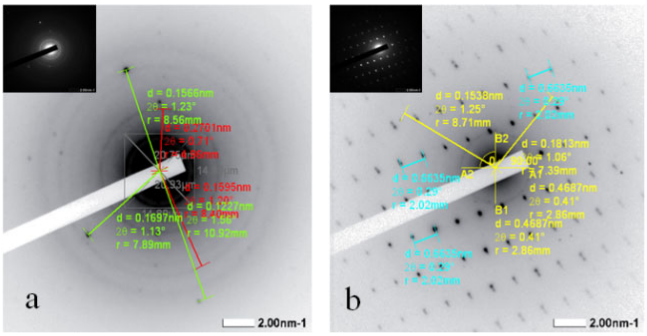


Fig. 7. TEM diffraction (a) Na-bentonite (b) ZrO_2-bentonite

Conclusion

Zirconia pillared bentonite has been synthesized successfully which can be proved from characterization results. Characterization towards bentonite pillared synthesis result was performed using XRF, XRD, TEM and analysis of N_2 adsorption/desorption. The analysis showed that the surface area and pore volume of ZrO_2 pillared bentonite increased from 52.830 m^2/g and 0.152 cc/g into 269.165 m^2/g and 0.204 cc/g. Through XRD and TEM analysis also showed that the presence of metal oxide ZrO_2 was able to increase the basal spacing of 1.38 nm to 1.89 nm and raised no damage to the structure of bentonite.

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REFERENCES

1. A. Olad, Polymer/Clay Nanocomposites, Advances in Diverse Industrial Applications of Nanocomposites, Publisher InTech Europe, Croatia, pp. 113-138 (2011).
2. I.P. Okoye and C. Obi, *Res. J. Appl. Sci.*, **6**, 447 (2011).
3. A. Gil and M. Montes, *Langmuir*, **10**, 291 (1994).
4. A. Gil, M.A. Vicente and L.M. Gandia, *Micropor. Mesopor. Mater.*, **34**, 115 (2000).
5. C.B. Molina, J.A. Casas, A.H. Pizarro and J.J.Rodriguez, Pillared Clays as Green Chemistry Catalysts: Application to Wastewater Treatment, Nova Science Publishers, Inc (2011).
6. S. Yamanaka and G.W. Brindley, *Clays Clay Miner.*, **27**, 119 (1979).
7. R. Burch and C.I. Warburton, *J. Catal.*, **97**, 503 (1986).
8. J.T. Kloprogge, *J. Mater. Porous*, **5**, 5 (1998).
9. F. Figueras, *Catal. Rev., Sci. Eng.*, **30**, 457 (1988).
10. S. Yamanaka and G.W. Brindley, *Clays Clay Miner.*, **26**, 21 (1978).
11. R.T. Yang and M.S.A. Baksh, *AIChE J.*, **37**, 679 (1991).
12. G. Fetter, V. Hernández, V. Rodríguez, M.A. Valenzuela, V.H. Lara and P. Bosch, *Mater. Lett.*, **57**, 1220 (2003).
13. P. Komadel, *Clay Miner.*, **38**, 127 (2003).
14. K. Katti and D. Katti, Effect of Clay-Water Interactions on Swelling in Montmorillonite Clay, Proc. ASCE Engineering Mechanics Conference, Seattle, WA, USA (2002).
15. K. Wijaya, *Indonesian J. Chem.*, **2**, 12 (2002).
16. R. Issaadi, F. Garin, C.E. Chitour and G. Maire, *Appl. Catal.*, **207**, 323 (2001).
17. K. Ohtsuka, Y. Hayashi and M. Suda, *Chem. Mater.*, **5**, 1823 (1993).