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The Textural properties of Zirconia pillared Indonesian Bentonite

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Abstract : Zirconia pillared bentonite is interesting for used in catalysis field as a support or catalyst. In this study, to prepare pillared bentonite intercalated with zirconia we used natural bentonite from Boyolali clays, one part of Indonesian region.The mixture was obtained by mixing the suspensions of bentonite and zirconium chloride octahydrate solution followed by drying (at 343 K) and calcination (at 673 K). The changes specific surface area; the pore volumes were studied by varying the zirconia concentration in the composite. The measurement of SEM and nitrogen adsorption results of the composite indicated that the zirconia was successfully distributed as pillars. The analysis showed that the surface area and pore volume of ZrO_2 pillared bentonite increased from 29.7 m^2/g and 0.09 cc/g to 194.2 m^2/g and 0.176 cc/g, respectively. The SEM analysis also showed that the presence of metal oxide of ZrO_2 was surface properties of pillared bentonitebe more porous than bentonite and it did not damage the structure of bentonite.
Key word : pillaredbentonite; zirconia; surface area; porous.

Introduction

Pillared interlayered clays include a new family of clays based on two-dimensional materials, and are used in adsorption and catalysis.Pillaring of clay with inorganic polycation results in producing thermally stable rigid cross-linked materials with a large surface area, a particular porous texture, and acidity.The properties of pillared clays depend on several factors such as preparation conditions of the polycations, the method of intercalation, washing and drying steps. The most commonly studied are the zirconium intercalated clay using zirconium chloride octahydrate solution ($ZrOCl_2 \cdot 8H_2O$) as a precursor has been used to form stable oxide pillars between layers in bentonite clays[1–6]. The pillared process can lead to the clay porosity getting bigger and homogeneous and inter-layered character becomes relatively more stable. The zirconia–pillared bentonite is a promising support for catalysts of several oil refining processes (hydrotreating, hydrocracking, and catalytic cracking). Bentoniteis a good binder because bentonite hydration results in the spontaneous decomposition ofits particles to smaller sizes than 1 mm and is an essential swelling of the system. The introduction of hydrated and activated bentonite into zirconium polycations enables to control of the structure porosity and texture of the resulting composite. The present work, we studied the formation of zirconia- pillared bentonite composition and to observethe textural properties of the zirconia- pillared bentonite as derivative supports.

Experimental

Clay sample

A sample of natural clay was collected from an open clay deposit in Boyolali, Central Java, Indonesia. The clay sample was dissolved in deionized water for 24 hours. Furthermore, colloidal solution filtrate was centrifuged to obtain its precipitate that was separated from its filtrate by evaporation to get the bentonite. The solid bentonite was dried at 110^{o}C and sieved to 150 mesh size, the resulting product was named as LFB.

ZrO_2-pillared bentonite synthesis

The transformation of natural bentonite into pillared clay required the use of pillaring solution prepared by variation in concentrations of 0.05; 0.10; and 0.20 M $ZrOCl_2.8H_2O$Then the solution was refluxed at 70^{o}C for 2 hours under constant stirring. After that, pillaring solution was added dropwise to ca. 8 g of clay in 800 mL suspensions with constant stirring and aged overnight at room temperature. Afterward, the pillared clay suspension was filtered and washed with distilled water, finally neutralized until Cl^-free. The pillared clay was air-dried at ambient temperature and 80°C for 8 hours, then calcinated at 400°C for 4 hours. The resulting product was sequentially named as LFBZ05; LFBZ10; LFBZ20.

Characterization of ZrO_2- pillared bentonite

BET NOVA 1994- 2010 Instrument version 11:0 was used to determine the specific surface area and porosity of bentonite. The Scanning Electron Microscopy (SEM) micrographs were obtained using JEOL JSM - 6510 at 20 kV to observe the surface morphology of the pillared clays.

Results and discussion

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 colloidal filtrate by centrifugation. The filtrate obtained was evaporated to get solid bentonite. The morphology and homogeneity of the bentonite and ZrO_2–pillared bentonite were investigated using SEM technique. The SEM micrographs show results that the surface properties of bentonite before pillarization is porous and dark. On the other hand, ZrO_2–pillared bentonite giving the surface properties image of which is more porous and clear.The SEM images in Figure.1 showed that there was an enlarging space between the layers due to the replacement of interlayers space by zirconium polycations, so the micrographs of surface properties of ZrO_2–pillared bentonitebe more porous than bentonite. Results of previous studies using XRD and TEM analysis reinforces these findings, which change in basal spacing showed that pillarization zirconia oxide in silicate interlayer of bentonite had been successfully carried out with silicate increasing in the interlayer distance. This indicates that the presence of metal oxide ZrO_2 on the bentonite interlayer no damage to the structure of bentonite[7-10].Based on Table 1 it can be seen that ZrO_2-bentonite 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 is due to the formation of card house structure during the pillarization process.

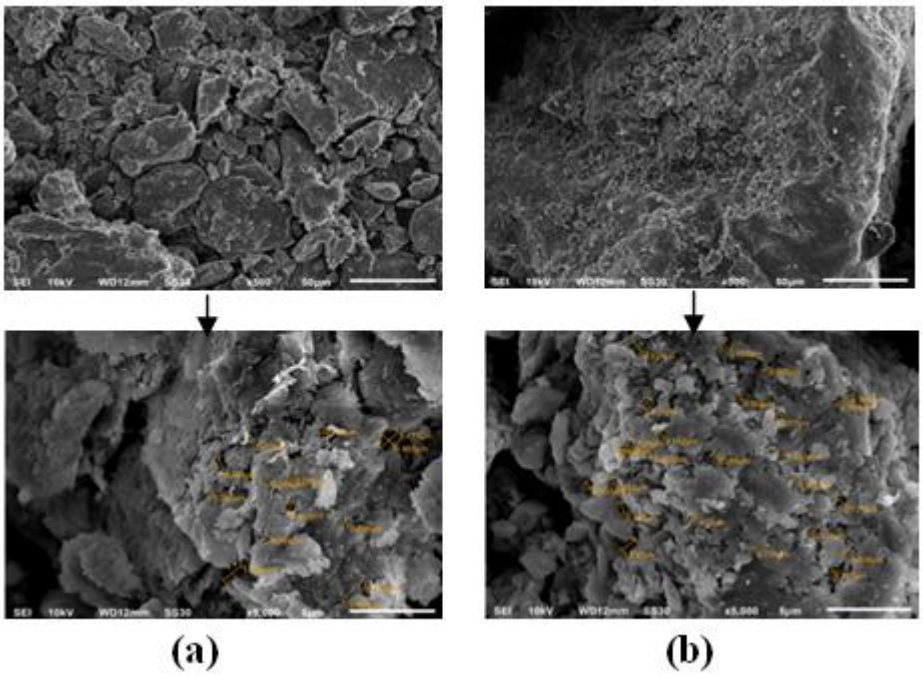

Figure1. SEM image of bentonite andZrO_2- pillared bentonite

Pillarization process caused new pores that form micro-porous, whereas the structure of the card caused the pore size becoming mesoporous. The natures of the intercalated species yield the idea of the presence of pore groups. Also, the pore quality is proportional to pillar concentration. Moreover, based on Table1 the particular total pore volume (V_t) derived from adsorption isotherms, increases with decreasing pillar population. The BET and Langmuir approaches were served to analyze N_2 adsorption isotherms.

Table 1.Textural properties of Bentonite and Zr-Pillared Bentonite

Sample	S_{Lang} (m^2/g)	S_{BET} (m^2/g)	$S_{\mu p}$ (m^2/g)	S_{ext} (m^2/g)	V_p (cc/g)	$V_{\mu p}$ (cc/g)	Pore Radius(Å)	$ZrOCl_2.8H_2O$ (M)
LFB	50.4	29.7	0.00	29.7	0.090	0.00	15.40	-
LFBZ05	277.1	194.2	74.5	119.7	0.176	0.032	17.27	0.5
LFBZ10	256.7	194.8	108.9	85.9	0.151	0.045	17.28	1.0
LFBZ20	272.3	176.2	96.4	79.8	0.154	0.052	17.33	2.0

The methods were applied for P/P_o values between 0.05 and 0.35 whose results are shown in Table 1. The adsorption isotherms give a good fit on both the Langmuir and BET equations for the Zr-pillared bentonite materials. Furthermore, Table 1 shows the increase of external surface areas obtained from the t-plots with the pillar density reduction.Table1.demonstrates the filling of pores with different sizes[11-12], with a general decrease in reduced pillar density. The total of pore volume was a 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[13-14] 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 resulted from the formation of mesoporous delamination in the bentonite structure. The analysis results of adsorption-desorption hysteresis graphs on Fig.2 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. The zirconium pillared bentonite isotherms are more of Type IV-like shown in Fig.2, suggesting a significant contribution of surface area, in particular for the sample LFBZ05. For the Zr-pillared bentonite materials, at relativelylow pressure, a reduction of the pillar density causes an adsorption decrease. The contribution of S_{ext} to the total surface area tends to increase with the reduced pillar density.

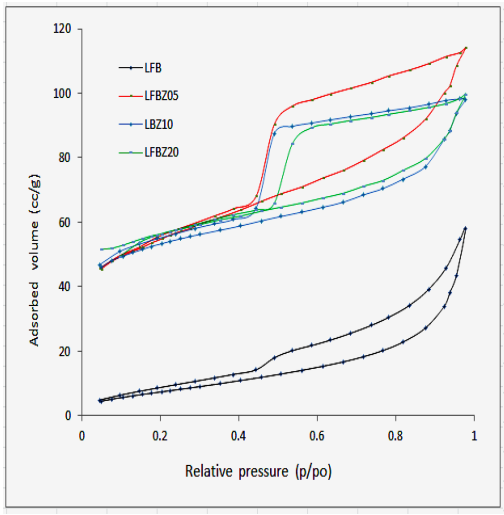

Figure 2.Nitrogen adsorption isotherm

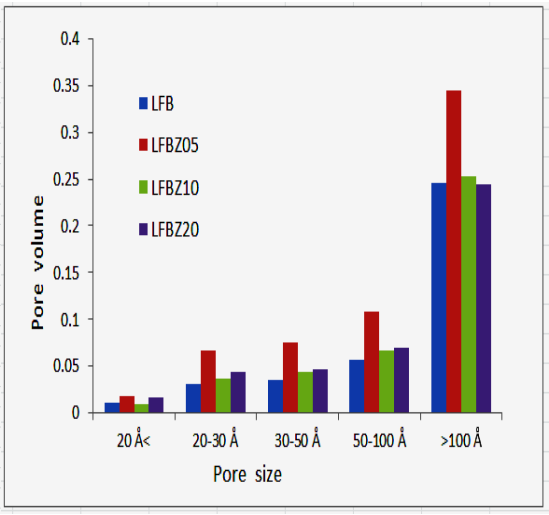

Figure 3. Distribution of pore size

The total pore volume increases systematically with decreasing pillar density. This can be explained by the increase in lateral pillar distance, leading to the development of a total sorption capacity of the pore system. It can be concluded that the porous structure of the Zr-pillared bentonite comprises of a huge amount of micropores. Based on works by[15], the N_2-adsorption isotherms of pillared bentonite related to the adsorption within the micropores is more valuable when the adsorption is made on the external surface. Table.1 indicates that the S_{ext} tends to increase with decreasing pillar concentration. From this work, it is noticeable that the t method provides important information about the porous structure of pillared bentonite. From Table 1 and plots presented in Fig.3, it follows that for the Zr-pillared bentonite, the adsorption isotherms are fitted by both the Langmuir and BET equations. Indeed, for those samples having the largest fraction of such pores LFBZ05, the difference between S_{Lang} and S_{BET} is the most pronounced. According to S_{Lang}, the surface area derived from the t-plots increases with decreasing pillar density. For the sample, LFBZ05 has the highest contribution of micropores, and the surface areas derived from both methods are very close to each other. Based on this work, it is possible to conclude that the BET method gives underestimate result, whereas the Langmuir approach gives overestimates resultthis is in good agreement with the results reported[15].Additionally, the pillar density results are decreased with an increase in the external surface of the samples. This provides valuable information about textural differences[16]. Moreover, for all kinds of pillared clays, the content of such surface micropores decreases when the pillar density decreases.

Conclusion

Zirconia pillared bentonite has been synthesized successfully which can be proved from characterization results. Through SEM analysis also showed that the presence of metal oxide ZrO_2 was more porous and clearand raised no damage to the structure of bentonite. The analysis with N_2 adsorption isotherms showed that the surface area and pore volume of ZrO pillared bentonite increased from 29.7 m^2 and 0.090 cc/g into 194.2 m^2/g and 0.176 cc/g, respectively. The BET method underestimates the total surface area of these pillared bentonite, whereas the Langmuir approach overestimates it. The methods applied show that the zirconia-pillared bentonite contain a significant amount of micropores and mesopores. Changes in the surface area, micropore volume and pore size distribution of these materials are caused by the variation of the pillar density.

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References :

1. Yamanaka S. and Brindley G.W.,1979,High Area Solids Obtained by Reaction of Montmorillonite with Zirconyl Chloride. *Clays Clay Miner*., 27(2), 119–124.
2. Farfan E.M., Sham E. and Grange P.,1992, Pillared Clay: Preparation and Characterization of Zirconium Pillared Montmorillonite. *Catal.Today*.,15, 515–526.
3. Farfan E.M., Dedeycker O. and Grange P.,1991, Zirconium Pillared Clays, Influence of Basic Polymerization of the Precursor on their Structure and Stability. *Catalyse et chimie des matériauxdivisés*.,63, 337–343.
4. Awate S.V., Waghmode S.B., Agashe M.S.,2004, Synthesis, Characterization and Catalytic Evaluation of Zirconia pillared Montmorillonite for Linear Alkylation of Benzene. *Catal.Communications*.,**5**, 407–411.
5. RangaRao G. and Gopal Mishra B. A.,2005,Comparative UV–vis-diffuse Reflectance Study on the Location and Interaction of Cerium Ions in Al- and Zr-pillared Montmorillonite Clays. *Materials Chemistry and Physics*.,89, 110–115.
6. Chen M**.**, Fan L., Qi L., Luo X., Zhou R., Zheng X.,2009,The Catalytic Combustion of VOCs Over Copper Catalysts Supported on Cerium-modified and Zirconium-pillared Montmorillonite. *Catal. Communications,*10, 838–841.
7. Suseno,A.,Wijaya ,K.,Trisunaryanti,W., and Shidiq, M., 2015, Synthesis and Characterization of ZrO_2-Pillared Bentonites, *Asian J Chem;* Vol. 27(7), pp 2619-2623
8. Utubira Y, Wijaya K, Triyono, Kunarti E.S,2016, Microwave Assisted Preparation of Zirconia-Pillared Bentonite , *Int J Chem Tech Res.* vol.9(04), pp 475-482
9. Muzakky, Prayogo I, Susiantini E,2015, Elimination of Hydroxo Zirconium Complex using the Combination of Polar Organic and Reflux at the Preparation of Zr-Pillared-Clay, *Int J Chem Tech Res.* vol.8(1), pp 22-29
10. Sekewael, S.J., Wijaya ,K.,Triyono and Budiman A., 2016, Microwave Assited Preparation and Physico-Chemical Properties of Mixed Oxides Silica-Zirconia Montmorillonite K10 Nanocomposite, *Asian J Chem;* Vol. 28(10), pp 2325-2330
11. Gil, A., Massinon, A., Grange, P.,1995, Analysis and comparison of the microporosity in Al, Zr and Ti pillared clays. *Microporous Mater*., 43: 69.
12. Gil.A., Montes. M.,1994, Analysis and comparison of the microporosity in pillared clays. *Langmuir*, 10: 291.
13. Wijaya, K., *Indonesian J. Chem.*, 2, 12(2002).
14. R.Issaadi, F.Garin,C.E.ChitourandG.Maire,*Appl.Catal.*,207,323 (2001).
15. Remy, M.J., Vieira, A.C., Coelho, G., 1996, Surface area and microporosity of 1.8 nm pillared clays from the nitrogen adsorption isotherm,*Poncelet Microporous Mater*., 7: 287.
16. Arfaoui-Rhouma, S., Frini-Srasra, N. and Srasra,E. 2011, The textural property of chromium pillared clay, *Afr. J. Pure Appl. Chem, Vol. 5(10),* 339-345

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