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Elimination of Hydroxo Zirconium Complex using the Combination of Polar Organic and Reflux at the Preparation of Zr-Pillared-Clay

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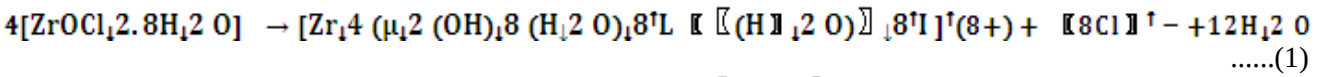
Abstract: The elimination of hydroxo zirconium complex using the combination of polar organic and reflux at the preparation of Zr-pillared-clay has been studied. This study also will introduce some imaging results of various zirconium concentrations before and after the calcination process at 600°C. The imaging results was observed by some instruments such as X-ray Diffraction (XRD), Transmission Electron Microscopy (TEM), UV-Vis Diffuse Reflectance Spectroscopy (UV-Vis DRS) and Surface Area Analysis *(SAA)*. The results of imaging by using XRD pattern showed the existing of displacement of angle 2 Θ towards the left from 9.08 2Θ to 5.92 2Θ, whereas the imaging by using UV-Vis DRS showed the shifting of wavelength from 120 nm to 145 nm. By varying Zr concentrations, the absorbance of results decreased due to an increasing degree of materials porosity. The observed of imaging result by using of TEM showed that the addition of glycerol seem more porous and opaque compared to that of which using ethylene glycol. The results of Zr-pillared clay at calcinating process showed the displacement of angle from 9.08 2Θ to 8.87 2Θ and 8.64 2Θ respectively for 0.01 M Zr with ethylene glycol and glycerol. While the visualization image of pillared of 0.01 M Zr with ethylene glycol was more opaque and porous compared to that of which using glycerol. Visualization of the image of N_2 adsorption on Zr-intercalated clay without ethylene glycol or glycerol, in fact had a smaller volume compared to that of which using ethylene glycol or glycerol. At the same concentration of Zr above, the volume of porous materials would not significantly increase and the existence of meso porous material (2-50 nm) was proven.
Key words : XRD, SEM, UV-Vis DRS, SAA, Zr-intercalated-clay, Zr-pillared-clay.

Introduction

One of superior home made products by Center for Acelerator Science and Technology (CAST) - National Nuclear Energy Agency-Yogyakarta is ZrOCl2.8H2O (ZOC). This product was as the result of an implemented National Research Projects funded via INSENTIF RISET SINAS in 2013-2014. As a superior ingredient , ZOC was economically and highly utilized as a Zirconium base catalysts in petrochemical industry and adsorption processes[1]. The basic phenomenon occured in the preparation of Zr-pillared clays is the occurance of ion exchange of interlamellar cations (1A or 2A groups of Mandeleiev) for bulky cationic species (oligomer is a cation with large size and high charge). It is obvious that only the swelling clay minerals of cation exchanger can be pillared, if the condition of Zr as precursor solution is satisfied[2]. The Zr-pillared clay difficulties has long been known by Farfan[3] since the freshly $ZrOCl_2$ solution have produce Zr oligomer whose forms zirconium square planar complex structure like $[Zr_4(OH)_{l4}(H20)^{2+}$, then It can be suppressed as a pillared

result. Hu[4] by using of high-energy X-ray scattering (HEXS), found that moiety of the average oligomerics Zr was larger than the tetrameric building unit of $[Zr_4(OH)_8(H2O)_{16}]^{(8+),}$ and Its species is generally understandably dominate in the solution. While Chaabene[5], by using of Nuclear Magnetic Resonance (NMR) have studied the tetranuclear hydroxo zirconium complex in aqueous solution. The freshly Zr prepared solution produced in this study was dominated by octameric polycations as depicted with the following reaction[5],



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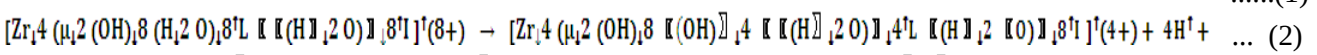

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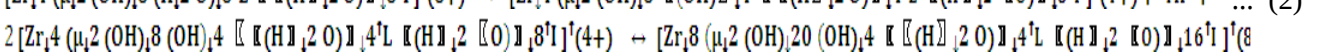
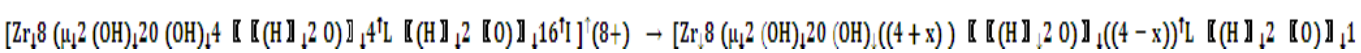


.....(3)

(L is labile and I is inert polyaquo complex)

The properties of freshly prepared $ZrOCl_2$ solution is acidic and hydrolysis of which producing labile water molecules that will decrease its pH as be explained below,



..(4)

Furthermore, the decrease of pH will precipitate the polymeric octamer species and immediately damage the Zr-pillared clay. There are several ways to overcome those problems such as by refluxing of pillared solution at 90°C - 1OO°C, but most materials are still in the form of macro-porous[3]. Then, by adding amount of SO_4^{2-} ions or ammonium sulfate salt, It will turn out to be a corrosive sulphate [5,6]. Other studies was conducted by adding the polar organic compounds for eliminating octameric polycations and It produced a meso porous but still in small degree [6,7]. It turns out that all previous studies were dissatisfied due to their high meso-porous products obtained. In this recent study, we combined an organic compound and refluxing method for gaining the greater number of meso porous products. It was studied further for eliminating hydroxo zirconium complex **by** using the combination of polar organic and reflux at the preparation of Zr-pillared-clay. The polar organic such as glycerol and ethylene glycol was chosen for eliminating the influence of the labile or inert water molecules of polyaquo zirconium complex as ionic cluster species. This study was experimentally conducted by varying of Zr concentrations to gain an optimal results before and after calcining process at 600°C. Evaluation of the results were done by some instruments such as X-ray Diffraction (XRD) and UV-Vis Diffuse Reflectance Spectroscopy (UV-Vis DRS) for imaging of intercalated and pillared products. Transmission Electron Microscopy (TEM) and Surface Area Analysis (SAA) for imaging the properties of surface materials.

Experimental

Materials

Clay as Na-bentonite, Zirconium oxide chloride ($ZrOCl_2.8H_2O$) or ZOC for short name was a home made product by the Center for Accelerator Science and Technology (CAST)- National Nuclear Energy Agency (NNEA)-Yogyakarta, Glycerol and Ethylene glycol made by E.Merck.

Zr-Intercalated and pillared clay methods

The Zr-intercalated and pillared clay methods were carried out in three stages, where as the first, the second and the third were series of the prepared ZOC solution containing 0.01 M Zr, 0.02 M Zr and Zr 0.05 M Zr respectively[8]. First series was added by 5 ml of ethylene glycol and the second series was replaced by glycerol[9]. Second, both of all series were added by 100 g Na-bentonite, then all of them were immediately refluxed at temperature of 100°C for 3 hours[10]. Furthermore, their anion impurities were removed by using hot water and the product of which was then dried at the room temperature as Zr-intercalated-clay product. Third, all of those Zr-intercalated-clay products were calcined at temperature of 600°C as Zr-pillared-clay. Then as much as 5 gr products were analyzed by some instruments such as X-ray Diffraction, Transmission Electron Microscopy (TEM),UV-Vis Diffuse Reflectance Spectroscopy (UV-Vis DRS) and *Surface Area Analysis (SAA)* for evaluation of image results.

Results and Discussion

1. Elimination of hydroxo zirconium complex by glycerol at Zr- Intercalated-clay

One of the successful intercalation process of Zr-intercalated clay is that by looking at the changing of XRD pattern or identified by other instruments[11,12]. The intercalation process of Zr-intercalated clay will be influenced by the concentration of Zr in aqueous phase due to the formation of zirconium hydroxo complex[5]. In the following figures can be seen the effect of glycerol as a polar organic compound on the XRD patterns changing in the intercalation process of Zr-intercalated clay.

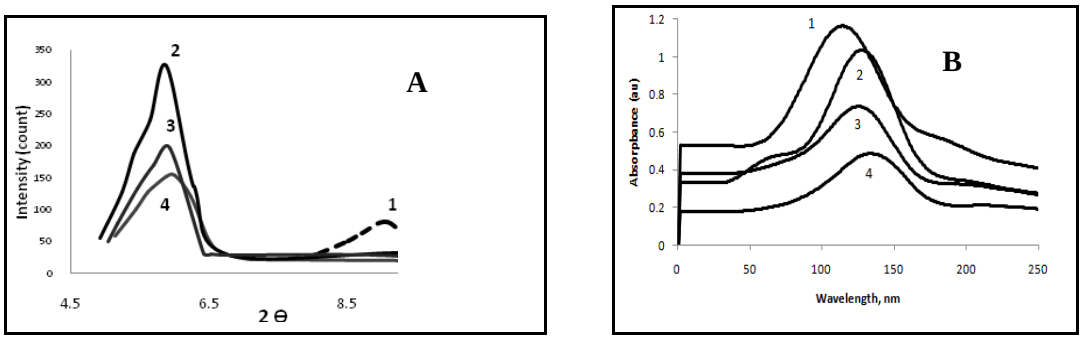


Figure 1, The image of XRD (A) and DRS UV-Vis (B) of Zr-intecalated clay without glycerol(1), and with glycerol at various concentrations of 0.01 M Zr (2), 0.02 M Zr (3) and 0.05 M Zr (4)

In Figure (1.A), it can be seen that the role of glycerol in intercalation process of Zr-intercalated clay lead to the significantly displacement of 2Θ angle compared to which process without glycerol. The displacement of that XRD pattern were obviously seen at the peak of 9.08 2 Θ angle (1.A.1) towards the left at the peak of 5.9 2Θ angle (1.A.2). This displacement proved that that labile and inert polyaquo zirconium can be eliminated by glycerol. Furthermore, the products of Zr-pillared clay at various Zr concentrations (1.A.2 , 1.A.3 and 1.A.4) turned out to be the cause of decreasing their intensity, which was influenced by the large number of Zr insertions into the interlayer as such that the clay interlayer structure would be more opened.

In Figure (1. B) can be seen the comparison results of DRS UV-Vis patterns of the products without glycerol (1.B.1) and with glycerol (1.B.2), that will lead to displacement of wavelength from 120 nm to 145 nm. The most probable one is that the occurence of delocalization of Zr with alkali cations such as Na or Ca on the bentonite clay interlayer. Furthermore, this phenomenon strengthen about elimination of labile and inert polyaquo zirconium by glycerol. At the moment , as the concentration Zr varied from Zr (1. B.2 : 1.B.3 and 1. B. 4) in fact that its absorbances result will be decreased. This experimental data agrees with the previous studies of Al-Kady[12] who proved that the images result of Zr-intercalated-clay identified by XRD which is shown by the displacement of 2Θ angle. This phenomenon will change the natural properties of those materials tobecome meso porous materials. Whereas Liu.Q[13] by using DRS UV-Vis had proven the incorporation of Zr into the framework of clay as Zr-intercalated-clay with the formation of porous materials. These evident will strengthen the decrease in the porosity properties of materials which can be seen in Figure 2,

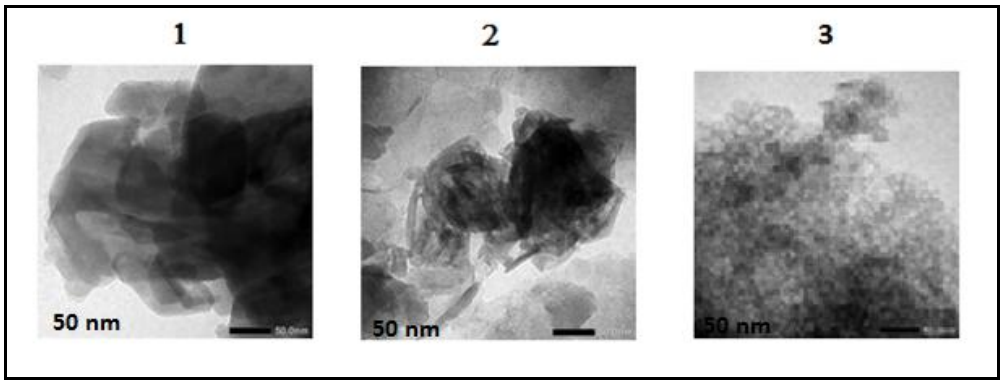


Figure 2, The TEM image of Zr-intercalated clay at the condition without (1) and with 0.01 M Zr (2), 0.02 M Zr *glycerol* (3) at 50 nm

In Figure 2, it can be seen the image of surface properties of Zr-intercalated clay without additing glycerol (2.1) is amorph, porous and dark. On the other hand, with the addition of glycerol to Zr-intercalated clay giving the surface properties image of which is more porous and clear (2.2). The TEM images in Figures (2.2 and 2.3) showed that there was an enlarging space between the layers due to the replacement of interlayers space by Zr cation so the image of surface properties of Zr-intercalated clay be more porous. Refer to Figure 2 , the images data of Zr-intercalated-Clay product of this recent finding agrees with the previuos finding of Samantaray[14] which is an evident that there were agglomerated particles in that product due to cation exchange process happened on interlayers of the clay.

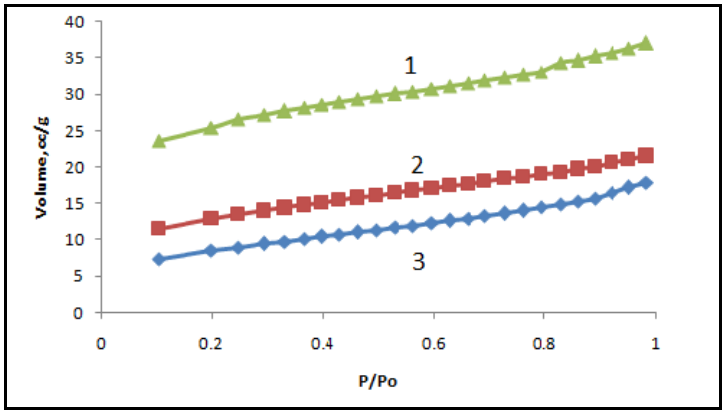


Figure 3, The graphs of isotherms N_2 adsorption at 77^{o}K for 0.01 M Zr (1), 0.02 M Zr (2) *with* glycerol and without glycerol(3)

In Figure 3, it can be shown the graphs of N_2 adsorption on Zr-intercalated clay without glycerol apparently having a maximum volume of 17.8 cc/g at maximum pressure (P/Po) (3.3). Whereas by increasing of Zr concentrations there would be an increase of volume from 21.55 cc/g to 37.00 cc/g at the maximum pressure (P/Po) (3.2 and 3.1). This recent finding agrees with the previous studies of Groan[10] and Zhang[11] in which the graphs of isotherms N_2 adsorption in Figure 3 were still linear, and the materials with a macro-size porous were dominant.

2. Elimination of hydroxo zirconium complex by ethylene glycol at Zr- intercalated-clay

Interlayer space of clay (bentonite) consist of many sheets of tetrahedral (T) and octahedral (O), between which 2 sheets space (2:1) as TOT layer were inserted. In the swelling condition, the spaces will adsorb the hydrated cations or polar organics. Due to its polar properties, therefore etylene glycol will dissolve the labile and inert polyaquo zirconium and eliminate the disturbance of intercalation process[9].

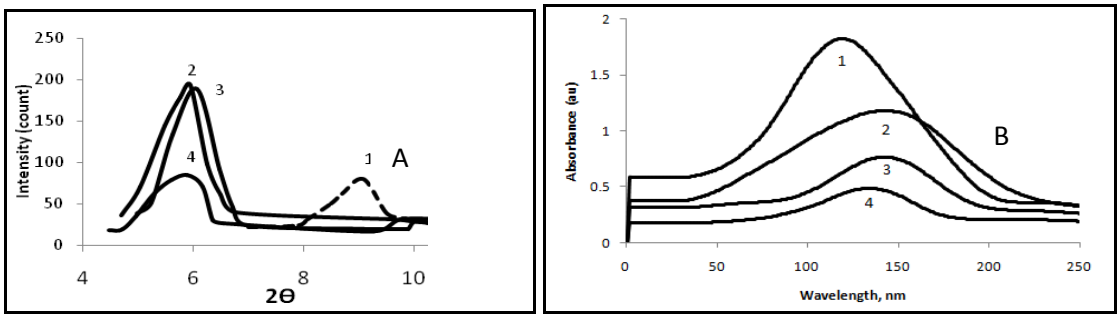


Figure 4, The image of XRD (A) and DRS UV-Vis (B) of Zr-intecalated clay without glycerol (1), and with ethylene glycol at various concentration of 0.01 M Zr (2), 0.02 M Zr (3) and 0.05 M Zr (4)

The same phenomenon is shown in Figure 4 (A) that there had been a displacement of 2 Θ angle towards the left as seen from Figures (4.A.1) to (4.A.2), consequently Zr will insert into the interlayers bentonite. Furthermore the higher of Zr concentration turned out to decrease the intensities of 2Θ angle (Figures 4 A.2 , 4.A.3 and 4.A.4). This might due to the increase of the porosity properties of materials formed. Then, this current study does agree with the studies of Samantaray[14] that the increase of intercalan materials such as Zr in interlayer clay will decrease its intensity.

This phenomenon was confirmed by experimental data shown in Figure 4(B), in which the occurence of the higher displacement of wavelength was happened. In addition to the occurence of Zr dislocation, this phenomenon proved that the more porous materials had been produced by the increase of Zr concentrations (Figures 4.B.2 ; 4.B.3 and 4.B.4). Therefore , this current finding was agree with the previous studies of Suraja[15] and Costa[16] in which there was a decrease of absorbance at DRS UV-Vis which is caused by an increase of intercalan such as Zr in the interlayer montmorillonite clay. This current finding data will be confirmed by the image products of surface properties as shown in Figure 5,

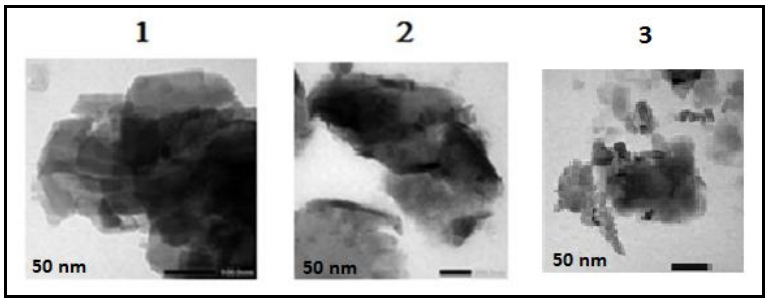


Figure 5, The TEM image of Zr-intercalated Clay without ethylene glycol (1) and with ethylene glycol of 0.01 M Zr (2), 0.02 M Zr (3) at 50 nm

In Figure 5, it can be shown in the TEM images of surface properties at 50 nm intercalation without Ethylene glycol (Figure 5.1) which was amorph and porous as well as dark. While the TEM image of intercalation products with ethylene glycol was apparently more porous and clear (Figure 5.2). Even if compared to Figure (5.3), its image was much more porous and clear. From figure 5, the current finding data agrees with the previous research of Srivastava[17] namely that TEM images of Zr-intercalated-Clay will become more porous with the increase in concentration of intercalan such as Zr in interlayer of montmorillonite clay

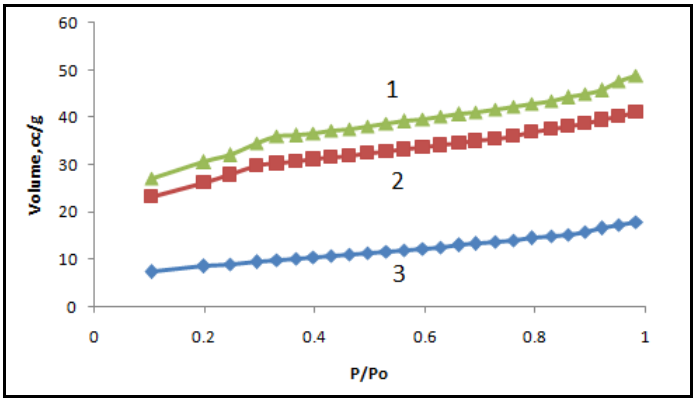


Figure 6, The graphs of isotherms N_2 adsorption at 77°K for 0.01 M Zr (1), 0.02 M Zr (2) *with* ethylene glycol and without ethylene glycol (3)

In Figure 6, the graphs of isothermically N_2 adsorpted to Zr-intercalated clay without ethylene glycol is shown (Figure 6.3) in which smaller volume of the product was obviously proven compared to that of which using etylene glycol (Figures 6.2 and 6.1). The increase of Zr concentration in that products would also increase their volume, and the current finding data agrees with the research data conducted by Groen[10] and Zhang[11] in which the graphs depicted in Figure 6 was still linear and the properties of materials formed was macro porous.

3. Calcination of Zr-pillarized-clay

The aims of calcination at 600°C were to eliminate the bonded water also the media of polar organic molecule such as glycerol and or ethylene glycol as well. Calcination also aimed at arranging ZrO2 molecules as the pillars in the arranged interlayer space so that formed the properties of porous surface such as cylinder, parallel-sided slit, wedge, cavity as well as ink-bottle[2]. The properties data of 600°C calcinated product shown in the following Figure 7.

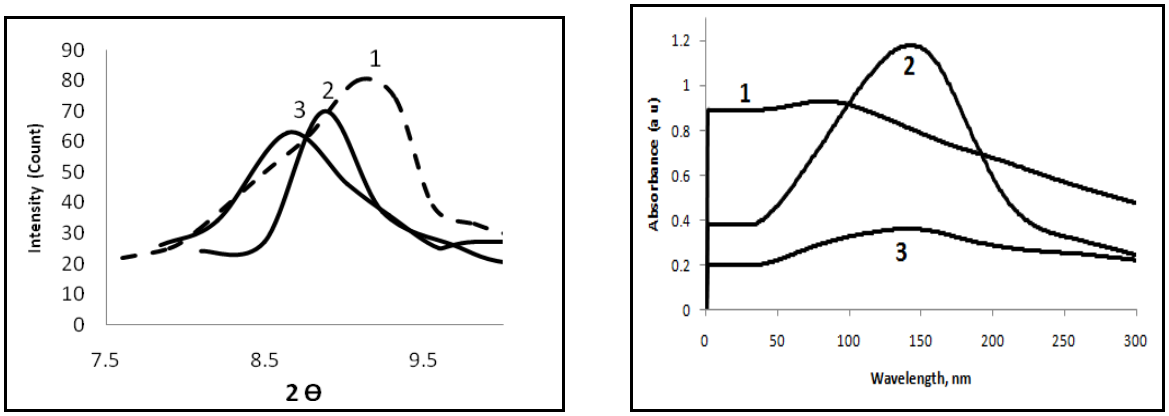


Figure7, The image of XRD (A) and DRS UV-Vis (B) of Zr-pillared clay without glycerol or ethylene glycol (1) and with ethylene glycol for concentrations of 0.01M Zr(2) and with glycerol for concentrations of 0.02 M Zr (3)

In Figure 7 (A) , the peak of pillared and 600^{o}C calcinated products without additing glycerol as well as ethylene glycol remained at 9.08 2Θ . While the peak of those pillared products for 0.01 M Zr with the addition of glycerol (Figure 7.2) will displace to the left from 9.08 2Θ to 8.7 2 Θ , then for 0.01 M Zr with glycerol (Figure 7.3) will displace from 9.08 2Θ to 8.64 2 Θ. The displacement of 2Θ angle leads to the release of bonded water and polar organic compounds of glycerol or ethylene glycol. The data of current finding agrees with the research data conducted by Bachir[18] which stated that the displacement of 2 Θ angle on Zr-pillared-clay after being calcinated was an indication the existing of an expansion in the layers structure as a result of pillaring process. Consequently, there would be rearranging of the surface to be more porous followed by pillarization with pillar center of ZrO2

Next to Figure 7 (B) in which there was displacement of wavelength of Zr-pillared clay to the right from 50 nm to 150 nm at the pillarization with ethylene glycol (Figure 7.2) and glycerol (Figure 7.3). Those phenomenon confirmed the occurence of the dislocation of Zr with the decrease of absorbance value which informed that at pillarization by using glycerol made the pillared materials to be more porous compared to that of which using ethylene glycol. The current researcher agrees with the research data conducted by Fatimah [19] in which the displacement of wavelength of Zr-pillared clay is due to the formation of meso porous size in the Zr-pillared-clay matrix.

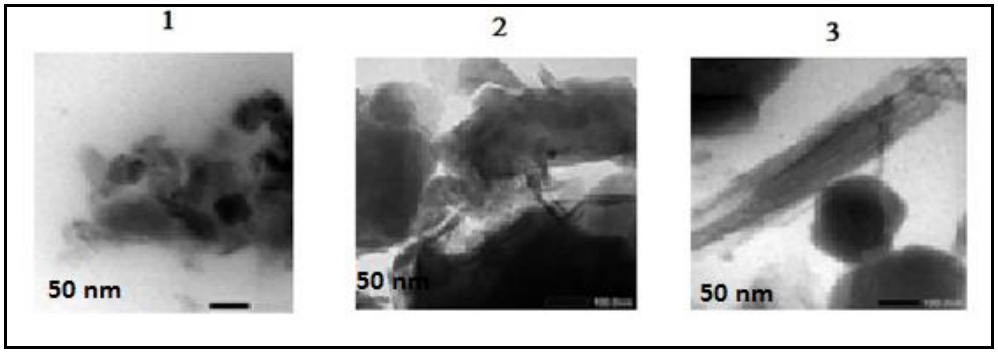


Figure 8, The TEM images of calcined product at 600^{o}C at pillarization without using glycol or glycerol (1) by using ethylene glycol for 0.01 M Zr (2), and by using glycerol for 0.01 M Zr (3)

Then in Figure 8, TEM images of calcining processed products at the pillarization on the Zr- clay pillared without ethylene glycol or glycerol (8.1) was not porous as well as dark. **Next, the** formed materials at pillarization with ethylene glycol (8.2) was obviously clear and porous, but they were obviously clearer with ZrO_2 as the pillar and by using glycerol (8.3.). In the calcining process of Zr-pillared clay products by using ethylene glycol or glycerol (8.2 and 8.3) , both of them were filled up with ZrO_2 as the pillar. Thus, by using the images of both of their calcining products the existence of the more real of pillarization processes was proven. In Figure 8, the current data agrees with the research data conducted by Chen[20] which stated that calcination phenomenon as a delaminated ZrO2 pillared-clay namely a kind of disordered of threedimensional of clay particles coaggregation. An intercalation process will also contribute to the formation of the disordered structure of the ZrO2-pillared-caly (Figure 2 or Figure 5)

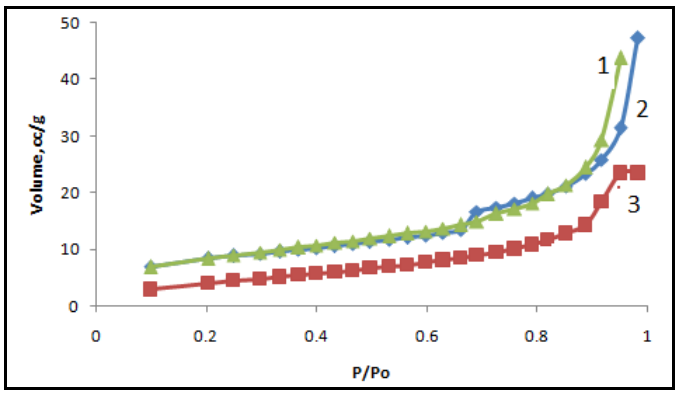


Figure 9, The graphs of isotherms N_2 adsorption at 77^{o}K with ethylene glycol for 0.01 M Zr (1), for 0.01 M Zr with glycerol (2) and without glycerol(3)

In Figure 9, the graphs of isotherms N_2 adsorption at 77^{o}K on Zr-pillared-clay without ethylene glycol or glycerol (9.3), showed the trend of products having smaller volume of compared to that of which using either ethylene glycol or glycerol (9.1 and 9.2). While at the same Zr concentration, there would not be significantly increase in their volume and all of experimental data findings in Figure 9 agree with the previous research data conducted by of Groen[10] and Zhang[11] by which the existence of meso porous material (2 nm -50 nm) in their products was proven.

Conclusion

Identification of the experimental results data by using XRD, UV-Vis DRS, TEM and SSA images had proven that by using the surface properties of Zr-intercalated-clay and Zr-pillared-clay as the products of combining an organic polar addition and reflux processes would be truely characterized. Elimination process of hydroxo zirconium complex by glycerol or ethylene glycol at Zr- Intercalated clay have shown the image of inserting Zr into the interlayers clay. All of the processes performed in this experimetal investigation conducted would not improved the characteristic of products with the presence of meso porous material as depicted by a linear curve of p/po versus volume. The TEM images of calcination processes of Zr-pillarized-clay showed that there would be rearranging of the surface to be more porous followed by the more real pillarization with pillar center of ZrO2. While the calcination process of Zr-intercalation-clay products will be expected to produce mesoporous material via an increase in the pressure (p/po) of 0.8 psi - 1.0 psi that generated a volume of 40.23 cc/g.

Akcnowledgment

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