The International Journal Of Engineering And Science (IJES)
|| Volume || 5 || Issue || 5 || Pages || PP -118-124 || 2016 ||
ISSN (e): 2319 – 1813 ISSN (p): 2319 – 1805

Chemical Formula of Al_xo_y on Synthesize Of Al_2o_3 For Buffer Catalyst by Sol-Gel Method Based On Variation of Calcination and Sintering Treatment

Dwita Suastiyanti[1] ,Maykel T.E. Manawan[2] ,Sri Handayani[3]
[1]*Mechanical Engineering Department, Institut Teknologi Indonesia,Indonesia*
[2]*Politeknik Negeri Jakarta (PNJ), Depok, West Java, Indonesia*
[3]*Chemical Engineering Department, Institut Teknologi Indonesia, Indonesia*

----------ABSTRACT----------
Heterogeneous catalyst used in the process of improving the oxidative stability of biodiesel is the Pt-Rh-Pd catalyst supported by γ-Al_2O_3 (γ-alumina). The purpose of this research was to know the effect of sintering and calcination treatment in sol-gel process on the atomic weight ratio of Al/O that could affect the formation of γ-alumina phase as buffer catalyst. Precursors used was Al $(NO_3)_3.9H_2O$, NH_4OH and ($C_6H_8O_7$) to be dissolved in Aquabidestilate. The calcination process was performed at a temperature which varied of 190°C, 275°C and 320°C for 4 hours respectively and sinter process carried out at a temperature of 420°C for 4,6 and 8 hours. XRD test results confirm that all of the powder has a single phase with different ratio of Al/O atomic weight. For calcination process at a temperature of 320°C for 4 hours and sintering at 420°C for 4, 6, and 8 hours was obtained powder with the atomic weight ratio of Al/O in accordance with ratio of Al/O in Al_2O_3 compound is 0.6667 (2/3). Alumina with the smallest particle size of 84.5 nm is owned by powder with ratio of Al/O = 0.6667. Morphology of the crystals is not homogen in size and shape and it is still agglomerated.

Keywords: catalyst, sol-gel, biodiesel, single phase

Date of Submission: 06 May 2016 Date of Accepted: 25 May 2016

I. INTRODUCTION

Being One of the stages of producing biodiesel has a purpose an increasing oxidation stability of biodiesel using heterogeneous catalysts of Pt-Rh-Pd supported by γ-Al_2O_3. Compound of γ-Al_2O_3 is most known transition alumina as a catalyst support compound, where the compound of γ-Al_2O_3 is stable at high temperature, physically stable, strong and malleable in the manufacturing process. However, commercially γ-Al_2O_3 is not available in single phase and still relatively expensive. This research produced heterogeneous catalyst of γ-Al_2O_3 in single phase, nanoparticle size and the atomic weight ratio of Al/O = 2/3 (0.6667) by method which is easier and more economically. The commercial catalyst activity is limited by the formation of coke and pores of the catalyst [1].

One way to improve the performance of the catalyst is made in size to nanoparticles. Use of the catalyst nanoparticles has been studied by several researchers using ZSM-5 catalyst in cracking LDPE (Low Density Poly Ethilen). The results showed that the nanoparticles ZSM-5 had higher catalytic activity than the microparticles. Therefore, in this study the size of the compound of γ-Al_2O_3 was produced in the size of the nanoparticles. The method used in this research was sol-gel method because this method has many advantages such as the process takes place at low temperatures, the process is relatively easy, could be applied in all circumstances (versatile), producing products with high purity and homogeneity if the parameter is varied. In addition, the most impressive of the sol-gel process is relatively cheap, and products in the form of silica xerogel produced non-toxic[2]. Alumina has had a relatively hard physical properties, relatively stable at high temperatures, low electrical conductivity, melting point high, large pore structure, and has a surface area in the range of 100-200 m^2/g. With these characteristics, causes the alumina is often used in industries, such as absorbents, abrasives, catalysts and catalyst support. In the active form, alumina has a polar surface that is able to adsorb polar compounds. These properties could vary according to the temperature and pH [3,4,5,6] In research conducted by Rahmanpour [7], γ-Al_2O_3 synthesized from $Al(NO_3)_3.9H_2O$ (0.26M), NH_4OH (3.2%), and deionized water at pH of 7.5-8.5 with a temperature of 310 to 340°C for 15 hours and had crystal size of 1-2 nm.

II. EXPERIMENTAL PROCEDURE

The precursors used include simple compound comprised of aluminum nitrate [$Al(NO_3)_3.9H_2O$], citric acid ($C_6H_8O_7$), ammonium hydroxide (NH_4OH) and Aquabidestilate. Overall the base material was a chemical compound Merck products. Characterization of the resulting powder was done by X-Ray Diffraction / XRD test

(Phillips type) to confirm the formation of phases and determine the atomic weight ratio of Al/O. Observation by Scanning Electron Microscope/SEM (type JEOL/EO, JEM-1400 Version 1.0) was to determine the morphology of the grains. To determine the particle size, it was used Particle Size Analyzer/PSA type of Beckman Coulter DelsaTM Nano by using a solution of dispersing Ethyl Alcohol left for 4 days then the particle/powder was broken again by using ultrasonic. Tests using TGA / DTA (Thermal Gravimetry Analyzer/Differential Thermal Analysis) performed on gel (before the sinter process) was to determine the temperature of the phase transition that could be observed through the reduction of powder mass and a decrease in energy when the gel was heated at temperatures of up to 1000°C. This research was conducted by the flow chart as shown in Fig. 1.

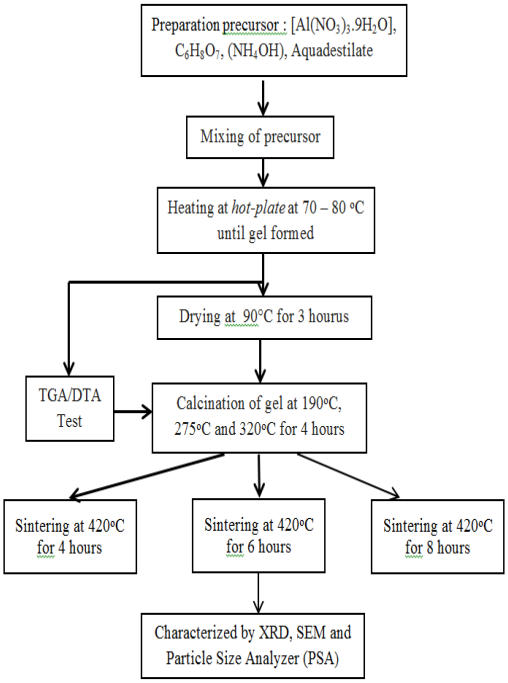


Fig.1. Synthesis of Alumina Powder by Sol-Gel Method

Sol-gel process was preceded by the formation of a gel by heating the solution on a hot plate at a temperature of 70-80°C until the gel was formed (approximately 4-5 hours). Gel was then tested by TGA / DTA to determine the temperature of phase transformation. The temperatures were used as the reference to the calcining and sintering temperatures. The parameters varied were the calcination temperature of 190°C, 275°C and 320°C respectively for 4 hours. The sintering process was done after the calcination at a temperature of 420°C for 4, 6 and 8 hours respectively for calcined process aboved.

III. RESULT AND DISCUSSION

To find out the calcination and sintering temperatures, they were tested by the TGA/DTA that the result is shown in Fig. 2.

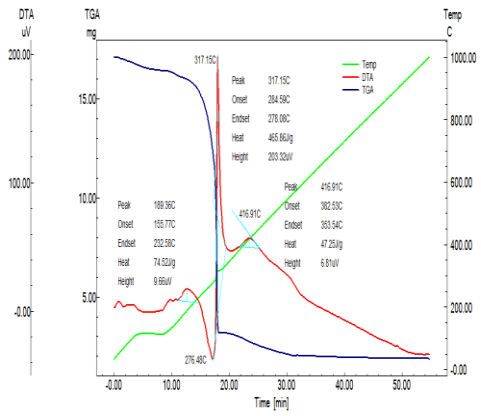
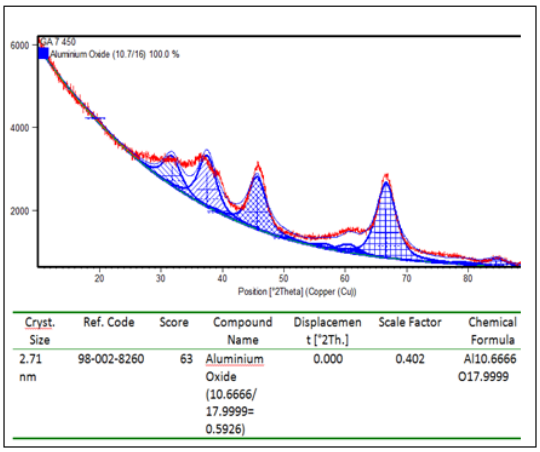


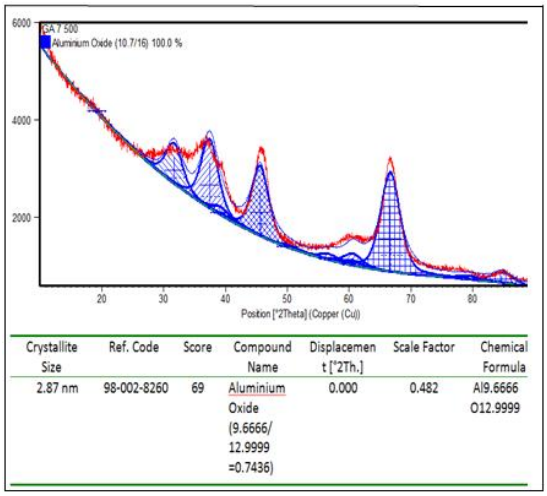
Fig.2. TGA/DTA Test Result of Citric Acid Gel-γ Al_2O_3

Figure 2 shows that the loss of mass and energy reduction occur simultaneously in a temperatures range of 189.36°C-317.15°C. In this temperature range, H_2O and other elements evaporated which is derived from precursor used. The calcination process is performed at temperature in the range that is at 190°C, 275°C and 320°C for 4 hours. The next energy changes on the diagram TGA / DTA occurs at temperatures 416.91°C. At this temperature it begins to form alumina phase and it happens crystallization of alumina. So Sinter process is carried out at 420°C for 4, 6 and 8 hours respectively for calcined process aboved. The XRD results are shown in Fig. 3-11.



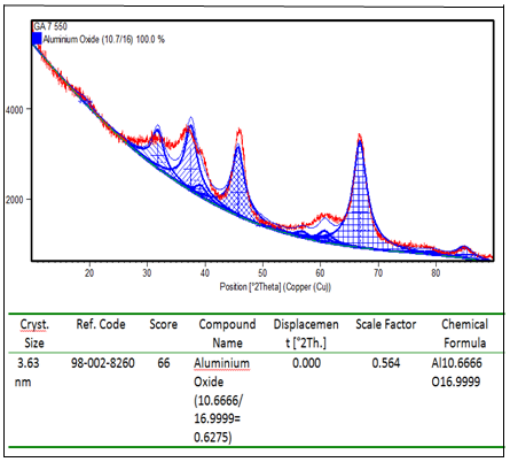
Cryst. Size	Ref. Code	Score	Compound Name	Displacement [°2Th.]	Scale Factor	Chemical Formula
2.71 nm	98-002-8260	63	Aluminium Oxide (10.6666/ 17.9999= 0.5926)	0.000	0.402	Al10.6666 O17.9999

Fig.3. XRD Pattern of Powder Calcined at 190°C, 4 Hours, Sintered at 420°C, 4 Hours



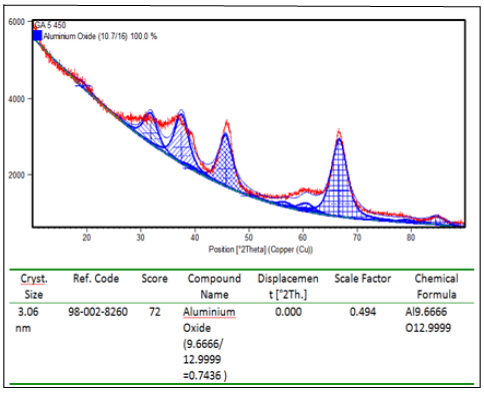
Crystallite Size	Ref. Code	Score	Compound Name	Displacement [°2Th.]	Scale Factor	Chemical Formula
2.87 nm	98-002-8260	69	Aluminium Oxide (9.6666/ 12.9999 =0.7436)	0.000	0.482	Al9.6666 O12.9999

Fig.4. XRD Pattern of Powder Calcined at 190°C, 4 Hours, Sintered at 420°C, 6 Hours



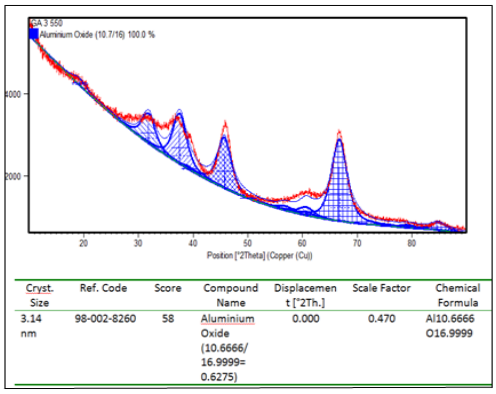
Cryst. Size	Ref. Code	Score	Compound Name	Displacement [°2Th.]	Scale Factor	Chemical Formula
3.63 nm	98-002-8260	66	Aluminium Oxide (10.6666/ 16.9999= 0.6275)	0.000	0.564	Al10.6666 O16.9999

Fig.5. XRD Pattern of Powder Calcined at 190°C, 4 Hours, Sintered at 420°C, 8 Hours



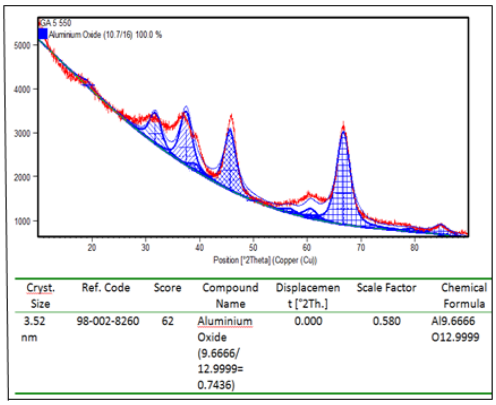
Cryst. Size	Ref. Code	Score	Compound Name	Displacement [°2Th.]	Scale Factor	Chemical Formula
3.06 nm	98-002-8260	72	Aluminium Oxide (9.6666/ 12.9999 =0.7436)	0.000	0.494	Al9.6666 O12.9999

Fig.6. XRD Pattern of Powder Calcined at 275°C, 4 Hours, Sintered at 420°C, 4 Hours



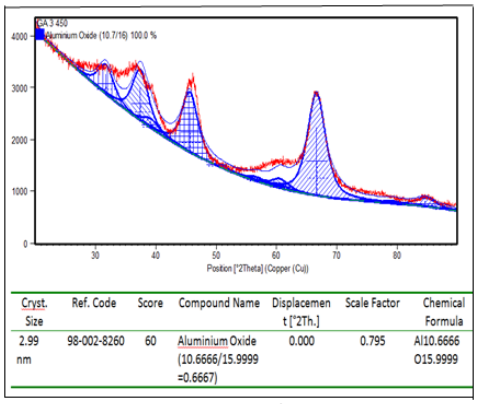
Cryst. Size	Ref. Code	Score	Compound Name	Displacement [°2Th.]	Scale Factor	Chemical Formula
3.14 nm	98-002-8260	58	Aluminium Oxide (10.6666/ 16.9999= 0.6275)	0.000	0.470	Al10.6666 O16.9999

Fig.7. XRD Pattern of Powder Calcined at 275°C, 4 Hours, Sintered at 420°C, 6 Hours



Cryst. Size	Ref. Code	Score	Compound Name	Displacement [°2Th.]	Scale Factor	Chemical Formula
3.52 nm	98-002-8260	62	Aluminium Oxide (9.6666/ 12.9999= 0.7436)	0.000	0.580	Al9.6666 O12.9999

Fig.8. XRD Pattern of Powder Calcined at 275°C, 4 Hours, Sintered at 420°C, 8 Hours



Cryst. Size	Ref. Code	Score	Compound Name	Displacement [°2Th.]	Scale Factor	Chemical Formula
2.99 nm	98-002-8260	60	Aluminium Oxide (10.6666/15.9999 =0.6667)	0.000	0.795	Al10.6666 O15.9999

Fig.9. XRD Pattern of Powder Calcined at 320°C, 4 Hours, Sintered at 420°C, 4 Hours

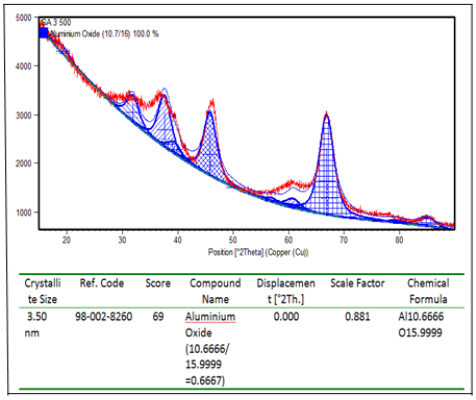


Fig.10. XRD Pattern of Powder Calcined at 320°C, 4 Hours, Sintered at 420°C, 6 Hours

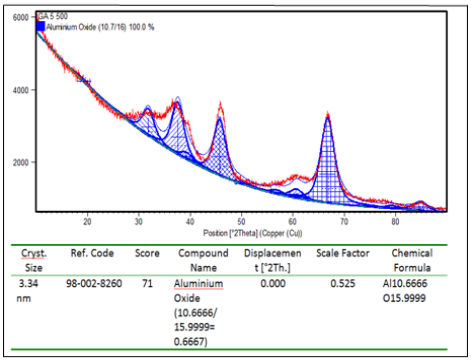


Fig.11. XRD Pattern of Powder Calcined at 320°C, 4 Hours, Sintered at 420°C, 8 Hours

Fig. 3-11 show that the whole powder calcined and sintered at varied condition having 100% of γ alumina phase. There is no impurity phase contained by the powder. It could be seen from the pattern shape in which all peak are swept by one color (blue). However ratio of Al/O atomic weight for powder calcined at 190°C and 275°C are not same with ratio of Al_2O_3 atomic weight (2/3). Powder calcined at 320°C, 4 hours for all sintering time condition has an atomic weight ratio of Al/O equal to the atomic weight ratio of Al/O on Al_2O_3 powder (2/3). From the results of this refinement can also be known that the γ alumina powder calcined at 190°C, 275°C and 320°C for 4 hours has crystallite size ranged 2.71 nm - 3.63 nm (nanosize). This leads to the formation of particles in nano size anyway (<100 nm). List of crystal data for all calcined temperatures is shown in Table 1.

Table.1. List of Crystal Data for All Sample

Treatment		**Al/O**	**Crystallite Size (nm)**
Calcination, 190°C,4 Hours	Sinter (420°C) 4 Hours	0.5926	2.71
	Sinter (420°C) 6 Hours	0.7436	2.87
	Sinter (420°C) 8 Hours	0.6275	3.63
Calcination 275°C, 4 Hours	Sinter (420°C) 4 Hours	0.7436	3.06
	Sinter (420°C) 6 Hours	0.6275	3.14
	Sinter (420°C) 8 Hours	0.7436	3.52
Calcination 320°C, 4 Hours	Sinter (420°C) 4 Hours	0.6667	2.99
	Sinter (420°C) 6 Hours	0.6667	3.50
	Sinter (420°C) 8 Hours	0.6667	3.34

Table.1. Shows that powder having ratio of atomic weight of Al/O = 2/3 (0.6667) has crystal size of < 3.50 nm.

To determine particle size of powder, the PSA test results are shown in Fig.12. The PSA test used a solution of ethyl alcohol to dissolve the powder tested, then the crushing process is carried out by ultrasonic. Crushing process is done to break down the particles of the powder to prevent agglomeration.

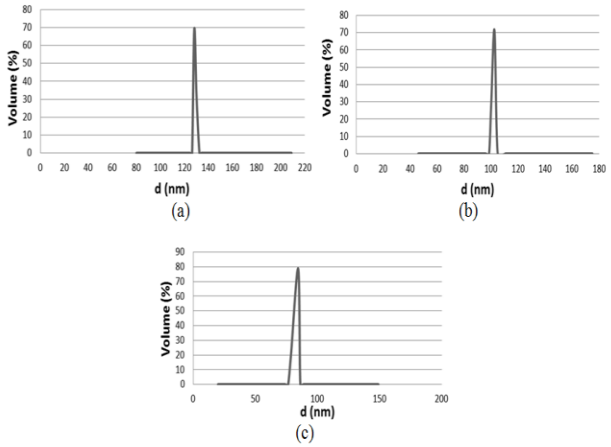


Fig.12. Particle Size Distribution (a) Calcined at 190^{o}C (b) Calcined at 275^{o}C (c) Calcined at 320^{o}C

Fig.12. shows graphic of particle size distribution for powder calcined at 190^{o}C, 275^{o}C and 320^{o}C and then sintered at 420^{o}C for 4 hours. Fig. 12 shows that the powder has particle in nanosize (<100 nm) except powders calcined at 190^{o}C for 4 hours. Powder with ratio of Al/O atomic weight = 2/3 has the finest particle (85 nm), it belongs to powder calcined at 320^{o}C. The results of the measurements of the particles showed that the sol-gel process has not yet reached the optimum conditions. Expected condition is a powder with a particle size of 20-30 nm when referring to crystal size of between 2.71 nm – 3.63 nm.

To determine the morphology of the grain is observed by Scanning Electron Microscope (SEM), the result is shown in Fig.13.

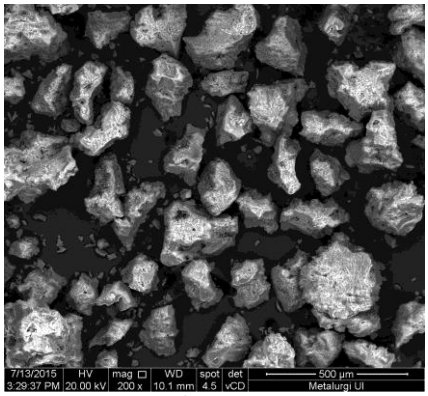


Fig.13. SEM Observation of Powder Calcined at 320^{o}C for 4 Hours, Sintered at 420^{o}C for 4 Hours Fig.13.shows that the powder is still in agglomeration and has not been homogenous in size and shape.

IV. CONCLUSION

Sol-gel process at the calcination temperatures of 190^{o}C, 275^{o}C and 320°C for 4 hours respectively and sintering temperature of 420^{o}C for all sintering time produce γ alumina in single phase without impurities phase. Powder of γ alumina having ratio of atomic weight Al/O = 2/3 is powder which is calcined at 320^{o}C for 4 hours for all sintering time. This ratio is equal with ratio of atomic weight in Al_2O_3 = 2/3. Meanwhile among the sintering time aboved (calcined at 320^{o}C 4 hours), powder which has the finest crystal and particles is powder with sintering time of 4 hours (2.99 nm and 85 nm respectively). The morphology of the grain is still heterogenous in size, shape and still agglomerated. Although powder has particle in nanosize but it is not as expected particle size is about 20-30 nm when referring to the crystal size is about of 2.71 nm - 3.63 nm. So, the best condition for producing γ Al_2O_3 is calcination at 320^{o}C for 4 hours and sintering at 420^{o}C for 4 hours. It could be the best condition to produce γ Al_2O_3 as buffer catalyst.

V. ACKNOWLEDGMENT

This research is supported financially by INSINas-RistekDikti Research Grant 2016 through letter of decree No. 266/SP2H/LT/DRPM/III/2016, Ministry for Research and Technology DIKTI, the Republic of Indonesia.

REFERENCES

[1]. Setiadi, F. Mailisa, Proses Katalitik Sintesis Hidrokarbon Fraksi Bensin Dari Minyak Sawit Menggunakan Katalis B_2O_3/Zeolit, Seminar Nasional MKICS, Universitas Indonesia , 2006, pp 94-98.

[2]. M.F. Zawrah, A.A. El-Kheshen, H. Abd-El-All, Facile and Economic Synthesis of Silica Nanoparticles, Journal of Ovonic Reasearch, vol.5, No.5 , 2009, pp.129-133.

[3]. Rogojan,Radica,et al,Synthesis and Characterization of Alumina Nano-Powder Obtained By Sol-Gel Method. U.P.B. Sci. Bull., Series B, Vol. 73, Iss. 2, 2011.

[4]. M.R. Karim et al, Synthesis of γ-Al_2O_3, Particles and Surface Characterization, The Open Colloid Science Journal , vol 4, 2011, pp 32-36.

[5]. Y.J.O. Asencios, M.R. Sun-Kou,Synthesis of High-Surface-Area γ-Al_2O_3 from Aluminum Scrap and its Use for The Adsorption of Metal : Pb(II), Cd(II), Zn(II). Applied Surface Science, vol 258, 2012, pp 10002-10011.

[6]. L.P.Singh, S.K.Agarwal, S.K. Bhattacharyya, U. Sharma, S. Ahalawat, Preparation of Silica Nanoparticles and Its Beneficial Role in Cementitious Materials, Nanomater Nanotechnol, vol.1, No.1,2011, pp. 44-51.

[7]. O. Rahman, et al, New Method For Synthesis Nano Size γ-Al_2O_3 Catalyst for Dehydration of Methanol to Dimethyl Ether. International Journal of Chemical Engineering and Applications, Vol. 3, No. 2, 2012.