Available online at https://ijcpe.edu.iq and www.iasj.net
Iraqi Journal of Chemical and Petroleum Engineering
Vol.19 No.1 (March 2018) 45– 49
ISSN: 1997-4884
IJCPE
Iraqi Journal of Chemical and Petroleum

Synthesis of Nano Crystalline Gamma Alumina from Waste Cans

Nada Sadoon Ahmedzeki [a], Sattar Jalil Hussein [b] and Waqar Abdulwahid Abdulnabi [a]

[a]*Chemical Engineering Department - College of Engineering - University of Baghdad – Iraq*
[b]*Petroleum Research and Development Center, Ministry of Oil-Baghdad-Iraq*

Abstract

In the present study waste aluminium cans were recycled and converted to produce alumina catalyst. These cans contain more than 98% aluminum oxide in their structure and were successfully synthesized to produce nano sized gamma alumina under mild conditions. A comprehensive study was carried out in order to examine the effect of several important parameters on maximum yield of alumina that can be produced. These parameters were reactants mole ratios (1.5, 1.5, 2, 3, 4 and 5), sodium hydroxide concentrations (10, 20, 30, 40, 50 and 55%) and weights of aluminum cans (2, 4, 6, 8 and 10 g). The compositions of alumina solution were determined by Atomic absorption spectroscopy (AAS); and maximum yield of alumina solution was 96.3% obtained at 2 mole ratios of reactants, 40% sodium hydroxide concentrations and 10g of aluminum cans respectively. Gamma alumina was acquired by hydrothermal treatment of alumina solution at pH 7 and calcination temperature of 550 ºC. The prepared catalyst was characterized by X-ray diffraction (XRD), N2 adsorption/ desorption isotherms, X-ray fluorescence (XRF) and atomic force microscopy (AFM). Results showed good crystallinity of alumina as described by XRD patterns, with surface area of 311.149 m^2/g, 0.36 cm^3/g pore volume, 5.248 nm pore size and particle size of 68.56 nm respectively.

Keywords: Gamma-alumina, Aluminum cans, Nano size materials, Waste recycling

1- Introduction

Alumina has many potential applications in industries and high-tech sectors due to high surface area, porosity and good mechanical properties. Numerous methods had been experienced for synthesis of alumina which were cost effective, requires conditions of high temperatures and pressures [1] such as Bayer process [2], sol-gel method [3], control precipitation method from aluminum salts [4] and extraction of alumina from kaoline [5].

Production of valuable materials from the recycle of waste materials is a process of dual benefit for reducing the accumulated amount of wastes from one side and to obtain a facile way for synthesizing new product having an important application on industrial scale on the other side [6]. Liu et al. (2011) **[7]** utilized the recycling of aluminum beverage cans as a raw material to prepare micron-sized α -alumina by sol–gel method.

Aluminum cans were reacted with ethanol to produce aluminum ethoxide which was converted to α-Al_2O_3 by calcinations at 900 ºC for 2 h. They analyzed the presence of some impure oxides and suggested purification of the ethoxide by vacuum distillation method. Asencios and Sun-Kou (2012) [8] prepared γ-Al2O3 by precipitation of sodium aluminate (which was derived from aluminum scrap) with sulfuric acid and calcinations at 500 ºC. The effect of pH, aging time and calcinations temperature were studied on the physicochemical properties of alumina produced.

The presence of various alumina phases was observed within thermal treatment step. The result showed that alumina with higher surface area and smaller pores were produced at low pH values.

The prepared alumina with 371 m^2/g surface area was used for the adsorption of Cd(II), Zn(II) and Pb(II) from aqueous solution. Chotisuwan et al. (2012) [3] synthesized a mesoporous alumina by template-free sol-gel method from aluminum isopropoxide and aluminum hydroxide from waste aluminum cans. A high surface area alumina was produced (421-556 m^2/g) at calcinations temperature of 500ºC and it was employed as a catalyst support for the oxidation of toluene.

Sheel et al. (2016) [1] investigated the preparation of alumina from industrial cans by acid and alkali method. They showed that acid method is more convenient and preferred to prepare alumina than alkali method because of its higher product quality and quantity.

The aim of this work is to synthesize gamma alumina from waste aluminum cans under mild conditions. A comprehensive study was carried out in order to examine the effect of several important parameters on maximum yield of alumina that can be produced. These parameters were reactants mole ratios, sodium hydroxide concentrations and weights of aluminum cans.

Corresponding Authors: Nada Sadoon Ahmedzeki, Email: **dr_ahmedzeki@yahoo.com**, Sattar Jalil Hussein, Email: NA, Waqar Abdulwahid Abdulnabi, Email: engweqar@yahoo.com

2- Experimental

2.1. Preparation of nano γ-Al_2O_3

Waste aluminum cans were washed with 50% sulfuric acid to remove paint films which may inhibit the contact between reactants. These cans were reacted with 40% sodium hydroxide solution at ambient condition in a batch reactor. Sodium aluminate solution is prepared from this reaction.

This solution was filtered and its pH value was adjusted at 7 using concentrated hydrochloric acid. This solution was left at 80º C for 6 h. Aluminum hydroxide gel was obtained from this step; the gel was washed many times with deionized water in order to get rid of sodium chloride salts that may dissolve in the solution. The solution were filtered and dried at 80º C for 6 h. Finally the sample was ground and calcined at 550º C for 3 h in air at a heating rate of 1º C/min.

2.2. Characterization of Catalyst

X-ray diffraction analysis of sample was conducted in order to check its crystallinity by X-ray diffractometer (Shimadzu SRD 6000, Japan) located at Research Center of Materials/ Ministry of Science and Technology using Cu radiation with wave length of 1.54060 cm^{-1}, in the 2θ range of 10-80º.

The chemical compositions of produced catalyst were estimated by X-ray fluorescence performed at College of Science / Department of Geology/ Baghdad University.

Particles size of sample and the morphology of their surface were implemented by atomic force microscopy (AFM) located in College of Science / Department of chemistry/ Baghdad University. BET surface area, pore volume and pore size of sample were determined from Nitrogen adsorption- desorption isotherm conducted at Petroleum Research and Development Center/ Ministry of Oil.

3- Results and Discussion

3.1. Effect of Reactants Mole Ratio

The effect of NaOH/Al mole ratios on alumina yield at 40% NaOH concentration and 4 g of aluminum cans were studied to find out the best values that will give optimum recovery of alumina. The mole ratios of reactants were more than the stoichiometric quantities at values of 1.5, 2, 3, 4 and 5. Usually in any recovery process, excess amounts of reactants are usually required because the stoichiometric quantities do not offer the optimum recovery [9].

Alumina yield (wt. %) was defined as [10]:

$$yield\ \% = \left(\frac{m_{Al,out}}{m_{Al,in}}\right) \times 100 \quad (1)$$

where; $m_{Al,in}$ and $m_{Al,out}$ were the mass of aluminum in the precursor and product respectively.

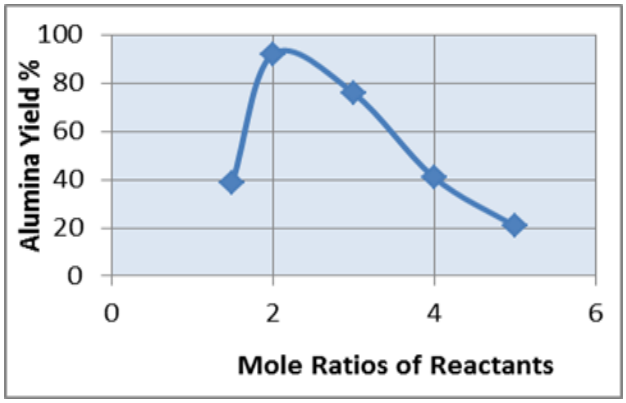

Fig. 1. The effect of reactants mole ratios on alumina yield

As shown in Fig. **1**, alumina yield was found to increase initially from 38.5 to 91.9 % with increasing the reactants mole ratios from 1.5 to 2.Further increase in reactants mole ratios showed a declining trend of alumina recovery to about 21% at mole ratio of 5.

The equations for complete reactions may be proposed as the following:

$$2\,Al_{(s)} + 2NaOH_{(aq)} + 6H_2O_{(l)} \rightarrow 2NaAl(OH)_{4(aq))} + 3H_{2(g)} \quad (2)$$

$$NaAl(OH)_{4(aq))} + HCl_{(l)} \rightarrow NaCl_{(s)} + H_2O_{(l)} + Al(OH)_{3(s)} \quad (3)$$

$$Al(OH)_{3\,(s)} \rightarrow \gamma - AlOOH_{(s)} + H_2O_{(l)} \quad (4)$$

$$2\gamma - AlOOH_{(s)} \rightarrow \gamma - Al_2O_{3\,(s)} + H_2O_{(l)} \quad (5)$$

More boehmite will be produced with the increasing of NaOH /Al molar ratio. This is due to the conversion of the aluminium precursor into $Al(OH)_3$ which will be hydrothermally treated to produce gamma alumina phase.

The chemical reactions were illustrated in equations 1 to 4. Further excess of NaOH/Al mole ratio, resulted in the drying of sodium aluminate which will become as a solid mass so that reducing alumina yield with additional excess of NaOH amounts. This trend agrees with Bell [10], but sodium aluminate was extracted from aluminium nitrate without acid addition.

During this study, it may be noted that with increasing the ratio of reactants, the yield percent initially increased and then decreased beyond a certain quantity.

This may be due to the fact that higher dissolution will be observed with increasing alkalinities; however, the rate of aluminium cans dissolution will be decreased with additional increasing of NaOH concentrations due to the loss amount of water in the mixture and as a result a solid mass of sodium aluminate will be formed.

Thus to obtain an optimum dissolution of alumina from these cans, a compromise between alkalinities and

hydroxide ions concentrations had to be confirmed in the reacted solution.

3.2. Effect of Sodium Hydroxide Concentration

To investigate the influence of the concentrations of the sodium hydroxide solution on alumina production, an experimental study was carried out at different concentrations of NaOH solution (10, 20, 30, 40, 50 and 55%), at constant reactants mole ratio (of 2) and aluminum cans weight (4 g). As shown in Fig. 2, a sharp increase in alumina yield from 25.8 to 91.9 % was occurred with increasing the concentration of NaOH solution from 10% to 40%, it was then followed an insignificant decrease in alumina recovery to about 79 % as NaOH concentration increased to 55%.

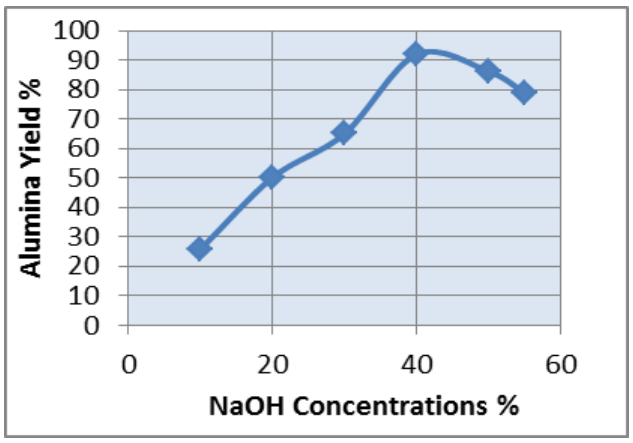

Fig. 2. Alumina yield as a function of NaOH concentration

The reaction between aluminum cans and water formed a dense film of protective oxide that covering the surface of these cans. The charge of this film was positive in the neutral solutions and it was easily dissolved in alkaline solutions generating hydrogen gas at ambient conditions.

It can be suggested that at low NaOH percentage, complete reaction cannot be obtained because of low rate of reaction. Higher NaOH concentration accelerated the hydrolysis of aluminum because the evolved hydrogen bubbles inhibit the precipitation of sodium aluminate from attaching on the aluminum surface reacted [11].

Anderson et al. (2003) [12] proposed that NaOH plays as a catalyst for aluminum hydrolysis and enhances the generating rate of hydrogen bubbles which increase agitation of the mixture and promote the reaction.

As can be seen from Fig. 2, the concentrated NaOH solutions resulted in low alumina recovery, this may be attributed to the less amounts of water that are present for aluminum cans dissolution causing low yield.

The reduction in alumina recovery up to 40% NaOH concentration could be explained by the fact that sodium aluminate is less soluble in concentrated solutions.

Considering this aspect it was clear that the presence of adequate amounts of NaOH as well as water strongly affects the dissolution kinetics essential for keeping the sodium aluminate in dissolved manner.

3.3. Effect of Aluminum Cans Weight

Figure 3 shows the behavior of alumina recovery as a function of aluminum cans weight (2, 4, 6, 8 and 10 g) at NaOH concentration of 40% and NaOH/ Al cans of 2. Alumina yield increased from 91.9 to reach a maximum value of 96.3 % as the weight of cans increased from 4 to 10 g.

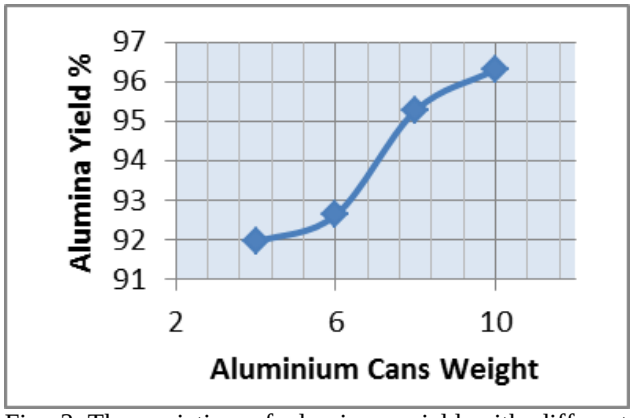

Fig. 3 The variation of aluminum yield with different weights of aluminum cans

As shown in Fig. **3** and according to equations 1-4, it is clear that alumina yield is increased by increasing the initial amounts of aluminum cans precursor. It is well known that increasing the reactants concentrations increases the rate of reaction so that the reaction occurs more quickly. The increase in alumina yield as the can weight is increased may be attributed to the increase in the number of molecules that are ready for reaction [13].

4- Characterization of Nano γ-Al_2O_3

4.1. X–Ray Diffraction (XRD)

The results of XRD patterns for the synthesized alumina can be referred to the formation of γ-Al_2O_3as a single phase through the comparison with the powder diffraction data [JCPS 29-0063]. Comparison revealed that the preparation method was successfully synthesized gamma alumina material through the recycle of waste aluminum cans.

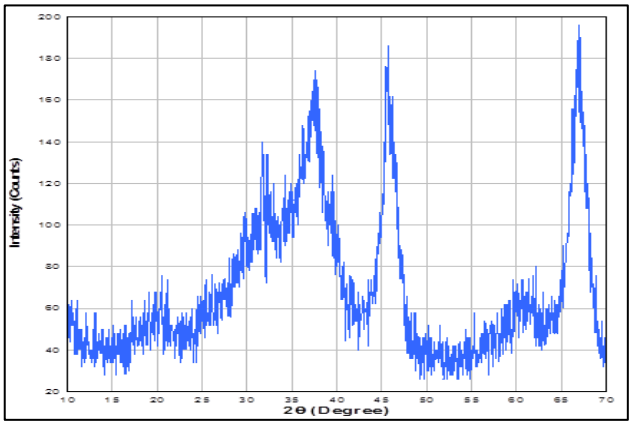

Fig. 4. XRD Pattern of the prepared alumina

As shown in Fig. 4, the XRD peaks can be assigned to gamma alumina structure characterized by 2θ at 66.87, 45.85 with broad peak at 37.42ºrespectively. It can be seen that these peaks tend to be amorphous due to their low intensities [14].

The degree of relative crystallinity of the synthesized alumina was determined according to equation 6 [15].

$$Average\ Crystallinity\ \% = \frac{\sum Intensities\ of\ peak\ of\ sample}{\sum Intensities\ of\ peaks\ of\ reference\ sample} \times 100 \qquad (6)$$

According to equation 2, it was clear that the calculated relative crystallinity is 91.4 referring to the crystalline gamma alumina product and the calculated crystallite size was as 4.542 nm.

4.2. Surface Area and Pore Volume Analysis

Surface area of sample calcined at 550ºC was 311.149m^2/g which refers to the crystalline porous structure of the prepared alumina. Pore volume of the sample and pore size of the sample were 0.36 cm^3/g and 5.248 nm respectively.

As reported in other studies [16], [17], maximum surface areas were obtained from smaller crystallite sizes. These crystallites contained high proportion of small pores. Increasing calcinations temperatures led to the increase in the rate of evaporation of water and gases (OH bond and CO gas) entrapped in the small pores towards larger ones and then to the bulk causing a drop in pressure. This pressure drop would be resulted in a partial loss of surface area due to the collapse of part of the pores.

4.3. Atomic Force Microscopy (AFM)

To investigate the topography of the prepared alumina AFM test was utilized. Fig. 5 and Fig. 6 showed topographical images on two and three-dimensional surface profile of alumina prepared at pH 7 and calcined at 550 ºC.

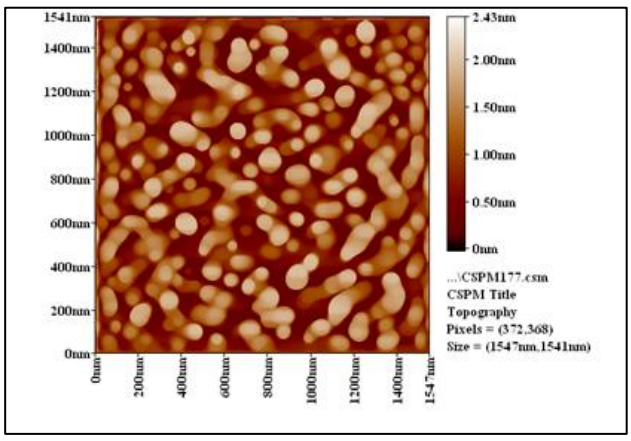

Fig. 5. Two-dimensional image of the surface of synthesized alumina

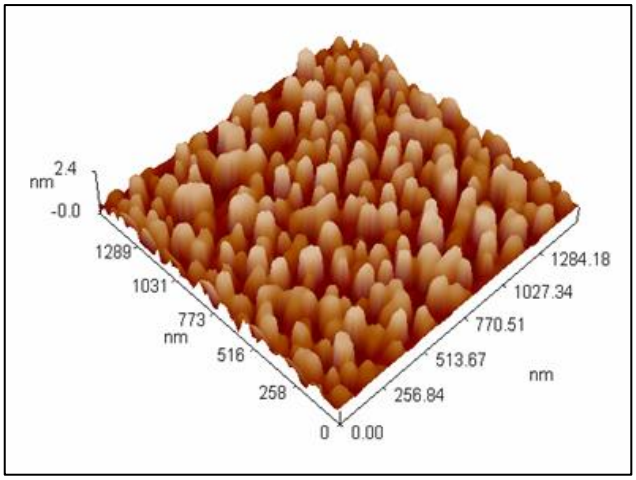

Fig. 6. Three-dimensional image of the surface of synthesized alumina

Particles of sizes in the range of 1 to 100 nm are classified as nano materials [18]. Fig. 7 illustrates the particles size distribution of synthesized alumina. These results confirmed that the prepared alumina is in the nano size region for the range of the diameters between 45 - 90 nm. Most volume percentage of particles is 16.81 % at size distribution of 80 nm particles size at 25% volume percentage is around 60 nm; while its size at 50 and 75% is less than 80 nm. The average particle size is 68.56 nm.

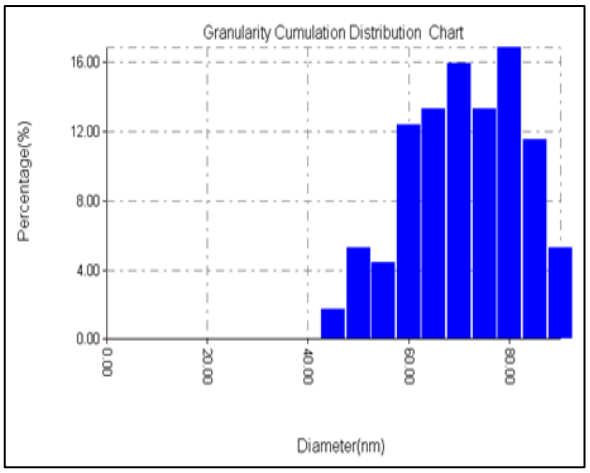

Fig. 7. Granularity Cumulation Distribution Report of synthesized alumina

4.4. X-Ray Fluorescence (XRF)

Alumina with high purity was confirmed by XRF analysis. The structural formula of prepared sample is listed in Table 1.

Table 1. Chemical composition of synthesized alumina

Symbol	Element	Wt%
Al_2O_3	Aluminum	79.46
Na_2O	Sodium	4.226
Cl	Chlorine	4.186
SiO_2	Silicon	1.000

The presence of NaCl salt in alumina structure affected the crystallinity of this sample but did not affect the surface area. The pronounced encouraging results are promising for adopting the present study for future applications.

5- Conclusion

Nano sized gamma alumina with purity of about 80% was successfully produced from waste aluminum cans. Maximum yield of 96.3% alumina solution was obtained at 2 mole reactants ratio, 40% sodium hydroxide concentration and 10 g of aluminium cans respectively.

The method adopted announced the preparation of potential material with striking results; high surface area of 311.149m^2/g, 0.36 cm^3/g pore volume, 5.248 nm pore size and particle size of 68.56 nm respectively. These results are promising for fruitful recycling of waste cans and in the boundaries of the green technology.

Acknowledgment

The authors are grateful to the Ministry of Oil in Iraq / Petroleum Research and Development Center for the financial support of the PhD degree project.

References

[1] Sheel, T. K., Poddar, P., Murad, A. W., Neger, A. T., & Chowdhury, A. S., 2016. Preparation of aluminum oxide from industrial waste can available in Bangladesh environment: SEM and EDX Analysis. *Journal of Advanced Chemical Engineering*, 6(2).

[2] Mohammed, A.-H.. K., Ibrahim, A. & Madhhoor, M.G., 2007. Alpha-alumina extraction from Al-Ga'ara Bauxite. *Iraqi Journal of Chemical and Petroleum Enginnering*, 8(2).

[3] Chotisuwan, S., Sririrak, A., Har-Wae, P., & Wittayakun, J., 2012. Mesoporous alumina prepared from waste aluminum cans and used as catalytic support for toluene oxidation. Materials Letters, 70, pp.125–127.

[4] Sarsenbay, G., Myltykbaeva, L. a, Abdulwalyev, R. a, & Sukurov, B. M., 2013. Influence of the precipitating reagents and dispersants on the formation nano-aluminum hydroxide. , 2013(October), pp.11–15.

[5] Asenciosa, Y.J.O. & Sun-Koub, M.R., 2012. "Synthesis of high-surface-area gamma-al_2o_3 from aluminum scrap and its use for the adsorption of metals : Pb (II), Cd (II) and Zn (II). *Optical Materials*, 34(9), pp.1553–1557.

[6] Birnin-Yauri, A.U & Aliyu, M., 2014. Synthesis and Analysis of Potassium Aluminium Sulphate (Alum) from Waste Aluminium Can. , 1(8), pp.1–6.

[7] Liu, W., Niu, T., Yang, J., Wang, Y., Hu, S., Dong, Y., & Xu, H., 2011. Preparation of micron-sized alumina powders from aluminium beverage can by means of sol-gel process. *Micro and Nano Letters*, 6(10), pp.852–854.

[8] Asenciosa, Y.J.O. & Sun-Koub, M.R., 2012. "Synthesis of high-surface-area gamma-al_2o_3 from aluminum scrap and its use for the adsorption of metals : Pb (II), Cd (II) and Zn (II). *Optical Materials*, 34(9), pp.1553–1557.

[9] Das, B. R., Dash, B., Tripathy, B. C., Bhattacharya, I. N., & Das, S. C., 2007. Production of g-alumina from waste aluminium dross. *Minerals Engineering*, 20, pp.252–258.

[10] Bell, T. E., Gonzalez-Carballo, J. M., Tooze, R. P., & Torrente-Murciano, L., 2015. Single-step synthesis of nanostructured [gamma]-alumina with solvent reusability to maximise yield and morphological purity. *J. Mater. Chem. A*, 3, pp.6196–6201.

[11] Zou, H., Chen, S., Zhao, Z., & Lin, W., 2013. Hydrogen production by hydrolysis of aluminum. *Journal of Alloys and Compounds*, 578, pp.380–384.

[12] Andersen, E. R., & Andersen, E. J. (2003). Method for producing hydrogen. *U.S. Patent No. 6, 506,360 B1. U.S. Patent and Trademark Office, Washington, DC.*

[13] Crowe, by J. & Bradshaw, T., 2010. *Chemistry for the Biosciences_ The Essential Concepts*, OUP Oxford; 2 edition.

[14] Du, X., Wang, Y., Su, X., & Li, J., 2009. Influences of pH value on the microstructure and phase transformation of aluminum hydroxide. *Powder Technology*, 192(1), pp.40–46.

[15] Alrubaye R. "Generation and Characterization of Ctalytic Films of Zeolite Y and ZSM-5 on FeCr Alloy Metal " : Ph.D. Thesis , University of Manchester, 2013.

[16] Chen, Y. F., Lee, C. Y., Yeng, M. Y., & Chiu, H. T., 2003. The effect of calcination temperature on the crystallinity of TiO_2 nanopowders. *Journal of Crystal Growth*, 247(3–4), pp.363–370.

[17] Richardson, J.T., 1989. Principles of Catalysts Development, Plenum, New York and London.

[18] Tiwari, A. & Tiwari, A., 2014. Bioengineered Nanomaterials, CRC Press, Boca Raton, London and New York.