Synthesis and Characterize of Porous Aluminum Oxide Nanoparticles

Anwar H. Ali Al-Fouadi[1], Randa Kamel Hussain[2*]

Abstract

Polyvinyl alcohol (PVA) surfactant and calcination effect on the properties of the alumina powder were investigated. A sol-gel method used to prepare porous alumina from nano alumina that synthesized from colloidal. Among the phases appeared, the XRD analysis evidenced α -phase predominated. The bonding FTIR characterization showed a formation alumina hydroxide referring to the O–H stretching vibration peak. The variation of microstructure texture and the particle morphology were observed by FESEM. The pore size, pore volume, surface area and particle size were determined by BET analysis: 69.22nm, 0.012cm3/g, 0.626m2/g and 9.57nm respectively. The calcination (at 400 °C) of mesoporousalumina showed a decreasing of the pores size and increasing the surface area.

Key Words: Sol-gel, Alumina Porosity, Polyvinyl Alcohol Surfactant, Surface Area, Mesoporosity.

DOI Number: 10.14704/nq.2020.18.1.NQ20115 **NeuroQuantology 2020; 18(1):109-116**

Introduction

Mesoporous aluminum oxide get attention due to their properties related to high surface area, nano pore size, porosity adjustable, is wide dispread in a lot of applications came from its morphology and structural properties[1]. Amorphous nonporous alumina ceramic employment as a catalyst, mesoporous alumina synthesized from boehmite sols using nonionic surfactants. The produced alumina showed high porosity and surfactant amounts displayed an effectively arising on size and volume of pore with surfactant concentrations [3 ,2]. Porosity a great sense feature in adsorption and filtering applications, adjustable pore size were done in micro- and nano- scales to be suitableas removals of dyes, heavy metals in membrane water treatments[4]. High mechanical properties of alumina make it suitable for reinforcement applications, provided a composite of alumina/ polyester an enhanced the mechanical hardness and stiffness [5]. The mechanical and thermal stability supposed that the alumina to be favorites in cutting tools[6].

Aluminum oxide posses several phases types of meta stable structures includingα-, β- , δ- , χ-, γ- , k-, and -θ, the most thermal stable among them is α-phase, and γ-phase have the porosity structural [7, 8]. Different phases could synthesize from tri hydroxide and oxy hydroxide compounds, phase's transitions take place under hydrothermal. The aluminum hydroxides first decompose into boehmite, then to γ→δ→θ→α-alumina which is the more stable phase. The dehydration temperature of around 500 °C produces alumina with high surface area of γ-alumina [9], while, others literature remarked that the phase transitions of alumina in sequence γ to δ to θ to α occurred through the heating duration from ambient temperature up to 1200 °C[10].

Corresponding author: Randa Kamel Hussain
Address: [1]Department of Physics, College of Science, Mustansiriyah University-Baghdad-Iraq; [2*]Department of Physics, College of Science, Mustansiriyah University-Baghdad-Iraq.
[1]E-mail: anwaral_fouadi@uomustansiriyah.edu.iq
[2*]E-mail: Dr.randa.kamel.Hussain@uomustansiriyah.edu.iq
Relevant conflicts of interest/financial disclosures: The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.
Received: 23 December 2019 **Accepted:** 17 January 2020

It is evidence a close relationship of the sintering rate with microstructure of alumina, pure α-alumina has hexagonal close packed structure, could generates β-alumina from thermal reaction of Al_2O_3 with Na_2O_3 at over 1000 ^{0}C. In contract, γ-alumina produced from calcination of α-alumina phase[11].

The phase transition of gamma alumina posses a very important peculiarity, it modulated textural features like surface area, volumeof pore, and pore uniformity, and its acidity (alkalinity) properties are strongly identifies the chemical component, local texture, and phase composition[12]. Gamma alumina is supposed as a spinal cubic structure, instance, it could prepared with tetragonal structure from crystallinity boehmite within 450^{0}C - 750^{0}C [6] according to synthesis method and controlling conditions that highly correlated to the microstructure and thermal. While, it fabricated in cubic structure as prepared by sol gel method from amorphous raw materials[13].Wet chemical method (sol gel) is preferred to produce of microporous and mesoporous alumina forms [14], due to fine size of obtained particles, covered the produces crystallinity, homogeneously, refined, pore size and high specific surface area [15, 16]. Porosity, morphology and structural is subjected to factors of sol gel synthesis such as the mixing, amount of added materials and filler distributed [17]. Further adjusting is including the experimental method parameters of solution concentrations, PH, temperature, and rawmaterials [18, 19]. Previously alumina of alpha and gamma transition phases were fabricated from aqueous solutions by sol gel method [20], very fine nanoparticles of gamma type synthesized from $NaAlO_2$ liquor using surfactants polymers polyethylene glycol (PEG) and polyvinyl alcohol (PVA). Stabilizer type has a significant effect on the crystal size achieved, pore size, and surface area[21]. Further parameters has a clearly influenced is calcinations temperature, for every calcination temperature displayed an effective effect on texture [22].

In sol gel method, the colloidal in solvent, translated to gel form then to solid phase. The precursor of alumina hydrolysis and undergo polymerization processes, the produced sol. Two phases including solid phase (collides) and liquid phase were separated by many methods such as filtering, centrifugation, and evaporation the solution to for the final materials. Poly condensation is usually obtained by thermal treatment. The materials achieved by sol gel method in form of powder, film, fiber according to final output process [23]and could produced a highly porosity alumina[24], figure (1) explains the sol gel mechanism.

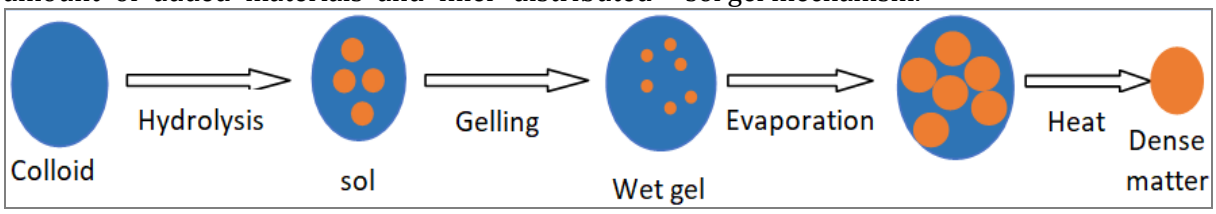


Fig. 1: Sol gel mechanism to form dense material

The goal of this work is to synthesis a nano alumina from bulk scale bycolliding it in solution, and then precipitatedthe produced nano alumina with surfactant polymer. In addition, this work aimed to fabricate porous alumina. Theproperties investigated and characterized by morphological, structural of XRD, FTIR, FESEM, and BET.

Experimental

The preparation of nano-alumina powder can be obtained by dispersed or scattered 25 g alumina (Al_2O_3) powder, GoH basisch type E supplied by Mereck company, with high purity of 99.99% in 100 cm^3 distilled water. Regulating the PH of the mixture to 2.0 with some drops of HCl and leaves it for 24 hours. Then, stirring for 30 min at 70 ^{o}C using magnetic stirrer, left up to 7 daysto grow. Pour the result dispersion solution in a cylindrical pyrex glass 1.30 m length and ≈10 cm in diameter, add distilled water to fill the cylinder, leave it to settle down, for 24 hours to separatethe particles> 1 μm depending on Stock's law. Poured out the upper dispersion solution used a special valve at the upper part of the cylinder as shown in figure (2). Regulating the PH≈9 with addition drops of NH_4OH, stirring using magnetic stirrer at 80^{o}C to get thick solution or slurry.Then dry by electrical oven at 70 ^{o}C to get powder.

The second stage in experimental is prepared γ-alumina by sol gel method, (2.4 g) of alumina previously prepared mixed with(9g) NaOH and dissolved them in (30mL) ethanol: water with volume ratio (3:1). Keeping continuous stirring on hot plate at 70 ^{o}C for 90 min, and then removed the

heat source and added (3 g) of polyvinyl alcohol (PVA) withstirring by using magnetic stirrer until a soft homogenousthick solution is formed. The gel separated with decantation, washed with ethanol and water to remove the extra PVA. Dried at 70 °C and calcination were done in air at 400°C for 2h to achieve the porous γ-alumina.

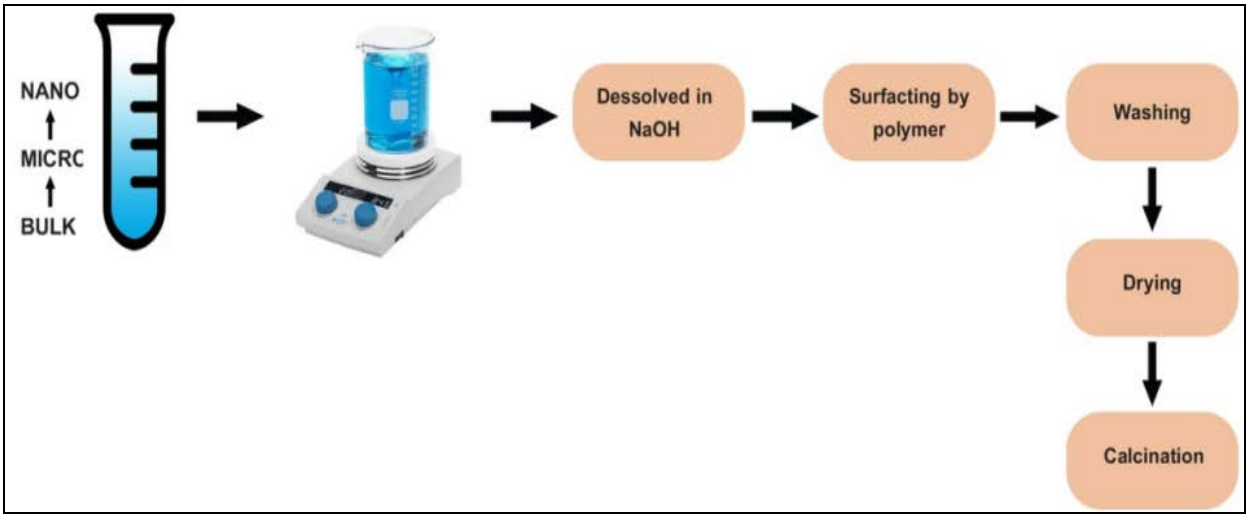


Fig. 2: Procedure diagram

Results and Discussions

XRD

The phase analysis of prepared alumina was analyzed using X-ray diffraction. The scanning was in range of 2θ from 10^0 to 80°. The average crystallite size of the synthesis alumina was calculated by the Sherrer's formula.Figure (3) displayed the profile of XRDrevealed the α- alumina particles and less quantity of γ-alumina.

The strongest peaks ofγ-alumina lie at 2θ =31.7^0 and 45.4^0 corresponding to planes (220) and (400) respectively. XRD revealedα- alumina nanoparticles of crystal size (44.83 nm) and d-spacing (2.73A^0) for the main peaks. The main peaks reflections (104), (113) and (116) posited at 35^0, 43.5^0, and 57.7^0 indicated to formation α –alumina phase. Polymer PVA surfactant treatment in presence of NaOH formed aluminum hydroxide $Al(OH)_3$ with less crystallinity which expected to assist in porous alumina created. The calcination to 400 ^{0}C for 2 hours assists to remove humidity and increased the crystallinity, metastable phases were appeared.It is clear that the crystal size of $Al(OH)_3$ is very smaller, this may due to PVA and NaOH effect on alumina structure, figure (4) compares the crystal structures obtained via XRD. The polymer surfactant lowered the surface tension of nano alumina with aid of sodium hydroxide which plays as a colloidal factor, and spread the crystals into smaller crystals accompanying with increasing of dislocations and micro strain. Calcination to 400 ^{0}C evaporates the PVA which has low boiling temperature, returns the aluminum to alumina structure size having porous pores.

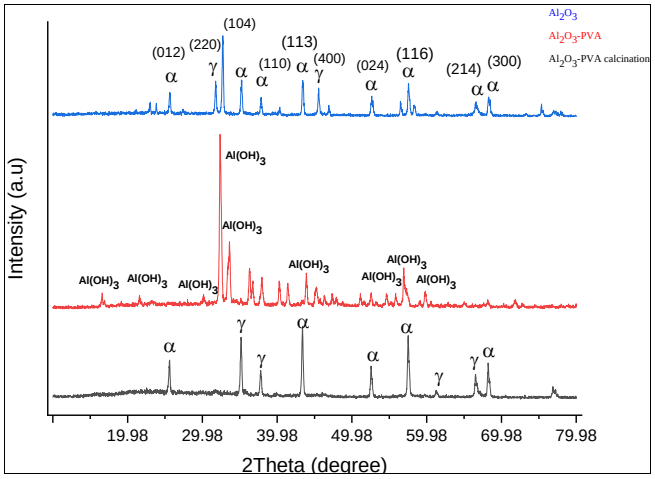


Fig. 3: XRD of fine pure alumina, Al_2O_3/PVA and Al_2O_3/PVA calcination at 400 ^{0}C

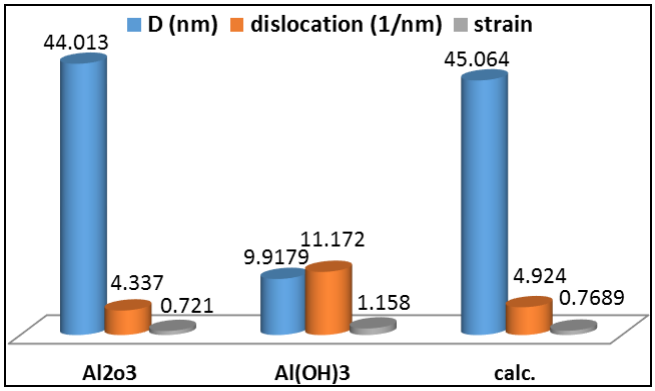


Fig. 4: Crystal size (D), dislocation density (dis.) and strain of alumina before and after hydroxylated and calcination samples

FTIR

FTIR spectra of the Al_2O_3 and Al_2O_3 /PVA are given in figures (5).The spectra in IR region showed two weak bandsat 3544 cm^{-1} and 1647 cm^{-1} of alumina belongs to the stretching and bending vibrations of OH groups respectively. The vibrations of Al–O–Al bonds displayed at 1065 cm^{-1}. For Al_2O_3 /PVA it is observed peaks referred to the O–H stretching vibration of the hydroxy group, asymmetric stretching vibration of CH_2, carbonyl stretch in C=O, C–H bending vibration of CH_2, C–H deformation vibration, C–O stretching of acetyl groups and C-C stretching vibration around 3133, 3033, 1683, 1456, 1397, 1063 and 634 cm^{-1}respectively[25].

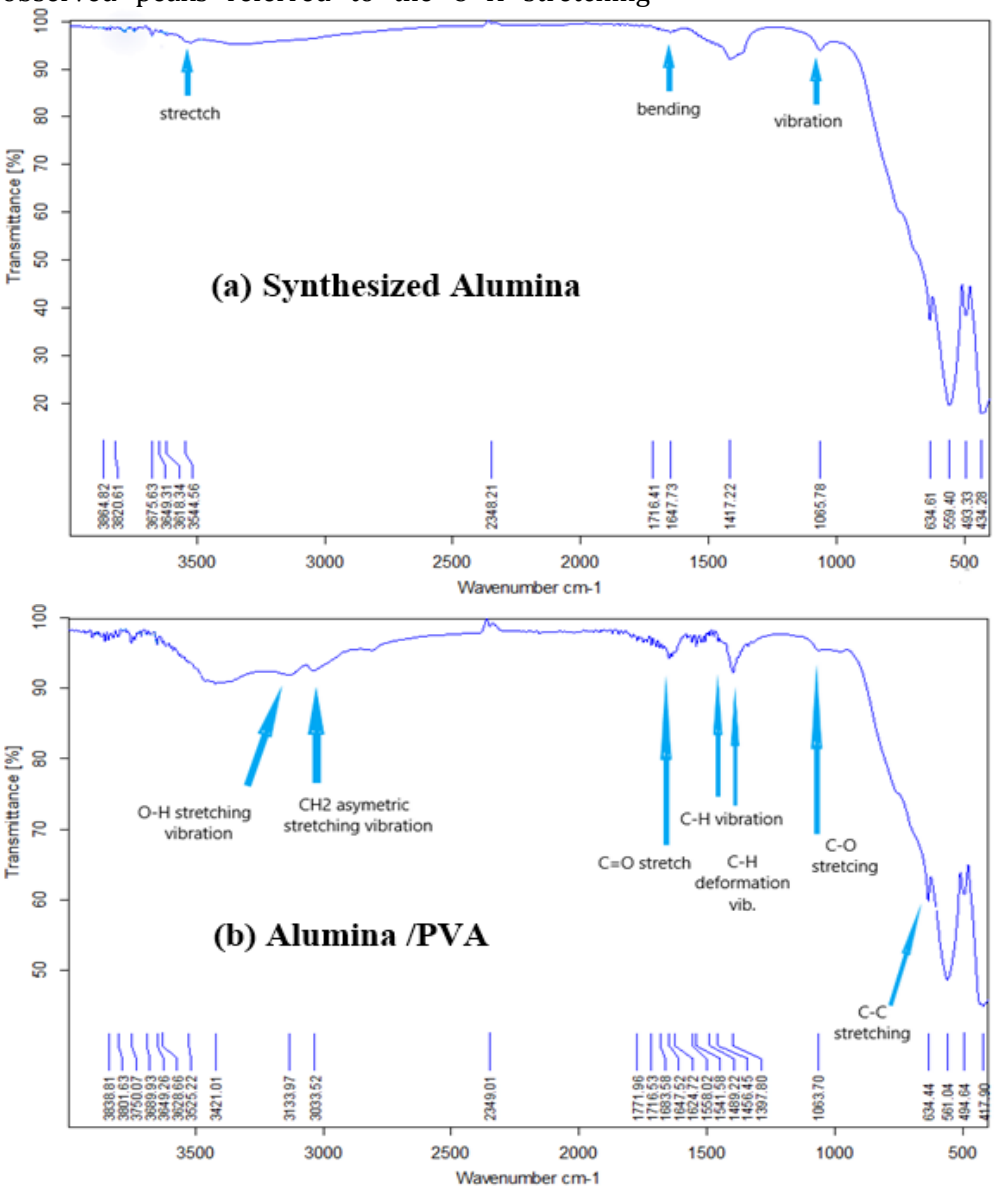
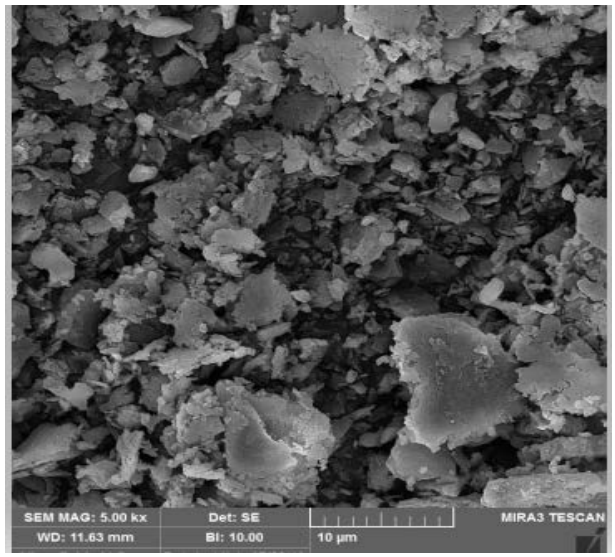
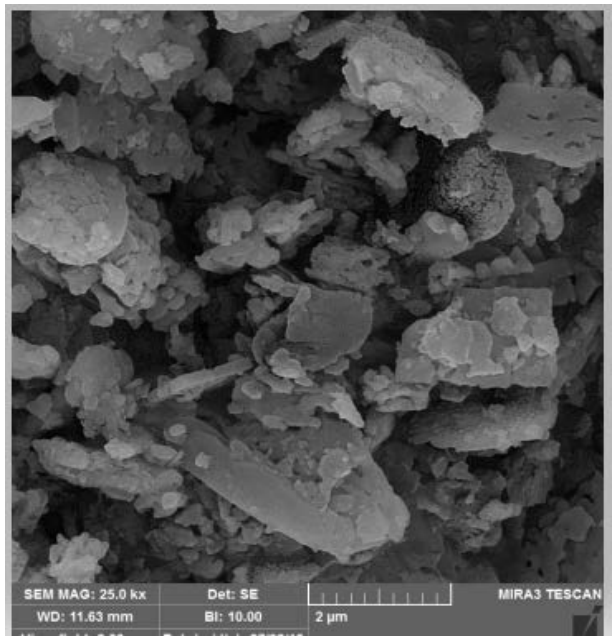


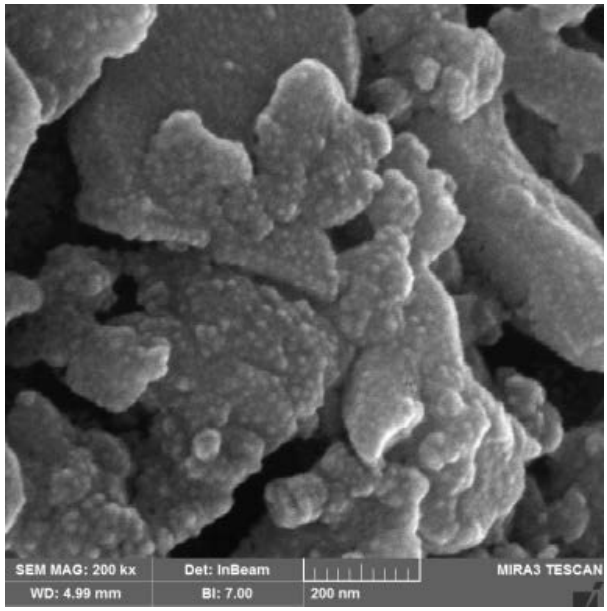
Fig. 5: FTIR spectra with peaks of: (a) alumina and (b) alumina/PVA

FESEM

The morphology of the alumina synthesizedin presence of Na_4OH is shown in figure (6). The FESM image shows different sizes of stony Rocky-shape particles surrounded with the big holes. The quantitative results illustrated from EDX showed that the aluminum element weight percent was 55.6% and oxygen was 28.36%, less quantity of other elements also appeared such as chloride and sodium.







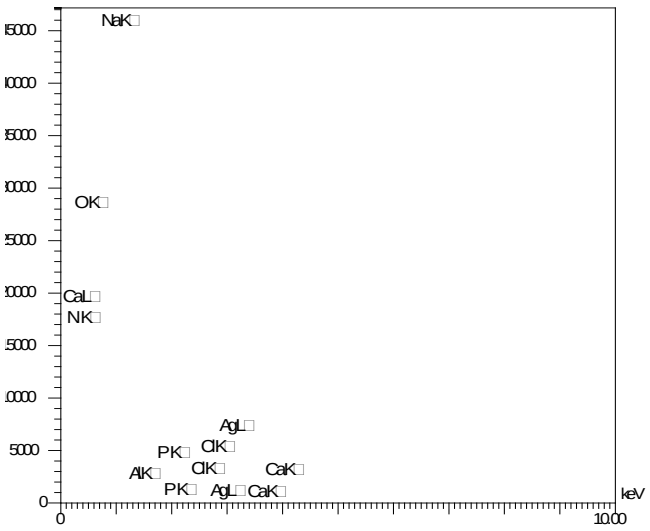
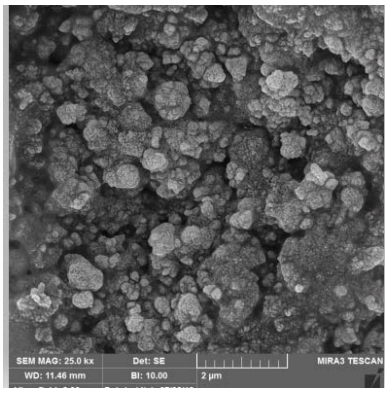
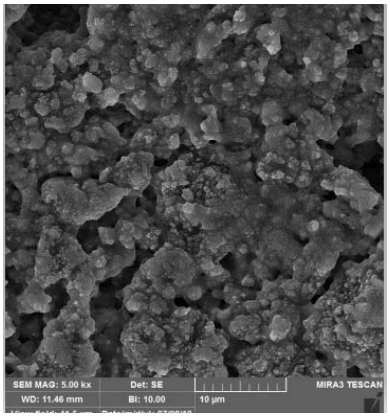


Fig. 6: FESEM and DEX of the Al_2O_3 at different magnification

The mesoporous structure of the alumina obtained using PVA has showed problematic particles, with diameter in range 23.81-26 .89 nm (fig. (7)). The main peaks appears in DEX is related to sodium element which has the weight percent 58.81%, aluminum element has only 4.4% and oxygen58.81%. Using NaOH provides extra sodium more than aluminum, and added PVA (the chemical formula of PVA is $(C_2H_4O)_x$) keep the oxygen content.





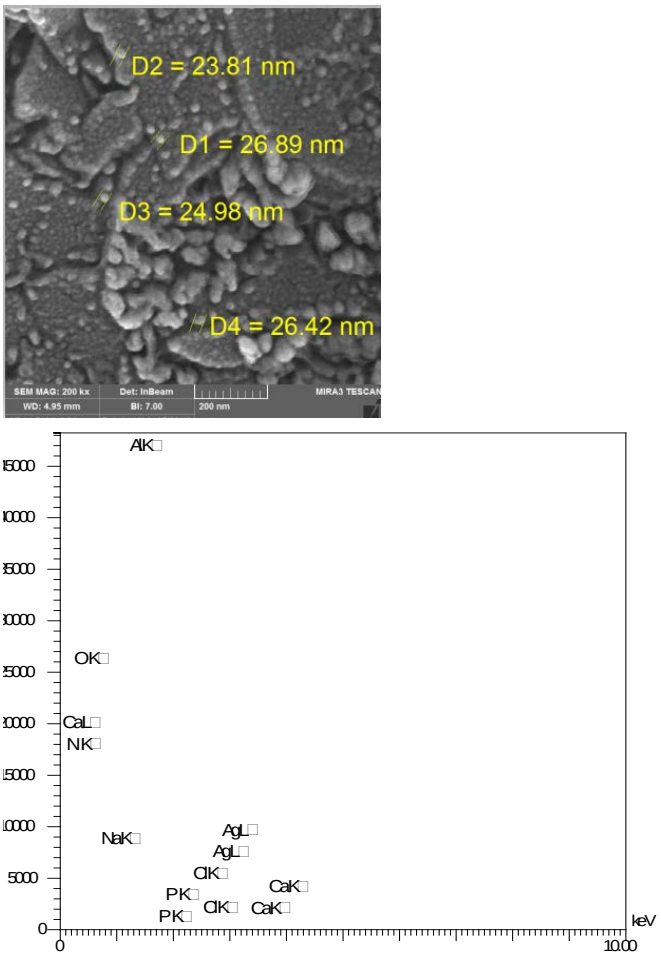
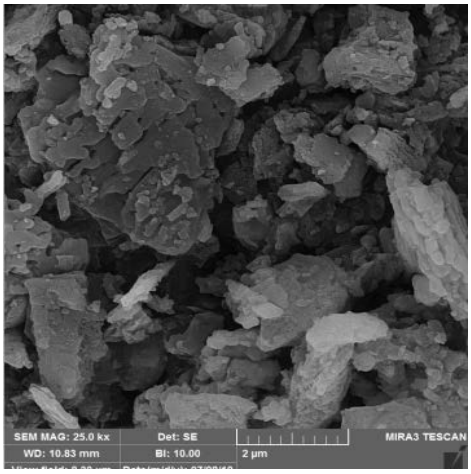
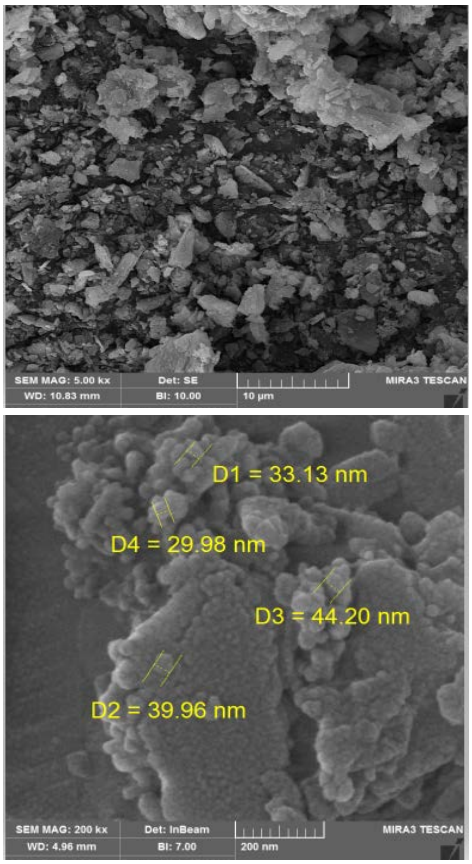


Fig. 7: FSEM and EDX (at different magnification) of Al_2O_3 synthesized with PVA

The FESEM images in figure (8) confirmed the increasing of thestony Rocky-shapedparticle size of Al_2O_3-PVA when calcination at 400 $^oC$to the range 29-44 nm. The larger crystals companying with smaller holes may remarked to a dense material formation. The microstructure is can assort as meso - structure (particle size smaller than 50 nm). Calcination succeeded to remove most quantity of sodium to be 9.63%, and the alumina has the sharp peak produced in EDX with 48.83% weight percent.





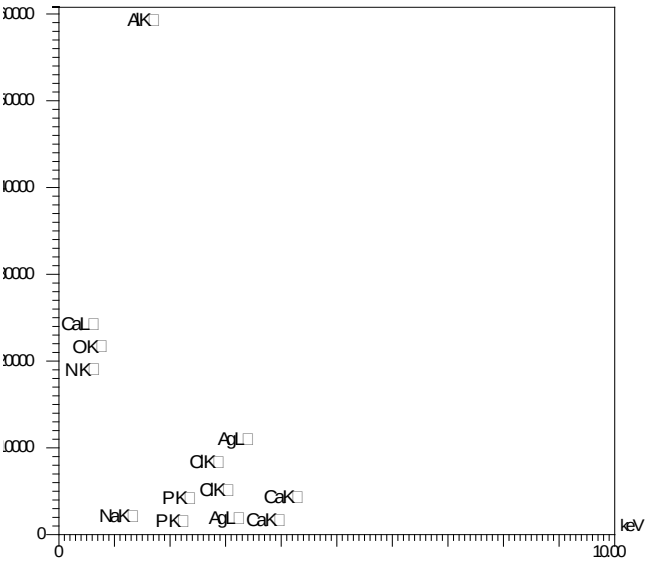


Fig. 8: FSEM and EDX (at different magnification) of Al_2O_3/ PVA calcination at 400 ^oC

BET Analysis

Isothermal linear plot curves were obtained by nitrogen (N_2) adsorption/desorptionanalysis BET method. The surface area, pore size and pore volume were determined by nitrogen adsorption/ desorption.

Figure (9) presents the amount gas with the relative pressure curves. The curves are partially

dissimilar in morphology, in spite of that the whole curve is concaved shapes. At the low relative pressure region ($0 < P/P0 \leq 0.4$) where the curve increment is slowly, this remarked to the mono-layer microporous surface. At a higher relative pressure (stage ($0.4 < P/P0 \leq 0.9$) a multi-molecular layer mesoporous adsorption/ desorption occurred, a smoothly transition frommicroporous to mesoporous were observed. The general shape in Figure (9-a) showed the adsorption and desorption branches are closed to overlap. The nearly absence in hysteresis loop may refers to macro-porosity of type III according to IUPAC classification [26]. The amount of adsorption/desorption gas increased rapidly, showing the hysteresis behavior (especially in fig. (9-b)).

A Raising of the relative pressure more than 0.9 to saturation led to sharply increment of the gas amount [27]. Figure (9) is fully agreements with the FESEM results; the decreasing in pore diameter (see table (1)) supposing led to increasing surface, i.e. the dense body becomes degassing referring by the negative sign.

Table (1) summarized the typical results determined by BET for samples Al_2O_3, Al_2O_3-PVA and calcination Al_2O_3-PVA. FromFigure (9) and table (1), the pure alumina showed a weak interaction and it categorized as a type III. A polymer surfactants converted alumina to type IV which have a mesoporosity structure. Thermal treatment at 400 ^{0}C removing the PVA polymer that effect on the mesoporosity structure which is denoted by decreasing in area of loop hysteresis (Fig.(9-c)).

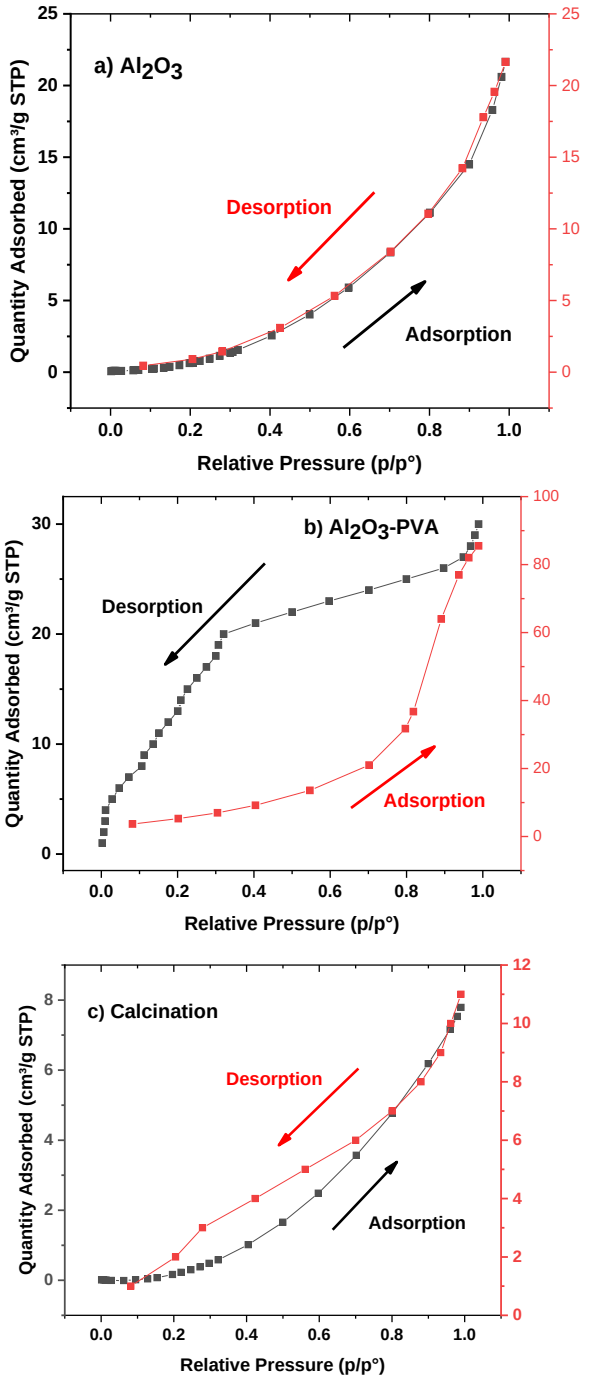


Fig. 9: Nitrogen desorption/adsorption isotherm plot for: a) Al_2O_3, b) Al_2O_3 / PVA and c) calcination Al_2O_3/PVA

Table 1: Typical BET results for Al_2O_3, Al_2O_3/PVA and calcination Al_2O_3/PVA

Sample	Surface area, m^2/g	Pore volume, cm^3/g	Particle size, nm	Pore size (4V/A by BET), nm	Average pore hydraulic radius (by MP method, nm
Al_2O_3	**0.626**	Adsorption: **0.010842** desorption: **0.010814**	**9.577**	Adsorption: **69.22478** Desorption:**69.04199**	**1.6071**
Al_2O_3 /PVA	**22.750**	Adsorption: **0.107958** desorption: **0.123523**	**263.725**	Adsorption:**18.98097** Desorption:**21.71752**	**1.835**
Al_2O_3 / PVA (calcination)	**-15.961**	Adsorption: **0.027237** desorption: **0.028977**	**375.916**	Adsorption: **-6.82593** Desorption: **-7.26187**	**1.863**

Conclusion

Ordered mesoporous alumina with stony Rocky-shapedstructure was synthesized by the sol-gel method. Polyvinyl alcohol polymer used as a surfactant agent to arrange the alumina into mesoporousstructure at the ethanol: water evaporated.

References

Ibrahim AR, Zhu L, Xu J, Hong Y, Su Y, Wang H, Li J. Synthesis of mesoporous alumina with CO2 expanded carbonation and its catalytic oxidation of cyclohexanone. The Journal of Supercritical Fluids, 2014; 92: 190-196.

Liu Q, Wang A, Wang X, Gao P, Wang X, Zhang T. Synthesis, characterization and catalytic applications of mesoporous γ-alumina from boehmite sol. Microporous and Mesoporous Materials, 2008; 111(1-3): 323-333.

Ecsedi Z, Lazău I, Păcurariu C. Synthesis of mesoporous alumina using polyvinyl alcohol template as porosity control additive. Process. Appl. Ceramics, 2007; 1(1–2): 5.

Zhou J, Tang C, Cheng B, Yu J, Jaroniec M. Rattle-type carbon–alumina core–shell spheres: synthesis and application for adsorption of organic dyes. ACS applied materials & interfaces, 2012; 4(4): 2174-2179.

Latief FH, Chafidz A, Junaedi H, Alfozan,A, Khan R. Effect of Alumina Contents on the Physicomechanical Properties of Alumina () Reinforced Polyester Composites. Advances in Polymer Technology, 2019. 2019.

Xiong Y, Shen, Q, Chen, F, Luo, G, Yu, K, Zhang, L. High strength retention and dimensional stability of silicone/alumina composite panel under fire. Fire and Materials, 2012. 36(4): p. 254-263.

Ruan HD, Frost RL, Kloprogge JT, Duong L. Far-infrared spectroscopy of alumina phases. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 2002. 58(2): p. 265-272.

Zahir MH, Nagano T, Rahman MM, Alhooshani K, Chowdhury S, Aziz, MA. Microstructural investigations of tubular α-Al2O3-supported γ-Al2O3 membranes and their hydrothermal improvement. Journal of the European Ceramic Society, 2017. 37(7): p. 2637-2647.

Munhoz Jr AH, De Paiva H, Figueiredo de Miranda L, De Oliveira EC, Andrades RC, Ribeiro RR. Study of Gamma alumina synthesis–analysis of the specific surface area. in Advances in Science and Technology. Trans Tech Publ. 2014; 87: 54-60.

Lamouri S, Hamidouche M, Bouaouadja N, Belhouchet H, Garnier V, Fantozzi G, Trelkat JF. Control of the γ-alumina to α-alumina phase transformation for an optimized alumina densification. Boletín de la sociedad española de cerámica y vidrio, 2017; 56(2): 47-54.

Boumaza A, Favaro L, Lédion J, Sattonnay G, Brubach JB, Berthet P, Tétot R. Transition alumina phases induced by heat treatment of boehmite: an X-ray diffraction and infrared spectroscopy study. Journal of solid state chemistry, 2009; 182(5): 1171-1176.

Segal FM, Correa MF, Bacani R, Castanheira B, Politi MJ, Brochsztain S, Triboni ER. A novel synthesis route of mesoporous γ-alumina from polyoxohydroxide aluminum. Materials Research, 2018. 21(1).

Minaei S. Micro/mesoporous quasi-zero-dimensional AlOOH and Al2O3 nanoparticles. Inorganic and Nano-Metal Chemistry, 2019: 1-8.

Chen X, Zhang W, Lin Y, Cai Y, Qiu M, Fan Y. Preparation of high-flux γ-alumina nanofiltration membranes by using a modified sol–gel method. Microporous and Mesoporous Materials, 2015; 214: 195-203.

Zaki T, Kabel KI, Hassan H. Preparation of high pure α-Al2O3 nanoparticles at low temperatures using Pechini method. Ceramics International, 2012; 38(3): 2021-2026.

Kango S, Kalia S, Celli A, Njuguna J, Habibi Y, Kumar R. Surface modification of inorganic nanoparticles for development of organic–inorganic nanocomposites—A review. Progress in Polymer Science, 2013; 38(8): 1232-1261.

Kritikaki A, Tsetsekou A. Fabrication of porous alumina ceramics from powder mixtures with sol–gel derived nanometer alumina: effect of mixing method. Journal of the European ceramic Society, 2009; 29(9): 1603-1611.

Wang J, Ge L, Li Z, Li L, Guo Q, Li J. Facile size-controlled synthesis of well-dispersed spherical amorphous alumina nanoparticles via homogeneous precipitation. Ceramics International, 2016; 42(7): 8545-8551.

Saengkwamsawang P, Pimanpaeng S, Amornkitbamrung V, Maensiri S. Synthesis and characterization of Al2O3 nanopowders by a simple chitosan-polymer complex solution route. Ceramics International, 2014; 40(4): 5137-5143.

Roque-Ruiz JH, Medellín-Castillo NA, Reyes-López SY. Fabrication of α-alumina fibers by sol-gel and electrospinning of aluminum nitrate precursor solutions. Results in Physics, 2019; 12: 193-204.

Nazari S, Karimi G, Ghaderi E, Moradian KM, Bagherpor Z. Synthesis and characterization of γ-alumina porous nanoparticles from sodium aluminate liquor with two different surfactants. International Journal of Nanoscience and Nanotechnology, 2016; 12(4): 207-214.

Dabbagh HA, Taban K, Zamani M. Effects of vacuum and calcination temperature on the structure, texture, reactivity, and selectivity of alumina: Experimental and DFT studies. Journal of Molecular Catalysis A: Chemical, 2010; 326(1-2): 55-68.

Kour S, Sharma RK, Jasrotia R, Singh VP. A brief review on the synthesis of maghemite (γ-Fe2O3) for medical diagnostic and solar energy applications. in AIP Conference Proceedings. AIP Publishing. 2019; 2142(1): 090007.

Poco J, Satcher Jr J, Hrubesh L. Synthesis of high porosity, monolithic alumina aerogels. Journal of non-crystalline solids, 2001; 285(1-3): 57-63.

Kharazmi A, Faraji N, Hussin RM, Saion E, Yunus WMM, Behzad K. Structural, optical, opto-thermal and thermal properties of ZnS–PVA nanofluids synthesized through a radiolytic approach. Beilstein journal of nanotechnology, 2015; 6(1): 529-536.

Sing KS. Adsorption methods for the characterization of porous materials. Advances in Colloid and Interface Science, 1998; 76: 3-11.

Wang F, Jiao L, Liu Z, Tan X, Wang C, Gao J. Fractal analysis of pore structures in low permeability sandstones using mercury intrusion porosimetry. Journal of Porous Media, 2018: 21(11).