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The Effectof pH on the Structural Properties of Crystalline Alpha Alumina Powders Synthesized by Co-Precipitation Method

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ABSTRACT

Crystalline alpha-alumina (α-A_2O_3) powders were prepared by using chemical co-precipitation method with different pH values. Prepared powders were fired at 1300°C in the air for 4 hours. Structural properties of the prepared powders were studied using Fourier transform infrared (FTIR) spectroscopy, X-ray diffraction (XRD), scanning electron microscope (SEM), and energy-dispersive X-ray spectroscopy (EDX). XRD results confirm that the powders have the α-Al_2O_3 phase with the main peak (113) of rhombohedral(hexagonal) crystal structure, where the average crystallite size of particles of the prepared samples increasefrom (32-38)nm with increases of pH value. FTIR results indicate that the samples contain the molecular functional groups of (Al-O) bonds that appear in (AlO_6) groupof the rhombohedral structure of α-Al_2O_3 with corundum structure which is built up only in this group, and this result supports the results of XRD. The SEM measurements results showed that the powders particles have apparent porosity, agglomerated size, and the size distribution of particles is mostly uniform where the particle size ranges from (93 to 189) nm.EDXwas used to confirm the chemical analysis of aluminium oxide powders and it showed that (Al) and (O) are the main components of alumina particles with no impurities, hence, confirmed the stoichiometric of the prepared alumina powder by the co-precipitation method.

Keywords: α -Alumina, pH, Co-Precipitation Method, EDX.

1. INTRODUCTION

Aluminium oxide (Al_2O_3) has unique properties that it becomes one of the most important engineering materials in the late 20th century due to its low cost, good crystalline composition, high melting point, high hardness,and high corrosion resistance[1-3].Alumina has chemical stability and it can be formed in several structural phases (γ, δ, θ, α) which made it widely used in many fields, especially in ceramics manufacturing[4], polishes and in the optics industry due to the transparency of its films[5], and it can also be used as an intermediary in some chemical reactions. In addition, alumina has many uses in medical applications in the dental or ceramic femur industry [6-8]. Since the material shows important properties such as high thermodynamic stability, hardness, high stability, and electrical insulation, therefore, scientific researches have been geared towards the synthesis of α-Al_2O_3 particles that isimportant in many ceramic applications. There are many structures of alumina (χ-Al_2O_3, η-Al_2O_3, κ-Al_2O_3, δ-Al_2O_3, β-Al_2O_3, γ-Al_2O_3, θ-Al_2O_3), which are called transitional aluminas. The thermal decomposition of aluminium trihydroxides, α-Al_2O_3 is the most stable phase and the final product of the thermal treatments of the transition aluminas[9].

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Alumina particles were prepared through the use of many chemical and physical methods, where chemical methods include chemical co-precipitation[4], combustion[7], sol-gel[10], and hydrothermal[11]. Meanwhile, physical methods include thermal plasma[12], lasers[13], and mechanical milling[14].Chemical co-precipitation method is a common technique in the preparation of many nanoscale materials. In this technique, many parameters such as temperature, time of calcinations, and pH; have an important role in the synthesis of ceramic powders, with desired size and shape [15]. Corundum structure of α-Al_2O_3 phase is more important than other phases, which has great importance in the field of catalytic applications due to the thermodynamic stability of the phase at standard conditions of pressure and temperature [16].α-Al_2O_3 can be prepared by the heat treatment of γ-Al_2O_3 phase and bohemite or any hydrous oxide above 1000˚C.

Calcinations at increasing temperatures give rise to the sequence γ-$Al_2O_3 \rightarrow \delta Al_2O_3 \rightarrow \theta$-$Al_2O_3 \rightarrow \alpha$-$Al_2O_3$ [17]. Furthermore, α-Al_2O_3 has a hexagonal crystalline closest packing structure (HCP), in which the aluminium cations and oxygen anions are arranged sequentially A-B-A-B according to dimensions ($a_0 = 4.7589 \times 10^{-8}$ cm and $c_0 = 12.991 \times 10^{-8}$ cm).The difference of crystalline structures of alumina from one phase to another is shown in Figure 1.

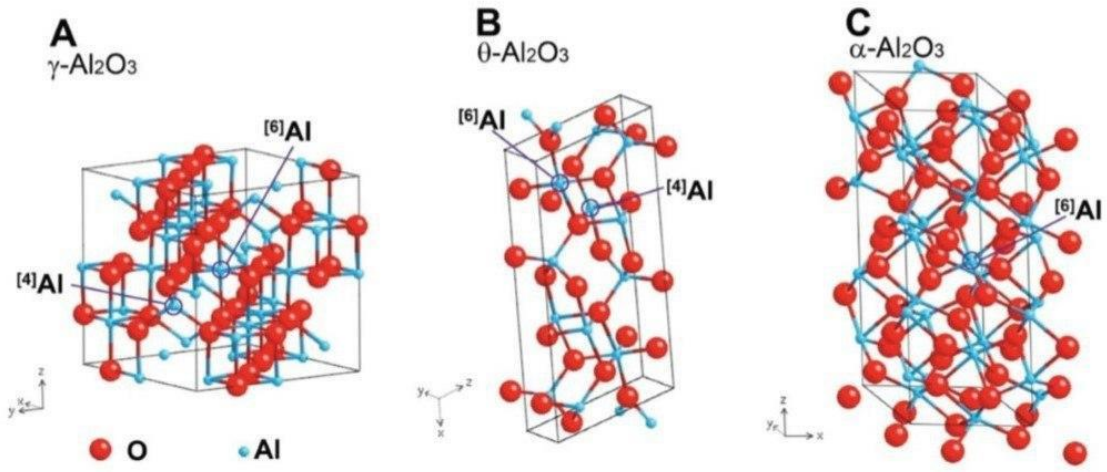

Figure 1. Molecular structures of alumina phases; A: γ-Al_2O_3; B: θ-Al_2O_3; C: α-Al_2O_3.

Aluminium hydroxides consist of many of polymorphs structures such as amorphous hydroxide, bayerite, gibbsite, monohydrates boehmite, nordstrandite, diaspore, boehmite, and tohdite. These structures can be transformed through several processes into metastable transition aluminas, which consist of two main groups of metastable transition aluminas structures: the first is a face centre cubic structure arrangement of oxygen anions which include γ-, η-, θ-, δ-Alumina, and the second is a hexagonal closed packed arrangement of oxygen ions which include χ, κ-, α-Alumina, which in turn are converted by dehydration process to α-Al_2O_3, as shown in Figure 2[1,18].

Aluminium hydroxides precursors are highly dependent on pH.By affecting the reaction of the solution and the structural transform, the change of pH leads to a change in the formation of powders and the phase structure of the prepared bohemite. The different structures of metastable transitions aluminas, nordstrandite, bohemite, diaspore, bayerite, gibbsite, and tohdite can be produced from precipitation of aluminium salts depending on the pH value when the pH value of the solution is adjusted to 4, a pure bohemite will be formed.When the pH value is increased to 7, bohemite and gibbsite phases will consist in the resulting powder. At pH value above 9, the product powder will be composed of bayerite and gibbsite phases[15].

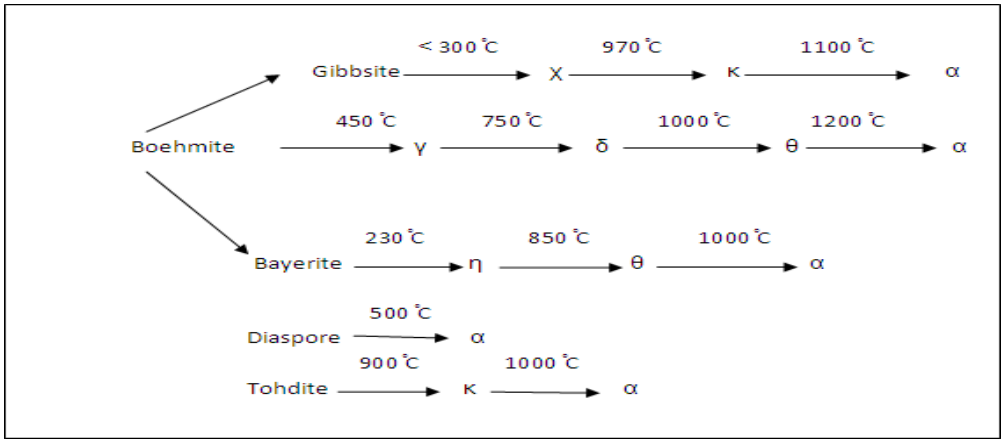

Figure 2. Phase transformation of transition alumina.

In the present work, the co-precipitation method was used in the preparation of aluminium oxide (Al_2O_3) particles at 1300˚C through the using of NH_4OH as a precipitating agent with different concentrations in the aqueous solutions of aluminium nitrate. The pH values were adjusted at different values (10 and 12) by the changing of NH_4OH concentration of the solution.The main aim of this project is to find the effect of pH on the structural characteristics of α-Al_2O_3 powders, and characterized it through many techniques: XRD, FTIR spectroscopy, scanning electron microscope (SEM), and energy dispersive spectroscopy (EDX). A few numbers of articles discuss the effect of the chemical co-precipitation process parameter as pH on structural properties of *α*-alumina particles.Amirsalari *et al*. [15] prepared aluminas with a different structure (γ, γ-, δ, θ) using the wet chemical method from the aqueous solution of Al $(NO_3)_3.9H_2O$ and NH_4OH as precipitant where pH values of the solution were adjusted within the range (7-10), and then the product powders were calcined at different temperatures (500,550, 700,750,900,950)˚C.They reported that the crystal structure and the particle size depend strongly on pH value of the solution,where the crystallite size will increase with an increase of pH value, and the best result was obtained at pH value (9) of the prepared alumina particles. Jian-hong *et al*. [19] prepared high purity powders of γ-Al_2O_3 from the aqueous solution of $NaAlO_2$ and oxalic acid by using the direct precipitation method where pH of the solution was adjusted at different values and it was kept in a suitable range for polymerization of $Al(OH)^-_4$to indissolubleγ-AlO(OH) with a porous structure.Then γ-AlO(OH) powder was annealedat different temperatures (300,350,400,450,500)˚Cfor 4 hours to obtain the final alumina powders, andthey showed that pH factor has an important effect on the preparation process, and they concluded that when the value of pH is less than 8.5,the product will be amorphous forms of AlO(OH).On the contrary, at higher values than 8.5 the product formation of AlO(OH) will be with cubic crystal structures as well as many structures of $Al(OH)_3$, β-Al $(OH)_3$ and γ-AlOOH can be formed as to where $Al(OH)_3$ can be easily converted into $(Al_2O_3.nH_2O)$,and they showedthat the best value of pHwas at 8.5, in which highly pure γ-AlOOH is formed after the calcinations process.

2. MATERIAL AND METHODS

Initially,aluminium nitrate ($Al(NO_3)_3{\cdot}9H_2O$) manufactured by (Sigma–Aldrich, USA,purity 99.7%) with Stoichiometric quantity of 0.2 mol was weighed and dissolved in 100 ml distilled water and stirred for (30 minutes) at 60C̊ to obtain a transparent solution and precipitating agent of the aqueous solution of ammonia NH_4OH(Sigma–Aldrich, USA, 33% Conc.) that was diluted with different amounts of distilled water, and added by drop-wise to the transparent solution of aluminium nitrate to maintain the pH of 10 and 12, and then stirred for 30 minutesat 60˚C. The white precipitate obtained from the preparation was filtered and washed several times using distilled water; filtration is an operation which was used to separate the

precipitate from the remaining impurities (residual ammonia, soluble nitrates, and ions that are contaminants of the raw material).

Finally, the white precipitate powders were dried through an oven at 80˚C for 48 hours. The resultant synthesis product has been pre-calcined at 700°C for 4 hours to remove water and unregent components.The obtained precipitate fine powder was ground and sieved with (75 microns) to obtain the pure phase. The obtained powder was fired in a furnace (Carbolite,England) under air atmosphere at 1300˚C for 4 hours with a temperature rate of 6ºC/min.The experimental procedure of synthesis α-A_2O_3 powders is shown in Figure (3).The structural characteristics of the prepared powders were studied by Fourier-transform infrared spectroscopy (FT-IR, model IR-Affinity, Shimadzu Corporation) to study the information concerning the different stretching and bending bonds of α-alumina powders prepared using the chemical co-precipitation method. The final product of the powders was characterized utilizing the X-ray diffraction patterns (XRD) studies of the prepared samples with different pH values of 10 and 12, which were performed in the 2θ range of 20° to 80° using a Philips XRD-6000-Shimadzu diffractometer that works with a radiation Cu Kα (λ =1.5406 Å) operating at 40 kV and 30mA to identify the current phases. Morphologies of the surface of the particles were performed using a FESEM model FEINOVA NANOSEM 450. Energy dispersive X-Ray spectroscopy (EDX) Model BRUKER X FLASH6l10 was used to investigate the elemental analysis of both aluminium and oxygen.All the measurements were performed at room temperature.The experimental procedure of synthesis α-alumina powders is shown in Figure 3.

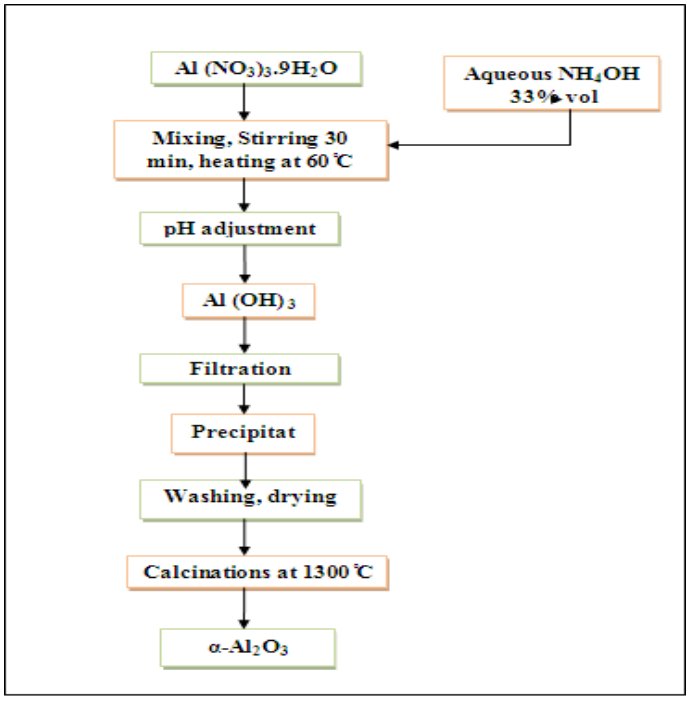

Figure 3. Flowchart of synthesis α-Al_2O_3 by co-precipitation process.

3. RESULTS AND DISCUSSION

3.1 X-ray Diffraction Patterns

X-ray diffraction patterns were used in the study of the structural properties of the α-Al_2O_3 particles prepared at different pH values 10 and 12 at 1300°C.The X-ray diffraction patterns of the desired α -Al_2O_3phase were studied [20].Figure 4 showed that the sharp intense peaks

recorded for α-Al_2O_3 phase identical with miller indices (012), (104), (113), (024), (116), (122), (214), (300) and (119), which correspond to JCPDS 00-010-173 structural parameters indicating that it has a rhombohedral crystal structure. The diffraction angles are shown at 2θ= 43.45, 43.42 for both alpha alumina powders prepared at pH 10 and 12 are back to the main peak (113) of the rhombohedral crystal structure. The XRD parameters for the prepared powders were included in Table 1.The crystallite sizes of the synthesized powders are calculated using Debye -Scherer's formula as shown in equation1 [21].

$$D = \frac{0.9\lambda}{\beta COS\theta}(1)$$

Where D refers to the crystallite size of the particles, λ refers to the radiant wavelength of the X-ray source, 0.94 refers to the value of the constant K, and β refers to the peak width at half maximum intensity. Single stable α-Al_2O_3 phase calcined at 1300˚C for 4 hours shows a highly crystalline nature where the temperature and the time of calcinations played a major role in the conversion to the corundum structure of alumina.The total conversion to the required phase (corundum) occurs on the calcinations temperature at 1300˚C [20].Crystal structure and the crystallite size of α-Al_2O_3 particles are highly dependent on the temperature and pH value [17,19]. The results indicated that the crystallite size of α-Al_2O_3 particles increases with increasing pH values in the solution as shown in Table 1. The reason for this is that the increase of ammonia conccausing the particles to be close to each other and thus results in slow nucleation when ammonia conc. The pH increases lead to the gathering of a large number of small particles and the chance of attraction increased through the process of nucleation, which in turn leads to form big crystalline sizes according to the following reaction [15].

$$Al(NO_3)_3 + 3(NH_4)OH \rightarrow Al(OH)_3 + 3(NH_4)NO_3$$

Table 1 X-Ray parameters of prepared α -Al_2O_3 particles at pH = (10, 12)

pH values	*hk*l	2θ (deg)	2θ (deg)	d(A)˚ Lattice distance	Lattice distanced (A) ˚	FWHM (deg)	Crystallite size$D$ (nm)	Standard valuesof lattice parameters(A˚)	Lattice parameters of prepared powders (A˚)
10	012	25.694	25.583	3.464	3.479	0.26610		a=b=4.758 ˚A C=12.991 ˚A	a=b=4.7602˚A C=13.0067˚A
	104	35.259	35.135	2.543	2.552	0.27040			
	110	37.881	37.783	2.373	2.379	0.27720			
	113	43.453	43.362	2.080	2.085	0.26630	32		
	024	52.642	52.551	1.737	1.740	0.28710			
	116	57.581	57.517	1.599	1.601	0.28990			
	018	61.338	61.343	1.510	1.510	0.39000			
	214	66.602	66.546	1.402	1.404	0.28900			
	300	68.290	68.196	1.372	1.374	0.33170			
	119	77.339	77.226	1.232	1.234	0.19000			
12	012	25.668	25.583	3.467	3.479	0.21920		a=b=4.758 ˚A C=12.991 ˚A	a=b=4.7618 ˚A C=13.0009 ˚A
	104	35.234	35.135	2.545	2.552	0.21660			
	110	37.858	37.783	2.374	2.379	0.20560			
	113	43.428	43.362	2.082	2.085	0.10660	38		
	024	52.615	52.551	1.738	1.740	0.21050			
	116	57.564	57.517	1.599	1.601	0.23110			
	018	61.339	61.343	1.510	1.510	0.35200			
	214	66.579	66.546	1.403	1.404	0.23170			
	300	68.262	68.196	1.372	1.374	0.22370			
	119	77.319	77.226	1.233	1.234	0.18000			

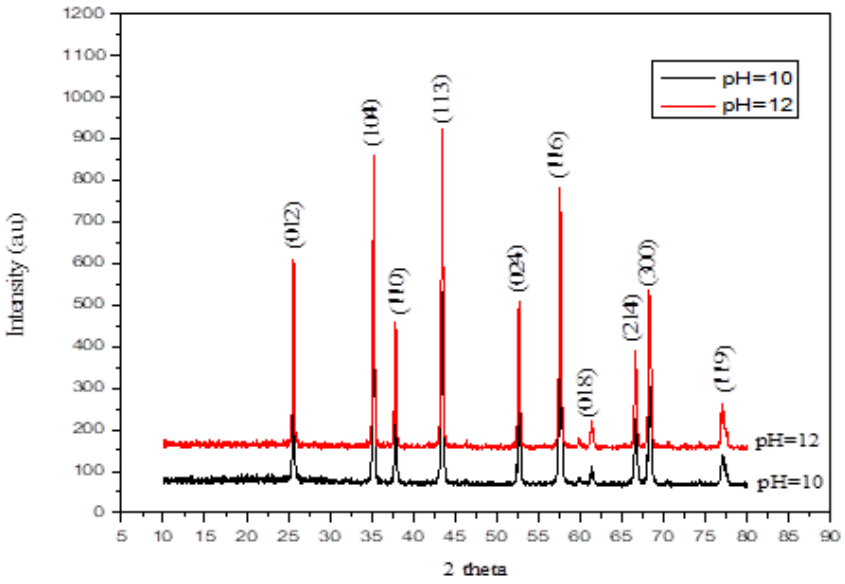

Figure 4. XRD patterns of α -Al_2O_3 particles prepared at different pH values at 1300˚C.

3.2 FT-IR Study

FT-IR spectroscopy of alumina powders was synthesized by chemical co-precipitation method with different pH values 10 and 12, calcined at 1300˚C for 4 hours as shown in Figure5.Spectra in Figure 5 showed many peaks of the absorption bands of the functional groups at (403.12,441.70,493.78,594.03,640.37,750.31)cm^{-1} for alumina powder synthesized at pH=10, and at (451.34,592.15,642.30)cm^{-1} for the alumina powder at (pH=12), where as the sharp absorption peaks of both pH values 10 and 12 observed at(403.12, 441.70, 451.34, 493.78, 592.15, 594.03, 640.37, 642.30)cm^{-1} are the stretching modes of (Al-O) bonds that appear in (AlO6) group of the rhombohedral structure of α-Al_2O_3 with corundum structure that is built up only in this group[22]. The peak observed at 750.31 cm^{-1} of alumina powder synthesized at pH=10 can be assigned to the stretching modes that appear in AlO4 group of θ-Al_2O_3[23]. The intensity peaks of the absorption bands are a good proportional to the XRD spectroscopy at 1300˚C.

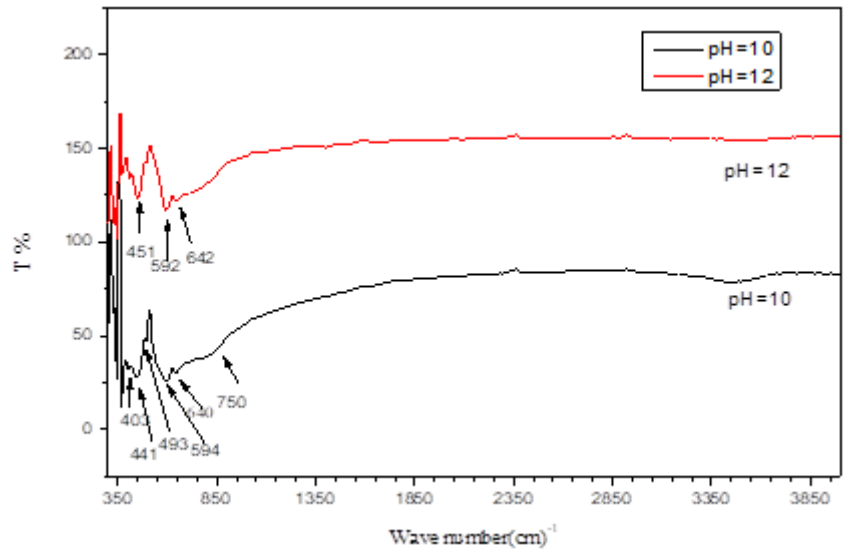

Figure 5.FT-IR spectroscopy of α -Al_2O_3 particles prepared at different pH values (10, 12) at 1300˚C.

3.3 FE-SEM Images and Elemental Analysis

Scanning electron microscope (FESEM) was used to study morphology and the crystal structure of the prepared α-Al_2O_3 particles with different pH values 10 and 12, which are calcined at 1300˚C.The SEM images are shown in Figure6. These images showed that powders particles prepared at 1300˚C were highly porous with highly agglomerated, and the size distribution of particles is mostly uniform[18].Through the SEM images, the particle size ranges from (93 to 189 nm) were observed. Besides that, the images also illustrate the formation of sintering necks and interconnection among grains.

Chemical analysis of the elements of alumina powders was performed through energy dispersive spectroscopy (EDS) as shown in Figure6 and Figure 7 at (0 KeV) for the reference peak. The results make it clear that the elements of aluminium and oxygen are the main components of alumina particles with no impurities which confirm the Stoichiometric of prepared alumina powder by the co-precipitation method [20].

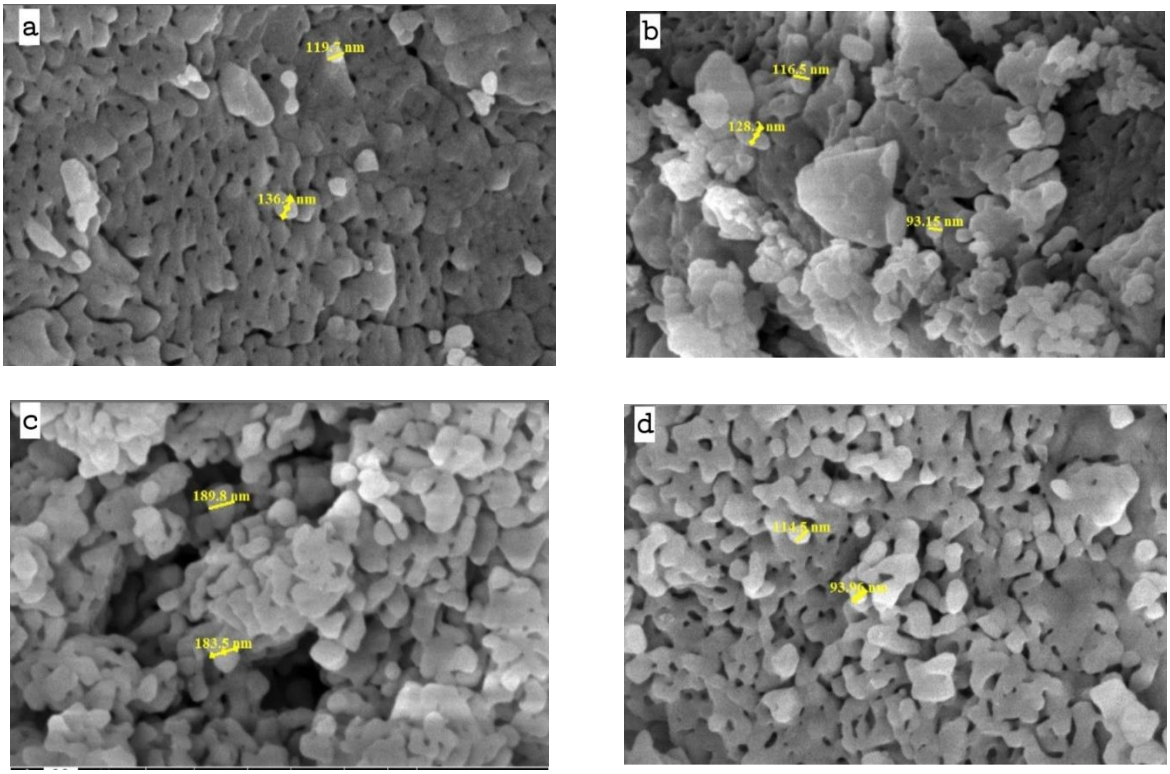

Figure 6.SEM images of α-Al_2O_3 powders prepared at 1300˚C (a, b, at pH=10): (c, d, at pH=12).

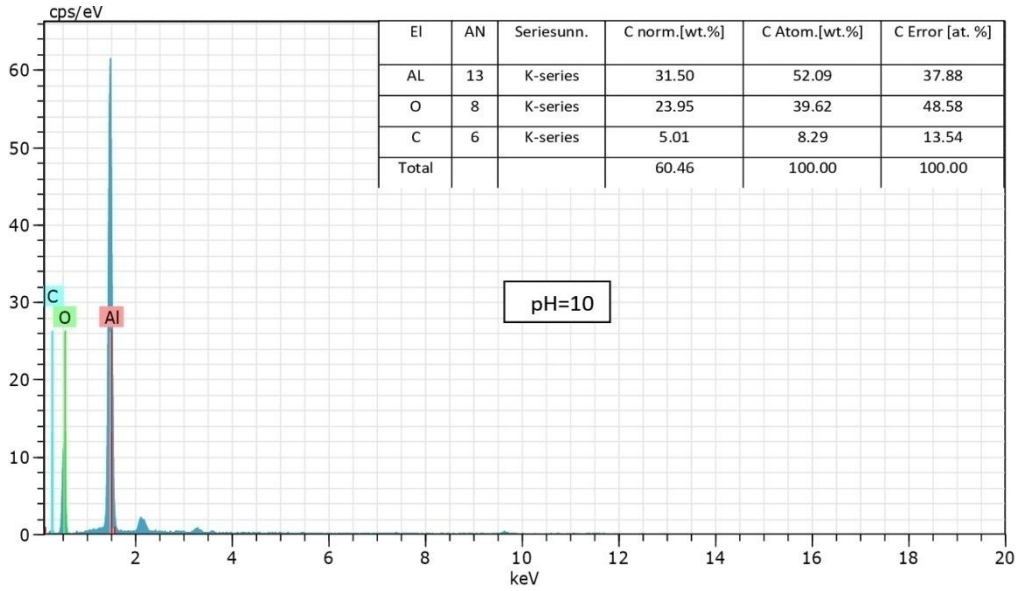

Figure 7.EDS spectrum of α-Al_2O_3 powder prepared at pH=10.

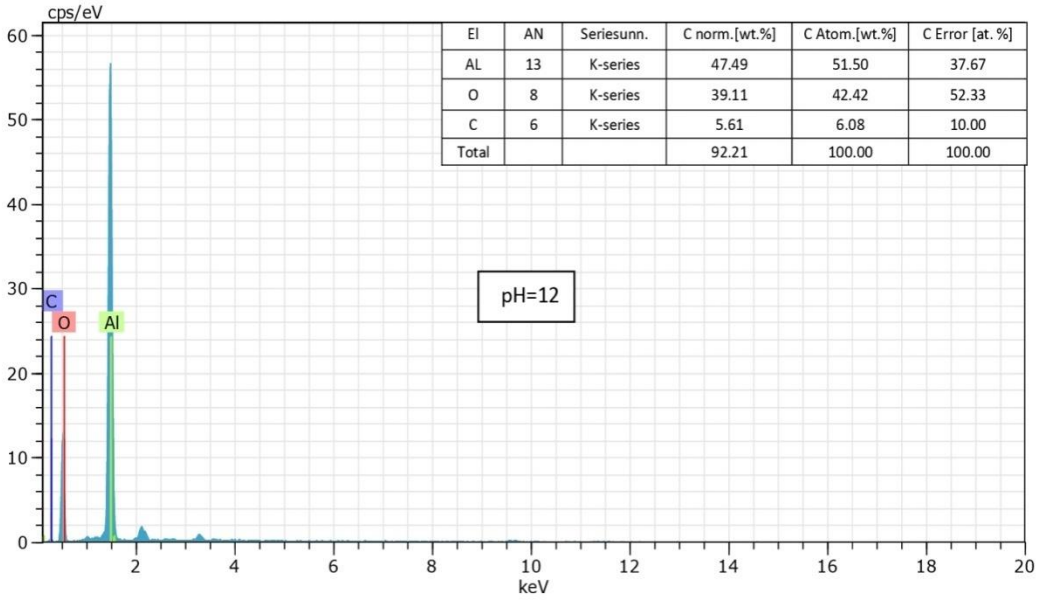

Figure 8.EDS spectrum of α-Al_2O_3 powder prepared at pH=12.

4. CONCLUSION

Alpha alumina particles were successfully synthesized using the co-precipitation method. XRD spectrum shows the rhombohedral (hexagonal) crystal structure of α-Al_2O_3 calcinations at 1300˚C. The crystallite size of alumina particles ranges from 32 nm to 38 nm with increasing pH value from 10 to 12 indicating that the crystallite size depends on pH value. X-ray diffraction showed that the prepared alumina powder does not contain any impurities. FTIR results showed that the samples containing the molecular functional groups of (Al-O) bonds that appear in (AlO_6) group of the rhombohedral structure of α-Al_2O_3 with corundum structure that is built up only in this group and this result supports the results of XRD. SEM images showed that the powders particles were highly porous among the particles with highly agglomerate and the size distribution of particles is mostly uniformwith the particle size ranges from (93 to 189 nm).EDS is used to confirm the chemical analysis of aluminium oxide powders and it showed

the existence of (Al) and (O) with weight percent are the main components of alumina particles with no impurities which confirmed the Stoichiometric of prepared alumina powder by the co-precipitation method. The results obtained in the research can be used in many ceramic applications.

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