IJCPE
Iraqi Journal of Chemical and Petroleum Engineering

Iraqi Journal of Chemical and Petroleum Engineering
Vol.17 No.4 (December 2016) 11- 23
ISSN: 1997-4884

University of Baghdad
College of Engineering

Synthesis Of Nano Ni-Mo/γ-Al_2O_3 Catalyst

Abdul-Halim A. K. Mohamed* and Hawraa H. Atta
Chemical Engineering Department – College of Engineering – University of Baghdad (Iraq)
* Email: prof.abdulhaleem@gmail.com

Abstract

Nano γ-Al_2O_3 support was prepared by co-precipitation method by using different calcination temperatures (550, 600, and 750) ^oC. Then nano NiMo/γ-Al_2O_3 catalyst was prepared by impregnation method were nickel carbonate (source of Ni) and ammonium paramolybdate (source of Mo) on the best prepared nano γ-Al_2O_3 support at calcination temperature 550 ^oC. Make the characterizations for prepared nano γ-Al_2O_3 support at different temperatures and for nano NiMo/γ-Al_2O_3 catalyst like X-ray diffraction, X-ray fluorescent, AFM, SEM, BET surface area, and pore volume.

The Ni and Mo percentages in the prepared nano NiMo/γ-Al_2O_3 catalyst determined by X-ray fluorescence were 2.924 wt % and 12.9 wt %, respectively. SEM of prepared nano γ-Al_2O_3 support at calcination temperature 550 ^oC. The average particles diameter of prepared γ-Al_2O_3 support determined by AFM at calcination temperatures 550, 600, and 750 ^oC and for prepared nano NiMo/γ-Al_2O_3 catalyst at calcination temperature 550 ^oC.

Key words: Nanoparticles, γ-Al_2O_3, NiMo/ γ-Al_2O_3, Co-precipitation method.

Introduction

Gamma Al_2O_3 is one of the important ceramic materials which are mostly used as adsorbent, catalyst, and catalyst support because its thermal, chemical, and mechanical stability. For use as catalyst or adsorbent alumina with desirable characteristics such as high surface area, and small particle size is required [1]. Morphology of synthetic gamma alumina can be changed by varying some of the reaction conditions such as: temperature, pressure, reaction time, thermal decomposition routes and methods of preparation, precursors, and reactants. The catalytic properties of gamma alumina depend on its physical properties such as surface acidity, porosity, and pore size of particles [2].

Alumina is a chemical compound with melting point of 2072 °C and specific gravity of 3.4. Alumina is insoluble in water and organic liquids and very slightly soluble in strong acids and alkalies [3]. Alumina occurs in two crystalline forms. Alpha alumina is composed of colorless spherical crystals shape. While gamma alumina is composed of minute colorless non spherical or irregular hexagonal crystals shape depending on the arrangement of oxygen anions [4].

The gamma phase is transform to the alpha form at high temperatures [3]. Also when high pressure the transformation is used, phase transformation occurs at low temperature. For example the phase of gamma alumina can be transformed to alpha alumina by changing temperature from750 to 1000 ^oC at 1 atm. But when increase the pressure from 1 atm to 8 GPa, gamma alumina transforms phase to alpha alumina at 460 ^oC because the high pressure decrease the thermodynamic energy barrier, and kinetic energy barrier required for nucleation also causes the phase transformation. High pressure caused enough number of nucleation sites to prevent the formation of the vermicular structure and take the equiaxed structure. The transition phase and temperature depend on the particles size chemical homogeneity, heating rate, and water vapor pressure [4].

The mechanical properties of gamma alumina depend on their nanostructure which are related with the shape, and size of the alumina particles. Alumina has many advantages: hard, highly resistance towards bases and acid, very high temperature application, and excellent wear resistance [5]. The phase of alpha alumina with microsize is more stable than gamma alumina phase, while the phase of gamma alumina in nano structure is more stable than alpha alumina. This is because of the change in the thermodynamic stability with the size of nano particle [6].

Potdar, et al., (2007) prepared nano sized γ-Al_2O_3 by precipitation / digestion method at calcination temperature 550 ^oC. The surface area of obtained nano alumina was 220 m^2/g and the average pore diameter was 4.5 nm [7]. Y. I. Tian-hong, el at., (2009) used precipitation method to prepare nano alumina at calcination temperature 450 ^oC and pH range 8 to 9. The surface area of obtained nano alumina was 269.9 m^2/g, the pore volume was 0.57 ml/g, with range of size from 40 to 50 nm [8]. Parida, et al., (2009) prepared nano spherical shape γ-Al_2O_3 by control precipitation method at calcination temperature 550 ^oC. The surface area of prepared catalyst was 190 m^2/g and the crystallite size was 5.7 nm [9]. Mandan, et al., (2010) prepared nano sized γ-Al_2O_3 by sol gel method at calcination temperature 600 ^oC. The surface area of obtained catalyst, the pore volume, and the average pore diameter were 242.9 m^2/g , 1.42 cm^3/g, and 16.5 nm respectively [10]. Sarah, et al., (2012) prepared nano sized γ-Al_2O_3 by sol-gel method at calcination temperature 500 ^oC. The surface area of obtained gamma alumina was 197 m^2/g, the pore volume was 0.38 cm^3/g and the average pore diameter was 8.6 nm [11]. Asencios, et al., (2012) prepared nano sized γ-Al_2O_3 by precipitation method at calcination temperature 500 ^oC. The surface area of prepared gamma alumina was 371 m^2/g, while the pH was 6, the pore volume was 0.275 cm^3/g, and the average pore diameter was 4.5 nm [12]. S.Y. Hosseini, et al., (2012) prepared nano γ-Al_2O_3 catalyst powder by precipitation/digestion method at calcination temperature 580 ^oC for 5 h^{-1} in air. The obtained gamma alumina surface area, average pore diameter and total pore volume are 251 m^2/g, 8.95 nm and 0.82 cm^3/g, respectively [13].

A. Rajaeiyan, et al., (2013) prepared nanostructured gamma alumina powder by sol gel and co-precipitation methods at 750 ^oC. The surface area of prepared sample by sol gel method was 30.72 m^2/g and pore diameter was 49.09 nm, while the surface area of the prepared sample by precipitation method, and the pore

diameter were 206.2 m^2/g, and 7.31 nm, respectively [14]. M. Edrissi, et al., (2013) prepared nano sized alumina by combustion synthesis. The surface area of prepared nano alumina and average pore diameter were 154m^2/g, and 10 nm respectively [15].

Ferechteh rashidi, et al., (2013) prepared nano γ-Al_2O_3 support by sol-gel method. The obtained nano γ-Al_2O_3 with surface area 404.05 m^2/g , pore volume 1.06 cm^3/g and average size 10.469 nm. HDS catalyst was prepared by wet co-impregnation method with percentage of 3% Co, 13 % Ni, and 3 % P on prepared γ-Al_2O_3. The surface area of obtained catalyst was 295.63 m^2/g, the pore volume was 0.62 cm^3/g, and the average pore diameter was 8.355 nm. This catalyst used for HDS diesel fuel which decreased the sulfur content from 150 ppm to 38 ppm [16]. A. Eliassi, et al., (2014) prepared nanosized γ-Al_2O_3 with surface area 413 m^2/g, average pore diameter 38 nm and pore volume 1.624 cm^3/g by using precipitation/digestion method. This catalyst used for methanol dehydration to dimethyl ether using fixed bed microreactor. The operation conditions were LHSV from 20 to 50 h^{-1} and temperature from 250 to 300 ^oC [17].

The aim of this work is to prepare nano gamma alumina then use it in the preparation of nano Ni-Mo/γ-Al_2O_3 catalyst which can be used for hydrodesulphurization of Iraqi gas oil.

Experimental

Synthesis of Alumina by Co-Precipitation Method

1 M of $AlCl_3$ was dissolved in 300 ml ethanol and 90 ml distilled water was added to get a transparent solution, then 120 ml NH_3 was added to the stirred $AlCl_3.6H_2O$ solution drop by drop with the rate of 2.5 ml/min until the precipitate became white as Al^{3+} gel hydroxides was formed. After gel filtering in vacuum system, it was dried at 80 °C over night in the oven, and calcinated at 550 °C, 600 °C for 2 h, and 750 °C for 1 h. A white fine alumina nano-powder was obtained.

Synthesis of Nano Ni-Mo/γ-Al_2O_3 Catalyst

The Ni-Mo/γ-Al_2O_3 catalyst was prepared by impregnation method. The device used for impregnation consisted of a conical flask with a separating funnel, vacuum pump, electric shaker and trap to absorb the moisture and gases (Figure 1). An impregnated aqueous solution was prepared by dissolving 2.7 g nickel carbonate, 4.2 g of ammonium para molybdate and 25 ml of distilled water with mixing at room temperature. This solution was poured in the conical flask of the impregnation apparatus which contains 15 g of dried nano gamma alumina. The impregnation took place drop by drop for 1.5 hours. The impregnated nano alumina was air dried at 80 °C for 16 hours and then calcined at 550 °C for 16 hours.

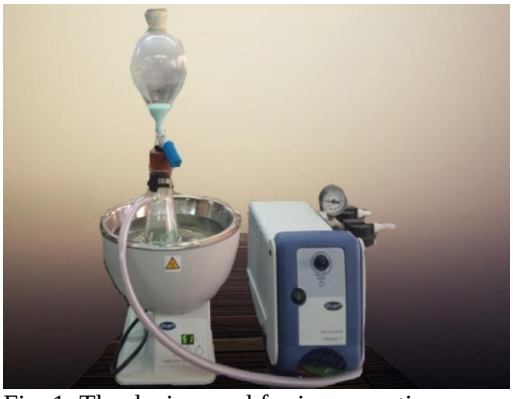


Fig. 1: The device used for impregnation

Results and Discussion

XRD Analysis and XRF Analysis

X-Ray Diffraction analysis for the samples was carried out using Rigaku X-Ray Diffractometer with CuK_α radiation under identical conditions. These conditions are:

wavelength (λ) = 1.5406 A^0, tube voltage = 40 kV, tube current = 30 mA, and scan range: 10 – 70 (deg).

The XRD spectrum gives the diffraction intensity verses 2θ plot. The XRD spectra of prepared nano alumina at different temperatures are shown in the Figures 2 - 4, while the XRD spectrum standard of gamma alumina is shown in Figure 5. The comparison of XRD spectra with standard spectrum shows that all peaks of prepared support approached the standard gamma alumina. This means that the prepared support at different temperatures is gamma alumina. The difference in the height of obtained peaks may be due to the change in the calcination temperature used during support preparation. This mean the prepared support is nano gamma alumina because of that the peaks is more wide than the standard peas.

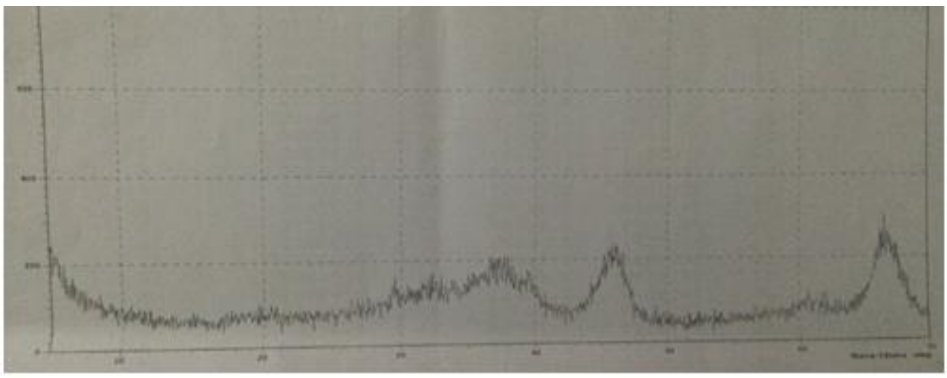


Fig. 2: The XRD spectrum for prepared nano gamma alumina at calcination temperature 550 ^oC

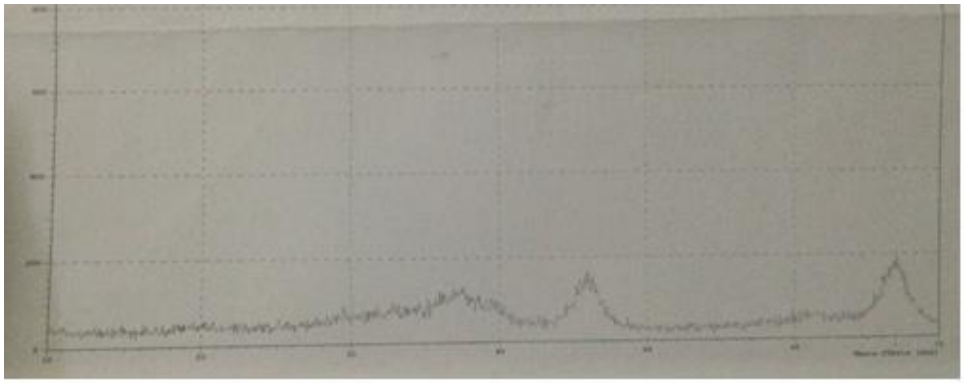


Fig. 3: The XRD spectrum for prepared nano gamma alumina at calcination temperature 600 ^oC

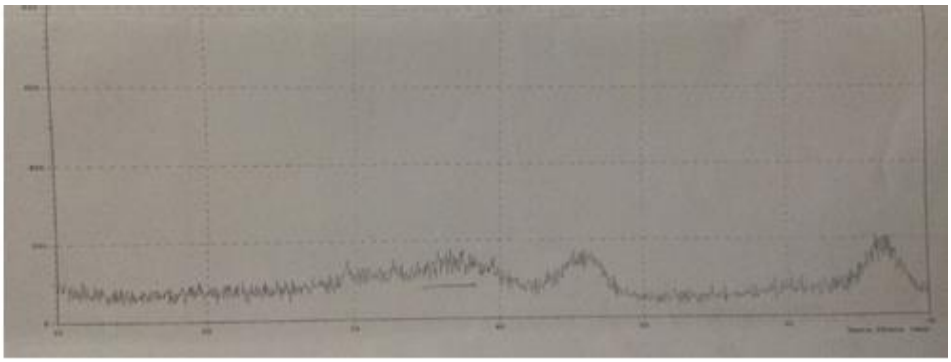


Fig. 4: The XRD spectrum for prepared nano gamma alumina at calcination temperature 750 ^oC

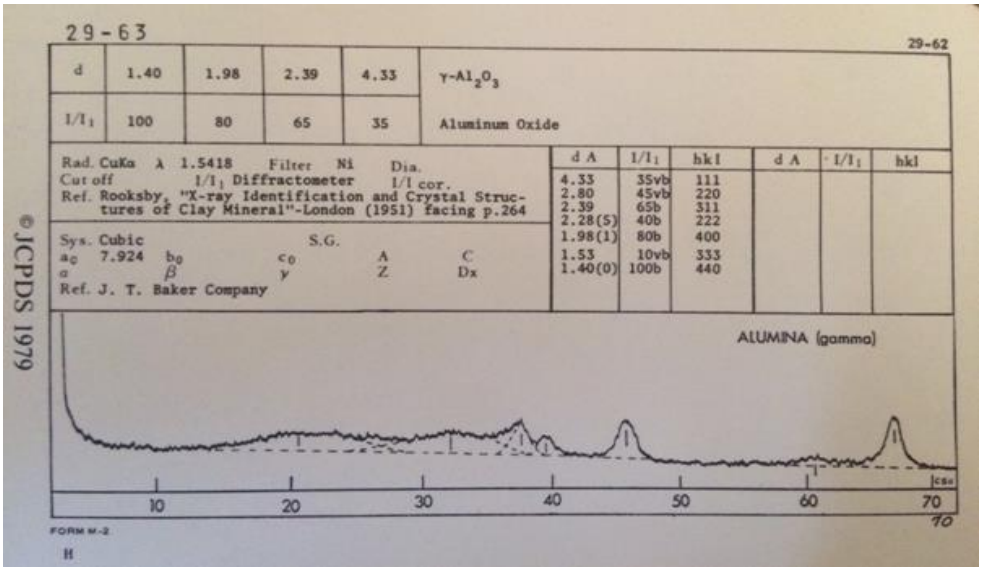


Fig. 5: The XRD spectrum of synthetic of standard gamma alumina

The purity of solid crystal was measured by comparing the X-ray diffractogram pattern of prepared nano alumina at different calcination temperatures with X-ray diffractogram pattern of standard gamma alumina shown in Table 1. This comparison proved that the prepared gamma alumina at calcination temperature 550 ^{o}C is more nearly to the standard.

The XRF analysis was used to find the percentage of Ni and Mo in the prepared catalyst. The percentages of Ni and Mo were 2.924 wt % and 12.920 wt %, respectively. The concentration of the metals on the support usually varies from 8 to 25 % for the active metal (Mo) and from 1 to 4 % for the promoter (Ni or Co) [20]. The percentage of Ni and Mo in prepared nano catalysts are not far from those obtained by Sandeep Badoga,el at., (2014), who prepared mesoporous NiMo/γ-Al_2O_3 by using the sequential impregnation (3% Ni, 13% Mo).

Table 1: Comparison between prepared nano gamma alumina at different calcination temperatures and standard synthetic gamma alumina

Gamma alumina 550 ^{o}C		**Gamma alumina 600 ^{o}C**		**Gamma alumina 750 ^{o}C**		**Standard gamma alumina**	
Angle (2ɵ) deg	**d,spacing (Å)**	**Angle (2ɵ) deg**	**d,spacing (Å)**	**Angle (2ɵ) deg**	**d,spacing (Å)**	**Angle (2ɵ) deg**	**d,spacing (Å)**
20.462	4.33	20.000	4.43	21.246	4.18	20.494	4.33
31.641	2.82	31.691	2.82	31.728	2.81	31.936	2.80
37.486	2.39	37.385	2.40	37.323	2.40	37.603	2.39
39.521	2.28	39.434	2.28	39.492	2.27	39.401	2.28
45.930	1.97	45.930	1.97	45.905	1.98	45.764	1.98
60.349	1.53	60.224	1.53	59.974	1.54	60.457	1.53
66.422	1.40	66.827	1.39	66.688	1.40	66.761	1.40

Atomic Force Microscopy (AFM)

The morphology of prepared alumina was studied using Atomic Force Microscope. Figures 6 – 8 show the images of AFM on two-dimensional surface profile at different calcination temperatures, while Figures 9 - 11 show AFM images for three-dimensional surface profile at different calcination temperature. The two dimensional surface images in Figures 6 - 8 show the irregular hexagonal structure of the gamma alumina crystal. Three dimensional surface

images shown in Figures 9 - 11 indicate that the agglomerates of gamma alumina nano crystal are in form of irregular hexagonal layers with height terraces up to 9.8 nm [5].

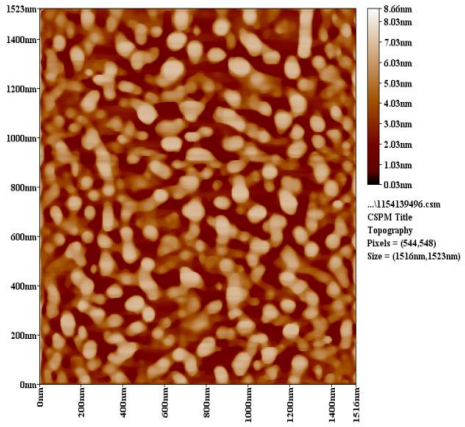


Fig. 6: AFM on two-dimensional surface of prepared nano alumina at calcination temp. 550 ^{o}C

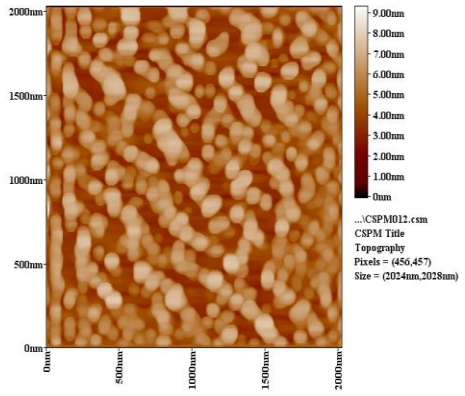


Fig. 7: AFM on two-dimensional surface of prepared nano alumina at calcination temp. 600 ^{o}C

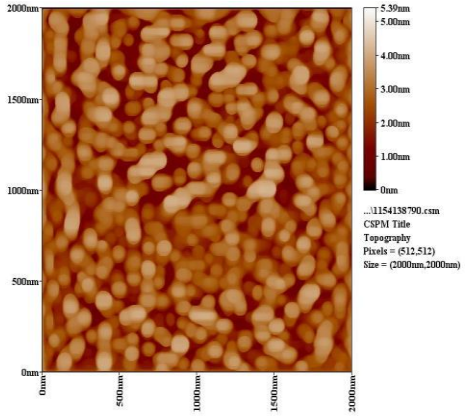


Fig. 8: AFM on two-dimensional surface of prepared nano alumina at calcination temp. 750^{o}C

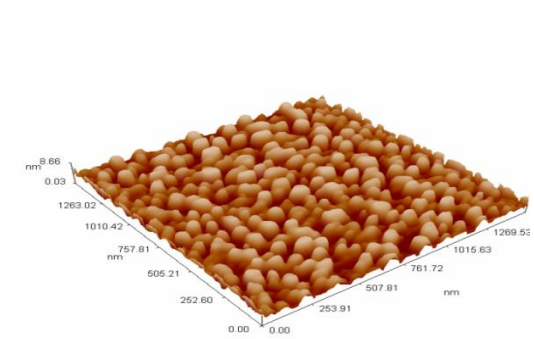


Fig. 9: AFM for three-dimensional surface of prepared nano alumina at calcination temp. 550 ^{o}C

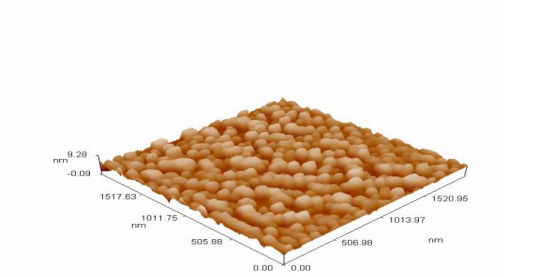


Fig. 10: AFM for three-dimensional surface of prepared nano alumina at calcination temp. 600 ^{o}C

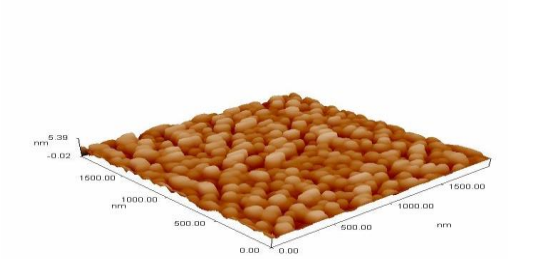


Fig. 11: AFM for three-dimensional surface of prepared nano alumina at calcination temp. 750^{o}C

Figures 12 – 14 show the particle size distribution for prepared gamma alumina at different calcination temperatures. At calcination temperature 550 ^{o}C the results confirm the largest volume percentage 19.27 % at 50 nm and the lowest volume percentage 0.36 % at 90 - 95 nm. The prepared gamma alumina at 550 ^{o}C consisted of particles with diameters ranged between 45 - 95 nm and average diameter of 56.91 nm this

result is near from that of A. Rajaeiyan, et al., (2013), who prepared nano structured gamma alumina powder 49.09 nm [5]. While at 600 ^{o}C the results confirm the largest volume percentage 7.11 % at 55 nm and the lowest volume percentage 0.22 % at 99 - 100 nm. The prepared gamma alumina at 600 ^{o}C consisted of particles with diameters ranged between 15 - 180 nm and average diameter of 68.72 nm. At 750 ^{o}C the results confirm the most volume percentage 11.18 % at 105 nm and the lowest volume percentage 0.62 % at 45 nm. The prepared gamma alumina at 750 ^{o}C consisted of particles with diameters ranged between 45 - 105 nm and average diameter of 77.27 nm.

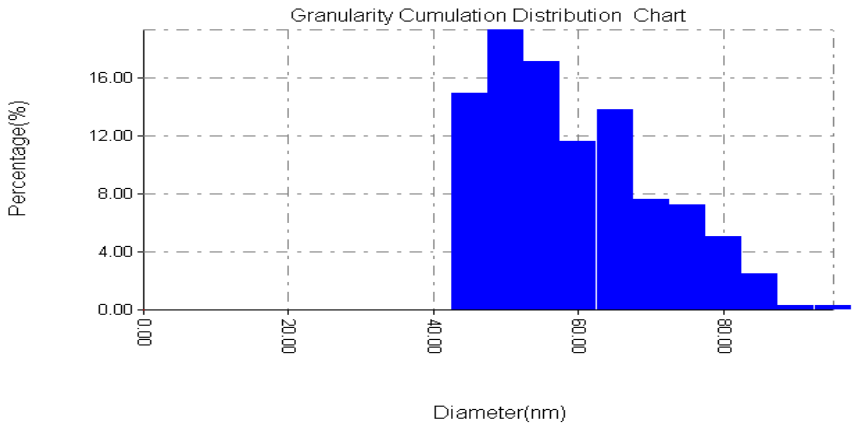


Fig. 12: Bar chart of particle size distribution for prepared alumina at calcination temperature 550 ^{o}C

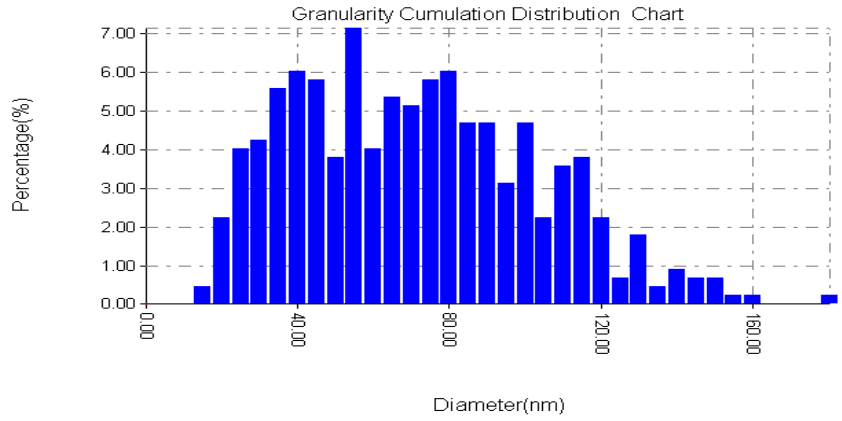


Fig. 13: Bar chart of particle size distribution for prepared alumina at calcination temperature 600 ^{o}C

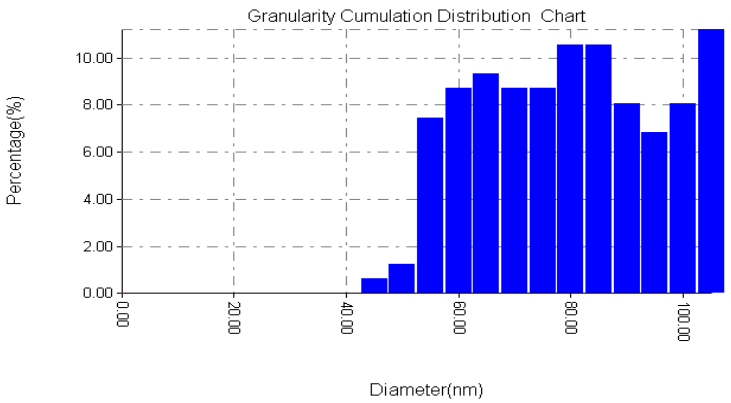


Fig. 14: Bar chart of particle size distribution for prepared alumina at calcination temperature 750 ^{o}C

Usually the range of nano particles is 1 – 100 nano meter [21]. Figures 12 – 14 show that all prepared alumina support at different calcination temperature are nano type. It was observed that the average particle diameter of nano gamma alumina increase with the increase in calcination temperature. This is due to the crystal sentering [22].

The AFM images of prepared NiMo/γ-Al_2O_3 catalyst using nano alumina support obtained at calcination temperature 550 ^oC are shown in Figures 15 - 16. The two dimensional surface images in Figure 15 show the irregular hexagonal structure of the gamma alumina crystal. Three dimensional surface images shown in Figure 16 indicating that the agglomerate of gamma alumina nano crystal are in form of irregular hexagonal layers with height terraces up to 3.96 nm [5].

Figure 17 show the particle size distribution for prepared gamma alumina and these results confirm the largest volume percentage 23.85 % of particle size distribution 70 nm and the lowest volume percentage 5.38%, 85 nm. It also show the prepared gamma alumina consisted of particles with diameters ranged between 55 - 85 nm and average diameter was 64.74 nm. This means that the particle of prepared nano NiMo/γ-Al_2O_3 catalyst was nano type. The increasee in average particle diameter of prepared catalyst occurs due to loading Ni and Co during impregnation on prepared support and crystal centering during impregnation method [22].

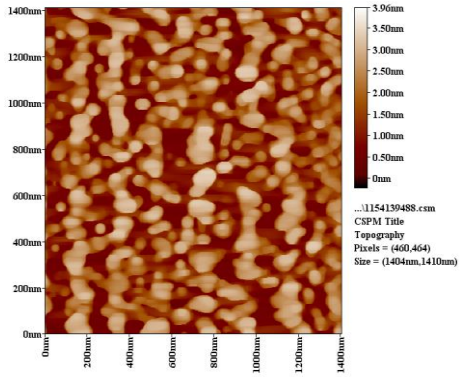


Fig. 15: For prepared NiMo/γ-Al_2O_3 AFM image on two-dimensional surface profile at 550 ^oC

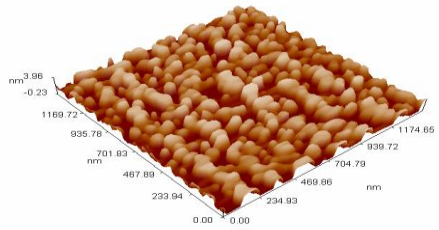


Fig. 16: For prepared NiMo/γ-Al_2O_3 AFM for three-dimensional surface profile at 550 ^oC

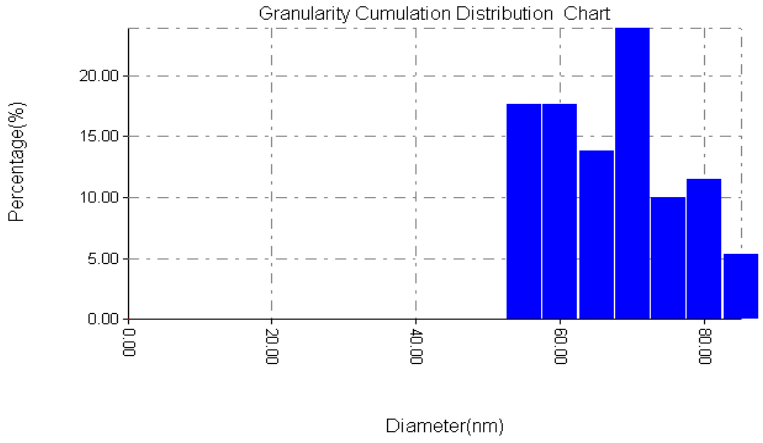
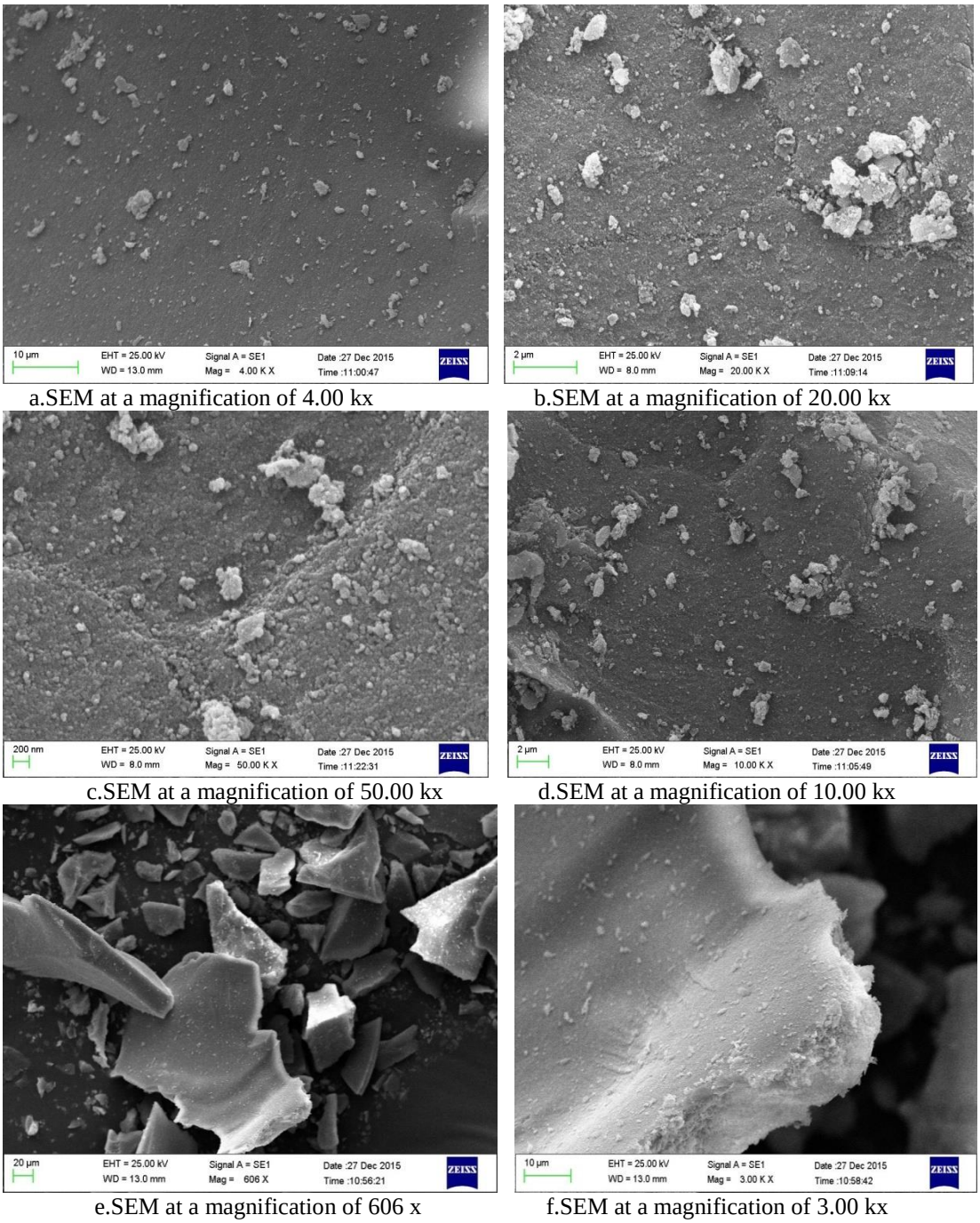


Fig. 17: Bar chart of particle size distribution for prepared nano NiMo/γ-Al_2O_3 catalyst at calcination temperature 550 ^oC

Scanning Electron Microscopy (SEM)

SEM images of prepared gamma alumina at calcination temperature 550 ^{o}C are shown in Figure 18, at magnification of 50.00, 20.00, 47.90, 10.00, 4.00, and 3.00 k x. It is very convenient to compare the prepared gamma alumina crystal with that prepared by A. Rajaeiyan, et al., (2013), as shown in Figure 19.

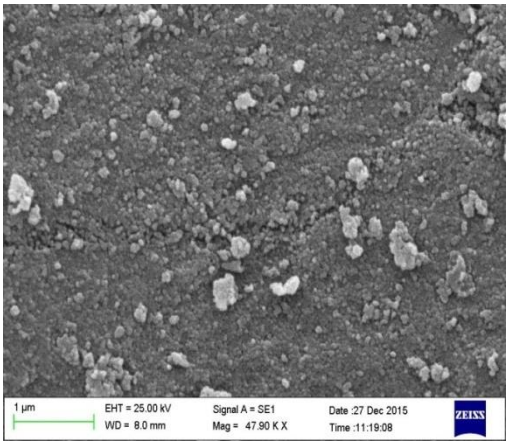


a.SEM at a magnification of 4.00 kx
b.SEM at a magnification of 20.00 kx
c.SEM at a magnification of 50.00 kx
d.SEM at a magnification of 10.00 kx
e.SEM at a magnification of 606 x
f.SEM at a magnification of 3.00 kx

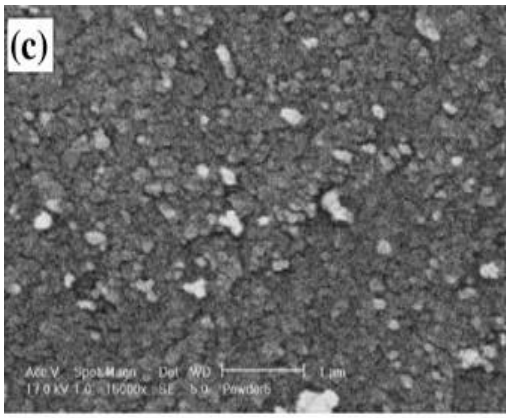
Fig. 18: SEM images of prepared nano gamma alumina

The comparison of SEM images for prepared gamma alumina with SEM for prepared nano gamma alumina by A. Rajaeiyan, et al., (2013) shows that both gamma alumina are irregular hexagonal shape particles with uniform

distribution and has not strong agglomeration [5].



a.SEM at a magnification of 47.90 kx of prepared gamma alumina



b.SEM at a magnification of 15.00 kx of prepared gamma alumina by A. Rajaeiyan,

Fig. 19: SEM images of prepared gamma alumina and nano gamma alumina prepared by A. Rajaeiyan, et al., [5]

General Properties of Catalyst

Physical and chemical properties of prepared catalyst at different calcinations temperature such as surface area, and pore volume were determined by BET device and presented in Table 2.

This table shows that the surface area decreased with increasing calcination temperature and maximum surface area 256.0 m^2/g is obtained at calcination temperature 550 ^oC while the surface area of prepared nano gamma alumina by A. Rajaeiyan, etal.,(2013) was 206.2 m^2/g. The higher surface area usually has a high percentage of small pores [5]. Also the using of high calcination temperature causes quick water evaporation from small pore to the large pore then to the bulk and this gives pressure drop. This pressure drop collapses part of pores especially in hydrogel step resulting in partial loss of surface area [9].

The pore volume of γ-Al_2O_3 decreases with the increase in calcination temperature increasing and the minimum pore volume 0.3742 cm^3/g obtained at calcination temperature 550 ^oC which was not far from 0.467 cm^3/g obtained by Parida et al. (2009) [1]. This occurs because high calcination temperature increases the reaction temperature, which rapidly leads the crystallites to contact each other. The contact occurs by two smaller crystallites agitated at higher temperatures resulting in coalescing to a larger one causing an increase of the pore volume and decrease the surface area by sintering or agglomeration of crystallites [9].

Table 5: Physical properties of prepared nano support γ-Al_2O_3

Calcined Temp ^oC	Surface Area m^2/g	Pore Volume cm^3/g	Pore volume distribution nm
550	256.0	0.3742	5
600	217.5	0.3715	-
750	213.5	0.4123	-

The prepared nano Ni-Mo/γ-Al_2O_3 catalyst obtained at calcination temperature 550 ^oC has surface area 215.82 m^2/g, and pore volume 0.2855 cm^3/g which was near that by Sandeep Badoga,el at., (2014) who prepared nano Ni-Mo/γ-Al_2O_3 catalyst with surface area of 225 m^2/g . The decrease

in surface area, and pore volume may be due to blockage of some pores by impregnation of Ni and Mo on the prepared support [21].

Conclusion

Nano γ-Al_2O_3 support was prepared by co-precipitation method from aluminum chloride as a source of alumina and ammonia hydroxide by using different calcination temperatures 550, 600, and 750 ^oC. From X-ray diffraction pattern and when compared it with the standard of gamma alumina found that prepared supports at different temperatures are mainly gamma alumina.

BET test found the surface area of prepared nano gamma alumina at 550, 600, and 750 ^oC are 256, 217, 213 m^2/g. The decreasing in surface area occur by increasing temperature.

From Atomic Force Microscopy test found that the average diameter of particles of prepared gamma alumina is 56.91 nm at 550 ^oC, 68.72 nm at 600 ^oC and 77.27 nm at 750 ^oC. While the average diameter of particles of prepared NiMo/γ-Al_2O_3 catalyst is 64.74 nm, and this means that the prepared γ-Al_2O_3 support and the prepared NiMo/γ-Al_2O_3 catalyst are in the range of nano type 1-100 nm.

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Appendix (A)

SPECTRO X-LabPro Job Number: 0

Description	Hawraa	Method	TurboQuant-Powders
Sample Name	3	Date of Receipt	05/27/2015 11:56:06

Z	Symbol	Element	Norm. Int	Concentration	Abs. Error
12	Mgo	Magnesium	38.0224	0.927 %	0.027 %
13	Al2O3	Aluminum	12382.5502	79.85 %	0.066 %
14	SiO2	Silicon	66.3879	0.2311 %	0.0051 %
15	P2O5	Phosphorus	254.9972	0.3699 %	0.0039 %
16	SO3	Sulfur	0.0000	< 0.00050 %	(0.0) %
17	Cl	Chlorine	428.9963	0.06085 %	0.00036 %
19	K2O	Potassium	6.5734	0.0374 %	0.0026 %
20	CaO	Calcium	31.9450	0.1230 %	0.0023 %
22	TiO2	Titanium	0.0000	< 0.00034 %	(0.0) %
23	V2O5	Vanadium	0.0000	< 0.00037 %	(0.0037) %
24	Cr2O3	Chromium	0.0000	< 0.00015 %	(0.0) %
25	MnO	Manganese	7.2168	0.00373 %	0.00034 %
26	Fe2O3	Iron	205.1929	0.06025 %	0.00040 %
27	CoO	Cobalt	96.6807	0.1328 %	0.0087 %
28	NiO	Nickel	19686.3359	2.924 %	0.002 %
29	CuO	Copper	40.2948	0.00447 %	0.00022 %
30	ZnO	Zinc	2537.4834	0.2390 %	0.0004 %
31	Ga	Gallium	0.0000	< 0.00005 %	(0.0) %
32	Ge	Germanium	0.0000	< 0.00005 %	(0.0) %
33	As2O3	Arsenic	0.0000	< 0.00007 %	(0.0) %
34	Se	Selenium	0.0000	< 0.00005 %	(0.0) %
35	Br	Bromine	10.9351	0.00032 %	0.00002 %
37	Rb2O	Rubidium	56.4448	0.00108 %	0.00002 %
38	SrO	Strontium	439.2818	0.00821 %	0.00004 %
39	Y	Yttrium	9.5877	0.00015 %	0.00003 %
40	ZrO2	Zirconium	44.4298	0.01603 %	0.00033 %
41	Nb2O3	Niobium	45.5775	0.01384 %	0.00053 %
42	Mo	Molybdenum	40962.1338	12.92 %	0.01 %
47	Ag	Silver	1.3400	0.00183 %	0.00055 %
48	Cd	Cadmium	8.6726	0.00797 %	0.0004 %
50	SnO2	Tin	12.2892	0.01152 %	0.00041 %
51	Sb2O5	Antimony	9.2371	0.01027 %	0.00048 %
52	Te	Tellurium	11.0299	0.00700 %	0.00030 %
53	I	Iodine	7.0907	0.00644 %	0.00067 %
55	Cs	Cesium	0.0000	< 0.00040 %	(0.0) %
56	Ba	Barium	0.0000	< 0.00020 %	(0.0) %
57	La	Lanthanum	3.8772	0.00188 %	0.00046 %
58	Ce	Cerium	0.0000	< 0.00020 %	(0.0) %
72	Hf	Hafnium	34.4012	0.00660 %	0.00019 %
73	Ta2O5	Tantalum	141.1496	0.0344 %	0.0011 %
74	WO3	Tungsten	21.4133	0.00436 %	0.00094 %
80	Hg	Mercury	0.0000	< 0.00010 %	(0.0) %
81	Tl	Thallium	15.2258	0.00058 %	0.00003 %
82	PbO	Lead	735.5520	0.05019 %	0.00016 %
83	Bi	Bismuth	0.0000	< 0.00010 %	0.00047 %
90	Th	Thorium	21.5463	0.00100 %	0.00005 %
92	U	Uranium	18.5451	0.00047 %	0.00002 %

Sum of concentration 54.88 %