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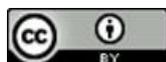
## Effect of Cationic Surfactant in the Synthesis Process of Nano $\gamma$ -Alumina for Petroleum Industry Application

Mustafa H. Flayyih\*, Mohammed S. Theib

Catalyst and Zeolite Section, Petroleum Research and Development Center, Ministry of Oil, Iraq

\*Corresponding Author E-mail: [mustafa.eng70@yahoo.com](mailto:mustafa.eng70@yahoo.com)

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### Abstract

Nanotechnology is widely used in industries, including catalyst synthesis for oil and gas industries to enhance and perform new Characteristics of materials. Cetyl tri methyl ammonium bromide (CTAB) cationic surfactant was used in the synthesis of spherical nanostructured  $\gamma$ -alumina to enhance the morphology of the prepared nano gamma alumina which is used as a catalyst support in the naphtha reforming process. The preparation was carried out by co-precipitation method by adding drop wise of ammonium hydroxide solution and aluminum nitrate nonahydrate solution simultaneously to a solution of surfactant medium, PH and temperature of reaction were kept at 8 and 30 c° respectively. The gamma alumina obtained were characterized by X- Ray Diffraction (XRD), nitrogen adsorption-desorption analysis (ASAP 2020, Micromeritics) and atomic force microscope (AFM). The sample of synthesized gamma alumina with the CTAB cationic surfactant showed that surface are (314 m<sup>2</sup>/g), pore volume (0.37 cm<sup>3</sup>/g), and pore size (3.6 nm).

**Keywords:** Nanotechnology; gamma alumina; surfactant; surface area; pore volume.

تأثير اضافة مواد تقليل الشد السطحي الموجبة في تصنيع نانو كاما ألومينا للصناعة النفطية

### الخلاصة:

تستخدم تقنية النانو على نطاق واسع في الصناعة ، بما في ذلك استخدام العوامل المحفزة في صناعات النفط والغاز للحصول على خصائص جديدة للمواد وتحسين مواصفاتها. تم استخدام Cetyl tri methyl ammonium bromide (CTAB) كعامل تقليل للشد السطحي في تصنيع كاما ألومينا النانوية لتحسين مواصفات وبنية العامل المساعد المستخدم في وحدات تحسن البنزين. تم إجراء التفاعل بطريقة الترسيب المزدوج لكل من محلول هيدروكسيد الأمونيوم ومحلول نترات الألومنيوم غير المائي في وقت واحد إلى وسط من محلول سيتيل ثلاثي مثيل بروميد الامونيوم، وتم المحافظة على الأس الهيدروجيني ودرجة حرارة التفاعل عند 8 و 30 درجة مئوية على التوالي. شخصت الألومينا النانوية المحضرة بواسطة جهاز حيود الاشعة السينية XRD، و جهاز الامتزاز الفيزيائي بالنيتروجين، ومجهر القوة الذرية (AFM).

أظهرت عينة الألومينا النانوية المحضرة باستخدام (CTAB) أن المساحة السطحية كانت بحدود ( 314 m<sup>2</sup>/g )، الحجم المسامي (0.37 cm<sup>3</sup>/g)، وقطر المسامات بحدود (3.6 nm).

## 1. Introduction

Aluminum oxide is useful in petroleum industry because of their excellent properties, such as high abrasion resistance, good insulation, high hardness, excellent dielectric strength at high voltage, thermal stability with a melting point of 2050 °C, and high resistance to chemical attack. As a result of its own textural properties and morphology, gamma alumina is commonly used as a catalyst support and adsorption. This is due to its improved properties, which include high thermal stability, surface area, pore volume, pore size, amphoteric and hydrolytic properties [1]. gamma alumina ( $\gamma$ -Al<sub>2</sub>O<sub>3</sub>) is possibly the most important transition aluminas known, with applications as a catalyst and catalyst support in the oil and gas industries. This oxide's usefulness can be attributed to a favorable combination of its textural properties, such as surface area, pore volume, and pore size distribution, and its acidity and basicity properties, which are primarily related to surface chemical components, structure, and phase composition. the chemical and hydrothermal stability of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> remains an issue for catalytic applications [2]. J.L. Contreras et al. used the precipitation method with Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, (NH<sub>4</sub>)OH, and the cationic surfactant cetyl-trimethyl ammonium bromide (CTAB) to create gamma alumina nano powder. CTAB concentration was varies from 0 to 0.1 M. The surface area of the prepared aluminas was (94-113) m<sup>2</sup>/g [3]. S. Faramawy et al synthesied crystalline nano alumina with high surface area (375 m<sup>2</sup>/g) via microwave irradiation at different times and watts using the sol gel method, aluminum hydroxide as starting material with ammonium hydroxide solution, and CTAB as template [4]. Jae Sung Lee et al. prepered nanotube gamma alumina with a large surface area and good thermal stability by combining aluminum alkoxide and cationic, ionic, and non ionic surfactants in an organic liquid. The final results shows that surface area (241-429 m<sup>2</sup>/g) and pore size (4.5-7.2 nm) [5]. L. A. Avinash Chunduri et al synthesized gamma alumina in nano size using aluminum nitrate as an oxidizer and urea or hexamethylenetetramine (HMT) as fuel with varies surfactants. Gamma alumina has a fairly uniform spherical morphology with a lower size distribution of (40–60 nm). The specific surface area obtained was (160–240 m<sup>2</sup>/g) [6]. Wen Qian Jiao prepared mesoporous gamma alumina by using Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O and NaAlO<sub>2</sub> as aluminum sources, and a template of cationic and anionic surfactants (CTAB) and dodecyl sodium sulfate (SDS) by using cationic-anionic double hydrolysis (CADH) method.

The obtained gamma  $\text{Al}_2\text{O}_3$  made up of nanoparticles with lengths ranging from 50 to 100 nm. Other characteristics include a high specific surface area ( $261 \text{ m}^2/\text{g}$ ), a large pore volume ( $0.79 \text{ cm}^3/\text{g}$ ), and a large pore size (12.1 nm) with a narrow pore size distribution [7]. Ming Bo Yue et al synthesized  $\gamma$ -alumina using CTAB as a surfactant,  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  and  $\text{NaAlO}_2$  as aluminum sources, citric acid and sodium citrate as structure direct agents, the resulting mesoporous gamma alumina with high specific surface area ( $398 \text{ m}^2/\text{g}$ ) and large pore volume ( $0.59 \text{ cm}^3/\text{g}$ ) [8]. Ming Bo Yue et al. also synthesized mesoporous alumina using (CTAB) and structure direct agents like sodium tartrate, citrate, or succinate. Aluminium Sulfate Octadecahydrate  $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$  as an aluminum source, and urea as a precipitating agent. Pore volume  $0.28\text{-}0.5 \text{ cm}^3/\text{g}$  and surface area  $172\text{-}325 \text{ m}^2/\text{g}$  [9]. Changhua Hu et al. created mesoporous aluminas with varying textural properties in aqueous solution using a combination of surfactants such as sodium dodecylsulphate (SDS), cetyltrimethyl ammonium bromide (CTAB), and polyethylene glycol (PEG). The results shows an alumina with a high specific surface area ( $267 \text{ m}^2/\text{g}$ ), pore volume ( $0.64 \text{ cm}^3/\text{g}$ ), and pore diameter (9.3 nm) [10].

For the high importance of gamma-alumina in the preparation of catalysts that are used in the many petroleum industries. moreover, nano gamma-alumina has unique specifications that were synthesized by the Co-precipitation method and characterized it to achieve this goal.

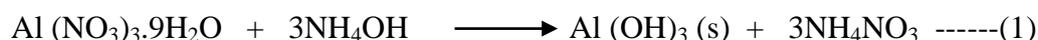
## 2. Materials & Methods:

### 2.1 Materials:

Aluminum nitrate nonahydrate  $\{\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}\}$  98% Assay (Thomas Baker Chemicals Pvt. Ltd. Co.) was used as a precursor of alumina, ammonium hydroxide  $\{\text{NH}_4\text{OH}\}$  25 weight% solution (Chem Lab NV Co.) as a source of hydroxide ions, cetyl tri methyl ammonium bromide  $\{\text{CTAB}\}$  99% assay (HiMedia Laboratories Pvt. Ltd. Co.), and deionized water.

### 2.2 Experimental Procedure of Preparation:

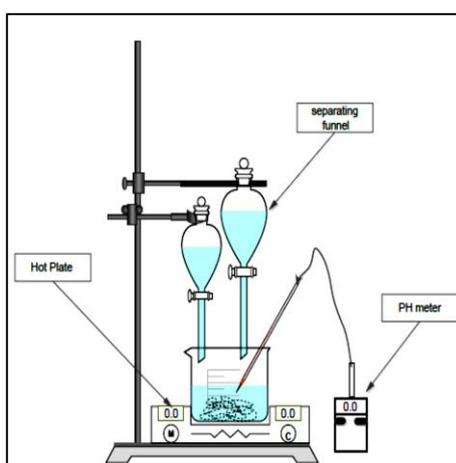
Nano  $\gamma$ - $\text{Al}_2\text{O}_3$  was synthesized as follows:



1 M of aluminum nitrate nonahydrate was poured into a separating funnel and 5 M of ammonia solution was poured into another separating funnel. After that, both solutions were allowed to drop wise into deferent concentration of CTAB solutions (0.0025, 0.005, and 0.01 M) as the reaction medium, and another reaction was carried out without surfactant, as shown in Table (1). These reactions were proceed under continuous stirring using a magnetic stirrer for two hours at room temperature taking into consideration adjusting the pH value at (7.5-8.5) by adding a nitric acid solution as shown in Figure (1). As a result a precipitate of  $\text{Al}(\text{OH})_3$  would appear, left it overnight for aging. The precipitate was separated from the solution by filtration and washing with two liters of deionized water, then filtrate again and drying at ( $60\text{ }^\circ\text{C}$ ) for 12 hours. Nano Gamma alumina was obtained from calcination powder for 2 hours at  $550\text{ }^\circ\text{C}$  at a rate of  $10\text{ }^\circ\text{C}/\text{min}$ .

**Table (1) Experimental Procedure**

	$\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	$\text{NH}_4\text{OH}$	CTAB
	Molarity (M)	Molarity (M)	Molarity (M)
A	1	5	0
B	1	5	0.0025
C	1	5	0.005
D	1	5	0.01



**Fig. (1): Schematic diagram of the laboratory glassware and tools used**

### 3. Results and Discussions:

The synthesized materials have been characterized by XRD (x-ray diffraction), AFM (atomic force microscope), and N<sub>2</sub> adsorption–desorption. Apparently spherical nano-sized particles were obtained with crystallite size in the range (nm) by peaks broadening calculation.

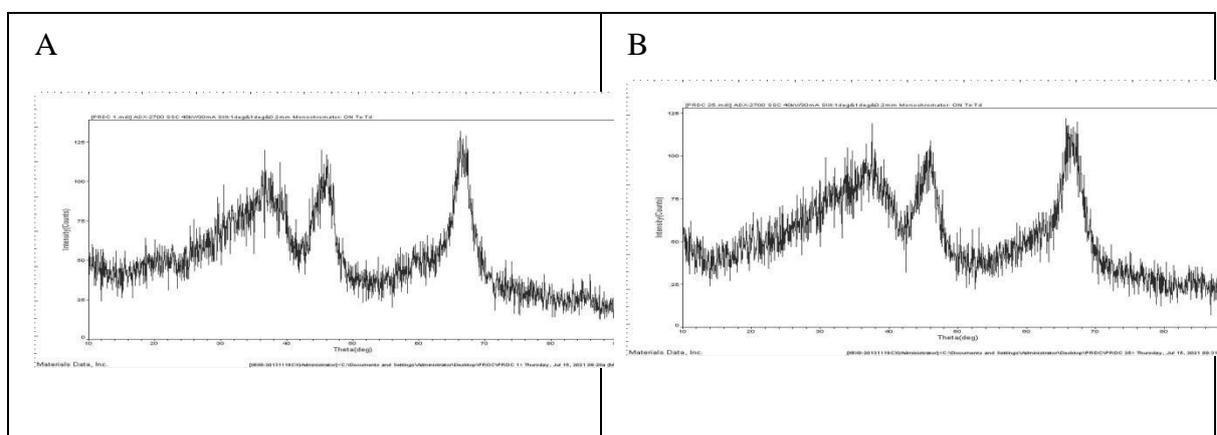
#### 3.1 XRD Patterns:

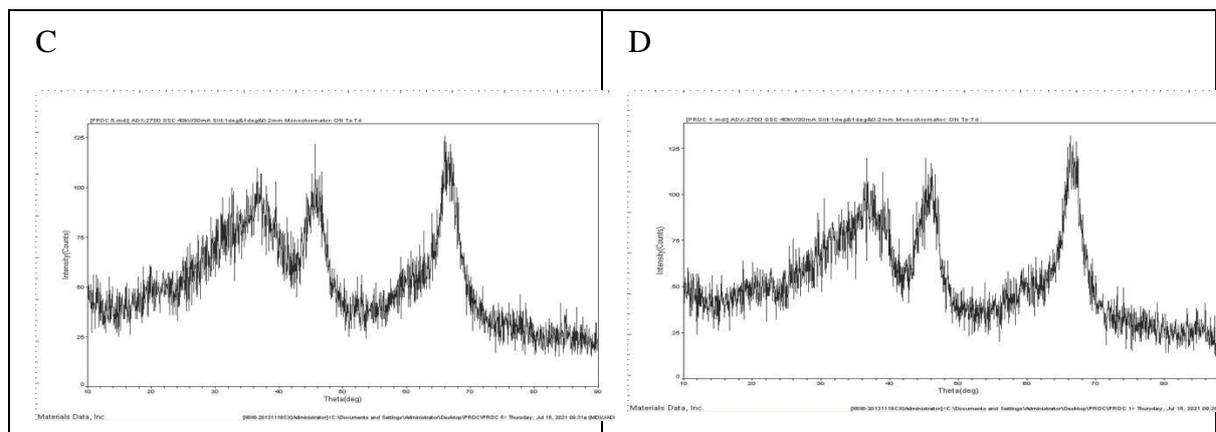
The XRD patterns of all samples shown below in (Figure 2 (a), (b), (c), and (d)) are in the gamma phase and crystalline. Crystallite sizes were calculated in comparison table (2) using Debye–Scherrer equation:

$$D = \frac{k \lambda}{\beta \cos \theta} \quad \text{----- (4)}$$

Where D is the crystallite size (nm), k is a constant (0.94 for spherical particles),  $\lambda$  is the wavelength of the x-ray radiation (Cu-K $\alpha$  = 0.1541 nm),  $\beta$  is the full width at half maximum (FWHM) of the intense and broad peaks and  $\theta$  is the Bragg's or diffraction angle.

XRD pattern shows big matches with the database standard (0010-0425 ICDD International Centre for Diffraction Data database) at three basic reflections ( $2\theta=37.6$ ,  $2\theta=45.8$  and  $2\theta=67.03$ ). Broadening of the peaks clearly shows the nano size nature of crystallites. From eq.(4) we see that the relation between Peak Width and crystallite size an inverse relation, i.e as the  $\cos \theta$  enlarged the crystallite became smaller and also peak intensity became shorten and as peaks became broaden the intensity became shorten also signifying greater degree of structural disorder [11].





**Fig. (2): XRD patterns of synthesized  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> at different concentration of CTAB.**

### 3.2 Atomic Force Microscope Characterization:

Atomic Force Microscopy shows that all samples in the nanosize range (nm). Particle size was analyzed by using the Atomic Force Microscope. The mean particle size for A, B, C, and D, samples were found to be (A: 43.8, B: 34.4, C: 17.06, and D: 40.01) nm as shown in Figure (3). The difference between values examined by AFM and XRD were illustrated in Table (2) i.e. due to the principle of measuring the AFM would be more accurate than XRD results.

**Table (2) Crystalline and particle size for different concentration of CTAB**

	A	B	C	D
Mean crystalline size XRD	55.3	17.6	15.6	23
Particle size AFM	43.8	34.4	17.06	40.01

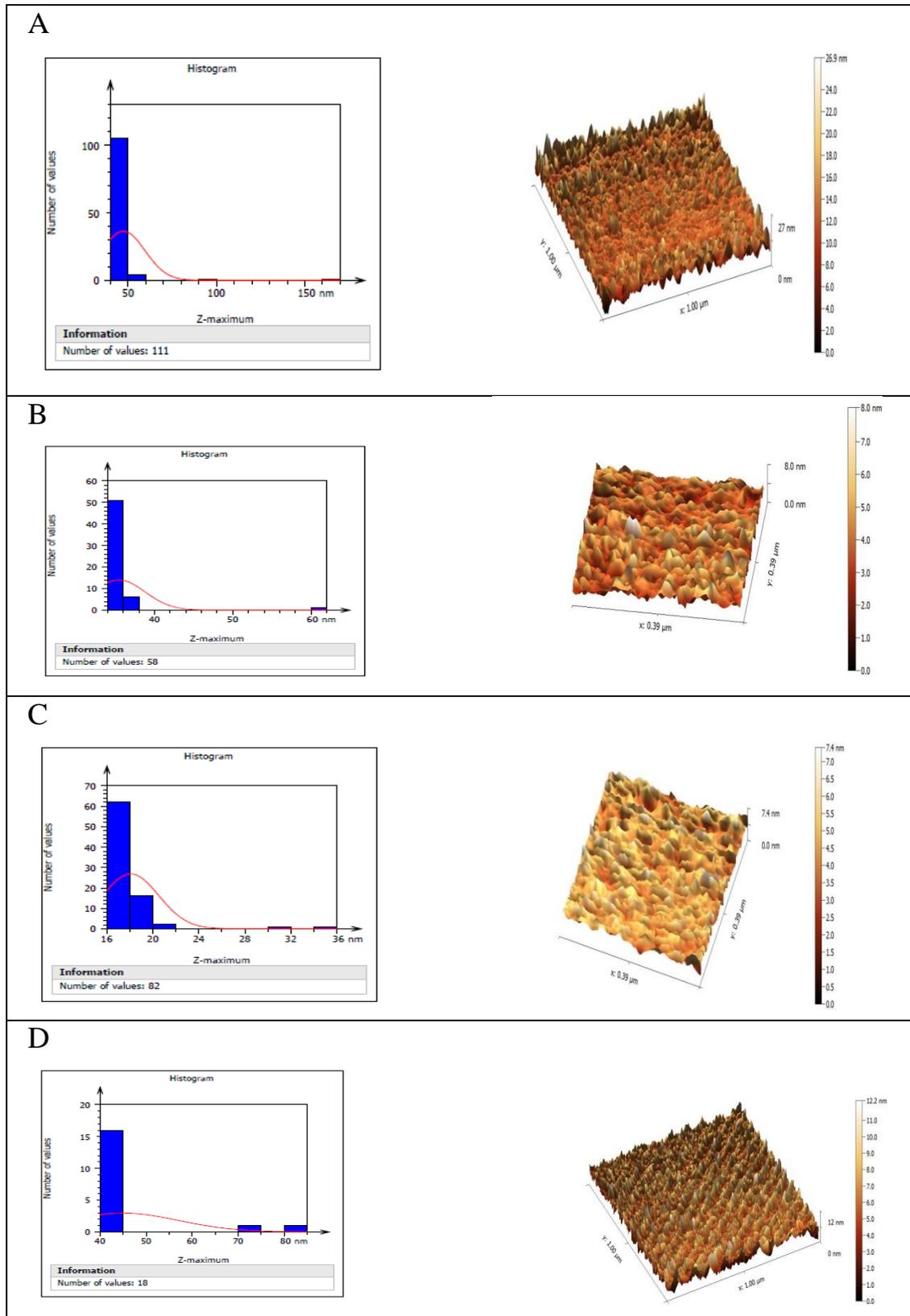


Fig. (3): AFM image of nano  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> prepared with different concentration of CTAB.

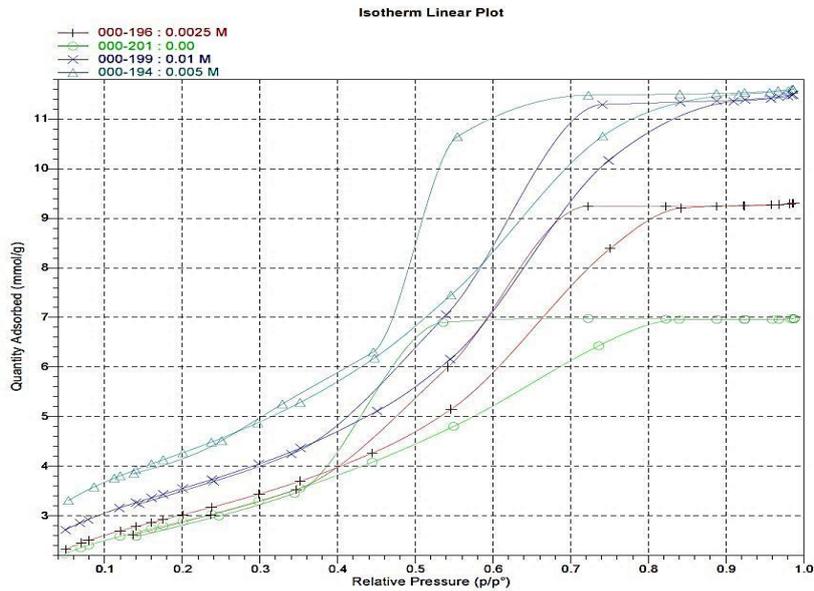
### 3.3 N<sub>2</sub> Physisorption Characterization

Catalytic performance was examined using Nitrogen adsorption isotherm at boiling temperature (-196 C°) to determine catalyst surface area and porous texture. According to IUPAC (International Union of Pure and Applied Chemistry) classification all synthesized samples were in mesopous (IV type) [12]. BET (Brunauer, Emmet and Teller) specific surface areas and pore volume were measured with an automatic sorptometer on a Micromeritics ASAP 2020 apparatus. Surface area and pore volume obtained were (314 m<sup>2</sup>/g) and (0.37 cm<sup>3</sup>/g) respectively at CTAB concentration of 0.005 molarity (figure 4).

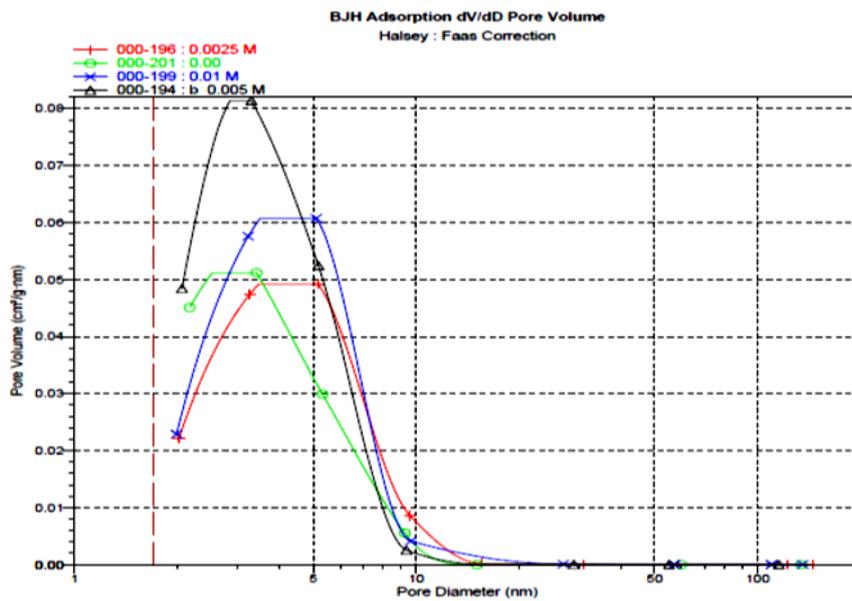
All results were tabulated in table (3) below, at different concentration of CTAB the optimum concentration is 0.005 M (run C) because surface area reach the best value and pore volume enlarged, above this concentration the CTAB solution tends to aggregate and surface tension be greater[13]. Also all samples were in narrow pore size distribution (figure 5).

**Table (3) Surface texture of synthesized nano gamma alumina**

Run	CTAB Molarity	Surface area (m <sup>2</sup> /g)	Pore volume (cm <sup>3</sup> /g)	Average Pore size (nm)
A	-----	234	0.24	3.0
B	0.0025	239	0.33	3.8
C	0.005	314	0.37	3.6
D	0.01	282	0.39	3.9



**Fig.(4) Isotherm behavior for nano gamma alumina prepared with different concentration of CTAB.**



**Fig. (5): Pore size distribution of nano gamma alumina prepared with different concentration of CTAB.**

#### 4. Conclusion

Nano Gamma alumina successfully prepared by co- precipitation method in presence of CTAB as a surfactant. Essential parameters were studied in our research, isotherm behavior, surface area, pore volume, and pore size. The properties of our synthesized nano gamma alumina and the commercial one specified by Eugene et al and antos, were matches in surface area and pore size while pore volume should be more than  $0.5 \text{ cm}^3/\text{g}$  to achieve excellent dispersion of active metals. Surface area enhancement from 234-314  $\text{m}^2/\text{g}$  while pore volume enlarged by approximately 13%.

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