Journal of Petroleum Research and Studies

Open Access
No. 39, June 2023, pp. 76-85

P- ISSN: 2220-5381
E- ISSN: 2710-1096

DOI: http://doi.org/10.52716/jprs.v13i2.665

Enhancement of the Texture & Morphology of Nano γ-Alumina as a Support for Naphtha Reforming Catalyst

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Received 6/9/2022, Accepted in revised form 25/10/2022, Published 15/6/2023

Abstract

The morphology of nano gamma alumina affects the molecule adsorption-desorption phenomena. In this case, manipulating the surface area, pore volume, and pore size by the technique of preparation to control the morphology and textural properties of gamma alumina. Washing of the synthesized boehmite gel with methanol has a significant effect. The co-precipitation method was used to prepare nano gamma alumina, which is involved by adding drop-by-drop ammonium hydroxide and aluminum nitrate nonahydrate solutions to a cetyltrimethylammonium bromide (CTAB) cationic surfactant solution at 30 C and adjust PH to 8. Nitrogen adsorption-desorption analysis (ASAP 2020), Atomic Force Microscope (AFM), and X-Ray Diffraction (XRD) were used to examine the obtained material. Surface area (362 m2/g), pore volume (0.51 cm3/g), pore size (5.2 nm), and narrow pore size distribution were obtained.

Keywords: nano gamma alumina, morphology control, methanol, drying, washing, pore texture.

تأثير الغسل بالميثانول على بنية وشكل نانو كاما الومينا كمادة ساندة للعامل المساعد في النفثا

الخلاصة:

تتأثر ظاهرة الامتصاص على اسطح المواد بشكل وتركيب هذه الاسطح، لذلك يتم السيطرة على بعض الخصائص مثل المساحة السطحية والحجم الفراغي والحجم الحبيبي وتوزيع الجزيئات بواسطة التقنيات المستخدمة في تحضير نانو كاما الومينا للسيطرة على هذه الخواص. غسل البوهمايت الهلامي بالميثانول له أثر كبير في ذلك. يتم تحضير كاما الومينا النانوية بترسيب كل من نترات الالمنيوم المائية وهيدروكسيد الامونيوم سويةً قطرة قطرة في محلول من سيتيل مثيل بروميد الثلاثي بدرجة حرارة 30 م ودالة حامضية 8. تم استخدام طريقة الامدصاص الفيزياوي بالنتروجين ومجهر القوة الذرية وحيود الاشعة السينية لتشخيص كاما الومينا النانوية. اظهرت النتائج ان المساحة السطحية (362 م/غم) والحجم الفراغي (0.47 سم/غم) وقياس المسام (5.2 نانوميتر) وتوزيع مسامي محدد.

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P- ISSN: 2220-5381
E- ISSN: 2710-1096

1. Introduction:

Gamma alumina has been used as catalyst support in a variety of industrial catalytic processes due to its relatively stable, acidic and basic site contents also provides a wide range of surface areas and porosities making it suitable for a wide range of catalytic applications [1]. The most common inorganic carrier of catalytic components is aluminum oxide (Al_2O_3). The applicability of this oxide can be attributed to a beneficial combination of textural properties and acid/base properties, all of which are primarily related to its surface composition, local microstructure, and phase composition [2]. Boehmite gels (AlOOH) formed by neutralization from their acid or a basic solution contain excesses of water and ions [3]. In general, the use of template materials is thought to be the most efficient way to prepare nanostructures that allow for pore size tuning [4]. The Co-precipitation method begins with a solution, which requires digesting the precursors in a soluble form and thereafter adding a precipitating agent to create a homogeneous, single-phase inorganic gel. Subsequently, the precipitate can be decomposed at a high temperature to yield the desired oxide material [5]. Drying has a direct effect on the reactant's diffusion and many factors can influence the morphology of the synthesis gel including temperature, aging time, synthesis gel composition, and structure-directing agent [6]. One of the most important steps in catalyst preparation using precipitation methods is drying the obtained precipitate and the drying method affects the final catalyst's structure, texture, porosity, surface area, and morphology [7]. Washing silica gels which were produced using tetraethylorthosilicate (TEOS) and ammonium hydroxide (NH_4OH) with various aprotic solvents show that the pore volume increased [8]. The pore volume and pore size enlarged when using methanol or ethanol to wash the synthesized porous alumina [9]. Nanosized γ-alumina powder was prepared via precipitated in ethanol and the aggregation of particles was studied [10]. Boehmite (AlOOH) was synthesized via Co-precipitation of aluminum nitrate nonahydrate $\{Al(NO_3)_3 \cdot 9H_2O\}$ or aluminum chloride ($AlCl_3$) in ethanol (C_2H_5OH) and sodium hydroxide (NaOH) solution, so the pore volume and surface area obtained were 0.37 cm^3/gm and 90 m2/g respectively [11]. Nano gamma alumina was prepared using Tween-80 as a nonionic surfactant, $AlCl_3.6H_2O$ as a source of aluminum, and NaOH. The precipitate of $Al(OH)_3$ was obtained and then washed several times with ethanol and water. The sizes of the nanoparticles are in the 30–50 nm range, the pore size is 4.13 nm and the surface area is 112.9 m^2/g [12]. The objectives of the present work are synthesis of nano gamma alumina (γ-Al_2O_3) using surfactant and enhancement the texture properties of it to extending catalyst life.

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2. Materials & Methods:

2.1 Chemicals:

Nano gamma aluminum oxide was produced via aluminum nitrate nonahydrate {Al(NO3)3.9H2O} 98% Assay (Thomas Baker Chemicals Pvt. Ltd. Co.) as an aluminum precursor, ammonium hydroxide {NH4OH} 25 weight% solution (Chem Lab NV Co.) as precipitating agent, cetyl tri methyl ammonium bromide {CTAB}99% assay (HiMedia Laboratories Pvt. Ltd. Co.) as a surface active agent, methanol (Scharlab S. L.) 99.9%, and deionized water as a cleaning agent.

2.2 Characterization:

2.2.1 X-Ray Diffraction

The morphological and structural information of the investigated nanomaterials can be obtained using X-ray and Bragg diffraction [13]. Scherrer equation can be used to estimate particle size [14].

$$D = \frac{(K)\,\lambda}{\beta\,\cos\theta} \quad \ldots\ldots\ldots\ldots (1)$$

Where: D size of the.

K Scherrer constant

λ XRD wavelength

β full width at half maximum (FWHM) measured in radians, and

ɵ diffraction angle.

2.2.2 Atomic Force Microscope [15]:

Atomic force microscope **(**AFM) is a fairly straightforward instrument. The creation of an AFM with nanometre-scale resolution, however, necessitates a significant amount of advanced engineering. The microscope stage itself, control electronics, and a computer make up the majority of an AFM. The sample holder, force sensor, and scanner the device that moves the AFM tip in relation to the sample are all found on the microscope stage.

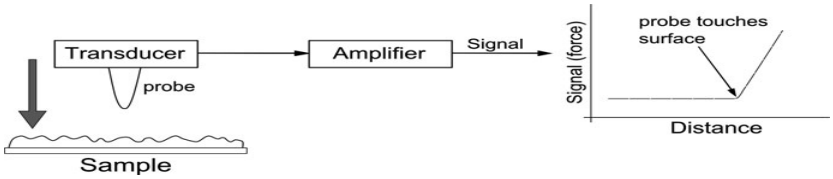

Fig. (1): Scheme of force transducer operation.

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2.2.3 Nitrogen Adsorption-Desorption Characterization

Nitrogen adsorption-desorption isotherms were measured at -196 C on an ASAP-2020 instrument. Samples were outgassed at 200 C° for 6 h. The total surface area was determined by the Brunauer–Emmett–Teller (BET) method, single point pore volume was measured at a relative pressure of 0.9856 cm^3/g, and average pore width was measured by the BET method at 4V/A.

Fig. (2): ASAP 2020 Instrument

2.3 Experimental Procedure:

The procedure used in the synthesis of nano gamma alumina was as follows, 1 M of aluminum nitrate solution $\{Al(NO_3)_3.9H_2O\}$ was used as a precursor for aluminum oxide and 5 M of ammonium hydroxide solution were precipitated together in the 0.005 M of cetyl tri methyl ammonium bromide solution (CTAB) as shown in fig. (3). Nitric acid was used for controlling the pH at 8. The temperature was kept at about 30 c° throughout the process and mixing of the mixture of course. The white gel of AlOOH was precipitated and left it 24 h for aging. Filtrate the solid, washing with deionized water and then with methanol, after that drying the gel at 60 c° for 12 h. Calcination was carried out at 550 ????? K or C at a rate of 10 c°/min. The representation of the samples is as follows: (CTAB) represents nano gamma aluminum oxide prepared using surfactant and washed with deionized water, and (CTAB) Me represents another sample of synthesized alumina but washed with methanol.

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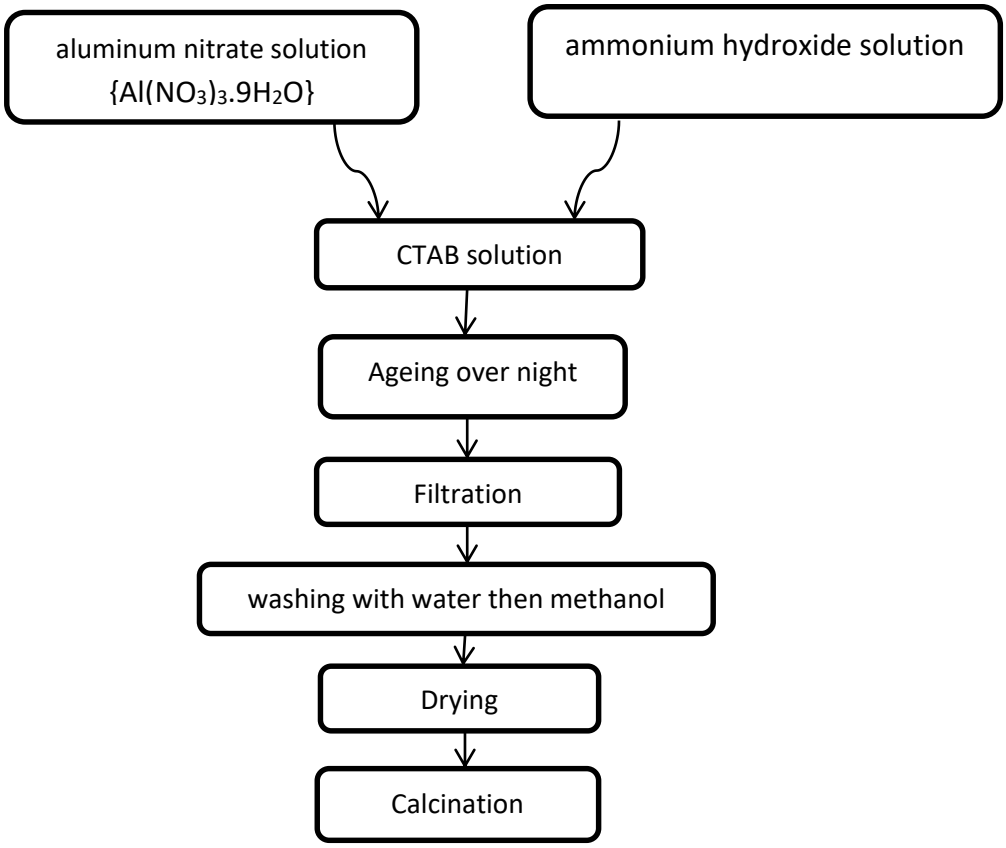

Fig. (3): Preparation scheme of nano gamma alumina.

3. Results and Discussions:

3.1 XRD Patterns:

Gamma alumina phase shows three basic reflections compared to save standard (0010-0425 ICDD International Centre for Diffraction Data database) cubic structure at (311), (400), and (440) diffraction peaks while peak (111) was clearly appeared in (CTAB) Me sample only. Approximately the mean crystallite size for tow samples calculated by eq. (1) of the prepared γ-Al_2O_3 using the full width at half-maximum peaks of 28, 11, and 10 nm respectively.

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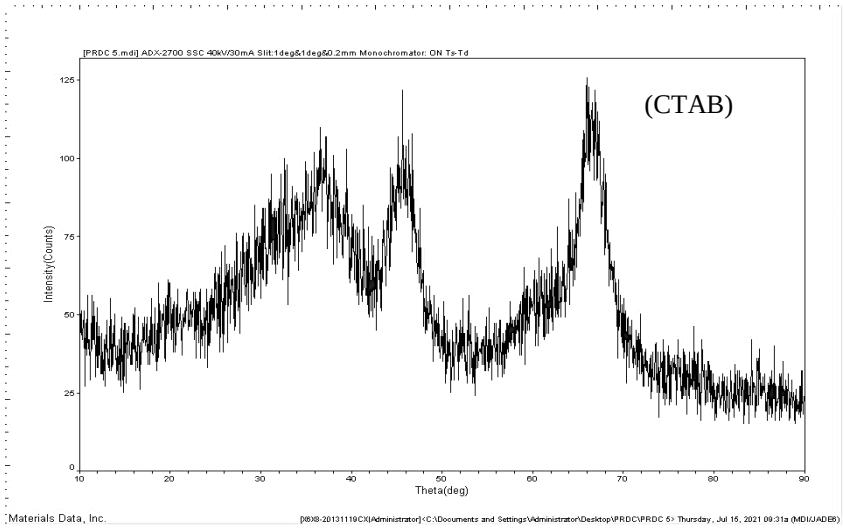

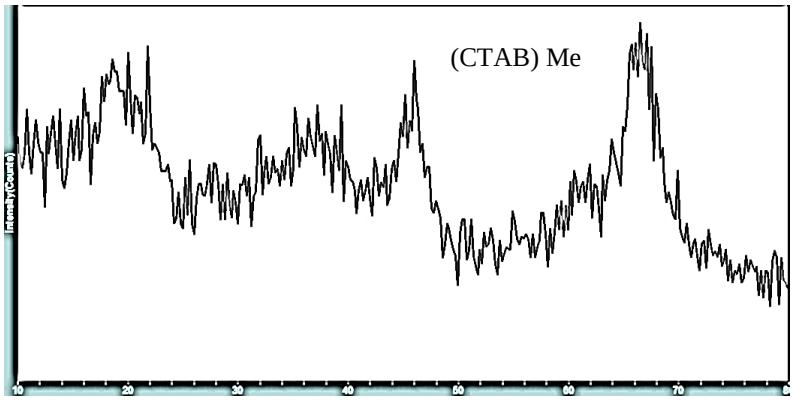

Fig. (4): XRD patterns of synthesized γ-Al_2O_3

3.2 Atomic Force Microscope Test:

Samples that dry with and without methanol are characterized with an atomic force microscope was shown in Figure (5). Nanoparticle size can be measured with three-dimensional structure and particle size distribution by some analysis software. The size of the particle was approximately 11 nm when the gel washed with methanol and 20 nm for the washing the gel with water only. Methanol pulled the water molecule from pores so it prevents shrinkage of pore wall at annealing.

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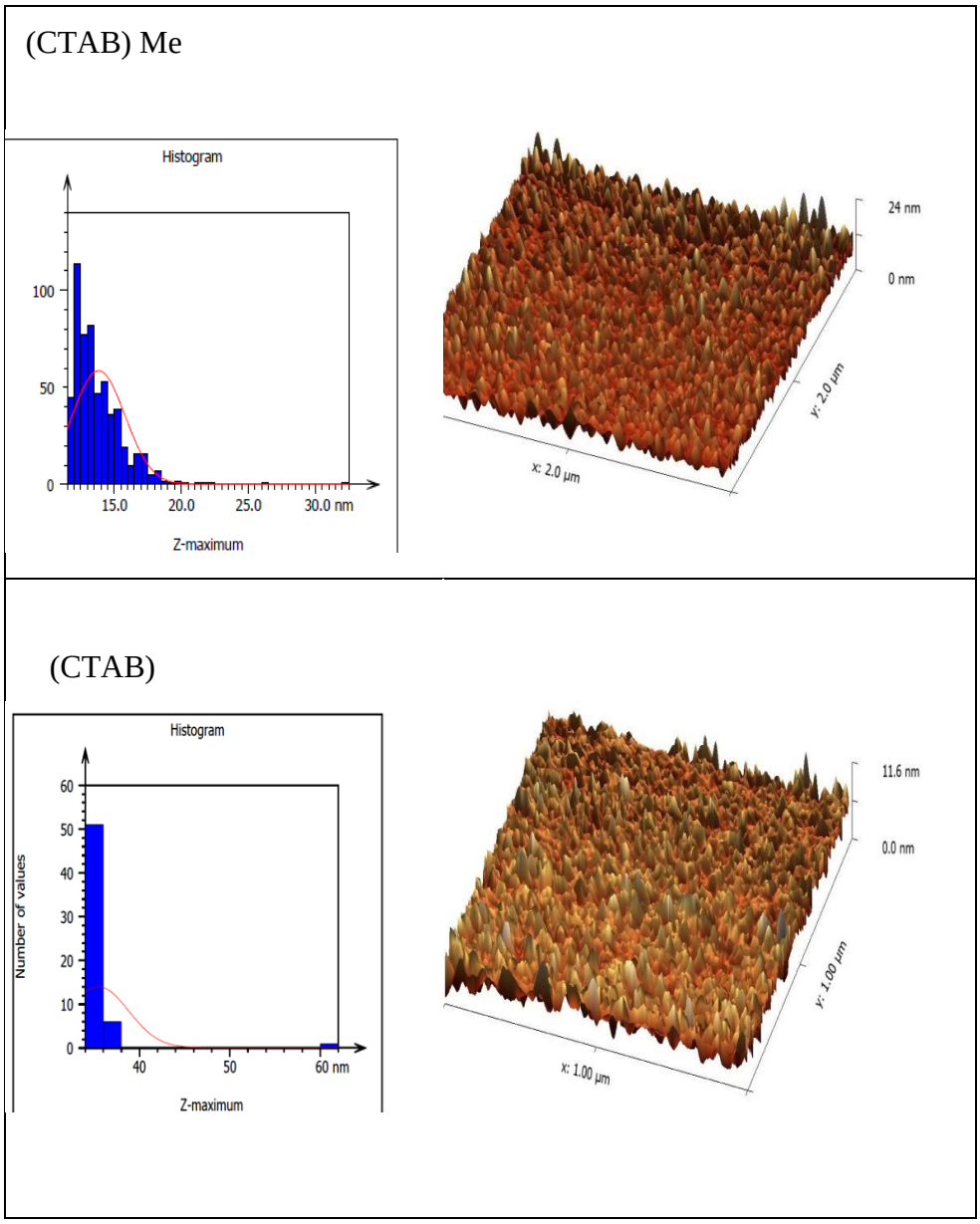

Fig. (5): AFM image of synthesized γ-Al_2O_3

3.3 Nitrogen Adsorption Test:

Two samples were in mesoporous type (IV) as shown in Figure (6) and the green line indicates that the sample that was washed with methanol has more quantity absorbed of nitrogen and larger pore volume as we see from Table (1) also.

Table (1) Surface texture of synthesized nano gamma alumina

Run	Surface area (m^2/g)	Pore volume (cm^3/g)	Pore width (nm)
(CTAB)	330	0.37	4.7
(CTAB) Me	362	0.51	5.2

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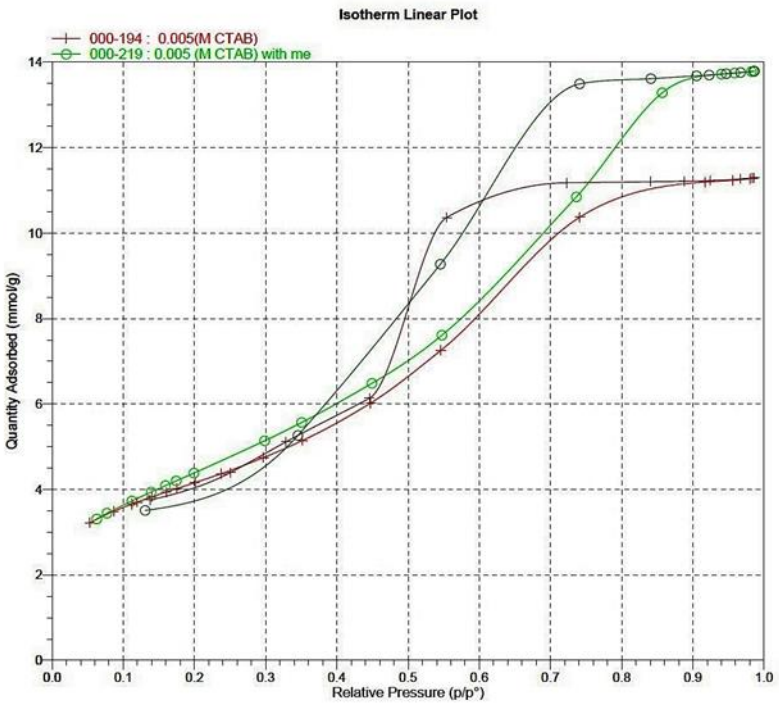

Fig. (6): Isotherm behavior for synthesized nano gamma alumina

4. Conclusion

The porosity of the support material is responsible for the transport of reacting subsistence. The pore structure for the desired reaction allows free entrance of reacting substances to the catalyst pores' mouth. Three factors were improved by washing the gel produced by methanol surface area, pore volume, and pore size. The use of methanol as a washing solvent for surfactant and moisture totally removed to avoid shrinkage of small particles and prevent losses of pore volume. The surface tension of methanol is lower than water and the capillary force of methanol is lower too.

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