Synthesis of high surface area γ-alumina by microwave irradiation process.

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Abstract: The preparation of crystalline nano-sized γ-Alumina with high surface area (375 m^2/g) using sol gel simple method , aluminum hydroxide as starting material and CTAB as template molar ratio (1:1) via microwave irradiation process at different times and watts. The prepared samples were characterize by DSC/TG, X-ray diffraction, nitrogen physisorption, and HRTEM techniques.
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Keywords: γ-aluminaand microwave irradiation.

1- Introduction:

Aluminas are important industrial chemicals that have found wide application in adsorbents, ceramics, catalysts and catalyst supports [1-4]. The catalytic performances of alumina-supported catalysts are largely dependent on the textural properties of the alumina supports. Alumina supports with large surface areas, large pore volumes, and narrow pore size distributions within the mesoporous range [5, 6]. Therefore, synthesis of mesoporous aluminas with high surface areas and uniform mesoporous has attracted much attention [7-9]. Many synthesis routes have been developed for the preparing of mesoporous aluminas. Among them, organic-inorganic assemblies involving complicated sol-gel processes by using surfactants as structure-directing agents [10, 11]. Microwave processing is a relatively new development in materials processing. The ability of microwaves to couple energy directly to the material is the primary advantage of microwave processing as compared to conventional techniques (thermal processes) [12, 13]; microwave synthesis has the advantages of short reaction time, small particle size, and high purity [14, 15]. In the present work, we used a new step to synthesize mesoporous γ-$Al_2O_3$with high surface areas and rich porosities using a cationic surfactant (CTAB) as directing agents and in the presence of a cyclic microwave irradiation at different operation times and watts.

2- Material and methods:

2.1. Materials:

Aluminum nitrate nonahydrate $Al(NO_3)_3.9H_2O$ (98.0% , Qualikems), ammonium hydroxide solution (30.0% NH_3 ADWIC), hexadecyltrimethylammonium bromide (CTAB, ≥ 98% Merck), glacial acetic acid (≥ 99.7%), ethanol (≥ 99.5%, absolute) were purchased from Sigma-Aldrich Company.

2.2. Preparation of aluminum hydroxide:

Enough ammonium hydroxide (30%) added dropwise to 0.64 M aluminum nitrate solution under vigorous stirring, to reach the pH ~ 8. The hydroxide gel was then left to age overnight then washing several times with deionized water and separate the filtrate using the centrifuge process. The solid was then dried at 80°Covernight.

2.3. Synthesis nano-sized γ-AL_2O_3 at different microwave operation times:

We prepared four different samples γ- Al_2O_3 powders using aluminum hydroxide as starting material which peptized by glacial acetic acid ($_PH$ ~ 3) and surfactant (CTAB) molar ratio (1:1) by microwave synthesis process, operation at different times (0, 4, 6 and 8 min) and 100 watts. were dissolved in deionized water. The mixture was titrated by ammonium hydroxide solution with continuous mechanical stirring; until the forming of gel at $_PH$ to ~ 8. The stirring continued for 10 min under the microwave irradiation. The product was left to be decanted and washed with warm water/ethanol mixture several times. Finally, the precipitate was dried at80°C. The γ-Al_2O_3 powders were obtained by carrying out calcinations step at 400 °C with heating rate 4°C /min for 6 h in a muffle furnace. The resulted samples were coded ***0mw/4, 4mw/4, 6mw/4 and 8mw/4*** regarding different microwave operation time respectively.

2.4. Synthesis nano-sized γ-AL_2O_3 at different microwave operation watts:

We preparedfour different samples γ- Al_2O_3 powders using aluminum hydroxide as starting material which peptized by glacial acetic acid ($_PH$ ~ 3) and surfactant (CTAB) molar ratio (1:1) via by microwave

synthesis process, operation at different watts (100, 300, 600 and 800) and time 8 min. were dissolved in deionized water. The mixture was titrated by ammonium hydroxide solution with continuous mechanical stirring; when the sol gel was formed at pH ~ 8 the addition process was stopped. The stirring continued for 10 min under the microwave irradiation at a power of (100, 300, 600 and 800 W). The product was washed by warm water/ethanol mixture several times. Separate white precipitate by centrifuge processes finally, dried the precipitate at 80°C and γ-Al_2O_3 powders were obtained by calcined in a muffle furnace at 400 °C with heating rate 4°C /min for 6 h. the resulted γ- alumina samples were coded ***8mw/100, 8mw/300, 8mw/600 and 8mw/800*** respectively regarding to different microwave operation watts.

2.5. Characterization of the prepared samples:

Thermogravimetric and differential thermal analysis (TG-DTA, TA Instruments) widely used to study the structural stability of as-synthesized forms of mesoporous materials during the calcinations of alumina and were performed with a heating rate of 10°C /min in air. To examine the crystallinity of the prepared materials, powder X-ray diffraction (XRD) analysis was carried out with a PAN analytical x' PERT PRO using CuKα X-ray radiation (λ= 0.1540 nm). The BET surface area and pore volume were determined from nitrogen adsorption and desorption isotherm data obtained at 77K on a constant-volume adsorption apparatus (Quantachrome NovaWin 3200). The pore volumes were determined at a relative pressure (p/p^o) of 0.99. The prepared samples were degassed at (150 ^oC) for overnight before measurements. A BJH (Barett-Joyner-Halenda) model from adsorption branch of the nitrogen isotherms determined the pore size distributions of prepared materials. To investigate the morphologies of the nanostructure alumina materials, transmission electron microscope (TEM) images were obtained on a JEOL JEM 2100F (Field Emission Electron Microscope) instrument operated at 200 kV.

3. Results and Discussion:

3.1. Characterization of alumina samples:

The differential thermal analysis (DTA) and thermal gravimetric analysis (TGA) are important techniques used to distinctly the effect of heating in the performance and thermal stability of the prepared alumina sample. All synthesized samples prepared at different microwave operation times and watts appeared similar thermal behavior. Fig. (1) Shows DSC/TG curves of synthesized samples. The TGA curves show that the sample has two major weight loss events. The first weight loss event below 151 °C is due to desorption of physically adsorbed water. The second weight loss event in the temperature range of 151–286 °C, may be the continuation of desorption of surface water. Also can be seen from the endothermic peak at 291 °C of the DSC curve, assigned to dehydroxylation of the sample during the transformation of the aluminum hydroxide into γ Al_2O_3 [16]. A small exothermic peak at about 966◦C is attributed to phase transformation from γ Al_2O_3 to δ- Al_2O_3[17].

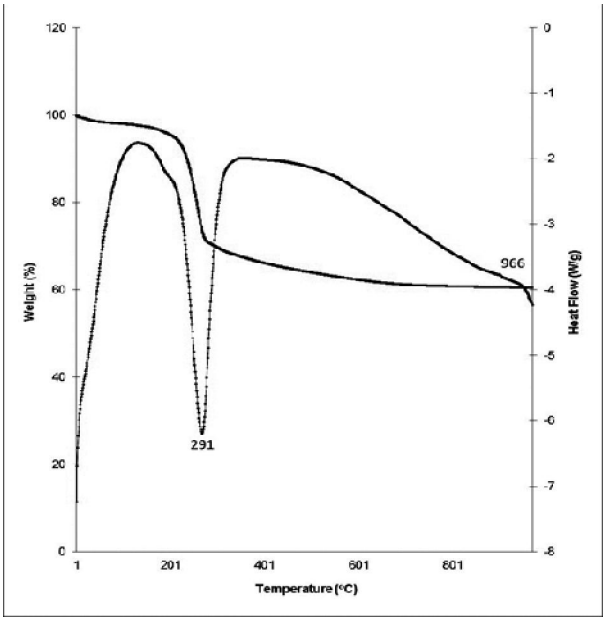


Fig. (1): DSC/TG curves for as-synthesized nano alumina sample.

The XRD patterns of the prepared alumina samples Fig. (2, 3) reveal that all samples exhibit broad peaks corresponding to γ-Al_2O_3 and Show the main reflections of γ-Al_2O_3 at d-spacing 1.39, 1.97, and 2.38 Å this is as compared with (JCPDS 48-0367) [18].It indicates that the resulting materials are amorphous, but have the characteristics of mesostructured materials and Success in achieving γ-Al_2O_3 via microwave process.

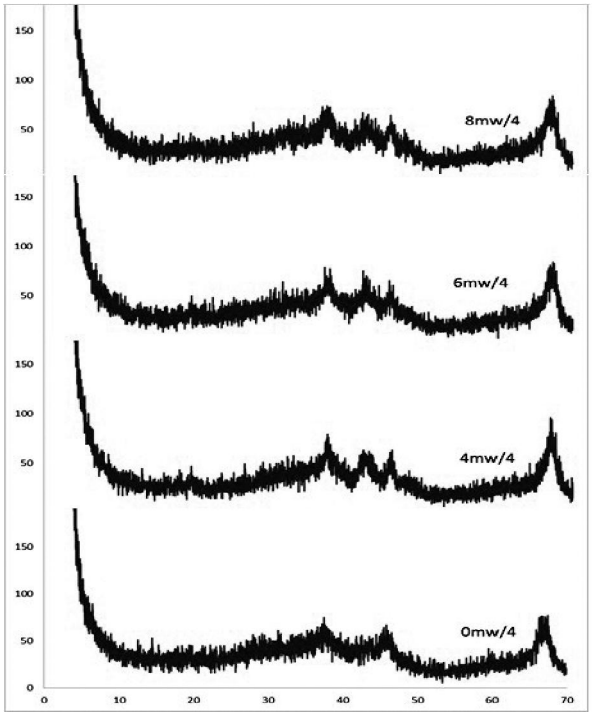


Fig.(2): X-ray diffraction patterns of alumina samples at different microwave operation times.

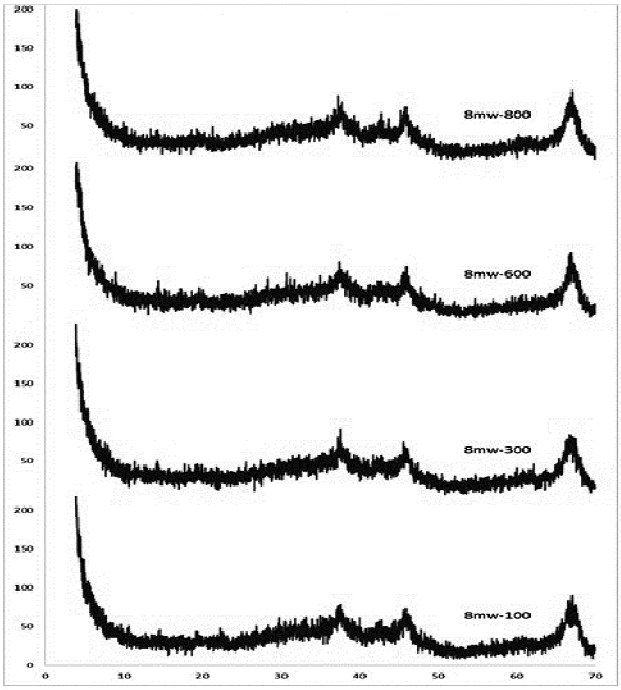


Fig.(3): X-ray diffraction patterns of alumina samples at different microwave operation watts.

Nitrogen adsorption–desorption isotherms at −196 °C for the prepared alumina samples at different microwave operation times and watts display the features of type IV isotherm according IUPAC classification [19]. The adsorption isotherms Fig. (4, 5)and the tabulated data in Table (1, 2) Showed the highest surface areafor sample coded 8mw/300and 8mw/4 are (~ 375 m^2/g and 352 m^2/g) and the total pore volume (~0.4145 cm^3/g and 0.9163cm^3/g) respectively. It is observed that the surface area and the total pore volumes of the γ-Al_2O_3 increased with increasing microwave operation watts and times. These indicate that,increase in watts and times of microwave irradiation usuallyenhancethe rate of grain growth of particles[18, 20].

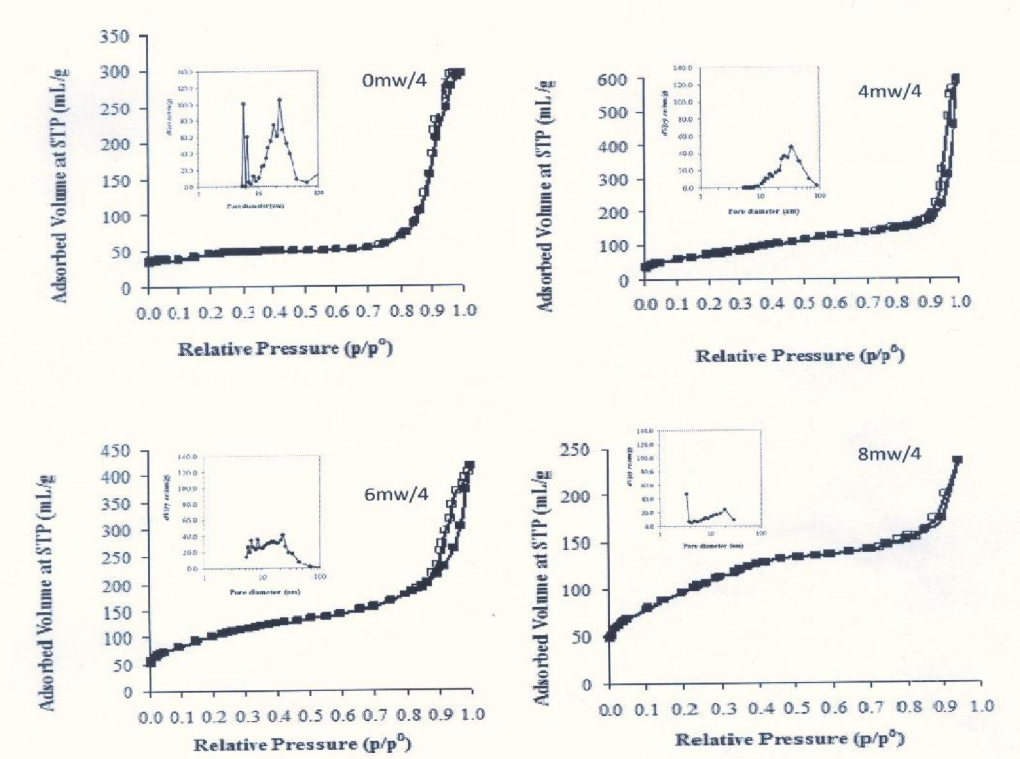
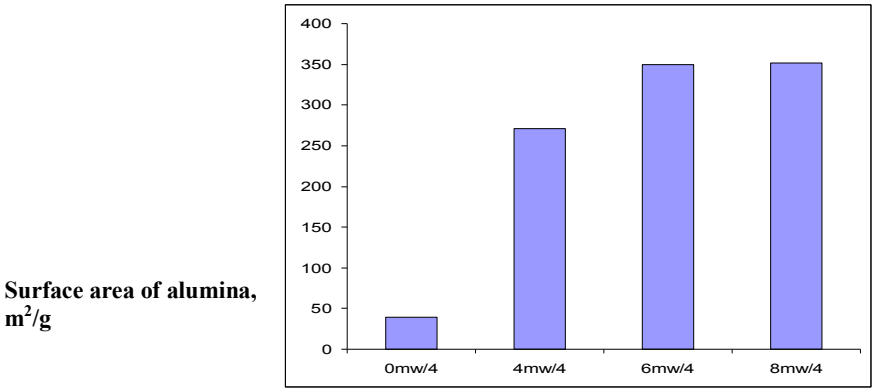


Fig. (4): Nitrogen adsorption–desorption isotherms for prepared alumina samples at different microwave times.



Effect of different microwave operation times on surface area of alumina samples.

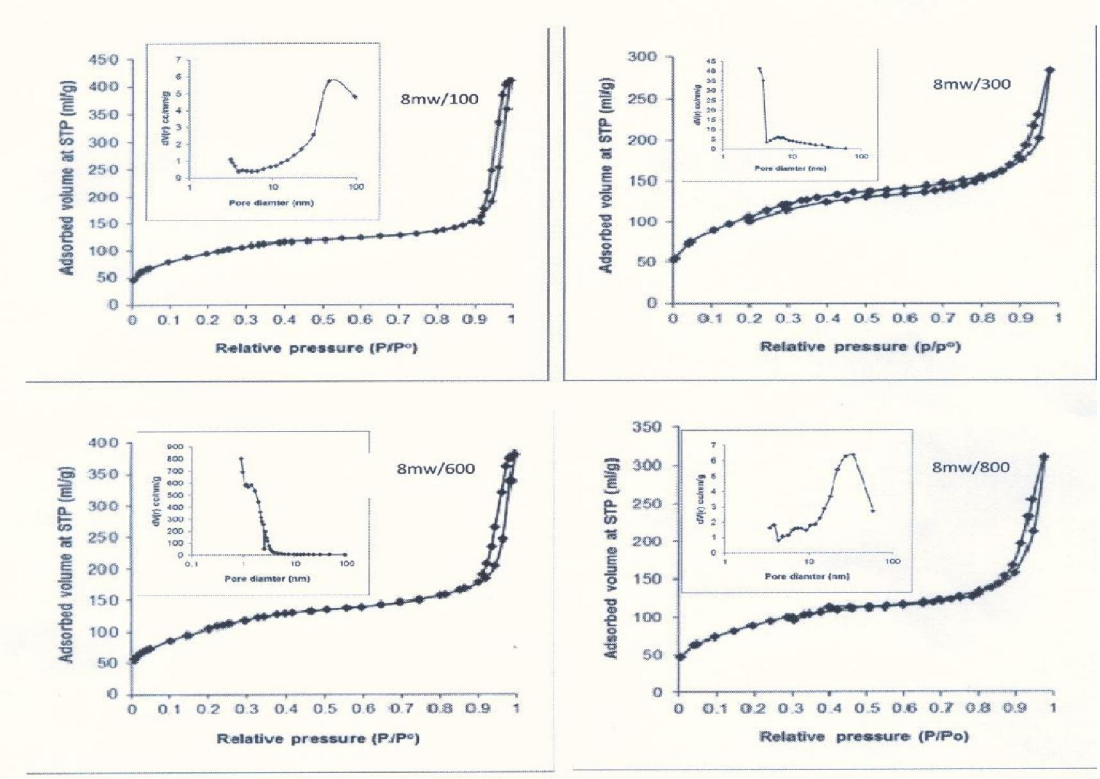
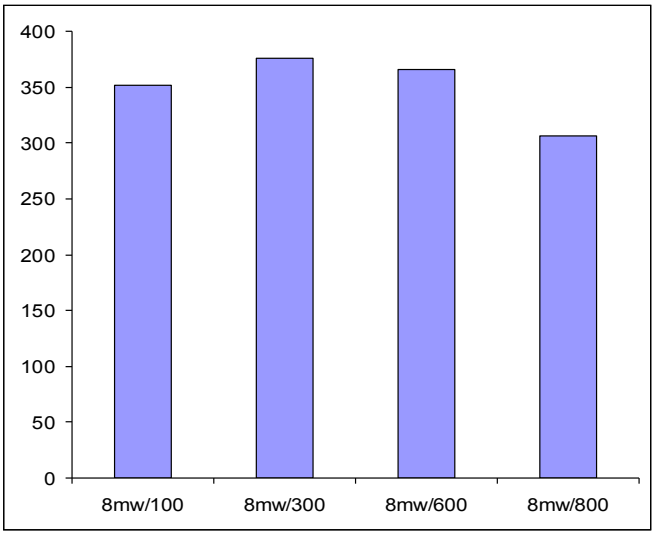


Fig.(5): Nitrogen adsorption–desorption isotherms for prepared alumina samples at different microwave watts.



Effect of different microwave operation watts on surface area of alumina samples.

Table (1): Textural properties of the synthesis alumina samples at different microwave operation times, S_{BET}: specific surface area and V_P: total pore volume.

Sample code	S_{BET} (m^2/g)	V_P (cm^3/g)
0mw/4	38.80	0.1754
4mw/4	270.79	0.3621
6mw/4	350.01	0.3674
8mw/4	352.03	0.3621

Table (2): Textural properties of the synthesis alumina samples at different microwave operation watts, S_{BET}: specific surface area and V_P: total pore volume.

Sample code	S_{BET} (m^2/g)	V_P (cm^3/g)
8mw/100	352.03	0.3621
8mw/300	375.78	0.4145
8mw/600	365.62	0.5893
8mw/800	306.49	0.4788

The TEM micrograph images of prepared alumina samples at different microwave operation watts and times Fig. (6) Showed nanoparticles that formed in hexagonal shape.

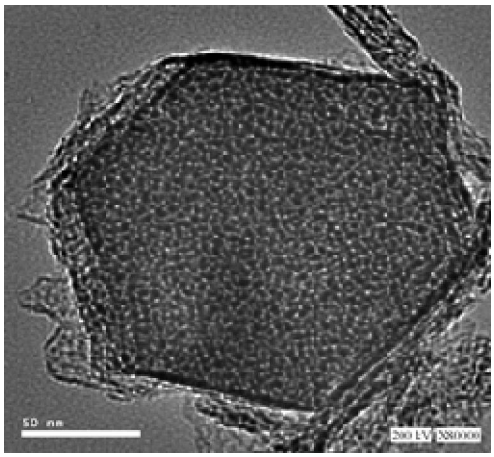


Fig. (6): HRTEM micrograph images for the prepared alumina sample.

4. Conclusions

In this study, Synthesis high surface area γ-alumina using cationic surfactant in the presence of microwave irradiation by consuming of a little of power for short time. The XRD results suggested that the crystallinity of alumina samples increase by increasing microwave operation times and watts.

Acknowledgments

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