

# Synthesis of $\gamma$ -Alumina Particles and Surface Characterization

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**Abstract:** Alumina was synthesized *via* sol-gel technique by the hydrolysis of aluminium ion controlled by urea in aqueous media. The resulting sol composed of Al(OH)<sub>3</sub> particles coalesced and became a transparent gel. The freshly prepared gel was heated at 280°C to obtain alumina particles. The obtained particles were found to be amorphous  $\gamma$ -alumina particles with high porosity, characterized by FTIR, XRD and S<sub>BET</sub> techniques. Electron micrograph shows that the particles are nano-sized having non-spherical shape. Comparatively higher magnitude of adsorption of cationic surfactant indicated that the surface of alumina particles is negatively charged.

**Keywords:** Alumina, Porosity, Adsorption, Surface characteristics

## INTRODUCTION

The oxides of aluminium materials are widely used in ceramics, refractories and abrasives due to their hardness, chemical inertness, high melting point, non-volatility and resistance to oxidation and corrosion [1-5]. The importance of alumina as catalyst or catalytic support has also been widely recognized for many chemical reactions [6-8]. The transparency of alumina film and wide range of properties extend its application in optics as well [9].

Recently many researchers are showing interest on the preparation and application of nano-sized alumina or alumina composites considering their diverse properties [10-16]. It is generally believed that the properties of such alumina particles are largely governed by the particle size, morphology, surface and phase homogeneity and these can be controlled by selecting a proper synthetic route [17].  $\gamma$ -Alumina with desirable surface properties such as high surface area and mesoporous properties is most commonly used as a high-temperature catalyst or catalytic support and as a membrane [18]. The synthesis of alumina by sol-gel technique generally produces a mixture of alumina phases ( $\alpha$ ,  $\gamma$  and  $\delta$ ) and these transform to a stable  $\alpha$ -alumina phase by heating at high temperature [10, 19-21]. In 2004, Macêdo *et al.*, reported the synthesis of  $\gamma$ -alumina by sol-gel method from a saturated aqueous solution of aluminium nitrate using urea as neutralizing and hydrolysis control agent [22].

In the present investigation similar method was used to prepare  $\gamma$ -alumina with slight modification. The produced alumina particles were characterized by XRD, FTIR and electron micrographs. The specific surface area (S<sub>BET</sub>) was measured by nitrogen adsorption applying BET method. Bulk (loose) and true densities were also measured. As the structure of the porous adsorbents plays a very important

role in the adsorption process [23, 24], porosity, and adsorption isotherms of different organic solvents such as ethyl acetate (EA), methanol (MeOH), tetrahydrofuran (THF) and methylethyl ketone (MEK) as well as anionic and cationic surfactants were investigated. It is to be mentioned that so far mostly commercially available  $\alpha$ -alumina particles have been used for such detail surface property measurement.

## MATERIALS AND METHODOLOGY

### Materials

Aluminium nitrate nonahydrate Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O from Hopkin & William Ltd., UK, urea and MEK from E-Merck, Germany, MeOH from Fisher Scientific Ltd., UK, EA from Biocraft Co. Ltd., India, and THF from Merck Ltd., India were used without further purification. Sodium dodecyl sulphate (SDS) and hexadecyl trimethyl ammonium bromide (HTABr) both from Fluka, Biochemica, Switzerland were used as anionic and cationic surfactants. Other chemicals used were of reagent grade. Distilled deionized water of conductivity less than 5  $\mu$ S/cm was used for all measurements.

### Instruments

Scanning electron microscope or SEM (Hitachi S-2460) and transmission electron microscope or TEM (Zeiss EM 912 Omega) were used to see the morphology of the particles. IR spectrophotometer (Shimadzu, FTIR-8900, Japan) was used for obtaining IR spectra (KBr). BET method was applied using Nova3000e apparatus from Yussa Ionocs Inc., Osaka, Japan, to measure the surface of alumina particles. The powder X-ray diffraction pattern was obtained in a diffractometer operating at 2°/min with CuK <sub>$\alpha$</sub>  radiation. Microprocessor pH and conductivity meters from HANNA Instruments, Portugal were used in this study.

### Preparation of $\gamma$ -Alumina

Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (35 g) was dissolved in 35 mL distilled deionized water at 22°C under magnetic stirring. Urea (72 g)

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was added keeping the molar ratio of  $\text{Al}^{3+}$ /urea at 1/13. The solution mixture was maintained at 22°C for 1 h and then filtered to remove any insoluble impurity. The aluminium/urea saturated solution was heated at 90°C for around 12 h. The pH of the solution mixture was initially 2.0. As the reaction proceeds the pH gradually increased and rose sharply from 3 to 6 producing alumina sol. The sol was heated for another 3 h to a transparent gel.

The freshly prepared alumina gel was dried at 280°C for 1 h in presence of air to eliminate the remaining urea and nitrate and resulted in porous, amorphous  $\gamma$ -alumina powder.

### Material Characterization:

Bulk density (loose) a property of particulate materials is the mass of many particles of the material divided by the volume they occupy. The occupied volume includes the space between particles as well as the space inside the pores of individual particles. This was measured at 22°C using a 10 cc graduated cylinder. Oven dried  $\gamma$ -alumina powder was poured into the cylinder. The weight and volume of the powder were recorded and the bulk density was obtained using the equation (1).

$$\text{Bulk Density} = \frac{\text{Weight of dry } \gamma\text{-alumina (g)}}{\text{Volume of dry } \gamma\text{-alumina (cc)}} \quad (1)$$

The particle density or true density is the density of the particles that make up the powder. This density was measured using a densimetric bottle at 22°C. The volume of the densimetric bottle was first calculated using the appropriate density value of water. Then, 5 to 6 g of oven dried  $\gamma$ -alumina powder was taken in the bottle. Distilled water was added and the contents in the bottle were gently boiled for 10 min to remove any entrapped air. The increase in weight over the alumina powder was used to obtain the volume of water in the bottle. The volume of the alumina powder in the bottle was obtained by subtracting this volume from the total volume of densimetric bottle. Equation (2) was used to calculate the particle density:

$$\text{Particle Density} = \frac{\text{Weight of dry } \gamma\text{-alumina (g)}}{\text{Volume of water displaced (cc)}} \quad (2)$$

Both bulk density and particle density were measured in duplicate and the average values are reported in Table 1.

The amount of pore space or porosity was obtained by density measurement using the equation (3).

$$\text{Porosity} = 1 - \left( \frac{\text{Bulk density}}{\text{Particle density}} \right) \times 100 \% \quad (3)$$

The specific surface area ( $S_{\text{BET}}$ ) of the powdered sample was measured by 6-point adsorption measurement using BET method at 77 K with NOVA3000e apparatus. Prior to the measurement the sample was dried in oven at 100°C.

For electron microscopic observation, dilute  $\gamma$ -alumina dispersion (0.1% solid) in water was prepared by sonication for 30 min. A few drop of the diluted dispersion was placed on a carbon coated copper grid and dried at ambient temperature prior to the observation by TEM. For SEM, diluted sample was placed directly onto aluminium stub, dried at

ambient temperature and then sputter-coated with an ultra-thin layer of gold before observation.

For adsorption measurement of different organic solvents (EA, MeOH, THF and MEK), specific amount of  $\gamma$ -alumina particles (0.1 g) was mixed with 5 mL of each organic solvent. The mixture was maintained at the respective temperature with occasional stirring for 45 min. Then  $\gamma$ -alumina was decanted and separated. The excess solvent adsorbed on the surface was removed by tapping with filter paper [25]. The increase in the weight of  $\gamma$ -alumina over the initial weight was used to calculate the amount of adsorption (mg/g of particles).

**Table 1. Experimental Values of Physical Parameters of  $\gamma$ -Alumina**

S. No.	Parameter	Value
1	Bulk density (loose), g/cc	0.9333
2	Particle density or true density, g/cc	1.9867
3	Porosity, %	52.46
4	Specific Surface area ( $S_{\text{BET}}$ ) $\text{m}^2/\text{g}$	4.49

The adsorption isotherms of anionic SDS and cationic HTABr emulsifiers were obtained at 30°C by the following method. A dispersion of  $\gamma$ -alumina (1.0 g) was prepared in 10 mL of distilled deionized water. For each measurement, a mixture of 30 mL was then prepared from alumina dispersion and emulsifier aqueous solution. The emulsifier aqueous solution was prepared in such a way that the concentration of the emulsifier in the mixture remained below the critical micelle concentration. The pH value of the mixture was immediately adjusted to 7.0 by dilute HCl/KOH aqueous solution. The alumina dispersion-emulsifier mixture was then allowed to stand for specified time at 30°C. In order to examine the adsorption behavior of the emulsifier onto the alumina particles the conductance was recorded at 30°C. The amount of emulsifier adsorbed was obtained by subtracting the emulsifier concentration in the medium from the initial concentration. The emulsifier concentration was obtained using calibration curves, representing the relationship between the concentration and the conductance of emulsifier aqueous solution at the pH value of 7.0 assuming that the adsorbed emulsifier molecules do not contribute to the conductance.

## RESULTS AND DISCUSSION

Experimental values of the physical property of alumina powder are shown in Table 1. Particle density or true density provides information about the kind of material present in the sample. The particle density higher than 1.0 g/cc is attributed to high alumina content in the sample rather than the organic matter. Porosity is also reasonably high as expected [23]. For application as catalyst or catalytic support, porosity is an important parameter as it tells how much water/hydrocarbons/gases can be stored in. This property also gives idea about the rate at which air/water/hydrocarbon can pass through in alumina packed chromatographic column.

Morphological studies were carried out using SEM and TEM photographs. Fig. (1a), shows the SEM photograph of alumina. The produced alumina particles are mostly nano-sized and a close observation by TEM Fig. (1b), indicates that the shape of particle is non-spherical. The particles are typically around 30-40 nm in length with an outer diameter of around 10 nm. The surface area ( $S_{BET}$ ) shown in Table 1 is lower than that estimated from electron micrographs. This

can be explained by considering the coagulation of particles in the dried state.

The X-ray diffraction pattern shown in Fig. (2), indicates that the produced alumina is completely amorphous. Two broad peaks appeared at around  $42^\circ$  and  $65^\circ$  respectively as indicated by arrows are the characteristics of  $\gamma$ -alumina phase [10, 22]. FTIR spectra of the alumina powder recorded in KBr pellet is shown in Fig. (3). The absorption bands ap-

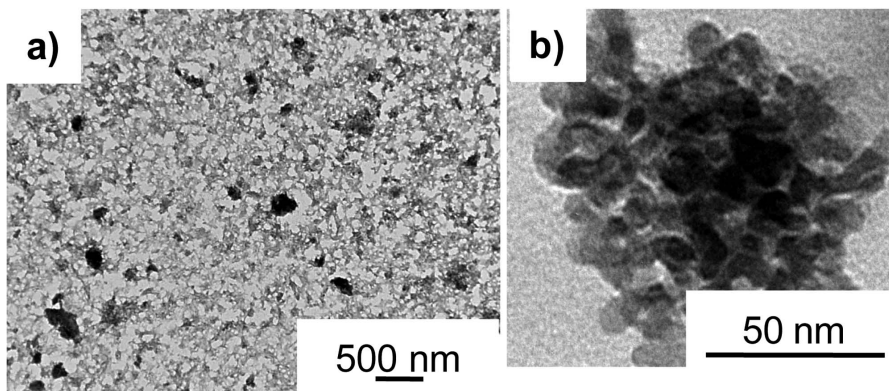


Fig. (1). Electron micrographs of  $\gamma$ -alumina particles: a) SEM and b) TEM.

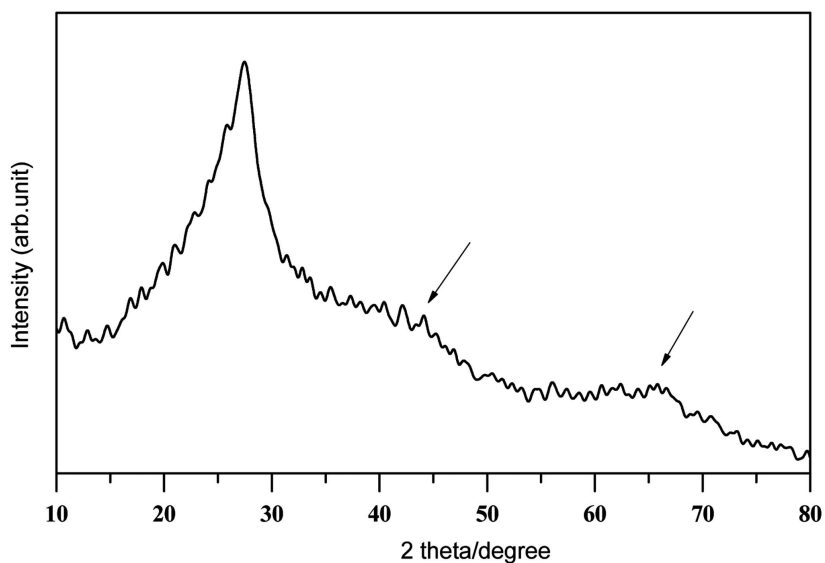


Fig. (2). X-ray diffraction spectra of  $\gamma$ -alumina particles.

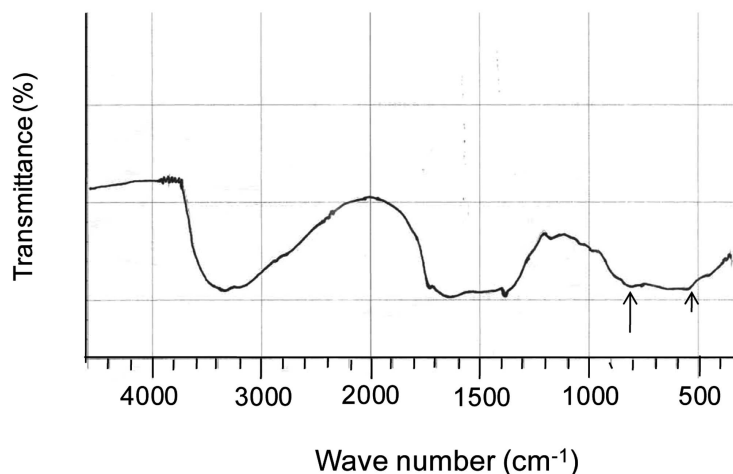


Fig. (3). FTIR spectra of  $\gamma$ -alumina particles.

peared at  $\sim 545$  and  $\sim 788$   $\text{cm}^{-1}$  represent aluminium ions in octahedral and tetrahedral environments. These results are in agreement with the FTIR spectrum of  $\gamma$ -alumina as reported elsewhere [26, 27]. Broad OH stretching band appeared at around  $3354$   $\text{cm}^{-1}$  reveals the presence of hydroxyl groups. The additional peaks appeared in the region of  $1100$ - $1700$   $\text{cm}^{-1}$  represent the presence of physisorbed water [26]. Calcination at the temperature of  $280^\circ\text{C}$  to produce  $\gamma$ -alumina is probably not enough to drive off this physisorbed water.

Fig. (4), shows the adsorption isotherms of different organic solvents on  $\gamma$ -alumina at different temperatures. The adsorption is a complex process and its magnitude is influenced by many factors such as pore volume or surface heterogeneity of alumina particles as well as molecular size, hydrophobicity of the alkyl chain of the adsorbate. The magnitude of adsorption of MeOH and THF increased with increasing temperature whereas those of MEK and EA decreased. Comparatively, the magnitude of adsorption for MeOH is much higher and almost levelled off at  $35^\circ$  to  $45^\circ\text{C}$ . This higher adsorption of MeOH on the alumina surface is probably accompanied by the formation of hydrogen bond as both alumina surface and MeOH contain hydroxyl groups. The levelling off in magnitude of adsorption at higher temperature indicates that alumina surface is saturated with layer of MeOH. The decrease in adsorption for MEK and EA with increase in temperature can be explained by considering two different adsorption processes at lower and higher temperatures [24]. The physical adsorption at lower temperature possibly changed into chemisorption at higher temperature.

The magnitude of adsorption for anionic SDS and cationic HTABr emulsifiers measured at pH 7.0 is shown in Fig. (5). The magnitude of adsorption for cationic emulsifier is relatively higher than that of anionic emulsifier. Moreover, the magnitude of adsorption for cationic emulsifier increased with immobilization time. These behaviour imply that surface of  $\gamma$ -alumina particles are negatively charged. The decrease in adsorption for anionic SDS with immobilization

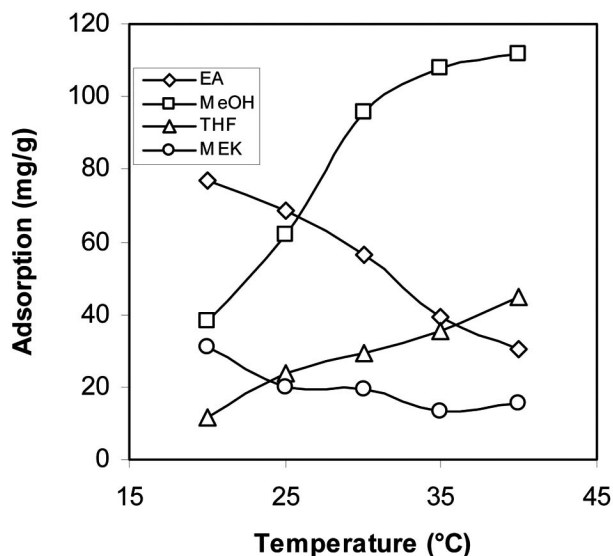


Fig. (4). Adsorption isotherms of different organic solvents on  $\gamma$ -alumina particles (0.1 g) at various temperatures.

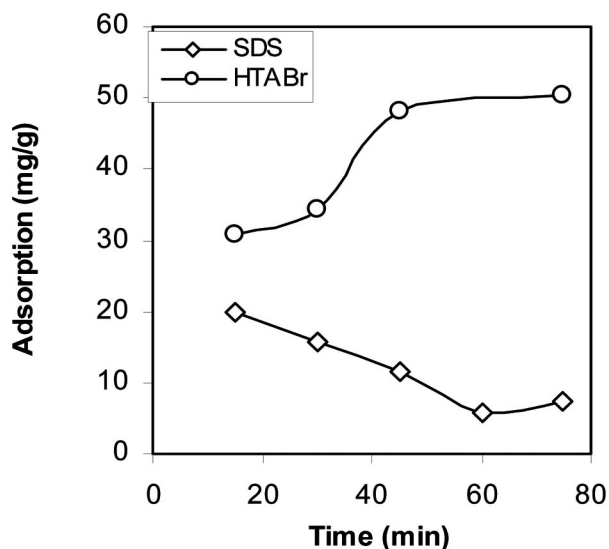


Fig. (5). Adsorption isotherms of anionic SDS and cationic HTABr emulsifiers on  $\gamma$ -alumina particles (0.1 g) at pH 7.0 and  $30^\circ\text{C}$ .

time is pretty unexpected. It is not clear whether the repulsion between negatively charged alumina surface and emulsifier molecules reduced the adsorption amount over prolonged immobilization time.

Above results suggest that prepared  $\gamma$ -alumina particles are anionically charged, amorphous and porous in character. The absorption capacity of  $\gamma$ -alumina particles is pretty high and can be used for chromatography. These particles may find application in biomedical field and can also be modified/functionalized to diversify their applications.

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