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Boehmite Nanoparticles by the Two-Reverse Emulsion Technique

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Boehmite (γ-AlOOH) nanoparticles were successfully synthesized by the two-reverse emulsion technique at 90°±1°C under constant agitation with varying Al^{3+} concentrations in the aqueous solution. A mixture of cyclohexane and the surfactant, sorbitan monooleate (Span 80), constituted the support solvent in the reverse emulsions. The synthesized particles were characterized by thermogravimetry, differential thermal analysis, Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), particle size analysis, and transmission electron microscopy (TEM). XRD and FTIR results confirmed crystalline boehmite formation at 90°±1°C. The average particle size of boehmite was found to be 10 nm. The spherical morphology of the boehmite nanoparticles was confirmed by TEM.

I. Introduction

The aluminum oxide-hydroxide boehmite (γ-AlOOH) nanopowder has been known to be used in the preparation of membranes, catalysts, coatings on different substrates, and more importantly, for alumina and alumina-based materials for various applications in the field of advanced ceramics.[1–5] Because of the above-mentioned applications, considerable work is still being carried out on the synthesis of boehmite powders and their characterization. Although numerous methods are reported for the synthesis of these particles,[1–9] generally hot water hydrolysis of aluminum alkoxides,[1,2,9] hydrothermal synthesis,[3,5,10] and precipitation under hot condition from aqueous inorganic salt solutions[4,11–13] are mainly followed. However, the morphology of the powders and properties of the final materials have been found to depend strongly on the chemical compositions and the experimental conditions used during the synthesis.[1,3,5,14] Further, very often, the final product becomes associated with other crystalline phases such as gibbsite and/or bayerite.[5] Catone and Matijevic[14] synthesized monodispersed spherical particles of hydrous aluminum oxide by hydrolysis of aluminum sec-butoxide in the presence of sodium, potassium, ammonium, and magnesium sulfate under controlled experimental conditions of pH, temperature, aging time, etc. On the other hand, boehmite fibrils were obtained after prolonged heat treatment of the basic aluminum chloride or nitrate solutions in an autoclave at 160°C or above.[6] Again, formation of plate-like boehmite has also been reported in the literature.[15]

Although various chemical methods have been developed to control the morphology, size, and distribution of nanoparticles, because of the large surface-to-volume ratio, the particles undergo aggregation. To overcome these problems, many recent studies followed emulsions to control the size and morphology of the nanoparticles.[16–24] In such cases, the dispersed aqueous microdroplets in water-in-oil (w/o)-type emulsions act as microreactors in which reactions are carried out. As the alkoxide route for the preparation of boehmite nanoparticles in bulk quantity is quite expensive, one has to look for the inorganic salts for its synthesis. Keeping in view the aforementioned points, the aim of the present work was to:

(1) develop a process, based on the two-reverse emulsion technique, for the synthesis of boehmite nanoparticles from an aqueous inorganic salt solution at a considerably low temperature,

(2) examine the process parameters for particle formation, and

(3) characterize the synthesized powders.

The synthesized particles in the present investigation were free-flowing and monodispersed in nature.

II. Experimental Procedure

(1) Preparation of Aluminum Nitrate Solutions

Aluminum nitrate solutions of concentrations 0.05*M* and 0.1*M* were prepared by dissolving the required amount of aluminum nitrate nonahydrate, $Al(NO_3)_3 \cdot 9H_2O$ (G.R., Merck, Mumbai, India, purity >99%) in deionized water of conductivity 1.4×10^{-5} Ω.

(2) Preparation of Support Solvents

Support solvents were prepared by mixing cyclohexane of dielectric constant 2.042 at 25°C (G.R., Merck, purity >99%) and 2 vol% of the emulsifier (surfactant) with respect to the cyclohexane under agitation. Sorbitan monooeleate (Span 80, Fluka Chemica AG, Switzerland), having a hydrophilic–lipophilic balance (HLB) value of 4.3, was used as the emulsifier in the present study.[18,19,24–26]

(3) Preparation of the Reverse Emulsion (w/o) of Aluminum Nitrate Solution (Emulsion A)

The reverse emulsion of aluminum nitrate solution (emulsion A) was prepared at ambient temperature by adding a measured volume of the salt solution to the support solvent in a closed glass container under a mechanical agitation of 500 rpm. The volume ratio of the salt solution: support solvent was 1:4 in all the experiments.

(4) Preparation of the Reverse Emulsion of Ammonia Solution (Emulsion B)

The emulsion B was prepared at ambient temperature by adding a measured volume of the ammonia solution (25 wt%, w/v, G.R., Merck) to the support solvent in a closed glass container under a mechanical agitation of 500 rpm. The volume ratio of the ammonia solution: support solvent was 1:4 in all the experiments.

(5) Preparation of Boehmite Nanopoarticles by the Two-Reverse Emulsion Technique[24]

The containers with the emulsion A and emulsion B were kept separately in an oil bath preheated to 90°±1°C (reaction temperature) and kept at that temperature for 10 min under magnetic stirring of 500 rpm to attain the reaction temperature. The temperature of both the emulsions was verified by thermometers dipped into the respective containers. After attaining a temperature of 90°±1°C, emulsion B was rapidly added to emulsion A

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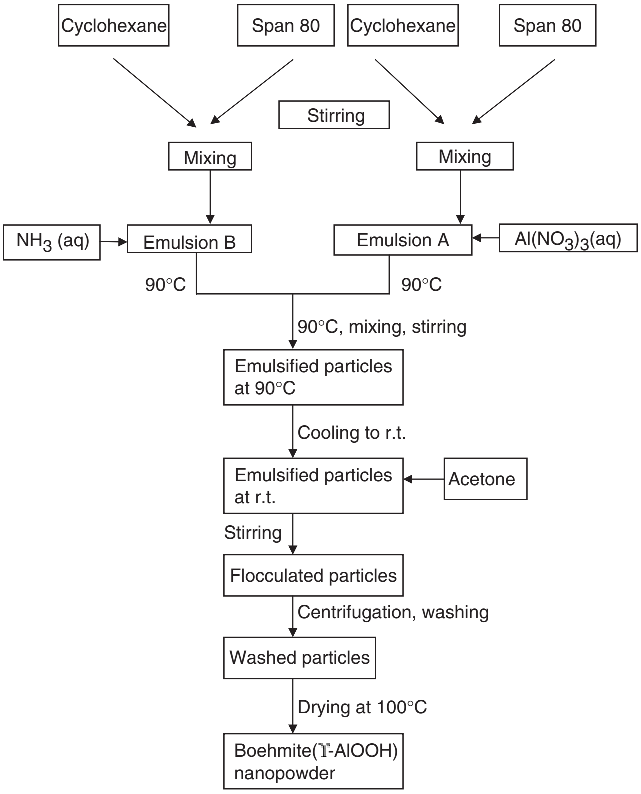

Fig. 1. Flow diagram for the synthesis of boehmite (γ-AlOOH) nanoparticles.

under stirring to obtain a single reverse emulsion (w/o) followed by simultaneous precipitation of the precursor powders. The aging at 90°±1°C was continued for 10 min, after which the container was removed from the bath and cooled down under a water tap to the ambient temperature.

The synthesized particles were obtained from the single reverse emulsions by adding a known volume of acetone (G.R., Merck). Immediate separation of the particles occurred. The particles were collected by centrifugation at 6000 rpm. To remove the last traces of adhered impurities, the above procedure was repeated twice, each time collecting the powders centrifugally. The washed particles were dried at 100°C, with a dwell time of 1 h, in an air oven under static condition. The yield of the product was found to be greater than 95%. Figure 1 presents the flowchart for the preparation of boehmite nanoparticles. Table I summarizes the experimental conditions and results obtained in the present investigation. To examine the effect of calcination temperature on phase transformation, the precursor powder corresponding to run no. 2 of Table I was calcined at different temperatures, i.e. from 400° to 1200°C in air, each with a dwell time of 1 h, under static conditions.

Table I. Crystal Phases Developed in Nanoparticles Under Different Experimental Conditions

Run no.	Concentration of $Al(NO_3)_3$ solution (*M*)	Reaction temperature (°C)	Final pH of the emulsion	Crystal phase
1	0.05	90±1	8.5	Boehmite (γ-AlOOH)
2	0.05	90±1	8.0	Boehmite (γ-AlOOH)
3	0.1	90±1	8.5	Boehmite (γ-AlOOH)
4	0.05	90±1	7.0	Boehmite (γ-AlOOH)+ bayerite
5	0.05	80±1	7.0	Bayerite
6	0.05	90±1	6.0	Bayerite
7	0.05	80±1	8.0	Bayerite+boehmite (ϒ-AlOOH) (little)

Aging time at 90°±1°C: 10 min.

The novelty of the developed technique primarily lies in providing a process that is economical, environmentally friendly, time-saving, and of high yield from inorganic-based precursors.

(6) Characterization of the Nanoparticles

The precursor and the calcined powders were characterized by differential thermal analysis (DTA) and thermogravimetry (TG; model STA 409C, Netzsch, Bayern, Germany), X-ray diffraction (XRD; model 1730, Philips, Almelo, the Netherlands) with Ni-filtered Cu*K*α radiation, Fourier transform infrared spectroscopy (FTIR) study (model 5PC, Nicolet, Madison, WI), particle size analysis (Otsuka Electronics Co. Ltd. model DLS 700, Osaka, Japan), and transmission electron microscopy (TEM; model JEJ-200X, JEOL, Tokyo, Japan).

III. Results and Discussion

(1) Stabilization of Aqueous Microdroplets in Reverse Emulsions

In a system composed of two immiscible liquids,[25–28] i.e. for the w/o-type emulsions (reverse emulsion) in the present investigation, dispersion of the water phase (aqueous Al^{3+} or ammonia solution) in the oil phase (cyclohexane) as small droplets under agitation causes an increase in the surface area of the dispersed phase. Thermodynamically, the increase in the surface area (ΔA) of the dispersed phase associated with a high free energy (ΔG) can be represented as[27,29,30]

$$\Delta G = \gamma \Delta A \qquad (1)$$

where γ is the interfacial tension. The equation indicates that a low interfacial tension favors droplet disruption. In fact, the high interfacial tension between the dispersed water phase and continuous oil phase is reduced by the addition of a system-compatible amphiphilic surface-active agent or surfactant (emulsifier in the present case), i.e. a molecule with a polar head and a non-polar tail.[18,24] The surfactant molecules orient themselves according to the polarities of the chemical constituents involved. Thus, because of the high polarity of water, the polar heads of the surfactant molecules at the water–oil interface are oriented toward the water droplets and become adsorbed on their surfaces and prevent the coalescence of the droplets by steric hindrance occurring between two droplets (steric stabilization). Thus, the emulsifier added to the system: (i) lowers the interfacial tension between two immiscible liquids, favoring droplet disruption and (ii) prevents re-coalescence of aqueous droplets by adsorbing on their surfaces, thus producing a stable emulsion. In the present investigation, reverse emulsions of aqueous Al^{3+} and ammonia solutions were used as precursors for the preparation of boehmite nanoparticls in the presence of sorbitan monooleate, Span 80, as the emulsifying agent.

(2) Formation of Spherical Boehmite Nanoparticles

The present method, based on the emulsion (w/o type) precipitation, involves emulsification of an aqueous metal salt solution (water phase) with a high dielectric constant in an organic solvent (oil phase) of low dielectric constant by agitation in the presence of a surfactant. The dispersed droplets act as microreactors for carrying out the precipitation reaction. The metal ions in the microdroplets are precipitated as hydroxides by increasing the basicity of the system.[19,22,25] The surfactants used for the stabilization of aqueous droplets are characterized by their HLB values. The surfactants in the span series, i.e. the Span 80 in the present case, are basically the fatty acid esters of anhydro sorbitols, which are good oil-soluble emulsifying agents.[27] In fact, a high HLB value of the surfactant indicates a strongly hydrophilic character, while a low value is an indication of a strong hydrophobic nature. Considering these points, a non-ionic, relatively pH-independent hydrophobic surfactant, i.e. sorbitan monooleate (Span 80) with an HLB value of 4.3, was selected

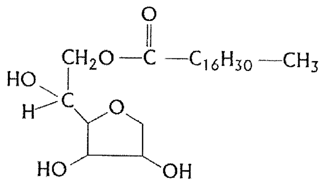

Fig. 2. Molecular structure of Span 80 showing the hydrophilic "head" (sorbitan) and the hydrophobic "tail" (oleic acid) parts.

for the present study. Figure 2 shows the molecular structure of the amphiphilic Span 80[18,25] where the hydrophilic sorbitan group acts as a "polar head" and the hydrophobic oleic acid group acts as the "non-polar tail."

For the synthesis of precursor particles in the single-emulsion technique, ammonia gas/organic amine/ammonia solution[19,23,26] is directly introduced into the emulsion system to cause precipitation of the metal hydroxide inside the dispersed aqueous microdroplets. As the main disadvantage of the single-emulsion technique is the non-uniform distribution of the added base, resulting in the formation of particles with wide size distribution, in the present investigation, the two-emulsion technique was followed. Compared with the single-emulsion system, the two-emulsion system is more advantageous in the sense that the precipitation and growth (by ripening) of the particles in the fused dimmer caused by collision of two reactant droplets is limited.[23,31,32] Figure 3 presents a schematic of the formation of fused dimmers during particle formation in the two-emulsion system. The steps involved can be visualized as follows:

Step I: Dispersion of the aqueous microdroplets of Al^{3+} and NH_3 solution in the organic phase (matrix) through steric stabilization.

Step II: Formation of fused droplets by collision because of Brownian motion followed by particle formation via exchange reaction (precipitation).

Step III: Dispersion of emulsified particles, i.e. surfactant-stabilized-precipitated particles by steric hindrance.

Step IV: Separation of spherical boehmite (γ-AlOOH) nanoparticles, by acetone treatment.

Based on the above mechanism, the size of the particles during precipitation, in the present investigation, was tailored by controlling the concentration of Al^{3+} in the starting solution and aging time at the reaction temperature. Further, the reaction temperature as well as the final pH of the system played important roles in the development of different crystal phases. This is clearly discernible from the results of Table I where both the low pH and low reaction temperature favor the formation of bayerite instead of boehmite particles.[1,2]

(3) Thermal Behavior of Boehmite Nanoparticles

The thermal behavior of the boehmite nanoparticles corresponding to run no. 2 of Table I was investigated by TG/DTA from 30° to 1210°C at 10°C/min in Ar atmosphere, and the TG/DTA traces of the samples have been presented in Fig. 4.

The TG study of the precursors corresponding to run no. 2 of Table I shows that weight losses because of the volatilization of water, and decomposition of nitrates, and organics mostly occurred up to about 500°C[33,34] accompanied by a weight loss of 41.56% (Fig. 4). An insignificant amount of weight loss of 1.66% for the sample was found from 500° to 1210°C. In the DTA curve of the same sample (Fig. 4) from 30° to 1210°C, a strong endothermic peak appeared at about 154°, which was because of the expulsion of loosely bound water molecules and some organics associated with the materials.[34–36] The first strong exothermic peak at 228° for the nanoparticles of run no. 2 corresponded to the decomposition of nitrates.[33,35,36] The second broad exothermic peak at ~600°C for the above sample indicates the formation of γ-Al_2O_3. The weak exothermic peak corresponding to 1038°C indicates the formation of δ-Al_2O_3. Finally, the appearance of a small exothermic peak at 1150°C for the sample is explained to be because of the crystallization of α-Al_2O_3.[4,36] It is to be noted that the precursor powders were heated separately in an Ar atmosphere to the corresponding exothermic peak temperatures obtained from DTA results at the same heating rate (10°C/min) and quenching to room temperature as in DTA analysis. The heated samples were analyzed by XRD, which confirmed the crystallization of the respective phases as observed from the exothermic peaks of DTA curves.

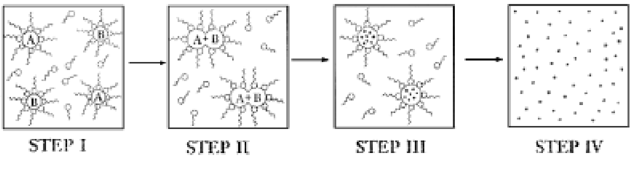

Fig. 3. Schematic for the formation of boehmite (γ-AlOOH) nanoparticles.

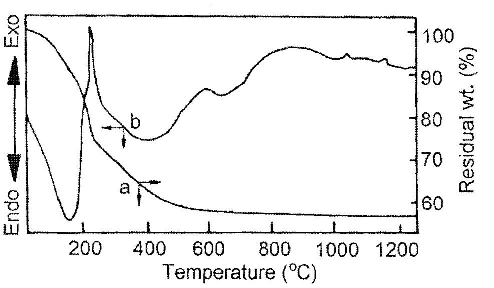

Fig. 4. Thermogravimetry and differential thermal analysis of boehmite (γ-AlOOH) nanoparticles (product of run no. 2 of Table I), from 30° to 1200°C.

(4) Phase Transformation of the Boehmite Nanoparticles

Crystalline phases identified by XRD in the precursor corresponding to run no. 2 of Table I calcined at different temperatures have been presented in Fig. 5. It indicates that the formation of γ-AlOOH (boehmite) occurs during its synthesis at 90°C. The peaks observed in the XRD patterns match well with the γ-AlOOH (boehmite) peaks reported in the JCPDS File no. 21-1307. The phase-pure γ-AlOOH was found to persist even after calcination at 400°C. At 600°C, δ-Al_2O_3 was identified, which persisted as the only phase at 800°C. At 1000°C, δ-Al_2O_3 co-existed as the major phase with the γ-Al_2O_3. The formation of γ-Al_2O_3 and δ-Al_2O_3 was also indicated in the DTA curve at ~600° and 1038°C, respectively, for the same sample. At 1200°C, α-Al_2O_3 was identified as the only phase. Therefore, based on the DTA and XRD results, the phase transformation of the boehmite nanoparticles during heat treatment from ambient temperature to 1200°C is represented as follows[4]:

$$\text{Boehmite}\,(\gamma\text{-AlOOH}) \rightarrow \gamma\text{-}Al_2O_3 \rightarrow \delta\text{-}Al_2O_3 \rightarrow \alpha\text{-}Al_2O_3$$

(5) FTIR Study

FTIR spectroscopic analysis was performed for the product of run no. 2 of Table I in the wavenumber range 4000–400 cm^{-1}. The spectra in the wavenumber range 1300–400 cm^{-1} are shown in Fig. 6. It is to be noted that the absorption bands appeared at around 1160, 1067, 895, 730, 624, and 490 cm^{-1} of the γ-AlOOH in the present investigation match with those obtained in the earlier studies,[5,9,10,15] thus further confirming the formation of boehmite (γ-AlOOH) at 90° ± 1°C.

(6) Particle Size Distribution and TEM of the Boehmite Nanoparticles

The average particle size of the product of run no. 2 of Table I (as-synthesized particle) was found to be the smallest, i.e. 10 nm,

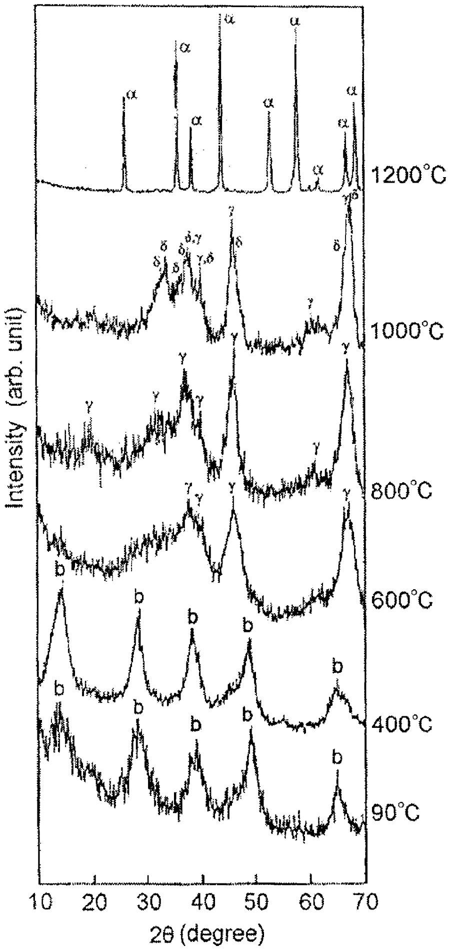

Fig. 5. Powder X-ray diffraction patterns of boehmite (γ-AlOOH) nanoparticles (product of run no. 2 of Table I) calcined at different temperatures (90°–1200°C). b = boehmite (γ-AlOOH), $\gamma = \gamma$-Al_2O_3, $\delta = \delta$-Al_2O_3, $\alpha = Al_2O_3$. *Note*: dwell time: 1 h at each temperature.

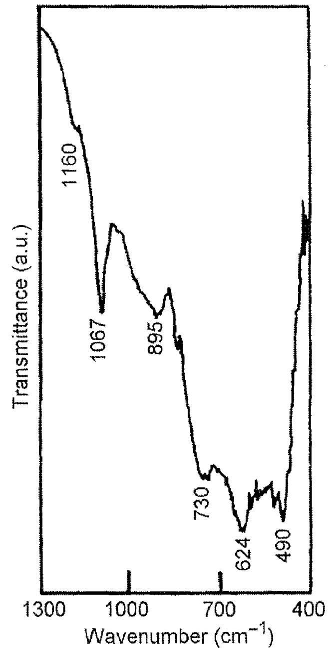

Fig. 6. Fourier transform infrared spectroscopy spectra of boehmite (γ-AlOOH) nanoparticles (product of run no. 2 of Table I).

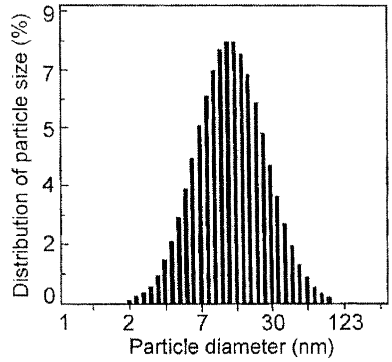

Fig. 7. Particle size distribution of boehmite (γ-AlOOH) nanoparticles (product of run no. 2 of Table I).

with a size distribution of about 2–85 nm. The distribution of particle size is monomodal in nature (Fig. 7). The average particle size of the product of other runs of Table I ranged from 265 to 735 nm.

The morphology of the product of run no. 2 of Table I (as-synthesized powder) and that calcined at 400°C, with a dwell time of 1 h, was examined by TEM. The investigation revealed that the as-prepared γ-AlOOH powder was free from agglomeration and they were spherical in morphology (Fig. 8(a)). At 400°C, the particles became agglomerated, although their sphericity was retained (Fig. 8(b)).

IV. Conclusions

1. The two-emulsion technique has been proved to be highly effective for the synthesis of spherical, agglomerate-free boeh-

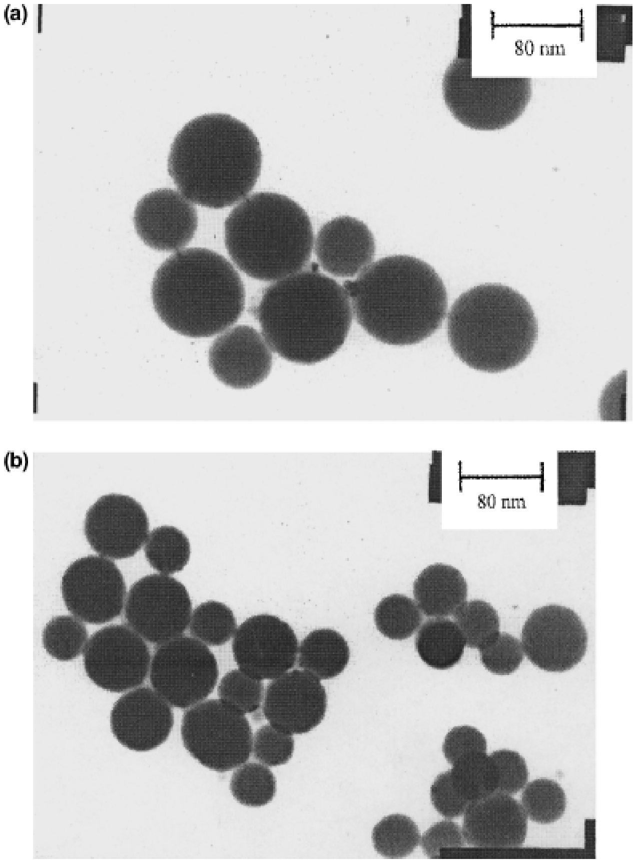

Fig. 8. Transmission electron microscopy photograph of boehmite (γ-AlOOH) nanoparticles (product of run no. 2 of Table I); (a) dried at 100°C/1 h dwell time, (b) calcined at 400°C/1 h dwell time.

mite (γ-AlOOH) nanoparticles at a considerably low temperature of 90°±1°C from inorganic-based precursors.

2. The TG result of the as-synthesized nanoparticles shows a weight loss of about 43% up to 1200°C, and polymorphic transformations of alumina, i.e. γ-Al_2O_3, δ-Al_2O_3, and α-Al_2O_3 from boehmite nanoparticles, take place at about 600°, 1040°, and 1150°C, respectively, which are confirmed by the same exothermic peak temperatures of the DTA curve.
3. XRD results confirm the crystallization of boehmite (γ-AlOOH) nanoparticles at 90°±1°C, which retains up to 400°C.
4. FTIR studies indicate the characteristic absorption bands of boehmite (γ-AlOOH) at around 1160, 1067, 895, 730, 624, and 490 cm^{-1} in the as-synthesized nanoparticles.
5. The particle size distribution is monomodal in nature. The average particle size of 10 nm of boehmite nanoparticles has been observed from particle size analysis.
6. TEM indicates the spherical morphology of boehmite nanoparticles.

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