



THE ROLE OF UREA ON THE HYDROTHERMAL SYNTHESIS OF BOEHMITE NANOARCHITECTURES

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The AlOOH nanoarchitectures have been successfully synthesized via hydrothermal method. The effect of urea/nitrate molar ratio 1, 2, and 4 were studied to obtain the various AlOOH nanoarchitectures. The products were characterized by XRD, FT-IR, FESEM, and TEM techniques. The specific surface area of samples was determined by N_2 adsorption-desorption measurements. Our experiments showed that AlOOH nanoarchitectures have been formed in all three ratios of urea/nitrate and the increase of urea/nitrate molar ratio from 1 to 2 then it favors for the formation of flowerlike AlOOH nanoarchitectures. The microscope analysis revealed that the flowerlike AlOOH are composed of nano-layers.

INTRODUCTION

Since the discovery of carbon nanotubes [1] nanostructures and nanomaterials have attracted much attention due to their remarkable mechanical, optical, electronic and magnetic properties [2] and it is well known, the development of materials with improved applications depends not only on the compositions but also on their morphologies [3]. On the other hand, the synthesis of inorganic nanoscale materials with special morphologies has been of great interest in recent years because the intrinsic properties of nano scale materials are mainly determined by their composition, structure, crystallinity, size and morphology [4]. Various methods, such as chemical vapour deposition [5], sol-gel process [6], solvothermal [7], dry gel conversion [8], anodic oxidation [9], co-precipitation [10], hydrothermal [11-13], sonochemistry [14], and combustion [15] were employed for the preparation of nanostructures. Among these synthesis methods the hydrothermal route has some distinct advantages such as the moderate condition and the easy control of the solution components [18].

 γ -Alumina is one of the most important oxides which it's can be obtained through the dehydration of the boehmite form of γ -AlOOH at temperatures in the range of 400 - 700°C. γ -Al₂O₃, which is obtained commonly from boehmite by calcination at 500°C in air [11,12], Also boehmite or aluminium oxide-hydroxide (AlOOH), is a versatile material employed in domains such as ceramics, surface coatings, morphology control, and pharmaceuticals [13, 19]. It is also an important precursor of preparing alumina, which is a low cost material most widely used as catalyst or catalyst supports [15-17] because of its high surface area, mesoporosity and surface acidity. Therefore, it is crucial to control the shape and size on AlOOH materials before use. Aiming at this goal, well-defined AlOOH nanostructures with various morphologies such as nanopowders [20], nanorods and nanoflakes [11, 21], nanofibers [22], nanobelts [23], hollow microspheres [3], nanoarchitectures [12, 24-26, 34], cantaloupe-like [27], microspheres [28] and three-Quarter-Sphere [29] have been prepared via many methods and conditions. Therefore, the method and conditions can be having an important role in the synthesis of special AlOOH.

In this paper, we introduce a hydrothermal route to synthesize AlOOH nanoarchitectures by the reaction between aluminium nitrate as the aluminium source and urea, as precipitating agent, and the effect of urea/nitrate molar ratio (U/N ratio) on the characterization of samples will be investigated which up to now, no publication has been issued.

EXPERIMENTAL

The aluminium nitrate nonahydrate, $Al(NO_3)_3 \cdot 9H_2O$ (Scharlau, Spain, extra pure) and urea, $CO(NH_2)_2$ (Scharlau, Spain, synthesis grade) were used without further purification.

AlOOH with layer/shell nanoarchitectures were prepared using the hydrothermal method. In a typical procedure, Al(NO₃)₃·9H₂O (18.75 g) was dissolved into 100 ml of distilled water at room temperature in a beaker and magnetically stirred to obtain a homogeneous solution (A). Then 25 ml aqueous solution of urea (B) was added to solution A, so that, the urea/nitrate molar ratios (U/N ratio) were 1, 2 and 4. Magnetic stirring (800 rpm) was maintained throughout the entire process and lasted for 5 min. The final solutions were transferred into a Teflon-lined stainless-steel autoclave of 200 ml capacity. The autoclave was sealed and maintained at 200°C for 24 h, then cooled to room temperature and a white precipitate was recovered. The products were collected by centrifugation and washed with distilled water several times. Finally, the samples were dried at 60°C for 24 h in air. Figure 1 shows schematic flow chart for the preparation of AlOOH nanoarchitectures.



Figure 1. Schematic flow chart for the preparation of AlOOH nanoarchitectures synthesized via hydrothermal route.

The X-ray Powder diffraction patterns (XRD) were recorded using BRUKER, model B8 ADVANCE, with Ni-filtered CuK α radiation ($\lambda = 1.54$ Å), Fourier transform infrared spectroscopy (FTIR) were performed on RAYLEIGH, model WQF-510. Field emission scanning electron microscopy (FESEM) images were obtained on a HITACHI, model S-4160, Vacc = 25 kV. Transmission electron microscopy (TEM) were taken with a PHILIPS, model CM30 at an accelerating voltage of 250 kV. The nitrogen adsorption-desorption isotherms

RESULTS AND DISCUSSIONS

analysis at -196°C were conducted using BEL SORP,

Figure 2 exhibits the effect of U/N ratio on the FTIR spectrum of the AlOOH nanoarchitectures. For AlOOH nanoarchitectures formed under U/N ratio of 1, 2 and 4, the FTIR spectra's were similar regardless of the difference in intensity peaks. There are three regions for the samples, which are ascribed as follows.

At the region of $400 - 1250 \text{ cm}^{-1}$ (I), well resolved sharper bands were observed. As shown in Figure 2, for the AlOOH nanoarchitectures, five strong bands at 486, 631, 750, 1082, and 1171 cm⁻¹ were observed. The sharp band at 486 cm⁻¹ is assigned to the angle deformation of O=A-(OH). The intensity of this band is stronger for sample with U/N = 2. The (OH)-Al=O angle bending results in the peak at 631 cm⁻¹, and 750 cm⁻¹ which is attributed to the (AlO)-O-H angle bending. The sharp peak at 1082 cm⁻¹ and small shoulder at 1171 cm⁻¹ are assigned to the (OH)-Al=O asymmetric stretching vibrations and the O-H bending, respectively [29, 30]. At the region of $1250 - 2500 \text{ cm}^{-1}$ (II), the peaks in this region were relatively weaker as compared with the other two regions regardless of the peak in 1385 cm⁻¹. The acute peak in 1385 cm⁻¹ corresponds to the nitrate anion, which was not thoroughly removed by washing.



Figure 2. The effect of U/N ratio on FTIR spectrums of AlOOH nanoarchitectures; a) U/N = 1, b) U/N = 2, c) U/N = 4.

As a comparison, the intensity of this band is stronger for the synthesized sample with U/N = 4 as has not been washed well. The weak band at 1640 cm⁻¹can be assigned to the stretching and bending modes of the adsorbed water molecule, and this absorbance in the spectra of AlOOH nanoarchitectures are very weak, indicating a very small amount of physically adsorbed water molecules. At the region of 2500 - 4000 cm⁻¹ (III), the samples showed two broad and resolved bands at 3099 and 3286 cm⁻¹, which can be assigned to the v_s(Al)O–H and v_s(Al)O–H stretching vibrations.

Figure 3 shows the XRD patterns of the samples obtained at 200°C with different U/N ratio (1, 2 and 4). As can be seen, with increasing the U/N ratio from 1 to 2, the diffraction peaks were intensified gradually regardless of (020), (080) and (171) planes which intensity peaks were decreased. By increasing the



Figure 3. The effect of U/N ratio on XRD patterns of AlOOH nanoarchitectures, (a) U/N = 1, (b) U/N = 2, (c) U/N = 4.

U/N ratio from 2 to 4, no significant differences in the intensity peaks were observed. In the XRD pattern of sample with U/N = 1, all the peaks could be identified clearly as orthorhombic AlOOH with calculated lattice constants of a = 3.69 Å, b = 12.21 Å and c = 2.86 Å (JCPDS card 01-083-2384). In the synthesized sample with U/N = 2 and 4, all of the deflection peaks of the product were in agreement with the standard data of orthorhombic AlOOH with calculated lattice constants of a = 3.70 Å, b = 12.22 Å and c = 2.86 Å (JCPDS card number 00-021-1307). No characteristic peaks were observed for impurities in all XRD patterns, indicating the high purity and crystallinity of the products. The remarkably increased intensity of the (020) diffraction peak of the sample with U/N = 1 compared with that of standard pattern suggests the highly anisotropic crystallographic nature of the particles in the product along the [010] axis [32].

The morphology of the samples was investigated using FESEM micrographs (see Figure 4). The comparison between the FESEM images of AlOOH nanoarchitectures with different U/N ratio shows that all these ratios shave a great impact on the morphology, and also aggregation of the AlOOH particles. When U/N = 1, then it forms uniform boehmite nanorods with average diameter about of 50 and length of 250 nm (Figure 4a). In contrast, with U/N = 2, the sample was composed of 3-dimensional flower-like nanoarchitectures [12] (Figure 4b). The microscope analysis revealed that the flowerlike AlOOH were nano-layers and nano-shells in terms of structure with their thickness of approximately 35 nm. A further magnification of Figure 3b clearly reveals that each architecture consists of a number of nanorods with the aspect ratio of 10 - 100. But when U/N = 4, the FESEM images (Figure 4c) show sample formation with irregular shape.

TEM analysis was conducted to clearly represent the structure characteristics of the samples. Figure 5 displays the TEM images of the samples. Figure 5a shows the representative TEM images of sample with U/N = 1. The sample consists of a large number of nanorods. To characterize the intrinsic structure of the AlOOH nanorods, we carried out the higher magnification analysis for the sample which exhibits a large quantity of nanorods with diameters of 10 - 30 nm and lengths of 20 to several hundreds of nanometre. Figure 5b shows the TEM images of the sample synthesized with U/N = 2, in which a nanoarchitectures of boehmite flowerlike can be seen. The magnified nanoarchitectures of boehmite flower-like exhibits that the average diameters of nanorods are about 25 nm. With U/N = 4 conditions, clearly displays that AlOOH nanorods attach together and assemble into irregular architecture (Figure 5c).

The Nitrogen adsorption-desorption isotherms for the AlOOH Nanoarchitectures are shown in Figure 6. These isotherms were measured on products outgassed at temperature of 120°C for several hours. The uptake of nitrogen by the AlOOH samples proceeded as monolayer–multilayer adsorption followed by capillary condensation, i.e. instantaneous filling of mesoporous with adsorbate, in the relative pressure (P/P_0) of 0.99. Upon desorption, pronounced hysteresis was observed for all samples under study. According to the common classification of adsorption isotherms [33], the isotherms for AlOOH nanoarchitectures can be considered type IV. This type of isotherm is characteristic for mesoporous samples and closely resembles the loops of type H1.



Figure 4. FESEM images of AlOOH nanoarchitectures synthesized via hydrothermal method; a) U/N = 1, b) U/N = 2, c) U/N = 4.

The pore size distributions for the samples, calculated from the desorption branches of isotherms using the Barrett-Joyner-Halenda (BJH) method, are shown in the inset of Figure 6. The general profiles of adsorption and desorption are not similar at high relative pressure $(P/P_0 = 0.99)$ for all samples, which indicates that significant changes were introduced in the porous structure of the AlOOH during U/N ratio changes.

The BET specific surface area, total pore volume and average pore size of AlOOH samples evaluated from nitrogen adsorption. The BET surface areas for U/N = 1, 2 and 4 were 79.73, 69.11, and 72.28 $m^2 \cdot g^{-1}$, the total pore volume were 0.56, 0.36, and 0.71 cm³ \cdot g^{-1}, and average pore size are 28, 21 and 39 nm, respectively. As can be seen, the specific surface area, total pore volume and average pore size of samples decrease with the increasing U/N ratio from 1 to 2, but with the increasing this ratio from 2 to 4, the characterization are increased, specially the total pore volume showed significant increase. The samples with U/N = 2 exhibited a lower surface area and pore volume, which may be due to the formation of larger nanostructures.



a) U/N = 1





b) U/N = 2



c) U/N = 4

Figure 5. TEM images of AlOOH nanoarchitectures synthesized via hydrothermal method; a) U/N = 1, b) U/N = 2, c) U/N = 4.



Figure 6. The effect of U/N ratio on the nitrogen adsorption/ desorption isotherms and pore size distribution of AlOOH nanoarchitectures, (a) U/N = 1, (b) U/N = 2, (c) U/N = 4.

CONCLUSIONS

The AlOOH nanoarchitectures were synthesized at 200°C, under hydrothermal route, using aluminum nitrate and urea as the reaction precursors and the effect of Urea/Nitrate molar ratio (U/N ratio) as the morphology-directing agent were studied. The sample morphologies were investigated systematically by XRD, FTIR, FESEM and TEM techniques. The morphology of AlOOH nanoarchitectures were influenced by U/N ratio from 1 to 4. Increasing U/N ratio from 1 to 2 favored the formation of the AlOOH nano-flowers. The AlOOH nanoarchitectures synthesized in the current work have the ability and potential applications in ceramic, sorbent and catalyst because of their structure and particle size, BET surface area, and porous properties.

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