Research Article

Mesoporous Alumina Microfibers In Situ Transformation from AACH Fibers and the Adsorption Performance

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Well-dispersed mesoporous γ -alumina microfibers with high surface were prepared by thermal decomposition of the ammonium aluminum carbonate hydroxide (AACH) precursors. The as-synthesized alumina retained the morphology of its precursor and exhibited memory effect. The structural, morphological, porous, and adsorptive properties of the samples were investigated by XRD, FTIR, TGA-DSC, SEM, TEM, and UV-vis spectroscopy. The prepared γ -alumina microfibers exhibited excellent ability to remove organic pollutants from waste water because of their mesoporous structures. The γ -alumina in situ converted from AACH synthesized without surfactant exhibited adsorption ability for Congo red as good as that synthesized with PEG2000 and better than PEG20000 that provided a facile method without surfactant to synthesize γ -alumina with excellent adsorption performance.

1. Introduction

In recent years, considerable attention has been paid to the environmental pollution problems. Materials with mesoporous structure are expected useful in the water treatments. Alumina are widely used as catalyst supports, adsorbents, ceramics, and abrasives, [1]. Alumina have been prepared in different morphologies including nanowhiskers [2], nanoflakes [3], nanowires [4], nanofibers [5], nanorods, and nanotubes [6]. They may be categorized as one- and two-dimensional nanostructures. A great deal of recent effort has been placed on the synthesis of mesoporous alumina with a high specific surface area and large pore volume using various templates, including surfactants, [7–10] carboxylic acids, [11] and single organic molecules (e.g., glucose [12], tetraethyl glycol [13, 14], and tartaric acid [15]). The introduction of hydrothermal process has provided a relatively simple and powerful method for synthesis of 1D mesoporous nanostructures [16].

Recently, many reports studied the preparation of the morphology-controlled alumina materials via a novel AACH precursor due to its special crystal structure [1, 16], which are benefits to the preparation of the morphology-controlled and mesopores-remained Al_2O_3 products. Herein, we present

a facile hydrothermal and thermal decomposition route to synthesis mesoporous γ - Al_2O_3 fibers with uniform diameters without or with different surfactant. The possible formation process and subsequently surfactant-induced growth mechanism is proposed. Finally, both of the as-obtained alumina fibers were used to adsorb Congo red from water solution.

2. Experimental

2.1. Preparation of Samples. In a typical synthesis of AACH precursors, 0.1 mmol of polyglycol (PEG)-20000 or polyglycol (PEG)-2000 was dissolved in 8 mL deionized water to form a transparent solution, to which 15.0 g of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Merck, 98.5%) was added under vigorous stirring. Then, urea (0.45 mol) was added. The final mixture was then transferred into Teflon-lined autoclave, which was then sealed and placed in an electric oven at 140°C . After 24 h, the autoclave was cooled naturally to room temperature. The product was collected by centrifugation then washed with distilled water and absolute ethanol for several times to remove the impurities and finally dried at 80°C .

The precursors synthesized above were calcined at 900°C for 2 h to obtain alumina.

FIGURE 1: XRD patterns of AACH samples prepared at 140°C for 24 h (a), together with its respective conversion to γ - Al_2O_3 sample calcined at 900°C for 2 h (b).

2.2. Characterization. X-ray diffraction (XRD) patterns were recorded on a powder X-ray diffractometer (D8 advance, Bruker, Germany) with Cu K α radiation. Scanning electron microscopy (SEM) images were obtained using a field-emission scanning electron microscope (LEO 1550, ZEISS, Germany) operated at 5 kV and a transmission electron microscope (JSM-6380LV, JEOL, Japan) operated at 200 kV. The nitrogen adsorption isotherms and special surface areas were obtained using a Quantachrome Nova2000e surface area and pore size analyzer. The sample was degassed at 250°C under a vacuum for 5 h. The special surface areas were calculated using the Brunauer-Emmett-Teller (BET) model from a linear part of BET plot ($P/P_0 = 0.10$ – 0.30). Average pore diameters were calculated using the Barrett-Joyner-Halenda (BJH) method from the desorption branch of isotherm. Chemical bonding information on product was recorded with a Nicolet IS-10 FTIR spectrometer (Thermo Fisher Scientific, USA) using the potassium bromide (KBr) pellet technique with a resolution of 4 cm^{-1} between 400 and 4000 cm^{-1} . The UV-vis absorption spectrum of the products was recorded using a UV-2045 UV-visible spectrometer. The thermal behavior of the products was characterized with a STA 449C TGA-DSC. In each experiment, about 10 mg of the sample was heated at a rate of 10°C/min from 30 to 1300°C.

2.3. Waste Water Treatment. Both of the alumina fibers were used to adsorb Congo red from water solution. 5 mg as-obtained particles were, respectively, added to 10 mL Congo red ($\text{C}_{20}\text{H}_{19}\text{N}_3$) solution (75 mg/L) under stirring continuously at room temperature. Analytical samples were taken from the suspension after various adsorption times and centrifuged to remove the particles. UV-vis absorption spectra were recorded at different intervals to monitor the process.

3. Results and Discussions

As shown in Figure 1, the as-synthesized sample at 140°C for 24 h (curve (a)) was identified as the hexagonal ammonium

FIGURE 2: FTIR spectrum of the synthesized AACH.

FIGURE 3: TGA-DSC curves of AACH precursor.

aluminum carbonate hydroxide (denoted as AACH) (JCPDS card no. 29-0106) by X-ray diffractometer. The high intensity of the XRD peaks of the as-synthesized samples indicated that the AACH phase synthesized in this work is highly crystalline. The respective sample calcined at 900°C for 2 h (curve (b)) can be identified as cubic γ - Al_2O_3 (JCPDS card no. 10-0425). The low intensity of the XRD peaks indicates the alumina products calcined at this temperature that have a low crystallinity.

The FTIR spectrum of the as-synthesized AACH was shown in Figure 2. The band at 1452–1539 cm^{-1} was attributed to the asymmetrical stretching vibration of CO_3 bonds. Peaks at 3446 and 978 cm^{-1} are due to stretching and bending of hydroxyl group in AACH. Bands at 3016–3173 cm^{-1} and 1385 cm^{-1} are due to symmetric and asymmetric stretching vibration of NH_4 . The bands at 468, 611, 733, and 848 cm^{-1} are ascribed to vibration modes of Al-O, while strong band at 1105 cm^{-1} is due to Al-O-Al symmetric vibrations. The absorption bands at 858 cm^{-1} and 482 cm^{-1} belong to C-O-C and $-\text{CH}_2-$ vibration, which originates from surfactant of PEG, and the result suggests that some PEG molecules are absorbed onto the surface of AACH particles.

The TGA-DSC curves of the AACH are shown in Figure 3. The TGA curve shows that the sample has two major

FIGURE 4: SEM images of AACH microfibers prepared with no surfactant: (a) PEG20000, (b) PEG2000, (c) SEM, and (e) TEM ((c), (d)) images of γ - Al_2O_3 microfibers prepared by calcination at 900°C for 2 h.

weight losses. The first weight loss below 208°C is due to the desorption of physically adsorbed water. The second weight loss in the temperature range of 208 – 251°C , corresponding to the large exothermic peak at 251°C of the DSC curve, is associated with the decomposition of PEG20000, together with the conversion of AACH to amorphous Al_2O_3 by release of H_2O , NH_3 , and CO_2 . With the consideration of the weight loss due to absorbed water and PEG, the total weight loss is about 63.8% which is in good agreement with theoretical calculations 63.3% according to the reaction: $2\text{NH}_4\text{Al}(\text{OH})_2\text{CO}_3 \rightarrow \text{Al}_2\text{O}_3 + 2\text{NH}_3$ (12.23% wt loss) + 2CO_2 (31.65% wt loss) + $3\text{H}_2\text{O}$ (19.42% wt loss). The two Endothermic peaks at 885°C and 1146°C on DSC curve without weight loss on TG curve should be attributed to the phase transformation into γ - Al_2O_3 and α - Al_2O_3 , respectively [17].

As shown in SEM images of AACH prepared with no surfactant (Figure 4(a)), PEG20000 (Figure 4(b)), and PEG2000 (Figure 4(c)), the sample is composed of microfibers with uniform size. The length of the fibers is about $10\text{ }\mu\text{m}$, and the diameter of the fibers is about 500 nm for Figures 4(a) and 4(c), and $1\text{ }\mu\text{m}$ for Figure 4(b). The formation of AACH follows the following equation:

The formation of the alumina nanofibers could be interpreted using a surfactant-induced fiber formation (SIFF) mechanism brought forward by Zhu et al. [18], that is, AACH nanocrystals adsorbed on the PEG micelles via hydrogen

FIGURE 5: (A) N_2 absorption and desorption isotherms and (B) pore-size distributions of $\gamma\text{-Al}_2\text{O}_3$ transformed from AACH prepared with surfactant of (a) no surfactant, (b) PEG20000, and (c) PEG2000, respectively.

bonding of the oxide groups of PEG with the OH groups of AACH. The hydrogen bonding reduces the free energy of the AACH crystallites, which allows the AACH crystallites to grow into AACH/PEG nanorods along the direction of the axis of the rod-shaped copolymer micelles. As shown in Figures 4(a)–4(c), AACH microfibers prepared with no surfactant have the same morphology with the samples prepared with PEG20000 and PEG2000. That is the result of preferred growth of AACH along the crystallographic *c*-axis. The diameter of the fibers derived from AACH prepared with PEG20000 was larger than the others that may be due to the larger rod-shaped micelles of PEG20000 formed from the longer carbochain.

SEM and TEM images of the $\gamma\text{-Al}_2\text{O}_3$ microfibers prepared by the thermal decomposition of the AACH fibers shown in Figure 4(b) at 900°C for 2 h were shown in Figures 4(d)–4(f). As shown in Figure 4(d), the alumina fibers are relatively small in diameter than its AACH precursors, and the microfibers were comprised of worm-like mesopores with the pore size about 10 nm (shown in Figure 4(f)) that is probably induced by shrinkage during calcination accompanied by release of H_2O and decomposition of PEG and AACH precursor. The corresponding selected area electron diffraction pattern (Figure 4(e) inset) indicated the typical diffraction rings of the polycrystalline phase.

The N_2 adsorption-desorption isotherm of the $\gamma\text{-Al}_2\text{O}_3$ microfibers calcined at 900°C for 2 h was presented in Figure 5. All of the samples exhibited type IV isotherm with hysteresis of type H1 in the relative pressure range of 0.6–1.0, indicating the presence of the inhomogeneous mesopores. The specific surface areas were $212.43\text{ m}^2/\text{g}$, $182.26\text{ m}^2/\text{g}$, and $235.84\text{ m}^2/\text{g}$, respectively, by the BET method for $\gamma\text{-Al}_2\text{O}_3$ transformed from AACH prepared with surfactant

of (a) no surfactant, (b) PEG20000, and (c) PEG2000. The corresponding pore size distribution curve (Figure 6) of the three samples all displayed pore size distribution from 3 to 25 nm, centered at 12 nm ((b) and (c)) and 15 nm (a), which is close to the result from the TEM images. The calculated pore volume by the BJH method is $0.4899\text{ cm}^3/\text{g}$, $0.3782\text{ cm}^3/\text{g}$, and $0.5089\text{ cm}^3/\text{g}$ for samples (a), (b), and (c), respectively. By comparison, $c > a > b$ for both of the specific surface area and pore volume.

The UV-vis spectra of Congo red solutions in the presence of $\gamma\text{-Al}_2\text{O}_3$ transformed from AACH prepared with surfactant of PEG2000 were taken over time at room temperature (Figure 6(A)). Where Congo red is a common azo-dye in the textile industry and was chosen as a model organic waste. When 5 mg of $\gamma\text{-Al}_2\text{O}_3$ was added into 10.0 mL Congo red solution (75 mg/L), the absorption of Congo red was decreased to 1.8% within 20 mins and Congo red was removed almost completely after 30 mins. The removal of Congo red can be attributed to the electrostatic attraction between the surface of mesoporous alumina microfibers and Congo red molecules [19]. For comparison, the removal efficiency under the same condition of the as-obtained alumina microfibers transformed from AACH prepared with surfactant of (a) no surfactant, (b) PEG20000, and (c) PEG2000, respectively, was shown in Figure 6(B) and indicated that both of the samples (a) and (c) can remove about 100% of the Congo red after 30 mins, while (b) can remove 75% of that. From the results, it can be deduced that the adsorption abilities should be related to their specific surface area and the pore volume. The large surface area and pore volume combined with excellent thermal stability enhance the potential applications of these mesoporous alumina fibers in water treatment, as well as catalysis and catalysis supports.

FIGURE 6: (A) Absorption spectrum of Congo red solution in the presence of γ - Al_2O_3 transformed from AACH prepared with surfactant of PEG2000. (B) Adsorption rates of the Congo red on γ - Al_2O_3 transformed from AACH prepared with surfactant of (a) no surfactant, (b) PEG20000, and (c) PEG2000, respectively.

4. Conclusions

In summary, γ -alumina microfibers with mesoporous of 3–25 nm were synthesized by a hydrothermal and the followed thermal decomposition route. AACH obtained by the hydrothermal method was used as the precursors and converted to Al_2O_3 after thermal-decomposition treatment without the morphology deformation. The formation of mesoporous structures is due to the release of H_2O and decomposition of PEG and AACH precursors. And the release of H_2O , NH_3 , and CO_2 from AACH when calcined has the most important influence to specific surface area and the pore volume. The γ -alumina microfibers exhibited excellent ability to remove organic pollutants from waste water because of their mesoporous structures. The γ -alumina converted from AACH synthesized without surfactant exhibited middle adsorption ability for Congo red between that synthesized with PEG20000 and PEG2000 which may provide a facile method to synthesize promising sorbent and catalyst.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Authors' Contribution

Adding Haibo Zeng to the authors list is because of his contribution to the revised paper.

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