γ-Alumina Nanofibers Prepared from Aluminum Hydrate with Poly(ethylene oxide) Surfactant

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Introducing poly(ethylene oxide) surfactant to aluminum hydrate colloids can effectively direct the crystal growth of boehmite and the crystal morphology of final γ-alumina crystallites. Fibrous crystallites of γ-alumina about 3−4 nm thick and 30−60 nm long are obtained. They stack randomly, resulting in a structure with a low contact area between the fibers but with a very large porosity. Such a structure exhibits strong resistance to sintering when heated to high temperatures. A sample retains a BET surface area of 68 m^2/g, after being heated to 1473 K. The surfactant molecules form micelles that interact with the colloid particles of aluminum hydroxide through hydrogen bonding. This interaction is not sufficient to change the intrinsic crystal structure of boehmite, but induces profound changes in the morphology of boehmite crystallites and their growth. The surfactant-induced fiber formation (SIFF) process has distinct features from templated synthesis but shows similarities in some respects to biomineralization processes in which inorganic crystals with complex morphological shapes can be formed in biological systems. SIFF offers an effective approach to create new nanostructures of inorganic oxide from aqueous media.

Introduction

In recent years, a "synthesis with construction" strategy has achieved great success in developing materials of nanostructures on a scale of several nanometers.[1] Surfactants are widely used as templates or directing agents for the effective control of mesophase structures in nanomaterial synthesis.[2] Outstanding examples include the synthesis of mesoporous molecular sieves of silica or aluminosilicate, M41S[3] and FSM-16[4] materials, using an ionic surfactant as a template. The molecular templating technique has since been used to synthesize a variety of mesoporous materials.[2,5] Porous alumina, also known as activated alumina, is extensively used as an industrial adsorbent, catalyst, and catalyst support.[6,7] The concept of surfactant templating has been applied to the synthesis of mesoporous alumina molecular sieves.[8−11] However, when quaternary ammonium surfactants were used as templates, the nanostructured mesophases collapsed upon surfactant removal.[8] Successes were achieved by using neutral surfactants[9,10] or carboxylic acids[11] as templates. It is noted that all the templated syntheses of aluminas were conducted in nonaqueous systems. However, most porous alumina is prepared from aqueous systems. The properties of aluminum species in aqueous systems, such as electrical charges, morphology, hydrolysis, and polymerization behavior, are remarkably different from those in nonaqueous systems. In aqueous systems aluminum hydroxides most likely exist in crystalline, such as in boehmite or gibbsite, rather than in amorphous phases.[12] It would be of great interest to know how the surfactants interact with aluminum hydrate colloids in the presence of abundant water and if such an interaction can lead to creation of advanced materials. It is highly possible that the underlying mechanism for the synthesis of mesoporous alumina in the presence of a surfactant in aqueous systems is distinctly different from that which has been reported.

In this study, we report the synthesis of aluminas with a fiber morphology and very large porosity from inorganic salts with nonionic poly(ethylene oxide (PEO) surfactants. In such a synthesis, the surfactant micelles induce important changes in the crystallite morphology and growth, rather than simply acting as templates for

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gel particles to condense around. We propose the alumina nanocrystallite formation and growth mechanism to be surfactant-induced fiber formation (SIFF), distinctly different from the templating mechanism as observed in M41S or FSM-16 synthesis.[3,4] This new mechanism could shed light on and provide insight into a new strategy of nanostructured solids.

Experimental Section

Materials. Four nonionic PEO surfactants, Tergitol 15S-*n* ($n = 5$, 7, 9, and 12), from Aldrich, were used in this study. The PEO surfactants have the general chemical formula $C_{12-14}H_{25-29}O(CH_2CH_2O)_nH$, and average molecular weights of about 420 for Tergitol 15S-5 ($n = 5$) and about 730 for Tergitol 15S-12 ($n = 12$). Analytical grade $NaAlO_2$ and acetic acid, from Aldrich, were used to prepare the aluminum hydrate precipitate.

Preparation. Aluminum hydrate is generally precipitated in an aqueous solution from an inorganic aluminum salt. For example, a $NaAlO_2$ solution was added dropwise to 5 N acetic acid solution under vigorous stirring. A white precipitate was formed, separated by centrifugation, and washed 3−4 times to remove Na^+ ions. The PEO surfactant was mixed with the washed precipitate at a predetermined molar ratio of surfactant to aluminum (PEO/Al). The mixture was transferred into an autoclave after a being stirred for 2 h and maintained at 373 K for 2 days. A wet cake was recovered, dried in air, and calcined at 773 K for 20 h. The temperature was raised at a rate of 2 K/min.

To examine the function of the surfactants in such a synthesis, the PEO/Al ratio was varied; for example, various amounts of a surfactant were mixed with a constant amount of precipitate, and PEO surfactants with different molecular weights were used.

Characterization. N_2 adsorption/desorption isotherms were measured at liquid nitrogen temperature, using a gas sorption analyzer (Quantachrome, NOVA 1200). The samples were degassed at 523 K in a vacuum below 10^{-3} Torr for 16 h prior to the measurement. The specific surface area was calculated by the BET equation, using the data in a P/P_0 range between 0.05 and 0.2.[13]

Thermal gravimetric analysis (TGA) of the samples as prepared was obtained on a Shimazu TGA-50. About 10 mg of solid before calcination was loaded onto a platinum pan and heated from room temperature to 1173 K in an air flow of 80 mL/min with a temperature ramp of 5 K/min. X-ray diffraction (XRD) patterns of the sample powder were recorded on a Philips PW 1050/25 goniometer equipped with a graphite monochromator. Cu Kα radiation and a fixed power source (40 kV, 40 mA) were used. The scan rate was 1 deg (2θ)/min. Fourier transform infrared (FTIR) spectra of the samples were recorded by a Perkin-Elmer 2000 FTIR spectrometer. Specimens for the measurements were prepared by mixing 2 mg of the sample powder with 100 mg of KBr and pressing the mixture into pellets. The spectra were acquired in a wavenumber range between 580 and 4000 at 2 cm^{-1} resolution and averaged over 100 scans. Transmission electron microscopy (TEM) images were taken with a JEOL 2010 microscope and a Philips Tecnai 20 microscope on powder samples deposited onto a copper mesh grid coated with a carbon film.

Results

TEM Images. Figure 1 shows the TEM images of the *γ*-alumina samples prepared with PEO/Al ratios of 0.47 (Figure 1A) and 0 (Figure 1B), respectively.

The two images are significantly different. The alumina crystallites in Figure 1A are lath-shaped, with a length over 50 nm and a constant thickness of about 3 nm. In contrast, alumina particles prepared with no PEO added as in Figure 1B show no regular shape. Evidently, introducing PEO surfactant results in the formation of alumina nanofibers. It is noted that when the PEO/Al ratio <0.47, platelike particles are observed. When the ratio >0.47 most of the samples are nanofibers.

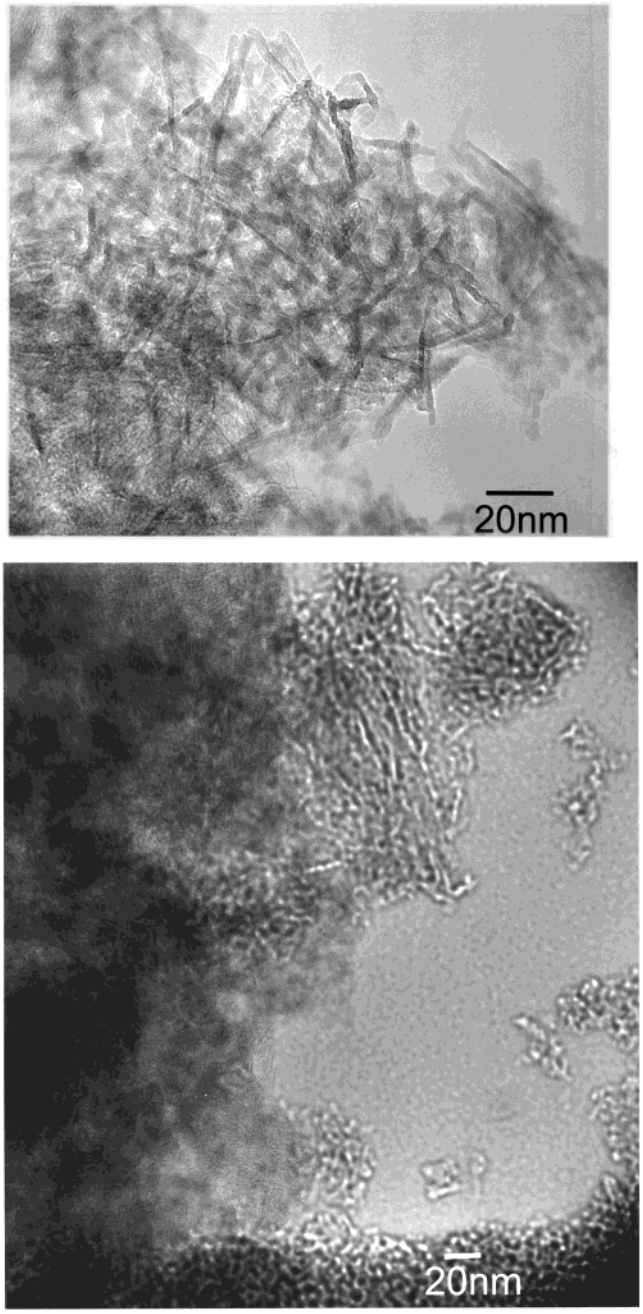

Figure 1. TEM images of the *γ*-alumina prepared with PEO/Al ratios of 0.47 (A, top) and 0 (B, bottom) Alumina nanofibers formed when prepared with PEO surfactant.

N_2 Adsorption. The significant changes in the texture of the product aluminas, as a result of the introduction of PEO surfactants, are also reflected in the nitrogen adsorption isotherms.

The adsorption capacity by alumina prepared without PEO is slightly over 300 cm^3/g STP, whereas that for the sample prepared in the presence of PEO is as high as 1050 cm^3/g STP (Figure 2). It is known that adsorption strongly depends on the porosity of porous solids.[13]

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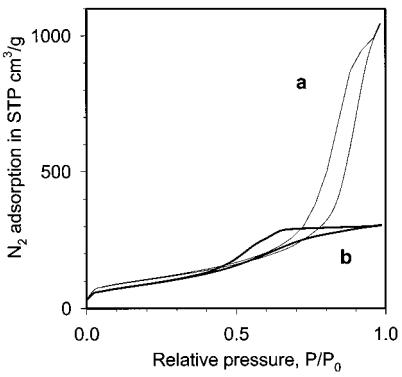

Figure 2. Nitrogen adsorption/desorption isotherms of the samples. For the sample prepared with PEO surfactant (curve a) a steep increase in adsorption commences from a P/P_0 of about 0.7, indicating a very large volume of mesopores in the solid. The isotherms for other samples prepared with PEO surfactants have a similar shape. Curve b is for the sample prepared without PEO surfactant.

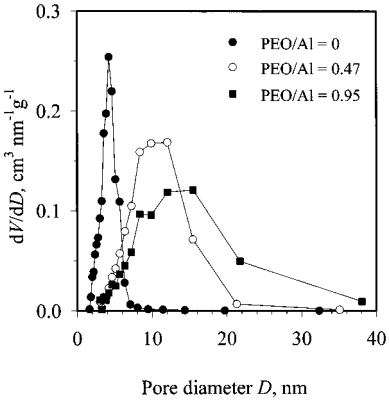

Figure 3. PSDs of a few γ-alumina samples, calculated from the data of N_2 isotherms. As the PEO/Al ratio increases, the PSD peak becomes broader and shifts to larger pore size.

The extraordinarily large nitrogen adsorption by the PEO-induced alumina samples indicates very large pore volumes in these samples. The pore volume should be attributed to the intercrystallite voids of the randomly stacked alumina nanolaths. Because the voids have no regular shape and size but very large volume, the pore size distributions of these samples are much broader than that of the reference sample prepared without PEO (Figure 3).

Figure 3 shows the pore size distributions (PSDs) of a few γ-alumina products, which were calculated from the data of N_2 isotherms using the Barrett−Joyner−Halenda method.[14] The pore sizes concentrate in a range of 5−20 nm for the samples prepared with PEO surfactants.

Most interesting is the impact of the surfactant properties on the PSDs. An evident trend is that both pore size (indicated by the peak position) and pore volume (indicated by the area under the PSD curve) increase with the amount of surfactant Tergitol TS-15-7 introduced in the synthesis. The impact of the PEO/Al ratio on the BET specific surface area (BET SA) and pore volume of the alumina is summarized in Table 1.

Generally, in a templating synthesis, the size of the pores in the product is closely related to the molecular size of the surfactant. It is well-known that the micelles of quaternary ammonium surfactants are uniform cylindrical rods and the diameter of the rods is proportional to the molecular size of the surfactants.[3−5,9−11] In contrast, the trend found in this work is distinctly different. The results derived from N_2 adsorption (Figure 3, Tables 1 and 2) suggest that the more surfactant molecules added during the synthesis, the larger the pore size and pore volume in the products (below a PEO/Al ratio of about 1). For all the samples in Table 2, the same amount (in mass) of the surfactant and $NaAlO_2$ were used in the preparation, while different surfactants were used. Evidently, the molecular size of the surfactant is not simply a determinant of the pore size of the product alumina. There exists a saturation limit of the surfactant around a PEO/Al ratio of 1. Above this limit, the excess surfactant does not appear to be intercalated with boehmite crystallites and shows no effect on the final pore structure. These findings also imply that the mechanism of the synthesis is different: the PEO surfactant does not act merely as a template.

Table 1. Impact of the PEO/Al Ratio on the BET Specific Surface Area (S_{BET}) and Pore Volume (V_p) of the Alumina Samples

PEO/Al ratio	S_{BET} (m^2/g)	mean D[a] (nm)	V_p (cm^3/g)
0	321.6	5.9	0.471
0.24	360.0	15.7	1.409
0.47	376.2	17.1	1.616
0.95	347.4	22.4	1.946
1.95	373.1	12.7	1.185

[a] Mean D is the mean hydraulic diameter of the pores.

Table 2. Impact of the Molecular Weight of the PEO Surfactant (MW) on the S_{BET} and Porosity of the γ-Alumina Samples

surfactant	MW	S_{BET} (m^2/g)	mean D (nm)	V_p (cm^3/g)
Tergitol 15-TS-5	420	371.4	20.3	1.889
Tergitol 15-TS-7	508	376.2	17.1	1.616
Tergitol 15-TS-9	596	360.0	18.1	1.631
Tergitol 15-TS-12	728	351.7	19.0	1.671

XRD Patterns. To derive the formation mechanism of the lath-shaped alumina, XRD patterns at various stages of the synthesis were determined and are depicted in Figures 4 and 5.

The fresh precipitate obtained from aqueous solution $NaAlO_2$, prior to the introduction of PEO surfactant, has poor crystallinity (Figure 4a) A hydrothermal treatment at 373 K was found to evidently enhance the crystallinity of boehmite, AlOOH (Figure 4b). According to the literature, the boehmite (AlOOH) phase forms from aluminum hydroxide, $Al(OH)_3$, at about 373 K.[12] In the presence of PEO surfactant, well-crystallized boehmite also forms during the hydrothermal treatment, according to the XRD patterns (Figure 4c). An XRD diffraction peak of the greatest intensity at $2\theta = 20.8°$, corresponding to $d = 0.43$ nm, is also observed. This peak is believed to be due to the configuration of oxide groups in the surfactants because we found the intensity of this peak is proportional to the number of oxide groups in the surfactant. For the same surfactant used, the intensity of this peak is proportional to the surfactant amount in the dried samples. This peak will be discussed further in the Discussion.

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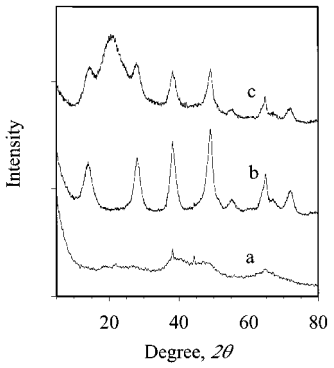

Figure 4. X-ray diffraction patterns: a, dried aluminum hydroxide without hydrothermal treatment; b, aluminum hydroxide after hydrothermal treatment (the pattern indicates that it is well-crystallized boehmite (AlOOH)); c, a mixture of aluminum hydroxide and a PEO surfactant after hydrothermal treatment.

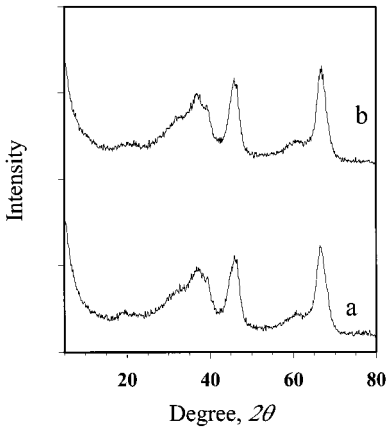

Figure 5. X-ray diffraction patterns of the γ-alumina samples prepared without (curve a) and with (curve b) PEO surfactant. The two patterns are almost identical.

The hydrothermally treated samples were dried in air and calcined subsequently at 773 K. During heating the PEO surfactants evaporated at about 473 K. If the calcination was carried out in a nitrogen flow that passes a cooling trap, the surfactant could be collected for reuse. This is an important merit in regard to environmentally friendliness and economy for the synthesis. The calcination converted nanocrystallite boehmite to γ-alumina. The XRD diffraction patterns of the resulting γ-alumina samples prepared with and without added surfactant are almost identical (Figure 5) although remarkable differences in porosity and crystal morphology have been observed between them.

TGA Results. The weight loss below 393 K (Figure 6a) is mainly due to dehydration. TGA results show that such weight losses for the dried samples prepared with and without surfactant are similar. Nevertheless, the aluminum content in the sample prepared without surfactant is much larger than that in the sample prepared with surfactant. In terms of the water amount per unit mass of boehmite, the latter has a low water content, as compared to the former. Besides, for the samples prepared with surfactant, the greatest weight loss is observed between 473 and 573 K (Figure 6b,c), due to volatilization of the surfactant. Such a surfactant volatilization was observed in sample calcination.

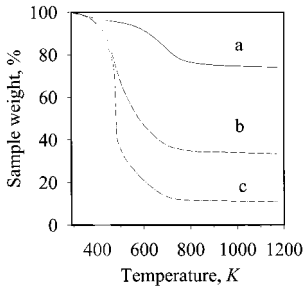

Figure 6. TGA curves of three samples before calcination at 773 K. Curve a is for the sample prepared without PEO surfactant. Curves b and c are for the samples prepared with PEO/Al ratios of 0.47 and 0.95, respectively.

We found that the pore volume (obtained from N_2 adsorption) is proportional to the weight loss. Both curves b and c in Figure 6 are for samples prepared with the same surfactant but in different amounts. We found a larger weight loss in the TGA curve for the sample prepared with more surfactant. This suggests that the mesopores were created, to a large extent, by the evaporation of the surfactant, which was located in the intercrystallite voids before the calcination step. Because the pore size is far beyond the molecular size of the surfactant, the surfactant should have existed in micelles rather than in single molecules. A number of studies have shown that PEO surfactants exist in rodlike or wormlike micelles in aqueous solutions.[15−18]

FTIR Spectra. In Figure 7A representative FTIR spectra of the samples prepared with PEO surfactant before calcination are shown (curve a). For comparison, the spectrum of a pristine surfactant is also given in the figure (curve b).

Figure 7A shows the spectra in the range between 1500 and 700 cm^{-1}, and the characteristic bands of the ethylene oxide chain[19] can be clearly seen at 1350, 1250, 1105, 950, and 845 cm^{-1} for the pristine surfactant, while only the most intense characteristic bands at 1350, 1250, and 950 cm^{-1} can be found for the sample prepared with the surfactant. The bands at 1187, 1132, and 1050 cm^{-1} observed for the sample are due to the vibration modes of −OH groups on the boehmite.[20] The bands at 2873 and 2928 cm^{-1} (Figure 7B) and 1466 cm^{-1} (Figure 7A) are due to the $-CH_2-$ groups of both the alkyl and ethylene oxide chains.[19] Consistent with the literature, Figure 7B also shows that the intensity ratio of the asymmetric band (2928 cm^{-1}) to the symmetric band (2873 cm^{-1}) is greater for the sample (2.11) than that for the pristine surfactant (1.32). According to Michot et al.,[19] this is due to the surfactant binding to the boehmite particles. The FTIR spectra confirm that there are strong interactions between the surfactant molecules and the surface boehmite, the precursor of γ-alumina.

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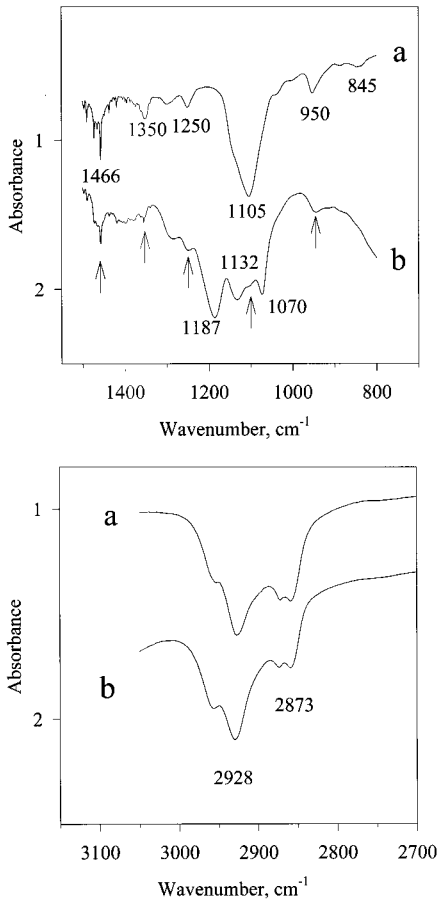

Figure 7. FTIR spectra of the PEO surfactant Tergitol 15-TS-7, and the uncalcined sample with a PEO/Al ratio of 0.47 (a mixture of this surfactant and boehmite): A, top, in the range between 1500 and 800 cm^{-1}; B, bottom, in the range between 3100 and 2700 cm^{-1}.

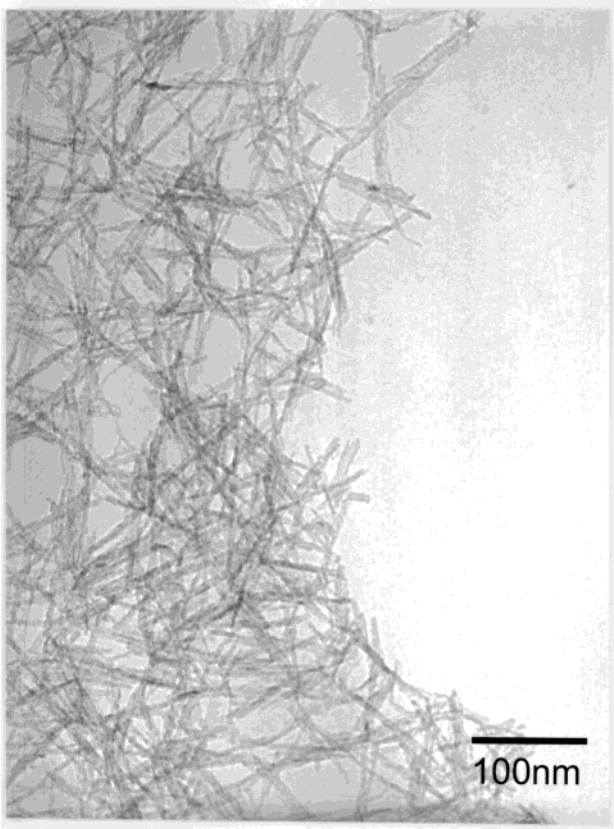

Figure 8. TEM images of the boehmite prepared with a PEO/Al ratio of 0.47. The scale bars in the images indicate 100 nm. This is the sample before calcination at 773 K but after the hydrothermal treatment at 373 K.

Discussion

Introducing polymer molecules of large molecular weight (10^4 to 10^6) to increase the porosity of activated alumina has been reported for a long time.[7,21] But the additives, such as polyalcohols and cellulose, were simply regarded as space fillers or pore-regulating agents. The effect of the additives on the morphology of aluminum hydroxide crystals, reflected by the results of this study, was ignored. As shown by TGA results, the dried samples prepared with surfactant have a low water content, compared to the sample prepared without surfactant. This fact can be explained as the affinity to the surfaces of boehmite crystallites allows the surfactant micelles to squeeze out part of the water molecules that were previously bonded on the surface. The nature of this affinity is the mutual interaction between the surfactant and boehmite surfaces.

Actually, in the TEM images of the boehmite prepared with a PEO surfactant prior to calcination, one can observe the nanofiber morphology clearly (Figure 8).

The thickness of these fibers is similar and close to that of the γ-alumina fibers observed in Figure 1a. Evidently, boehmite fibers first formed from aluminum hydrate at moderate hydrothermal conditions. Because the conversion of boehmite to γ-alumina mostly takes place at above 573 K and the PEO surfactants evaporate at lower temperatures than this temperature, we believe that the surfactant micelles induce the formation of nanolath morphology and the subsequent growth of the nanocrystallites through such a mutual interaction.

For the dried samples prepared with surfactant, an XRD diffraction peak of the greatest intensity at $2\theta = 20.8°$, corresponding to a d value of 0.43 nm, is observed (curve c in Figure 4), while the rest of the peaks are well matched with the patterns of boehmite. This peak is due to the configuration of oxide groups in the surfactants because its intensity is proportional to the number of oxide groups in the surfactant. For the same surfactant used, the intensity of this peak is proportional to the surfactant amount in the dried samples, and if various surfactants are introduced by the same amount, this increases with n, the number of oxide groups in a surfactant molecule. Indeed, a strong peak is also found in the XRD pattern of the pristine surfactant liquid at room temperature at a lower angle, $2\theta = 18.6°$ (Figure 9), corresponding to $d = 0.43$ nm. The comparison of the XRD patterns for the same surfactant in different states, solid, partially melted, and in a mixture of boehmite and surfactant (Figure 9), suggests that the surfactant in boehmite is in an intermediate state, with more close packing than that in the pristine liquid. This can only be attributed to the interaction of the surfactant micelles with the boehmite crystallite surfaces. Even in the liquid phase the PEO surfactants exhibit regular packing. Their alkyl chains prefer to stack close to each other, and so do the oxide

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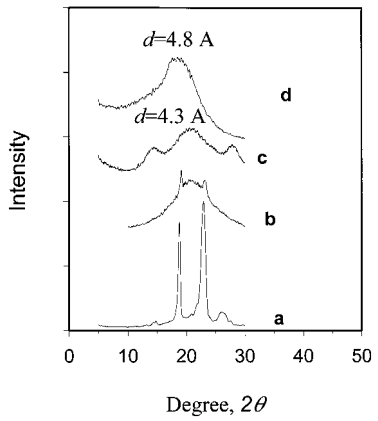

Figure 9. XRD patterns of a PEO surfactant in various states: a, pure solid; b, partial melt; c, in boehmite; d, pure liquid.

groups, forming micelles. When the surfactant is dispersed in a polar medium, such as in aqueous systems or polar surfaces, the oxide groups form the outer surface of the micelles, being in contact with the polar medium,[15−17] in this case, the surface of boehmite crystallites. The shift in the diffraction peak of the surfactant to a higher angle is indicative of the interaction between the oxide groups of the surfactants and the surface of boehmite crystallites. The changes in the infrared absorption bands also support the surfactant binding to aluminum hydroxide.

As shown by XRD patterns, this interaction seems not to be sufficiently high to alter the intrinsic structure of boehmite crystallites. Instead, it results in changes in the stacking of the surfactants because their stacking is more flexible. Therefore, such an interaction should be hydrogen bonding, and the micelles should be closely bonded to the surface of boehmite crystallites through hydrogen bonding. More importantly, this close bonding combined with the regular stacking of the PEO surfactant regulates the growth of the boehmite crystallites to a certain direction during aging. This is the fundamental mechanism underlying SIFF.

The proposed SIFF process is schematically shown in Figure 10a. The structure of a boehmite crystallite is given in Figure 10b. The corrugated layers of boehmite nanocrystallites are linked by hydrogen bonds.[20,22] The surfactant micelles should take the configuration in which the oxide groups lie on the surface of the boehmite crystallite, while the alkyl chains head away from the surface (Figure 10b). The layered aggregates of boehmite crystallites are intercalated with surfactant micelles. The stacking of the surfactant micelles on the boehmite crystallite surface is more closely packed than in the pristine surfactant liquid. Therefore, the surfactant micelles attain the maximum number of hydrogen bonds with the OH groups on boehmite surfaces. It is believed that the hydrogen bonding between the oxide groups and the boehmite surface reduces the free energy of the crystallites with low dimensions. This allows the boehmite crystallites to grow along one direction. Such a situation has similarity to the formation of silica nanotubes reported recently.[23,24] In addition, the formation of nanofibers may undergo the Ostwald ripening process in which larger crystallites grow at the expense of smaller crystallites being dissolved.[25]

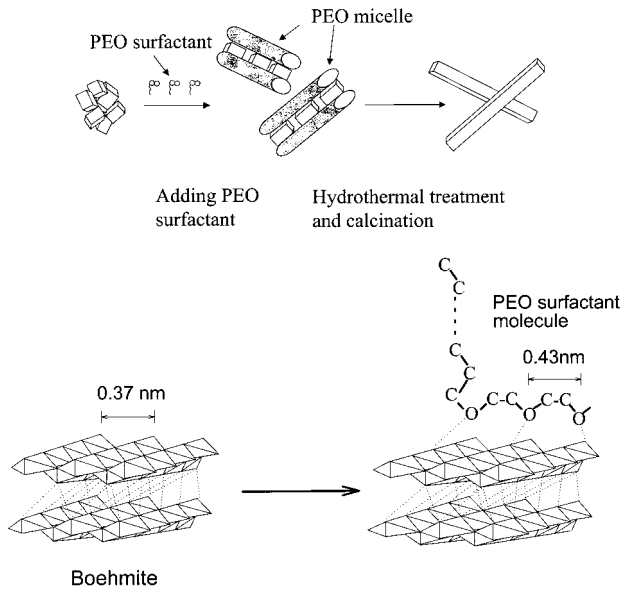

Figure 10. Schematic illustration of the surfactant-induced fiber formation change mechanism. (A, top) Fine particles of boehmite disperse into the PEO surfactant medium, where surfactants form micelles of one-dimensional structure. The growth of boehmite crystals is regulated by the micelles through hydrogen bonding, which allows the oxide groups of the surfactant to strongly bind to the surface of boehmite (as shown in B). During the heating the fibers harden, the surfactant is removed, and boehmite nanolaths are converted to γ-alumina nanofibers. Panel B (bottom) shows the boehmite structure and interplay between the surfactant molecules and corrugate surface of boehmite. The micelles are close packed on the surface of boehmite.

Boehmite is converted to γ-alumina during the subsequent heating, as elimination of H_2O between boehmite layers takes place. Nevertheless, the conversion from boehmite to γ-alumina does not lead to substantial changes in morphology.[7,26] Thus, the lath-shaped boehmite crystals will result in γ-alumina with nanofiber morphology.

In contrast to the templated synthesis of M41S and FSM-16 materials[3−5] and the synthesis of mesoporous alumina in nonaqueous systems,[9−11] where the precursors of silica and alumina have no crystalline structure and are sufficiently flexible to condense around the surfactant micelles, in the SIFF process the inorganic precursor has its own intrinsic crystallite structure and does not mimic the shape of the surfactant micelles. Thus, the surfactant micelles do not act simply as a template. The surfactants also act as a "shape-inducing" reagent.[27] As discussed, boehmite crystallites grow during the aging period, in particular under moderate hydrothermal conditions[12] (Figure 4). At this stage, boehmite crystallites grow in the direction parallel to the corrugated surface due to strong bonding of the surfactant micelles to the boehmite surface, and due to

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Table 3. S_{BET} and V_p in Alumina Nanofibers Calcined at High Temperatures

PEO/Al ratio	1173 K		1473 K	
	S_{BET} (m^2/g)	V_p (cm^3/g)	S_{BET} (m^2/g)	V_p (cm^3/g)
0	154.2	0.433	4.6	0.032
0.24	179.4	1.131	13.4	0.077
0.47	198.7	1.406	48.6	0.391
0.95	189.3	1.545	50.2	0.404
1.95	183.9	1.129	43.4	0.333

the configuration of the micelles, leading to the formation of lath-shaped nanocrystallites. In these respects, the SIFF process leading to the formation of the nanolath morphology is quite similar to the biomineralization process, in which the nucleation, growth, morphology, and assembly of the inorganic crystals are regulated by organized assemblies of organic macromolecules (the organic matrix).[28] Both processes are aqueous synthesis processes of inorganic solids under moderate conditions, and the interaction at the interface of organic and inorganic nanophases in both cases is hydrogen bonding.

The proposed SIFF mechanism can also be applied to interpret a common problem in alumina refinery: humic substances in the Bayer liquor result in a fine and fragile alumina hydrate precipitate that is undesirable for the industry.[29] The humic compounds act similarly to the PEO surfactants in this study, leading to products with very fine crystallites and very large porosity. In fact, we prepared an γ-alumina sample using a Bayer liquor as the alumina source and achieved a very large surface area (630 and 450 m^2/g after calcination at 623 and 773 K, respectively). This fact further supports the above discussion.

At a higher PEO/Al ratio, some of the surfactant micelles may not be able to access the boehmite crystallite surface. They exist in the intercrystallite voids, acting as a space filler. The fraction of the space filler surfactant increases with the PEO/Al ratio, resulting in an increased pore volume (so that the trend in Figure 4 is observed). From the trend shown in Figure 4, we can control the pore size distribution of the alumina products by adjusting the ratio of surfactant to aluminum.

Another merit of γ-alumina nanofibers is their strong resistance to sintering when heated to high temperatures. It is known that sintering causes serious loss of specific surface area and porosity. For instance, after heat treatment at 1173 K for 3 h, a sample of alumina nanofiber still retains a BET surface area of 240 m^2/g and pore volume of 1.1 cm^3/g. The sample still retains a surface area of 68 m^2/g, even after being heated at 1473 K.

As shown in Figure 1a the nanofibers stack randomly, having a very large porosity and very low contact area between the fibers. In such a structure the sintering propensity is low. Therefore, the alumina fibers retain a substantially large surface area after being heated to high temperatures. For instance, after calcination at 1473 K for 3 h, the BET surface area and pore volume of several alumina nanofiber samples are about 10 times those for normal alumina samples (Table 3). The data in Table 3 demonstrate that the peculiar morphology of the nanoparticles has significant influence on the properties of the materials.

This is an important advantage for alumina particularly when used as a catalyst support. First, high-temperature calcination may also create acid sites with stronger acidity, which are more favorable for some catalytic reactions, such as toluene alkylation, or a surface structure that results in high performance of catalysts. We have found that Ni catalysts supported by our SIFF-derived mesoporous alumina calcined at 1173 K exhibit a superior performance for NO_x reduction, compared to catalysts supported on a commercial γ-alumina. Second, there are numerous reactions requiring that catalysts be used or regenerated at high temperatures. The alumina nanofibers can be a good substrate for preparing high-temperature catalysts. For instance, barium hexaaluminate (BHA) shows outstanding thermal stability even above 1473 K, and it retains a surface area of around 10 m^2/g after heat treatments at 1473 K.[30,31] BHA has been used to develop useful catalysts for combustion for energy generation, or a steam re-forming reaction. Some researchers used aluminum alkoxide as starting material[9−11] and an advanced technique, reverse microemulsion synthesis,[32] to prepare BHA with a surface area up to 100 m^2/g. As a comparison, we simply impregnated the alumina nanofibers with $Ba(NO_3)_2$ solution and calcined the solid at 1473 K. The calcined catalyst, which still has a surface area of 35 m^2/g, is a mixture of barium hexaaluminate and barium aluminate according to their XRD patterns. This result demonstrates that alumina fibers are a very promising substrate for the synthesis of BHA catalysts. The nanofibers are not only promising potential catalysts, catalyst supports (on which the catalytic active components can well disperse, forming nanosized active sites), and advanced adsorbents (due to the large surface area and pore volume), but also an ideal structural reinforcement for various composite materials.

Conclusions

TEM images indicate that introducing poly(ethylene oxide) surfactant to aluminum hydrate colloids leads to γ-alumina nanofibers about 3 nm thick and 30−60 nm long. Such a structure exhibits large porosity and strong resistance to sintering when heated at high temperatures so that these γ-aluminas can be used as supports for catalysts working at high temperatures or for developing combustion catalysts.

A surfactant-induced fiber formation mechanism is proposed. The surfactant micelles interact with the colloid particles of aluminum hydroxide through hydrogen bonding as boehmite crystals form and grow. This interaction is not sufficient to change the intrinsic crystal structure of boehmite, but can effectively direct the crystal growth of boehmite, inducing profound changes in the morphology of the crystallites. During the subsequent heating, the surfactant volatizes, leaving a highly porous framework. At the same time the

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boehmite crystals are converted to γ-alumina, retaining the fiber morphology. In the SIFF process boehmite has its own intrinsic crystallite structure and does not mimic the shape of the surfactant micelles. There is no relation between the pore sizes in the product alumina and the molecular size of the surfactant, which is generally observed in templated synthesis. SIFF offers an effective approach to create new nanostructures of inorganic oxide from aqueous media.

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