

Synthesis of acicular goethite with surfactants

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Frost, Ray and Wu, Peter and Bostrom, Thor and Zhu, Huai Yong (2005) Synthesis of acicular goethite with surfactants. *Materials Letters* 59(17):2238-2241.

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Abstract:

Goethite nanotubes have been synthesised using polyethylene oxide surfactant as a directing agent. The surfactant enables the goethite to crystallise along a specific pathway and does not affect the crystal structure of the mineral but rather the agglomeration of the mineral. The crystals reach an optimum size at which the surfactant can bond.

Introduction:

The growth of goethite (α -FeOOH) particles has been controlled by directing the aggregation of goethite nanocrystallites through the use of PEO (polyethylene oxide) surfactant. Being able to control the growth and morphology of particles at a nanometer scale forms an integral part of nanomaterials research [1]. It is therefore of no surprise that there has been considerable research interest in developing such methods. Surfactants have received particular attention in this field due to their self-assembling capabilities [2]. There has been considerable success in the use of surfactants as templates for the synthesis of mesoporous materials [3] Lamellar mesoporous structures of silica, [4] alumina [5] and more recently, iron oxide, [6] have been reported.

Lately an interesting new synthesis method using surfactants has been reported by Zhu et al. [7] Rather than acting as templates as for the synthesis of the mesoporous materials, the surfactant was able to direct formation of boehmite (AlOOH) fibres, and the fibres can grow to over 100 nm long when reaction conditions are well-controlled [8]. It was also reported that a much higher Al concentration and lower temperatures can be used compared to traditional methods for the synthesis of boehmite nanofibres. This is an efficient approach of producing the nanofibres in large quantity. The boehmite can then be converted to fibrous γ -alumina through a topotactic transition by subsequent heating [9] Moreover, the new mechanism for formation and growth of nanofibres, directing by micelles, is of significance for fundamental research. If such a method can be extended to other systems, it will provide a new methodology for the synthesis of nanomaterials with controlled size and morphology.

This study investigates the applicability of this synthesis method to iron systems, in particular lepidocrocite (γ -FeOOH) and goethite (α -FeOOH) which have similar chemistry to boehmite. The method could potentially produce highly fibrous (acicular) goethite and lepidocrocite nanosized particles which has applications as precursors for heterogeneous catalysts, anticorrosion coatings and magnetic recording media [10,11].

The initial iron oxyhydroxide precipitate was synthesised by a modification of the method reported by Nunez et al.¹² as the method is simple to perform and the goethite to lepidocrocite ratio of the product can be easily controlled by the Fe/OH ratio. The precipitate was then grown in an autoclave under hydrothermal condition, with and without PEO surfactant, by addition of fresh precipitate. Evidences for the effect of surfactant on the growth of iron oxyhydroxide particles were observed with XRD, IR, TEM and N₂ adsorption/desorption.

2. Experimental

The detailed experimental procedure is as follows. FeSO₄·7H₂O (from Mallinckrodt) was dissolved in ultrapure water to form a 0.05M FeSO₄ solution. NaOH was then added in a Fe/OH ratio of 0.35. Oxidation was achieved by bubbling air through the solution with stirring at 40°C for 100 minutes. The solution was then centrifuged and washed 3 times. An orange precipitate was obtained.

This precipitate was then split into two batches. Polyethylene oxide (PEO) surfactant (Tergitol 15-S-7 from Aldrich) with a general chemical formula C₁₂₋₁₄H₂₅₋₂₉O(CH₂CH₂O)₇H, was mixed with the first batch of precipitate at a PEO:Fe molar ratio of 0.47. The second batch was used as a reference. Both batches of precipitate were then put into autoclaves at a temperature of 100°C. A fresh batch of iron precipitate synthesized at a Fe/OH ratio of 1.75 was added to both autoclaves everyday for 3 days to examine the applicability of the method for high iron concentration. A sample was taken out of each autoclave daily before the addition of fresh precipitate.

Transmission electron microscope images and diffraction patterns were taken using a Phillips CM200 TEM operated at 200kV from powdered samples deposited from dilute suspension onto film-coated Cu grids. Infrared spectra were obtained using Nicolet Nexus 870 FTIR spectrometer fitted with a Smart Endurance single bounce diamond ATR cell. The spectra were acquired over the range of 4000 cm⁻¹ and 580 cm⁻¹ at 4 cm⁻¹ resolution and averaged over 64 scans. X-ray diffraction patterns of the powdered samples were obtained using a Philips X'Pert Multi-Purpose Diffractometer at a scan rate of 0.03°/sec. Cu radiation was used. N₂ absorption/desorption isotherms were measured at liquid nitrogen temperature using a Tristar 3000 nitrogen adsorption instrument. The samples were degassed at 100°C for 4 hours prior to the analysis.

3. Results and discussion

The XRD patterns (Fig. 1) showed that the fresh precipitate produced with 5 times the iron concentration (b) formed goethite with a minor amount of other phases. There is an absence of any lepidocrocite peaks in the final samples c and d, indicating that the initial lepidocrocite was converted into goethite during the hydrothermal treatment. The definitive mechanism for this is uncertain although Wirnsberger et al.¹⁰ proposed that the corners of the lepidocrocite structure can interlink to form the goethite structure in solution.

The major point to note in the XRD patterns is the similarity between the sample with surfactant and the sample without surfactant. Calculating the full width at half maximum (FWHM) showed that they have similar crystallinity and both are more crystalline than the fresh precipitate (see Table 1).

The similarity between the samples with and without surfactant is in correspondence with that documented by Zhu et al. [7] for alumina. Despite the similarity it is observed that the sample with surfactant shows higher orientation effect in the XRD compared to the sample without surfactant. This suggests that the particles in the sample with surfactant have morphology of lower dimension (1-D or 2-D).

The IR spectra (Fig. 2) show that the O-H stretching band of goethite (~3100 cm⁻¹) shifts approximately 15 cm⁻¹ to lower wavenumber due to the surfactant despite the XRD showing that there is no difference in crystal structure between the two samples. This suggests that there are interactions between the goethite particles and the surfactant.

The lower wavenumber region of the IR spectra showed a similar effect (Fig. 3). Shifts of approximately 10 cm^{-1} to lower wavenumber were observed for one of the O-H bending vibration ($\sim 890\text{ cm}^{-1}$) and the Fe-O stretching vibration ($\sim 620\text{ cm}^{-1}$) of the goethite for the sample containing surfactant which again demonstrates that the goethite particles are interacting with the surfactant. The IR result also suggests that the interaction is due to hydrogen bonding. When the PEO surfactant is dispersed in a polar medium, the oxide groups would form the outer surface of the micelles, being in contact with the polar media, in this case, the surface of goethite crystallites. Evidently such an interaction facilitates the dispersing of PEO surfactant micelles among the goethite nanocrystallites. Moreover, under the synthesis conditions the PEO surfactant should form linear micelles 13 which can promote aggregation of goethite crystallites in the elongating direction through the interaction, as shown in TEM images.

The goethite particles observed in the TEM images for the sample with surfactant have dimensions in the order of $20\times 200\text{ nm}$, which is significantly greater than the crystallite size calculated according to the Scherrer equation. This suggests that the larger particles may be aggregates of small individual crystallites. This was confirmed by more details examination in the TEM and by electron diffraction of a large particle (see Fig. 4) where the pattern shows spots from a number of crystalline orientations.

In the sample without surfactant, small clusters of particles with the approximate dimensions of that calculated by the Scherrer equation are observed frequently throughout the sample (see Fig. 5(b)). It was also observed that the larger polycrystalline crystals in the sample without surfactant have a more irregular morphology than that in the sample with surfactant.

The evidence from XRD and TEM demonstrate that the interaction between the micelles and goethite nanocrystallites is insufficient to change the intrinsic crystal structure of goethite, but it is capable of inducing changes in the morphology. It is proposed from the evidences that the interaction with PEO surfactant can promote aggregation of goethite crystallites and also influence the direction of its aggregation.

The BET surface area calculated from the nitrogen adsorption/desorption isotherms (see Fig. 6) for the sample with surfactant is $24.0\text{ m}^2/\text{g}$, which is substantially smaller than the surface area of $39.4\text{ m}^2/\text{g}$ for the sample without surfactant. The larger surface area of the latter is attributed to the small and irregular particles in this sample, as observed in the TEM image, while the PEO surfactant in the former sample promoted aggregation of small goethite crystallites to form larger one-dimensional nanoparticles.

The isotherm also indicated that there are no micropores ($> 2\text{ nm}$) in the particles. This is supported by the TEM which showed that the particles are essentially solid. Therefore it implies that the surfactant did not exhibit a templating effect as seen for the synthesis of M41S type materials. 3

This study has shown that PEO surfactant can be used to control the growth of goethite particles by a mechanism that is markedly different from that used for the M41S type materials. The PEO surfactant influences the aggregation of small nanosized goethite crystallites by interaction with their surfaces. The goethite crystallites therefore act as nanoscale building blocks from which larger particles can be constructed. Further understanding of the mechanism for this type of synthesis can potentially allow production of goethite particles with controlled size and morphology that can be tailored to specific applications.

References

1. C. Rao, A. Cheetham, *Journal of Materials Chemistry*, 2001, 11(12), 2887-2894.
2. I. Soten, G. Ozin, *Supramolecular Organization and Materials Design*, 2002, 34-82.
3. C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Vartuli, J. S. Beck, *Nature*, 1992, 359, 710.
4. K. Edler, S. Roser, *International Reviews in Physical Chemistry*, 2001, 20(3), 387-466.
5. S. A. Bagshaw, T. J. Pinnavaia, *Angew. Chem., Int. Ed. Engl.*, 1996, 35(10), 1102.
6. G. Wirnsberger, K. Gatterer, H. Fritzer, W. Grogger, B. Pillep, P. Behrens, M. Hansen, C. Bender Koch, *Chemistry of Materials*, 2001, 13, 1453-1472.
7. H. Y. Zhu, J. D. Riches, J. C. Barry, *Chemistry of Materials*, 2002, 14(5), 2086-2093.
8. H. Zhu, W. Martens, Z. Gao, J. D. Riches, X. Gao, R. Frost, E. Vansant, *J. Phys. Chem.* 2004, 108, 4245-4247.
9. J. Sterte, J. Otterstedt, *Mat. Res. Bull.*, 1986, 21, 1159.
10. G. Wirnsberger, K. Gatterer, H. Fritzer, W. Grogger, B. Pillep, P. Behrens, M. Hansen, C. Bender Koch, *Chemistry of Materials*, 2001, 13, 1453-1466.
11. D. Cook, S. Oh, R. Balasubramanian, M. Yamashita, *Hyperfine Interactions*, 1999, 122(1,2), 59-70.
12. N. Nunez, M. Morales, P. Tartaj, C. Serna, *Journal of Materials Chemistry*, 2000, 10, 2561-2565.
13. P. G. Cummins, E. Staples, J. Pemfold, *Langmuir*, 1989, 5, 1195.

Table 1: Crystallite size calculations for the 110 peak using the Scherrer equation

Sample	FWHM	Crystallite size (nm) a
Fresh Precipitate	0.62	19
Sample after 3 days without surfactant	0.54	23
Sample after 3 days with surfactant	0.53	24

a After adjusting for instrumental broadening.

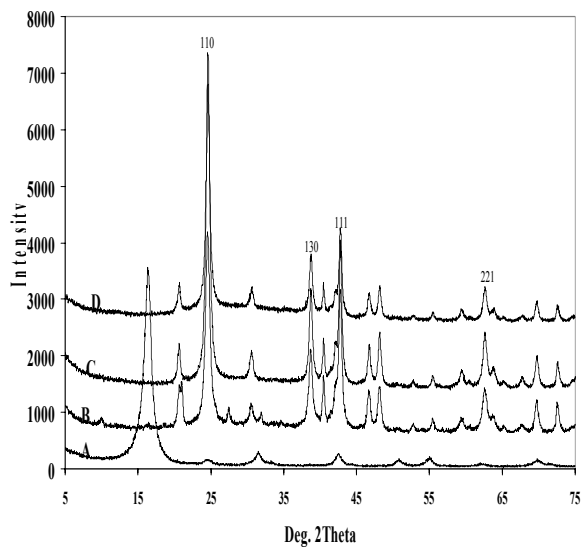


Fig.1:XRD patterns (a) Starting material (b) Fresh precipitate (c) Sample after 3 days without surfactant (d) Sample after 3 days with surfactant

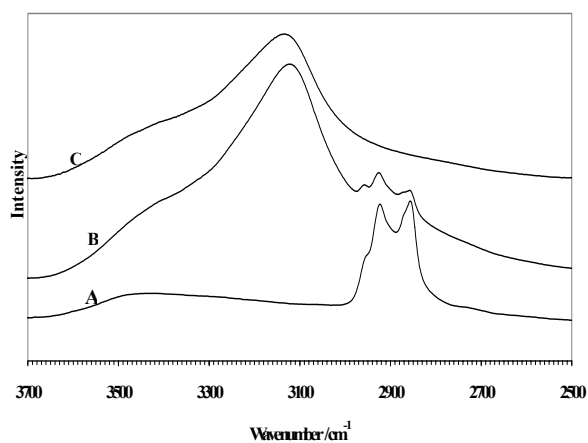


Fig.2:ATR spectra of 2500 to 3700 cm^{-1} region (a) PEO surfactant (b) Sample after 3 days with surfactant (c) Sample after 3 days without surfactant.

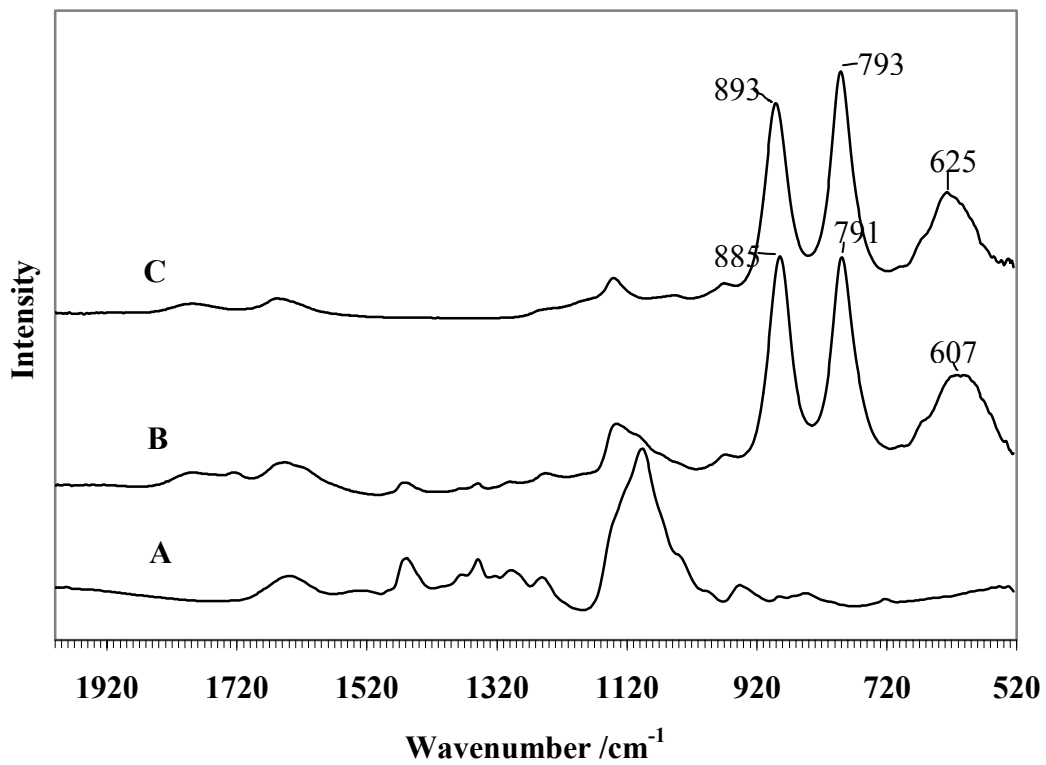


Fig. 3 ATR spectra of 520 to 2000 cm⁻¹ region (a) PEO surfactant (b) Sample after 3 days with surfactant (c) Sample after 3 days without surfactant.

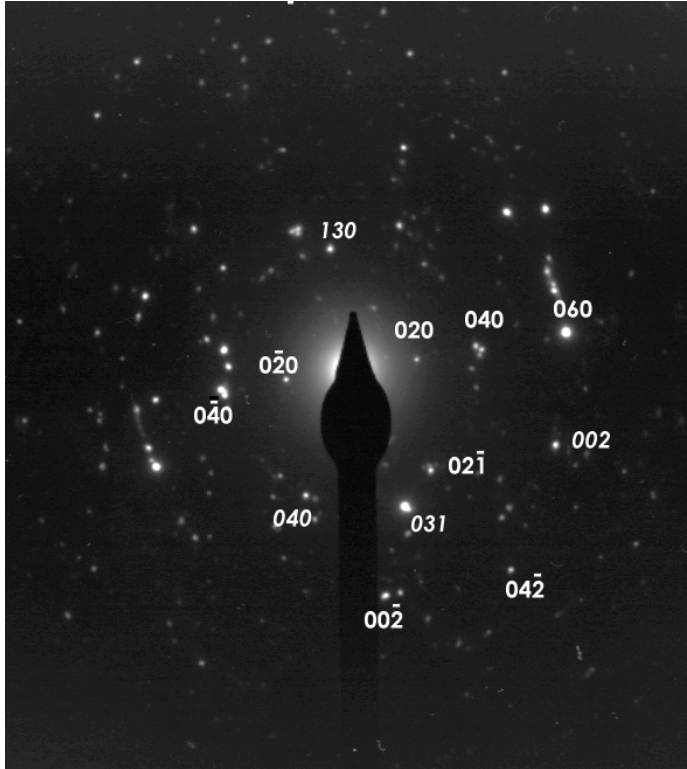


Fig. 4: Electron diffraction pattern of a goethite particle in the sample with surfactant. Indexed spots are mainly from a [100] orientation, but many additional spots are from other orientations (some indicated by indices in italics).

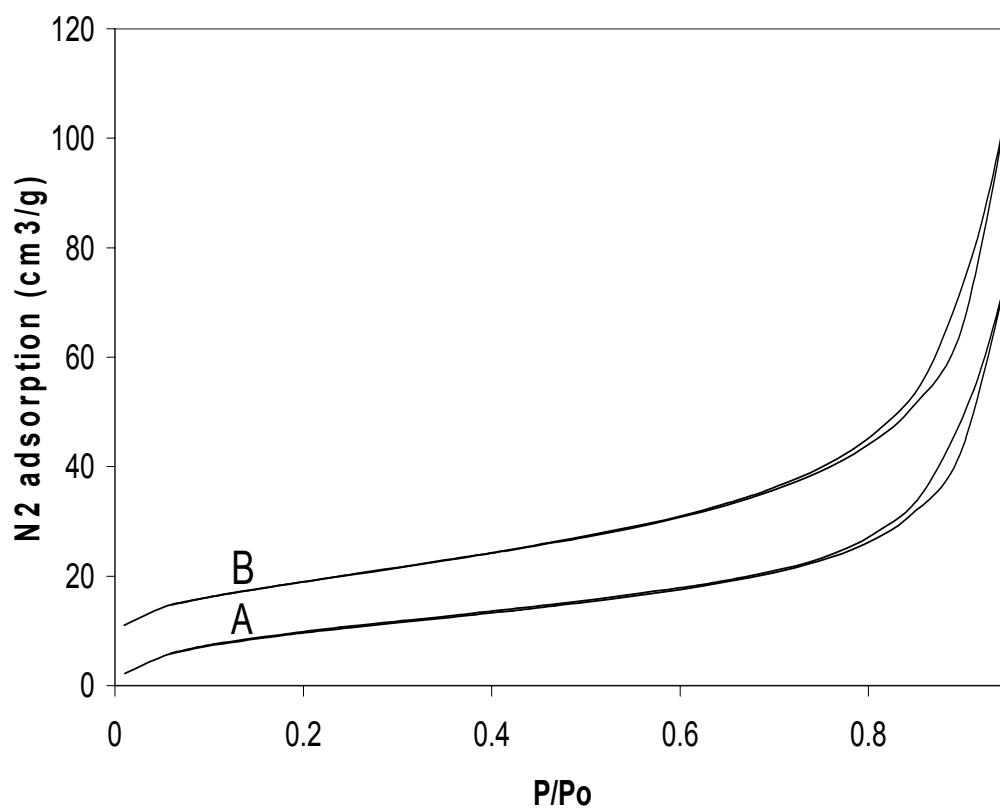


Fig. 6: N₂ adsorption/desorption isotherms (a) Sample after 3 days with surfactant (b) Sample after 3 days without surfactant.

Fig. 5: TEM images (a) Sample with surfactant showing particles with well defined fibre morphology; (b) Sample without surfactant showing particles with more irregular morphology and clusters of undeveloped material (arrows).

