Mesoporous Akaganeite of Adjustable Pore Size Synthesized using Mixed Templates

Y Zhang, D L Ge, H P Ren, Y J Fan, L M Wu and Z X Sun*
School of Chemistry and Chemical Engineering, University of Jinan, 250022 Jinan, China

*Corresponding email: sunzx@ujn.edu.cn

Abstract. Mesoporous akaganeite with large and adjustable pore size was synthesized through a co-template method, which was achieved by the combined interaction between PEG2000 and alkyl amines with different lengths of the straight carbon chain. The characterized results indicate that the synthesized samples show comparatively narrow BJH pore size distributions and centered at 14.3 nm when PEG and HEPA was used, and it could be enlarged to 16.8 and 19.4 nm respectively through changing the alkyl amines to DDA and HDA. Meanwhile, all the synthesized akaganeite possess relativity high specific surface area ranging from 183 to 281 m²/g and high total pore volume of 0.98 to 1.5 cm³/g. A possible mechanism leading to the pore size changing was also proposed.

1. Introduction
Akaganeite (β-FeOOH) nanoparticles have extensive applications in the field of ion exchange [1], sorbents [2], and catalysts [3]. In addition, due to the fact that pores significantly increase the surface area/volume ratio of a material, mesoporous iron oxide films offer great potential as advanced materials for electrodes [4] and pharmaceutical drug delivery [5]. In order to synthesize nanocrystalline akaganeite, different methods such as precipitation, sol–gel as well as surfactant assisted methods have been employed [4, 6]. However, most of the synthesized akaganeite have either comparatively irregular pore size distributions [7] or have not reported on information about pores [6]. Up to now, synthesis of pore size adjustable mesoporous akaganeite material still represents a challenge. On the other hand, different templates have been successfully employed as the regulator to control the pore size and the pore channel architecture of silica and alumina [8, 9]. The idea in synthesizing size tunable silica and alumina mesoporous materials could also hopefully throw some lights in the synthesis of pore size adjustable mesoporous akaganeite materials.

To the best of our knowledge, however, there is no report on the synthesis of mesoporous akaganeite with large and adjustable pore size so far, although Bruce et al. [10] have synthesized two- and three-dimensional mesoporous iron oxides with micro-porous walls by using decylamine as the template. Furthermore, the mechanisms for the formation of mesoporous akaganeite using surfactant as a template are still unclear. Herein, we report, the synthesis of mesoporous akaganeite with large and adjustable pore size from 14 to 20 nm using PEG and alkyl amine with different chain length as mixed templates, and propose a possible mechanism leading to various pore sizes.
2. Experiments

2.1. Sample preparation
All the chemical reagents are of analytical grade and used as-received without any further purification, double distilled water was used throughout the experiment. In a typical synthesis, 12.0 mmol FeCl₃·6H₂O and 0.3 mmol PEG2000 were dissolved in 20 mL distilled water forming a yellow solution in a 100 mL beaker. 12.0 mmol n-Heptylamine (HEPA) (or other amine) was dissolved in 20 mL ethanol and added drop wise to the beaker forming a dark brown solution under magnetic stirring. The solution was then heated to 60 °C and maintained at this temperature for 3 h. After that, 16 mL 2.5% NH₃·H₂O was added to the solution, which remained dark brown with some precipitation, and the system was then heated up to 80 °C. After washing three times with distilled water and ethanol respectively, the precipitates were dried for characterization.

2.2. Characterizations
Powder X-Ray diffraction (XRD) measurements of samples were carried out with a Bruker D8-Advance powder diffractometer in a scanning range of 20-70° at a scanning speed of 0.02° s⁻¹ using a Ni-filtered Cu Kα radiation (wavelength 1.542 Å). The infrared spectra of samples were recorded on a Bruker VERTX-70 FT-IR spectrometer using KBr pellets containing about 1% weight sample in KBr. The surface area and pore parameter of prepared samples were determined by N₂ adsorption–desorption technique and relevant data were collected on a Nova 2000e Surface Area and Pore Size Analyzer at -196 °C. The surface area was calculated by the BET (Brunauer – Emmett – Teller) method and the pore size distributions were calculated from the desorption data of the isotherms by Barrett - Joyner - Halenda (BJH) model. Total pore volume was estimated from the amount adsorbed at P/P₀ = 0.99.

3. Results And Discussion
XRD measurements were carried out to investigate the crystal structure of the prepared samples and the result is shown in Figure 1. Only the results for samples synthesized with PEG2000 and HEPA are shown here because the others show basically the same XRD results.

![Figure 1](image)

**Figure 1.** XRD patterns of samples synthesized with PEG2000 + HEPA: (a) precursor; (b) calcinated at 250°C.

It can be found from Figure 1 that the as synthesized material with broader peaks, which is typical for nanosized akaganete [11, 12] (β-FeOOH, JCPDS No. 34-1266). According to the Scherrer’s formula: \( D = \frac{0.89\lambda}{\beta \cos\theta} \), where \( D \) is the crystal size, \( \lambda \) is the X-ray wavelength, \( \beta \) is FWHM (full
width at half maximum) of the diffraction peak and θ is the diffraction angle, the average crystallite size of as prepared akaganeite particle is about 6.6 nm. However, after being calcinated at temperature of 250 °C, it converted to hematite (α-Fe2O3, JCPDS No. 24-0072) with crystallite size of about 29.8 nm calculated using Scherrer’s formula.

The surface area calculated from the Brunauer - Emmett - Teller (BET) method was determined to be more than 184 m²g⁻¹. The diameter of a solid spherical particle may be calculated using the formula

\[ S = \frac{6}{\rho d} \]

where S, ρ and d denotes specific surface area, particle density and particle size, respectively. The average size calculated in this way is about 4 nm.

N₂ adsorption-desorption isotherms (Figure 2) for three template-extracted samples show type IV adsorption isotherm with an H1 hysteresis loop, which is a characteristic of mesoporous materials, as defined by IUPAC. The pore size distributions show a narrow range of 14.5 - 20.5 nm (centered at 16.8 nm), which is calculated from Barret - Joyner - Halenda (BJH) equation \[14, 15\] using the desorption data. The narrow pressure range for capillary condensation is also indicative of a narrow pore size distribution.

![Figure 2](image_url)

**Figure 2.** N₂ adsorption/desorption isotherms for three template-extracted samples (a) PEG + HEPA (b) PEG + DDA (c) PEG + HAD and the inset is the pore size distribution curves of the corresponding samples.

The BET specific surface area, average pore diameter and the pore volume of template-extracted samples are listed in Table 1.

| Composition of template | Surface area (m²g⁻¹) | BJH pore size (nm) | Pore volume (cm³g⁻¹) |
|-------------------------|----------------------|--------------------|----------------------|
| PEG                     | -                    | 11.1               | -                    |
| PEG + HEPA              | 218                  | 14.3               | 0.99                 |
| PEG + DDA               | 281                  | 16.8               | 1.50                 |
| PEG + HDA               | 184                  | 19.4               | 0.98                 |

Obviously, from table 1, the pore size increases as the alkyl amine chain length increases. However, the specific surface and pore volume have not the orderliness as the alkyl amine chain length increases, it is interesting to note that the specific surface area and pore volume of product prepared using PEG + DDA as co-template is the highest among them.
Restrained hydrolysis and condensation of the inorganic species appears to be important for forming mesophases of most of the non-silica oxides in order to slow down the hydrolysis and condensation rates [16]. According to our results, on the other hand, the PEG has a complexation tendency with Fe$^{3+}$, implying that the inorganic particles were more apt to combine with polar PEG than with the neutral alkylamine. On the basis of these considerations, a strategy was devised as presented in Scheme 1. The alkyl amines: n-Heptylamine (HEPA), Dodecylamine (DDA) and n-Hexadecylamine (HDA), used as the expanding agents, were supposed to occupy the interior of the micelle (aggregate formed by a physisorption).

![Scheme 1. Schematic representation of the process synthesizing mesoporous iron oxide with various pore sizes using PEG2000 and alkyl amine as mixed templates](image)

In order to explain these results, a possible mechanism leading to mesostructure and varying pore size is proposed, as illustrated in Scheme 1, which mainly comprises a two-step procedure: (i) the complexation interaction of the PEG and Fe$^{3+}$ and (ii) the combination of alkyl amines with PEG through weak hydrogen bonding. In fact, it is well-documented that alkyl amines are also good templates for mesoporous transition metal oxides [12]. Therefore, the alkyl amines are supposed to play the role of adjusting the pore size through changing its chain length in conjunction with PEG. The chain length of different alkyl amines have been calculated. Amazingly, the increases of pore size is nearly quantitatively agreeable with the increase of the carbon chain length (obsd. 16.8 nm and 19.4 nm, calcd. 16.9 and 19.0 for sample using template PEG + DDA and PEG + HDA respectively). For the product prepared from PEG + DDA systems, its highest specific surface area and pore volume may be due to DDA having the optimal chain length, with incorporation and organization properties different from the other two amines in the process of forming mesoporous iron oxide. Unlike the optimal swelling effects of decane which expands the pore diameter of mesoporous silica, reported by Ulagappan et al. [17], our results indicate the optimal effects of DDA, which fit in with the surface area and pore volume of iron oxide particles. The mechanisms involved are largely unexplored, it should be relevant with the physicochemical properties of the system, such as solubility, interaction among particles, PEG and the surfactants.

4. Conclusions
PEG and alkyl amines with different chain length as mixed templates can be used to produce pore size adjustable mesoporous akaganeite nanoparticles with high surface area and pore volume. We have proposed a mechanism with a two-step sorption effect, which comprises chemical interaction between ferric ions and PEG and hydrogen bonding between PEG and alkyl amines for the synthesis process.
Acknowledgement

Financial support from Chinese Natural Science Foundation (No.51274104; No.50874052; No. 20677022) is gratefully acknowledged.

References

[1] Cai J, Liu J, Gao Z, Navrotsky A, Suib S L, Synthesis and anion exchange of tunnel structure akaganeite. Chem. Mater. 13, 4595 (2001).
[2] Peak D, Regier T, Direct observation of tetrahedrally coordinated Fe(III) in ferrihydrite. Environ. Sci. Technol. 46, 3163 (2012).
[3] Mazéina L, Deore S, Navrotsky A, Energetics of bulk and nano-akaganeite, β-FeOOH: Enthalpy of formation, surface enthalpy, and enthalpy of water adsorption. Chem. Mater. 18, 1830 (2006).
[4] Poizot P, Laruelle S, Grugeon S, Dupont L, Tarascon J M, Nano-sized transition-metal oxides as negative-electrode materials for lithium-ion batteries. Nature 407, 496 (2000).
[5] Wu P C, Wang W S, Huang Y T. et al, Porous iron oxide based nanorods developed as delivery nanocapsules. Chem. Eur. J. 13, 3878 (2007).
[6] Xiong H, Liao Y, Zhou L, Xu Y, Wang S, Biosynthesis of nanocrystal akaganéite from FeCl₂ solution oxidized by acidithiobacillus ferrooxidans cells. Environ. Sci. Technol. 42, 4165 (2008).
[7] Gash A E, Tillotson T M., Satcher J H. et al, Use of epoxides in the sol-gel synthesis of porous iron (III) oxide monoliths from Fe (III) salts. Chem. Mater. 15, 3268 (2003).
[8] Zhao D, Feng J, Huo Q, Melosh N. et al, Triblock copolymer syntheses of mesoporous silica with periodic 50 to 300 angstrom pores. Science. 279, 548 (1998).
[9] Bagshaw S A, Pinnavaia T. J, Mesoporous alumina molecular sieves. Angew. Chem. Int. Ed.. 35, 1102 (1996).
[10] Jiao F, Bruce P G, Two- and three-dimensional mesoporous iron oxides with microporous walls. Angew. Chem. Int. Ed. 43, 5958 (2004).
[11] Chitrakar R, Tezuka S, Sonoda A. et al, Phosphate adsorption on synthetic goethite and akaganeite. J. Colloid Interf. Sci. 298, 602 (2006).
[12] Yusan S, Erenturk S A, Adsorption equilibrium and kinetics of U (VI) on beta type of akaganeite. Desalination 263, 233 (2010).
[13] Sun Z X, Su F W, Forsling W, Samskog P O, Surface characteristics of magnetite in aqueous suspension. J. Colloid Interf. Sci. 197, 151 (1998).
[14] Barrett E P, Joyner L G, Halenda P P, The determination of pore volume and area distributions in porous substances. I. Computations from nitrogen isotherms. J. Am. Chem. Soc. 73, 373 (1951).
[15] Krusk M, Jaroniec M, Sayari A, Application of large pore MCM-41 molecular sieves to improve pore size analysis using nitrogen adsorption measurements. Langmuir 13, 6267 (1997).
[16] Antonelli D M, Ying J Y, Synthesis of hexagonally packed mesoporous TiO2 by a modified sol-gel method. Angew. Chem, Int. Ed. 34, 2014 (1995).
[17] Ulagappan N, Rao C N R, Evidence for supramolecular organization of alkane and surfactant molecules in the process of forming mesoporous silica. Chem. Commun. 24, 2759 (1996).