Synthesis and Anion Exchange of Tunnel Structure Akaganeite

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Akaganeite (β-FeOOH) has been prepared by the hydrolysis of $FeCl_3$ solutions. The effects of microwave heating, pH of the solution, and addition of manganese with different valence states have been studied for the optimization of its synthesis. The nucleation and growth of akaganeite crystallites are accelerated by microwave heating. A low pH favors the crystallization of akaganeite, and a high pH favors the crystallization of hematite. Addition of manganese appears to impede crystallization at low pH but improves it at high pH. The anion exchange of Cl-akaganeite with F^-, Br^-, and OH^- and some properties of different anion-exchanged akaganeites has been investigated. The exchange rate and capacity depend on the nature of the anions. Anion exchange significantly changes the loss of chloride and affects the decomposition of akaganeite upon being heated.

Introduction

Akaganeite (β-FeOOH) has been found as a natural product of the corrosion of iron in chloride-containing environments.[1–5] Akaganeite is widely used in the pigment industry as a catalyst and absorbent.[6] β-FeOOH is of industrial importance in the preparation of ferromagnetic materials such as γ-Fe_2O_3.[6] Akaganeite with a tunnel structure is a promising catalytic material in chemical reactions. The band gap is 2.12 eV, making akaganeite a semiconductor.[7,8] This property makes it suitable for catalyzing oxidation/reduction reactions, and its amphoteric properties may allow it to be used as an acid/base catalyst.[9,10] Pradel et al.[11] have reported high catalytic activity of akaganeite for the hydroprocessing of coal.

Akaganeite has a tetragonal structure consisting of double chains of edge-shared octahedra running parallel to the *c* axis.[12–17] The Fe^{3+} ions are in octahedral sites. The double chains are corner-shared with neighboring double chains to form a three-dimensional tunnel structure. The unit cell formula can be written as (X, $H_2O)_2$-Fe_8(O, $OH)_{16}$, where X is Cl^- or F^-.[17] A certain number of extraframework anions (usually halide ions) are necessary in the structure to balance the extra protonation of oxides in the iron octahedra since akaganeite is synthesized in acidic solutions.[18]

The hydrolysis of $FeCl_3$ is usually used to synthesize akaganeite instead of oxidation and hydrolysis of a mixture of $FeCl_2$–NH_4OH, because the former method is more effective and faster. $FeCl_3$ solutions have to be heated to 70–100 °C for hydrolysis to occur, and the reaction time ranges from several hours to a few days. Recently, microwave heating has emerged as a new and effective way of material synthesis,[19,20] which accelerates reactions and may produce better quality products.[21,22] In this work, microwave heating was employed in the synthesis of akaganeite and the effect of microwaves on the hydrolysis of $FeCl_3$ was studied.

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(1) Heller, W.; Kratky, O.; Nowotny, H. *Compt. Rend.* **1936**, *202*, 1171.

(2) Tassel, R. V. *Bull. Soc. Belge Geol.* **1959**, *68*, 360.

(3) Mackay, A. L. *Min. Mag.* **1962**, *33*, 270.

(4) Misawa, T.; Hashimoto, K.; Shimodaira, S. *Corros. Sci.* **1974**, *14,* 131.

(5) Taylor, L. A.; Mao, H. K.; Bell, P. M. *Geochim. Cosmochim. Acta* **1973**, *41,* 829.

(6) Ceus, J. W. E.; Tacobus, J. M. *Chem. Abstr.* **1973**, *78*, 32167m.

(7) Leland, J. K.; Bard, A. J. *J. Phys. Chem.* **1987**, *91*, 5076.

(8) White, A. F. *Reviews in Mineralogy 23*; Mineral Society of America: Washington, DC, 1990; 447.

(9) Ellis, J.; Giovanoli, G.; Stumm, W. *Chimia* **1976**, *30*, 194.

(10) Cornell, R. M. *The Iron Oxides*; VCH Publishers: New York, 1996; pp 474–477.

(11) Pradel, J.; Simone, C.; Traverse, J.; Grezes-Besset; Darcy, M. *Ind. Eng. Chem. Res.* **1993**, *32* (9), 1801.

(12) Mackey, A. L. *Mineral. Mag.* **1960**, *32*, 545.

(13) Bernal, J. D.; Dasgupta, D. R.; Mackey, A. L. *Clay Miner. Bull.* **1959**, *4*, 15.

(14) Keller, P. *N. Jb. Min. Abh.* **1970**, *113*, 29.

(15) Szytula, A.; Ballanda, M.; Dimitrijevic, Z. *Phys. Status Solidi A* **1970**, *3*, 1033.

(16) Feitknecht, W.; Giovanoli, R.; Michaelis, W.; Muller, M. *Helv. Chim. Acta* **1973**, *56*, 2847.

(17) Childs, C. W.; Goodman, B. A.; Paterson, E.; Woodhams, F. W. D. *Aust. J. Chem.* **1980**, *33*, 15.

(18) Post, J. E.; Buchwald, V. F. *Am. Mineral.* **1991**, *76*, 272.

(19) Sutton, W. *Ceram. Bull.* **1989**, *68*, 376.

(20) Wan, J. K. S. *Res. Chem. Intermed.* **1993**, *19*, 147.

(21) Zhang, Q. H.; Luo, J.; Vileno, E.; Suib, S. L. *Chem. Mater.* **1997**, *9*, 2090.

(22) Ma, Y.; Vileno, E.; Suib, S. L.; Dutta, P. K. *Chem. Mater.* **1997**, *9*, 3023.

There are many preparative factors affecting the formation of akaganeite. For example, Atkinson, Collepard, and Parida showed that the pH of the solution affects its structure and properties.[23–25] However, a systematic study of the influence of pH on the formation, crystallization, and properties of akaganeite is lacking. Therefore, this was addressed in the present study.

Studies of the effect of foreign ions may give a better understanding of the mechanisms of formation, the structure, and phase transformations.[26–30] The chemical similarity between Mn and Fe makes Mn a logical element to investigate. The influence of manganese on the formation of akaganeite was studied in this paper.

Gallagher first predicted the potentially interesting ion-exchange properties of akaganeite in 1970.[31] Anion exchange was later studied by Ellis et al.[32] Fluoride was found to replace chloride. Then, Paterson et al.[33,34] showed that akaganeite had a variable pH-dependent anion-exchange capacity and perchlorate could not exchange freely with chloride in the tunnels of akaganeite because of an ion sieve effect. To gain insight into the roles that anions play in the structure and properties of akaganeite, akaganeite-containing chloride ions (Cl-akaganeite) and akaganeite-containing fluoride ions (F-akaganeite) in the tunnels were ion-exchanged with OH^-, Br^-, and F^- (for Cl-akaganeite) or Cl^- (for F-akaganeite) anions. The exchange rates and capacities of different anions were measured, and the properties of the anion-exchanged samples were studied.

Experimental Section

Synthesis of Akaganeite. Akaganeite was prepared from the hydrolysis of an $FeCl_3$ (FeF_3 for F-akaganeite) solution. A solution of 150 mL containing 8.1 g of $FeCl_3$ and 9.0 g of urea was prepared at room temperature in a 200 mL flask. The pH was adjusted to 1.5 with ammonia. The temperature was maintained at 100 °C, either with a water bath or by microwave heating, and kept for 6 h. The heat was then turned off, and the solution was kept still overnight. The solution was centrifuged, and the precipitate was washed three times with 1000 mL of deionized water. Then, the sample was dried at 60 °C for 2 days.

Microwave heating was carried out in a model 10-1300 microwave furnace from Microwave Materials Technologies, Inc. A thermocouple connected to a Micristar heat-processing controller system was used to control the temperature. Microwaves were generated at 2.45 GHz with a maximum output power of 1300 W.

To study the synthesis of akaganeite at different pH values, before it was heated, the pH of solutions was adjusted to 1.5, 2, 4, 6, and 8 using an ammonia solution. The rate of hydrolysis

was reduced by lowering the temperature to 65 °C, for an easier study of the effects of pH. The hydrolysis was finished after 5 days.

To study the influence of Mn^{2+}, $MnCl_2 \cdot 4H_2O$ was added to the solution before it was heated. $KMnO_4$ and $MnCl_2 \cdot 4H_2O$ were used together to produce oxidation states greater than 2+ for Mn and study their effects on the synthesis of akaganeite. Amorphous manganese and iron oxides were removed by extracting 1 g of the dry precipitate overnight with 1000 mL of pH = 3 ammonium oxalate solution.[35–38]

Anion Exchange. A 1 g portion of akaganeite was added to 100 mL of 0.5 M of NaOH, NaF, or NaBr solution at 55 °C. A blank test was also done by exchanging 1 g of akaganeite with deionized water at 55 °C. The anion exchange was stopped at 10, 30, 60, 90, 120, 240, 300, or 600 min, respectively, by immediate separation of the sample from the solution. The ion-exchanged samples were washed with 100 mL of deionized water three times and then dried at 60 °C for 2 days.

The filtrate was placed in a 500 mL volumetric flask. Mohr titration was used to determine the amount of chloride ions released from the akaganeite sample in the anion exchange.[39] The determination of chloride left in the anion-exchanged samples was done by chemical analysis using energy-dispersive X-ray analysis (EDAX).

Characterization. Powder X-ray diffraction (XRD) data were collected on a Scintag XDS 2000 diffractometer with Cu Kα radiation. All of the X-ray diffraction patterns were made under identical conditions so that in the XRD patterns, the peak intensities (more precisely, peak areas) reflected the relative crystallinity of a given phase.

Thermogravimetric analyses (TGA) were performed on a Hi-Res TGA 2950 model thermogravimetric analyzer (TA instruments). Differential scanning calorimetry (DSC) experiments were done on a DSC 2900 model differential scanning calorimeter (TA instruments). The temperature ramp for TGA and DSC was 10 °C min^{-1}, and the carrier gas was either nitrogen or oxygen.

Scanning electron microscope (SEM) photographs were taken on an AMRAY 1810 scanning electron microscope. Chemical compositions of samples were determined by EDAX on a Philips PV9800 EDAX spectrometer with a Super Quant program. The voltage used for SEM and EDAX was 20 kV.

Inductively coupled plasma (ICP) analysis was performed using a Perkin-Elmer 7-40 instrument equipped with an autosampler. Samples were dissolved in HCl solutions.

IR spectra were taken on a Nicolet Magna-IR System 750 FT-IR spectrometer with an MCT-B detector, using standard measurement procedures.

Results

Syntheses of Akaganeite by Conventional and Microwave Heating. Akaganeite was prepared at boiling temperature by both methods. Urea was added to the reactant solution for better control of the reaction. The XRD patterns of the products synthesized are shown in Figure 1. *d* spacing values of strong peaks of all products match the values for akaganeite in JCPDS card 34-1266 that is: 3.33 (100), 2.55 (65), 7.47 (40), 2.30 (35), 1.64 (35), 5.28 (30), 2,63 (25), 1.95 (20).

In conventional heating, akaganeite was formed after being heated at 100 °C for 60 min. Its XRD peaks were

(23) Atkinson, R. J.; Posner, A. M.; Quirk, J. P. *Clays Clay Miner.* **1977**, *25*, 49.

(24) Collepardi, M.; Massidda, L.; Rossi, G. *Trans. Inst. Min. Metall.* **1972**, *81*, C43.

(25) Parida, K. M. *J. Mater. Sci. Lett.* **1987**, *6*, 1476.

(26) Sampson, C. F. *Acta Crystallogr., Sect. B* **1969**, *25*, 1683.

(27) Detourney, P. J.; Giovanoli, M.; Derie, R. *Z. Anorg. Allg. Chem.* **1975**, *412*, 184.

(28) Stiers, W.; Schwetmann, U. *Geochim. Cosmochim. Acta* **1985**, *49*, 1909.

(29) Krishnamurti, G. S.; Huang, P. M. *Clays Clay Miner.* **1988**, *36* (5), 467.

(30) Krishnamurti, G. S.; Huang, P. M. *Clays Clay Miner.* **1989**, *37* (5), 451.

(31) Gallagher, K. J. *Nature* **1970**, *226*, 1225.

(32) Ellis, J.; Giovanoli, G.; Stumm, W. *Chimia* **1976**, *30*, 194.

(33) Paterson, R.; Rahman, H. *J. Colloid Interface Sci.* **1983**, *94*, 60.

(34) Paterson, R.; Rahman, H. *J. Colloid Interface Sci.* **1984**, *97*, 423.

(35) Schwetmannn, U. *Z. Pflanzenernaehr. Bodenkd.* **1964**, *105*, 194.

(36) Stiers, W.; Schwertmann, U. *Geochim. Cosmochim. Acta* **1985**, *49*, 1909.

(37) Ebinger, M. H.; Schulze, D. G. *Clays Clay Miner.* **1989**, *37*, 151.

(38) Cornell, R. M.; Giovanoli, R.; Schneider, W. *Clays Clay Miner.* **1990**, *38*, 21.

(39) Harris, D. C. *Quantitative Chemical Analysis*, 4th ed.; W. H. Freeman and Company: New York, 1995; p 173.
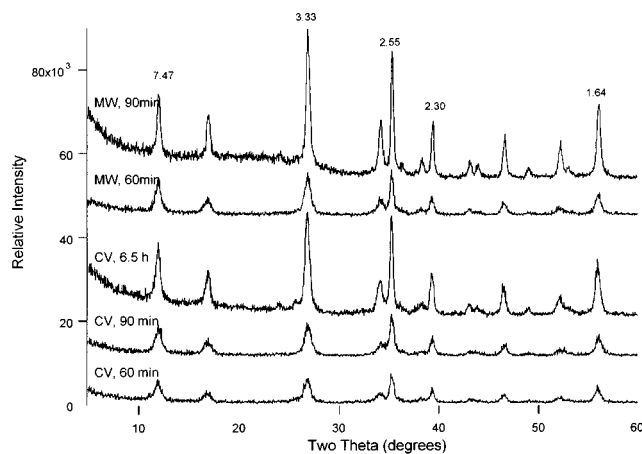
Figure 1. XRD patterns of akaganeite prepared by conventional and microwave heating at 65 °C for different times (CV, conventional heating; MW, microwave heating).

Figure 2. XRD patterns of akaganeite prepared at different pH values (H, hematite; G, goethite).

weak and broad, indicating that the crystallinity of the structure was poor. The peak with a d spacing of 3.33 Å ($2\theta = 26.9°$), which is the strongest line in the standard XRD pattern, was actually the second strongest line. Relative intensities of other peaks were also in poor agreement with the standard XRD pattern. Some minor peaks of akaganeite were absent in the XRD patterns. The akaganeite prepared by conventional heating for 90 min displayed increases in all peak intensities without much change in their relative intensities. The peak intensities of akaganeite increased significantly after it was heated in boiling water for 6.5 h. The peak with a d spacing of 3.33 Å became the strongest peak as shown in the JCPDS card. Other peaks were also in better agreement with the standard data after such heating. Thus, a better-crystallized akaganeite was formed after 6.5 h of being heated.

The XRD pattern of akaganeite synthesized by microwave heating for 60 min was similar to that of akaganeite prepared by conventional heating for 90 min in the number of peaks, the peak intensity, and the peak width. When the reaction time under microwave radiation was increased to 90 min, the XRD pattern of akaganeite showed the narrowest reflections in all akaganeite samples. The relative intensities of all peaks present showed very good agreement with the relative intensities in the JCPDS card. The crystallinity of the akaganeite prepared by microwave heating for 90 min was higher than that prepared by conventional heating for 6.5 h. Therefore, the time for the synthesis of akaganeite is considerably shortened with microwave heating. Crystallization can be accomplished within 90 min instead of 6.5 h, and the product has a better crystallinity.

The SEM photographs showed that akaganeite prepared under conventional or microwave heating had the same morphology. The crystallites in both products had similar cigarlike shapes and similar crystal sizes.

Effect of pH. XRD patterns of akaganeite synthesized at different pH values at 65 °C are shown in Figure 2. Nucleation and growth of akaganeite took place only at relatively low pH in the presence of chloride or fluoride. When the $FeCl_3$ solution was hydrolyzed at a pH of 1.5, the XRD pattern of the product indicated a clear akaganeite structure with
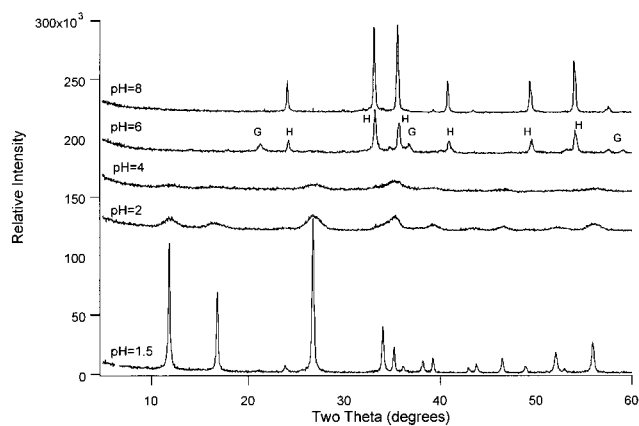
narrow peaks. As the pH of the starting solution increased to 2, the peaks became much broader and less intense, indicating that the crystallinity of the product was poorer. Products other than akaganeite were formed when the pH was raised to 6. XRD showed that hematite was the dominant phase coexisting with other minor peaks due to goethite. No akaganeite was found in this product. In basic solutions, hematite was the only product.

Therefore, pH of the $FeCl_3$ solution is one of the major determining factors in the synthesis of akaganeite. Low pH favors the nucleation and growth of akaganeite while high pH favors the crystallization of hematite. Akaganeite can be synthesized via hydrolysis of $FeCl_3$ only in strongly acidic solution.

Influence of Manganese. When akaganeite was prepared in the presence of Mn^{2+}, the intensities of XRD peaks decreased with increase in the Mn/Fe ratio and the relative intensities differed from the akaganeite prepared in the absence of Mn^{2+}. The ICP analysis showed that only about 0.05% of Mn was present in the akaganeite, indicating that the substitution of Mn^{2+} in the akaganeite was small.

In the syntheses where akaganeites were prepared in the presence of higher oxidation states of Mn, Mn^{3+} was first formed and then a part of the Mn^{3+} disproportionated to Mn^{4+} and Mn^{2+} in solution. Only weak peaks of akaganeite were seen above a rather strong background. The strong background in the XRD patterns of akaganeite disappeared and no Mn was left by elemental analyses after ammonium oxalate treatment, suggesting that the Mn existing in the products was probably amorphous manganese oxide and Mn was not incorporated into the akaganeite structure.

Anion Exchange. The ion exchange of Cl-akaganeite with various anions was studied at 55 °C, and the results are given in Figure 3. A blank test was done to determine the release of chloride from Cl-akaganeite in water at this temperature. The release of chloride in water was fast at the beginning, and about 0.15 mmol g^{-1} of chloride was found in water in 10 min. Then, the release rate slowed gradually until equilibrium was obtained at 120 min. At equilibrium, around 0.24 mmol g^{-1} of chloride had been released from akaganeite into water. In the anion exchange of Cl-akaganeite with hydroxide, fluoride, and bromide, the release rates of chloride showed the same rapid increase in the first 10
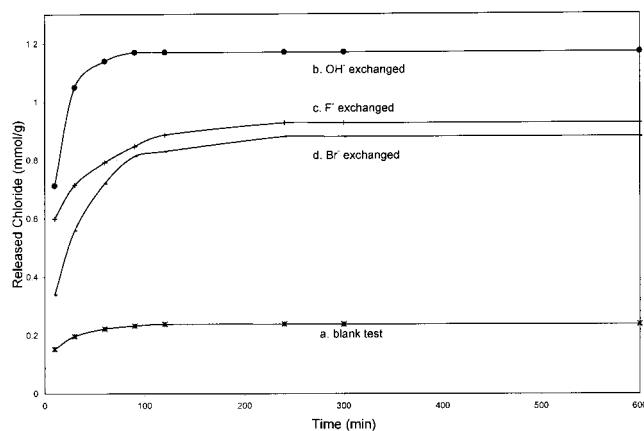
Figure 3. Rate and amount of chloride released from different ion-exchanged akaganeite samples.

Figure 4. IR spectra of untreated and anion-exchanged akaganeite.

min. The hydroxide exchange continued to proceed rapidly for another 20 min. Then, the release rate dropped significantly, and about 1.2 mmol g^{-1} of chloride was detected in solution when the exchange reached equilibrium at 90 min. Earlier, the release rates of chloride dropped for the fluoride and bromide exchanges and their equilibrium time was extended to 240 min. The amounts of chloride released at equilibrium for fluoride and bromide exchanges were 0.93 and 0.88 mmol g^{-1}, respectively.

The release rates of chloride during anion exchange showed that the anion exchange of akaganeite was rather rapid at 55 °C. The exchange of chloride with hydroxide was faster than the exchanges with fluoride and bromide. The amounts of chloride released at equilibrium corresponded to the exchange capacities of various anions with chloride ions in akaganeite. The sequence of exchange capacities is in the order hydroxide > fluoride > bromide.

F-Akaganeite, synthesized by the hydrolysis of FeF$_3$ solution, was treated with OH$^-$, Cl$^-$, and Br$^-$ anions to investigate the possibility of anion exchange. Cl and Br were not found in the treated akaganeite using EDAX chemical analysis. About 0.2 mmol g^{-1} of fluoride was detected in the hydroxide solution.

IR Spectroscopy of Anion-Exchanged Akaganeite. IR spectra of akaganeite samples are presented in Figure 4. There was not much difference in the IR spectra of Cl-akaganeite and the anion-exchanged samples. The two bands at 3480 and 1640 cm^{-1} were due to bulk O–H vibrations, and a very weak band at 3650 cm^{-1} was assigned to surface OH groups.[39] Asymmetric and symmetric Fe–O stretches appeared at 750, 550, and 480 cm^{-1}. The only significant difference between F-akaganeite and Cl-akaganeite was the band at 1500 cm^{-1}. Since the radius of F$^-$ (1.33 Å) is close to that of O^{2-} (1.40 Å) and OH$^-$ (1.37 Å), F$^-$ may substitute for O^{2-} and OH$^-$ in the akaganeite structure.[40–42] The band observed at 1500 cm^{-1} may be related to F. Because F can form strong hydrogen bonds with H, the bend vibration of the O–H bond may be reduced from 1640 to 1500 cm^{-1}.
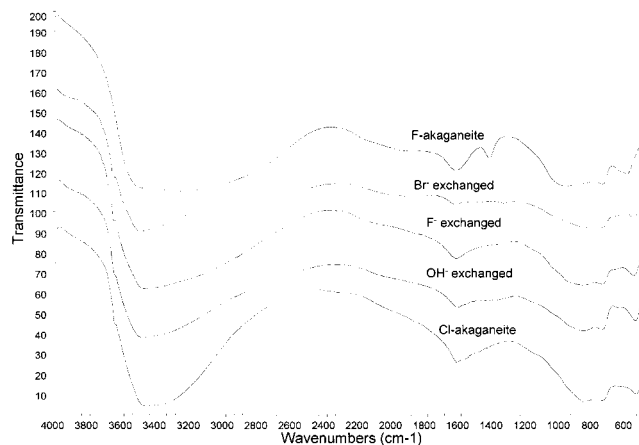
Phase Transformation of Akaganeite upon Being Heated. XRD analysis of samples was done directly after anion exchange, and no phase change was observed. The effect of anions on the tunnel structure of akaganeite was then studied by analyzing the samples heated to 220, 320, 420, and 550 °C. Nitrogen and oxygen were both used to study the influence of atmosphere.

XRD patterns of akaganeite heated at 320, 420, and 550 °C in nitrogen are given in Figure 5. When heated to 220 °C, the intensities of peaks of akaganeite dropped about 10–20% but their positions remained the same. After it was heated at 320 °C, only a few major peaks remained, and the second strongest peak became the strongest one. Since the peaks of akaganeite and hematite with *d* spacings of 2.55 and 2.52 Å, respectively, are very close to each other, this change could be due to the formation of some hematite in the sample. The appearance of the strongest peak of hematite at a *d* spacing of 2.70 Å, in the XRD patterns of the samples heated to 320 °C, confirmed the formation of hematite. After being heated, the color of samples turned more red, indicating that hematite was formed. As the temperature was raised to 420 °C, Br$^-$-and OH$^-$-exchanged samples were transformed to hematite. The more intense peaks of hematite in the pattern of Br$^-$-exchanged akaganeite suggested that upon being heated, Br$^-$-exchanged akaganeite might be decomposed and transformed to hematite earlier than OH$^-$-exchanged akaganeite. Cl-Akaganeite and F$^-$-exchanged akaganeite still displayed weak and broad akaganeite peaks as the hematite peaks became more intense. After being heated to 550 °C, all the samples were transformed to hematite except the F$^-$-exchanged akaganeite and F-akaganeite. Compared with Cl-akaganeite, the phase transformation from akaganeite to hematite took place at higher temperatures due to the presence of fluoride in the tunnels, whereas the transformation took place at lower temperatures when Br$^-$ and OH$^-$ substituted for Cl$^-$ in the tunnels. The effect of tunnel anions on the thermal transformation of akaganeite can be summarized by the order of temperatures in which the akaganeite phase disappeared and the hematite phase

(40) Ishikawa, T.; Nitta, S.; Kondo, S. *J. Chem. Soc., Faraday Trans. 1* **1986**, *82*, 2401.

(41) Lide, D. R. *CRC Handbook of Chemistry and Physics,* 73rd ed.; CRC Press: 1992; pp 12–8.

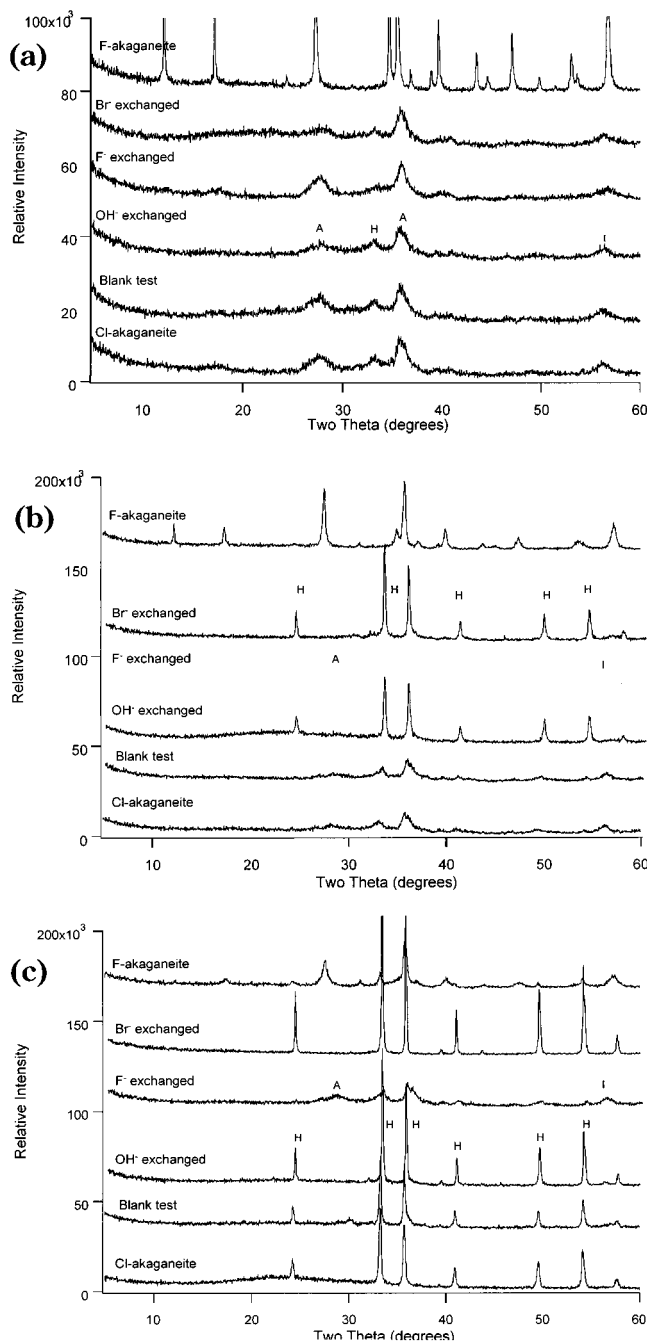(42) Ohyabu, M.; Ujihira, Y. *J. Inorg. Nucl. Chem.* **1981**, *43* (12), 3125.

Figure 5. XRD patterns of akaganeite heated in nitrogen to different temperatures (A, akaganeite; H, hematite; I, intermediate) (a) 320 °C, (b) 420 °C, and (c) 550 °C.

appeared in the products in a nitrogen atmosphere: Br⁻-exchanged akaganeite ≅ OH⁻-exchanged akaganeite < Cl-akaganeite < F⁻-exchanged akaganeite < F-akaganeite.

In oxygen, the akaganeite structure remained at 220 °C, but the intensity of the peaks decreased. Hematite peaks appeared, and akaganeite peaks were very broad at 320 °C. At 420 °C, the akaganeite peaks almost disappeared for the Br⁻- and OH⁻-exchanged samples but were readily observed for F⁻-exchanged akaganeite. As the heating temperature reached 550 °C, akaganeite samples were all transformed to hematite but the intensity of the hematite peaks of F⁻-exchanged akaganeite was the lowest. In an oxygen atmosphere, ion-exchanged akaganeite samples behaved in a similar way
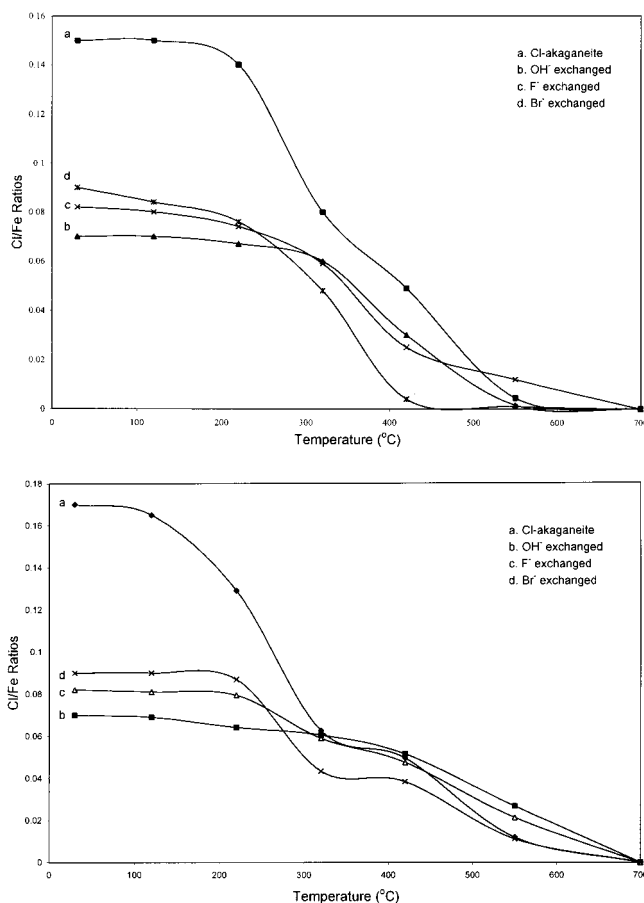

Figure 6. Cl/Fe ratio of akaganeite heated in different atmospheres: (a) N_2 and (b) O_2.

in their decomposition temperatures except that the differences were much smaller.

Loss of Chloride Ions upon Being Heated. The chloride ions in akaganeite stabilize the tetragonal tunnel structure. The loss of chloride ions may cause a change from the tetragonal structure of akaganeite to the rhombohedral structure of hematite. The Cl/Fe ratio of samples was measured after they were heated to different temperatures in nitrogen or oxygen, and the results are shown in Figure 6.

Figure 6a shows the change of Cl/Fe ratio with an increase of temperature in nitrogen. Not much Cl⁻ was lost up to 200 °C. Starting at 200 °C, the loss of Cl⁻ increased significantly, especially for the untreated and Br⁻-exchanged akaganeites. At 420 °C, the Br⁻-exchanged akaganeite lost almost all of the Cl⁻ in its structure. As the temperature reached 550 °C, the Cl remaining in the akaganeite samples had a Cl/Fe ratio order of Br⁻-exchanged akaganeite ≅ OH⁻-exchanged akaganeite < Cl-akaganeite < F⁻-exchanged akaganeite. Such an order was consistent with the order of the decomposition temperatures of akaganeite samples. Cl⁻ almost totally disappeared in all the samples as the temperature reached 700 °C.

Figure 6b shows the loss of Cl⁻ for the samples heated in oxygen. For the first 300 °C, the loss of Cl⁻ was similar to that of samples heated in nitrogen. Then the loss of Cl⁻ was slow in the range of 300−400 °C. After 400 °C, the ratio of Cl/Fe gradually dropped to zero as the heating temperature was raised to 700 °C. The
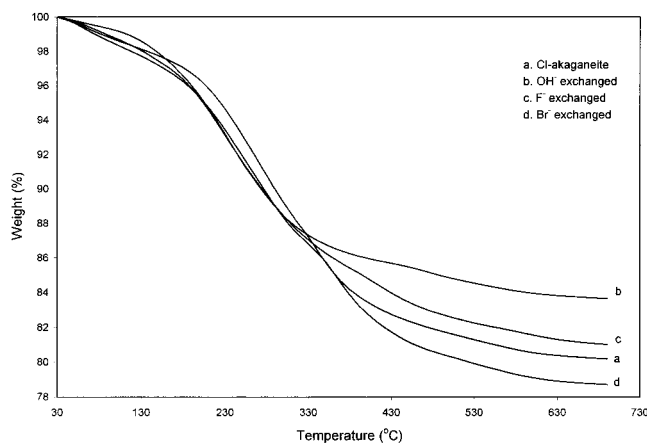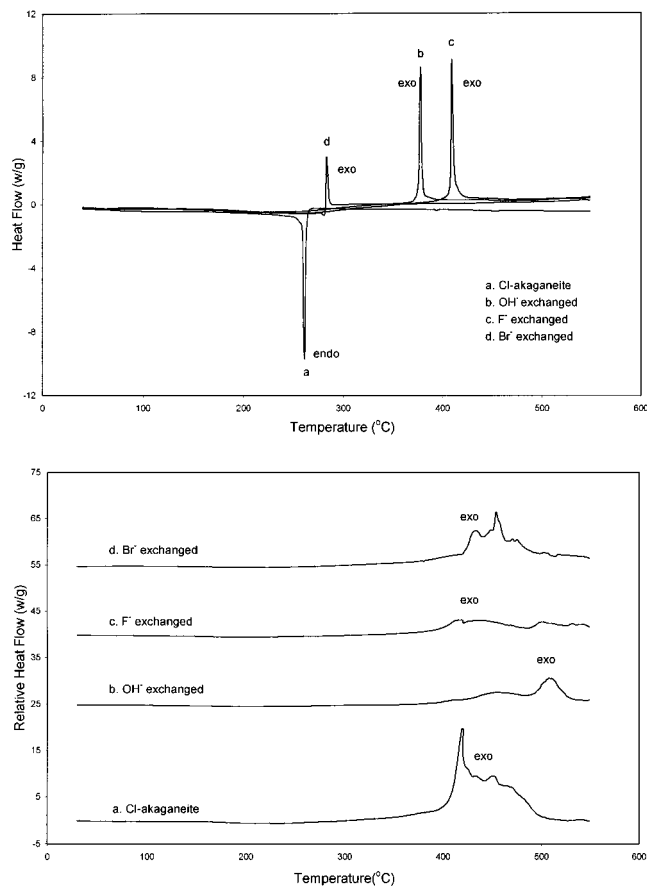
Figure 7. TGA of akaganeite samples in N_2.

Figure 8. DSC of akaganeite samples in different atmospheres: (a) N_2 and (b) O_2.

chloride content of samples heated in oxygen was generally higher than that in the materials heated in nitrogen.

Thermal Analyses of Akaganeite. TGA and DSC of the samples were done in both nitrogen and oxygen. The TGA and DSC data are shown in Figure 7 and Figure 8, respectively.

Since there was not much difference in the results of TGA for nitrogen and oxygen atmospheres, only the TGA results in nitrogen are shown in Figure 7. In the oxygen atmosphere, the weight losses were slightly shifted to higher temperatures compared with losses in the nitrogen atmosphere. The samples started to slowly lose weight as soon as heat was applied until the

temperature reached 150 °C. In the range of 150−300 °C, the weight loss was more significant for all samples. After 300 °C, the weight loss continued but gradually slowed at 700 °C. Weights of samples became constant around 700 °C, and the total weight losses of samples ascended in the order of OH^--exchanged akaganeite < F^--exchanged akaganeite < Cl-akaganeite < Br^--exchanged akaganeite. This trend is consistent with the order of the exchange capacities of the different exchanging anions.

The atmospheres in which the samples were heated significantly influenced the DSC of akaganeite samples. Figure 8a shows DSC data for samples heated in a nitrogen atmosphere. The Cl-akaganeite had only one sharp endothermic peak at 260 °C in the whole temperature range from room temperature to 550 °C. In the Br^--exchanged akaganeite, a very weak endothermic peak appeared at 281 °C and then was followed by a sharp exothermic peak immediately at 283 °C. The OH^-- and F^--exchanged akaganeite samples had only one exothermic peak at 378 and 409 °C, respectively. The heat flows of these three exothermic peaks have the following order: Br^--exchanged akaganeite < OH^--exchanged akaganeite < F^--exchanged akaganeite. Figure 8b shows DSC data of samples heated in an oxygen atmosphere. All samples had one broad endothermic peak with a low heat flow in the range of 100−300 °C. Then a broad exothermic peak appeared in the temperature range of 400−520 °C. The difference of DSC in nitrogen and oxygen could be due to the effect of oxygen, which delayed and prolonged the release of anions in tunnels and hence delayed and prolonged the release of energy in the thermal transformation.

Discussion

Microwave synthesis is generally faster, cleaner, and more economical than conventional methods. Reactions occur faster under microwave irradiation than conventional heating. In the present study, the synthesis of akaganeite via the hydrolysis of $FeCl_3$ was accelerated by microwave heating. The synthesis time of akaganeite was shortened from 6.5 to 1.5 h under the same conditions. The acceleration of the formation of akaganeite can be attributed to the microwave coupling of water molecules bound to Fe^{3+} ions in the hydration spheres because of the high dielectric constant of water (78.54 at 25 °C).[43,44] The influence of microwave fields also results in a rotational motion of the usually hydrogen-bonded water molecules and destroys the hydration spheres.[45] The rotational excitation of the water molecules by microwaves disengages them from Fe^{3+} ions and from each other and promotes the nucleation and growth of akaganeite crystals. The same effect may also help the anions, such as Cl^- and F^-, to be incorporated into the tunnels of akaganeite to balance the electrical charges of the framework and to stabilize the structure. An increase in the mobility of
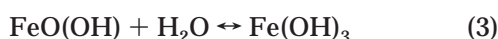
(43) Douglas, B. E.; McDaniel, D. H.; Alexander, J. J. *Concepts and Models of Inorganic Chemistry,* 3rd ed.; John Wiley & Sons: New York, 1994; p 235.
(44) Kingston, H. M.; Haswell, S. *Microwave-Enhanced Chemistry*; American Chemical Society: Washington, DC, 1997; p 525.
(45) Girnus, I.; Jancke, K.; Vetter, R.; Richter-mendau, J.; Caro, J. *Zeolites* **1995**, *15*, 33.

the ions in the solution under the influence of an oscillating electric field that is oscillated with the microwave may also enhance the growth of akaganeite crystals,[44,45] so the crystallite size of the akaganeite product obtained by microwave heating is larger. However, in terms of industrial economics, profits gained from the shortened reaction time could be undercut by expensive electric energy if short reaction time is not a priority.

Akaganeite (β-FeOOH) precipitates from $FeCl_3$ or FeF_3 solution, whereas $Fe(NO_3)_3$ and $Fe_2(SO_4)_3$ solutions give goethite (α-FeOOH) upon hydrolysis.[46,47] The tunnel structure of β-FeOOH often contains interstitial anions such as Cl^- or F^-. The hydrolysis of Fe^{3+} in aqueous solution proceeds as follows

$$Fe^{3+} + 2H_2O \leftrightarrow FeO(OH) + 3H^+ \qquad (1)$$

$$Fe^{3+} + 3H_2O \leftrightarrow Fe(OH)_3 + 3H^+ \qquad (2)$$

$$FeO(OH) + H_2O \leftrightarrow Fe(OH)_3 \qquad (3)$$

The results of this work indicate that low pH slows down hydrolysis and favors the formation of β-FeOOH, resulting in better crystallinity of akaganeite. On the other hand, high pH favors the formation of α-FeOOH and $Fe(OH)_3$.[23] Amorphous $Fe(OH)_3$ may slowly transform to α-FeOOH and hematite (α-Fe_2O_3). After results are obtained for a wide range of pH values, it is clear that an akaganeite product with good crystallinity can be obtained when the initial pH of the $FeCl_3$ solution is adjusted to 1.5. At a pH of 6, only hematite is present in the product.

Since the synthesis of akaganeite is carried out at low pH, Mn^{2+} ions are not fully hydrolyzed in acidic solution because the precipitation of $Mn(OH)_2$ occurs only at a pH above 8.[48] The ionic radius of Mn^{2+} (0.83 Å) is considerably greater than that of Fe^{3+} (0.55 Å). The substitution of Mn^{2+} for Fe^{3+} in the structure of akaganeite was small for this reason. Adding a mixture of Mn^{2+}, Mn^{3+}, and Mn^{4+} into the $FeCl_3$ solution impedes the formation of akaganeite. Although Mn^{3+} is hydrolyzed in acidic solution[48] and the ionic radii of Mn^{3+} (0.58 Å), Mn^{4+} (0.53 Å), and Fe^{3+} (0.55 Å) are very close to each other, the substitution of Mn^{3+} and Mn^{4+} for Fe^{3+} in the akaganeite structure appears to be minimal. The low stability of Mn^{3+} and the insolubility of MnO_2 in acidic solution may account for the lack of substitution.

Crystalline Cl-akaganeite with a tunnel structure is an inorganic shape-selective anion exchanger. There are two types of exchange sites in akaganeite, tunnel sites and surface sites.[33,34] Large anions, such as perchlorate ions, are excluded from the tunnel sites, whereas surface sites are accessible to perchlorate and all other anions regardless of their size. About 13% of the exchange sites are surface sites, which can be ion-exchanged freely and

rapidly at ambient temperature.[34] The anion exchanges in this work were done at 55 °C. At this temperature, the ion-exchange rate is accelerated, and the exchange equilibrium can be achieved in 1.5−4 h instead of several days or weeks at 25 °C. For the anion exchange of Cl-akaganeite with OH^-, F^-, and Br^- ions, there is no explicit boundary between the two types of exchange sites on the ion-exchange curves. After the first 10 min of rapid exchange, the amounts of chloride ions replaced by OH^-, F^-, and Br^- ions are 0.71, 0.60, and 0.34 mmol g^{-1}, respectively, which constitute 60, 64, and 39% of the exchange capacities of these anions at equilibrium. The ionic radii of OH^-, F^-, Cl^-, and Br^- ions are 1.37, 1.33, 1.81, and 1.96 Å, respectively. The tunnels in akaganeite seem to be accessible to all these anions at 55 °C. The rapid exchange implies that these foreign anions can enter tunnels in the crystals through micropores rather freely while Cl^- ions readily depart at 55 °C. The equilibrium times of OH^-, F^-, and Br^- exchanges are 1.5, 4.0, and 4.0 h, and their exchange capacities at equilibrium are 1.20, 0.93, and 0.88 mmol g^{-1}, respectively. In acidic solution, β-FeOOH crystals uptake protons from solution as depicted in eq 4

$$FeO(OH) + H^+ \leftrightarrow FeO(OH_2{}^+) \qquad (4)$$

At the same time, a stoichiometric amount of chloride counterions is taken up by the crystals. The degree of protonation is a function of the solution pH. Hence, the anion-exchange capacities for chloride are not only dependent on the concentration of the anions but also pH dependent. The OH^- exchange of Cl-akaganeite was done in a 0.5 M NaOH solution, while the other exchanges were done in 0.5 M sodium salt solutions. The deprotonation of samples at high pH accounts for the large exchange capacity and the short equilibrium time of OH^- exchange in comparison to other anion exchanges.

The thermal decomposition and phase transition of Cl-akaganeite and various anion-exchanged Cl-akaganeites have been investigated using TGA, DSC, XRD, and wet chemical methods. All forms of akaganeite lose physically adsorbed water below 150 °C. The dehydroxylation of samples occurs over the temperature range of 150−300 °C. The product of dehydroxylation is a hematite with low crystallinity and small crystallite size, whose XRD peaks are small and broad. After it was heated to 420−550 °C, the XRD peaks of the hematite become narrow and intense, showing that a well-crystallized hematite has been formed. For some of the samples, an exothermic peak appears on the DSC curve in this temperature region. The origin of this exotherm can be ascribed to a release of energy due to a decrease in microstrain, grain growth, and decrease of surface area or a sintering process of the hematite crystallites.[49] The evolution of hydrogen chloride begins around 200 °C as shown in the curves of Cl/Fe ratio. The loss of chlorine proceeds continuously until 700 °C. The release of the last trace of chloride in the samples at temperatures higher than 500 °C is probably due to sublimation of iron(III) chloride at elevated temperatures.[50,51] When heated, the chloride ions in the struc-

(46) Parida, K.; Das, J. *J. Colloid Interface Sci.* **1996**, *178*, 586.

(47) Van der Woude, J. H. A.; Verhees, P.; Debruyn, P. L. *Colloids Surf.* **1983**, *8*, 79.

(48) Baes, C. F. *The hydrolysis of Cations*; John Wiley & Sons: New York, 1976; pp 219−237.

(49) Morales, J.; Tirado, J. L.; Macias, M. *J. Solid State Chem.* **1984**, *53*, 303.

(50) Ishikawa, T.; Enouye, T. *J. Therm. Anal.* **1976**, *10*, 399.

(51) Naona, H.; Fujiwara, R.; Sugioka, H.; Sumiya, K.; Yanazawa, H. *J. Colloid Interface Sci.* **1982**, *87*, 317.

tural tunnels are lost more easily in nitrogen than in oxygen. Paterson et al. reported the same phenomena of the influence of oxygen on Cl-akaganeite upon heating, and they proposed that the evolved hydrogen chloride is formed by reaction between the chloride ions and the water molecules produced by dehydroxylation[52]

$$2H_2O + 4Cl^- \leftrightarrow 4HCl + O_2 + 4e^- \qquad (5)$$
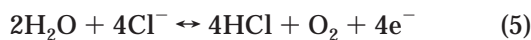
The presence of oxygen will shift the reaction balance to the left and delay the release of hydrogen chloride.

The temperatures of the decomposition of various anion-exchanged akaganeites are different depending on the nature of the anions held in the tunnel structure. In the structure of akaganeite, $Fe(O, OH)_6$ octahedra form double chains extended along the c axis. The chains share corners with adjacent chains to give a structure with tunnels along the c axis. The tunnels of Cl-akaganeite or F-akaganeite synthesized from $FeCl_3$ or FeF_3 solutions contain Cl^- or F^- and water. The charges on Cl^- or F^- ions balance the charges of extra protons in the lattice, and the stability of the tunnels in the akaganeite structure is associated with the interaction between the halide ions and the lattice. The Cl^- ions are partly replaced by F^-, Br^-, and OH^- ions after anion exchange. In this work, it has been observed that the decomposition temperatures of akaganeites containing different halide ions decrease in the order $F^- > Cl^- > Br^-$. The electronegativities of F^-, Cl^-, and Br^- ions are 4.0, 3.2, and 3.0, respectively. The anions in tunnels are essential to balance the framework charges and to stabilize the tunnel structure of akaganeite.[18] The decrease in the ability of akaganeite to keep its tunnel structure, from F^--exchanged akaganeite to Br^--exchanged akaganeite, upon being heated can be ascribed to a decrease in the strength of the interaction between the halide ions in the tunnels with the lattice. A stronger interaction between an anion and the tunnels would help akaganeite retain the anion at a higher temperature. F^- leaves the tunnels at a higher temperature since it binds more strongly with the tunnels than Cl^-, resulting in a higher decomposition temperature for F^--exchanged akaganeite. On the contrary, Br^-

leaves the tunnels at a lower temperature because it is less electronegative than Cl^-, resulting in a lower decomposition temperature for Br^--exchanged akaganeite. OH^- ions had a similar ability to hold the tunnels of akaganeite as Br^- ions. The low ability of OH^- ions to keep the akaganeite tunnel structure from collapse upon being heated can be explained in two ways. On one hand, the dehydroxylation of akaganeite occurs at a lower temperature than the evolution of hydrogen halide upon heating. On the other hand, an abundance of hydroxyl groups increases the amount of water molecules evolved in the system and enhances the loss of chloride via the reaction of water with chloride ions. The easier release of OH^- and Cl^- ions from the akaganeite tunnels must have contributed to the collapse of the tunnel structure of OH^--exchanged akaganeite at a lower temperature.

Conclusions

Akaganeite with good crystallinity can be prepared via hydrolysis of $FeCl_3$ in strong acidic solution. A pH of 1.5 is most favorable for nucleation and growth of akaganeite at 100 °C. At a pH $\geq$ 6, hematite is formed instead of akaganeite. Microwave heating accelerates the synthesis of akaganeite. With the use of microwave heating, the synthesis time is shortened to 1.5 h. Adding Mn with different valence states into $FeCl_3$ solution impedes the crystallization of akaganeite at pH 1.5 and improves the crystallization slightly at pH 4. Cl-Akaganeite is an inorganic anion exchanger. Anion exchange of Cl-akaganeite with F^-, Br^-, and OH^- ions can reach equilibrium in the range of 0.88–1.20 mmol g^{-1}. The dehydroxylation product is hematite. The loss of chloride starts at 200 °C and continues until 700 °C. The temperature of the thermal decomposition of tunnel structure akaganeite is determined kinetically by the ability of anions to retain themselves in the tunnels upon being heated. Anions with higher electronegativities can bind more strongly with the framework of akaganeite and keep the tunnel structure at a higher temperature.

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(52) Paterson, E.; Swaffield, R.; Clark, D. R. *Thermochim. Acta* **1982**, *54*, 201.