Hydrothermal Synthesis of Fe-montmorillonite in Si-Fe-Mg System

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Fe-montmorillonite ($Na_{0.3}Fe^{3+}_{1.7}Mg_{0.3}Si_4O_{10}(OH)_2 \cdot H_2O$) was synthesized hydrothermally for 24 hours at 100 and 200 °C. XRD analysis showed the synthesized material to be crystalline Fe-montmorillonite without impurities, with d_{001}=11-14.3 Å and d_{06}=1.52-1.53 Å, respectively. The particle size of the material was found to be > 500 Å by TEM. The X-ray photoelectron binding energy of Fe indicated that iron is present in smectite as Fe^{3+}.

There are copious applications of smectite as rheological additives in many industrial fields such as oil drilling mud, paint, cosmetics, etc., and as sorbent in buffer materials for clay barriers system for forth coming geological disposal of high level nuclear waste.

Fe-montmorillonite is one of the iron rich species of smectite, having a chemical formula;

$Na_xFe^{3+}_{2-x}Mg_xSi_4O_{10}(OH)_2 \cdot H_2O$, where 0.2<x<0.6.

Use of Fe-montmorillonite has been found to be advantageous, in terms of adaptability in a disposal system, because Fe^{3+} in the octahedral site of montmorillonite is reduced in the ground water which results in an increase of layer charge leading to enhancement of cation exchange capacity.[1]

A survey of previous studies reveals that it is difficult to synthesize a single phase of ferric smectite and the synthetic conditions are chaotic and different depending on experiments. For example, Ewell and Insley[2] attempted to synthesize iron-rich smectite by aging a mixture of silica gel and iron(III) oxide. However, they could only synthesize a mixture of iron-free smectite with hematite. Similar results were obtained by Hamilton and Furtwangler,[3] who used a mixed solution of sodium silicate and iron(III) chloride as a starting material. Harder[4] synthesized nontronite only in reducing condition where the precipitation of iron oxide can be avoided. Hydrothermal synthesis of Fe(III)-bearing smectite in the Si-Fe system under oxidizing conditions under 150 °C was succeeded by Decarreau et al.[5] However, the product consisted only of the poorly crystalline material even after 12 days treatment. The chemical formula of the smectite was $Ca_{0.26}Si_4Fe_{1.83}O_{10}$ $(OH)_2$ and the layer charge was derived solely from the octahedral defects.

This paper describes the study on hydrothermal synthesis of Fe-montmorillonite. The intention was to obtain good crystalline variety in a short duration.

For estimating the synthetic condition for the smectite, the solubility curves of hematite (Fe_2O_3), aegirine ($(Na_{1-n}Ca_n)(Fe_{1-n}Mg_n)Si_2O_6$) and Fe-montmorillonite ($Na_{0.3}Fe_{1.7}Mg_{0.3}Si_4O_{10}$ $(OH)_2$) were calculated.

Considering that Fe^{3+} containing solution is saturated with hematite in the equilibrium condition, the following expression is derived;

$$2Fe^{3+} + 3H_2O \leftrightarrow Fe_2O_3 + 6H^+ \qquad (1).$$

When pH and temperature of the solution are kept constant, activity of Fe^{3+} in the solution can be determined as follows;

$$\log a^*_{Fe^{3+}} = -3pH - 0.5 \log K_{HM} \qquad (2),$$

where $\log K_{HM}$ is equilibrium constant of formation of hematite, and $a^*_{Fe^{3+}}$ is activity of Fe^{3+} in the solution saturated with hematite. Hence, formation of hematite is feasible when,

$$\log a_{Fe^{3+}} > \log a^*_{Fe^{3+}} = -3pH - 0.5 \log K_{HM} \qquad (3),$$

where $a_{Fe^{3+}}$ is activity of Fe^{3+} in solution.

From the formation reaction of aegirine it can be deduced that aegirine will crystallize when Ca^{2+} is absent in the system and

$$\log a_{Fe^{3+}} > -4pH - \log K_{EG} - \log a_{Na^+} - 2 \log a_{H_4SiO_4} \qquad (4),$$

where $\log K_{EG}$ is equilibrium constant of formation of aegirine, a_{Na^+} is activity of Na^+ in solution, and $a_{H_4SiO_4}$ is activity of aqueous silica in solution.

The saturation field of Fe-montmorillonite is also obtained by the same methodology as follows;

$$\log a_{Fe^{3+}} > -3.54pH - 0.59 \log K_{MON} - 0.18 \log a_{Na^+} - 0.18 \log a_{Mg^{2+}} - 2.36 \log a_{H_4SiO_4} \qquad (5),$$

where $\log K_{MON}$ is solubility product of Fe-montmorillonite and $a_{Mg^{2+}}$ is activity of Mg^{2+} in solution.

The equilibrium constant of hematite (K_{HM}) is taken from the data of Helgeson.[6] The equilibrium constant of aegirine (K_{EG}) and the solubility product of Fe-montmorillonite (K_{MON}) are calculated from the equilibrium constants of some phyllosilicates, analcime, and jadeite, using the data and method of Tardy and Fritz,[7] Helgeson,[6] and Bowers et al.[8]

From the equations (3)-(5), the solubility curves and the saturation fields of hematite, aegirine and Fe-montmorillonite can be obtained in terms of pH and $\log a_{Fe^{3+}}$ by assuming $a_{Na^+} = a_{OH^-}$, $\log a_{H_4SiO_4} = -2$, and $\log a_{Mg^{2+}} = -3$ at Temp. = 200 °C (Figure 1).

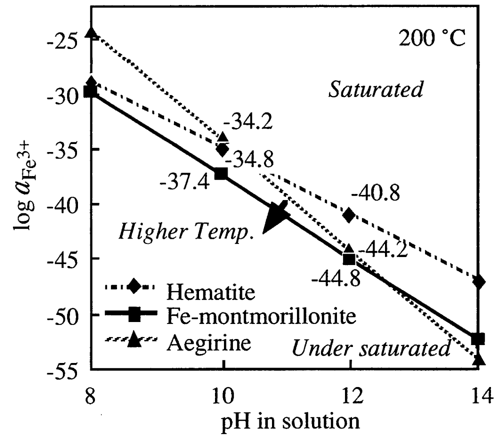

Figure 1. Solubility curves of hematite, aegirine and Fe-montmorillonite calculated thermodinamically using data from Helgeson,[6] assuming $\log a_{Na^+} = \log a_{OH^-}$, $\log a_{H_4SiO_4} = -2$, $\log a_{Mg^{2+}} = -3$.

The upper side of each solubility curve is the saturation field of the mineral. The order of the calculated activity of Fe^{3+} in solution is found to be smaller than the experimental activity due to high alkalline condition and no consideration of formation of hydroxide complex ions, $Fe(OH)_n^{3-n}$. To obtain Fe-montmorillonite as a single phase, it is necessary to keep the activity of Fe^{3+} and pH in solution lower than the value on the solubility curves of impurities such as hematite and aegirine. At higher temperature, the solubility curves shifts lower (as indicated in Figure 1) and it becomes difficult to avoid the formation of impurities.

As starting material of the synthesis, hydrous oxide was prepared by mixing acidic sodium silicate solution with iron(III) chloride and magnesium chloride solutions to set the atomic ratio at Si-Fe-Mg = 4-1.7-0.3. Mixed hydrous oxides were precipitated at pH 9.9 because Mg content was dissolved in solution when the pH is lower than 9. After washing with distilled water, hydrous oxide (ca. 2.5 m mol/g) was dispersed in water and the pH was adjusted with NaOH solution or aqueous ammonia. Then, the slurry was sealed in a teflon container and hydrothermally treated at 100 or 200 °C for 24 hrs. Smectite was crystallized when the initial pH was ≥12. At pH >13 aegirine and hematite precipitated, while at pH < 12 an amorphous or liquid phase appeared. The optimum pH range was found to be in the range of 12-12.4 for obtaining smectite as a transparent yellowish-brown gel without impurities (Table 1).

The interpretation of XRD patterns (Figure 2) indicate the range of d(001) and d(06) spacings of synthesized Fe-montmorillonites using sodium hydroxide are to be 13.1-14.3 Å and 1.52 Å, respectively. After treatment with ethylene glycol, the d(001) spacing expanded to ca. 17-19 Å, which coincide with those of dioctahedral smectites. The size of crystallites along the b-axis calculated from 06 peak using Scherrer's equation are ca. 90-134 Å. Fe-montmorillonite sample synthesized using ammonia has smaller d(001) spacings of 11 Å and do not expand even after treatment with ethylene glycol. TEM analysis indicated the particle size of the smectite obtained at 200 °C was > 500 Å. The chemical composition analyzed by TEM-EDS was found to be Si-Fe-Mg=4-1.65-0.3 by atomic ratio.

Table 1. Hydrothermal conditions of synthsis of Fe-montmorillonite

Run No.	Initial pH	Temp	Alkali
1	12.3	100	NaOH
2	12.4	200	NaOH
3	12.0	200	aqueous ammonia

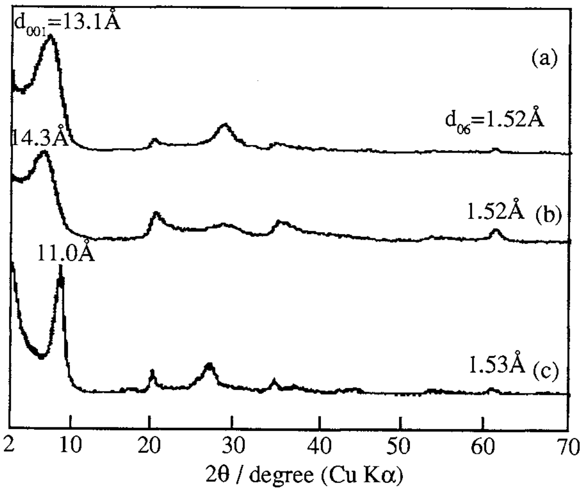

Figure 2. X-ray powder diffraction patterns of the sodium Fe-montmorillonites synthesized at 200°C (a) and 100°C (b), and the ammonium Fe-montmorillonite synthesized at 200°C (c).

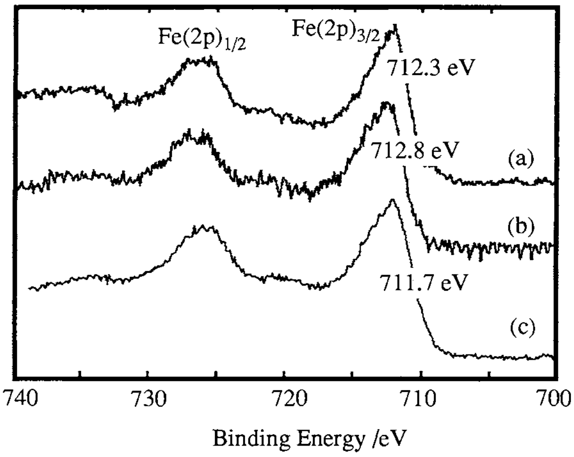

Figure 3. Fe(2p) XP spectra of the sodium Fe-montmorillonites synthesized at 200°C (a) and 100°C (b), and the ammonium Fe-montmorillonite synthesized at 200°C (c).

The X-ray photoelectron binding energy of $Fe(2p)_{3/2}$ spectra (Figure 3) coincide indicates that iron exists in the smectite structure as Fe^{3+},[9] as confirmed by the d(06) spacing of the XRD pattern.

These results imply that Fe-montmorillonite was synthesized under relatively mild hydrothermal condition, and low concentration of iron in the solution and high pH were needed to accomplish the smectite formation.

References and Notes

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