# Preparation of Iron-Containing Hectorite-Like Swelling Silicate

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Iron-containing hectorite-like layered silicate was synthesized by the reaction of LiF, $Mg(OH)_2$, colloidal silica, and $FeCl_3$ in aqueous suspension at 100 °C for 2 days. From X-ray diffraction and infrared spectroscopic analysis, the formation of hectorite-like layered silicate was shown. Dimethyldioctadecylammonium and 1,1′-dimethyl-4,4′-bipyridinium (methyl viologen) ions were intercalated by cation-exchange reactions into the interlayer space of the iron-containing silicate. The intercalated amounts of both cationic species were larger compared to iron-free layered silicate, showing increase in the layer charge density of the silicate by the incorporation of iron(III). The increase in the layer charge was thought to be derived from isomorphous substitution of silicon(IV) by iron(III) in the silicate layer. The structural iron(III) was reduced to iron(II) by reaction with sodium dithionite, which was shown by a color-change (yellow to green) and the increase in the intercalated amounts of dimethyldioctadecylammonium and 1,1′-dimethyl-4,4′-bipyridinium ions.

Host–guest complexation has extensively been investigated to control the physicochemical characteristics of both host and guest and to construct hybrids with unique functions to which neither host nor guest alone can access.[1] Layered solids offer two-dimensional nanospaces to accommodate guest species (Intercalation). Inorganic–organic hybrid materials with varied chemical composition and nanostructures have been synthesized by the intercalation reaction.[2] Among possible layered materials capable of accommodating guest species, smectite layered clay minerals have most widely been investigated due to their stability, large surface area, natural abundance, and rich host–guest chemistry.[3,4] Smectites are comprised of superimposed crystalline aluminosilicate layers. A silicate layer is composed of two silicon tetrahedral sheets and one aluminum octahedral sheet. To avoid problems such as qualitative and quantitative differences of impurities and inconsistent quality stemming from the natural smectites, the syntheses of layered silicates, which possess swelling properties similar to natural smectites, have been conducted. In addition to the commercialized products such as “Laponite” (a synthetic hectorite),[5] “Sumecton SA” (a synthetic saponite),[6] and Na-fluorotetrasilicic mica,[7,8] there are several reports on the preparation of smectite-like silicates[9] and intercalation compounds.[10]

One of the advantages of smectites as host material for hybrid materials is the variation of their chemical compositions. The isomorphous substitution of octahedral and/or tetrahedral sheets is known to control the properties of smectites. Therefore, the syntheses of smectites with various chemical compositions are worth conducting. The amounts of isomorphous substitution, the variation of cation-exchange capacity (CEC), which closely correlates to the amount of negative layer charge, has been used to control the distances of adjacent interlayer cations, resulting in controlled molecular sieving functions[11] of pillared clays and photoprocesses of adsorbed cationic dyes.[12] In a previous report, smectites (trioctahedral group, hectorite-like) with CEC ranges from 60 to 90 mequiv (100 g clay)$^{-1}$ were successfully prepared by changing molar Li:Mg:Si ratios in the starting mixture.[13] The preparation of smectites with a series of CEC can be achieved without modifying other characteristics such as location of isomorphous substitution and particle size, giving materials to discuss the effects of CEC on the physicochemical properties of smectites and their intercalation compounds.

In addition to the variation of CEC, incorporation of transition-metal elements which possess such abilities as charge variation by redox reactions and some catalytic activities is worth conducting in order to prepare smectites with additional functions. Depending upon the nature of incorporated elements (Zn, Ni, Co, and Ti) in the layers, catalytic activities, and adsorptive properties have been reported to be different.[14] Structural $Fe^{3+}/Fe^{2+}$ ions in smectites have been known to affect fundamental properties including layer charge, hydration of interlayer cations, and swelling pressure in response to the iron oxidation states.[15] Although it has been reported that iron-containing layered silicates were synthesized under various conditions (reaction temperature, pH, and so on) and by using various starting materials,[16,17] the structural irons are not well utilized for functionalization of smectites and their intercalation compounds. Here we report the incorporation of ferric ion into the structures of smectite to impart redox activity as well as to vary CEC.

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## Experimental

**Materials.** LiF, $Mg(OH)_2$, and $FeCl_3$ were obtained from Kanto Kagaku Co., Inc. Silica sol ($SiO_2$: 20.3 mass %, $SiO_2/Na_2O = 95$) was kindly donated by Nissan Chemical Ind., Co. Dimethyldioctadecylammonium (abbreviated as $2C2C_{18}N^+$) chloride, 1,1′-dimethyl-4,4′-bipyridinium (abbreviated as $MV^{2+}$) chloride, sodium citrate, and sodium hydrogencarbonate were purchased from Tokyo Kasei Ind. Co. Sodium dithionite was purchased from Junsei Chemical Co., Ltd. All these chemicals were used without further purification.

**Sample Preparation.** $Mg(OH)_2$ was added to an aqueous solution of LiF and the mixture was vigorously mixed by magnetic stirring for 30 min at room temperature. The molar ratio of LiF:$Mg(OH)_2$:$SiO_2$ in the starting mixture was 1.4:5.3:8.0. To the suspension was added silica sol and $FeCl_3$ at a molar ratio of $Si/Fe = 25$, and the suspension was mixed with a homogenizer for another 30 min at room temperature. The slurry was brought to reflux with stirring at 100 °C for 2 days. The product was separated by ultracentrifugation (25000 rpm for 20 min) and dried at 60 °C.

Reduction of structural iron was carried out following a literature procedure[16] as follows: sodium dithionite (0.75 g, 4.6 mmol) was added to an aqueous suspension (0.050 $dm^3$) of the silicate (0.25 g, 0.2 mmol of Fe) containing sodium citrate (0.42 mmol) and sodium hydrogencarbonate (11 mmol) and the mixture was subsequently mixed with stirring for 1 week under nitrogen flow. After washing with 1 M NaCl aqueous solution, the product was dispersed in water/ethanol mixed solution. After the subsequent centrifugation (25000 rpm for 20 min) to collect solid, the product was dried under reduced pressure in order to avoid the oxidation by oxygen in air.

The ion-exchange reactions of the silicates thus obtained were examined using $2C2C_{18}N^+$ chloride and $MV^{2+}$ chloride. The aqueous solution of the organic salt was mixed with an aqueous suspension of the silicate and the mixture was mixed with stirring at room temperature for 1 day. After the ion exchange, the product was washed until a negative $Cl^-$ test was obtained. The product was then collected by centrifugation and was dried under reduced pressure.

**Characterization.** XRD patterns were obtained by a Rigaku RAD IB diffractometer (Cu K$\alpha$ radiation) operated at 20 mA, 40 kV. UV–vis spectra were recorded on a Shimadzu UV-3100PC spectrophotometer. The diffuse reflectance spectra were recorded on a Shimadzu UV-3100PC spectrometer equipped with an integrated sphere attachment. TG-DTA curves were recorded on a Rigaku TG8120 instrument at a heating rate of 10 °C $min^{-1}$ and using $\alpha$-alumina as the standard material. FT-IR spectra were recorded on a Shimadzu FT-IR8200 by KBr disk. ICP-AES was performed using a Rigaku Spectro Ciros CCD.

## Results and Discussion

The color of iron-free hectorite-like silicate is colorless, while that of the iron-containing product is yellow. From the ICP result, the amount of iron content was determined to be $Si/Fe = 21$ (molar ratio). In the X-ray diffraction patterns of the iron-free[13] (Figure 1a) and iron-containing (Figure 1b) samples, the (00*l*) and (*hk*0) reflections were observed at 8–9° ($2\theta$) for (001) and 20 and 40° ($2\theta$) for (*hk*0) reflections. The *d*-value of (060) reflection for the iron-containing sample was 0.152 nm, showing that the product is tri-octahedral group 2:1 type silicate (hectorite-like). There are some reports on the preparation of iron-containing layered silicates under mild conditions (≦100 °C, 1 atm),[17] where co-precipitation of iron oxides and hydroxides as by-products was often observed, depending on pH and reaction temperature. In the XRD pattern of the present product (shown in Figure 1b), reflections ascribable to smectite were observed, while those ascribable to by-products were not observed. The intensities of the reflections are low and the reflections are broad, indicating that the product is composed of finite particles with poor crystallinity. This is consistent with the reported characteristic features of the synthetic smectites-like minerals prepared under relatively mild conditions.[9,10,13,14,17]

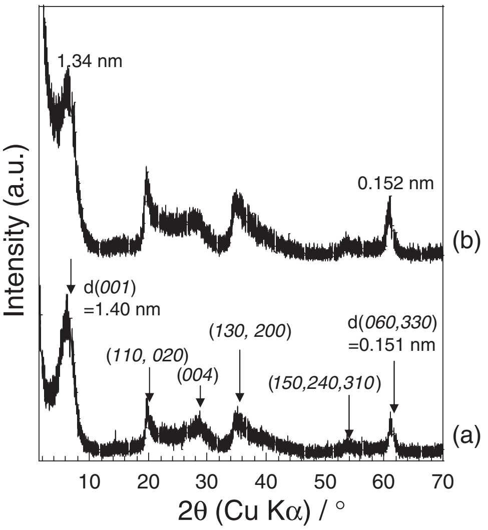

**Figure 1.** XRD patterns of (a) iron-free and (b) iron-containing layered silicates.

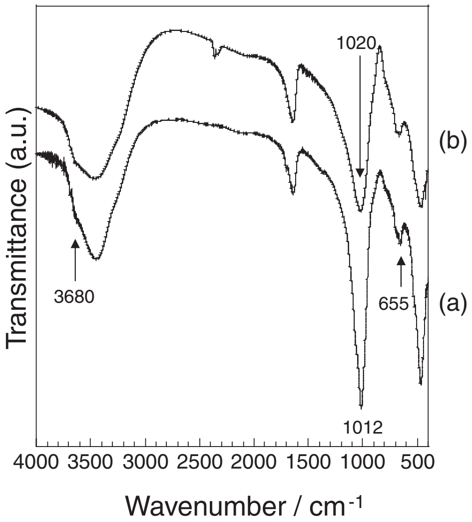

**Figure 2.** FT-IR spectra of (a) iron-free and (b) iron-containing layered silicates.

The IR spectrum of the iron-containing sample is shown in Figure 2b, where the absorption bands such as OH stretching at 3680 $cm^{-1}$, Si–O stretching at 1020 $cm^{-1}$, and Mg–O at 655 $cm^{-1}$, which are characteristic to smectites,[18] were observed. The band due to Si–O stretching observed at 1020 $cm^{-1}$

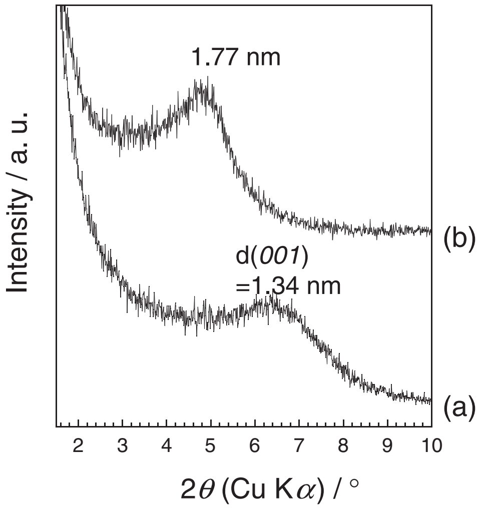

**Figure 3.** The change in XRD patterns by reaction with ethylene glycol. Traces (a) before and (b) after the reaction.

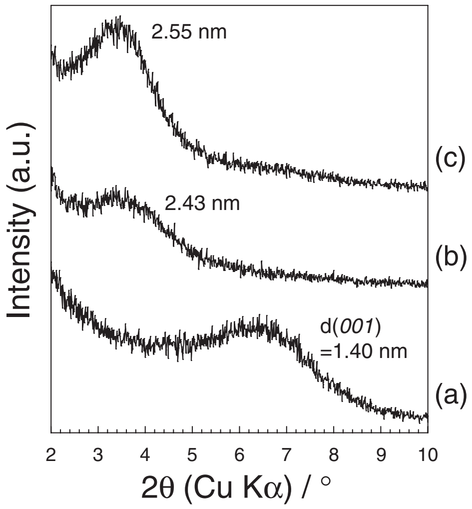

**Figure 4.** XRD patterns of (a) iron-containing layered silicate and the products after the intercalation of $2C2C_{18}N^+$ (b) without reduction, (c) with reduction by sodium dithionite.

**Table 1.** The Adsorbed Amounts and Basal Spacings of $MV^{2+}$- and $2C2C_{18}N^+$-Exchanged Samples

| Sample | Adsorbed amount /mequiv (100 g clay)$^{-1}$ | | Basal spacing/nm | |
|---|---|---|---|---|
| | $MV^{2+}$ | $2C2C_{18}N^+$ | $MV^{2+}$-exchanged form | $2C2C_{18}N^+$-exchanged form |
| Iron-free silicate | 65 | 62 | 1.31 | 2.26 |
| Iron-containing silicate | | | | |
| Before reduction | 76 | 74 | 1.31 | 2.43 |
| After reduction | 85 | 96 | 1.31 | 2.55 |

was in a longer wavenumber region compared to that for iron-free material (Figure 2a: 1012 cm$^{-1}$), while the Mg–O band (at 655 cm$^{-1}$) was in the same position, indicating that iron had been immobilized in mainly the tetrahedral sheet of the silicate layer rather than the octahedral sheet. The sample expands its basal spacing to ca. 1.8 nm after the reaction with ethylene glycol (Figure 3). All these data indicate the formation of iron-containing swelling hectorite-like layered silicate.

The cation-exchange reactions of the present hectorite-like silicate with $MV^{2+}$ chloride were examined to observe the cation-exchange ability. The basal spacing of the $MV^{2+}$-exchanged product was 1.31 nm, which was consistent with the values reported for the $MV^{2+}$–smectite intercalation compounds.[19a,20] Judging from the interlayer expansion obtained by subtracting the thickness of silicate layers from the observed basal spacing ($0.35\,nm = 1.31 - 0.96\,nm$) and the size of $MV^{2+}$ ($0.63 \times 1.34 \times 0.3\,nm^3$),[19] the adsorbed $MV^{2+}$ ions are thought to be arranged as a monomolecular layer with the molecular planes of pyridinium rings (0.3 nm) parallel to the silicate layers. The adsorbed amount of $MV^{2+}$ was determined by the difference in the concentration of $MV^{2+}$ in aqueous phase by means of UV absorption spectroscopy (absorption maximum at around 260 nm). In our previous reports, the adsorbed amounts of $MV^{2+}$ were shown to be close to the CECs of smectites.[11b,13,20] The adsorbed $MV^{2+}$ amount was 76 mequiv (100 g clay)$^{-1}$, which was larger than that on the iron-free hectorite-like silicate [65 mequiv (100 g clay)$^{-1}$][13] (Table 1).

The ion-exchange reactions with $2C2C_{18}N^+$ chloride were also examined. By the reactions, the basal spacing was increased from 1.40 to 2.43 nm (Figure 4). It has been reported that $2C2C_{18}N^+$ takes paraffin type arrangements in the interlayer spaces of smectites [cation-exchange capacity: >70 mequiv (100 g clay)$^{-1}$] and their structural analogs.[21–30] Due to the large size of $2C2C_{18}N^+$, the intercalated $2C2C_{18}N^+$ took paraffin type arrangements when intercalated in the interlayer space of smectite. The adsorbed $2C2C_{18}N^+$ amount derived from the weight loss (26%) in the TG curve (Figure 5) of the product [74 mequiv (100 g clay)$^{-1}$] was close to that of the $MV^{2+}$ [76 mequiv (100 g clay)$^{-1}$], confirming the successful ion exchanges. The adsorbed amount of $2C2C_{18}N^+$ [74 mequiv (100 g clay)$^{-1}$] was also larger compared to the iron-free silicate system[14] (Table 1). The variations of the adsorbed amounts observed both for $2C2C_{18}N^+$ and $MV^{2+}$ are derived from the increase in the layer charge density (cation-exchange capacity) of hectorite-like silicate by incorporating iron. We assume that tetravalent silicon in tetrahedral sheets of smectite has been substituted by trivalent iron to increase the layer charge density.

The layer charge density is successfully changed by the reduction of iron in the presently prepared layered silicate. After the reactions of the iron-containing hectorite-like silicate with sodium dithionite, the color changed from yellow to green (Figure 6), indicating the reduction to divalent iron in smectite. The color returned to yellow under ambient air atmosphere.

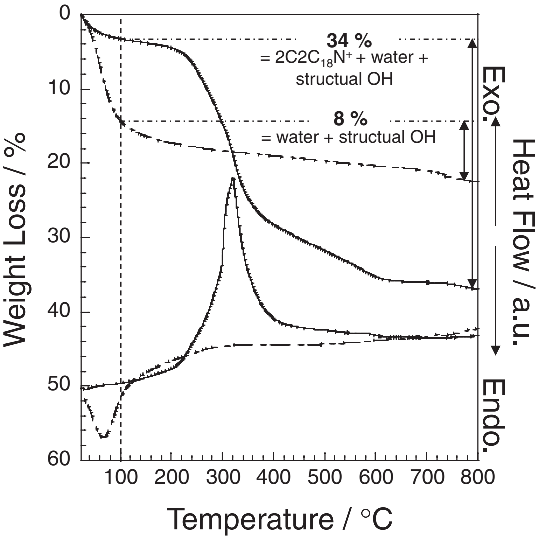

**Figure 5.** TG-DTA curve of samples before (dotted lines) and after (solid line) ion exchange with $2C2C_{18}N^+$.

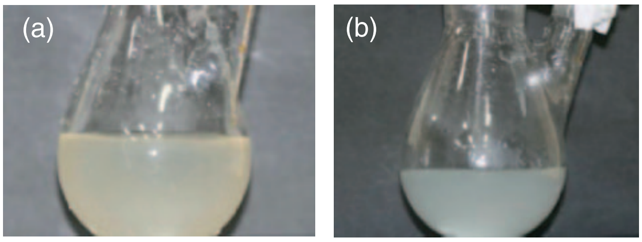

**Figure 6.** Photographs of aqueous suspensions of iron-containing layered silicates; (a) before and (b) after reduction by sodium dithionite.

When the sample after the reduction was used for the cation exchanges, the adsorbed amounts of $2C2C_{18}N^+$ and $MV^{2+}$ increased to 96 and to 85 mequiv (100 g clay)$^{-1}$, respectively, showing the increase in the layer charge density (Table 1). In the $2C2C_{18}N^+$ system, the basal spacing, which corresponds to the inclination of the alkyl chains, increased (from 2.43 to 2.55 nm) with the layer charge, reflecting the inclination. Assuming that all of the immobilized iron in the silicate was reduced, the increases in the adsorbed amounts [22 and 9 mequiv (100 g clay)$^{-1}$ for $2C2C_{18}N^+$ and $MV^{2+}$, respectively] are smaller than the calculated values [$6 \times 10^1$ mequiv (100 g clay)$^{-1}$ based on the ratio of Si/Fe = 21]. A portion of $Fe^{3+}$ was possibly located in the interlayer space or was not reduced to decrease the adsorbed amounts of both cations.

Furthermore, the iron-containing silicate synthesized here possibly shows redox activity, considering that the adsorbed $MV^{2+}$ partially reduced to methyl viologen radical cation ($MV^{\bullet+}$) by divalent iron as shown by diffuse reflectance spectrum (Figure 7); the absorption bands ascribable to $MV^{\bullet+}$ or its dimer, $(MV)_2{}^{2+}$, were observed at around 400 and 600 nm.[20b,31] Electron transfer occurred from iron(II) to $MV^{2+}$, and then adsorbed $MV^{\bullet+}$ may partially re-oxidize in aqueous media by dissolved oxygen. This is a possible speculation on the observed difference of the adsorbed amounts of $MV^{2+}$ and $2C2C_{18}N^+$ (relatively smaller adsorbed amount of $MV^{2+}$ than that of $2C2C_{18}N^+$).

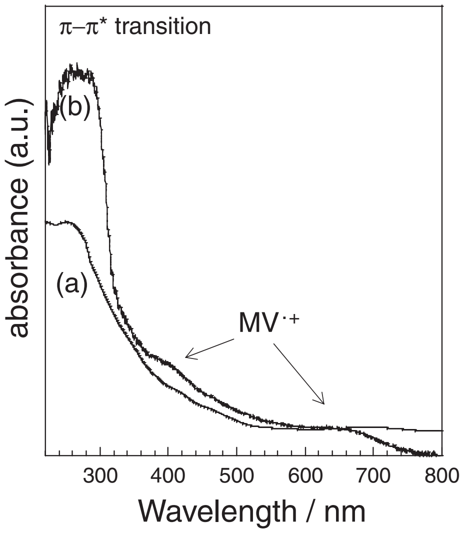

**Figure 7.** UV–vis diffuse reflectance spectra of iron-containing layered silicates (a) before and (b) after the adsorption of $MV^{2+}$.

## Summary

We report the synthesis of iron-containing hectorite-like layered silicate by the reaction of LiF, $Mg(OH)_2$, colloidal silica, and $FeCl_3$ in aqueous suspension at 100 °C for 2 days. The cation-exchange capacity was successfully increased from 70 to 90 mequiv (100 g clay)$^{-1}$ by reduction of the incorporated iron.

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