

Formation of Layered Manganese Oxide in the Gallery of Smectite Clay, and its Characterization

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Formation of monolayer of manganese oxide inside the gallery of smectite clay through the oxidation of manganese hydroxide layer with an oxidizing agent at room temperature has been investigated. It was found that a new type nanocomposite adopting an expanded structure with basal spacing of 2.0 nm could be synthesized. In this structure, a monolayer of manganese oxide is sandwiched by two monolayers of hydrated sodium ions inside the gallery. The expanded structure was thermally stable at least up to the 773K and reversible dehydration - rehydration behavior was observed in the temperature range between room temperature and 773K.

Key words: Layered Manganese Oxide, Oxidation, Clay Gallery, Nano-Composite, Expanded Structure

1. INTRODUCTION

Much attention has been paid on manganese oxides with layer or channel structure in the fields of energy storage, catalysts, as well as giant magnetoresistance devices. The synthetic chemistry of these low-dimensional manganese oxides proceeding at low temperatures has been recently developed so that various types of materials, e.g. birnessite [1], hollandite [2] and todorokite [3] can be artificially synthesized under hydrothermal conditions. Along this direction, room temperature chemistry of manganese oxide should be still facilitating to design the structure aiming at new properties. To lower the reaction temperature in forming layered manganese oxide, use of interlayer space (gallery) of layered clay materials as a micro reactor seems to be effective because of low dimensional nature of the space. It is well known that the gallery has ability to the various chemical reactions including hydrolysis [4, 5, 6] and oxidation [7, 8] of cations as well as swelling and cation exchange properties. It has already been demonstrated that various transition metal hydroxides (TM = Mn²⁺, Co²⁺, Fe²⁺, Ni²⁺) can be formed between the silicate layers in a monolayer fashion at room temperature [4, 5, 6]. In addition, the authors have recently reported that room temperature oxidation of the hydroxide sheets can proceed inside the gallery for Ni and Co cases [7, 8]. This time, we focussed our attention on manganese containing material, and have studied the gallery oxidation and structural and physicochemical properties attached to the resultant composite.

The purpose of this paper is to demonstrate a possibility of oxidation with using proper oxidative reagents at room temperature for formation of monolayer of manganese oxide inside the gallery affording a new type of nanometer scaled layered composite. The structure and physicochemical properties will be examined with XRD, FT-IR, TG as well as conventional chemical analyses. Thermal stability of the structure and reversible dehydration-rehydration behavior will be shown as well.

2. EXPERIMENTAL

2. 1 Intercalation of Manganese Hydroxide in the

Gallery of Sodium Fluoride Tetra Silicic Mica

Manganese hydroxide intercalated sodium fluoride tetra silicic mica nano composites were prepared by titrating manganese (II) chloride solutions in the presence of the sodium fluoride tetra silicic mica with sodium hydroxide after the previewed method by Ohtuka et al. [5]. The reaction starts as ion exchange between sodium and manganese cations in the gallery, then followed by hydrolysis of the manganese ions. The hydrolysis of the cations occurs preferentially inside the gallery rather than in outer space in solution.[6] The titration was performed under nitrogen flow to avoid formation of oxidation of manganese hydroxide throughout the procedure. The preparation procedure was as follows. 2.0 g of sodium fluoride tetrasilicic mica (SOMASIF ME 100-DS: CO-OP CHEMICAL CO.,LTD., nominal formula = Na₂Mg₅Si₈O₂₀F₄, CEC=115 meq. / 100g-clay) was dispersed into 150 ml of 0.1M MnCl₂ aqueous solution. After stirring for 1 day, this suspension was titrated with an appropriate volume of 0.1M sodium hydroxide solution at the rate of 2ml / h under vigorous stirring. After the titration, the suspension was further stirred for 2 days. The resulting products separated by centrifugation, washed with 0.01M-HCl (100ml) and deionized water to remove electrolyte, and then dried at 313K in vacuo. For convenience, we will refer this material as hydroxide composite hereafter.

2. 2 The Oxidation of Manganese Hydroxide Inside the Gallery

Oxidation of the above hydroxide composites was performed with about 4 mol / l sodium hypochlorite basic solution in the aqueous suspension system. The oxidation procedure was as follows. The hydroxide composite of 500 mg was dispersed 50 ml of about 4 mol / l sodium hypochlorite solution. The suspension was vigorously stirred for 12 hours at room temperature (298±3 K) for sufficient oxidation. The change in color from light brown to dark brown as well as formation of small bubbles of oxygen gas were clearly observed in the initial stage of the reaction. The resulting products were repeatedly washed with deionized water and then dried at 313K in vacuo. For

convenience, we will refer this material as hydroxide composite hereafter.

2.3 Techniques of Characterizing the Composites

Chemical analyses of the hydroxide composite and the oxidized one were carried out by atomic absorption analysis using a polarized Zeeman atomic absorption spectrophotometer, HITACHI Z-6100, and by thermogravimetric analysis (TGA) using SHIMADZU TG-40 from room temperature to 1273 K in air, the heating rate of 10 K min⁻¹.

The X-ray diffraction (XRD) patterns were obtained with a Rigaku RAD-C diffractometer, using a Cu K α radiation, for powder composites. Infrared spectra were obtained from 4000 to 400 cm⁻¹ with a resolution of 8 cm⁻¹ on a PERKIN ELMER 1640 model FT-IR spectrometer by the KBr method.

3. RESULTS AND DISCUSSION

3.1 Intercalation of Manganese Hydroxide in the Gallery of Mica

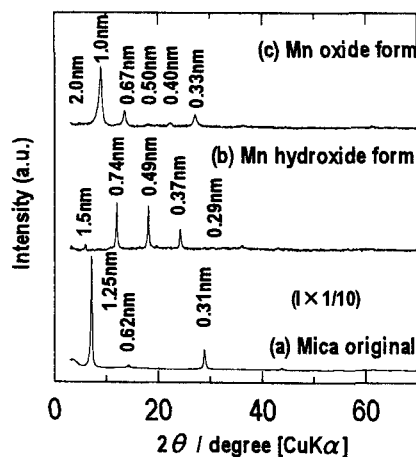


Fig. 1 The XRD patterns of (a) sodium fluoride tetra silicic mica, (b) manganese hydroxide / mica composite, (c) manganese oxide / mica composite.

The observed number of manganese atoms and sodium atoms in the hydroxide composite per O₂₀F₄ silicate unit are shown in Table 1. The values of manganese and sodium atoms were calculated from atomic absorption analysis data taking account the results of the thermogravimetric analysis. It was confirmed that the hydroxide composites contained 6.0 manganese atoms and only a little amount of sodium ones below 0.01 mol per O₂₀F₄ silicate unit. This result indicates that ion exchange reaction followed by hydrolysis proceeded mostly to the expected degree. The x-ray diffraction (XRD) patterns of hydroxide composite were shown in Fig. 1 (b). The basal spacing d(001) of the composite is about 1.5 nm. The extinction of (001) reflection and the strengthening of (002) and (003) reflections give an evidence for the growth of manganese hydroxide monolayer in the gallery, resulting in a chlorite-like structure [6] (Fig. 2).

The FT-IR absorption spectra of the hydroxide

composite is shown in Fig. 3 (b). Strong absorption bands appeared at about 3650 cm⁻¹ in the composite. This band is known due to the OH stretching vibration in the metal hydroxide.

The result of TG analysis for the hydroxide composite is shown in Fig. 4 (b). There observed a

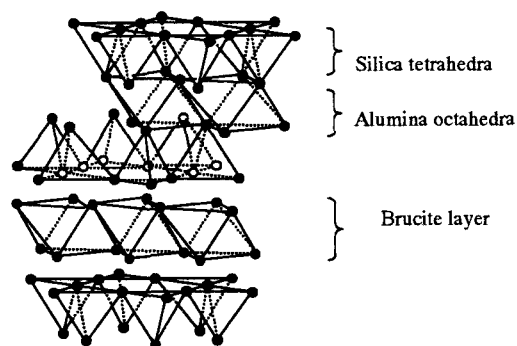


Fig. 2 The schematic illustration of the structure of chlorite.

small weight loss of about 1.5% up to 500K and a sudden weight loss about 5% from 520K up to 700K. These weight losses can be assigned to dehydration of the water molecules mainly adsorbed on outer surface of the composite and dehydroxylation of manganese hydroxide layer, respectively. From 700K to 1100K, a gradual weight loss of about 2% was observed, which can be assigned to additional dehydroxylation. The weight loss above 1100K can be assigned to defluorination of the mica.

3.2 Oxidation of the Manganese Hydroxide in the Gallery of Mica

The observed number of manganese ions and sodium ions in the oxide composite per O₂₀F₄ silicate unit are shown in Table 1. The oxide composite contained manganese ions of 5.8 per O₂₀F₄ silicate unit. Although the small amount of manganese ions were released, about 97 % manganese remained in the composite. Meanwhile, it was found that the oxide composite contains significant amount of sodium ions, which rarely existed before oxidation reaction, as shown in Table 1. The average valence of manganese ions determined by iodometric titration ranged from 3.8 to 3.9. The chemical change here occurred will be discussed the following section.

The XRD pattern of oxide composite was shown in Fig. 2 (c). The oxide composite showed an

Table 1 Inter layer composition of Mn and Na in the hydroxide and oxide composite. (The values are given in mol / O₂₀F₄-unit.) and observed average valence of Mn.

composite	Content (mol / mol-day)		Average valence of Mn
	Mn ²⁺)	Na ⁺)	
manganese hydroxide composite	6.0	less than 0.1	—
manganese oxide composite	5.8	2.8	3.8~3.9

*) Calculated from weight loss of oxide heated until 1273K in TG and atomic absorption analysis data for manganese and sodium atoms.

expanded basal spacing different from the hydroxide composite. Quite similar XRD patterns corresponding to basal spacing of 1.96 nm have been found for Ni and Co containing oxide composites. [7, 8] The value of $d = 2.0$ nm is considered to correspond to tetra layers of oxygen atoms packing in gallery.

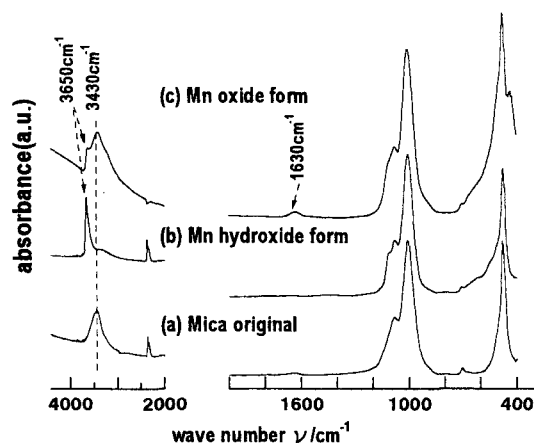


Fig. 3 IR absorption spectra of (a) sodium fluoride tetra silicic mica, (b) manganese hydroxide / mica composite, (c) manganese oxide / mica composite.

The IR absorption spectra of the oxide composite was shown in Fig. 3 (c). The 3650 cm^{-1} band, which is due to the OH stretching vibration, became weak instead of strengthening of 1630 cm^{-1} and 3430 cm^{-1} band, which can be assigned H_2O . These changes of adsorption bands suggested that the change from the manganese hydroxide to oxide through gallery oxidation with NaClO associated with intercalation of water molecules. The result of TG analysis for the oxide composite is shown in Fig. 4 (c). This result is obviously different from the hydroxide composite. There observed a sudden weight loss of about 10% at 400 K. This weight loss was mainly attributed to the dehydration of the water molecules adsorbed on the internal surface of the composite. From 400 to 1050 K, the weight loss was observed about 4%, which can be assigned to gradual reduction of MnO_2 . Further weight loss of about 5% was observed from 1050K to 1273 K. This weight loss can be assigned to decomposition of

silicate layer with defluorination.

3. 3 The Model for the Oxidation Reaction and the Structure.

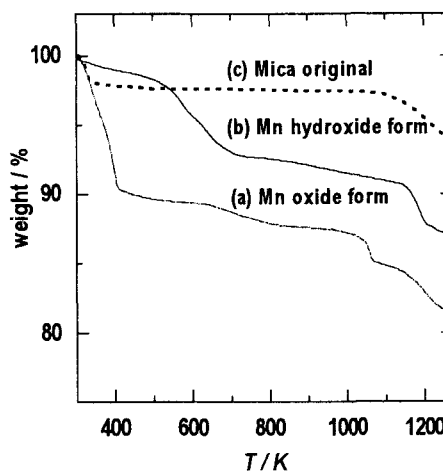


Fig. 4 TGA curves, for (a) sodium fluoride tetra silicic mica, (b) manganese hydroxide / mica composite, (c) manganese oxide / mica composite.

Gathering the above results, we attempted to construct the model of oxidation reaction and the structure of oxide composites.

The scheme of oxidation reaction and the change of the structure are shown in Fig. 5. This reaction contains at least three processes. The first is the oxidation of the manganese ions from di- to tri- or tetra valent states. The second is the release of protons from the hydroxide sheet. This process makes the manganese oxide layer negative. The third is intercalation of sodium ions hydrated with water molecules into the space between silicate and manganese oxide layers. In this way, the expanded structure with 2.0 nm basal spacing is considered to be generated. The validity of this type of structure model has been examined for Co containing material elsewhere [8] with the aid of one-dimensional Fourier analysis using peak intensity of XRD data. We will report the details for this manganese case in the paper followed after.

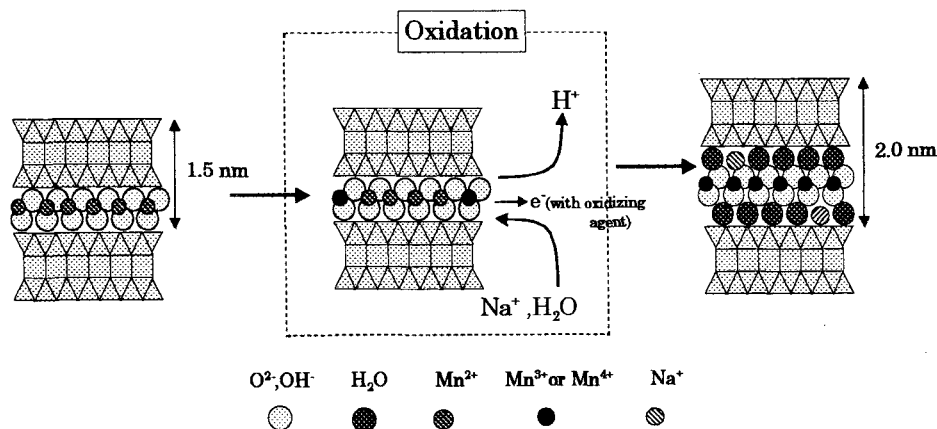


Fig. 5 Schematic illustration of formation of manganese oxide in the gallery by oxidation.

The similar structural change was observed, when we use KMnO_4 as the oxidizing agent. On the other hand, when we used H_2O_2 as the oxidizing agent, the basal spacing was found 1.5 nm and relative intensity clearly changed. This result indicated that intercalated hydroxide layer was released from the gallery by oxidation with H_2O_2 . However, when we oxidized the hydroxide composite with coexistence of NaOH , essentially the same XRD pattern as the expanded phase with basal spacing of 2.0 nm was observed ever in H_2O_2 oxidation.

These results indicated that coexistence of alkali ions with the oxidizing agent played an important role to maintain the MnO_2 layer inside the gallery.

3.4 The Reversible Dehydration - Rehydration Behavior of the Oxidized Composite

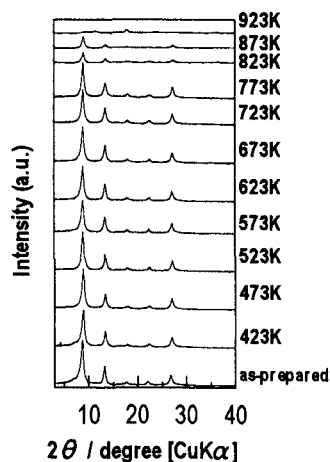


Fig. 6 The XRD patterns for the oxidized composite calcined in air at different temperatures from 373 to 773 K with 50 K interval.

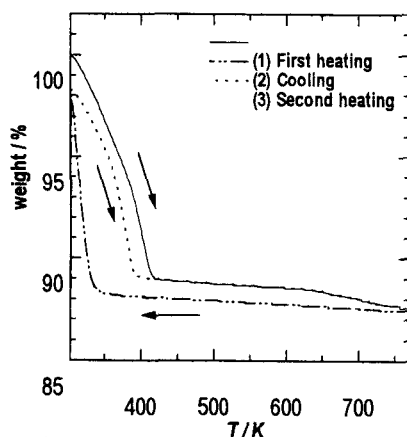


Fig. 7 TGA cycle for the oxide composite of (1) first heating, (2) cooling, (3) second heating at constant rate of 10 K min^{-1} , demonstrating reversible dehydration - rehydration behavior.

To examine thermal stability of the expanded phase, the oxidized composite was calcined in air from 373 to 773 K with 50 K interval. It was found that the XRD pattern was substantially unchanged except for a slight reduction in basal spacing. The basal spacing

value was shown in Fig. 6 as a function of calcination temperature. The basal spacing of as-prepared was 2.0 nm whereas calcined composite showed basal spacings from 1.98 to 1.99 nm. These results indicate that the expanded structure was thermally stable up to 773 K by calcination. The decomposition temperature of the structure was found in the range from 873 to 923 K.

It is noteworthy that rehydration occurs reversibly in temperature range below 773 K. The TGA profile was shown in Fig. 7 for heating and cooling cycle between room temperature and 773 K. In heating path, there was observed a sudden weight loss of about 9 % at 400 K. Total weight loss of this path up to 773K was 10 %. On the other hand, there observed a fast weight increase at 340 K in cooling path, approaching to the initial weight at room temperature. It was confirmed that this cycle except for the first heating path reproduced at least five times for the identical sample. Taking account of the stability of the structure mentioned above, it is likely that dehydration and rehydration in the interlayer space reversibly occurs. The similar hydration behavior was reported in the case of birnessite by Rongji Chen et al.[1]

Conclusion

In conclusion, a new expanded phase with basal spacing of 2.0 nm containing manganese oxide layer was synthesized at room temperature by oxidation reaction in the gallery. It is considered that, in this structure, manganese oxide layer is sandwiched by two monolayers of hydrated sodium ions in the gallery. This manner of hydration and the structure in the gallery seem to be similar to appear in birnessite type layered manganese oxide. In this reaction, the alkali ions coexisting with the oxidizing agent played an important role, compensating the negative charges both on manganese oxide and silicate layers. The expanded structure was stable at least up to the 773K and reversible dehydration-hydration behavior was observed in the temperature range between room temperature and 773K. It was suggested that the expanded structure could be a new type open framework structure.

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