

CHANGES THE STRUCTURE AND CAFFEINE ADSORPTION PROPERTY OF CALCINED MONTMORILLONITE

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ABSTRACT: Montmorillonite is widely used as a natural adsorbent. It is generally considered that the adsorption properties of montmorillonite are largely due to its characteristic layer structure. The structure of montmorillonite changes under different temperature conditions. In this study, changes in the structure of montmorillonite with temperature are analyzed using Synchrotron X-Ray Powder Diffraction (SR-XRD). Observations are made on how montmorillonite with a modified structure is affected by the adsorption of nonionic organic compounds in a water system. The object of this study is to elucidate the mechanism by which montmorillonite adsorbs nonionic organic compounds. It is confirmed that, without calcination treatment, adsorption of caffeine on montmorillonite changes its layer structure. Calcination treatment at above 573 K causes irreversible dehydration in the structure of montmorillonite. Samples of montmorillonite calcined at 673 K and 873 K show a reduction in the amount of caffeine adsorbed. In addition, calcination treatment of montmorillonite at 673 K and 873 K causes less intercalation into the layers. These results show that adsorption of caffeine on montmorillonite without calcination treatment occurs with the intercalation of caffeine between layers of montmorillonite. On the other hand, montmorillonite calcined at 873 K is confirmed to adsorb approximately 20 % of caffeine compared to untreated montmorillonite. It suggested the possibility of the adsorption of caffeine even on the surfaces and end faces of layers of montmorillonite.

Keywords: Montmorillonite, Synchrotron X-Ray Powder Diffraction (SR-XRD), Calcination, Adsorption, Caffeine

1. INTRODUCTION

Montmorillonite is a clay mineral and is a principal component of bentonite, which is mined naturally. This material is low cost and highly stable, and has been used in a wide range of fields. Due to the swelling property, plasticity, and adsorption function of the material, it is used as a soil amendment and a binder for agricultural chemicals in the agricultural sector. In the civil engineering field, it is used, for example, as a wall-building agent and lubricity agent, and as a water impermeable material for waste disposal. It also has practical applications in various areas other than agriculture and civil engineering, such as a solidification material for animal excrement [1].

Montmorillonite is a plate crystal with a thickness of about 1 nm, and it consists of tetrahedral silicate and octahedral alumina [2]. Several plate crystals are stacked to form a layer structure. The plate crystal has a three-layer structure consisting of the central layer of $\text{Al}(\text{OH})_6$ and both outer layers of $\text{Si}_4\text{O}_6(\text{OH})_4$. Partial isomorphous substitution of Al by Mg and Fe takes place in the central layer. Isomorphous substitution causes each layer to take on a negative charge. To cover for the negative charge, cations are retained between the layers. In water, the adsorption of water molecules between the layers

causes the material to swell, and the interlayer distance varies [3], [4]. Montmorillonite that is swollen in water readily exchanges cations that are present in the solution with those ones retained between the layers [5]. For this reason, the material is often used as a cation exchanger in a water system. On the one hand, nonionic organic compounds are thought to be adsorbed at different sites depending on factors such as the polarity of the chemical compound [6], [7]. A chemical compound that can get into the layers is believed to be adsorbed by its intercalation between the layers [8], [9]. Because of the very large surface area between the layers, the adsorption capacity is extremely high. On the other hand, a chemical compound that cannot get into the layers is thought to react with and be adsorbed on the surfaces and end faces of the layers [10].

In this study, montmorillonite is calcined to remove water molecules from its structure and change the distance between layers. The structural change caused by calcination is determined and analyzed with Synchrotron X-Ray Powder Diffraction (SR-XRD). In addition, calcined montmorillonite is suspended in caffeine solutions to quantify variations in the adsorption of caffeine. To examine the hypothesis that the layer structure of montmorillonite may play a key role in the adsorption of caffeine, changes caused by

calcination in the structure and the adsorption of caffeine are observed.

2. MATERIALS AND METHODS

2.1 Calcination Treatment of Montmorillonite and Adsorption Test of Caffeine

Samples of commercially available montmorillonite (from Mizusawa Industrial Chemicals, Ltd.) of 20 g each were placed in a heat-resistant crucible and calcined at 373 K, 473 K, 573 K, 673 K, or 873 K for two hours. Then, the samples of calcined montmorillonite were cooled at room temperature for one hour.

Caffeine (from Wako Pure Chemical Industries, Ltd.) was dissolved in ultrapure water and the concentration was adjusted to 400 mg/L to prepare a caffeine solution. Montmorillonite of 4.0 g was added to the caffeine solution of 400 mL and was suspended. The montmorillonite kept in contact with the caffeine solution for 60 minutes. The suspension was centrifuged (3000 rpm, 10 minutes) and the precipitated clay mineral was dried in an oven (EYELA) at 378 K overnight. The dried clay mineral was ground into a powder with a mortar to prepare a sample for analysis.

Adsorption of caffeine was tested using caffeine solutions with concentrations adjusted from 10 to 5000 mg/L. Montmorillonite of 4.0 g was added to the caffeine solution of 400 mL and was suspended. The montmorillonite kept in contact with the caffeine solution for 60 minutes. The suspension was centrifuged (3000 rpm, 10 minutes) to obtain the supernatant solution. The supernatant solution was filtered through a membrane filter (0.45 µm, PTFE). The concentration of caffeine in the filtrate was measured using HPLC-UV/Vis. The measurement conditions of HPLC are shown in Table 1. Adsorption of caffeine per unit weight was calculated.

Based on the results of the caffeine adsorption test, Langmuir adsorption isotherm was obtained. The concentration of caffeine in the filtrate was used as an equilibrium concentration C_{eq} . Based on the concentration of caffeine in a supernatant solution, adsorption per weight of montmorillonite Q_{eq} was calculated. In addition, using the Langmuir adsorption isotherm equation as in Eq. (1), the maximum adsorption capacities (Q_{max}) and the equilibrium constants (K_{Lang}) were calculated.

$$Q_{eq} = \frac{K_{Lang} \cdot Q_{max} \cdot C_{eq}}{1 + K_{Lang} \cdot C_{eq}} \quad (1)$$

Table 1 HPLC-UV/Vis condition for analysis of caffeine.

Column	Shodex Asahipak ODP-50 2D (2.0mmI.D. x 150mm)
Mobile phase	A: 0.1% formic acid B: 100%MeOH/Acetonitrile = 50/50 A/B = 0 to 10min : 90/10,
Step gradient	10 to 15min : 10/90, after 10min : 90/10
Flow rate	1 mL/min
Detector	UV (275nm)
Column temp.	40 °C

2.2 Synchrotron X-Ray Powder Diffraction (SR-XRD)

The diffraction patterns of calcined montmorillonite were obtained using a large synchrotron radiation facility (SPring-8 BL19B2, Japan Synchrotron Radiation Research Institute: JASRI). A large Debye-Scherrer camera (286.48 mm in diameter, Rigaku Corporation) was mounted on the rear hatch and an imaging plate (0.01 °, BAS2500, FUJIFILM Corporation) was used for detection. The X-ray source was derived from the synchrotron radiation and a monochromatic X-ray beam with a wavelength of about 1 Å is used. The beam size was 0.3 (H) mm x 3 (W) mm. A measurement samples were filled in a glass capillary with a diameter of 0.3 mm. The exposure time for measurement was 5 minutes for each sample.

2.3 Quantitative Analysis of Exchangeable Cation

Ammonium chloride (from Wako Pure Chemical Industries, Ltd.) was dissolved in ultrapure water and the concentration was adjusted to 1.0 mol/L to prepare an ionic solution. Calcined montmorillonite was added to the ionic solution to prepare a 1 wt% solution, and then was suspended. The solution and montmorillonite were kept in contact with each other for 60 minutes. The suspension was centrifuged (3000 rpm, 10 minutes) to obtain the supernatant solution. The supernatant solution was filtered through a membrane filter (0.45 µm, PTFE). The filtrate was analyzed for Na, K, Ca, and Mg ions by ICP-AES.

3. RESULTS AND DISCUSSION

The SR-XRD patterns of montmorillonite after calcination treatment are shown in Fig. 1. The samples of montmorillonite with calcination treatment at 373 K and 473 K show no change in

diffraction peaks, which indicates their basal distances. The change of basal distance indicates the change of interlayer distance in the layer structure. Samples of montmorillonite with calcination treatment at 373 K and 473 K show no change of interlayer distance. These results suggest that, during calcination, water such as adsorbed water and interlayer water was partially removed. Then, water molecules in the atmosphere rehydrated when cooled to normal temperature after calcination. Rehydration during the cooling process is considered to have led to the same interlayer distance as that of the montmorillonite before calcination. Montmorillonite with calcination treatment at 573 K showed no diffraction peak indicating the basal distance. This result indicates that dehydration within the structure of montmorillonite with calcination treatment at 573 K was to be an irreversible change. It is considered that montmorillonite calcined at 573 K was dehydrated within the structure, and it is considered to be an irreversible change. In other words, the structure of montmorillonite calcined at 573 K, after dehydration during calcination, cannot return to the structure before calcination. For montmorillonite samples calcined at 673 K and 873 K, a diffraction peak, which had not been present with the montmorillonite before calcination, was identified at about 6.1° . These results mean that calcination treatment at 673 K and 873 K appreciably changed the structure of montmorillonite compared to that before calcination.

Basal distances were calculated based on the diffraction peaks shown in Fig. 1 (Table 2). For Ca-type montmorillonite, three basal distances (two water phases: 1.5 nm, one water phase: 1.17 nm, no water phase: 1.03 nm) depending on water absorption condition were reported [11]. Basal distances of montmorillonite samples calcined at 373 K and 473 K were similar to the reported values of two water phases. This is because, after calcination and subsequent cooling, montmorillonite adsorbed atmospheric water molecules, which rehydrated to the level of two water phases. In addition, samples of montmorillonite calcined at 673 K and 873 K had basal distances approaching 1.03 nm. The calcination treatment at 673 K and 873 K caused irreversible structural changes, which does not allow rehydration and results in a montmorillonite structure with no water phase. For montmorillonite calcined at 573 K, no diffraction peak indicating a basal distance was identified.

There are several reports on the calcination of montmorillonite. First, for montmorillonite after calcination treatment, water molecules that are not involved in the montmorillonite structure, such as

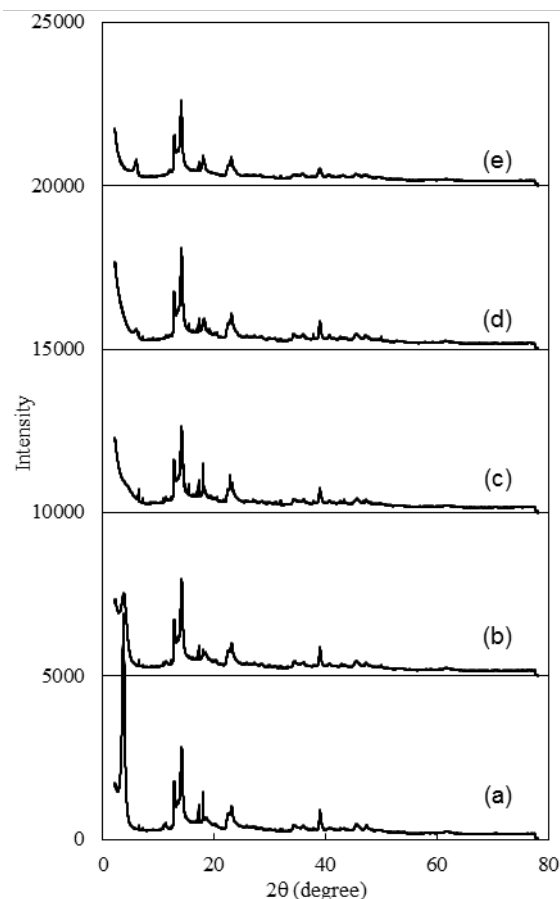


Fig. 1 SR-XRD pattern of montmorillonite calcined at (a) 373 K, (b) 473 K, (c) 573 K, (d) 673 K, and (e) 873 K.

Table 2 Basal distances with montmorillonite after calcination treatment.

	basal distance (nm)
373 K	1.54
473 K	1.51
573 K	n.d.
673 K	0.94
873 K	0.95

adsorbed water and interlayer water, are removed. It is reported that this dehydration is reversible, and rehydration takes place with calcined smectite when it is cooled after calcination [12]. Besides, it is reported that montmorillonite calcined at a high temperature above 773 K results in the removal of water molecules involved in the montmorillonite structure, and dehydration due to calcination above 773 K is irreversible [13]. We observed an irreversible structural change caused by calcination treatment above 573 K. Based on the results shown in Fig. 1, montmorillonite calcined below 473 K showed rehydration when cooled after calcination

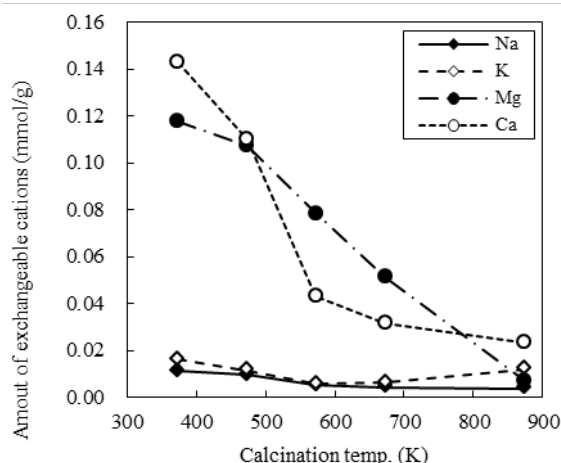


Fig. 2 The amount of cations eluted from montmorillonite after calcination treatment.

Table 3 Cation exchange capacity of montmorillonite after calcination treatment.

temperature of calcination treatment (K)	cation exchange capacity (meq/100 g)
373	54.9
473	45.6
573	25.4
673	17.7
873	7.8

treatment, while montmorillonite calcined above 573 K showed no rehydration after being cooled.

Fig. 2 and Table 3 show the cation exchange capacity of calcined montmorillonite samples. The cation exchange capacity (CEC) is calculated by summing the products of the amounts of exchangeable cations multiplied by the electric charge for each ion. The amounts of Ca and Mg ions, which are exchangeable cations, decreased with montmorillonite calcined above 573 K compared to that calcined at 373 K. Ca ions decreased by 70 % with calcination at 573 K, 78 % at 673 K, and 84 % at 873 K compared to montmorillonite calcined at 373 K. Cation exchange is less likely to occur in montmorillonite samples with calcination treatment at 573 K, 673 K, and 873 K. This is because less rehydration tends to occur with treatment. The cation exchange with montmorillonite in a water system occurs when cations such as Ca or Mg ion retained between the layers of montmorillonite are exchanged with water molecules, or other cations present in the solution [5]. Therefore, it is considered that montmorillonite samples calcined at 573 K, 673 K, and 873 K had no exchange of

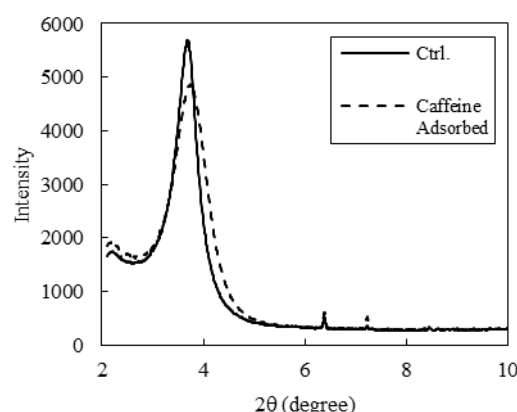


Fig. 3 The SR-XRD pattern of montmorillonite after caffeine adsorption treatment.

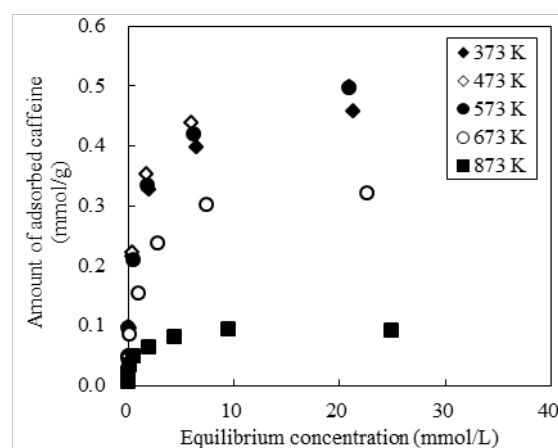


Fig. 4 Adsorption isotherms of caffeine on montmorillonite with calcination treatment.

water molecules for cations between the layers and did not take in water molecules between the layers. This result shows, based on Fig. 1, that rehydration within the structure of calcined montmorillonite at 573 K, 673 K, and 873 K were prevented.

The SR-XRD patterns of montmorillonite after a caffeine adsorption test are shown in Fig. 3. The region from about 2 to 10 ° where diffraction peaks, indicating reflection corresponding to the basal distance in the structure (basal reflection), is magnified. Montmorillonite without adsorbed caffeine was confirmed to have a diffraction peak at 3.69 ° indicating its basal distance. On the other hand, a diffraction peak at 3.75 ° was identified with its strength decreased to 85 % for montmorillonite having adsorbed caffeine. According to the change of diffraction peak, it is probable that caffeine molecules are intercalated between the layers of montmorillonite.

Fig. 4 shows the results when measuring the amount of adsorbed caffeine on montmorillonite

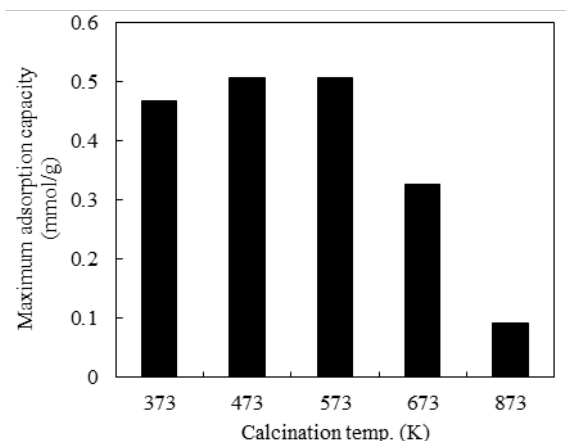


Fig. 5 Maximum adsorption capacity determined from the adsorption isotherm.

with calcination treatment. Fig. 4 plots test results for the adsorption of caffeine on montmorillonite. The horizontal axis shows the equilibrium concentration (mmol/L) after adsorption equilibrium is reached, and the vertical axis shows the amount of adsorbed caffeine (mmol/g) at adsorption equilibrium. The maximum adsorption capacities (Q_{max}) were also determined from the adsorption isotherm equation (Eq. 2) based on the adsorption test of caffeine. The maximum adsorption capacities are shown in Fig. 5. The maximum adsorption capacity was 0.51 mmol/g for the samples of montmorillonite calcined at 473 K and 573 K. It is 1.08 times higher than the adsorption capacity of montmorillonite calcined at 373 K. The maximum adsorption capacity of montmorillonite calcined at 673 K was 0.33 mmol/g, and that of montmorillonite calcined at 873 K was 0.09 mmol/g. These reduced maximum adsorption capacities occur because the intercalation of caffeine between the layers of montmorillonite is less likely due to the structural changes in montmorillonite as shown in Fig. 1. It is considered that the montmorillonite samples calcined at 673 K and 873 K had a reduced adsorption capacity for caffeine because caffeine molecules are no longer intercalated between the layers. It is indicated that the adsorption of caffeine on the samples of montmorillonite calcined at 673 K and 873 K were occurred on the surfaces and end faces of adsorbent. In addition, according to the results shown in Table 3 and Fig. 5, no correlation was found between cation exchange capacity (CEC) and amount of adsorbed caffeine at all calcination temperatures ($R=0.54$). Based on this result, it is probable that the adsorption of caffeine on montmorillonite does not involve electrostatic adsorption to which cation exchange capacity makes a contribution.

In the future, the effects of water molecules on structural changes of montmorillonite during

calcination treatment need to be observed. The structure of montmorillonite in water and in a wet state should be analyzed accurately, and the reversibility/irreversibility of its dehydration and rehydration should be observed and quantified.

4. CONCLUSION

The measurement results show the following:

1. Montmorillonite with calcination treatment above 573 K shows irreversible dehydration in its structure. Two types of analysis—structure analysis with SR-XRD and quantitative evaluation of exchangeable cations—were performed, and both support this conclusion.
2. Because the montmorillonite samples that had been calcined at 673 K and 873 K indicated a reduction in the amount of caffeine adsorbed, adsorption of caffeine on montmorillonite without a calcination treatment is shown to involve intercalation between the layers of montmorillonite.
3. Montmorillonite calcined at 673 K and 873 K is confirmed to adsorb caffeine. Therefore, regarding the adsorption phenomenon of caffeine on montmorillonite, the possibility of adsorption even on the surfaces and end faces of layers of montmorillonite is suggested, as well as intercalation into the layers.

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