

MODIFIED METHOD FOR BENTONITE PURIFICATION AND CHARACTERIZATION; A CASE STUDY USING BENTONITE FROM TSUNAGI MINE, NIIGATA, JAPAN

TAKAYUKI HAYAKAWA¹, MAKOTO MINASE¹, KEN-ICHI FUJITA¹, AND MAKOTO OGAWA^{2,*}

¹ Laboratory of Applied Clay Technology, Hojun Co., Ltd., An-naka, Gunma 379-0133, Japan

² School of Energy Science and Engineering, Vidyasirimedhi Institute of Science and Technology (VISTEC), 555 Moo 1 Payupnai, Wangchan, Rayong 21210, Thailand

Abstract—A modified procedure for bentonite purification and a new method for the quantitative characterization of bentonite using smectite content are reported. Bentonite found in a drill core of Tsunagi Mine, Niigata, Japan was evaluated by the new method to demonstrate the substantial increase in smectite content from 40% in the original bentonite to 75% after purification using a new procedure. Powder samples were prepared by putting blocks of bentonite into acetone to remove water without mechanical crushing. The powdered, acetone-dried bentonite was purified by a dispersion-sedimentation method in water after cation exchange of the interlayer Ca^{2+} ion with Na^+ ion by the reaction of raw bentonite with aqueous NaCl. The purification was evaluated using X-ray diffraction and thermogravimetric analyses (TG). The raw bentonite contained feldspar, quartz, and cristobalite, and feldspar and quartz were removed by the new purification procedure. The purification was evaluated quantitatively by comparing the TG data before and after the purification. The purified bentonite swelled in water to give a stable aqueous suspension and 3 g of purified bentonite dispersed in 60 mL of water was stable for several days. The replacement of interlayer sodium with dibehenyldimethylammonium gave an organophilic clay, which swelled in toluene. The bentonite has potential practical uses as a purified bentonite and an organophilic bentonite.

Key Words—Dibehenyldimethylammonium, Didococylidimethylammonium, Ion Exchange, Organic Modification, Purified Bentonite, Suspension, Transparency, Viscosity.

INTRODUCTION

The industrial application of bentonite is widespread from civil engineering to the food industry (Grim, 1962; van Olphen, 1977; Bergaya *et al.*, 2006). In addition to the on-going industrial applications, advanced materials application of montmorillonite (or purified bentonite) has been investigated extensively in the fields of chemistry and biochemistry related areas (Ogawa, 1998; Bergaya *et al.*, 2006; Takagi *et al.*, 2006; Ruiz-Hitzky *et al.*, 2011; Okada *et al.*, 2012, 2014; Takagi *et al.*, 2013). The performance of raw bentonite is determined by the smectite content and type (composition, particle size, and *etc.*) as well as the kind and the amounts of other minerals such as quartz and cristobalite. When the bentonite purification is complete and non-smectite minerals removed effectively, the purified bentonite properties can be determined by such chemical aspects as cation exchange capacity, interlayer cation type, type of isomorphous substitution, and smectite particle size. Accordingly, the variation of natural resource materials and the proper understanding of bentonite properties are important issues in bentonite industries to seek materials with better performing

materials as well as identify emerging new applications of bentonites and bentonite derivatives.

In this paper, a modified procedure for bentonite purification and a new method for the quantitative characterization of bentonite based on smectite content in bentonite are reported. Bentonite found in a drill core of Tsunagi mine, Niigata, Japan, was used in the present study, because the mine is new and bentonite from it has not been characterized yet. Powdered raw bentonite was obtained by placing blocks of bentonite into acetone in order to remove water and to avoid the mechanical effect of crushing. The acetone-dried bentonite was used as the starting material for purification and organic modification.

The bentonite interlayer cations were replaced with Na^+ cations to obtain a stable aqueous dispersion (van Olphen, 1977). The stable bentonite suspension was suitable for efficient smectite purification by the conventional dispersion-sedimentation method. In addition, the interlayer Na^+ cations were exchanged with a cationic surfactant to produce an organophilic clay. Organophilic clays prepared from purified bentonite and raw bentonite by cation exchange with surfactants are recognized as important materials for a wide variety of practical uses (Jordan, 1950; Barrer, 1978; Lagaly, 1981; Pinnavaia *et al.*, 2001; Okada *et al.*, 2014) and have been investigated, more recently, for advanced materials application (Bergaya *et al.*, 2006; Takagi *et al.*, 2006;

* E-mail address of corresponding author:

makoto.ogawa@vistec.ac.th

DOI: 10.1346/CCMN.2016.0640303

Heinz *et al.*, 2007, 2008; Heinz, 2012; Okada *et al.*, 2012, 2014).

Among quaternary ammonium surfactants, dialkyldimethylammonium salts, namely dioctadecyldimethylammonium chloride ($C_{40}H_{80}NCl$), are unique materials with the ability to form lamellar mesophases in aqueous solution as well as in the solid state. (Dubois *et al.*, 1993, 1994; Hubert *et al.*, 2000; Isayama *et al.*, 1993; Kunitake *et al.*, 1977a, 1977b; Machida *et al.*, 2014; Ogawa, 1997; Zhang *et al.*, 2007). Intercalation of dialkyldimethylammonium ions into the interlayer space of smectites and other layered silicates has been reported and large basal spacings due to the large molecular size have been observed (Lagaly, 1981, 1986; Inukai *et al.*, 1994; Nagase *et al.*, 2002; Minase *et al.*, 2008; Kinashi *et al.*, 2009; Ogawa and Iwata, 2010; Fujii *et al.*, 2011). Taking advantage of the highly hydrophobic nature, the dioctadecyldimethylammonium-montmorillonites have been used as rheology-controlling reagents and several commercially available products are available. Dialkyldimethylammonium-smectites are able to adsorb organic contaminants from environments (Kukkadapu and Boyd, 1995; Xu *et al.*, 1997). In addition, these materials have been used as supports to accommodate various functional molecular species to control photochemical reactions (Seki and Ichimura, 1990; Ogawa *et al.*, 1995, 1996, 1999, 2008, 2009; Kakegawa and Ogawa, 2002; Sasai *et al.*, 2003) and to produce membranes for catalytic reactors and for separations (Okahata and Shimizu, 1989; Kleinfeld and Ferguson, 1994; Ahmadi and Rusling, 1995).

In the present study, dibehenyldimethylammonium (abbreviated hereafter as 2C22) was used for the organic

modification of bentonite because the long alkyl chain is suitable for preparation of a highly organophilic clay and can be used to estimate the layer-charge density. The cation exchange capacity (CEC, or layer charge density) is recognized as an important parameter to determine the performance of smectites and, therefore, several methods have been used to determine the layer charge (Lagaly, 1981; Mermut, 1994). As far as the authors are aware, no study on the preparation and characterization of dibehenyldimethylammonium-exchanged smectites has been reported previously.

EXPERIMENTAL

Materials and methods

Bentonite was obtained from a drill core of Tsunagi mine, Niigata, Japan, and the bentonite fraction at a depth of 5 m from the ground surface was collected. Acetone, toluene, ethanol, 2-propanol, ammonium acetate, potassium chloride, and sodium hydroxide were purchased as extra-pure grade from Kanto Chem. Co. (Chuo-ku, Japan) and used as received. Dibehenyldimethylammonium chloride ($(C_{22}H_{45})_2(CH_3)_2NCl$, also called didococyltrimethylammonium chloride) was obtained from Lion Co. (Tokyo, Japan) and used without further purification.

A block of bentonite (200 g) was placed in acetone (400 mL) to dehydrate and collapse the block as shown in Figure 1. Then, the solid was separated from acetone by decantation, and air dried to obtain a powder sample without mechanical crushing. For comparison, another block of bentonite was oven dried at 120°C and subsequently crushed mechanically into a powder.

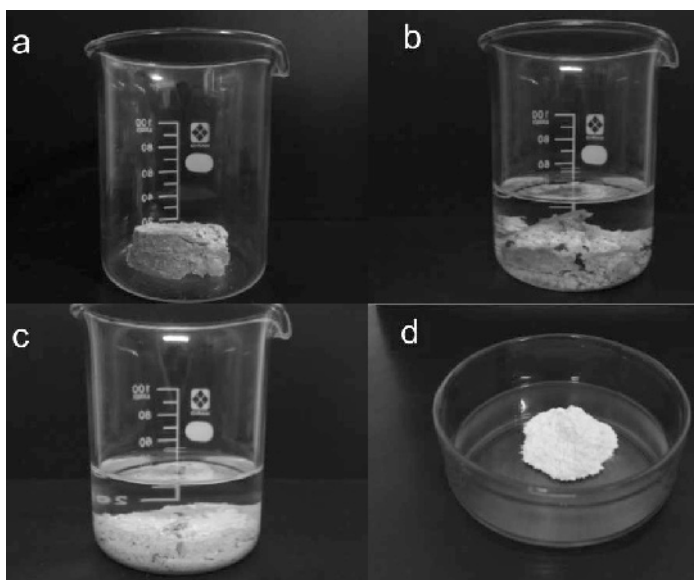


Figure 1. Photographs of: (a) a bentonite block from the drill core; (b, c) the bentonite block during contact with acetone. Part d shows the bentonite powder thus obtained.

The powder sample (designated as raw material; ~100 g) was dispersed into water (1 L), and NaCl (58 g) was added to the suspension. The 58 g of NaCl is equal to one equivalent of Na^+ per 100 g clay and is significantly in excess of the CEC of montmorillonite (Grim, 1953, 1962; van Olphen, 1977; Bergaya *et al.*, 2006). The mixture was stirred vigorously with an homogenizer (1000 rpm) for 1 h. After the mixture was stored for 3 days, the solid sample was separated from the suspension by centrifugation (3000 rpm for 7 min; $1,086 \times g$) and dried at 60°C in air (this sample was designated as the Na-exchanged form).

The Na-exchanged form of the bentonite was used in the following two experiments, one for purification and the other for organic modification. These two forms (purified bentonite and organophilic bentonite) are common and useful bentonite-derived products. Purified bentonite was produced from the Na-exchanged form by a conventional dispersion-sedimentation method, in which an aqueous clay suspension was prepared carefully using an homogenizer to disperse the clay and centrifugation was used to separate the $<2 \mu\text{m}$ fraction to remove non-expandable impurities. Organic modification of the purified bentonite was done by ion exchange with dibehnyldimethylammonium cations using an aqueous 2-propanol solution (25% 2-propanol, 75% water) of 2C22 chloride, where the amount of 2C22 added was equal to 100 meq/100 g of clay. An homogenizer was used for mixing and ion exchange was conducted at room temperature for 1 day. The samples were washed with water repeatedly until a negative AgNO_3 test for chloride was obtained.

Characterization

Powder X-ray diffraction (XRD) patterns of the products were recorded on a Rigaku Ultima IV powder diffractometer (Rigaku, Tokyo, Japan) equipped with Ni-filtered $\text{CuK}\alpha$ radiation operated at 40 mA and 40 kV with the step width of 0.0200° , scan speed of $2.00^\circ/\text{min}$, divergence slit (DS) of $1/2^\circ$, scattering slit (SS) of $1/2^\circ$, and receiving slit (RS) of 0.3 mm. The powder sample was mounted in a sample holder. Thermogravimetric (TG) and differential thermal analysis (DTA) curves were recorded on a Rigaku Thermoplus TG8120 (Rigaku, Tokyo, Japan) in air (no flow) at a heating rate of $10 \text{ K}/\text{min}$ using alpha-alumina as the standard. The CEC was determined by the ammonium acetate method (Schollenberger and Simon, 1945). Interlayer cation sites were saturated with ammonium ion by reaction with aqueous ammonium acetate. The eluent was analyzed by atomic absorption (AA) spectroscopy (Shimadzu atomic absorption spectrometer AA-7000, Shimadzu Co., Kyoto, Japan) to determine the types of interlayer cation. Then, the ammonium was desorbed by reaction with excess KCl and the amount of eluted ammonium ion was determined by the Kjeldahl method and used to calculate CEC (Kjeldahl and Christoffer, 1883)

RESULTS AND DISCUSSION

Powdered bentonite was obtained by means of the treatment of a bentonite block with acetone and subsequent air drying (Figure 1). The X-ray diffraction patterns of the bentonite powders obtained by the two different procedures (acetone immersion and mechanical crushing) are shown in Figure 2 (traces a and b). In the conventional industrial process as well as in laboratory experiments, bentonite was dried and crushed mechanically to obtain a powder sample. The drying and crushing procedures are thought to alter the performance of the products. The procedure developed here to prepare bentonite powder by immersion in acetone is better because heating and mechanical crushing were unnecessary.

The powdered bentonite was ion exchanged with sodium and purified subsequently by a dispersion-sedimentation method. In the XRD patterns of the raw bentonites (Figures 2a, 2b), the diffraction peaks characteristic of smectite are seen clearly. The diffraction peaks observed for the purified bentonite (Figure 2c) are sharp compared with those observed for powdered bentonite prepared by conventional means (drying and mechanical crushing). The diffraction peaks characteristic of the layered structure of smectite with the basal spacing of 1.25 nm and $(hk0)$ reflection at 0.45 nm were observed to confirm the presence of Na-smectite in the sample after the purification (Figure 2c). The basal spacing of the raw bentonite was 1.39 nm, typical of Ca-smectite (Grim, 1953, 1962).

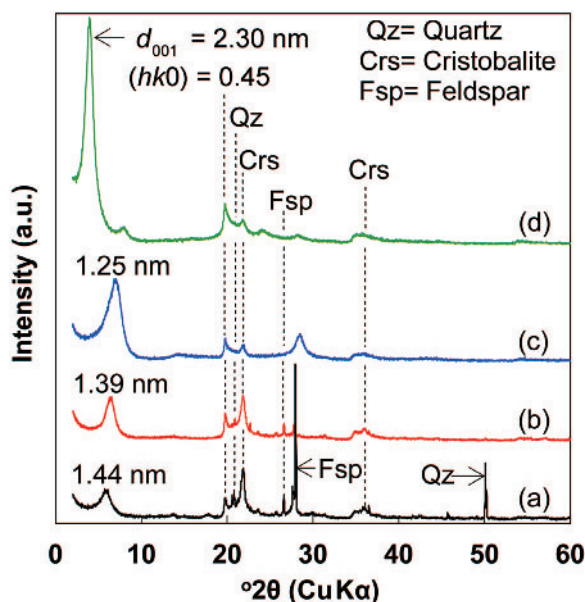


Figure 2. XRD patterns of the raw bentonites: (a) obtained by conventional drying and crushing; and (b) obtained by immersion of bentonite block in acetone; (c) purified bentonite; and (d) 2C22-exchanged form.

Quartz, feldspar, and cristobalite were detected in the raw bentonite XRD pattern, while quartz and feldspar were largely removed by the purification procedure as shown by the differences in the XRD patterns before and after purification (Figure 2, compare traces b and c). In order to remove cristobalite completely, the purification procedure must be improved, *e.g.* by repeating the procedure, prolonged aging time, and more careful dispersion using such techniques as sonication and milling, and longer sedimentation times.

In order to examine the purification procedure in a more quantitative manner, thermal analysis was used here. In the TG-DTA curves of the purified and the raw bentonites (Figure 3), typical thermal decomposition of smectite was observed; two endothermic reactions in the DTA curves starting from room temperature and at $\sim 500^\circ\text{C}$ accompanied weight losses in the corresponding TG curves due to the loss of adsorbed water and dehydroxylation of the silicate layer. Non-smectite minerals, such as quartz, cristobalite, and feldspar, were found in the unpurified Tsunagi bentonite. The non-smectite minerals are thermally stable and show no weight loss by heat treatment in air below 800°C as used in the TG-DTA analyses. The mass losses observed in the TG curves were from the smectite portion (Grim, 1962; Bergaya *et al.*, 2006). Weight losses were smaller for the raw bentonite (Figure 3) and suggest that quartz and cristobalite, which are thermally stable in the temperature range ($\sim 1000^\circ\text{C}$) of the TG-DTA analyses and give no weight loss, were removed by the purification procedure. For the raw bentonite, the mass loss due to the dehydroxylation at $\sim 400\text{--}700^\circ\text{C}$ was 2%. The resulting ash, which formed as a result of dehydration and dehydroxylation of bentonite, was 90%. From the weight-loss values, the ratio of the hydroxyl group (2%) in the silicate layer to the ash (90%) was calculated to be 2.2%, $2/(90+2)$. Hereafter, this value was designated as OH/ash ratio. The OH/ash ratio of pure montmorillonite was also calculated from the ideal formula $[\text{Ca}_{0.17}\text{Si}_8(\text{Al}_{3.34}\text{Mg}_{0.66})\text{O}_{20}(\text{OH})_4]$ of Ca-montmorillonite (Grim, 1953) to be 5.2%. The ratio (relative OH/ash ratio to the ideal value) was used as a measure of montmorillonite content in bentonite. The OH/ash ratio of the Tsunagi bentonite (2.2%) was divided by the ideal value (5.2%) to give 40%, which corresponds with the smectite content in the bentonite. Because the method is based on the mass loss in the

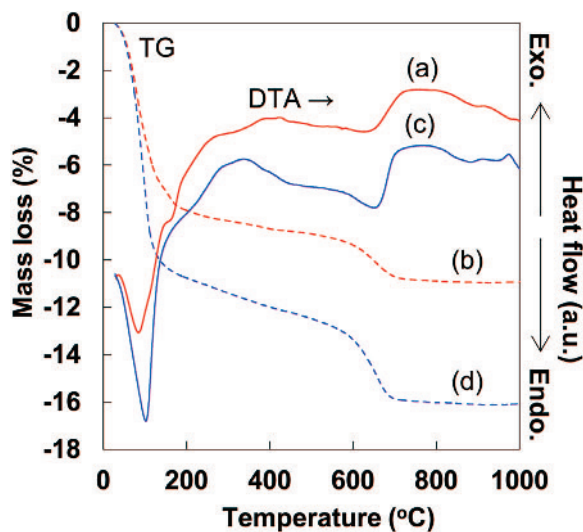


Figure 3. TG and DTA curves of raw bentonite (a = DTA, b = TG) and purified bentonite (c = DTA, d = TG).

temperature range of $400\text{--}700^\circ\text{C}$, any kind of associated minerals which decompose in this temperature range might affect the estimated smectite content. To use this method effectively, hydroxyl-bearing minerals and carbonates should not be present as associated minerals. The amount determined from the OH/ash ratio is a rough estimate based on the ideal chemical formula of montmorillonite.

The OH/ash ratio was compared between the samples before and after purification. After the purification procedure, the OH/ash ratio increased to 3.5%, which corresponds to a smectite content of 75%. This confirms the successful and efficient purification (or concentration of smectite) in the bentonite (Table 1). Because the smectite content of bentonite (*i.e.* purity) is one of the most important parameters needed to characterize bentonite quality, the quantification of the montmorillonite fraction in bentonite has been reported previously (Kaufhold *et al.*, 2002, 2012; Lopez-Galindo *et al.*, 2007) and each method has its advantages and disadvantages. The method proposed here, using TG analysis may be a simple way to determine the smectite content in bentonites.

The interlayer cation compositions of raw bentonite, the Na-exchanged form, and the purified bentonite were determined by AA for the eluents obtained by ion

Table 1. Quantitative data derived from TG results.

Sample	Mass loss of dehydroxylation (mass %)	Ash (mass %)	Dehydroxyl/ash (%)	Calculated purity (%)
Ideal montmorillonite	5	95	5.2	100
Raw bentonite	2	90	2.2	40
Purified bentonite	3	84	3.5	75

Table 2. Bentonite sample cation exchange capacity and interlayer cation composition (meq/100 g clay).

Sample	CEC	Interlayer cation				Total
		Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	
Raw bentonite	60	12	3	27	24	66
Na-exchanged form	62	38	2	15	14	69
Purified bentonite	100	67	1	18	22	108

exchange of the samples with ammonium acetate (Table 1). The CEC values of raw bentonite, of the Na-exchanged form, and of the purified bentonite were determined to be 60, 62, and 100 meq/100 g of clay, respectively. These values were within the range of a typical smectite (Bergaya *et al.*, 2006). The increase in the CEC value by the purification (from 60 to 100 meq/100 g clay) was important evidence of the successful removal of low-CEC impurities such as quartz and feldspar based on the differences in the XRD patterns and TG curves before and after purification.

For the raw bentonite, calcium was the major interlayer cation as shown by the chemical analysis (AA spectroscopy) of the ammonium acetate eluent. Only part of the calcium was exchanged successfully with Na⁺ by ion exchange with NaCl (Table 2). As a result, the Na-exchanged form was prepared to give a stable aqueous suspension as seen in Figure 4. Thus, due to efficient swelling of the Na-exchanged form, the sample was purified by the dispersion-sedimentation method. From the difference in the CEC (from 60 to 100 meq/100 g of clay), the smectite content increased by 1.7 times using the purification procedure.

As for organic modification of the bentonite, the XRD pattern of the 2C22-exchanged form (Figure 2, trace d) clearly has diffraction peaks due to the (00 l) plane. From the observed d_{001} value (2.3 nm), the intercalated 2C22 might form a pseudo-trimolecular layer in the interlayer space of montmorillonite (Lagaly, 1981; Ogawa *et al.*, 1995, 2008, 2009). In the TG-DTA curves of the 2C22-exchanged bentonite sample (Figure 5), exothermic reactions accompanied mass loss in the TG curve due to oxidative decomposition of adsorbed 2C22 ion were observed in the temperature range of 200–700°C. From the TG analysis (mass loss of 35% and the amount of the ash as dehydroxylated clay), the amount of 2C22 adsorbed was calculated as 70 meq/100 g clay. The mass loss due to the decomposition of 2C22 was determined by subtracting the hydroxyl-group content of the purified montmorillonite, 3%, from the ash, which was derived from the TG curve (Figure 3d) of the purified bentonite from the observed mass loss (35%) in the temperature range of 200–700°C. The value is smaller than the CEC of the purified bentonite (100 meq/100 g of clay), which was determined by the ammonium acetate method. When the unpurified Na form was modified with 2C22, the

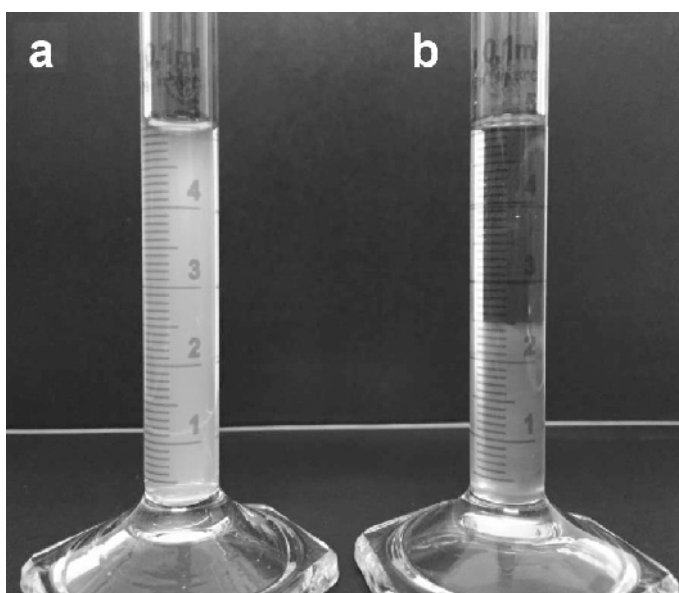


Figure 4. Photographs of (a) purified bentonite aqueous suspension and (b) the 2C22-exchanged form suspended in toluene.

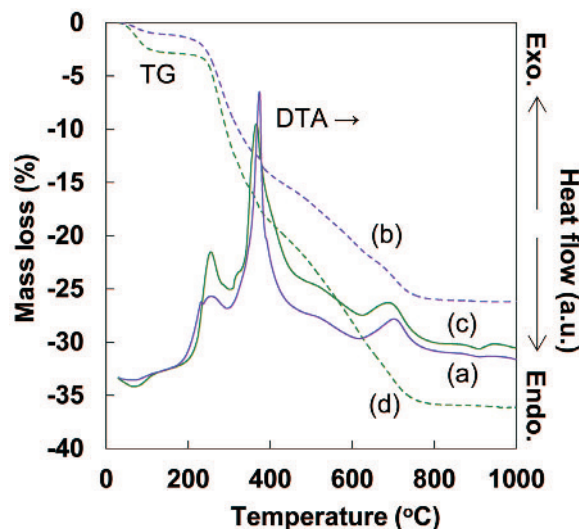


Figure 5. TG and DTA curves of 2C22-exchanged Na-form: (a = DTA, b = TG), and purified bentonite (c = DTA, d = TG). Exo. = exothermic and Endo. = endothermic.

amount of 2C22 adsorbed was 42 meq/100 g of clay as determined from TG analysis (25% mass loss). Based on the XRD pattern with the single-phase (00 l) diffraction peaks, the interlayer cations of the present bentonite had clearly been c exchanged efficiently with 2C22.

The 2C22-exchanged form swelled in organic solvents. As an example, the 2C22-exchanged, purified bentonite suspended in toluene (0.1 g in 5 mL of toluene) is shown in Figure 4b as an example. The volume of the 2C22, purified bentonite suspended in toluene, was estimated to be 25 mL/g sample, quite high when compared with commercial organophilic bentonites. The origin of the favorable swelling characteristics was thought to be due to the moderate CEC of the Tsunagi smectite and the molecular nature of 2C22, which is more hydrophobic than the 2C18 (dioctadecyldimethylammonium) commonly used for organic modification of smectite (Okahata and Shimizu, 1989; Seki and Ichimura, 1990; Inukai *et al.*, 1994; Kleinfeld and Ferguson, 1994; Ahmadi and Rusling, 1995; Ogawa *et al.*, 1995, 1996, 1999; Kakegawa and Ogawa, 2002; Nagase *et al.*, 2002; Sasai *et al.*, 2003; Kinashi *et al.*, 2009; Fujii *et al.*, 2011).

In order to clarify the origin of the favorable swelling in toluene, organic modification of the Tsunagi purified bentonite using other cationic surfactants is under investigation. The rheological properties of the suspension (both Na-form in water and 2C22-form in organic solvents) and the adsorptive properties of organic derivatives of the Tsunagi bentonite toward various organic species in vapor or in solution are also worth investigating because bentonites with different origins have been reported to have different properties (Boyd *et al.*, 1988; Kukkadapu and Boyd, 1995; Xu *et al.*, 1997; Okada *et al.*, 2012, 2014).

CONCLUSIONS

A method for quantifying the smectite fraction in bentonites and a method for bentonite sample preparation were reported using bentonite found in a drill core of Tsunagi Mine, Niigata, Japan. A bentonite powder sample, which was obtained by drying a block of bentonite in acetone without mechanical crushing, and purifying the acetone-dried bentonite by a conventional dispersion-sedimentation method in water. The bentonite powder was cation exchanged with excess aqueous NaCl before dispersion/sedimentation in order to achieve efficient purification. Quartz and feldspar were effectively removed by the purification, while complete removal of cristobalite was difficult. The purification was monitored by XRD and TG. The increase in smectite content by the purification procedure was evaluated quantitatively using TG analysis. The purified bentonite had a CEC of 100 meq/100 g of clay as determined by the ammonium acetate method and gave a stable aqueous suspension. Ion exchange of the purified bentonite with dibehnyldimethylammonium chloride successfully produced an organophilic clay, which swelled in organic solvents. These results confirmed the potential of the bentonite found in Tsunagi Mine, Niigata, Japan, as a raw material for important products including purified bentonite and organophilic bentonite.

REFERENCES

- Ahmadi, M. and Rusling, J.F. (1995) Fluorescence studies of solute microenvironment in composite clay-surfactant films. *Langmuir*, **11**, 94–100.
- Barrer, R.M. (1978) *Zeolites and Clay Minerals as Sorbents and Molecular Sieves*. Academic Press, London.
- Bergaya, F., Theng, B.K.G., and Lagaly, G. (editors) (2006) *Handbook of Clay Science*. Elsevier Science, Amsterdam.
- Boyd, A.S., Lee, J., and Mortland, M.M. (1988) Attenuating organic contaminant mobility by soil modification. *Nature*, **333**, 345–347.
- Dubois, M. and Cabane, B. (1994) Polymerization of silicic acid in a collapsed lamellar phase. *Langmuir*, **10**, 1615–1617.
- Dubois, M., Guik-Krzywicki, T., and Cabane, B. (1993) Growth of silica polymers in a lamellar mesophase. *Langmuir*, **9**, 673–680.
- Fujii, K., Kuroda, T., Sakoda, K., and Iyi, N. (2011) Fluorescence resonance energy transfer and arrangements fluorophores in integrated coumarin/cyanine systems within solid-state two-dimensional nanospace. *Journal of Photochemistry and Photobiology A: Chemistry*, **225**, 125–134.
- Grim, R.E. (1953) *Clay Mineralogy*. McGraw-Hill, New York.
- Grim, R.E. (1962) *Applied Clay Mineralogy*. McGraw-Hill, New York.
- Heinz, H. (2012) Clay minerals for nanocomposites and biotechnology: surface modification, dynamics and responses to stimuli. *Clay Minerals*, **47**, 205–230.
- Heinz, H., Vaia, R.A., Krishnamoorti, R., and Farmer, B.L. (2007) Self-assembly of alkylammonium chains on montmorillonite: effect of chain length, head group structure, and cation exchange capacity. *Chemistry of Materials*, **19**, 59–68.

- Heinz, H., Vaia, R.A., and Farmer, B.L. (2008) Relation between packing density and thermal transitions of alkyl chains on layered silicate and metal surfaces. *Langmuir*, **24**, 3727–3733.
- Hubert, D.H.W., Jung, M., Fredrik, P.M., Bomans, P.H.H., Meiddijk, J., and German, A.L. (2000) Vesicle-directed growth of silica. *Advanced Materials*, **12**, 1286–1290.
- Inukai, K., Hotta, Y., Taniguchi, M., Tomura, S., and Yamagishi, A. (1994) Formation of a clay monolayer at an air-water interface. *Journal of the Chemical Society, Chemical Communications*, 959–960.
- Isayama, M., Sakata, K., and Kunitake, T. (1993) Preparation of a self-supporting, multilayered film of montmorillonite. *Chemistry Letters*, **22**, 1283–1286.
- Jordan, J.W. (1950) Organophilic bentonites. I. Swelling in organic liquids. *The Journal of Physical and Colloid Chemistry*, **54**, 294–306.
- Kakegawa, N. and Ogawa, M. (2002) The intercalation of β -carotene into the organophilic interlayer space of dialkylmethylammonium-montmorillonites. *Applied Clay Science*, **22**, 137–144.
- Kaufhold, S., Dohrmann, R., and Meyer, M.F. (2002) Comparison of methods for the quantification of montmorillonite in bentonite. *Applied Clay Science*, **22**, 145–151.
- Kaufhold, S., Hein, M., Dohrmann, R., and Ufer, K. (2012) Quantification of the mineralogical composition of clays using FTIR spectroscopy. *Journal of Vibrational Spectroscopy*, **59**, 29–39.
- Kinashi, K., Kita, H., Misaki, M., Koshihara, Y., Ishida, K., Ueda, Y., and Ishida, M. (2009) Fabrication and optical properties of photochromic compound/clay hybrid films. *Journal of Thin Solid Films*, **518**, 651–655.
- Kjeldahl, J.G. and Christoffer T. (1883) Neue Methode zur Bestimmung des Stickstoffs in organischen Körper. *Zeitschrift für Analytische Chemie*, **22**, 366–382.
- Kleinfeld, R.E. and Ferguson, S.G. (1994) Stepwise formation of multilayered nanostructural films from macromolecular precursors. *Science*, **265**, 370–373.
- Kukkadapu, R.K. and Boyd, S.A. (1995) Tetramethylphosphonium- and tetramethylammonium-smectites as adsorbents of aromatic and chlorinated hydrocarbons: effect of water on adsorption efficiency. *Clays and Clay Minerals*, **43**, 318–323.
- Kunitake, T. and Okahata, Y. (1977a) A totally synthetic bilayer membrane. *Journal of the American Chemical Society*, **99**, 3860–3861.
- Kunitake, T., Okahata, Y., Tamaki, K., Kumamaru, F., and Takayanagi, M. (1977b) Formation of the bilayer membrane from a series of quaternary ammonium salts. *Chemistry Letters*, 387–390.
- Lagaly, G. (1981) Characterization of clays by organic compounds. *Clay Minerals*, **16**, 1–21.
- Lagaly, G. (1986) Interaction of alkylamines with different types of layered compounds. *Solid State Ionics*, **22**, 43–51.
- Lopez-Galindo, A., Viseras, C., and Cerezo, P. (2007) Compositional, technical and safety specifications of clays to be used as pharmaceutical and cosmetic products. *Applied Clay Science*, **36**, 51–63.
- Machida, S., Yoshida, T., Hashimoto, R., and Ogawa, M. (2014) Well-defined plate and hollow disk shaped particles of silica-dialkylmethylammonium hybrids. *Journal of Colloid and Interface Science*, **420**, 66–69.
- Mermut, A.R. (1994) *Layer Charge Characteristics of 2:1 Silicate Clay Minerals*. CMS workshop lectures, Vol. 6, The Clay Minerals Society, Aurora, Colorado, USA.
- Minase, M., Kondo, M., Onikata, M., and Kawamura, K., (2008) The viscosity of organic liquid suspensions of trimethyldecylammonium-montmorillonite complexes. *Clays and Clay Minerals*, **56**, 49–65.
- Nagase, T., Takahashi, Y., Suzuki, M.T., Ebina, T., Wakui, Y., and Onodera, Y. (2002) Fluorometric detection of *p*-chlorophenol by ZnTPP-intercalated dialkyl ammonium smectite. *Chemistry Letters*, 776–779.
- Ogawa, M. (1997) Preparation of silica-dialkylmethylammonium bromide nanocomposites. *Langmuir*, **13**, 1853–1855.
- Ogawa, M. (1998) Organized molecular assemblies on the surfaces of inorganic solids. *Annual Reports, Progress of Chemistry Section C: Physical Chemistry*, **94**, 209–257.
- Ogawa, M. and Iwata, D. (2010) Arrangements of interlayer quaternary ammonium ions in a layered silicate, octosilicate. *Crystal Growth and Design*, **10**, 2068–2072.
- Ogawa, M., Wada, T., and Kuroda, K. (1995) Intercalation of pyrene into alkylammonium-exchanged swelling layered silicates: the effects of the arrangements of the interlayer alkylammonium ions on the states of adsorbates. *Langmuir*, **11**, 4598–4600.
- Ogawa, M., Kimura, H., Kuroda, K., and Kato, C. (1996) Intercalation and the photochromism of azo dyes in the hydrophobic interlayer spaces of organoammonium-fluor-tetrasilicic micas. *Clay Science*, **10**, 57–66.
- Ogawa, M., Hama, M., and Kuroda, K. (1999) Photochromism of azobenzene in the hydrophobic interlayer spaces of dialkylmethylammonium-fluor-tetrasilicic micas. *Clay Minerals*, **34**, 213–220.
- Ogawa, M., Matsutomo, T., and Okada, T. (2008) Preparation of hectorite-like swelling silicate with controlled layer charge density. *Journal of the Ceramic Society of Japan*, **116**, 1309–1313.
- Ogawa, M., Matsutomo, T., and Okada, T. (2009) Preparation of iron containing hectorite-like swelling silicate. *Bulletin of the Chemical Society of Japan*, **82**, 408–412.
- Okada, T., Ide, Y., and Ogawa, M. (2012) Organic-inorganic hybrids based on ultrathin oxide layer-designed nanostructures for molecular recognition. *Chemistry – An Asian Journal*, **7**, 1980–1992.
- Okada, T., Seki, Y., and Ogawa, M. (2014) Designed nanostructures of clay for controlled adsorption of organic compounds. *Journal of Nanoscience and Nanotechnology*, **14**, 2121–2134.
- Okahata, Y. and Shimizu, A. (1989) Preparation of bilayer-intercalated clay films and permeation control responding to temperature, electric field, and ambient pH changes. *Langmuir*, **5**, 954–959.
- Pinnavaia, T.J. and Beall, G.W. (2001) *Polymer-Clay Nanocomposites*. John Wiley & Sons Ltd., New York.
- Ruiz-Hitzky, E., Aranda, P., Darder, M., and Ogawa, M. (2011) Hybrid and biohybrid silicate based materials: molecular vs. block-assembling bottom-up processes. *Chemical Society Reviews*, **40**, 801–828.
- Sasai, R., Sugiyama, D., Takahashi, S., Tong, Z., Shichi, T., Itoh, H., and Takagi, K. (2003) The removal and photodecomposition of *N*-nonylphenol using hydrophobic clay incorporated with copper-phthalocyanine in aqueous media. *Journal of Photochemistry and Photobiology A: Chemistry*, **155**, 223–229.
- Schollenberger, C.J. and Simon, R.H. (1945) Determination of exchange capacity and exchangeable bases in soil-ammonium acetate method. *Soil Science*, **59**, 13–24.
- Seki, T. and Ichimura, K. (1990) Thermal isomerization behaviors of a spiropyran in bilayers immobilized with a linear polymer and a smectitic clay. *Macromolecules*, **23**, 31–35.
- Takagi, S., Eguchi, M., Tryk, D., and Inoue, H. (2006) Porphyrin photochemistry in inorganic/organic hybrid materials: clays, layered semiconductors, nanotubes, and mesoporous materials. *Journal of Photochemistry and Photobiology C: Photochemistry Reviews*, **7**, 104–126.
- Takagi, S., Shimada, T., Ishida, Y., Fujimura, T., Masui, D.,

- Tachibana, H., Eguchi, M., and Inoue, H. (2013) Size-matching effect on inorganic nanosheets: control of distance, alignment, and orientation of molecular adsorption as a bottom-up methodology for nanomaterials. *Langmuir*, **29**, 2108–2119.
- Theng, B.K.G. (1979) *Formation and Properties of Clay-Polymer Complexes*. Elsevier Scientific Publishing Company, Amsterdam.
- van Olphen, H. (1977) *An Introduction to Clay Colloid Chemistry*, 2nd edition. Wiley-Interscience, New York.
- Xu, S., Sheng, G., and Boyd, A. S. (1997) Use of organoclays in pollution abatement. *Advances in Reviews*, **59**, 25–62.
- Zhang, L., Li, P., Liu, X., Du, L., and Wang, E. (2007) The effect of template phase on the structures of as-synthesized silica nanoparticles with fragile didodecyldimethylammonium bromide vesicles as templates. *Advanced Materials*, **19**, 4279–4283.

(Received 27 November 2015; revised 17 May 2016; Ms. 1073; AE: W.D. Huff)