PHYSICOCHEMICAL PROPERTIES OF BENTONITES: AN OVERVIEW

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ABSTRACT

Bentonites and their major clay mineral smectites have been among the more important industrial raw materials. Some of the applications are paint, paper, plastics, decolorization, chemical carriers, liquid barriers, foundry bondants, drilling fluids, desiccants, sealants, cosmetics, adhesives and catalysts. The purification and physicochemical modifications of pure smectites have a great importance to prepare some high technology materials such as pillared clays, organoclays, and polymer/smectite-nanocomposites. In this paper, besides general properties of bentonite, crystal structure, swelling, porosity, surface area, surface acidity, and ion exchange properties of smectites were discussed.

INTRODUCTION

Bentonites are the clay rocks altered from glassy igneous material such as a volcanic ash or tuff [1-3]. Bentonites have been used as industrial raw materials in numerous applications such as palletizing iron ores, foundry bond clay, ceramic, drilling mud, sealant, animal feed bond, bleaching clay, agricultural carrier, cat box adsorbent, adhesive, catalyst and catalyst support, desiccant, emulsion stabilizer, cosmetic, paint, pharmaceutical, civil engineering, pillared clay organoclay, and polymer-clay nanocomposites [4-8].

Bentonites are greatly affected from the acid activation, ion exchange, heating and hydrothermal treatments, and some other physicochemical processes [9-16]. For example, physicochemical properties such as strength, swelling, plasticity, cohesion, compressibility, particle size, cation-exchange capacity, pore structure, surface area, surface acidity and catalytic activity as well as the mineralogy can change considerably by these modifications [17-24].

Commercial importance of bentonites depends on the contents of their clay and nonclay minerals. Dominant clay minerals in bentonites are smectites such as montmorillonite, beidellite, saponite, nontronite, and hectrorite [25].

Bentonites are seldom found as monomineralic clays and may contain other clay and nonclay minerals and also some organic impurities. Nonclay minerals produce sharper X-ray diffraction (XRD) peaks than the smectites and other clay minerals, and this distinction is an important diagnostic criterion for their identification. The most common nonclay minerals in bentonites are silica polymorphs (silicas: quartz and opals), feldspars, zeolites, carbonates, sulfites, sulfides, sulfates, oxides and hydroxides [26].

STRUCTURE OF SMECTITES

Smectite is a 2:1 layer clay mineral and has two silica tetrahedral (T) sheets bonded to a central alumina octahedral (O) sheet as seen in Fig. 1 [27].
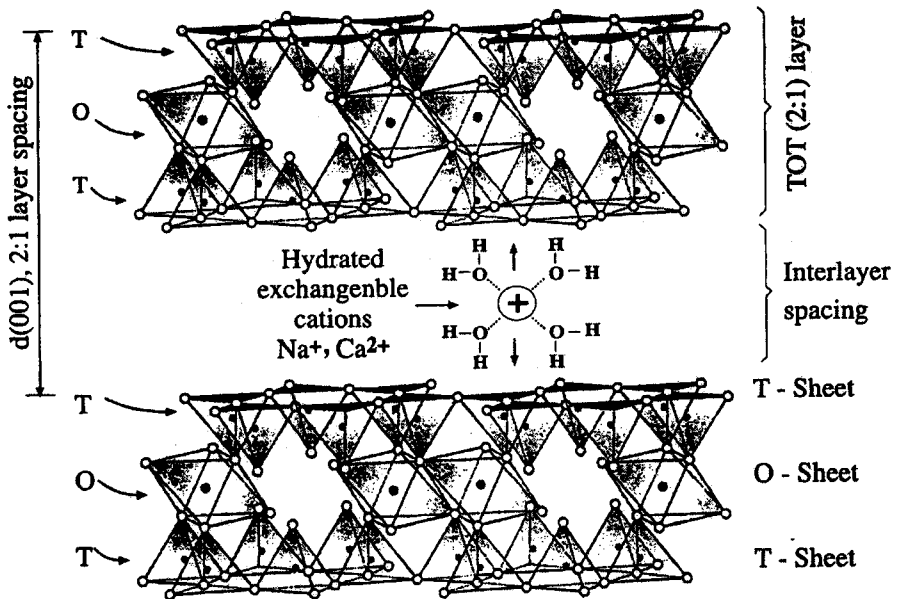
Fig. 1. The tetrahedral (T) and octahedral (O) sheets, TOT (2:1) layers, TOT (2:1) layer spacing [d (001)], interlayer spacing and hydrated exchangeable cations in a dioctahedral smectite mineral.

The net negative charge of the 2:1 (TOT) layers arising from the isomorphic substitution in the octahedral sheets of Fe^{2+} and Mg^{2+} for Al^{3+} and in tetrahedral sheets of Al^{3+} for Si^{4+} is balanced by the exchangeable cations such as Na^+, and Ca^{2+} located between the layers and around the edges. The mineral is called Na-smectite (NaS) or Ca-smectite (CaS) corresponding to the exchangeable cation which in Na^+ or Ca^{2+}. Industrial bentonites predominantly contain either Na-montmorillonite (NaM) or Ca-montmorillonite (CaM), and to much lesser extent other smectites. Bentonites are called Na-bentonite (NaB); Ca-bentonite (CaB) and NaCa-bentonite (NaCaB) corresponding to the abundance of the exchangeable cations. The equivalent amount of exchangeable cations in one kilogram smectite as well as other clay minerals and clays is defined cation exchange capacity (CEC).

The basal spacing, (d001), of the anhydrous smectites is approximately 1.0nm. The air dried NaS and CaS have respectively one water layer and two water layers in the interlayer, and their basal spacings are 1.26nm and 1.54nm respectively.

SWELLING

The physical state of smectite and corresponding bentonite may be changed with increasing water content, from an anhydrous solid to a hydrated material, semi-rigid plastic, gel, and suspension, respectively [28-31]. Smectite-water systems are of great importance for the agricultural, industrial, environmental and civil engineering activities such as barriers for water, protection nuclear waste, preparation desiccant, sealant, ceramic, cat box adsorbent, iron ore pellet, molding sand for foundry, and drilling mud for oil recovery [32-36].

The change in the physical state of a bentonite from an anhydrous solid to gel is called swelling [37,38]. The swelling of smectites occurs between the 2:1 (TOT) layers in agglomerated particles. Depending on the extent of the increase in the basal spacing, d(001), between two 2:1 layers, two types of SWE mechanisms can be purposed such as crystalline (initial or microscopic) SWE and osmotic (macroscopic) SWE [39-41].

Crystalline SWE results from the multimolecular adsorption of water on the basal crystal surface. Crystalline SWE occurs in a series of discrete steps, corresponding to the intercalation of 0, 1, 2, 3, and 4 layers of water molecules by adsorption from vapor phase [42-44]. Crystalline SWE is controlled by a balance between strong electrostatic-attraction and hydration-repulsion forces [45-49]. Thus, basal spacing is restricted in the range from 1.0nm to 2.2nm by the crystalline SWE. In this range, some of the physicochemical behaviors of swelling-shrinkage were investigated extensively [50-55].

The basal spacing, d(001), of a smectite may increase abruptly up to several decades nanometers depending on water content by osmotic swelling in liquid water [56,57]. Osmotic swelling was examined generally based on the diffuse double layer theory [58-61]. The increase in the basal spacing by SWE depends on the bentonite

mineralogy, extend of up taken water, and also size, valance, electronegativity, and hydration energy of exchangeable cations.

POROUS STRUCTURE

Smectites are porous clay minerals. The voids in a solid located among and within particles are called pore. The shape of the pores having different sizes can be cylindrical, parallel-sided silt, wedge, cavity, and ink-bottle. The empty spaces in a solid whose widths smaller than 2nm, between 2nm and 50nm, and greater than 50nm are called micropores, mesopores, and macropores, respectively [62-65]. The radius of a pore assumed to be cylindrical, can be taken as half of the pore width. The volume of pores in 1g solid is defined as specific pore volume. The area of the inner and outer walls of the pores in 1g of solid is taken as specific surface area. Surface area approximately originates from the walls of micropores and mesopores. The contribution of the macropore surface to the total surface area is negligible.

A number of methods have been used to obtain pore volume, surface area, and pore-size distribution. They include mercury porosimetry, low temperature gas adsorption-desorption, scanning electron microscopy, low angle X-ray diffraction, thermoporometry, filtration, and fluid-flow techniques [66-78].

ADSOPTION NON-POLAR MOLECULES

Smectites and other clay minerals do not adsorb non-polar molecules such as nitrogen, argon and ethane at elevated temperatures. These molecules can be adsorbed on smectites at their liquefaction temperatures but can not penetrate between the 2:1 (TOT) layers. Thus, the pore volume and the surface area obtained from an apolar molecule adsorption are less than whose theoretical values. Van der Waals forces are effective by the adsorption. Nitrogen is used generally as a non-polar molecule to determine the specific surface area and specific pore volume [79-83].

Several studies have been realized about the adsorption and desorption of nitrogen at the liquid nitrogen temperature (~77K) on the smectites, bentonites and their products [84-89]. The adsorption isotherms of all samples are similar to type II of the BDDT classification [90]. The adsorption and desorption isotherms show that the smectites and derivatives are micro-and mesoporous solids.

The specific surface area of the smectites as well as other porous materials can be determined from the nitrogen adsorption data by using the standard Brunauer, Emmett and Teller (BET) method and the others such as Lippens and de Boer (t-method), Sing (α_s-method), and Harkins and Jura (HJ) methods [91-95]. Monomolecular adsorption capacity and mean molecular area for nitrogen molecule must be used in BET method but in the other method do not use. The t-method and α_s-methods based on the t-curve and α_s-curve, respectively. These curves were determined previously from the nitrogen adsorption on the preselected reference

solids. The Harkins and Jura adsorption isotherm equation was derived thermodynamically. The specific surface area is determined absolutely by the HJ method without using other data. Langmuir, and Dubinin equations valid only for the monomolecular adsorption on the nonporous or microporous solids can not be used to determine of the specific surface area for the micro-mesoporous smectites [97,98].

The adsorption capacity as liquid nitrogen volume estimated from desorption isotherm at the relative equilibrium pressure of $p/p^0 = 0.96$ is taken as the specific micro-mesopore volume (V/cm^3g^{-1}) of a smectite as well as other porous solids. The specific micro-mesopore volumes can be also calculated by similar way at the relative pressures between 0.96 and 0.35. The corresponding pore radii (r/nm) at same interval are calculated from the corrected Kelvin equation by using desorption data. The plots drawn as V-r and dV/dr-r are called mesopore size distribution (MPSD) curves. The average mesopore radius is read from the maximum points of the dV/dr-r curve.

ADSOPTION POLAR MOLECULES

There are molecules between the 2:1 (TOT) layers of the natural smectites. Polar water molecules are adsorbed strongly by outgassed smectites and some other clay minerals [99]. The naturally interlayer water molecules in air dried smectites may replace by a variety of polar organic molecules such as short chain alcohols, glycerol, carbohydrates, ethylene glycol, ethylene glycol monoethyl ether (2-etoxyethanol), aliphatic and aromatic amines, and organic dyes [100-102]. Many organic molecules displace the water molecules from the interlayer cations more or less quantitatively. A part of the polar organic molecules more or less strongly solvate the interlayer cations, the others are associated between the solvation shells. Like the solvation of ions in solution the bonding strength between the interlayer cations and the solvent molecules covers the range from loose aggregates to complex bonding [103-108]. The specific surface area of smectites and other clay minerals can be determined from ethylene glycol, ethylene glycol monoethyl ether and polyvinylprolidone retentions measured gravimetrically [109-114].The surface areas obtained from these methods are greater 5-10 fold than the nitrogen surface areas and approach the theoretical values.

SURFACE ACIDITY

Smectites and some of other clay minerals behave as solid acid. Brönsted and Lewis acid sites on their surfaces are proton donors and electron pair acceptors respectively. The quantity of acid sites as moles (or number) in one gram solid is defined specific surface acidity ($n_m/molg^{-1}$) The acid strength of a solid surface is defined as its proton-donating and electron pair accepting abilities. Acid strength of a surface can be characterized by the equilibrium constant of its neutralization

reaction with a weak base. Surface acidity and acid strength have extensive and intensive properties respectively. They have been determined by different methods such as amine titration in presence of Hammett indicators, adsorption of some polar organic molecules having weak base character like as n-butylamine, pyridine, pyrine and trimethylamine nonaqueous solution and also vapor-phase adsorption of ammonia at elevated temperatures [115-127].

PILLARED CLAYS

The interlayer cations may exchange all inorganic and organic cations, and also hydrated hydroxy-polynuclearmetal cations. Layer-charge density and cation-exchange capacity have been determined by measuring one or more of these ion exchanges [128-136]. Na-smectite and H-smectite form by soda and acid activations, respectively. Pillared clays have been synthesized by intercalation of various polynuclearmetal cations in the interlayers after replacing by the exchangeable cations such as Na^+, H^+, and Ca^{2+} [137-141]. H-smectites and pillared clays are more porous materials than their natural forms with attractive catalytic properties [142-147].

ORGANOCLAYS

Bentonites or their major clay mineral smectites known to be an efficient gellent for water systems, were not effective in gelling organic liquids. However, smectites and corresponding bentonites have limited use as coagulant to remove organic pollutants from both drinking water and wastewater [148-151]. The increased threat of the environmental pollution by different organic compounds and especially pesticides promoted investigations to modify of bentonites on the use as sorbents for organic compounds instead of activated carbon used before. The focus of the researchs was on developing new hydrophilic and expanding lattice structure materials from natural bentonites.

It was seen that a bentonite having high swelling properties in water showed an aversion to water and a tendency to swell in various organic liquids after reaction with some organic ammonium salts [152-153]. An organophilic compound obtained by exchange of organic cations for inorganic interlayer cations in called generally as organoclay. The organoclays were found to be effective gellents for organic fluids.

Several investigations have been conducted since the first preparation of organoclays by Jordan in 1949. The surface properties of bentonites were modified greatly by replacing natural inorganic exchangeable cations by larger alkylammonium cations [154-163]. The metal cations are released into solution by the formation of organoclays. The intercalated organic cations act as pillars which hold the 2:1 layers permanently apart [164-169].

Organoclays may be prepared by using alkylammonium, α, w-alkyldiammonium and quaternary ammonium cations of the general forms $[CH_3(CH_2)_n\ NH_3]^+$, $[NH_3(CH_2)_n\ NH_3]^{2+}$ and $[(CH_3)_3\ NR]^+$ or $[(CH_3)_2\ NRR']^+$ respectively. Here, R and

R'are large non-polar alkyl groups with the 12 or greater C atoms and they may contain aromatic rings [170-180].

It was shown that quaternary ammonium cations with relatively large R groups such as hexadecyltrimethylammonium cation improved adsorptive capabilities of organoclays for the organic compounds. On the contrary, organoclays prepared by smaller organic cations like tetramethylammonium showed very weak adsorptive capabilities for the organic compounds especially for the phenolic compounds tested.

Furthermore, organic cations are fixed on smectite surface form an organic phase derived from alkyl groups [181]. This organic phase functions as a partition medium for non-polar organic compounds and is highly effective in removing such compounds from water [182-183]. Such small organic cations exist as discrete species on the smectite surface and do not form an organic partition phase. In this organoclays quaternary ammonium cations are separate from each other and function as pillars to permanently open the interlayers of smectite.

POLYMER-SMECTITE NANOCOMPOSITES

Recently, polymer-smectite nanocomposites have great importance, both in science and industry, because they often exhibit remarkable improvement in materials properties when compared with pure polymer or conventional micro-and macro-composites [184]. Some of these improvements are high module, increased biodegradability, increased strength and heat resistance and decreased gas permeability and flammability [184-200].

Such materials may be three different types such as intercalated, flocculated, and exfoliated nanocomposites. The intercalated nanocomposites form by the insertion of a polymer matrix between the 2:1 layers of smectite without collapsing of the crystal structure and any definite smectite to polymer ratio. The flocculated nanocomposites form same as intercalated nanocomposites, but 2:1 layer flocculated due to hydroxylated edge-edge interaction Exfoliated nanocoposites the individual 2:1 layers are separated in a continuous polymer matrix by an average distances that depends on smectite content. The smectite content is usually much lower than of an intercalated nanocomposite.

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BENTONİTLERİN FİZİKOKİMYASAL ÖZELİKLERİ: GENEL BAKIŞ

ÖZET

Bentonitler ve onların ana kil mineralleri olan simektitler en önemli endüstriyel hammaddeler arasında yer almaktadır. Bazı uygulamalarını boya, kağit, plastikler, renk giderici kimyasallar, barajlar, döküm bağlayıcılar, sondaj sıvıları, nem tutucular, sızdırmazlık maddeleri, kozmetikler, aşındırıcılar ve katalizörlerin üretimi şeklinde sıralayabiliriz. Sütunlaşmış kil, organokil ve polimer-simektit nanokompozitleri gibi yüksek teknoloji malzemelerinin hazırlanmasında, bentonitlerin saflaştırılması ve elde edilen simektitlerin fizikokimyasal modifikasyonları büyük öneme sahiptir. Bu çalışmada, bentonitlerin genel özelikleri yanında simektitlerin kristal yapısı, şişmesi, gözenekliliği,yüzey alanı, yüzey asitliği ve iyon değiştirme özeliği tartışılacaktır.

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