TRANSFORMATIONS OF AI-INTERLAYERED MONTMORILLONITE UPON AGING

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ABSTRACT

Al-interlayered montmorillonite, gibbsite and boehmite have been synthesized at room temperature and 100°C. The Al-interlayered montmorillonite, which shows a basal spacing of 13 Å after heating at 600°C, is the most stable at room temperature for 2 weeks. Over a longer period, gibbsite at room temperature or boehmite at 100°C grows from the Al-interlayered montmorillonite. The hexagonal plates of gibbsite and the laths of boehmite are usually associated with, and grow on, films of the montmorillonite. Gibbsite and boehmite develop well in the X and Y directions, but have a limited thickness. At room temperature, the SiO$_2$/Al$_2$O$_3$ ratio of the film ranges from 0.9 to 1.25, which is close to that of dioctahedral chlorite and different from that of the film at 100°C (range from 1.8 to 2.7). The gibbsite and boehmite have a SiO$_2$/Al$_2$O$_3$ ratio of 0.19 and 0.56, respectively, which suggests that they grew on the surface of the Al-interlayered montmorillonite films. The pH, CEC, and surface area changed with aging, which suggests that Al-interlayered montmorillonite is sufficiently unstable to peel off the Al-interlayer after longer periods at room temperature and 100°C.

Keywords: Al-interlayered montmorillonite, gibbsite, boehmite, transmission electron microscopy, energy-dispersion analysis.

SOMMAIRE

On a synthétisé montmorillonite interstratifiée avec Al(OH)$_3$, gibbsite, et boehmite à la température ambiante et à 100°C. La montmorillonite ainsi aluminée, qui montre un espacement interfoliaire de 13 Å après chauffage à 600°C, est la plus stable à la température de la pièce pour deux semaines. A plus long terme, c'est la gibbsite à température ambiante ou boehmite à 100°C qui croît aux dépens de cette montmorillonite. La gibbsite a une morphologie hexagonale, et la boehmite se présente en lattes. Les deux montrent une association avec les films de montmorillonite aluminée, et croissent sur la surface de ces films. Gibbsite et boehmite sont bien développées dans les directions X et Y, mais sont d'épaisseur restreinte. Les films à température ambiante ont un rapport SiO$_2$/Al$_2$O$_3$ entre 0.9 et 1.25, qui est proche de la valeur attendue d'une chlorite dioctaédrique, et qui diffère de celle pour le même maté-

| TABLE 1. CHARACTERIZATION OF THE PRODUCTS WITH AGING |

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<thead>
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<th>X-RAY DIFFRACTION</th>
<th>TRANSMISSION ELECTRON MICROSCOPY</th>
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Abbreviations: non-treat: nontreatment, glyc glycerol, gibbs gibbsite, boehm boehmite, hex hexagonal, surf surface, tr trace, comm common, abund abundant. Units: CEC in meq/100 g, surface area in m$^2$/g. $\Theta$ SiO$_2$/Al$_2$O$_3$ determined by energy-dispersion analysis. (Results are quoted in parentheses).
The fact that aluminum hydroxide can enter in the interlayer of montmorillonite to form Al-interlayered montmorillonite is well known. Investigators have prepared aluminum-interlayered complexes by several methods and have studied their properties extensively, e.g., surface area, cation-exchange capacity and activation energy of chloritization (Shen & Rich 1962, Barnhisel & Rich 1966, Brydon & Kodama 1966, Sawhney 1968, Barnhisel 1969, Lahav et al. 1978, Brindley & Kao 1980). But there are very few chemical data on micromorphology of such montmorillonite and associated products. The object of this paper is to illustrate, by transmission electron micrographs (TEM) with energy-dispersion analyses (EDX), the stages of formation of the Al-interlayered montmorillonite, gibbsite and boehmite, which have developed on the surface of films.

INTRODUCTION

The fact that aluminum hydroxide can enter in the interlayer of montmorillonite to form Al-interlayered montmorillonite is well known. Investigators have prepared aluminum-interlayered complexes by several methods and have studied their properties extensively, e.g., surface area, cation-exchange capacity and activation energy of chloritization (Shen & Rich 1962, Barnhisel & Rich 1966, Brydon & Kodama 1966, Sawhney 1968, Barnhisel 1969, Lahav et al. 1978, Brindley & Kao 1980). But there are very few chemical data on micromorphology of such montmorillonite and associated products. The object of this paper is to illustrate, by transmission electron micrographs (TEM) with energy-dispersion analyses (EDX), the stages of formation of the Al-interlayered montmorillonite, gibbsite and boehmite, which have developed on the surface of films.
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TEM samples. The clay suspensions spread well over the TEM grids.

Electron-optical studies were done with a Philips EM 400 transmission electron microscope equipped with an EDX 9100/60 analyzer, operating at 100 kV acceleration voltage, spot size 2 μm, condenser aperture 100 μm, objective aperture 30 μm for images, and at 120 kV acceleration voltage, spot size 2000 Å, condenser aperture 50 μm, selected aperture 150 μm, objective aperture 10 μm for electron-microdiffraction patterns. Polystyrene latex particles of 0.109 μm diameter were used to standardize the measurement of thickness by tungsten shadow.

The EDX 9100/60 analyzer contains an anticontamination trap cooled with liquid nitrogen and a beryllium specimen-holder to reduce background noise. The following conditions were used throughout the study: condenser aperture 100 μm; no objective aperture, no diffraction aperture, tilting angle of the specimen holder toward the detector 21°, accelerating voltage 100 kV, spot size 400 Å, emission current 13 A. Under these conditions, AlKα X-ray counts (1.41 to 1.51 kV) and SiKα X-ray counts (1.66 to 1.76 kV) were measured in a 50-second point analysis on each morphologically distinct particle. Background subtraction was made in the semiquantitative analysis mode in the EDX system by using the following 4 points: 1.11, 1.46, 1.72 and 2.36 kV. The Si/Al intensity ratio was determined by comparing the signal with that of pure and standard kaolin KGa-1 (Washington Co., Georgia).

Electron micrographs of aged products at 100°C.
A. After aging for 28 days; B. after aging for 44 days.

The EDX system was operated at an accelerating voltage of 100 kV, spot size 2 μm, condenser aperture 100 μm, objective aperture 10 μm for images.

The CEC of the products was determined by the silver thiourea method of Chhabra et al. (1975). The surface area of these products was determined by the ethylene glycol monomethyl ether method of Carter et al. (1965).

RESULTS AND DISCUSSION

XRD

X-ray data for the products collected at room temperature and aged 1 to 99 days are shown in Table 1. After the montmorillonite was aged for 2 weeks, a basal spacing between 16.37 and 17.67 Å was observed. This spacing changes slightly with ethylene glycerol treatment; it changes to 13 Å after heating at 600°C and may then be called Al-interlayered montmorillonite. Furthermore, montmorillonite in the solution aged more than 28 days gives the 4.85 Å basal spacing of gibbsite. Although X-ray diffraction of gibbsite aged for 99 days shows the strong 4.85 Å peak, the basal spacing (13.81 Å) expanded to 19.21 Å with ethylene glycerol treatment, which indicates typical montmorillonite.

After only one day at 100°C, the Al-interlayered montmorillonite was formed; but at longer periods, instead of gibbsite, boehmite of basal spacing 6.2 Å and montmorillonite were observed (Table 1).

The products aged for 99 days at room temperature and 100°C were further confirmed by DTA. The endothermic peaks at 270 and 240°C correspond to gibbsite and boehmite, respectively. Other endothermic peaks at about 100, 660, 940 and 960°C and exothermic peaks at 970 and 990°C correspond to montmorillonite.

Observations by electron microscopy

The montmorillonite starting material shows only film morphology, whereas the product held at room temperature and 100°C shows the following three kinds of morphology: film, hexagonal plate and lath. After aging for 2 weeks at room temperature, films were observed, but they possess a different value of SiO2/Al2O3, which ranges from 0.9 to 1.25.
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Fig. 3. Electron micrograph of tungsten-shadowed particles after aging 83 days at 100°C, with calibration specimen of Latex (diameter 1090 Å).

These values on crystal size and thickness suggest that hexagonal particles of gibbsite developed well in the X and Y directions, but were limited in the Z direction, and therefore appear as hexagonal plates. Lath-shaped particles of boehmite also are of limited thickness. Note that the hexagonal and lath-shaped particles always form on the surface of the films, which suggests that aluminum hydroxide once situated between montmorillonite layers later dissociated and precipitated as Al(OH)₃ or AlO(OH) on the surface of montmorillonite layers. The EDX data support these observations.

The electron-microdiffraction patterns for each hexagonal and lath-shaped single crystal (Fig. 4) conform with these observations (Figs. 1, 2, 3). Gibbsite in hexagonal crystals was distinguished by a strong diffraction-maximum at 4.4 Å, along with an isolated major diffraction-maximum at 2.2 Å (Fig. 4A). Boehmite of the lath habit (orthorhombic) was detected by the appearance of the set of three major diffraction-maxima at 1.83 (c), 1.42 (a) and 1.12 Å (b). The vertical direction of the lath-shaped crystals corresponds to the diffraction spot at 1.4 Å (Fig. 4B).

Point analysis by EDX

By using a TEM equipped with an energy-dispersion electron-microprobe analyzer (EDX), genetic relationships between morphology and chemical composition of the samples collected at room temperature, aged 1 and 83 days, and at 100°C, aged 83 days, were investigated (Table 1). These observations reveal that the chemical compositions of the reaction products, which have three kinds of morphology, are all different. The EDX data contribute to the identification of minerals of the same or similar morphology, such as films under different conditions, and also establish the chemical purity of the gibbsite and boehmite.

The chemical composition of the films at room temperature shows that the SiO₂/Al₂O₃ value ranges from 0.9 to 1.25; this finding is in agreement with the values for dioctahedral chlorite, which ranges from 0.6 to 1.2 (Brydon et al. 1961, Weaver & Pollard 1973, Sudo & Shimoda 1978). The films aged 83 days at 100°C gave a different SiO₂/Al₂O₃ value, in the range from 1.8 to 2.7, closer to the value of starting montmorillonite, in the range from 2.1 to 2.8, than that of dioctahedral chlorite.

The chemical composition of the films and hexagonal and lath-shaped particles, rich in Al, range from 0.05 to 0.25 and from 0.45 to 0.70 in SiO₂/Al₂O₃ value, respectively. Their averages are 0.19 and 0.56, respectively (Table 1). A small amount of SiO₂ in the hexagonal or lath-shaped particles reflects the chemical composition of the films underneath the particles (see Figs. 1B, 2B) that have not individually formed.
The EDX data also support the X-ray results, which identify the products as Al-interlayered montmorillonite, montmorillonite, gibbsite and boehmite. This effect might suggest that the suspensions with a OH/Al value of 2.7 are immediately contributed to the formation of the dioctahedral chlorite or Al-interlayered montmorillonite, which is unstable enough to peel off after longer period because the aluminum hydroxide minerals are formed on the surface. The CEC data (Table 1) are in agreement with the "pillar" concept. The CEC of the Na-montmorillonite, which is about 80 meq/100 g, decreases to 0–20 meq/100 g as a result of the formation of the Al-interlayered montmorillonite. The surface area for Na-montmorillonite, which is about 650 m²/g, decreases to 200–300 m²/g upon deposition of Al-interlayers. The surface area of the aged Al-interlayered montmorillonite with gibbsite or boehmite is over 350 m²/g during the pH decrease from 6–7 to 3–4 with aging. Aluminum hydroxide cannot fill up the vacant interlayer of montmorillonite under these conditions, but aluminum hydroxide partly enters the interlayer to make the pillar complex or cross-linked montmorillonite (Lahav et al. 1978, Pinnavaia 1983) as an Al-chlorite-like mineral.

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