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TEM observation of iron oxide pillars in montmorillonite

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The microstructures of iron oxide-pillared montmorillonite have been investigated by high-resolution transmission electron microscopy. The iron oxide is incorporated in the interlayer space of montmorillonite as Fe_2O_3 crystallites. The crystallites are present in two different morphologies: isolated particles $\sim$10 nm long and $\sim$4 nm thick, and bands (possibly plates) with a thickness $\lesssim$1 nm running parallel to the basal plane.

1. Introduction

Recently, a new kind of nano-composite prepared by incorporating fine particles such as metal oxide microcrystallites and organic polymers into the interlayer space of montmorillonite, has been intensively studied owing to its extremely large specific surface area, and its potentially wide application [1–4]. For example, intercalated montmorillonites are intended for use as catalysts [5, 6], molecule adsorbents and other advanced functional solids. The microstructures of the intercalated montmorillonite have been studied mainly by such techniques as X-ray diffraction and optical absorption spectroscopy, and thus the local topographic features of the microstructures have not yet been elucidated. In the present work, on the basis of this premise, the microstructures of iron oxide-pillared montmorillonite have been investigated by high-resolution transmission electron microscopy (HRTEM).

2. Experimental procedure

2.1. Preparation of iron oxide-pillared montmorillonite

Iron oxide-pillared montmorillonite was prepared through procedures essentially the same as those reported by Yamanaka *et al.* [3]. First, 0.125 M aqueous trinuclear acetato-hydroxo iron(III) nitrate, $[Fe_3(OCOCH_3)_7OH \cdot 2H_2O]NO_3$, was prepared and then the solution was mixed with an aqueous suspension of 1 wt % clay by continuously stirring at 308 K. The final volume ratio of the latter aqueous solution to the former was 0.4. The clay used was sodium montmorillonite, having a cation exchange capacity of 100 meq/100 g. The montmorillonite in the mixed suspension was then centrifuged, followed by washing with deionized water. The washed samples were spread on glass plates, air dried, and then annealed at 673 K for 72 ks in air. The resultant film products were approximately 20 μm thick and brown in colour. X-ray diffraction (XRD), using CuK_α radiation, of the products gave a diffraction peak at $2\theta = 5.35°$, from which an average basal spacing of 1.65 nm was obtained for the iron oxide-pillared montmorillonite. Subtraction of the silicate layer thickness of 0.96 nm from the average basal spacing gives 0.69 nm as the average interlayer spacing which may correspond to the pillar height of the incorporated iron oxide. The amount of the incorporated iron oxide in montmorillonite, which was determined by absorptiometry using *o*-phenanthroline, was 36 wt % iron oxide.

2.2. Transmission electron microscopy

The size and shape of the iron oxide pillars in montmorillonite were examined by HRTEM. For imaging the interstratified structure, it was necessary to use TEM foils perpendicular to the basal plane which were prepared in the following manner. The film products formed on glass plates (see Section 2.1), were peeled off and embedded in an epoxy resin (Epok 812). After 43.2 ks in a drying oven at 333 K the resin was fully hardened. Sections perpendicular to the basal plane were then cut using an ultramicrotome (Model ULTRACUT N, Reichert-Nissei) at room temperature. In addition to this conventional ultramicrotome sectioning, the freeze-sectioning was also employed to obtain foils free from artefacts associated with embedding. In this technique, no resin was used and the film products themselves were fixed at the tip of the arm of the ultramicrotome and were hardened by cooling down to approximately 120 K. Sectioning was carried out at this reduced temperature. The HRTEM investigation was carried out with a Hitachi H-9000 instrument equipped with a tilting device (± 10°) and operating at 300 kV ($C_s = 0.9$ mm). Images were recorded under axial illumination at approximate

0022–2461

Scherzer focus, with a point resolution better than 0.19 nm.

3. Results

A HRTEM image of the layer structure in the as-received sodium montmorillonite, the starting material used in this work, is shown in Fig. 1, which serves as a standard image depicting the original microstructures of the clay before intercalation. Layer stacks consisting of almost straight, parallel ~ 1 nm layers, are evident. This is essentially similar to that reported in the literature [7].

A low-magnification HRTEM image of the iron oxide-pillared montmorillonite is shown in Fig. 2 in which a number of isolated particles, which appear dark, and are absent in Fig. 1, are noticed. The particles are somewhat elongated in the direction parallel to the basal plane, and their typical size is 10 nm in the long axis and 4 nm thick. It is easily recognized that particle A is sandwiched between two silicate layers which are smoothly bent at the particle. An enlargement of the framed portion in Fig. 2 is shown in Fig. 3. All the lattice fringes appearing in the particles are assignable to those of Fe_2O_3. For example, the 0.37 nm spaced fringes in Particle B can be indexed as the (0 1 2) plane of Fe_2O_3. Another feature to be noted in Fig. 3 are the dark, rather thin bands running parallel to the basal plane. An example is seen at Band C in Fig. 3. In such bands, there appear again lattice fringes assignable to those of Fe_2O_3, as shown at Band C in Fig. 3. The thickness of the bands shows a somewhat wide variation but is generally below 1 nm. The bands are considered to be a section of plate-shaped Fe_2O_3 crystallites.

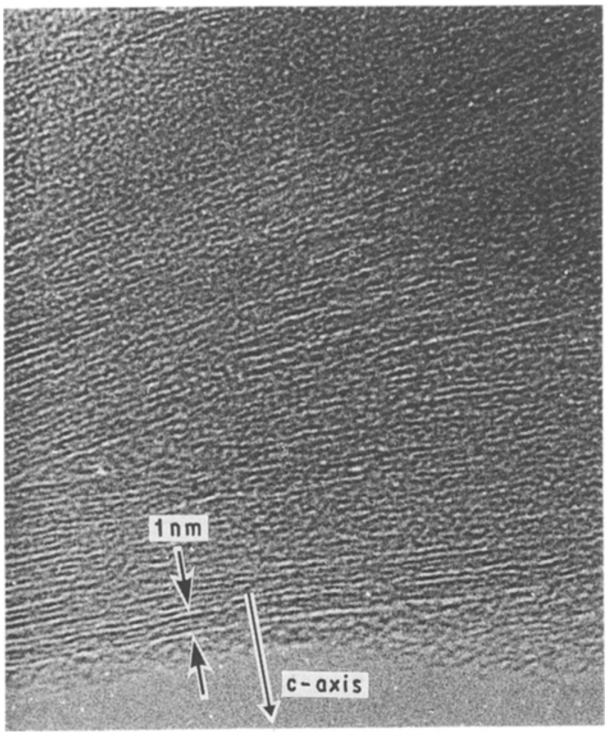

Figure 1 HREM image of the layer structure in the sodium montmorillonite before intercalation. The section is perpendicular to the basal plane, prepared by conventional ultramicrotome sectioning.

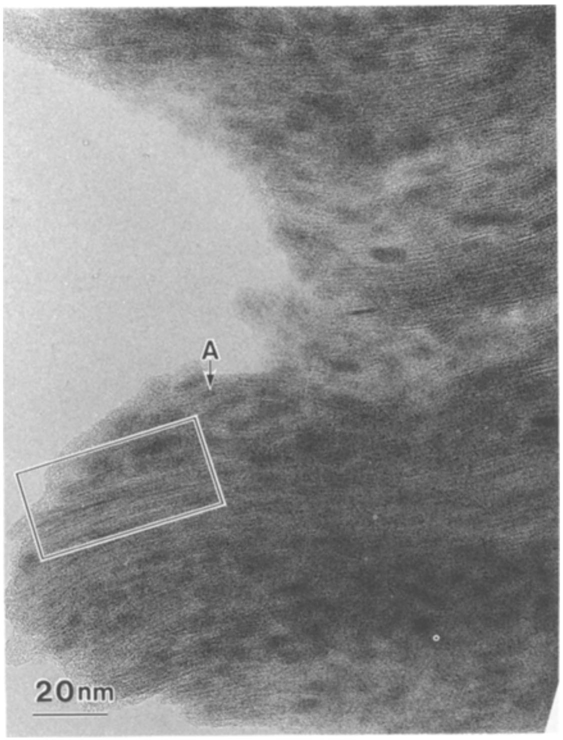

Figure 2 Low-magnification HREM image of iron oxide-pillared montmorillonite. The section is perpendicular to the basal plane, prepared by the freeze sectioning technique.

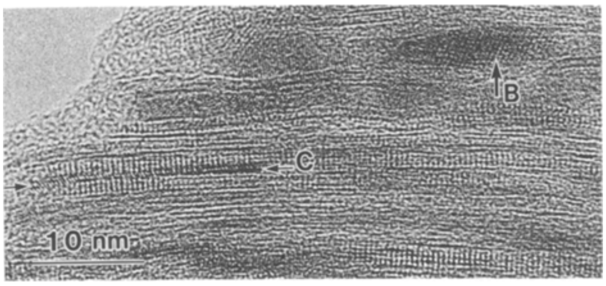

Figure 3 An enlargement of the framed portion in Fig. 2.

4. Discussion

Based upon the results obtained, it is safely concluded that iron oxide is incorporated into the interlayer space of montmorillonite as Fe_2O_3 crystallites and that they are present in two different morphologies. One is the isolated particles with dimensions ~ 10 nm long and ~ 4 nm thick and the other is the bands (possibly plates) with a thickness below ~ 1 nm running parallel to the basal plane. The presence of the isolated, rather large Fe_2O_3 particles is revealed for the first time in the present work. Although XRD studies have failed to predict the presence of the particles, an indication of the aggregation of iron oxide in montmorillonite has been obtained in spectral measurements. It has been reported that a long tail is formed in the absorption spectra of the iron oxide pillars in montmorillonite over the wavelength range above 450 nm [5]. The long tail in the spectra is an indication that iron oxide particles with larger dimensions must be included in the clay. The present observation is in qualitative agreement with the indication obtained by spectral measurements.

As described in Section 2.1, XRD data give an average interlayer spacing of 0.69 nm for the intercalated montmorillonite. The spacing is roughly in agreement with the thickness of the Fe_2O_3 bands (or plates) running parallel to the basal plane. Unfortunately, however, the bands are highly sensitive to radiation damage and are prone to disappear during detailed observations. Accumulation of further results is necessary before drawing a concrete conclusion on the nature of the average interlayer spacing.

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