NOTES

LOW TEMPERATURE SYNTHESIS OF A 10-Å HYDRATE OF KAOLINITE USING DIMETHYLSULFOXIDE AND AMMONIUM FLUORIDE

Key Words—Ammonium fluoride, Dimethylsulfoxide, Halloysite, Intercalate, Kaolinite.

In 1961 Wada succeeded in intercalating kaolinite by dry grinding with potassium acetate (KAc), thereby forming a 14-Å product. He subsequently intercalated dickite, nacrite, and hydrated halloysite with KAc (Wada, 1965). After washing the intercalates with water to remove the KAc, he found that kaolinite, dickite, and hydrated halloysite reverted to their original spacings, but that nacrite formed a well-defined hydrate with d(001) equal to 8.35 Å. Weiss *et al.* (1963) reported a 8.33-Å phase formed by the water washing of a kaolinite which had been expanded by urea but did not identify this material as a hydrated phase of kaolinite. By means of KAc- and urea-intercalates, van Olphen and Deeds (1963) obtained a 8.45-Å spacing for a well-defined hydrate of what they considered to be dickite. It was later shown (Deeds *et al.*, 1966) that the reactive mineral was really nacrite in a nacrite/dickite mixture. In the latter paper, Deeds *et al.* mentioned an ill-defined 7.6-Å hydrate of kaolinite. Range *et al.* (1969) reported a 10.04-Å hydrate that formed from the expansion of a disordered kaolinite by washing a hydrazine intercalate. Disregarding the ill-defined phases, there appears to be no report in the literature of a well-characterized kaolinite hydrate formed from a well-crystallized kaolinite at low temperature. In view of the problems associated with the nature and origin of hydrated halloysite, such a synthesis is of interest and is reported here.

EXPERIMENTAL

A 10.01-Å kaolinite dihydrate with the formula $Al_2Si_2O_5(OH)_4 \cdot 2H_2O$ has been produced from the well-crystallized St. Austell china clay (RLO 1415) (Figure 1A). The hydrated phase appeared as an unexpected product in a series of experiments designed to exchange inner surface hydroxyls by fluorine as suggested by Wolfe and Giese (1978). As shown in Figure 1B, the first step in the procedure was to expand completely the clay to a spacing of 11 Å using dimethylsulfoxide (DMSO) and water. The presence of water in DMSO is known to increase the rate and the completeness of intercalation (Olejnik *et al.*, 1970). In a typical experiment, 1.6 ml of distilled water and 20.0 ml of DMSO were added to 3.0 g of clay in a polyethylene centrifuge tube. The tube was held in a water bath at 60°C for at least 5 hr to intercalate the clay completely. After expansion had taken place, 1.3 g of ammonium fluoride (NH_4F) was dissolved in the suspension. The amount used was sufficient to exchange all of the OH by F. The suspension was heated for another 5 hr under the same conditions with the tube open so that ammonia could escape. After remaining undisturbed overnight, the suspension was centrifuged and examined by X-ray powder diffraction. Figure 1C shows that the addition of the NH_4F to the suspension had little effect on the X-ray powder diffraction pattern of the DMSO intercalate other than to weaken the (003) reflection. After washing with distilled water at least three times to remove the DMSO and NH_4F, the clay was allowed to remain in contact with the water of the last washing for at least 1 hr. A diffractogram of this product is shown in Figure 1D. The product consists of a mixture of the 10-Å hydrate and collapsed 7-Å kaolinite. The yield for this particular experiment, as indicated by the relative intensities of the (00l) reflections, was about 60%.

RESULTS AND DISCUSSION

Infrared spectrometry (IR) of the final product showed no detectable DMSO or ammonia, but chemical analysis indicat-
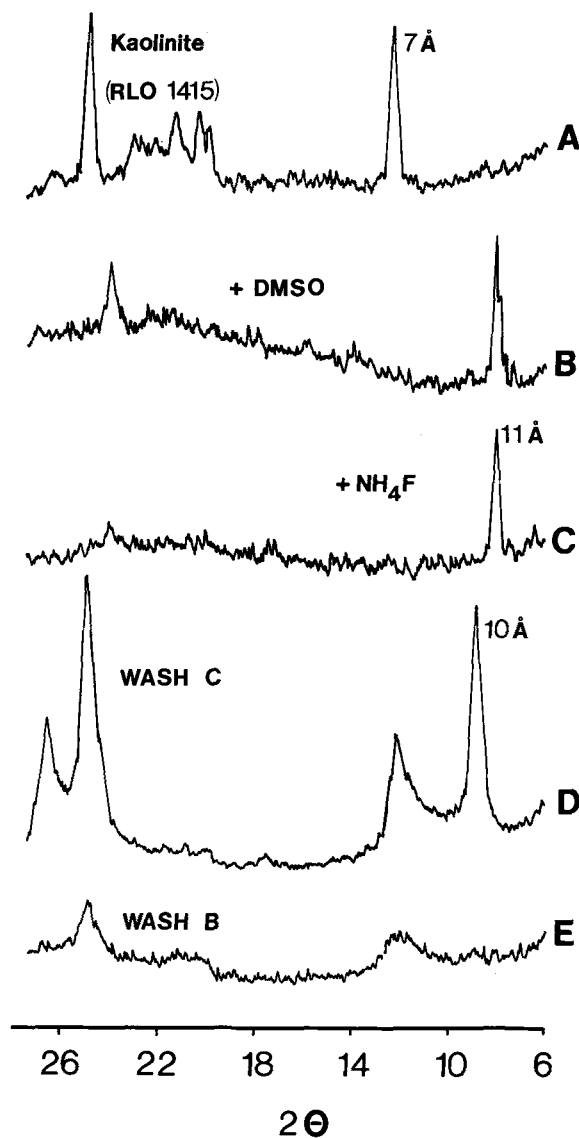

Figure 1. X-ray diffraction patterns illustrating the steps in the synthesis of the 10-Å kaolinite dihydrate. St. Austell china clay RLO 1415 (A); the clay intercalated with DMSO and 8% water (B); the intercalate after the addition of the ammonium fluoride followed by heating (C); the final product, a mixture of 7-Å and 10-Å phases (D); and the final product when no ammonium fluoride is used (E). (CuKα radiation)

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ed that the fluorine content of the clay increased from 0.2% to 2.30%. Thus the intercalating molecule and the NH_4F themselves were not responsible for the 10-Å spacing of the hydrate. Thermogravimetric measurements indicated that the weight loss is adequately accounted for by the decomposition of a dihydrate. The NH_4F was necessary for the formation of the hydrate because without it no 10-Å phase resulted (Figure 1E). Other work suggests that an initial extraction with absolute methanol prior to the final water washings substantially increases the yield of the 10-Å phase. At present, the role of the NH_4F is not clear, but the increase in fluorine content as indicated by the chemical analysis suggests that the F–for–OH substitution is important in forming the hydrate. Work on this problem is continuing.

The synthetic kaolinite dihydrate and a natural 10-Å halloysite gave similar d(001) values for the hydrated and dehydrated forms; both readily dehydrated under ambient conditions, both glycolated, and both lost similar weight upon dehydrating. They differ in that the IR spectra of the dehydrated synthetic sample showed strong, well-resolved peaks in the OH-stretching region, while IR spectra of the dehydrated form of Spruce Pine halloysite did not. This difference may simply reflect the greater crystallinity of the parent St. Austell kaolinite, or it may be the result of a more profound difference in the crystal structures. The effects of the DMSO–NH_4F treatment on other kaolin minerals are presently under investigation.

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