Control of the Distance between the Silicate Layers of Hectorite by Pillaring with Alumina in the Presence of Polyvinyl Alcohol

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Varying the concentration of an aluminium chlorohydroxide solution is found to result in a systematic alteration of the distance between the silicate layers on pillaring hectorite with alumina in the presence of polyvinyl alcohol.

By pillaring with appropriate oxide clusters, swellable layered clay minerals can be converted to thermally stable microporous materials.[1] For alumina-pillared clay, for example, pillaring is initiated by ion-exchange of the clay in an aluminium hydroxide solution followed by drying and calcination. As a result of pillaring, the distance between the silicate layers is expanded to *ca.* 0.9 nm. It was reported that several kinds of Al cations exist in an aluminium hydroxide solution.[2,3] The dimension of the cations, probably different from one cation to another, seems to be of primary importance in determining the distance between the silicate layers of alumina-pillared clay. However, no research has yet succeeded in altering widely the distance.

Unlike conventional pillaring methods, we found previously that the distance can be expanded to *ca.* 3 nm by pillaring clays with alumina in the presence of polyvinyl alcohol (PVA).[4,5] Methods for preparing pillared clays with control of the distance between the silicate layers in a desired way have not hitherto been established, and we now describe a method for systematically altering the distance between the silicate layers of alumina-pillared hectorite.

Synthetic fluorohectorite was obtained from Topy Industries, Ltd. Aqueous PVA (5 wt%; 1 dm^3) was added to a suspension of the hectorite (25 g in 1 dm^3 of distilled water), followed by further addition of distilled water (500 cm^3). Takibine-powder from Taki Chemical Co., Ltd. [formula authorized by the company, $Al_2(OH)_5Cl{\cdot}2.4\,H_2O$] was used as an aluminium chlorohydroxide salt. A 2 wt% solution (volume varied from 8 to 80 cm^3) of this salt was added dropwise to 100 cm^3 of the hectorite–PVA; the resulting final concentration of the salt was 0.15 to 0.89 wt%. The mixture was aged at 333 K for 3 days followed by washing, drying and calcination at 773 K for 2 h.

Fig. 1 illustrates X-ray powder diffraction patterns of non-pillared and alumina-pillared hectorites prepared from different concentrations of aluminium chlorohydroxide. While the 001 reflection appeared at 7° for non-pillared hectorite, pillared hectorites exhibited the 001 reflection at lower diffraction angle, indicating expansion of the distance between the silicate layers. The absence of the 001 reflection at 7° in all pillared hectorites provides evidence for the homogeneous pillaring. Fig. 2 summarizes the distance between the silicate layers as a function of the final concentration of aluminium chlorohydroxide. It is obvious that the distance increased with the concentration, although convex curvature is evident. The amount of alumina incorporated in hectorite as pillars was determined by atomic absorption spectroscopy. Fig. 2 also summarizes these results. The amount of alumina pillars increased linearly with increasing concentration of aluminium chlorohydroxide, which supports the expansion of the distance between the silicate layers.

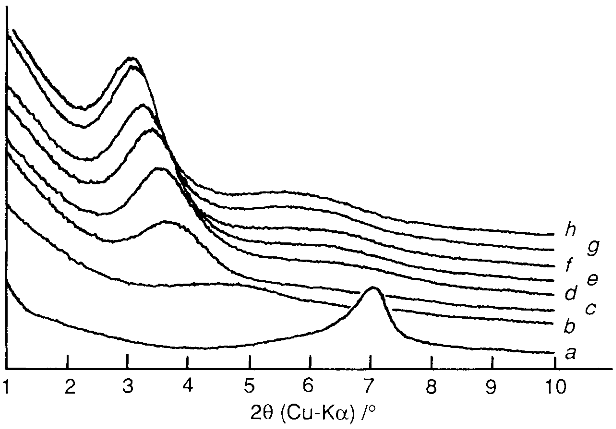

Fig. 1 X-Ray powder diffraction patterns for non-pillared and alumina-pillared hectorites prepared in the presence of PVA. Final concentration of aluminium chlorohydroxide (wt%): *a*; 0 (non-pillared hectorite), *b*; 0.15, *c*; 0.39, *d*; 0.49, *e*; 0.57, *f*; 0.65, *g*; 0.78, *h*; 0.89.

Alumina-pillared hectorite was similarly prepared in the absence of PVA. In contrast with the pillaring in the presence of PVA, the amount of alumina pillars was almost the same irrespective of the concentration of aluminium chlorohydroxide. The distance between the silicate layers was also independent of the concentration, as shown by the closed circles in Fig. 2: the value, *ca.* 0.8 nm, was in accordance with that in literature.[6] This indicates that the presence of PVA during pillaring is necessary for an expansion of the distance between the silicate layers of > 0.8 nm.

Our previous studies revealed that added PVA is incorporated in the interlayer space of the clay without disturbing the ion exchange for the pillaring process.[4,7] This finding, together with the present results, indicates that PVA may play

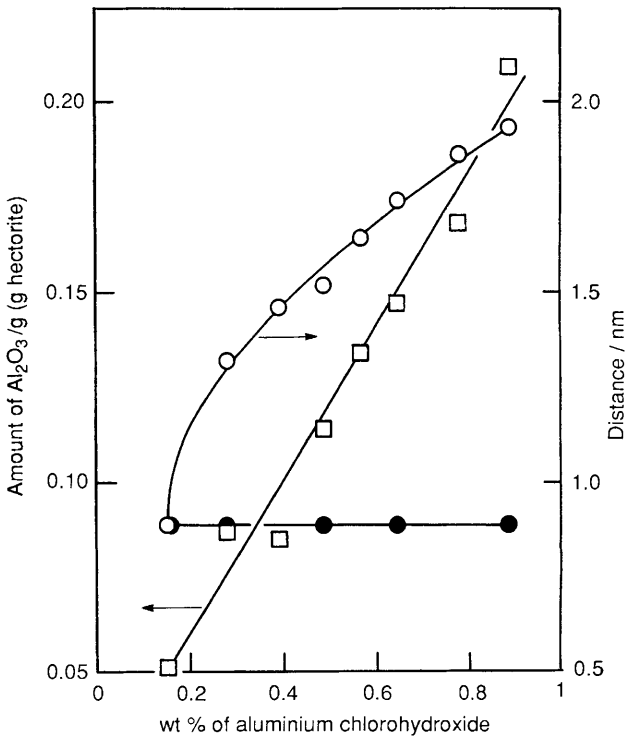

Fig. 2 Effects of the concentration of aluminium chlorohydroxide on the amount of alumina pillars incorporated in 1 g of hectorite (□) and the distance between the silicate layers (○) of alumina-pillared hectorite prepared in the presence of PVA. The distance between the silicate layers on pillaring in the absence of PVA (●).

a role as a template in the pillaring. In the absence of PVA, the clay is immediately coagulated on adding Al cations to a suspension. In the presence of PVA, on the other hand, the PVA present in the interlayer space leaves the distance between the silicate layers expanded. This provides favourable conditions under which smaller Al cations are hydrolysed to grow to larger ones. As a result, the distance between the silicate layers is expanded more than that on pillaring without PVA. An unambiguous identification of the mechanism of pillaring, especially in the presence of PVA, is required to verify the validity of this speculation.

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