Synthesis of Alumina-pillared Clay with Desired Pillar Population using Na-Montmorillonite having Controlled Cation Exchange Capacity

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Alumina-pillared montmorillonite with the desired pillar population was prepared by the ion-exchange of Na-montmorillonite, controlling the cation exchange capacity, with aluminium chlorohydroxy oligomers.

By pillaring with oligomeric hydroxy–metal cations, smectite clay minerals can produce a new class of porous and high surface area materials, the pore size of which is of molecular dimensions.[1] Since the starting smectite has a lamellar structure of silicate layers, the pore of the pillared smectite is composed of a two-dimensional interlayer space, characterized by both interlayer and lateral distances. The interlayer distance is determined by the size of the oligomeric cations, while the lateral distance is determined by the population of pillars. Controlling the pillar population may lead us to develop further the shape selective properties of the resulting pillared clay, which is desired for heterogeneous catalysis or separation.[2] The pillar population can be varied by altering the extent of the ion-exchange. It is, however, difficult to prepare the pillared clay with the desired pillar population, because the extent of hydrolysis and therefore the exact equivalent number of cationic oligomers are not known.[3]

According to our preliminary experiments, calcination at

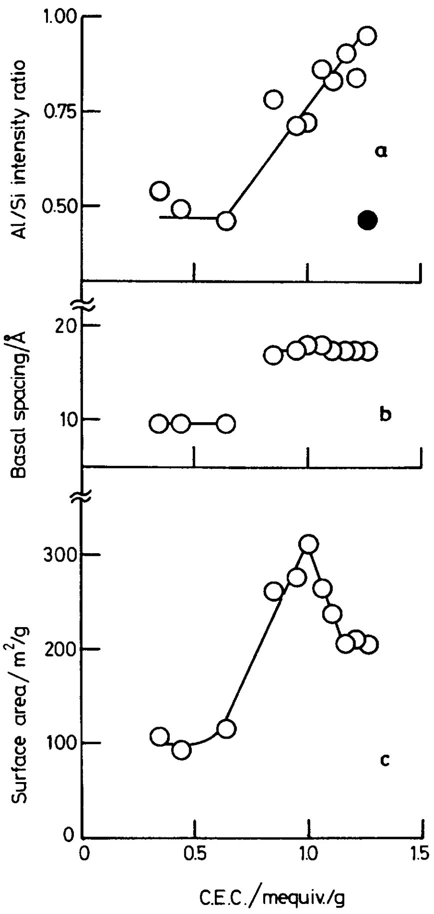

Figure 1 (a) Al/Si intensity ratio determined by *X*-ray fluorescence spectroscopy; (b) basal spacing; (c) surface area of the alumina-pillared montmorillonite against the C.E.C. of the starting (Na/Ni)-montmorillonite calcined. The filled circle in (a) is the Al/Si intensity ratio for the original Na-montmorillonite.

673 K resulted in a decrease in the cation exchange capacity (C.E.C.) of Ni-montmorillonite to *ca.* 25% of the original, while the C.E.C. does not alter for Na-montmorillonite. We therefore expect to control the C.E.C. of the resultant clay by calcining the montmorillonite containing both cations, Ni^{2+} and Na^{+}. It is known that by heating an Li-type smectite at a temperature as low as 423 K, its C.E.C. can be reduced to the same extent as that described above.[4] Controlling the C.E.C. with the latter method is not easy because of the sensitivity to temperature. In the former method, the C.E.C. of a resultant clay is exactly determined by the total amount of Na^{+} remaining unexchanged and the 25% of Ni^{2+} initially replaced. In the present study, alumina-pillared clays with desired pillar population were prepared by the ion-exchange of (Na/Ni)-montmorillonite by controlling the C.E.C.

(Na/Ni)-montmorillonites with various (Ni^{2+}/Na^{+}) ratios were prepared by ion-exchange of Na-montmorillonite (Kunipia-F, Kunimine Industries) with NiCl$_2$ solution having a fixed amount of Ni^{2+}. The montmorillonites containing the mixed cations were calcined at 673 K for 1 h, which results in a decrease in the ion-exchange ability by 75% of the Ni^{2+} initially replaced. Therefore the C.E.C. decreased by the corresponding amount of the non-exchangeable Ni^{2+}. The pillar population can, therefore, be varied using these montmorillonites controlling the C.E.C. This is because the amount of oligomeric hydroxy–metal cations, and therefore the population of pillars introduced in the clay, is primarily determined by the C.E.C. The alumina-pillared clay was prepared by ion-exchanging the calcined (Na/Ni)-montmorillonite with an aqueous solution of aluminium chlorohydroxide (Takibine-powder, Taki Chemical), followed by calcination at 773 K for 1 h.

Figure 1(a) shows the Al/Si intensity ratio determined by *X*-ray fluorescence for the alumina-pillared clay against the C.E.C. of the starting calcined (Na/Ni)-montmorillonite. For C.E.C. below 0.6 mequiv./g, the intensity ratio is almost the same as that in the original Na-montmorillonite, indicating that the clay is not pillared at all. In this range of C.E.C., *X*-ray diffraction showed that the starting (Na/Ni)-montmorillonite lost its swelling ability, which may be responsible for the absence of the pillar in the resultant clay. Above the C.E.C. of 0.6 mequiv./g, the intensity ratio is always larger in the pillared montmorillonite than in the original Na-montmorillonite, and it increases with the C.E.C. This indicates that the amount of alumina incorporated in the clay increases with increasing C.E.C. Figure 1(b) shows the basal spacing (d_{001}) of the alumina-pillared montmorillonite. For C.E.C. above 0.6 mequiv./g, d_{001} is almost constant (*ca.* 17.5 Å). The increase in the amount of alumina introduced as pillars into the interlayer space, keeping the interlayer distance constant, indicates clearly that the population of the alumina-pillars in the pillared montmorillonite increases with increasing C.E.C. This means that the alumina-pillared clay with desired pillar population can be prepared by choosing the starting Na-montmorillonite with a suitable C.E.C.

Figure 1(c) shows the surface area of the alumina-pillared montmorillonite against the C.E.C. Owing to the microporous structure, the clays pillared by alumina have larger surface area than those without pillars. In Figure 1(c), it is interesting that above the C.E.C. of 0.6 mequiv./g, with increasing C.E.C. and therefore with decreasing pillar population, the surface area first increases to the maximum value and then decreases. This indicates that the optimum pillar population is shown in the pillared montmorillonite which has the maximum surface area: in the present case, the maximum surface area (*ca.* 310 m^2/g) was obtained for a C.E.C. of 1.00 mequiv./g.

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