Unique Pore Structure formed in Montmorillonite in the Presence of Polyvinyl Alcohol and Aluminium Chlorohydroxide

Kenzi Suzuki, Toshiaki Mori,* Kaoru Kawase, Hiroshi Sakami, and Shozo Iida

Government Industrial Research Institute, Nagoya, Hirate-cho, Kita-ku, Nagoya 462, Japan

Porous montmorillonite, having a sharp pore size distribution (most abundant pore size *ca.* 30 Å), was prepared by the ion exchange of Na–montmorillonite with aluminium chlorohydroxy oligomers in the presence of polyvinyl alcohol.

Recently much attention has been directed to the study of heat-stable intercalated clay minerals, because, like zeolites, they have a pore structure of a molecular dimension.[1—5] This type of clay, called a pillared clay, is prepared by ion-exchange of the swollen clay with cationic hydroxy oligomers of aluminium,[1,2,4] zirconium,[3] or chromium,[5] followed by drying and calcination. Typically the pillared clay prepared in this way has an interlayer distance of *ca.* 10 Å, but larger interlayer distances are required because of limitations on the utility of both conventional pillared clays and zeolites owing to their small pore size. It is known that swelling of expandable clays is less pronounced in solution with a high concentration of cationic oligomers.[6] This may lead to difficulty in preparing pillared clays with larger interlayer distances.

It was found in our previous study that Na-montmorillonite

(Na-mont) swelled in an aqueous solution of polyvinyl alcohol (PVA) and that, owing to the incorporation of PVA into the interlayer space of Na-mont, the layers remained expanded after drying.[7] This suggested to us that pillared Na-mont with larger interlayer distances could be prepared *via* ion-exchange in the presence of PVA, since in PVA solution, Na-mont is significantly expanded even under high concentrations of cationic oligomers. On this basis, we have prepared porous Na-mont with quite large interlayer distances, and now report our results.

The following materials were obtained commercially: Na-mont (Kinipia-F, Kunimine Industries), and 10% (w/w) solutions of both PVA (Gohsenol NH-20, The Nippon Synthetic Chemical Industry) and aluminium chlorohydroxide (Takibine-powder, Taki Chemical). Typically, Na-mont (1.0
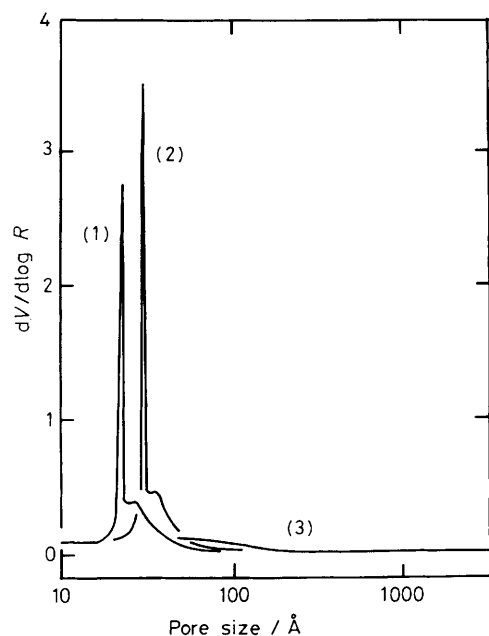
Figure 1. Pore size distribution of the porous montmorillonite determined from the N_2 adsorption/desorption isotherm on the basis of the cylindrical capillary model (1) and of the parallel plate pore model (2). Line (3) is determined from mercury porosimetry based on the cylindrical capillary model.

g) was added to the PVA solution (10 ml) with stirring, and then the Takibine solution (2 ml) was added with further stirring. Even in PVA solution, the Na^+ ions in Na-mont underwent complete exchange with cationic aluminium hydroxide oligomers.[7] The resultant paste was aged at room temperature for 1 day then dried at 333 K for another day. The sample was calcined at 773 K for 1 h, to remove the incorporated PVA. The mixing order of the components (Na-mont, aluminium chlorohydroxide solution, and PVA solution) greatly affected the properties of the prepared porous montmorillonite; the method described above gave the best results. The surface area of the prepared porous montmorillonite was found to be as large as 330 m^2 g^{-1}.

Figure 1 shows the pore size distribution determined from N_2 adsorption/desorption isotherms and mercury porosimetry methods using a Sorptomatic 1800 and Porosimeter 2000 (both from Carlo Erba Strumentazione), respectively. The adsorp-

tion isotherm observed was in agreement with the Brunauer–Emmett–Teller (B.E.T.) equation, indicating that the pores formed in the montmorillonite were large enough to assure the multi-layer adsorption of N_2. The pore size distribution determined from the cylindrical capillary model[8] was very sharp, most pores having a pore radius ca. 25 Å. Considering the layer structure of the parent montmorillonite, the pore size distribution was also determined from the parallel plate pore model[9] (line 2 in Figure 1). A similar distribution was also observed; the main distance between the plates was ca. 30 Å. The result obtained from mercury porosimetry (line 3 in Figure 1) showed that macropores (namely, pore size >100 Å) were absent in the prepared porous montmorillonite.

Because incorporation of PVA into the interlayer space does not affect the ion-exchange process between Na^+ and cationic aluminium hydroxide oligomers,[7] it is likely that an alumina pillar is formed in the interlayer space of the resultant montmorillonite. The incorporated PVA does not destroy the layer structure of the parent Na-mont,[7] which leads us to expect that the layer structure also remains in the prepared montmorillonite. However, X-ray diffraction showed no reliable evidence for the layer structure. One possible explanation is that, as a consequence of the 'delamination',[10] the long range ordering in the silicate laminae which is responsible for the diffraction is missing, although the definite cause of the 'delamination' is not known.

The precise structure of the porous montmorillonite together with its application is now being investigated.

References

1 G. W. Brindley and R. E. Semples, *Clay Miner.*, 1977, **12**, 229.
2 N. Lahav, U. Shani, and J. Shabtai, *Clays Clay Miner.*, 1978, **26**, 107.
3 S. Yamanaka and G. W. Brindley, *Clays Clay Miner.*, 1979, **27**, 119.
4 D. E. W. Vaughan and R. J. Lussier, Proc. 5th Internat. Conf. Zeolites, Naples, 1980, ed. L. V. C. Rees, Heyden, London, p. 94.
5 T. J. Pinnavaia, M.-S. Tzou, and S. D. Landau, *J. Am. Chem. Soc.*, 1985, **107**, 4785.
6 K. Norrish, *Discuss. Faraday Soc.*, 1954, **18**, 120.
7 K. Suzuki, H. Masuda, T. Mori, M. Horio, and E. Watanabe, *Chem. Express*, 1987, **2**, 265.
8 R. W. Cranston and F. A. Inkley, *Adv. Catal.*, 1957, **9**, 143.
9 W. B. Innes, *Anal. Chem.*, 1957, **29**, 1069.
10 T. J. Pinnavaia, M.-S. Tzou, S. D. Landau, and R. H. Raythatha, *J. Mol. Catal.*, 1984, **27**, 195.