Preparation and Property of Zirconia-Pillared Montmorillonite Having Different Pillar Populations

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Synopsis. Zirconia-pillared clay was prepared by ion-exchanging montmorillonites having different cation exchange capacities (CEC's) in an aqueous solution of $ZrOCl_2$. The amount of zirconia incorporated as pillars varied depending on the CEC of the starting clay. The interlayer distance was almost the same: ca., 0.8 nm. These findings suggest that the distance between pillars or the lateral distance should be different from one zirconia-pillared clay to another. As a result of pillaring the surface area was 200—260 $m^2 g^{-1}$. The thermal stability was examined in terms of a decrease in the surface area after heating at elevated temperatures.

By pillaring with alumina,[1] zirconia,[2] chromia,[3] titania,[4] or other kinds of oxide clusters,[5] a swellable layered clay mineral has been converted to a zeolite-like high surface area material. The resultant pillared clay has pores with sizes comparable to the dimension of many simple molecules. It is, therefore, expected that pillared clay can be used as a shape-selective catalyst or a molecular sieving separation material.[6,7]

The pore structure of pillared clay is characterized by both the distances between the silicate layers and between pillars, which are called, respectively, the interlayer distance and the lateral distance. It is not easy to prepare pillared clay with the desired interlayer distances. On the other hand, the lateral distance may be readily altered by altering the number of pillars: i.e., the lateral distance should be smaller in pillared clay with a larger number of pillars, as long as the interlayer distance is the same. By pillaring a montmorillonite having different CEC's with alumina we prepared a pillared clay with different lateral distances and studied its catalytic property.[7,8]

In the present study we similarly altered the pillar population in zirconia-pillared montmorillonite in order to change the lateral distance. Thermal stability was also investigated by measuring the surface area after heating at elevated temperatures.

Experimental

Na-montmorillonite [Kunipia-F, CEC; 1.28 mequiv g^{-1}] was obtained from Kunimine Industries, Co. The CEC was similarly altered by partially exchanging Na-montmorillonite with Ni^{2+}, followed by heating.[9] Zirconia-pillared clay was prepared by suspending the (Na, Ni)-montmorillonite with the CEC previously altered from 1.28 to 0.51 mequiv g^{-1} in an aqueous solution of $ZrOCl_2$, followed by washing chlorine free, drying at 333 K overnight and then calcined at elevated temperatures for 2 h. The amount of zirconia incorporated as pillars was determined by inductively coupled plasma (ICP) emission spectrometry (Shimadzu, ICPQ-1000). X-Ray powder diffraction was taken using a diffractometer with Ni-filtered monochromatic Cu$K\alpha$ radiation (Philips, APD-1700). The surface area was measured using an automatically controlled nitrogen-adsorption apparatus (Carlo Erba, Sorptomatic 1800).

Results and Discussion

Incorporation of Zirconia. The amount of zirconia introduced in the clay is plotted in Fig. 1 as a function of the CEC of the starting montmorillonite. Above 0.5 mequiv g^{-1}, the amount of zirconia increased linearly with increasing CEC, which is natural, since zirconia pillars are introduced in clay via ion-exchange. The tetrameric cation, $[Zr_4(OH)_{14}(H_2O)_{10}]^{2+}$ has been proposed as a plausible precursor for the zirconia pillar.[2a,d] Therefore, the number of zirconia pillars observed can be compared with the number expected from the divalent tetrameric cation. For a CEC of 1.28 mequiv g^{-1}, the observed number was 338 mg-ZrO_2 g^{-1}, while that expected was 315 mg-ZrO_2 g^{-1}, showing good agreement. However, it is obvious from a precise examination of Fig. 1 that when CEC decreased, the amount of observed zirconia was smaller than that expected, the possible reason for

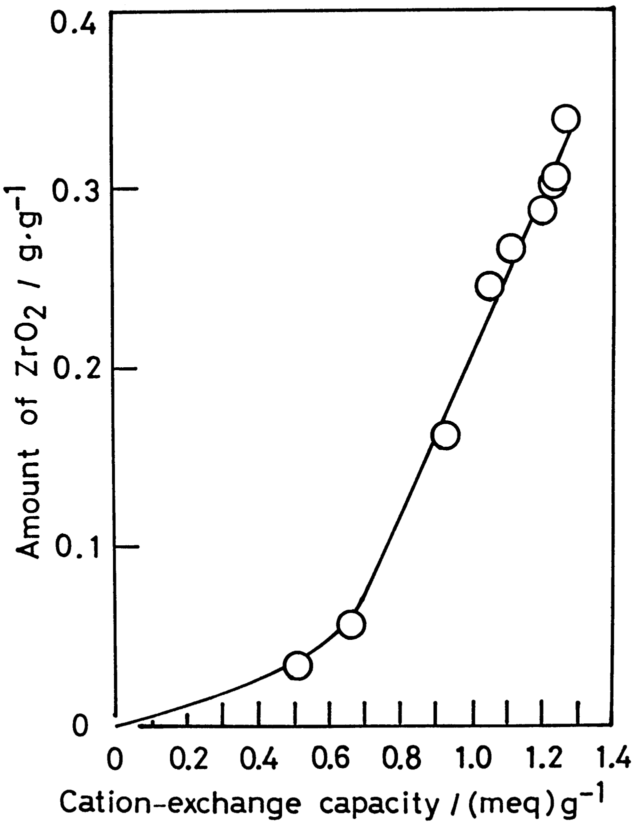

Fig. 1. The amount of ZrO_2 incorporated in montmorillonite with various CEC.

which is discussed below.

X-Ray Powder Diffraction. Since, as described below, the present zirconia-pillared montmorillonite was less thermally stable, X-ray powder diffraction was taken mainly for samples before calcination. Figure 2 summarizes the results. A diffraction peak, attributable to the 0 0 1 reflection, was observed at 4.5—5 ° for the CEC of the starting montmorillonite from 1.28 to 0.93 mequiv g^{-1}. The intensity of the 0 0 1 reflection increased with decreasing CEC to 1.06 mequiv g^{-1} and then decreased again for a CEC of 0.93 mequiv g^{-1}. Alumina-pillared montmorillonite also showed a similar variation in the intensity of the 0 0 1 reflections.[8] The intensity of the 0 0 1 reflection indicates the extent of the long-range ordering of the stacking of the silicate layers. Therefore, a favorable range of CEC seems to be present for preparing pillared clay well ordered in the longrange. From 0.93 to 1.28 mequiv g^{-1} of CEC, an additional peak also appeared at 8—9°, probably attributable to the 0 0 2 reflection. The variation in the intensity of the 0 0 2 reflection was found to be similar to that in the intensity of the 0 0 1 reflection, which may support the validity of the attribution.

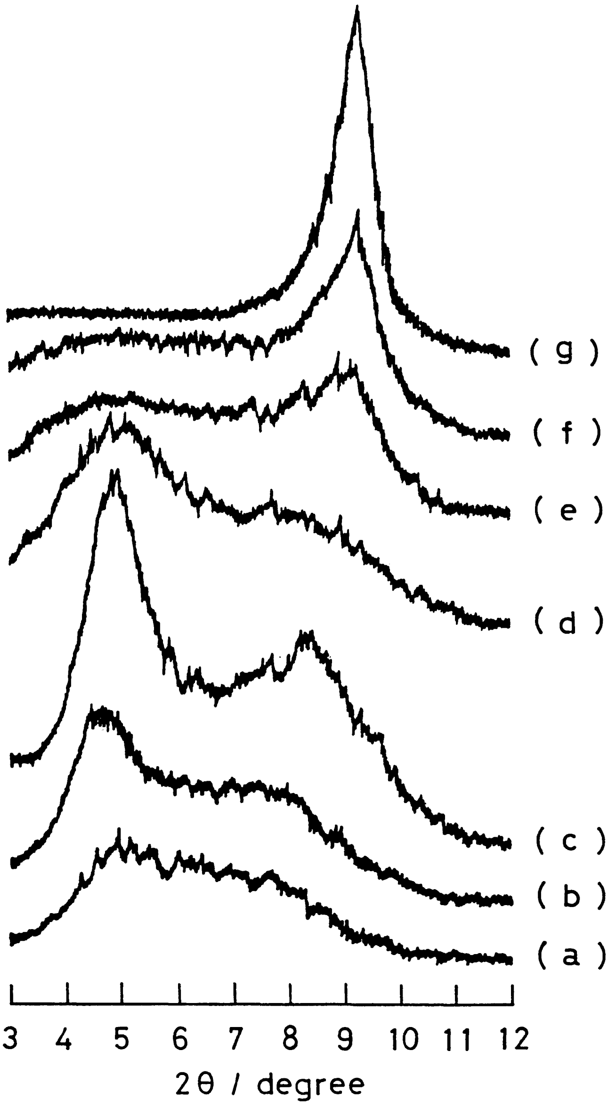

Fig. 2. X-Ray powder diffractions for the montmorillonite involving zirconium tetrameric cations in it. The CEC of the starting montmorillonite is 1.28 (a), 1.21 (b), 1.06 (c), 0.929 (d), 0.660 (e), and 0.506 mequiv g^{-1} (f). X-ray powder diffraction was taken for Ni-montmorillonite in a different scale (g).

For a CEC of 0.66 or 0.51 mequiv g^{-1}, a new main peak appeared at 9°, accompanying a very broad peak at 4.5—5°. The latter peak is again attributed to the 0 0 1 reflection. The diffraction for Ni-montmorillonite indicates that the former main peak is attributed to the 0 0 1 reflection of the non-pillared montmorillonite. The non-pillared portion present explains why the number of zirconia pillars was smaller than that expected. The reduced charge montmorillonite was reported to show a heterogeneous property with respect to a layer charge reduction.[9] This heterogeneity may be responsible for the presence of the non-pillared portion.

Interlayer Distance and Lateral Distance. The 0 0 1 basal spacing, d(0 0 1), was about 1.8 and 1.0 nm for the peak at 4.5—5 and at 9°, respectively. Since the thickness of the silicate layer was 0.96 nm, the respective interlayer distance was ca. 0.8 and 0.05 nm. The former interlayer distance assures pillaring, while the latter assures non-pillaring.

Figures 1 and 2 show that the number of zirconia pillars varied with the CEC of the starting montmorillonite from 1.28 to 0.93 mequiv g^{-1}, while the interlayer distance was virtually the same: ca., 0.8 nm. This suggests that the lateral distance is different from one zirconia-pillared montmorillonite to another: i.e., the greater number of zirconia pillars, the smaller is the lateral distance.

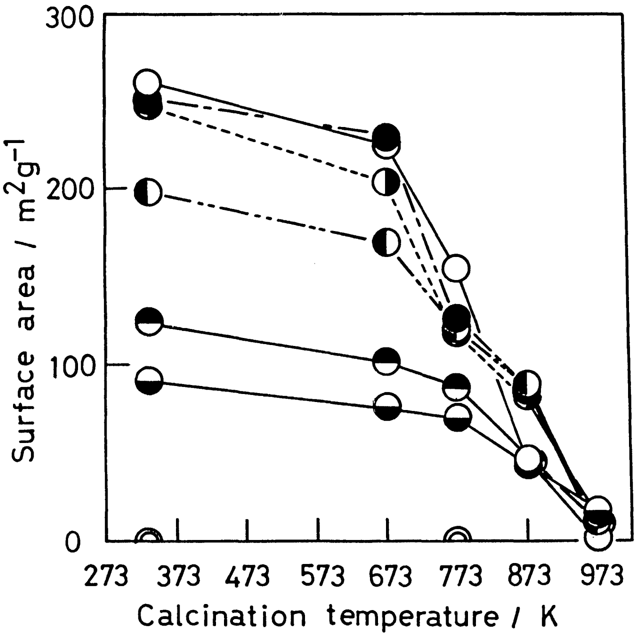

Fig. 3. Surface areas varied with calcination temperatures for typical zirconia-pillared montmorillonites. The CEC of the starting montmorillonite is 1.28 (◐), 1.21 (●), 1.06 (○), 0.929 (◑), 0.660 (◓), and 0.506 mequiv g^{-1} (◒). ⊚; Ni-montmorillonite.

Surface Area Varied with Calcination at Elevated Temperatures. As a result of pillaring, the surface area was 200—260 $m^2 g^{-1}$. The surface area of montmorillonite partially pillared was also much larger than that of Ni-montmorillonite: 120 or 90 $m^2 g^{-1}$ vs. >1 $m^2 g^{-1}$. The surface area is plotted in Fig. 3 as a function of the calcination temperature. For all pillared montmorillonites, the surface area slightly decreased up to 673 K accompanying a drastic decrease for a further elevation of the calcination temperature.

Our previous study showed that the decrease in the surface area caused by high-temperature calcination was much less pronounced for an alumina-pillared montmorillonite: the surface area was 285, 260, and 180 $m^2 g^{-1}$ after calcination at 773, 873, and 973 K, respectively.[10)] Compared with this pillared montmorillonite, the thermal stability of the present zirconia-pillared montmorillonite does not seem to be high. Here, the thermal stability was evaluated on the basis of a decrease in the surface area caused by high-temperature calcination. It is known that for zirconia-pillared clay the preparation method strongly affects the thermal stability.[2d)] Samples synthesized from refluxed $ZrOCl_2$ solutions were reported to have higher surface areas than those prepared using fresh, unrefluxed solutions. The highest thermal stability was obtained by refluxing a $ZrOCl_2$ solution prior to mixing with dispersed clay, combined with a subsequent refluxing of the mixture, while the lowest stability was produced by using a fresh solution followed by mixing at room temperature. Lower thermal stability of the present zirconia-pillared montmorillonite may be due to the preparation method: the fresh solution was used followed by mixing at room temperature.

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