Control of Pore Structure of Trioctahedral Magnesium-Smectite Materials

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Micro-mesoporous smectite-type materials are prepared from water glass and magnesium chloride by a hydrothermal treatment and calcination without template materials. The addition of dialkyldimethyl ammonium chloride during or after the hydrothermal synthesis enlarged their pore volumes and mesopore sizes, due to changes in the size and orientation of constituent smectite fragments.

Smectite-type materials have layered structures in which each layer is composed of one octahedral sheet sandwiched by two tetrahedral sheets. The octahedral sheets contain divalent or trivalent cations surrounded by six oxygen atoms in octahedral structure and the tetrahedral sheets contain Si^{4+} ions surrounded by four oxygen atoms in tetrahedral structure. The trilayers are negatively charged and are held together by the electrostatic interaction with exchangeable cations in the interlayer region. Pillared clays are prepared by exchanging the cations in the interlamellar position of smectite materials with larger inorganic hydroxyl cations.[1] When the exchanged samples are subjected to a thermal treatment, dehydration and dehydroxylation occur, forming stable metal oxide clusters which serve to separate the layers, creating a two dimentional gallery with an open space. Torii et al. have synthesized hectorite materials with micropores and mesopores of 40 Å from sodium silicate and magnesium chloride with a hydrothermal reaction.[2] They explained the formation of the mesopores of 40 Å by pillaring small fragments between smectite layers during the hydrothermal synthesis.

In this paper, we report that the pore structure (surface area, pore volume and pore diameter) of synthesized smectite materials is enlarged by adding quaternary ammonium chloride during or after the hydrothermal treatment followed by calcination at 873 K.

The synthetic procedure was as follows. Si-Mg hydrous oxide was prepared from water glass (SiO_2 29.04%, Na_2O 9.40%, NIHON KAGAKU KOGYO) and magnesium chloride. A Si-Mg hydrous precipitate was obtained by adding an aqueous solution of magnesium chloride to an aqueous water glass solution controlled in pH with an aqueous ammonia solution. The Si/Mg ratio was fixed at 8/6. After filtration and washing of the precipitate with distilled water, a slurry was prepared from the Si-Mg hydrous oxide precipitate and an aqueous ammonia solution (slurry A). Following a hydrothermal reaction, the resulting slurry (slurry B) was filtrated and dried at 353 K and calcined at 873 K, and then the final white product (SM(Mg)) was obtained. We prepared two other smectite materials with dialkyldimethyl quaternary ammonium chloride containing 75% octadecyl, 24% hexadecyl, and 1% octadecenyl groups as alkyl groups (trade name: 2HT-75, Lion Akzo Co., Ltd.). The dialkyldimethyl quaternary ammonium chloride was added to the slurry B. The Si/2HT-75 ratio was fixed at 8/0.7, corresponding to estimated maximum ion-exchange capacity. The slurry was filtrated, washed, dried at 353 K and calcined at 873 K. The final white-gray product (SM(Mg)+S) was obtained. The other smectite sample was prepared by the hydrothermal treatment from the mixture of slurry A and 2HT-75. Following the hydrothermal reaction, the slurry product was treated in the same way, and the final white-gray product (SM(Mg+S)) was obtained.

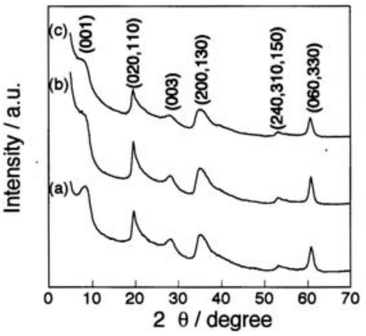

Figure 1. X-Ray powder diffraction patterns of smectite materials hydrothermally synthesized at 523 K; (a) SM(Mg), (b) SM(Mg)+S (c) and SM(Mg+S).

Figure 1 shows the XRD patterns of SM(Mg), SM(Mg+S) and SM(Mg)+S hydrothermally treated at 523 K. All the samples prepared show similar XRD patterns to those of smectite-type materials.[2b,2c] The (001) peak for SM(Mg) was much developed than those of the other two smectites, which indicates that more silicate fragments in the SM(Mg) sample stacked in parallel than those in the SM(Mg)+S and SM(Mg+S) samples.

The nitrogen adsorption-desorption isotherms at 77 K and pore size distributions evaluated from desorption isotherms with the BJH method are shown in Figure 2. Surface area (SA) and pore volumes (PV) are also shown. Average pore size (D) determined, using an equation of $D = 4PV/SA$, corresponds with maximum of the pore size distribution. The measured isotherms are of type IV in the classification of Brunauer et al.[3] It suggests that the pore structure of the smectite samples is of bottle-neck types. Figure 2 shows that the addition of 2HT-75 changes the pore structures of smectite materials.[4] SM(Mg) is a micro- and mesoporous material in which mesopore size is 40 Å. The pore diameter distribution calculated from adsorption isotherms also showed that micro- and meso pores exist in the SM(Mg) sample. SM(Mg)+S is a mesoporous material, with pore-size distribution from 20 to 80 Å, and has no micro-pores. SM(Mg)+S prepared at 523 K has higher surface area and larger pore volume than SM(Mg) prepared under similar hydrothermal conditions (temperature and time). SM(Mg+S) is a mesoporous material; pore-size ranges from 20 to 100 Å,

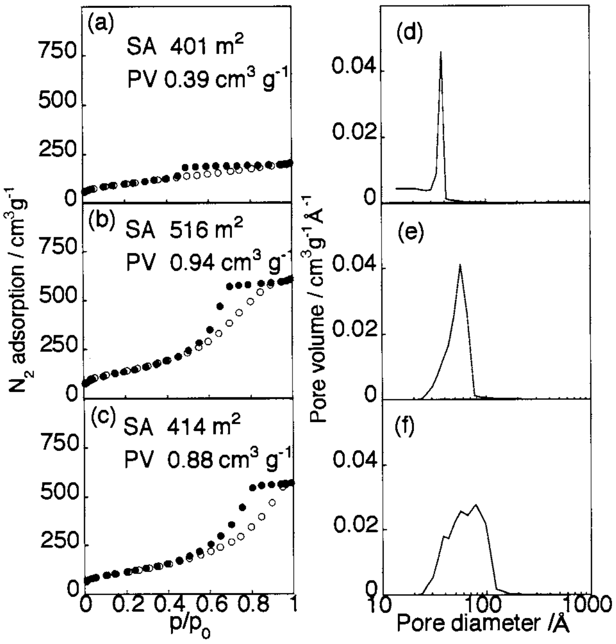

Figure 2. Nitrogen adsorption-desorption isotherms (○: adsorption and ●:desorption) and pore size distribution of synthesized smectite materials at 77 K; (a, d) SM (Mg) prepared at pH 10.0 at 523 K, (b, e) SM(Mg)+S prepared at pH 10.0 at 523 K, (c, f) SM(Mg+S) prepared at pH 8.64 at 523 K.

without micropores. SM(Mg+S) prepared at 523 K has larger surface area than that of SM(Mg); however, they have almost the same pore volumes. The pore diameter distribution calculated from adsorption isotherms also shows that micro pores do not exist in the SM(Mg)+S and SM(Mg+S) samples and that the sizes of meso pores of the SM(Mg+S) is larger than those of the SM(Mg)+S sample.

The pore structure of the synthesized smectite materials is related to the size and orientation of small silicate fragments between silicate layers. All the smectites prepared in this study have large surface area and high pore volume after calcination at 873 K. Small fragments of smectite would exist as pillars between silicate layers (smectites fragments intercalated in smectite layers), and pores would be formed between the layers.[2d] Torii et al. explained that the distance between ion-exchangeable sites of a silicate layer was 40 Å, which suggests that the lateral separation between silicate pillars may be of the order of 40 Å.[2d]

The addition of 2HT-75 after the hydrothermal treatment enlarges the surface area and pore volume. The pore size of SM(Mg)+S is larger than that of SM(Mg). The size distribution of silicate fragments in SM(Mg) would be similar to that of SM(Mg)+S because the hydrothermal conditions were the same. Moreover, the molecular size of 2HT-75 (dimethyldistearyl ammonium chloride) is much smaller than 40 Å. The dispersion of each silicate fragment during drying and calcination would relate to the pore structure of synthesized smectite materials. Bulky dialkyldimethyl ammonium cations would be adsorbed on the exchangeable sites on silicate layers and the orientation of the fragments would be changed.[5] After calcination the silicate fragments would be higher pillars which make larger mesopores. There is no micropore in SM(Mg)+S because all silicate fragments become pillars or disperse in mesopores. The mechanism of pore formation in the present smectites is different from those of MCM-41 and FSM-16, for which pore sizes are the same as templates materials (micelle of surfactant in solution).[6,7]

The size of mesopore in SM(Mg+S) is much larger than that of SM(Mg)+S. The dialkyldimethyl ammonium cations would be adsorbed on silicate and the silicates could be well dispersed in the slurry during the synthesis of SM(Mg+S). It means that larger silicate fragment would grow in SM(Mg+S) during the hydrothermal treatment compared with SM(Mg) and SM(Mg)+S. Thus, much larger mesopore is formed in SM(Mg+S) because of the larger size of pillared smectite.

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References and Notes

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4 Smectite materials prepared with dimethyldistearyl ammonium chloride showed similar pore structures to those prepared with 2HT-75.

5 We did not measure the CEC of the smectite materials prepared because carbonaceous materials would be adsorbed on the ion exchangeable sites. Similar samples prepared by the same hydrothermal method without dialkyldimethyl ammonium chloride have the smectite structure and CEC, as reported previously.[2]

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