Control of Pore Structure of Mesoporous Smectite-type Materials Containing Cobalt Cations in Octahedral Sheets

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Mesoporous materials with a smectite-type structure containing cobalt divalent cations in octahedral sheets (MST(Co)) are synthesized by the calcination of the mixture of dimethydistearyl ammonium chloride and silicate fragments synthesized with a hydrothermal method, their pore properties of the MST(Co) samples being able to control with hydrothermal conditions.

Thermally stable mesoporous materials containing catalytically active species are preferable for the diffusion of large molecules and for preventing blockage of pores by carbonaceous materials during reactions.[1] Porous smectite-type materials having catalytically active divalent cations (MST) in the octahedral sheets are synthesized by a hydrothermal method without adding any template.[2] Cobalt divalent cations in the lattice of the smectite-type materials synthesized showed high activities for hydrodesulfurization of thiophene.[3] The enlargement of pores is desirable for hydrodesulfurization of such large substrates as benzothiophene and dibenzothiophene in light oil and also less susceptible to blockage of pores by coking.

In this paper, we report a new preparation to control their pore properties of mesoporous materials having catalytically active species in lattice by the calcination of mixture of dimethyldistearyl ammonium chloride and silicate fragments having a smectite-type structure synthesized with the hydrothermal method.

The synthetic procedure was as follows. Si–Co hydrous oxide was prepared from water glass (SiO_2 29.04%, Na_2O 9.4%, NIHON KAGAKU KOGYO) and cobalt chloride. A Si–Co hydrous precipitate was obtained by adding an aqueous solution of cobalt chloride to an aqueous water glass solution, followed by filtration and washing the precipitate with distilled water. The Si/Co ratio was fixed at 8/5.8. An aqueous slurry at pH = 13.0 was prepared from the Si–Co hydrous oxide precipitate and an aqueous sodium hydroxide solution. Following hydrothermal reactions of the slurry at various temperatures, the resulting slurry (slurry A) was filtrated and mixed with an aqueous ammonium chloride (NH_4Cl) solution for 1 day at room temperature. After filtration, the resulting slurry (slurry B) was dried at 353 K and dark pink material was produced. The dried sample was calcined at 823 K for 2 h, and then the final black product was obtained. Other smectite materials were also prepared; dimethyldistearyl ammonium chloride (C18d) was added to the slurry A after hydrothermal treatment. The Si/C18d ratio was fixed at 8/2.1. Following the mixing of C18d and the slurry A at 313 K for 1 day, the resulting slurry was filtrated, washed, and dried at 353 K. Dark pink material thus produced was calcined at 823 K for 2 h, and then the final black product was obtained. Synthetic conditions, pore structures and chemical compositions of final products are summarized in Table 1.

The XRD patterns of the MST(Co) samples prepared with and without C18d were similar to those of other smectite-type materials[4] and that peaks ascribed to cobalt oxide (Co_3O_4) were not seen. Fourier transforms of Co K-edge EXAFS spectra of both MST(Co) samples with and without C18d were similar to those for smectite-type materials including nickel and zinc cations in octahedral sheets[5] and no peaks ascribed to cobalt oxide were seen. Both XRD and EXAFS results indicated that cobalt cations were incorporated in the lattice and that the MST(Co) materials were composed of only silicate fragments having smectite structure. The (001) peaks in the XRD patterns of MST and MST-a samples were very weak compared with those of natural smectite-type clays, indicating that silicate fragments in MST samples are small and not so stacked in parallel well as in natural smectite-type clays.

The samples prepared without C18d were porous (Table 1).

Table 1. Preparation conditions and porous properties of MST(Co) in the absence and presence of additives[1]

	Hydrothermal			Pore structure			Composition	
Sample[2] code	Temperature /K	Time /h	Additive	Surface area /m^2g^{-1}	Pore volume /cm^3g^{-1}	Pore diameter /nm	Si : Co	Remarks
MST-1	423	2	no	337	0.22	2.6	8 : 6.4	
MST-1a	423	2	yes	516	1.07	8.3	8 : 5.7	Fig. 1(a)
MST-2a	473	4	yes	491	1.24	10.0	8 : 5.5	
MST-3	523	4	no	247	0.25	4.0	8 : 6.0	
MST-3a	523	4	yes	409	1.13	11.0	8 : 5.7	Fig. 1(b)
MST-13a	423 + 523	2 + 4	yes	486	1.20	9.9	—	Fig. 1(c)
MST-13p[3]	423 + 523	2 + 4	yes	497	1.21	9.7	—	Fig. 1(d)

[1] Dimethyldistearyl ammonium chloride. [2] All samples were calcined at 823 K for 2 h.
[3] Physical mixture of MST-1a and MST-3a in 1 : 1 in weight.

The surface areas of natural smectite clays are less than $20\,m^2g^{-1}$;[6] however, those of MST(Co) materials were much larger even after calcination at 823 K. Pillared clays are thermally stable above 773 K, having surface areas of 200–500 m^2g^{-1}, because small oxide particles (pillars) induce micropores in montmorillonite.[7] In the case of the smectite-type materials synthesized, smectite-type crystal is the only phase and silicate fragments do not stacked well in parallel, then silicate fragments having smectite structure would be intercalated between silicate layers, and large surface areas and pores would be formed.[4]

Other MST(Co) samples were prepared from the mixture of C18d and slurry A. The surface area and pore volume values of the mixture were almost zero after drying at 353 K, but increased to maxima at 823 K and then decreased with increasing calcination temperature. The surface areas, pore volumes and pore sizes of the MST(Co) materials prepared with C18d are much larger than those prepared without C18d. The sizes of silicate fragments of MST(Co) samples with and without C18d would be similar, because the hydrothermal conditions were the same (X-ray diffraction peaks and amplitudes for EXAFS Fourier transforms of both samples were similar). Cobalt oxide was not observed with XRD and EXAFS analyses, indicating that the mesopores of MST(Co) samples prepared with C18d are not produced by cobalt oxide particles (pillars). The pore properties of MST(Co) materials are related to the orientation of small silicate fragments between silicate fragments. Bulky dimethyldistearyl ammonium cations would be adsorbed on the exchangeable sites on silicate fragments which are negatively charged and the orientation of the fragments would be changed.[4] The silicate fragments would be pillars and the space between the fragments would become large mesopores after calcination. The formation of the large mesopore by pillaring of silicate fragments would lead to the increase of the surface area and pore volume. The hydrothermal condition is also related to pore structure of MST(Co) materials. With increasing hydrothermal temperature and time, the pore diameters of the MST(Co) materials, which were prepared with the same amount of C18d, increased. The MST(Co) materials prepared at higher hydrothermal temperature with longer time would have larger silicate fragments. The larger silicate fragments would become higher pillars, and then the size of mesopore becomes larger for the MST(Co) materials prepared at higher hydrothermal temperature and longer time. The mechanism of pore formation in the present MST materials is different from those of MCM-41 and FSM-16, for which pore sizes are the same as template materials (micelle of surfactant in solution).[8]

Based on the pore formation mechanism of MST samples described above (silicate fragment pillared smectite), we have developed a method for controlling the pore structure of MST(Co) materials. The mixture of a slurry A treated at 423 K, a slurry A at 523 K, and C18d were calcined at 823 K to prepare MST-13a. The mesopore size and surface area of MST-13a were between those of MST-1a and MST-3a. The pore distribution of MST-13a was narrower than that of MST-13p (the physical mixture of MST-1a and MST-3a in 1 : 1 in weight). Mesopores with around 65 Å size of MST-1a sample were formed with (smaller) silicate fragments hydrothermally synthesized at 423 K for 2 h, and mesopores with around 100 Å of MST-3a were formed with (larger) silicate fragments at 523 K for 4 h. Mesopores with around 80 Å size of MST-13a were formed with the mixture of the smaller and larger silicate fragments.

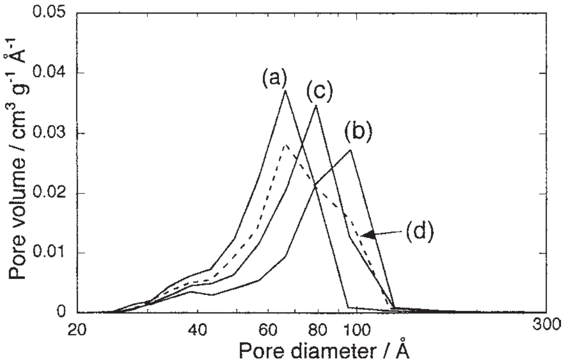

Figure 1. Pore size distributions of smectite-type materials synthesized; (a) MST-1a, (b) MST-3a, (c) MST-13a, and (d) MST-13p (physical mixture of MST-1a and MST-3a in 1 : 1 in weight) (broken line).

The present results demonstrate that mesopore sizes of smectite-type materials can be enlarged by the calcination of the mixture of C18d and silicate fragments prepared with a hydrothermal method. Further study for measuring the silicate size is needed to prove the mechanism of pore formation proposed.

References

1 A. Corma, *Chem. Rev.*, **97**, 2373 (1997).
2 M. Shirai, K. Aoki, K. Torii, and M. Arai, *Appl. Catal., A*, **187**, 141 (1999).
3 M. Arai, Y. Minato, K. Torii, and M. Shirai, *Catal. Lett.*, **61**, 83 (1999); K. Aoki, Y. Minato, K. Torii, M. Shirai, and M. Arai, *Appl. Catal., A*, **215**, 47 (2001).
4 M. Shirai, K. Aoki, T. Miura, K. Torii, and M. Arai, *Chem. Lett.*, **2000**, 36.
5 M. Shirai, K. Aoki, Y. Minato, K. Torii, and M. Arai, *Stud. Surf. Sci. Catal.*, **129**, 435 (2000).
6 D. E. W. Vaughan and R. J. Lussier, *Proceeding of Fifth International Conference of Zeolites*, **1980**, 94.
7 J. T. Pinnavia, *Science*, **220**, 365 (1983).
8 T. Yanagisawa, T. Shimizu, K. Kuroda, and C. Kato, *Bull. Chem. Soc. Jpn.*, **63**, 988 (1990).