

Microporous ZrO₂-Pillared Clays Derived from Three Kinds of Zr Polynuclear Ionic Species

Kunio Ohtsuka,* Yoshimasa Hayashi, and Mitsuru Suda

Ceramics Research Institute, Mitsubishi Materials Corporation, 2270 Yokoze,
Yokoze-machi, Chichibu-gun, 368 Japan

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Depending on the degree of polymerization of the zirconium species in zirconium oxychloride solutions, three kinds of microporous clay intercalation compounds have been prepared by cation exchange of a swelling clay with the zirconium polynuclear ionic species. These are products with 7-, 12-, and 14-Å interlayer spacings (=gallery heights). The major species in zirconium oxychloride solutions at room temperature is the zirconium tetramer, $[\text{Zr}_4(\text{OH})_{8+x}(\text{H}_2\text{O})_{16-x}]^{(8-x)+}$, giving the intercalation compound with a 7-Å interlayer spacing. Upon hydrolytic polymerization of the zirconium tetramer in solution, the more highly polymerized zirconium species are generated that can provide the intercalation compounds with 12- or 14-Å interlayer spacings; the concentration of halogen ions in the solutions governs the kinds of the intercalates. The two polymeric species forming the intercalates with 12- and 14-Å interlayer spacings are composed of three-dimensionally polymerized clusters based upon the tetramer. Examination of the intercalation compounds sheds light on the structure of the ionic species in solution.

Introduction

There has been intense research activity on the subject of layer silicate intercalation compounds cross-linked with inorganic or organic clusters, which are called pillared interlayered clays (PILC) or cross-linked clays (CLC).¹ These materials may have a two-dimensional pore size larger than conventional zeolites and exhibit specific properties depending on the nature of the pillar. PILCs have received much interest as a new type of microporous solid that can serve as shape-selective catalysts, separating agents, supports, sorbents, etc. In particular, clays pillared by metal oxides are of great importance because they show high thermal stability, high surface areas, and intrinsic catalytic activity.

These zeolite-like materials are usually prepared by ion-exchanging cations in the interlayer region of swelling clays with bulky alkylammonium ions, polynuclear complex ions bearing inorganic ligands (hydroxo ligand, chloro ligand), large metal complex ions bearing organic ligands (in some cases followed by the hydrolysis of the species in the interlayer space), or positively charged colloidal particles. The intercalated species are capable of preventing the collapse of the interlayer spaces, propping open the layers as pillars, and forming interlayer space, i.e., a two-dimensional porous network. On heating, the intercalated inorganic species are converted to metal oxide clusters, generating a stable microporous structure with a high surface area. So far several metal oxide pillared clays have

been considered that include aluminum oxide,²⁻²⁵ zirconium oxide,^{4,13,17,28-39} chromium oxide,⁴⁰ titanium oxide,⁴¹⁻⁴³ silicon oxide,^{16,25,44-46} iron oxide,⁴⁷⁻⁵² niobium oxide,^{53,54}

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(1) For review articles, see: (a) Barrer, R. M. *Zeolites and Clay Minerals as Sorbents and Molecular Sieves*; Academic Press: New York, 1978; Chapter 8. (b) Pinnavaia, T. J. *ACS Symp. Ser.* 1982, 192, 241. (c) Pinnavaia, T. J. *Science* 1983, 220, 365. (d) Vaughan, D. E. W. *ACS Symp. Ser.* 1988, 368, 308. (e) Vaughan, D. E. W. *Catal. Today* 1988, 2, 187. (f) Burch, R., Ed. *Pillared Clays. Catalysis Today*; Elsevier: New York, 1988; Vol. 2, Nos. 2-3. (g) Barrer, R. M. *Pure Appl. Chem.* 1989, 61, 1903. (h) Mitchell, I. V., Ed. *Pillared Layered Structures: Current Trends and Applications*; Elsevier: London, 1990. (i) Bellussi, G.; Fattore, V. *Chim. Ind.* 1992, 74, 166.

- (2) Brindley, G. W.; Sempels, R. E. *Clay Miner.* 1977, 12, 229.
- (3) Lahav, N.; Shani, U.; Shabtai, J. *Clays Clay Miner.* 1978, 26, 107.
- (4) Vaughan, D. E. W.; Lussier, R. J.; Magee, J. S., Jr. *U.S. Patent* 4,176,090, 1979.
- (5) Vaughan, D. E. W.; Lussier, R. J. In *Proc. 5th. Int. Conf. Zeolites*; Rees, L. V. C., Ed.; Heyden: London, 1980; p 94.
- (6) Shabtai, J.; Rosell, M.; Tokarz, M. *Clays Clay Miner.* 1984, 32, 99.
- (7) Shabtai, J.; Massoth, F. E.; Tokartz, M.; Tsai, G. M.; McCuley, J. In *Proc. 8th Int. Congr. Catal.*; Verlag Chemie: Weinheim, 1984; Vol. 4, p 735.
- (8) Plee, D.; Borg, F.; Gatineau, L.; Fripiat, J. J. *J. Am. Chem. Soc.* 1985, 107, 2362.
- (9) Tokarz, M.; Shabtai, J. *Clays Clay Miner.* 1985, 33, 89.
- (10) Pinnavaia, T. J.; Landau, S. D.; Tzou, M. S.; Johnson, I. D. *J. Am. Chem. Soc.* 1985, 107, 7222.
- (11) Occelli, M. L.; Finseth, D. H. *J. Catal.* 1986, 99, 316.
- (12) Sterte, J. *Catal. Today* 1988, 2, 219.
- (13) Jones, S. L. *Catal. Today* 1988, 2, 209.
- (14) Tichit, D.; Fajula, F.; Figueras, F.; Ducourant, B.; Mascherpa, G.; Gueguen, C.; Bousquet, J. *Clays Clay Miner.* 1988, 36, 369.
- (15) Suzuki, K.; Mori, T. *J. Chem. Soc., Chem. Commun.* 1989, 7.
- (16) Zheng, L.; Hao, Y.; Tao, L. *Zeolites: Facts, Figures, Future, Part A* 1989, 481.
- (17) Tsvetkov, F.; Mingelgrin, U.; Lahav, N. *Clays Clay Miner.* 1990, 38, 380.
- (18) Shen, Y. F.; Ko, A. N.; Grange, P. *Appl. Catal.* 1990, 67, 93.
- (19) Suzuki, K.; Mori, T. *Appl. Catal.* 1990, 181.
- (20) Malla, P. B.; Komarneni, S. *Clays Clay Miner.* 1990, 38, 363.
- (21) Tsvetkov, F.; Mingelgrin, U. *Clays Clay Miner.* 1990, 38, 380.
- (22) Sakurai, H.; Urabe, K.; Izumi, Y. *Bull. Chem. Soc. Jpn.* 1991, 64, 227.
- (23) Coelho, A. V.; Poncelet, G. *Appl. Catal.* 1991, 77, 303.
- (24) Bradley, S. M.; Kydd, R. A. *Catal. Lett.* 1991, 8, 185.
- (25) Zheng, L.; Hao, Y.; Tao, L.; Zhang, Y.; Xue, Z. *Zeolites* 1992, 12, 374.
- (26) Yamanaka, S.; Brindley, G. W. *Clays Clay Miner.* 1979, 27, 119.
- (27) Bartley, G. J. J.; Burch, R. *Appl. Catal.* 1985, 19, 175.
- (28) Burch, R.; Warburton, C. I. *J. Catal.* 1986, 97, 511.
- (29) Bartley, G. J. J.; Burch, R. *Appl. Catal.* 1986, 28, 209.
- (30) Burch, R.; Warburton, C. I. *J. Catal.* 1986, 97, 503.
- (31) Bartley, G. J. J. *Catal. Today* 1988, 2, 233.
- (32) Dyer, A.; Gallardo, T.; Roberts, C. W. *Zeolites: Facts, Figures, Future, Part A* 1989, 389.
- (33) Figueras, F.; Mattrud-Bashi, A.; Fetter, G.; Thierri, A.; Zanchetta, J. V. *J. Catal.* 1989, 119, 91.
- (34) Suzuki, K.; Horio, M.; Masuda, H.; Mori, T. *Bull. Chem. Soc. Jpn.* 1991, 64, 732.

tantalum oxide,⁵³ gallium oxide,^{23,24,55} mixed oxide clusters,^{11,23,24,56-60} and oxide modified with phosphate or sulfate.^{18,36}

The most extensively studied materials are aluminum oxide and zirconium oxide pillared clays derived from polynuclear complex ions; these pillared clays are stable in both oxidizing and reducing atmosphere and exhibit high thermal stability and a uniform pore size. Zr-pillared clays are of particular interest, because they are usually more stable than Al-pillared clays, and the formation of products with large interlayer spacings of over 10 Å has been reported.^{4,38} In the synthesis of Zr-pillared clays, zirconium oxychloride solutions are usually employed as the pillaring solution. Addition of a base to the solutions or heating or aging of the solutions brings about hydrolytic polymerization of the zirconium ions in the solutions (eventually resulting in the formation of a gelatinous, amorphous, hydrous oxide).⁶¹⁻⁶³ The resulting zirconium polymeric cations are intercalated into the clay layers by ion exchange with the interlayer cations of the clay, forming Zr-pillared clays.

Despite many experiments on Zr-pillared clays, the nature of the zirconium solutions, especially the polymerized species on hydrolytic polymerization, remains unclear, and the clay intercalates derived from these species are not definitely identified.

In this article, we demonstrate that three kinds of polynuclear cations are generated, depending upon the degree of polymerization of the zirconium cations in zirconium oxychloride solutions, and form three kinds of

intercalation compounds having different pore openings that correspond to the size of the zirconium species. Furthermore the occurrence and structure of the polynuclear species are discussed.

Experimental Section

I. Materials. Synthetic sodium fluoride tetrasilicic mica ($\text{NaMg}_{2.6}\text{Si}_4\text{O}_{10}\text{F}_2$) from Topy Ind., Ltd., was used as the starting material. A supplied 10 wt % sol of the silicate was diluted with water and impurities, i.e., α -cristobalite and magnesium fluoride richterite ($\text{Na}_2\text{Mg}_6\text{F}_2(\text{Si}_4\text{O}_{11})_2$), were separated by centrifugal sedimentation techniques. The purified sol was then condensed with an evaporator and dried at 100 °C. Distilled-deionized water was used for all the experimental work.

Sodium fluoride tetrasilicic mica has a 2:1 layered structure consisting of two layers of silica tetrahedra with a central octahedral layer containing magnesium. Na^+ ions exist between the silicate layers to compensate the negative layer charge arising from a deficiency of Mg^{2+} in the octahedral layer. These Na^+ ions are ion-exchangeable in water and the theoretical cation-exchange capacity is 254 mequiv/100 g of clay. The structural formula of the clay determined by chemical analyses is $\text{Na}_{1.00}\text{Mg}_{2.63}(\text{Si}_{3.86}\text{Al}_{0.05}\text{Mg}_{0.01}\text{O}_{10})\text{O}_{0.19}\text{F}_{1.81}$.⁶⁴ Further details concerning the characteristics of the layer silicate are described elsewhere.^{65,66}

II. Synthesis of the Zr-Pillared Clays. Solutions of zirconium oxychloride ($\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$, guaranteed reagent from Wako Pure Chem. Ind., Ltd.) was used as the pillaring agent. Reactions were carried out under the conditions of both room temperature and boiling temperature (reflux). Refluxing the zirconium oxychloride solutions was done before and after addition to the clay. Furthermore the concentration of the zirconium oxychloride solutions was varied in the range 0.1–1.5 M.

Room-Temperature Reaction System. To 0.1, 0.5, 1.0, and 1.5 M aqueous solutions of zirconium oxychloride, the clay was added to give a Zr/clay mole ratio of 5:1, and the suspensions were stirred for 24 h at room temperature to complete ion exchange. Next the resulting solids were centrifuged, washed repeatedly to remove all excess ions, and dried at 100 °C for 24 h.

Elevated-Temperature Reaction System. Aqueous solutions (0.1, 0.5, 1.0, and 1.5 M) of zirconium oxychloride were refluxed while being stirred for 1 h to permit hydrolysis and polymerization. Then the vessel was chilled with cold water to terminate the reaction. Next the clay was added to the solutions to give a Zr/clay mole ratio of 5:1 at room temperature and stirred for 2 h. The suspensions were then refluxed with vigorous stirring for 1 h. After cooling with cold water, the resulting solids were collected by centrifugation, washed repeatedly with water, and dried at 100 °C for 24 h.

The products so prepared by both room-temperature and elevated-temperature reactions were calcined at 200–700 °C for 4 h.

III. Characterization of the Pillared Clays. Powder XRD analysis was done with a Rigaku RU-200 diffractometer using $\text{Cu K}\alpha$ radiation. Pore sizes in the pillared clays were characterized in terms of both interlayer spacing (longitudinal pore size) and interpillar spacing (lateral pore size). The interlayer spacing was obtained by subtracting 9.6 Å, the thickness of the clay unit layer, from the XRD (001) basal spacing of the Zr-pillared clays. The interpillar distance was estimated by molecular probe studies,^{5,7,40} that is, by measurements of adsorption of molecules of different molecular dimensions. Referring to the method of Shabtai et al.,⁷ the measurements were done as follows.

The probe molecules used were octaethylporphyrin (from Aldrich Chem. Co.) and tetraphenylporphyrin (from Tokyo Kasai Kogyo Co. Ltd.); these polycyclic aromatic compounds are flat

(35) Farfan-Torres, E. M.; Dedecker, O.; Grange, P. In *Preparation of Catalysts V*; Poncelet, G., Jacobs, P. A., Grange, P., Delmon, B., Eds.; Elsevier: Amsterdam, 1991; p 337.

(36) Farfan-Torres, E. M.; Grange, P. In *Catalytic Science and Technology*; Yoshida, S., Takezawa, N., Ono, T., Eds.; Kodansha-Elsevier: Tokyo, 1991; Vol. 1, p 103.

(37) Farfan-Torres, E. M.; Grange, P. *Stud. Surf. Sci. Catal.* 1991, 60, p 97.

(38) Yang, R. T.; Baksh, M. S. A. *AIChE J.* 1991, 37, 679.

(39) Farfan-Torres, E. M.; Sham, E.; Grange, P. *Catal. Today* 1992, 15, 515.

(40) Tzou, M. S.; Pinnavaia, T. S. *Catal. Today* 1988, 2, 243.

(41) Sterte, J. *Clays Clay Miner.* 1986, 34, 658.

(42) Yamanaka, S.; Nishihara, T.; Hattori, M.; Suzuki, Y. *Mater. Chem. Phys.* 1987, 17, 87.

(43) Bernier, A.; Admaia, L. F.; Grange, P. *Appl. Catal.* 1991, 77, 269.

(44) Endo, T.; Mortland, M. M.; Pinnavaia, T. J. *Clays Clay Miner.* 1980, 28, 105.

(45) Endo, T.; Mortland, M. M.; Pinnavaia, T. J. *Clays Clay Miner.* 1981, 29, 153.

(46) Moyni, A.; Pinnavaia, T. J. *Solid State Ionics* 1988, 26, 119.

(47) Yamanaka, S.; Doi, T.; Sako, S.; Hattori, M. *Mat. Res. Bull.* 1984, 19, 161.

(48) Warburton, C. I. *Catal. Today* 1988, 2, 271.

(49) Yamanaka, S.; Hattori, M. *Catal. Today* 1988, 2, 261.

(50) Martin-Luengo, M. A.; Martins-Carvalho, H.; Ladriere, J.; Grange, P. *Clay Miner.* 1989, 24, 495.

(51) Rightor, E. G.; Tzou, M. S.; Pinnavaia, T. J. *J. Catal.* 1991, 130, 29.

(52) Mori, H.; Miyoshi, H.; Takeda, K.; Yoneyama, H.; Fujita, H.; Iwata, Y.; Otsuka, Y.; Murata, Y. *J. Mater. Sci.* 1992, 27, 3197.

(53) Christiano, S. P.; Wang, J.; Pinnavaia, T. J. *Inorg. Chem.* 1985, 24, 1222.

(54) Farfan-Torres, E. M.; Grange, P.; Delmon, B. *NATO ASI Ser B* 1987, 172, 489.

(55) Bellaloui, A.; Plee, D.; Meriaudeau, P. *Appl. Catal.* 1990, 63, L7.

(56) Shen, Y. F.; Ko, A. N.; Grange, P. *Appl. Catal.* 1990, 67, 93.

(57) Sterte, J. *Clays Clay Miner.* 1991, 39, 167.

(58) Skaribas, S. P.; Pomonis, P. J.; Grange, P.; Delmon, B. *J. Chem. Soc., Faraday Trans.* 1992, 88, 3217.

(59) Yamanaka, S.; Inoue, Y.; Hattori, M.; Okumura, F.; Yoshikawa, M. *Bull. Chem. Soc. Jpn.* 1992, 65, 2494.

(60) Gonzalez, F.; Pesquera, C.; Blanco, C.; Benito, I. *Inorg. Chem.* 1992, 31, 727.

(61) Clearfield, A. *Inorg. Chem.* 1964, 3, 146.

(62) Clearfield, A. *Rev. Pure Appl. Chem.* 1964, 14, 91.

(63) Clearfield, A. *J. Mater. Res.* 1990, 5, 161.

(64) Goto, S.; Sugimori, K.; Hayashi, T.; Kondo, R. *Nendo Kagaku* 1977, 17, 18.

(65) Ohtsuka, K.; Suda, M.; Ono, M.; Takahashi, M.; Sato, M.; Ishio, S. *Bull. Chem. Soc. Jpn.* 1987, 60, 871.

(66) Ohtsuka, K.; Suda, M.; Tsunoda, M.; Ono, M. *Chem. Mater.* 1990, 2, 511.

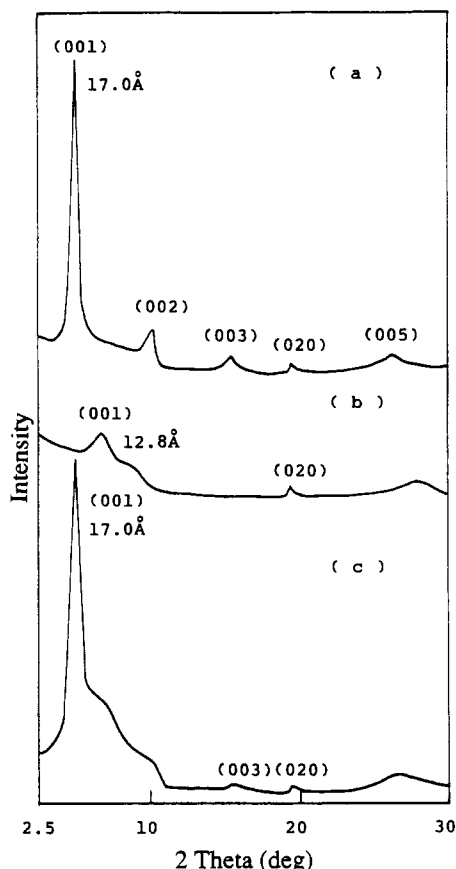


Figure 1. XRD patterns of (a) a Zr-pillared clay with a 7-Å interlayer spacing (the 7-Å phase) obtained by reaction of a clay with a 0.1 M zirconium oxychloride solution at room temperature, (b) the product obtained from calcining (a) at 500 °C for 4 h, and (c) the product obtained by reaction of a clay with a 1.0 M zirconium oxychloride solution at room temperature.

with a kinetic diameter of 15.3 and 19 Å, respectively. These compounds were dissolved in cyclohexane (guaranteed reagent from Wako Pure Chem. Ind., Ltd.) to give an initial concentration of 20 mg/L. Cyclohexane was treated with calcined NaX-type zeolites to remove water prior to use. Samples of 10–50 mg of Zr-pillared clays were calcined at 500 °C for 4 h and added to 40 mL of the cyclohexane solutions. Then the suspensions were shaken at 20 °C for 10 days to allow the concentration to come to equilibrium. The final concentration of the solutions was determined by UV spectrometry using a Shimadzu Model UV-200; the adsorbed amount was calculated by difference with the starting concentration. The equilibrium concentration was in the range 9–12 mg/L at each run. To estimate the amount adsorbed at the external surface, the same adsorption measurements were carried out with the reference sample. The reference sample, having a collapsed pore opening, was obtained by heating at 500 °C for 4 h a Zr-pillared clay prepared by refluxing a 0.5 M zirconium oxychloride solution for 1 h, adding clay and refluxing the suspension with a Zr/clay mole ratio of 1:1 for 1 h.

Surface areas were estimated with a Carlo Erba Sorptomatic Series 1800 by the Langmuir and the BET methods using N₂ gas adsorption. Although the pore sizes of the Zr-pillared clays are too small to adopt the BET method that is based on multilayer adsorption, Langmuir surface areas tend to overestimate these areas.

Results and Discussion

I. Room-Temperature Reaction System. As illustrated in Figure 1a, the intercalate obtained by the reaction of the clay with a 0.1 M zirconium oxychloride solution at room temperature had an interlayer spacing of 7.4 Å (d_{001} = 17.0 Å; hereafter designated the 7-Å phase). In general, the predominant species in aqueous zirconium oxychloride

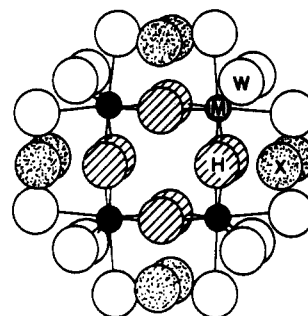


Figure 2. Model⁶⁷ for the zirconium tetrameric cation $[\text{Zr}_4(\text{OH})_8(\text{H}_2\text{O})_{16}\text{X}_2]^{(8-2)+}$ in solution: (M) Zr⁴⁺, (H) hydroxyl group, (W) H₂O, and (X) Cl⁻ and Br⁻.

Table I. Elemental Composition of Zr-Pillared Clays Prepared by Reaction of a Clay* with Zirconium Oxychloride Solutions Having Various Concentrations at Room Temperature

| ZrOCl ₂ concn (M) | composition ^b (mol) | | | | Cl/Zr (mol ratio) | ion-exchange ratio ^c (%) |
|---------------------------------|--------------------------------|------|------|------|----------------------|--|
| | Si | Zr | Cl | Na | | |
| 0.1 ^d | 4.00 | 0.67 | 0.01 | 0.23 | 0.01 | 77 |
| 0.5 ^e | 4.00 | 0.67 | 0.04 | 0.25 | 0.06 | 75 |
| 1.0 ^e | 4.00 | 0.59 | 0.04 | 0.23 | 0.07 | 77 |
| 1.5 ^e | 4.00 | 0.56 | 0.03 | 0.24 | 0.05 | 76 |

^a The clay employed was sodium fluoride tetrasilic mica, NaMg_{2.5}Si₄O₁₀F₂. ^b Normalized per 4 mol of Si. ^c Ion-exchange ratio was calculated by means of $\{1 - \text{Na (mol)}\} \times 100$. ^d The resulting product in this condition was the 7-Å phase. ^e The resulting product in this condition was the mixture of the 7-Å phase and other phases.

solutions is the zirconium tetrameric cation, $[\text{Zr}_4(\text{OH})_8(\text{H}_2\text{O})_{16}\text{X}_2]^{(8-2)+}$ (X = Cl, Br), where the zirconium atoms lie in a square and are each linked by a pair of hydroxyl bridges, as shown in Figure 2.^{67–69} Since the 0.1 M zirconium oxychloride solution used has a pH of 1.3 and the pH remained unchanged after the addition of clay, the major species in the solution is the zirconium tetramer.⁶⁸

Yamanaka and Brindley suggested formation of an intercalate with the tetramer by reaction of montmorillonite with a zirconium oxychloride solution at room temperature.²⁶ The dimensions of the zirconium tetramer are 8.98 Å in width and length and 5.82 Å in thickness.⁷⁰ Hence, one layer of the square tetramer lies flat between the silicate layers in this intercalate with a 7-Å interlayer spacing. The average chemical composition of the tetramer between the silicate layers is computed to be $[\text{Zr}_4(\text{OH})_{11.2}(\text{H}_2\text{O})_{12.7}\text{Cl}_{0.1}]^{4.7+}$ from the results of chemical analyses (Table I). The reduction of the cluster charge from $[\text{Zr}_4(\text{OH})_8(\text{H}_2\text{O})_{16}]^{8+}$ occurs through hydrolysis in the solution with clay and hydrolysis in the interlayer space of the clay induced by the polarization of the cation.

The interlayer spacing after calcination at 100, 200, 300, 400, 500, and 600 °C was 7.4, 5.2, 4.3, 3.7, 3.2, and 2.8 Å, respectively; upon heating, the intercalates had a lower structural regularity (Figure 1b).

XRD spectra of the intercalates derived from higher concentration (0.5, 1.0, and 1.5 M) solutions of zirconium oxychloride at room temperature gave patterns similar to that from the 0.1 M solution, but a broad shoulder at the base of the (001) reflection line emerged (Figure 1c). This

(67) Muha, G. M.; Vaughan, P. A. *J. Chem. Phys.* 1960, 33, 194.

(68) Baes, C. F., Jr.; Mesmer, R. E. *The Hydrolysis of Cations*; Wiley-Interscience: New York, 1976; p 152.

(69) Aberg, M. *Acta Chem. Scand.* 1977, B31, 171.

(70) Fryer, J. R.; Hutchison, J. L.; Paterson, R. *J. Colloid Interface Sci.* 1970, 34, 238.

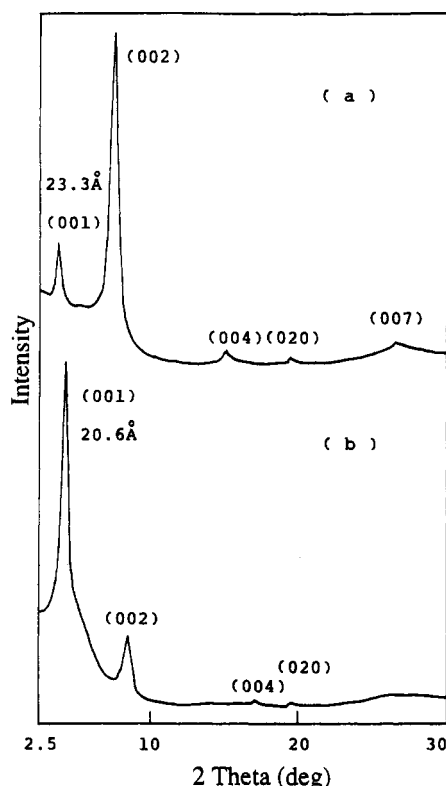


Figure 3. XRD patterns of (a) a Zr-pillared clay with a 14-Å interlayer spacing (the 14-Å phase) obtained by refluxing a 0.5 M zirconium oxychloride solution before and after addition to a clay, and (b) the product obtained from calcining (a) at 500 °C for 4 h.

indicates that the zirconium tetramer is dominant at the higher concentrations of zirconium oxychloride solutions, while there is a small amount of other species in these more acidic solutions.

II. Elevated-Temperature Reaction System. Low Concentration (0.1 and 0.5 M) Solutions of Zirconium Oxychloride. A Zr-pillared clay with a larger interlayer spacing of 13.7 Å ($d_{001} = 23.3$ Å; designated the 14-Å phase) was prepared by refluxing a 0.5 M zirconium oxychloride solution before and after addition to the clay (Figure 3a). In the case of a 0.1 M zirconium oxychloride solution, the 7-Å phase, which is the intercalate with the zirconium tetramer, was generated together with the 14-Å phase. Therefore, at low concentrations (0.1 and 0.5 M) of aqueous zirconium oxychloride solutions, the tetramer undergoes hydrolysis and polymerization by aging (refluxing), the higher polymerized species being generated that provides the 14-Å phase.

As shown in Table II, the amount of zirconium introduced into the silicate is higher in the intercalate prepared from the 0.5 M solution than in the intercalate prepared from the 0.1 M solution. This is ascribed to the fact that the 14-Å phase forming species is more hydrolyzed than the 7-Å phase forming species and has a reduced charge.

XRD patterns for the Zr-pillared clay with a 14-Å interlayer spacing showed several orders of 00 l reflection, indicating that the 14-Å phase has a regular structure and that the pillared clay can exhibit a homogeneous pore structure even after heat treatment at elevated temperature (Figure 3b). The 14-Å phase as-prepared has (002) as the most intense peak, but on heating (above 300 °C) (001) becomes the most intense peak. This is probably the result of dehydroxylation of the surface hydroxyl

Table II. Elemental Composition of Zr-Pillared Clays Prepared by Refluxing Zirconium Oxychloride Solutions Having Various Concentrations before and after Addition to a Clay^a

| ZrOCl ₂ concn (M) | composition ^b (mol) | | | | Cl/Zr (mol ratio) | ion-exchange ratio ^c (%) |
|---------------------------------|--------------------------------|------|------|------|----------------------|--|
| | Si | Zr | Cl | Na | | |
| 0.1 ^d | 4.00 | 1.01 | 0.06 | 0.20 | 0.06 | 80 |
| 0.5 ^e | 4.00 | 1.54 | 0.20 | 0.20 | 0.13 | 80 |
| 1.0 ^f | 4.00 | 0.99 | 0.21 | 0.19 | 0.21 | 81 |
| 1.5 ^g | 4.00 | 0.96 | 0.22 | 0.19 | 0.23 | 81 |

^a The clay employed was sodium fluoride tetrasilicic mica, NaMg_{2.5}Si₄O₁₀F₂. ^b Normalized per 4 mol of Si. ^c Ion-exchange ratio was calculated by means of $\{1 - \text{Na (mol)}\} \times 100$. ^d The resulting product in this condition was the mixture of the 14-Å phase and the 7-Å phase. ^e The resulting product in this condition was the 14-Å phase. ^f The resulting product in this condition was the mixture of the 12-Å phase and the 14-Å phase. ^g The resulting product in this condition was the 12-Å phase.

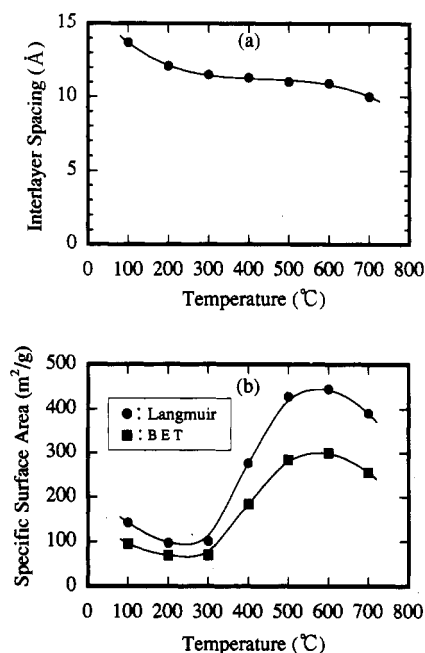


Figure 4. Changes in (a) interlayer spacings and (b) specific surface areas by the Langmuir and the BET models with heating temperature for a Zr-pillared clay with a 14-Å interlayer spacing (the 14-Å phase).

groups of the 14-Å forming species accompanied by structural rearrangement of the cluster between 300 and 500 °C. The structure of the cluster is discussed later.

Changes in the interlayer spacings and specific surface areas of the 14-Å phase as a function of the heating temperature are shown in Figure 4. The intercalates showed the highest Langmuir surface area of 445 m²/g at 600 °C and a high thermal stability up to 700 °C.

High Concentration (1.0 and 1.5 M) Solutions of Zirconium Oxychloride. Refluxing a 1.5 M zirconium oxychloride solution before and after addition to the clay produced an intercalate with a 11.7-Å interlayer spacing ($d_{001} = 21.3$ Å, designated the 12-Å phase; Figure 5a). On the other hand, refluxing a 1.0 M zirconium oxychloride solution produced the 12-Å phase and a small quantity of the 14-Å phase, which was obtained from refluxing low concentration solutions of zirconium oxychloride.

Hence, when high concentration solutions of zirconium oxychloride are aged (refluxed), the tetramer in the solutions is hydrolyzed and polymerized to the higher polymerized species that provides the 12-Å phase.

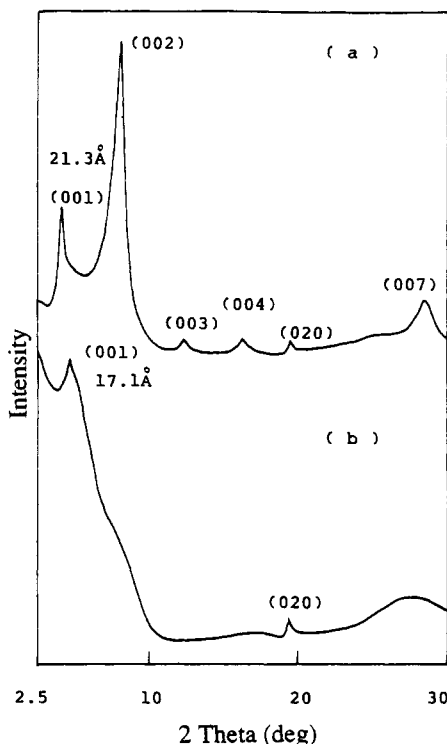


Figure 5. XRD patterns of (a) a Zr-pillared clay with a 12-Å interlayer spacing (the 12-Å phase) obtained by refluxing a 1.5 M zirconium oxychloride solution before and after addition to a clay, and (b) the product obtained from calcining (a) at 500 °C for 4 h.

This 12-Å phase easily dehydrates at low temperature (under 200 °C); upon calcination at 200 °C, the interlayer spacing changes to 9.8 Å. Probably water molecules are loosely associated with the zirconium polynuclear cations within the interlayer of the silicate. Hence, the 12-Å phase might be called the 10–12-Å phase.

A XRD pattern for the Zr-pillared clay indicates that the structure became heterogeneous or disordered upon calcination at elevated temperature (Figure 5b). The interlayer spacing after calcination at 100, 200, 300, 400, and 500 °C was 11.7, {9.8, 7.6 (weak)}, {9.8 (weak), 7.6}, 7.6, and 7.5 Å, respectively.

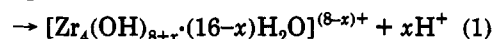
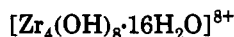
III. Zr Polynuclear Species Forming Zr-Pillared Clays. As mentioned above, we demonstrated the following results:

(1) The major species in zirconium oxychloride solutions at room temperature is the zirconium tetramer, giving rise to a product with a 7-Å interlayer spacing (the 7-Å phase) by intercalation with the clay.

(2) Refluxing low concentration (0.1–0.5 M) solutions of zirconium oxychloride causes hydrolytic polymerization of the tetramer, forming the higher polymerized species that gives a product with a 14-Å interlayer spacing (the 14-Å phase).

(3) Refluxing high concentration (1.0–1.5 M) solutions of zirconium oxychloride generates the higher polymerized species that gives a product with a 12-Å interlayer spacing (the 12-Å phase).

Clearfield suggested the following sequence of events during the aging of aqueous zirconium oxychloride solutions:^{61–63}



Aqueous solutions of zirconium oxychloride are highly acidic owing to hydrolysis, as depicted in eq 1. Heating the zirconium oxychloride solutions accelerates the process, shifting the equilibrium to the right (addition of base has the same effect). Subsequent polymerization results in formation of colloidal zirconia in which the particles are crystallized in the monoclinic phase (eqs 2 and 3).

The polymerization is suggested to occur in the following way.^{61–63,70} Upon heating, the tetramers are hydrolyzed and polymerized, two-dimensional polymers based upon the original tetrameric units being formed by theolation of the hydrolyzed zirconium tetramers: the tetramers are joined by ol bridges (hydroxy bridges) to form edge to edge bonding (Figure 6). Three-dimensional polymerization proceeds by oxolation between the two-dimensional layers: the layers are joined by oxo (–O–) bridges to form face-to-face bonding with elimination of water by condensation of hydroxyl groups (Figure 7a). In this face-to-face bonding, the tetramer layers stack together in such a way that the fluorite-type lattice of tetragonal zirconium dioxide can be formed, as illustrated in Figure 7b; the three-dimensional cluster has water and hydroxyl groups on the surface. When the three-dimensional assembly approaches a size of 12–24 tetramers, precipitation occurs and attains a 30-Å crystallite size. Then on prolonged refluxing, crystal growth and crystal perfection with transformation of the tetragonal to the monoclinic form takes place.

We think that the three-dimensionally polymerized species based upon the tetrameric units (Figure 7a) exist between the silicate layers of the Zr-pillared clays with 12- and 14-Å interlayer spacings; the *a*–*b* plane of the zirconium cluster orients in the galleries parallel to the silicate layers.

Since the dimension of the Zr tetramer is 5.8 Å in thickness,⁷⁰ the thickness of the cluster consisting of two two-dimensional layers joined together by face-to-face bonding, calculated using a diameter of oxygen anion of 2.5 Å, is 9.1 Å, and the thickness of the cluster consisting of three two-dimensional layers joined together by face-to-face bonding is 12.4 Å.

The thicknesses of these three zirconium species are in reasonable accord with the observed three interlayer spacings of the Zr-pillared clays, especially with the values calcined at 200 °C where adsorbed water is completely dehydrated. The interlayer spacings changed to a considerable extent between 100 and 200 °C.

(1) The zirconium tetramer (thickness = 5.8 Å) corresponds to the 7-Å phase (7.4-Å interlayer spacing (at 100 °C); 5.2-Å interlayer spacing (at 200 °C)). (2) The cluster consisting of two two-dimensional layers joined by face-to-face bonding (thickness = 9.1 Å) corresponds to the 12-Å phase (11.8-Å interlayer spacing (at 100 °C); 9.8-Å interlayer spacing (at 200 °C)). (3) The cluster consisting of three two-dimensional layers joined by face-to-face bonding (thickness = 12.4 Å) corresponds to the 14-Å phase (13.7-Å interlayer spacing (at 100 °C); 12.1-Å interlayer spacing (at 200 °C)).

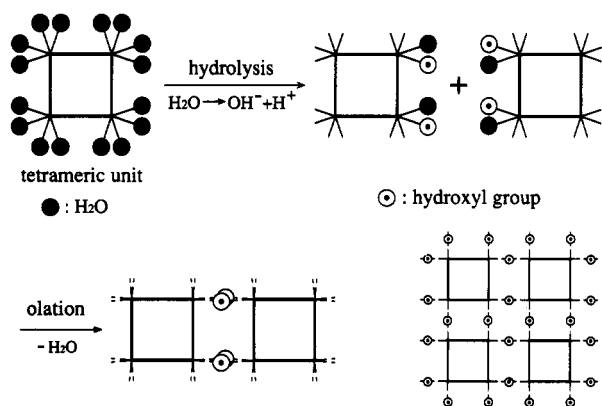


Figure 6. Formation of the two-dimensional sheet polymeric species by olation between the tetrameric units. The solid lined squares indicate the original tetrameric units and the dashed lines denote new ol bridges.

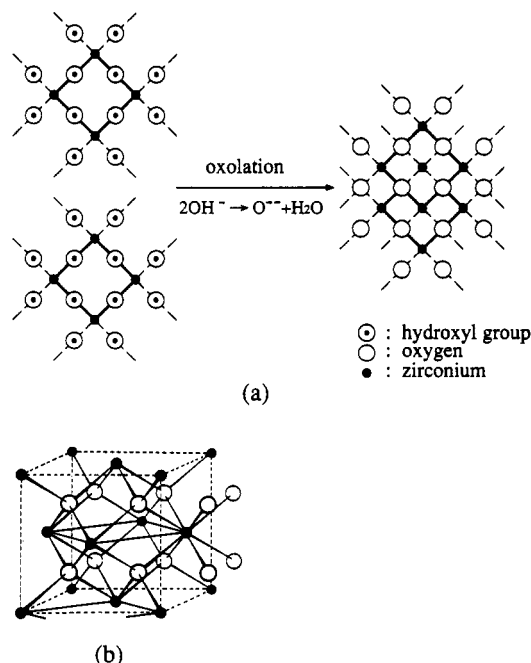


Figure 7. Formation of (a) the three-dimensional polymeric species by oxolation between the tetrameric units, and (b) the fluorite structure of ZrO₂.

Assuming that the 14-Å phase forming species may represent the upper limit of the size of the polymers obtained in solution and comprises 12 tetramers (as mentioned earlier, when the cluster approaches a size of 12–24 tetramers, precipitation occurs), the cluster cation is composed of three two-dimensional layers, and the two-dimensional layer is composed of four tetramers linked by olation.

It should be noted that the amount of Zr introduced into the Zr-pillared clays increased in the order the 7-Å phase < the 12-Å phase < the 14-Å phase: the amount of Zr in the 7-Å phase is (0.67 mol of Zr)/(formula unit of clay), the amount of Zr in the 12-Å phase is (0.96 mol of Zr)/(formula unit of clay), and the amount of Zr in the 14-Å phase is (1.54 mol of Zr)/(formula unit of clay) (Tables I and II). This indicates that the degree of hydrolytic polymerization of the species increases in the order, the 7-Å phase, the 12-Å phase, the 14-Å phase, that is, the charge of the species decreases in this order.

Murase and Kato found that two kinds of precipitates were formed by refluxing zirconium oxychloride solutions

depending on the concentration of hydrochloric acid in the solutions.⁷¹ Hydrochloric acid is formed by the hydrolysis of zirconium oxychloride solutions (eq 1). Hence both the concentration of the zirconium oxychloride solutions and the addition of hydrochloric acid to the solution govern the kinds of precipitates. Low-concentration solutions (under approximately 0.5 M) of zirconium oxychloride favor the precipitate of hydrous zirconium oxide, whereas high concentration solutions (over 0.5 M) of zirconium oxychloride favor the compound containing about 5 wt % Cl. Both the hydrous zirconium oxide and the Cl-containing compound have the monoclinic zirconium oxide crystal structure, but the latter is less three-dimensionally developed.

Hence, we may represent the following mechanism for the formation of the intercalates through hydrolytic polymerization of zirconium oxychloride solutions. Upon aging, hydrolytic polymerization of the zirconium tetramer leads to the more highly polymerized cation that produces the 14-Å phase. The 14-Å phase forming species consists of three two-dimensional layers linked by oxolation. Further polymerization causes the nucleation of hydrous zirconium oxide followed by precipitation. If the concentration of halogen ions (Cl⁻, Br⁻) is high, that is, the concentration of zirconium oxychloride is high or halides are added to the zirconium oxychloride solution when the tetramer is hydrolyzed and polymerized, the more highly polymerized cation containing a high amount of halogen is generated that forms the 12-Å phase.⁷² The 12-Å phase-forming species, being less highly polymerized than the 14-Å phase-forming species, consists of two two-dimensional layers joined by oxolation and halogen ions are held in this structure. These halogen ions probably exert an effect by inhibiting the oxolation of Zr tetramer units, and the precipitate formed by subsequent polymerization has less three-dimensionally developed zirconium dioxide structure containing a high amount of halogen.

In fact the polymeric species forming the 12-Å phase has a Cl/Zr mole ratio of 0.23, which is about twice as large as the amount of Cl of the polymeric species forming the 14-Å phase that has a Cl/Zr mole ratio of 0.13, as shown in Table II.

IV. Effects of Prereflux and Postreflux of ZrOCl₂ Solutions. Refluxing zirconium oxychloride solutions promotes hydrolysis and polymerization of the zirconium species in solution. The Zr-pillared clays were prepared by first refluxing the zirconium oxychloride solutions for 1 h, mixing the refluxed solutions with the clay for 2 h at room temperature and then a second refluxing of the suspension for 1 h.

The rate of the hydrolysis of the tetramer, depending on the concentration of the solutions, is slow in the absence of the clay.⁷³ Postrefluxing in the presence of the clay accelerates the hydrolysis of the tetramer owing to the migration of the sodium ions between the clay layers into the solutions, and causes rearrangement of the large

(71) Murase, Y.; Kato, E. *Nippon Kagaku Kaishi* 1976, 425.

(72) Refluxing for 1 h a 0.5 M zirconium oxychloride solution before and after addition to the clay led to the formation of the 14-Å phase. However refluxing for 1 h a 0.5 M zirconium oxychloride–0.5 M hydrochloric acid solution led to the formation of the 12-Å phase together with the 14-Å phase.

(73) Refluxing for 1 h a 0.5 M zirconium oxychloride solution before and after addition to the clay produced the 14-Å phase. However refluxing for 2 h a 0.5 M zirconium oxychloride solution and mixing it with the clay at room temperature generated the 7-Å phase along with the 14-Å phase. In both experiments the time for refluxing is equal.

Table III. Sorption of Probe Molecules on a Zr-Pillared Clay^a

| probe molecule | kinetic diameter (Å) | amount sorbed (mol/g) |
|----------------------|----------------------|--|
| octaethylporphyrin | 15.3 | 60 × 10 ⁻⁶ (16 × 10 ⁻⁶) ^b |
| tetraphenylporphyrin | 19 | 17 × 10 ⁻⁶ (13 × 10 ⁻⁶) ^b |

^a Obtained from calcining a Zr-pillared clay with a 14-Å interlayer spacing (the 14-Å phase) at 500 °C for 4 h. ^b Sorption on the reference sample having no pore opening, which is a collapsed Zr-pillared clay.

polymerized species between the layers.⁷⁴ However the pH of the suspensions is so low that too long postrefluxing causes the degradation of the clay structure. Therefore homogeneous intercalates are obtained with ease on the second refluxing, if intercalates have been prepared partially in advance by mixing the clay with the first refluxed solutions.

Apparently the Zr-pillared clays with 14- and 12-Å interlayer spacings are prepared even without postrefluxing if zirconium oxychloride solutions are aged for a long time to convert all the tetramers to the polymerized species (14-Å phase-forming species or 12-Å phase-forming species). For example, refluxing a 0.5 M zirconium oxychloride solution for 24 h and mixing the refluxed solution with the clay at room temperature produces the 14-Å phase.

V. Pore Sizes in the Zr-Pillared Clays. As mentioned above, the Zr-pillared clay with a 14-Å interlayer spacing has a uniform structure; the gallery height (interlayer spacing) of the pillared clay after calcination at 500 °C is 11.0 Å. Its lateral pore size (interpillar spacing) was determined by molecular probing; sorbed quantities on external surfaces were measured for the reference sample having no pore mouth. As shown in Table III,

(74) Refluxing for 1 h a 0.5 M zirconium oxychloride solution before and after addition to the clay gave the 14-Å phase (Zr-pillared clay with a 13.7-Å interlayer spacing). By further aging this compound in water (clay/water = 1 g/100 mL) at 100 °C for 24 h, the interlayer spacing was shifted by nearly 1 Å (from 13.7 to 14.8 Å) due to the ordering of pillars.

appreciable adsorption was found within the interlamellar space of the Zr-pillared clay for octaethylporphyrin with a kinetic diameter of 15.3 Å but not for tetraphenylporphyrin with a kinetic diameter of 19 Å. Thus the pores in the Zr-pillared clay are 11 Å in height and 15–19 Å wide.

Conclusions

Zirconium oxychloride solutions (0.1–1.5 M) were aged at room temperature and elevated temperature and reacted with a swelling clay. The predominant species in the zirconium oxychloride solutions at room temperature is the zirconium tetramer, giving rise to the Zr-pillared clay with a 7-Å interlayer spacing by intercalation with the clay. In general when this Zr tetramer is further hydrolyzed and polymerized, the higher polymerized species is generated that gives the Zr-pillared clay with a 14-Å interlayer spacing (the 14-Å phase). Eventually hydrous zirconium oxide precipitates with further polymerization of the species. On the other hand, if the concentration of halogen ions (Cl⁻, Br⁻) is high when the tetramer is hydrolyzed and polymerized, a higher polymerized species is generated that contains a high amount of halogen, giving the Zr-pillared clay with a 12-Å interlayer spacing (the 12-Å phase). Since this 12-Å interlayer spacing changes to a 10-Å interlayer spacing at low temperature, the 12-Å phase might be called the 10–12-Å phase. Upon further polymerization of the species, a compound containing a high amount of halogen precipitates. The 12- and 14-Å phases forming species are composed of three-dimensionally polymerized clusters based upon the tetramer.

The Zr-pillared clay with a 14-Å interlayer spacing showing a high thermal stability up to 700 °C has a regular structure and homogeneous pore structure even after heat treatment at elevated temperature. The lateral pore size of the 14-Å phase calcined at 500 °C is in the range 15–19 Å.

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