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Pillared Tetrasilicic Mica Catalysts Modified by Fixed Interlayer Cations. Classification of Fixation Mode by Cations

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Fluor-tetrasilicic mica (TSM) exchanged with various types of cations was calcined at 300 °C for 3 h, and a part of the cations were fixed, followed by Al-pillaring. Thus, acidic pillared clay catalysts were prepared with a modification of the silicate layer by cations. Active catalysts for cumene cracking were obtained when modified by Sr^{2+}, Ca^{2+}, La^{3+}, and Li^+. The structural changes in the catalysts affecting the reaction activity was examined through X-ray diffraction, surface area, and ^{29}Si-MASNMR measurements. The mode of cation fixation could be classified into five types, depending on the valence and size of the cations to be fixed. A group-2 cation (Na^+) gave no modification effect compared with conventional nonmodified PTSM and managed only meager catalytic activity. The catalyst modified by group-5 by (Sr^{2+}, Ca^{2+}, La^{3+} etc.) cations or a group-1 (Li^+) cation had a distinct pillared structure, characterized by an 18 Å basal spacing. These cations could be fixed either onto the basal oxygen surface for group-5 cations or into the octahedral vacancy for a group-1 cation. Though group-4 (Al^{3+}, Mg^{2+}) and group-3 (Cs^+, K^+) cations should also be fixed into the vacant sites and onto the surface, respectively, both types of modified catalysts formed unstable pillared structures, giving low catalytic activities.

The intercalation of aluminum hydroxy cluster cations between the layers of swellable clay minerals followed by calcination leads to bidimensional porous materials which are called pillared clays.¹⁾ The pillared clays prepared from smectite clay minerals are acidic and effectively catalyze organic reactions, such as the cracking of aromatic hydrocarbons.

Through the application of different kinds of material clays to the preparation of a pillared clay as catalyst, we found that fluor-tetrasilicic mica (TSM) gave a microporous, but acidless, pillared derivative.²⁻⁵⁾ While the pillared TSM (PTSM) was inactive for toluene alkylation by methanol, when the silicate-layers of TSM were modified by lanthanum ions, the modified pillared catalyst (La^{3+}–PTSM) showed high activity for alkylation, roughly comparable to that of the conventional pillared montmorillonite (PM).⁶,⁷⁾ The La^{3+}–PTSM was prepared as follows: TSM was first exchanged with La^{3+}, calcined at 300-400 °C and pillared by aluminum hydroxy cluster cations. During the calcination process, a part of the thermally dehydrated La^{3+} ions were fixed onto silicate layers while losing their exchangeability. We attributed the acidity genesis in La^{3+}–PTSM to the fixed La ions which remained even after Al-pillaring. Other polyvalent cations, having large ionic radii (such as Ce^{3+}, Sr^{2+}, Ca^{2+}) were also effective as modifiers. In this connection, a similar fixation of large cations by heating has been reported on La^{3+}–montmorillonite⁸⁾ and Ca^{2+}–bentonite.⁹⁻¹²⁾

On the other hand, the thermally induced irreversible fixation of small cations, such as Li^+, into the layer structure of montmorillonite is well-known as the Hofmann–Klemen effect,¹³,¹⁴⁾ and large monovalent cations, such as K^+ and NH_4^+, are known to be readily fixed by vermiculite without any thermal treatment.¹⁵,¹⁶⁾ The ease of fixation, thus, seems to be much dependent on the nature of the cation (especially valence and cation size), the layer structure of the clay, and the conditions at thermal treatment.

In this work, employing various cations having different valences and ionic radii as modifiers, we evaluated the catalytic properties of modified pillared TSM (M^{n+}–PTSM), and classified the fixation mode by the cations which affect the catalytic activity.

Experimental

Material Clay and Pillaring Agent. The sodium form of TSM was obtained from Topy Ind. The TSM, with or without refinement, was used for catalyst preparation. Unrefined TSM contained α-cristobalite and small amounts of tremolite-like mineral etc. as impurities. The refinement was made by the use of a conventional sedimentation technique and a <2 μm or <5 μm fraction was collected and dried to obtain the sodium form of the powder material. Various types of cations were exchanged with the original sodium ions of these TSM. In the case of Ca^{2+}–TSM, an in-situ cation exchange was also performed at the sedimentation stage; that is, aqueous calcium nitrate was added to an aqueous dispersion of clay containing a <5 μm or about <1 μm fraction of TSM particles.

The resulting cation-exchanged TSM is abbreviated M^{n+}–TSM(m); here, m(=1, 2, or 5) denotes the particle size (μm) of refined TSM. Unrefined TSM is represented by M^{n+}–TSM(U).

As a reference clay, synthetic Li^+–taeniolite supplied from Topy Ind. was used without further refinement.

An aluminum hydroxy cluster cation solution was prepared according to a previously reported method.⁷⁾

Catalyst Preparation. Various types of cation-modified pillared TSM (M^{n+}–PTSM) were prepared according to a method described in a preceding paper.⁷⁾ The preparative procedure is outlined below. Cation-exchanged TSM

(M^{n+}-TSM) was firstly calcined at 300 °C for 3 h. This calcination operation is referred to as calc. 1. The calcined M^{n+}-TSM was dispersed in a mixed solution of acetone and water, and an aluminum cluster cation solution was added as a pillaring agent and stirred for 12 h. After air-drying at 60 °C, the TSM with intercalated cluster cations was finally calcined at 300 °C at 3 h and used for the reaction. The second calcination operation is referred to as calc. 2.

The preparation of conventional nonmodified pillared TSM (PTSM) was described elsewhere.[2,3]

Reaction Procedure and Analysis. Cumene cracking was carried out using a conventional continuous-flow system under atmospheric pressure. The liquid products collected in an ice trap were analyzed by GLC using Bentone 34 and DNP column (4 m).

Characterization. X-ray diffraction (XRD) measurements were made with oriented clay films spread on glass slides.

The amount of nitrogen adsorbed on catalysts at 78 K was measured after evacuation at 300 °C for 1 h, and the BET or Langmuir surface area was determined.

The acidity of catalysts was examined by temperature programmed desorption (TPD) of adsorbed NH_3 with a He flow rate of 20 ml min^{-1} and a temperature rising rate of 10 °C min^{-1}. The measurement was started at 200 °C in order to eliminate any contribution of weakly adsorbed NH_3.

The ^{29}Si-MASNMR spectra were recorded on a JEOL JNM-GSX270 FT NMR spectrometer at 53.7 MHz. All of the clay samples for MASNMR measurements were prepared from unrefined clay materials, and the calcination operation after cation exchange or pillaring was carried out at 400 °C for 4 h.

Results

Cumene Cracking Activity. Table 1 shows the cumene cracking activities of various cation-modified pillared TSM (M^{n+}-PTSM) along with the values of the basal spacing (d_{001}) and surface area of the catalysts. On the right side of Table 1, the ionic radii[17] of modification cations and the group numbers which correspond with the mode of fixation (vide infra) are indicated.

Though Na^+-PTSM had a basal spacing of 18.8 Å and a large surface area of 207 $m^2\,g^{-1}$, it exhibited only a 0.27% cumene conversion, being as inactive as the conventional nonmodified PTSM. In the case of other modified PTSM, the activity greatly depended on the kind of modification cations. Particularly effective modifiers (such as Sr^{2+}, Ca^{2+}, La^{3+}, and Li^+) gave more than about 5% cumene conversion. All PTSM modified by these cations had distinct pillared structures characterized by 17—18 Å basal spacings, by N_2 adsorption isotherms of Langmuir type, and by surface areas more than 140 $m^2\,g^{-1}$. On the other hand, Al^{3+}, Mg^{2+}, Cs^+, and K^+ modified PTSM showed 10—11 Å basal spacings, indicating that their interlayer space collapsed. These modified PTSM showed only low activities.

A series of Ca^{2+}-PTSM prepared from Ca^{2+}-TSM with different particle sizes showed similar basal spacings (17.4—18.2 Å), though, the surface areas were noticeably different from one another. The cracking activities of these Ca^{2+}-PTSM catalysts were apparently influenced by the difference of surface area, and varied from 4.7 to 7.8% cumene conversion. The effect of particle size on the catalytic activity was rather small for Li^+-modified catalysts: Li^+-PTSM(5) showed 6.7% conversion, which is almost the same level as that of Li^+-PTSM(U). Thus, the difference in the degree of refining of material clay affected the catalytic activity to a certain extent, though the difference is not so influential as to void the classification in question.

Activity-Acidity Relationship. The acidity of M^{n+}-PTSM was estimated by temperature programmed desorption (TPD) of NH_3. All catalysts examined showed ammonia desorption peaks at around 370 °C. The amount of desorbed ammonia, which can be regarded as a measure of solid acidity, was calculated from the TPD peak area. Cumene cracking activity

Table 1. Catalytic Activities[a] of M^{n+}-PTSM for Cumene Cracking

Catalyst	d_{001}/Å	Surface area/$m^2\,g^{-1}$	Cumene conv./%	Cation radius/Å	Group No.
PTSM(5)	—	—	0.18		
Na^+ -PTSM(2)	18.8	207[c]	0.27	1.16	2
Al^{3+} -PTSM(2)	9.9	26.8[b]	0.26	0.68	4
Mg^{2+}-PTSM(2)	9.9	175[c]	1.2	0.86	4
Ba^{2+} -PTSM(2)	18.4	312[c]	0.92	1.49	5
Ce^{3+} -PTSM(2)	18.0	247[c]	2.7	1.15	5
Sr^{2+} -PTSM(2)	16.7	249[c]	6.9	1.32	5
Ca^{2+} -PTSM(1)	17.6	422[c]	7.8	1.14	5
Ca^{2+} -PTSM(5)	18.2	360[c]	4.7	1.14	5
Ca^{2+} -PTSM(U)	17.4	267[c]	4.7	1.14	5
La^{3+} -PTSM(2)	18.4	303[c]	7.5	1.17	5
Li^+ -PTSM(U)	17.7	138[c]	7.3	0.90	1
K^+ -PTSM(U)	9.9	—	0.22	1.52	3
Cs^+ -PTSM(U)	10.8	34.3[c]	0.21	1.81	3

a) Reaction temp 300 °C, W/F=33 g cat. h mol^{-1} (W=weight of catalyst, F=feed rate of reactant), flow rate of N_2 carrier gas 600 ml h^{-1}, averaged initial activity for 1 h after feeding of reactant. b) B.E.T. type N_2 adsorption isotherm. c) Langmuir type N_2 adsorption isotherm.

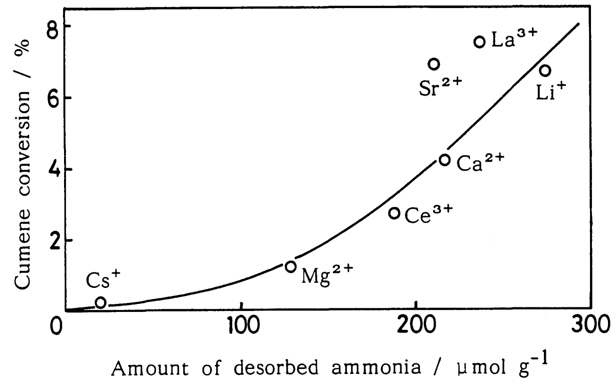


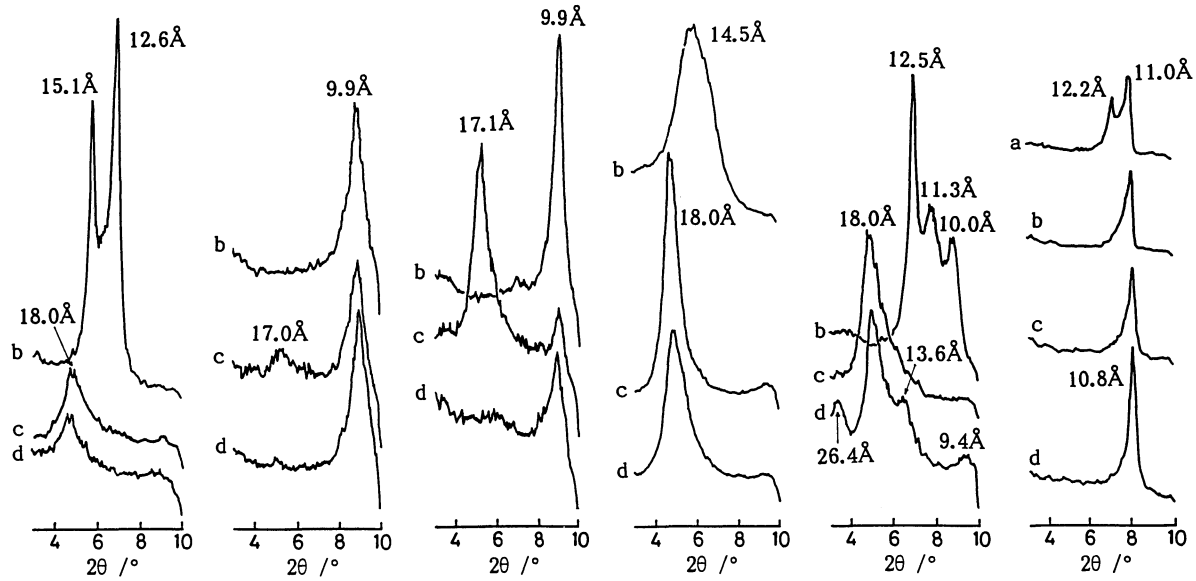
Fig. 1. Cumene cracking activities of various catalysts as a function of the amount of desorbed ammonia.

was plotted against the desorbed amount of NH_3 (Fig. 1). A good correlation between the acidity and activity was obtained. A similar relationsphip has already been ascertained for toluene alkylation by methanol with some pillared clays and HY zeolite.[3,4] Any catalyst which desorbed ammonia more than 200 μmol g^{-1} showed a high cracking activity, exceeding 4% cumene conversion.

X-Ray Powder Diffraction Data. Table 2 shows the change of the basal spacing in the course of the catalyst-preparation process, and some typical diffraction patterns are shown in Fig. 2. No difference was found in the behavior of the change in the basal spacing among several clays of different particle size. Cation exchanged TSM samples before pillaring

Table 2. Change in Basal Spacings in the Course of the Catalyst Preparation Process

Catalyst	Basal spacing d_{001}/Å				Group No.
	Before calc. 1 (M^{n+}-TSM)	After calc. 1 (M^{n+}-TSM)	After pillaring (M^{n+}-PTSM)	After calc. 2 (M^{n+}-PTSM)	
Na^+ -PTSM(2)	—	15.1/12.6	18.0	18.8	2
Al^{3+} -PTSM(2)	15.5	9.9	17.0/9.9	9.9	4
Mg^{2+}-PTSM(2)	—	9.9	17.1/9.8	9.9	4
Ba^{2+} -PTSM(2)	15.7	15.9	18.5	18.4	5
Ce^{3+} -PTSM(2)	—	14.2/9.8	18.0	18.0	5
Sr^{2+} -PTSM(2)	15.4	—	17.3	16.7	5
Ca^{2+} -PTSM(1)	15.8	14.5	18.0	17.7	5
La^{3+} -PTSM(2)	15.8	14.2/9.8	18.0	18.4	5
Li^+ -PTSM(U)	15.2	12.5/11.3/10.0	18.0	26.4/17.7	1
K^+ -PTSM(U)	10.0/12.4	9.9	9.9	—	3
Cs^+ -PTSM(U)	12.2/11.0	10.9	10.8	10.8	3



Na^+-PTSM Al^{3+}-PTSM Mg^{2+}-PTSM Ca^{2+}-PTSM Li^+-PTSM Cs^+-PTSM

Fig. 2. Change in XRD patterns during the preparation of M^{n+}-PTSM catalysts. (a) M^{n+}-TSM dried at 60 °C, (b) after calc. 1 at 300 °C for 3 h, (c) M^{n+}-PTSM after Al-pillaring and drying at 60 °C, (d) after calc. 2 at 300 °C for 3 h.

showed different basal spacings, depending on the degree of hydration. The following different spacings were observed: 14—15 Å (double-layer hydrated form[18]), 12—13 Å (single-layer hydrated form[18]), and 9—10 Å (anhydrous form[18]). After calc. 1, only an anhydrous form was observed for Al^{3+}, Mg^{2+}, K^+, and Cs^+–TSM. Cs^+–TSM had a larger d_{001} value (10.9 Å) than those of other anhydrous clays, the value of which is the same as a reported value for Cs^+-exchanged taeniolite in its anhydrous form.[19] After pillaring manipulation, the diffraction peaks at 17—18 Å were observed, indicating that Al hydroxy cluster cations were actually intercalated, except for the cases of K^+ and Cs^+–PTSM. Most of the pillared catalysts maintained approximately 18 Å peaks, even after the calc. 2 procedure. Particularly, the catalysts which exhibited high cracking activity (e.g., Sr^{2+}, Ca^{2+}, La^{3+}, and Li^+–PTSM) maintained their intense peaks. However, the peaks due to pillaring almost disappeared after the calc. 2 procedure for Al^{3+} and Mg^{2+}–PTSM because of their thermally unstable pillared structures.

In addition to a 18 Å peak, Li^+–PTSM after calc. 2 showed three weak peaks at 26.4, 13.6, and 9.4 Å. Singh et al. observed analogous diffraction peaks at 27.0, 14.3, and 9.6 Å for Al-pillared montmorillonite.[20] They prepared Al hydroxy cluster cations by extremely slow titration of an Al solution with diluted NaOH and reacted them with montmorillonite. They concluded that the pillared montmorillonite had a relatively regular interstratified structure of 9.6 and 18.9 Å component layers. Therefore, Li^+–PTSM may have similar interstratified phase after calc. 2.

^{29}Si-MASNMR Spectra. Figure 3 shows the ^{29}Si-MASNMR spectra of cation-exchanged TSM (M^{n+}–TSM) after a calc. 1 operation. For comparison, the spectra of cation-exchanged taeniolite (M^{n+}–T) are also displayed. The spectrum of Na^+–TSM showed a ^{29}Si signal at −93.8 ppm, which was assigned to the Q^3(0Al) signal observed when the central tetrahedral Si had no Al in the adjacent tetrahedra (0Al) at the tetrahedral layer structure formed by sharing three oxygens out of four in the SiO_4 unit (Q^3).[21—23] This chemical shift is somewhat different from the reported values of synthetic micas (−92.9 ppm for fluorophlogopite and −89.5 ppm for muscovite).[24]

While La^{3+}–TSM showed a distinct Q^3(0Al) signal at −94.5 ppm before the calc. 1 procedure, the signal was markedly broadened and its peak position shifted to around −98 ppm after calcination, approaching the chemical shift of neutral clay (−98.5 ppm for talc). This broadening means that the micro environment of the Si nuclei in a tetrahedral sheet of La^{3+}–TSM was inhomogenized;[25] the shift of the peak position suggests that a neutralization of the layer charge in TSM occurred.[21,26,27] These changes are probably due to the fixation of La^{3+} ions onto the silicate layers in a random fashion (vide infra).

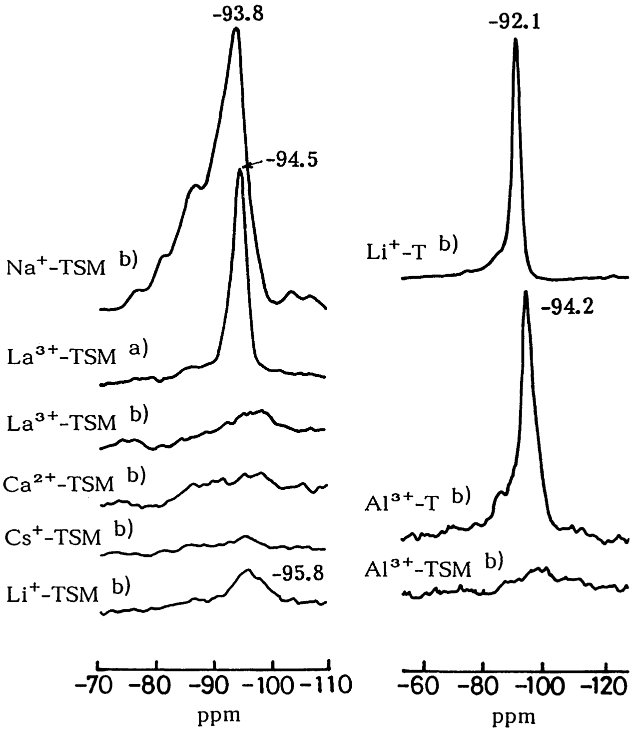


Fig. 3. ^{29}Si-MASNMR spectra of clay samples. a) Dried at 60 °C (before calc. 1). b) After calc. 1 at 400 °C for 4 h.

Broad ^{29}Si signals were also observed for the other cation-exchanged TSM (Al^{3+}–, Ca^{2+}–, Cs^+–, and Li^+–TSM) after calc. 1, except for Na^+–TSM. In these cases, monovalent cation (Cs^+ and Li^+)-exchanged TSM showed signals near −96 ppm, divalent cation (Ca^{2+})-exchanged TSM near −96 and −98 ppm, and trivalent cation (Al^{3+} and La^{3+})-exchanged TSM near −98 ppm. This order of chemical shift suggests that the higher valence of the exchanged cation, the more effectively is the negative charge of TSM neutralized.

In the case of taeniolite, the original Li^+ form (Li^+–T) showed a sharp Q^3(0Al) signal at −92.1 ppm, even after calc. 1. This chemical shift is very close to that of fluorophlogopite (−92.9 ppm)[24] which belongs to the same synthetic trioctahedral mica as taeniolite. Al^{3+}-exchanged taeniolite (Al^{3+}–T) showed a sharp Q^3(0Al) signal as well as Li^+–T, even after calc. 1, suggesting that these cations were not fixed by taeniolite.

Discussion

When the catalytic and structural data shown in Tables 1 and 2 and Fig. 2 are put together, it is possible to classify the cations as modifier into five groups, depending on the valence and size with respect to the mode of fixation. Each cation which belongs to the same group must be fixed by the same mechanism.

Group 1 (Li^+): Monovalent and small cation (<1 Å). Li^+–PTSM had a distinct pillared structure, and was very active for cumene cracking.

Group 2 (Na^+): Monovalent and large cation (1—1.5 Å). No modification effect was found for Na^+–PTSM, compared with the nonmodified conventional PTSM.

Group 3 (K^+, Cs^+): Monovalent and fairly large cations (>1.5 Å). The modified catalysts had small basal spacings due to an interlayer collapse, and pillared structures were not formed. The resulting catalysts were almost inactive for cumene cracking.

Group 4 (Mg^{2+}, Al^{3+}): Polyvalent and small cations (<1 Å). The pillared structures of the catalysts were very unstable upon heating during the calc. 2 operation, and displayed relatively low cracking activity.

Group 5 (Ba^{2+}, Ce^{3+}, Sr^{2+}, Ca^{2+}, and La^{3+}): Polyvalent and large cations (>1 Å). All of the modified catalysts have distinct pillared structures. Cracking activity varied by modifiers from 0.9 (Ba^{2+}–PTSM) to 7.5% (La^{3+}–PTSM) cumene conversion.

M^{n+}–PTSM catalysts could show high catalytic activity (>4% cumene conversion) when modified either by group-5 cations (Ca^{2+}, Sr^{2+}, and La^{3+}) or by a group-1 cation (Li^+). The already reported La^{3+}-modification mechanism[7)] can be commonly applicable to the acid-site generation caused by the modification with group-5 cations. An outline of the mechanism is as follows. During the calc. 1 operation, a part of the thermally dehydrated cations is fixed onto the basal-oxygen surface of TSM, where the cations are almost lodged in hexagonal holes. Consequently, the negative charge of TSM, which is expressed as the cation exchange capacity (CEC), is reduced according to the progress of fixation. After Al-pillaring, the fixed ions remain between layers where reactant molecules can be easily accessible, and the cations take charge of the genesis of acidic sites. Thus, the large-size modification cations with high electric fields can effectively function as acid sites. In this study, a broad ^{29}Si-MASNMR signal of calcined La^{3+}–TSM was observed in a higher magnetic field compared with uncalcined La^{3+}–TSM, which directly proves the above-mentioned reduction in negative charge of the silicate layer.

On the other hand, the PTSM modified by group-1 cation (Li^+–PTSM) showed a high catalytic activity, like La^{3+}–PTSM, despite the very low elecronegativity of the Li^+ ion. Another modification mechanism, different from that for group-5 cations, should be suggested. When a Li^+-exchanged montmorillonite is heated, the interlayer Li^+ ions migrate irreversibly into the layer structure (Hofmann–Klemen effect).[13,14)] The destination of the migrated Li^+ ions is still controversial. While Hofmann and Klemen originally advocated migration into vacant octahedral sites of montmorillonite,[13)] Tettenhorst considered, based on infrared data, that the migrated cations moved into the hexagonal holes, but did not penetrate into the octahedral sites.[28)] Anyhow, this type of Li^+-migration phenomenon is supposed to take place only when clay mineral is a dioctahedral and octahedrally substituted type.[29)] The layer structure of TSM fulfills the above-mentioned requisites, and similar irreversible migration, that is fixation, of Li^+ cations into the layer structure is unambiguously expected. Further, our observation of the difference in broadness between ^{29}Si signals of Li^+–TSM and Li^+–taeniolite supports the migration mechanism for Li^+ into octahedral vacant sites, since taeniolite has no octahedral vacancy and does not cause any broadening. If migrated Li^+ ions occupy the octahedral vacancies, the TSM layer may change to a hectorite-like structure.

$$Li^+(Mg_{5/2})^{oct}\cdot(Si_4)^{tet}\cdot O_{10}F_2 \longrightarrow Li_{1/2}{}^+(Mg_{5/2}Li_{1/2})^{oct}\cdot(Si_4)^{tet}\cdot O_{10}F_2$$

In contrast to TSM, hectorite possesses the ability to generate acidity in itself,[30)] and Al-pillared hectorite (calcined at 350 °C for 1 h under N_2 gas flow) prepared from synthetic fluor-hectorite showed a relatively high activity for toluene alkylation by methanol (7.5% toluene conversion), which roughly corresponds to two thirds of the activity of conventional pillared montmorillonite (11.5% toluene conversion).[3)] Therefore, it is reasonable that a pillared derivative of Li^+-fixed TSM comes to show appreciable activity.

Both Al^{3+} and Mg^{2+} (group-4 cations) are still smaller than Li^+, and a similar fixation mechanism may also be expected for these cations. The group-4 cations, however, are polyvalent, and presumably almost completely neutralize the negative charge of TSM layers. Such neutralization must lead to a remarkable decrease in the uptake of aluminum hydroxy cluster cations in the following pillaring step, resulting in an unstable pillared structure. Actually, though both Al^{3+}–PTSM and Mg^{2+}–PTSM showed basal-reflection peaks at 17 Å in the XRD spectra (Fig. 2), the peaks disappeared after heating at 300 °C for 3 h (calc. 2 procedure). In addition, compared with Mg^{2+}, when more positive Al^{3+} was employed as a modifier, the pillaring manipulation gave a less stable pillared structure, as suggested by a weaker 17 Å diffraction peak in Fig. 2. This fact also supports the migration-neutralization mechanism for the fixation of group-4 cations.

Recently, Suzuki et al. prepared Al-pillared montmorillonite with a controlled pillar population.[31)] They obtained a charge-reduced montmorillonite by calcining partially Ni^{2+}-exchanged Na^+-montmorillonite at 400 °C and pillared by Al hydroxy cluster cations. When Ni^{2+} ion was highly exchanged, a basal spacing of about 10 Å was observed after pillaring manipulation followed by calcination at 500 °C, indicating a lack of the pillared structure. Because the

Ni^{2+} ion is small (cation radius 0.83 Å)[17] and polyvalent, Ni^{2+} also belongs to group-4 according to our classification, and causes the lack of the pillared structure, presumably like Al^{3+} and Mg^{2+}.

When group-3 cations (Cs^+, K^+) were used for the modification, the obtained M^{n+}–PTSM catalysts were quite inactive for cumene cracking. Without calc. 1 operation, Cs^+-exchanged TSM showed two diffraction peaks which correspond to a single-layer hydrated phase (d_{001}=12.2 Å) and an anhydrous phase (d_{001}=11.0 Å), respectively. The single-layer hydrated phase disappeared after the calc. 1 operation. Similarly, K^+–TSM before calc. 1 showed both an intense 10.0 Å (anhydrous phase) and a weak 12.4 Å basal reflection peak (single-layer hydrated phase); only the anhydrous phase was observed after calc. 1. Such an anhydrous phase without heating has also been observed for K^+-saturated vermiculite, but K^+-saturated montmorillonite must be heated to form an anhydrous phase.[15] In K^+-exchanged vermiculite, K^+ ions are captured between the depressions formed by the hexagonal rings of basal oxygens, and are eventually fixed. Close fitting of the cation size of K^+ for hexagonal depressions and the low hydration energy of the ion are considered to be important factors in K^+ fixation.[15,16] In Cs^+– and K^+–TSM, both cations must be fixed by TSM because the negative layer charge of TSM is larger than that of smectite and because both cations have low hydration energies. Cs^+– and K^+–TSM showed no expansion by pillaring operation and kept their anhydrous forms, which indicates they have the character similar to K^+– or Cs^+-saturated vermiculite which have no expandability when they were immersed in water.[32]

In conclusion, each cation which belongs to group 1, 3, 4, and 5 could be fixed by TSM in different ways and affected differently the catalytic behavior of M^{n+}–PTSM. Only a group-2 cation (Na^+) exhibited no modification effect at all, suggesting that Na^+ ions could not be fixed by TSM. In fact, the result of chemical analysis of two Na^+–PTSM samples, one of which was treated on the calc. 1 operation at 300 °C and the other at 60 °C, showed no significant difference in the residual amount of Na^+ (Na/Si molar ratio was 0.04±0.01 for the former sample and 0.05±0.01 for the latter). This fact implies that a heat-induced fixation of Na^+ did not occur. Notable broadening of the ^{29}Si-MASNMR signal in M^{n+}–TSM was observed after calc. 1 at 300 °C, except for the case of Na^+–TSM. This broadening effect must be caused by the fixation of cations in a random fashion, either onto the basal oxygens (group 3,5) or into the layer structure (group 1,4) of TSM. No observation of such broadening in the MASNMR spectrum of Na^+–TSM supports the conclusion that Na^+ was not fixed by TSM.

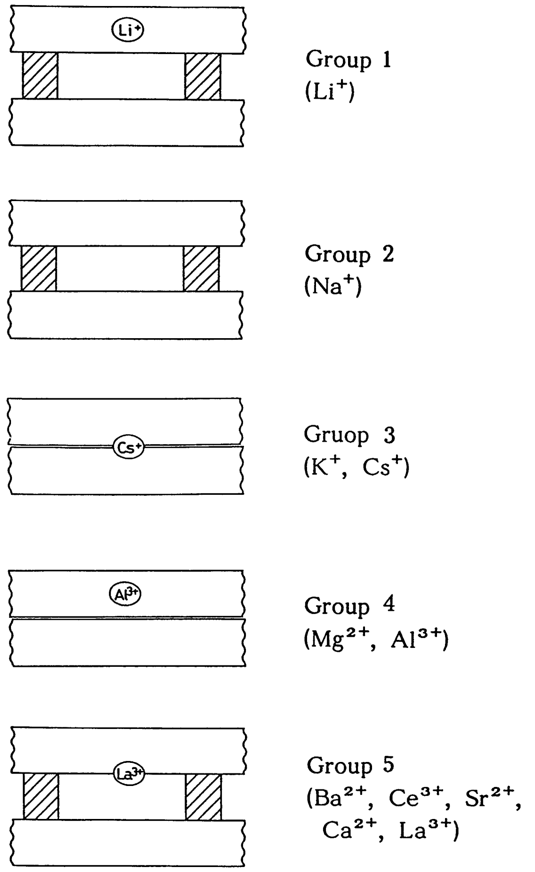


Fig. 4. Schematic representation of M^{n+}–PTSM catalyst in five cation groups.

On the basis of the above-mentioned consideration, the schematic structures of M^{n+}–PTSM after the calc. 2 operation can be depicted as shown in Fig. 4 in connection with the mode of fixation of group 1—5 cations. The cation-fixation mechanism and the effect of fixed cations on the pillaring process could be discriminated among the groups to give different catalytic activity.

Concluding Remarks

Here, employing TSM as a unique clay mineral which has a large layer charge and octahedral vacancies, and examining the effect of fixed cations on pillared clay catalysis, we showed that the fixation mode is primarily determined by the size and valence of the cations. Clay-mineralogically, we can regard this classification as being a chemical extension of the so-called "Hofmann–Klemen effect", which is a diagnostic method of octahedrally-substituted and dioctahedral clay. Also, from the catalytic point of view, the modification of clay layers by such a cation-fixation phenomena is considered to be useful for designing pillared clay catalysts at the molecular level, since the method can incorporate in order various types of cations, which function as the active sites, onto a clay surface or into the layer structure.

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