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Acidity Enhanced Pillared Clay Catalysts. Modification of Exchangeable Sites on Fluor-tetrasilicic Mica by the Fixed Interlayer Cations

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By the use of fluor-tetrasilicic mica (TSM) as a starting material, La^{3+}-modified pillared TSM was prepared by calcining La^{3+}-exchanged TSM followed by Al-pillaring. Nonmodified pillared TSM managed only a 0.1% conversion for toluene alkylation with methanol, but the alkylation activity was greatly enhanced by the modification to give more than a 7% conversion, the activity level of which was roughly comparable to that of the conventional pillared montmorillonite. The effect of modification greatly depended on the calcination temperature at the pretreatment of La^{3+}-exchanged TSM prior to a pillaring operation; the optimum calcination temperature was between 300 and 400 °C. Other multivalent cations with large ionic radii, such as Ce^{3+}, Ca^{2+}, and Sr^{2+}, were also useful as modifiers. On the basis of the results of measurements involving X-ray diffraction, cation-exchange capacity and IR spectra of the adsorbed pyridine, it was concluded that a part of the thermally dehydrated La^{3+} ions lost their exchangeability to be fixed on the cation exchange sites of layers, remained between layers even after Al-pillaring, and took charge of the genesis of acidic sites.

Pillared clays, which function as acid catalysts having good thermal stability and a molecular sieve property, are obtained by the intercalation of aluminum hydroxy cluster cations into the region between the silicate sheets of clay minerals.[1-4] Several kinds of polyoxocations other than Al, e.g., Zr, Cr, Ti, and Fe are also available as guest species, and the clays pillared by these guest species have been extensively studied.[5] In these studies, smectite clay minerals are exclusively employed as host clays: namely, montmorillonite,[2,3] hectorite,[6] fluor-hectorite,[6] laponite,[7,8] beidellite,[9-11] and saponite.[12-14] Through the examination of the acid catalysis of various types of clays, we have recently demonstrated the catalytic efficiency-determining factors in Al-pillared clay catalysts.[13] The factors on host clays include particle size, cation-exchange capacity (CEC) and the position of isomorphous substitution.

Fluor-tetrasilicic mica (TSM) is another interesting material clay, since it has a large CEC and a well-arranged layer structure. The sodium form of TSM, which was first synthesized as $Na(Mg_{5/2})^{oct.}(Si_4)^{tet.}O_{10}F_2$ by Kitajima and Daimon,[15] is known to have a free swelling property and a high cation-exchange ability. Morikawa et al.[16] reported an unusual property of TSM: that it possesses no acidic sites, even in the proton-exchanged form. By employing TSM as a starting material we could prepare an Al-pillared TSM (PTSM).[12,14] Due to its large CEC, TSM could be effectively pillared and the PTSM, thus obtained, showed a pore structure similar to that of pillared montmorillonite (PM); unexpectedly, however, it had few acid sites effective for toluene alkylation with methanol. We thus induced that a principal part in acidity genesis in pillared clays is played not by the pillars as guests but by the sheet silicate itself as a host.[14,17] It is therefore promising to modify not the pillars, but the silicate sheets of pillared clay in order to build up more acidic and active clay catalysts.

There have already been some examples of pillared clays modified through cation exchange. Shabtai et al.[18-20] introduced La^{3+} and Ce^{3+}, Vaughan et al.[21] introduced La^{3+} and Suib et al.[22,23] introduced Cr^{3+} and Fe^{3+}, into pillared montmorillonites or pillared bentonites (montmorillonite is a principal clay mineral of "bentonite" rock). However, the modification effects reported by them on activity improvement for some typical acid-catalyzed reactions remained obscure, because each nonmodified pillared montmorillonite used by them already had a substantial activity by itself. We recently found that the acidity of PTSM can be greatly enhanced when the silicate sheets of pillared TSM are modified by La^{3+} ions.[24,25] After native TSM was exchanged with La^{3+} and calcined at 300—400 °C, successive pillaring by aluminum hydroxy cluster cation was carried out in a mixture of acetone and water. The resulting catalyst gave a much higher catalytic activity for the toluene alkylation with methanol than nonmodified pillared TSM.

In this paper we described the preparative conditions of this La^{3+}-modified pillared TSM to give highly active catalysts in detail, and discuss the mechanism of acid-site generation by La^{3+} modification.

Experimental

Material Clay and Pillaring Agent. Samples of synthetic fluor-tetrasilicic mica were supplied from Topy Ind. and refined by means of the conventional sedimentation technique. The refined TSM contained only trace amounts of impurities, such as α-cristobalite. Reportedly, the composition of this clay by chemical analysis is[26] $Na_{1.00}Mg_{2.63}^{oct.}(Si_{3.94}Al_{0.05}Mg_{0.01})^{tet.}O_{10.19}F_{1.81}$. As a reference clay, refined natural montmorillonite (Kunipia F) was supplied by Kunimine Ind.

An aluminum hydroxy cluster cation solution (OH/Al=2.0) was prepared according to a known method.[2] An aqueous 0.5 M NaOH solution (1M=1 mol dm^{-3}) was slowly added (100 ml h^{-1}) to a 0.2 M $Al(NO_3)_3$ solution at 60 °C, and the mixture was aged for 2 h at the same temperature. The product solution was stored at room temperature.

Catalyst Preparation. The preparative procedure of various types of metal-modified pillared TSM (M^{n+}-PTSM) is illustrated in Fig. 1. First, metal ion-exchanged TSM (M^{n+}-TSM) was prepared using a metal nitrate solution followed by calcination at 200—500 °C for 3 h (procedure of calc.1). Al-pillaring manipulation was then achieved in a mixture of acetone and water according to the method of Yamanaka et al.[27] The calcined M^{n+}-TSM (1.2 g) was dispersed in a mixed solution of acetone and water (50 ml each) and stirred for 30 min; then, 150 ml of the aluminum hydroxy cluster cation solution (vide supra) was added to the dispersion. After stirring for 12 h, the product was filtered, washed repeatedly with deionized water and air-dried overnight at 60 °C. The M^{n+}-PTSM, thus obtained, was calcined in air (procedure of calc.2) and served as a catalyst. Nonmodified pillared TSM (PTSM) and pillared montmorillonite (PM) were prepared according to a previously reported method.[12,14]

Reaction Procedure and Analysis. Toluene alkylation with methanol and 2-propanol dehydration were both carried out using a conventional continuous-flow system under atmospheric pressure. The liquid products collected in an ice trap were analyzed by GLC using a Bentone 34 and DNP column (4 m) for toluene alkylation and a Porapack S column (1 m) for 2-propanol dehydration, respectively.

Characterization. X-Ray diffraction (XRD) analysis was carried out employing an oriented clay film spread on a glass slide. The nitrogen adsorption on the catalyst was measured at 78 K using constant-volume adsorption equipment; the surface area was calculated according to either the B.E.T. or to the Langmuir equation, depending on the type of adsorption isotherm.

Cation-exchange capacities (CEC) of clay samples were determined based on the amount of the Ca^{2+} which was replaced by Na^{+}[28] in a similar way to the conventional CEC determination.[29] Each clay sample (0.3 g) was diluted with quarts sand and packed in a Pyrex column (18 mm diameter). Aqueous $Ca(CH_3COO)_2$ (0.5 M) was added and the clay was saturated with Ca^{2+} ion. The clay was washed with a 90% EtOH solution and again exchanged to the sodium form with 1.71 M aqueous solution of NaCl. The Ca^{2+} ions leached out were determined by chelatometric titration.

IR spectra were recorded on a JASCO IR-810 spectrophotometer at room temperature. Each wafer sample of clay was mounted in a Pyrex-made IR cell and evacuated for 1 h at 300 °C. After cooling, the background spectrum was recorded, and pyridine was adsorbed at 150 °C. The sample was then treated at a given temperature between 150 and 450 °C in vacuo followed by cooling, and the corresponding spectrum was recorded. Finally, water was adsorbed on the sample at 200 °C, and the sample was evacuated at the same temperature, then the spectrum was recorded to examine the transformation of Lewis into Brϕnsted acid sites.[30]

Results and Discussion

Time Course of Catalytic Activity. The activities for the toluene alkylation with methanol over three kinds of catalysts (La^{3+}-modified pillared TSM (La^{3+}-PTSM), nonmodified pillared TSM (PTSM) and pillared montmorillonite (PM)) are compared in Fig. 2. La^{3+}-PTSM exhibited a high activity by the modification almost comparable to that of the conventional PM, whereas nonmodified PTSM showed only a meager conversion. Owing to carbon deposition, the toluene conversion was rapidly decreased with the

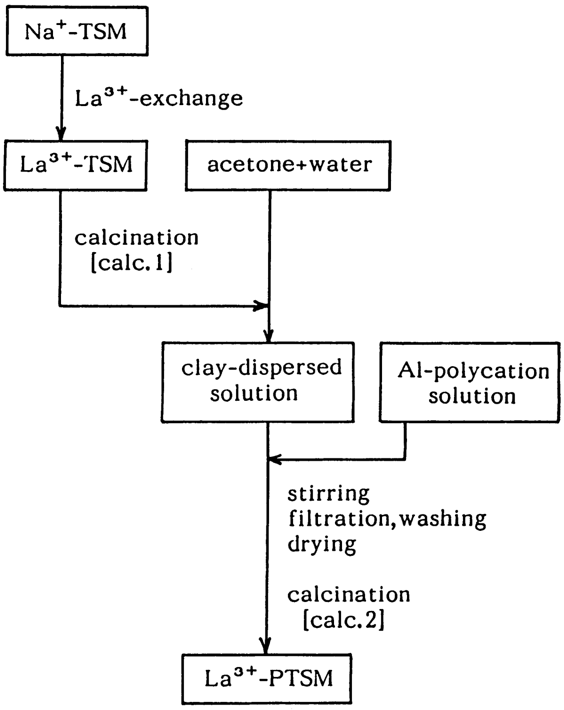

Fig. 1. Preparation procedure of La^{3+}-PTSM.

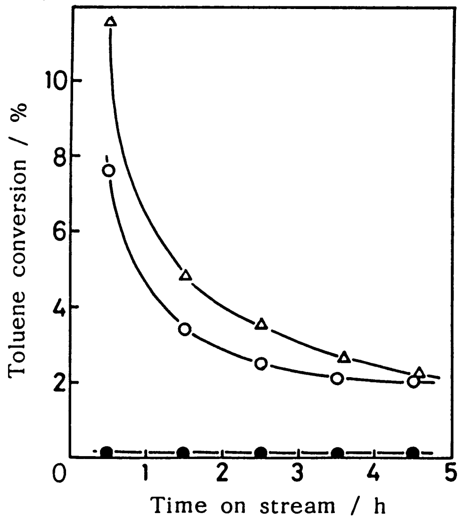

Fig. 2. Time course of catalytic activity for toluene alkylation. Reaction temp 350 °C, W/F=60 g h mol^{-1}, toluene : methanol=2 : 1 (mole ratio), flow rate of N_2 carrier gas 200 ml h^{-1}. (△) PM, (○) La^{3+}-PTSM, (●)PTSM.

time on stream for all catalysts tested. Incidentally, the deactivation rate was somewhat slower for La^{3+}-PTSM than for PM. Taking such deactivation into account, the averaged toluene conversion and xylene selectivity obtained 1 h after the reactant feed was initiated were subsequently taken as standard data to evaluate the catalytic efficiency.

Influence of Modifying Procedure on Catalytic Activity. Table 1 shows the initial conversions of the toluene alkylation by the catalysts obtained through various preparation methods, together with the data of basal spacing and surface area of the catalyst. Over the TSM-based catalysts, xylene was found to be a major product with a selectivity of more than about 80%. The Al-pillared, but nonmodified, catalyst (PTSM; No.1) showed a large surface area (197 $m^2 g^{-1}$) and a basal spacing of 18.4 Å. Considering the layer thickness of the clay itself (9.6 Å), the catalyst has an interlayer spacing (8.8 Å) large enough to accept the reactant organic molecules, though the nonmodified PTSM gave a very low activity. In the case of the La^{3+}-exchanged but nonpillared catalyst (La^{3+}-TSM; No. 2), the interlayer region collapsed (d_{001}=9.7 Å) on heating at 400 °, and the reaction did not proceed. In connection with the La^{3+}-modified and Al-pillared catalyst (La^{3+}-PTSM; Nos. 3—7), the activity varied widely, depending not only on the order of Al-pillaring and La^{3+}-exchange manipulation procedures, but also on the kind of clay-dispersion medium used in Al-pillaring and on the calcination conditions. When La^{3+} was ion-exchanged after Al-pillaring (No.3), the activity improved only slightly (from 0.1% to 0.7% conversion). In this case, La^{3+}-PTSM probably incorporated only a small amount of La^{3+}, because the CEC of once calcined pillared clay is greatly reduced to 10 to 20% of the initial CEC of the parent clay.[10,21] In order to prepare a highly active catalyst, the La^{3+}-exchange procedure prior to the Al-pillaring operation was indispensable. When non-calcined La^{3+}-TSM was pillared, the activity of the resulting La^{3+}-PTSM (No. 4) remained unaltered from that of nonmodified PTSM. On the other hand, when the La^{3+}-TSM was calcined at 400 °C and subsequently pillared in water without acetone (No. 5), the product clay showed a small basal spacing of 9.9 Å, indicating that aluminum hydroxy cluster cations were not intercalated. Thus, only when La^{3+}-TSM was first calcined, followed by Al-pillaring in a mixed medium of acetone and water (No. 6), a very active catalyst was obtained to afford high toluene conversion (3.2%). The best catalyst, which gives a higher toluene conversion (7.6%), was obtained when calc. 1 was operated at 300 °C and calc. 2 was omitted (No. 7).

Effect of Calcination Conditions. Since both calc.

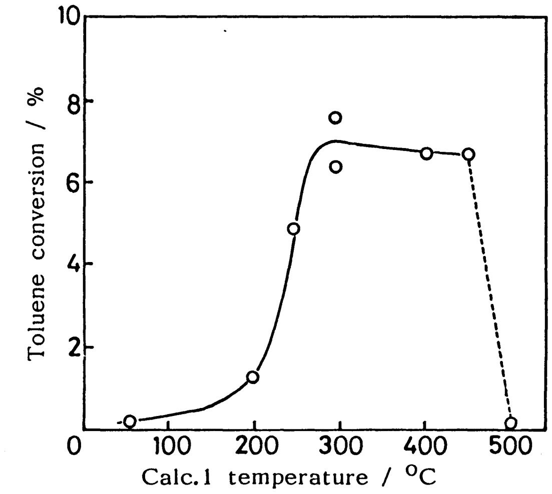

Fig. 3. Effect of the temperature of calc. 1 on toluene aklylation activity of La^{3+}-PTSM. Reaction temp 350 °C, W/F=60 g h mol^{-1}, toluene : methanol=2 : 1 (mole ratio), flow rate of N_2 carrier gas 200 ml h^{-1}.

Table 1. Catalytic Activities[a)] of the Catalysts Prepared by Various Methods for Toluene Alkylation by Methanol

No.	Catalyst	Preparation method[b)]	Clay dispersion medium[c)]	Calcination temp Calc. 1[d)] /°C	Calc. 2[e)] /°C	d_{001} /Å	Surface area[f)] /$m^2 g^{-1}$	Toluene conv. /%	Xylene selec. /%	p-Xylene fraction[g)] /%
1	PTSM	A	W	—	400	18.4	197[j)]	0.11	100	27.1
2	La^{3+}-TSM	B	—	—	400	9.7	—	0.0	—	—
3	La^{3+}-PTSM	C	W	—	400	18.0	—	0.7	100	30.2
4	La^{3+}-PTSM	D	W	h)	400	18.0	—	0.12	100	27.4
5	La^{3+}-PTSM	D	W	400	400	9.9	—	0.0	—	—
6	La^{3+}-PTSM	D	W+A	400	400	17.0	163[j)]	3.2	88.7	35.0
7	La^{3+}-PTSM	D	W+A	300	i)	17.7	242[j)]	7.6	77.5	40.1
8	PM	A	W	—	400	17.3	228[j)]	11.6	73.6	43.2

a) Reaction temp 350 °C, W/F=60 g cat. h mol^{-1} (W=weight of catalyst, F=feed rate of reactants), toluene : methanol=2 : 1 (mole ratio), flow rate of N_2 carrier gas 200 ml h^{-1}, averaged initial activity for 1 h after feeding of reactants. b) A: Al-pillaring only B: La^{3+}-exchange only C: La^{3+}-exchange after pillaring D: Al-pillaring after La^{3+}-exchange. c) Used for Al-pillaring (W: water W+A: mixture of water and acetone). d) Calcined for 3 h. e) Calcined for 4 h. f) Measured after evacuation at 300 °C for 1 h. g) p-Isomer fraction among the xylenes produced. h) Dried at 60 °C. i) Pretreated at 350 °C for 1 h under nitrogen gas flow before reaction. j) Langmuir type N_2 adsorption isotherm.

1 and calc. 2 procedures greatly affect the catalytic activity, appropriate calcination conditions were explored. Figure 3 shows the alkylation activities of La^{3+}-PTSM as a function of the temperature of calc. 1. The activity of the catalyst dried at 60 °C as calc. 1 was as low as that of nonmodified PTSM. When the calc. 1 temperature rose to over 200 °C, the activity rapidly increased with a rise in temperature and reached a maximum at 300 °C. The activity was maintained at over 6% conversion until the temperature reached 450 °C, but became almost inactive at 500 °C. This activity loss is due to the unsuccessful formation of a pillared structure of the catalyst (vide infra).

To evaluate the effect of the calc. 2 temperature, 2-propanol dehydration, which proceeds effectively even at a relatively low reaction temperature of 200 °C, was examined. As shown in Fig. 4, 2-propanol conversion rapidly decreased with increasing calcination temperature for both La^{3+}-PTSM and PTSM, but La^{3+}-PTSM exhibited a much higher activity than PTSM at every temperature. La^{3+}-PTSM showed 23% conversion at 300 °C, while PTSM dropped the conversion below 2% at the same temperature. Over either catalyst, the main product was propylene with a selectivity of more than 75%.

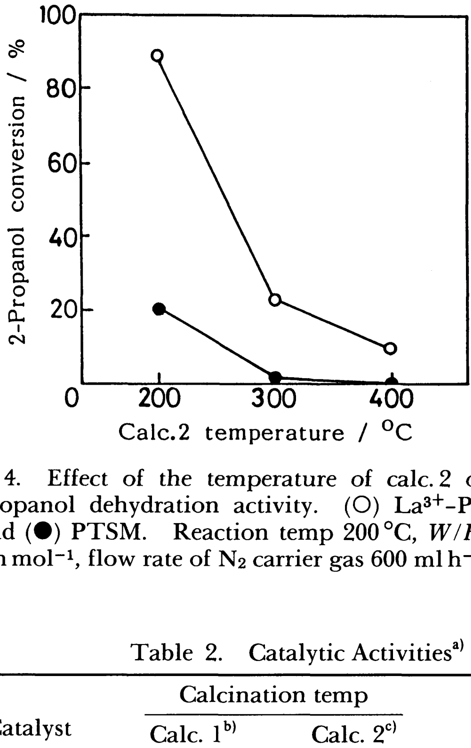

Fig. 4. Effect of the temperature of calc. 2 on 2-propanol dehydration activity. (○) La^{3+}-PTSM and (●) PTSM. Reaction temp 200 °C, W/F=2.1 g h mol^{-1}, flow rate of N_2 carrier gas 600 ml h^{-1}.

Modification by Various Cation Species. The modification of PTSM by various types of cations was performed in the same manner as in the case of La^{3+}-PTSM. As listed in Table 2, the modified pillared catalysts with large basal spacings of more than 17 Å were obtained, except for Al^{3+}-PTSM. These pillared catalysts, whose N_2 adsorption isotherms fitted with the Langmuir equation, showed specific surface areas of more than 160 m^2 g^{-1}. These catalysts have distinct pillared structures in this regard, but displayed different catalytic activities, depending on the modifying cation species used. With respect to monovalent cation Na$^+$, no differences in terms of both basal spacing and catalytic activity were found between Na$^+$-PTSM and PTSM (Table 1). With each of the divalent and trivalent cations (Ca^{2+}, Sr^{2+}, Ce^{3+}, and La^{3+}), the catalytic activity was greatly enhanced along with an increase of the p-xylene fraction. The highest modification effect was found for La^{3+}-PTSM. On the other hand, Al^{3+}-PTSM showed a "collapsed" basal spacing (9.8 Å) and N_2 adsorption isotherm obeyed the B.E.T. equation. The catalyst, hence, showed only very low activity (not more than 0.1% toluene conversion).

Structure Change of Clay. The structural change of clay in the course of the catalyst preparation process was traced by the use of XRD (Fig. 5). La^{3+}-TSM dried at 60 °C [(a) in Fig. 5(A)] had a double-layer hydrated form (d_{001}=15.8 Å); upon heating to 300 °C, another diffraction peak appeared which corresponds

Table 2. Catalytic Activities[a] of M^{n+}-PTSM for Toluene Alkylation by Methanol

Catalyst	Calcination temp		d_{001} /Å	Surface area[d] /m^2 g^{-1}	Toluene conv. /%	Xylene selec. /%	p-Xylene fraction[e] /%
	Calc. 1[b] /°C	Calc. 2[c] /°C					
Na$^+$-PTSM	300	f)	—	—	0.4	97.1	29.4
Na$^+$-PTSM	400	400	17.7	—	0.07	85.4	24.1
Al^{3+}-PTSM	300	f)	—	—	0.10	100	27.5
Al^{3+}-PTSM	400	400	9.8	22.0[g]	0.06	100	—
Ce^{3+}-PTSM	300	f)	—	—	2.0	94.9	32.5
Ce^{3+}-PTSM	400	400	17.0	182[h]	1.8	83.6	36.0
Ca^{2+}-PTSM	300	f)	17.3	—	4.9	82.5	34.6
Sr^{2+}-PTSM	300	f)	17.6	—	3.1	89.4	32.0
La^{3+}-PTSM	300	f)	17.7	242[h]	7.6	77.5	40.1
La^{3+}-PTSM	400	400	17.0	163[h]	3.2	88.7	35.0

a) Reaction temp 350 °C, W/F=60 g cat. h mol^{-1} (W=weight of catalyst, F=feed rate of reactants), toluene: methanol=2 : 1 (mole ratio), flow rate of N_2 carrier gas 200 ml h^{-1} averaged initial activity for 1 h after feeding of reactants. b) Calcined for 3 h. c) Calcined for 4 h. d) Measured after evacuation at 300 °C for 1 h. e) p-Isomer fraction among the xylenes produced. f) Pretreated at 350 °C for 1 h under nitrogen gas flow before reaction. g) B.E.T. type N_2 adsorption isotherm. h) Langmuir type N_2 adsorption isotherm.

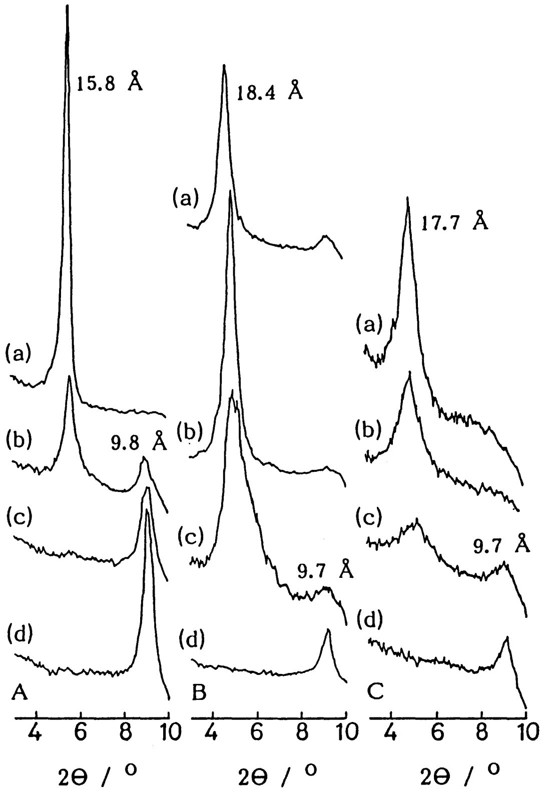

Fig. 5. Change in XRD patterns during the preparation of La^{3+}-PTSM. (A) La^{3+}-TSM after calc. 1, (B) La^{3+}-PTSM after Al-pillaring and drying at 60 °C, (C) after calc. 2 at 400 °C for 4 h. Calcined before Al-pillaring (calc. 1) at 60 °C (a), at 300 °C (b), 400 °C (c), and at 500 °C (d).

to an anhydrous form (d_{001}=9.7 Å) [(b) in Fig. 5(A)]. At 400 °C or above, only this anhydrous form was observed [(c) and (d) in Fig. 5(A)].

Such anhydrous clays could swell no longer in water, and it was impossible to introduce pillars between the layers by the conventional pillaring technique (see Table 1; No. 5). When a mixture of acetone and water was adopted as a clay dispersion medium, the basal spacing of La^{3+}-PTSM expanded to a definite level (17—18 Å) [(a), (b), and (c) in Fig. 5(B)]. When calc.1 was performed at 500 °C, the expansion of basal spacing by pillaring occurred no longer [(d) in Fig. 5(B)]. The low catalytic activity of the La^{3+}-PTSM which underwent heating at 500 °C in calc.1 (vide supra) is ascribed to the lack of an actual pillared structure.

The diffraction peak intensity after calc. 2 at 400 °C also altered, depending upon the calc. 1 temperature. The diffraction peak became weaker with increasing temperature of calc. 1. No collapsed basal spacing after calc. 2 was found, provided the calc.1 temperature remained below 300 °C [(a) and (b) in Fig. 5(C)], indicating a heat-stable pillared structure was obtained.

Thermal Change in CEC of La^{3+}-TSM. Figure 6 shows a change in the CEC of lanthanum-exchanged TSM (La^{3+}-TSM) with the calc.1 temperature. A La^{3+}-TSM sample dried at 60 °C had a CEC of 78 mequiv/100 g-clay. This value is much smaller than the reported CEC of native Na^{+}-TSM (190 mequiv/100 g)[31] but quite the same as that of Al^{3+}-TSM (78 mequiv/100 g). The discrepancy between the CEC values of Na^{+}-TSM and Al^{3+}-TSM has been reported to be due to a partial hydrolysis of the Al^{3+} ion.[26] Since the La^{3+} ion[32] is as the easily hydrolyzed as Al^{3+} ion, the small CEC value observed with dried La^{3+}-TSM is not unexpected.

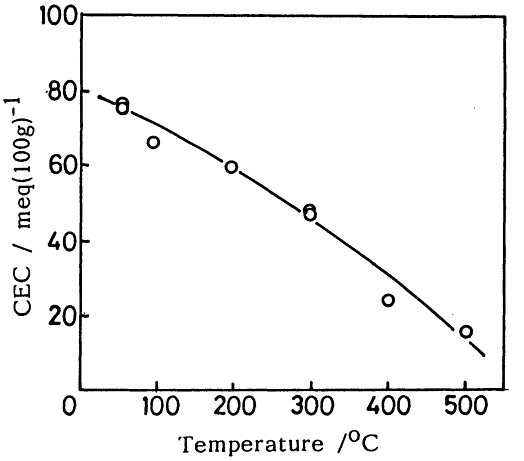

Fig. 6. Cation-exchange capacity of La^{3+}-TSM as a function of temperature of calc. 1.

The CEC value of La^{3+}-TSM linearly decreased from 78 to 15 mequiv/100 g with an increase in the temperature of calc.1 from 60 to 500 °C. This means that a part of the La^{3+} ions lost their exchangeability with other metal cations and became fixed between the silicate layers during the course of calcination. In other words, the amount of the fixed La^{3+} must increase with an increase in temperature. Such a reduction of CEC by heating was reported by Mozas et al.[33] in respect of La^{3+}-montmorillonite. Hofmann et al.[34] and Kondo et al.[35—37] also reported that the fixation of exchangeable cations in Ca^{2+}-bentonite occurred upon heating and that the CEC linearly reduced with increasing temperature.

It is well-known that when Li^{+}-exchanged montmorillonite is heated, small Li^{+} ions migrate into the vacant octahedral sites and neutralize the negative charge of montmorillonite, resulting in the reduction of CEC (Hofmann-Klemen effect).[38,39] Since the diameter of La^{3+} (2.34 Å) is larger than that of Li^{+} (1.80 Å), such migration of La^{3+} ions into an octahedral vacancy is considered to be unfeasible. Another mechanism must therefore be proposed for the case of La^{3+}-TSM.

Figure 7 shows the oxygen framework of TSM. The oxygen atoms which face an interlayer region (basal oxygens) form a repeated pattern of hexagons, and there is a depression which is called a "hexagonal hole" in the center of this network. When 2 : 1 type

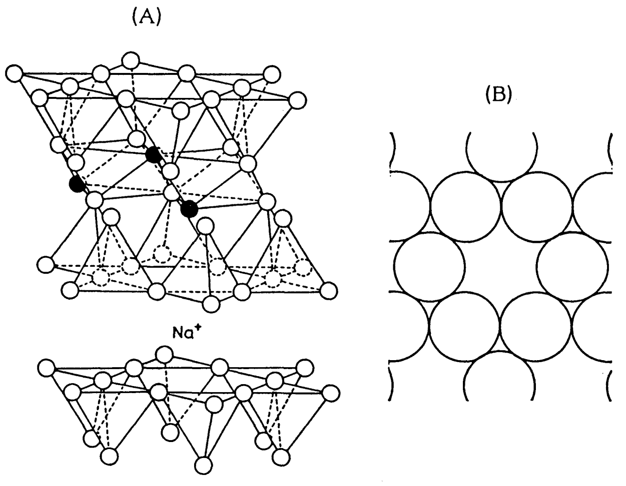

Fig. 7. Structure of fluor-tetrasilicic mica. (A) Layer structure, (○) oxygen, (●) fluorine. Every tetrahedral site is occupied by silicon and octahedral sites are occupied by magnesium or vacancy. (B) Hexagonal network of basal oxygens. "Hexagonal hole" is located in a center.

clay minerals, such as smectites and vermiculites, are heated so as to be converted to anhydrous forms, the interlayer cations are situated more or less within the hexagonal holes.[39] Taking account of the ionic diameter of La^{3+} (2.34 Å) and the fact that the basal spacing of La^{3+}-TSM heated at above 300 °C (9.7 Å) is very close to the layer thickness of TSM (9.6 Å), it seems probable that La ions are almost lodged in the hexagonal holes. The actual form of the fixed La ions in the dehydrated La^{3+}-TSM is not obvious at the present stage. The existence of a species such as $La(OH)^{2+}$, $(La\text{-}O\text{-}La)^{4+}$ or $(La{<}^{O}_{O}{>}La)^{2+}$ [40—42] has been suggested in the case of La^{3+}-exchanged Y-type zeolite. The bridged species are unlikely to exist in dehydrated La^{3+}-TSM, considering the small size of the hexagonal depression.

Kondo et al. found that the fixation of interlayer cations did occur in Ca^{2+}-bentonite, but not in Na^{+}-bentonite below 500 °C.[35—37] Above this temperature the clay lost its structural OH groups due to thermal dehydroxylation. The ease of the fixation of Ca^{2+} was ascribed to its greater electrostatic force than that of Na^{+} ion acting toward negatively charged surface oxygens.[37] If the La species exists in the form of La^{3+} or $La(OH)^{2+}$, such a nonbridged small-size species is also likely to be easily fixed onto silicate sheets.

Because the La^{3+}-fixed and charge-reduced TSM had a lower swelling ability than the original TSM, the intercalation of large aluminum hydroxy cluster cations into the interlayer spaces became difficult in an aqueous solution, and a pillared clay with an expanded basal spacing was not obtainable. To overcome this situation, the use of a mixture of acetone and water as a clay dispersion medium was effective and indispensable. Such a mixed medium was already reported by Yamanaka and Brindley[27] to be helpful for the Zr-pillaring of charge-reduced montmorillonites which was prepared by applying the Hofmann-Klemen effect described above. The larger dipole moment of the acetone molecule than that of water (water, 1.84×10^{-18} e.s.u.; acetone, 2.71×10^{-18} e.s.u.) must assist in the solvation of the residual exchangeable cations.[43]

Surface Acidity Generated by La-Modification. It has already been ascertained through the temperature-programmed desorption (TPD) of adsorbed NH_3 that the enhancement of the alkylation activity by La^{3+}-modification is attributable to an increased acidity.[25] To examine the characteristics of the acid sites generated by the modification in more detail, the IR spectra of the pyridine adsorbed on both PTSM and La^{3+}-PTSM were analyzed (Fig. 8). After pyridine adsorption at 150 °C followed by evacuation at the same temperature, three apparent absorption peaks of the adsorbed pyridine were observed at 1615, 1490, and 1450 cm^{-1} for La^{3+}-PTSM. The band at 1450 cm^{-1} indicates the presence of coordinatively adsorbed pyridines on the Lewis acid sites and both 1615 and 1490

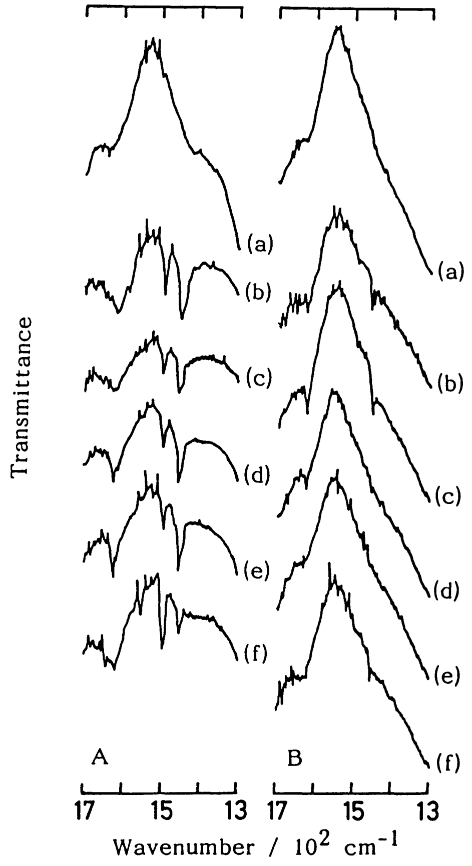

Fig. 8. IR spectra of pyridine adsorbed on La^{3+}-PTSM(A) and PTSM(B). (a) Back ground spectra, (b) after pyridine adsoption followed by evacuation at 150 °C, (c—e) followed by successive evacuation at 250 °C (c), 350 °C (d), and at 450 °C (e), (f) followed by water vapor adsorption and evacuation at 200 °C.

cm^{-1} bands are ascribed to the contribution of the pyridines adsorbed on both the Brϕnsted acid sites and the Lewis acid sites.[30] The 1490 cm^{-1} band gradually decreased its intensity ratio to the 1450 cm^{-1} band with increasing evacuation temperature up to 450 °C, whereas the intensity of 1450 cm^{-1} band remained nearly constant. This means that La^{3+}-PTSM contains both relatively weak Brϕnsted acid sites and strong Lewis acid sites. After water adsorption at 200 °C followed by evacuation at the same temperature, the intensity ratio of 1490 cm^{-1} to 1450 cm^{-1} reversed, and a new absorption band appeared at 1550 cm^{-1}. Apparently, some parts of the Lewis acid sites were converted to the Brϕnsted acid sites by adsorption of water.

For PTSM, the adsorbed pyridine was detected at 1620 and 1455 cm^{-1} after pyridine adsorption followed by evacuation at 150 °C. These bands, however, vanished readily upon evacuation at temperatures higher than 350—450 °C.

These results indicate that the fixed La^{3+} ions which remained between layers after Al-pillaring took charge of the genesis of acidic sites. Probably the fixed La^{3+} ions themselves function as Lewis acid centers; some part of them dissociate water molecules to liberate protons. Multivalent cations, such as La^{3+}, with a high electric field could thus effectively modify PTSM.

Concluding Remarks

Here, we succeeded for the first time in obtaining an acidity-enhanced pillared clay catalyst by making use of a unique phenomenon which occurred over the hexagonal network of a clay tetrahedral array, or the fixation of large interlayer cations, such as La^{3+} ions, onto the hexagonal cavities as cation exchange sites through thermal treatment. Recalling the very weak acidic nature or very low catalytic activity, shown by nonmodified PTSM, we can regard La^{3+}-modified pillared TSM as a well-organized pillared clay which possesses almost all of its acidic sites not on the pillars as guests, but on the walls of silicate sheets as hosts. Studies on the peculiar catalytic performance and microstructure of this modified pillared TSM are in progress through the application to other types of organic reactions and through the analysis by ^{27}Al, ^{29}Si-MAS NMR spectroscopy etc.

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