Pillared Tetrasilicic Mica Catalysts Having Fixed Interlayer Ca Ions. Comparison with Other Clays

Hiroaki Sakurai,† Kazuo Urabe,* and Yusuke Izumi*
Department of Synthetic Chemistry, Faculty of Engineering, Nagoya University,
Furo-cho, Chikusa-ku, Nagoya 464

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Three kinds of Ca^{2+}-modified pillared clays (TSM, taeniolite, and montmorillonite) were prepared from Ca^{2+}-exchanged clays. The cumene cracking activity over the TSM-based catalyst was greatly dependent on the calcination temperature before pillaring, and gave a maximum at 300—400 °C. In contrast, no appreciable increase in the activity with the calcination temperature before pillaring was observed in montmorillonite- and taeniolite-based catalysts. The amount of residual Ca in the modified pillared TSM was increased with a rise in the calcination temperature before pillaring, whereas the amount of Al incorporated through pillaring was decreased, showing the progress of Ca^{2+} fixation during the stage of thermal treatment of Ca^{2+}-exchanged unpillared TSM. Thus, the cracking activity was greatly enhanced by the fixation of Ca^{2+}. The cracking activity, however, dropped due to a pretreatment above 400 °C, since the Al-pillars which prop silicate layers are reduced while causing a decline in the surface area of the resulting pillared TSM; also, the strong acid sites were decreased due to excessive packing of Ca^{2+} fixed over the surface of silicate layers. In the cases of montmorillonite and taeniolite, the remaining amounts of Ca and Al were almost constant, irrespective of the calcination temperature before pillaring. This indicates that Ca^{2+} fixation does not occur in these clays.

Since pillared clay as a heat-stable porous material was synthesized by Brindley and Sempels in 1977,[1] clay minerals have attracted attention as potential catalytic materials, since pillared clays have both acidity and a molecular sieve ability. Pillared clay can be regarded as being an intercalated compound comprising a host silicate and guest oxide pillars. An aluminum hydroxy cluster cation, $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$, with a diameter of ca. 9 Å is most widely employed as a precursor of a pillar. To intercalate such a large cation between layers, the host clay, which has a free-swelling property in an aqueous medium, must be employed. Besides smectite clays (such as montmorillonite, hectorite, and saponite), the sodium form of fluor-tetrasilicic mica (TSM) fulfills the above-mentioned requisites; the clay is also swellable and cation exchangeable, and can form a porous pillared variant. Though the resulted pillared TSM (PTSM) had few acidic sites and was unattractive as an acidic catalyst, the acidity of the PTSM can be greatly enhanced by the fixation of interlayer cations onto the silicate layer of pillared TSM.[2] The fixation mode was classified into five types according to the valence and size of the cation to be fixed.[3] In these studies, TSM was employed as a host layer silicate. Since cation fixation into or onto a layered structure is due to an electrostatic force between dehydrated positive cations and negatively charged silicate layers, the ease of fixation might be affected not only by the nature of the cation, but also by the structure of the silicate layer.

The migration of small cations (such as Li^+, Al^{3+}, and Mg^{2+}) into a layer structure is known as the Hofmann-Klemen effect,[4-6] and occurs only in dioctahedral and octahedrally substituted clay minerals.[7] This principle, therefore, has been applied to the diagnostic method for montmorillonite.[7,8] It was found that the TSM layer with octahedral vacancies also gave rise to this type of migration-fixation.[3] The fixation of monovalent and fairly large cations (such as K^+ and Cs^+) has also been investigated in detail, and some factors that contribute to this type of fixation have already been reviewed in connection with both the interlayer cations and the silicate layer.[9,10]

On the other hand, the detailed controlling factors concerning the silicate layer are not yet known regarding the fixation of polyvalent and large cations. Only a few examples of La^{3+} and Ca^{2+} fixation by montmorillonite can be found in the literature.[11-13] No notable improving effect on the catalytic activity of pillared clay by the fixation of these cations has been ascertained in the case of clays other than TSM.

In this study, a similar modification of pillared clay was applied to other two clays, montmorillonite and taeniolite. Although the highest catalytic activity was exhibited by La^{3+}–PTSM among various cation modified catalysts, Ca^{2+} was employed here as a modifier, because Ca^{2+} is less susceptible to hydrolysis than is La^{3+}; a more quantitative discussion may be possible concerning fixation. Three kinds of pillared clays (Ca^{2+}–PTSM, Ca^{2+}–PM, and Ca^{2+}–PT) were compared with respect to their cracking activity. The residual cations (Ca^{2+}, Na^+) and the incorporated Al as a pillar component were determined. We also discuss here the relationship between cation-fixation and the change in the catalytic activity. Moreover, the distribution of Ca on the silicate surface was calculated based on a random distribution modes as a function of the amount of fixed Ca and is discussed in connection with the catalytic activity.

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† Present address: Government Industrial Research Institute of Osaka, Midorigaoka 1, Ikeda 563.

Experimental

Material Clay. Both the sodium form of fluor-tetrasilicic mica and the lithium form of taeniolite were supplied from Topy Ind. These samples were refined by means of a conventional sedimentation technique, and a <5 µm fraction was collected. The refined TSM contained only small amounts of impurities, such as α-cristobalite. Reportedly, the composition of TSM by chemical analysis is[14,15] $Na_{1.00}(Mg_{2.63})^{oct.}(Si_{3.94}Al_{0.05}Mg_{0.01})^{tet.}O_{10.19}F_{1.81}$.

Refined natural montmorillonite (Kunipia F) with high purity was supplied by Kunimine Ind., and used without further purification. The chemical formula of this montmorillonite is[15] $(K_{0.01}Na_{0.43}Mg_{0.01})(Al_{1.57}Fe^{3+}_{0.08}Fe^{2+}_{0.02}Mg_{0.34})^{oct.}(Si_{3.88}Al_{0.12})^{tet.}O_{10}(OH)_2$.

These clays were Ca^{2+}-exchanged by the use of either aqueous calcium nitrate or calcium chloride. In the case of TSM and taeniolite, an in situ cation exchange was performed during the sedimentation stage; that is, aqueous calcium chloride was added to an aqueous dispersion of clay containing a <5 µm fraction of TSM or taeniolite particles. Ca^{2+}-exchanged clays were washed repeatedly with deionized water until salt free; they were then dried at 60 °C.

Catalyst Preparation. Ca^{2+}-modified pillared clays (Ca^{2+}–PTSM, TSM; Ca^{2+}–PM, montmorillonite; Ca^{2+}–PT, taeniolite) were prepared according to a previously reported method.[2] The preparative procedure is as follows. Ca^{2+}-exchanged clays (Ca^{2+}–TSM, Ca^{2+}–M, and Ca^{2+}–T) were first calcined at 60—700 °C for 3 h (procedure of calc. 1). The calcined clays were dispersed in a mixed solution of acetone and water; an aluminum cluster cation solution (OH/Al=2.0)[2] was then added as a pillaring agent and stirred for 12 h. After air-drying at 60 °C, the clay samples were finally calcined at 300 °C for 3 h. The second calcination operation is referred to as calc. 2.

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

Characterization. X-Ray diffraction (XRD) analysis was carried out employing oriented clay films formed on glass slides.

The nitrogen adsorption over the catalyst was measured at 78 K after evacuation at 300 °C for 1 h; its surface area was calculated by either BET or Langmuir equation according to the type of adsorption isotherm. The pore-size distribution was computed from the isotherm according to the Cranston–Inkley method.[16]

The solid acidity of various catalysts was examined by the temperature-programmed desorption (TPD) of the adsorbed ammonia. The experimental conditions have already been described in a previous paper.[3]

The IR spectra of adsorbed pyridine were recorded on a JASCO IR-810 spectrophotometer according to a method described in a previous paper.[2]

Quantitative measurements of Ca, Al, and Na were carried out by use of an X-ray fluorescence spectrometer, VF-310 (Shimadzu Co., Ltd.). The clay sample (0.3 g) was fused with $Li_2B_4O_7$ (5.0 g) at 1100 °C, cooled in air, and a glass bead sample was obtained for the measurement.

Results and Discussion

Catalytic Activity Change. Figure 1 and Table 1 show the cumene cracking activity as a function of the calc. 1 temperature over a Ca^{2+}-modified pillared TSM catalyst (Ca^{2+}–PTSM). When the catalyst was dried at 60 °C as calc. 1, the cumene conversion (0.21%) was almost the same as that of nonmodified PTSM (0.18%). Beyond 200 °C, the activity drastically increased with a rise in temperature, and reached a maximum at 300—400 °C; it then decreased monotonously. The maximum conversion was 4.2%, which was about half the conversion on La^{3+}–PTSM (max. 7.6% at 300 °C).[2] While La^{3+}–PTSM became almost inactive at 500 °C (0.1% conversion) due to an interlayer collapse, Ca^{2+}–PTSM maintained a >1.5% conversion, even at 700 °C.

In the case of the other two clays Ca^{2+}–PM, montmorillonite; Ca^{2+}–PT, taeniolite), both catalysts dried at 60 °C already had a >10% conversion (Table 1). The conversion of Ca^{2+}–PM (13.3%) was about the

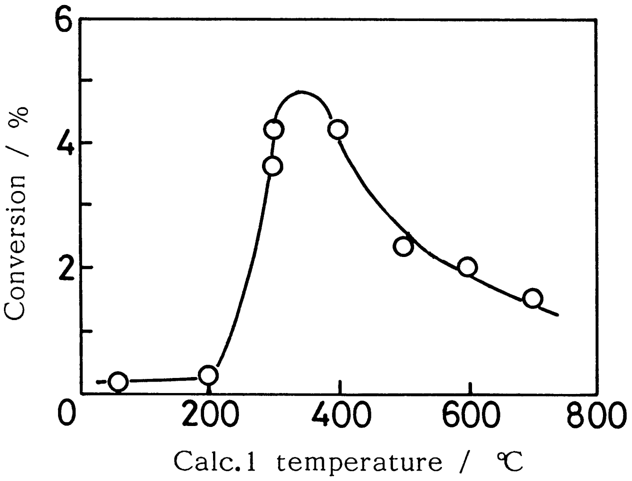


Fig. 1. Effect of the temperature of calc. 1 on cumene cracking activity of Ca^{2+}–PTSM. Reaction temp 300 °C, W/F=33 g h mol^{-1}, flow rate of N_2 carrier gas 600 ml h^{-1}.

Table 1. Cumene Cracking Activity of Ca^{2+}-Modified Pillared Clays[a)]

Calc. 1 Temp	Conversion over each catalyst/%		
°C	Ca^{2+}–PTSM	Ca^{2+}–PM	Ca^{2+}–PT
60	0.21	13.3	11.9
200	0.30	—	—
300	4.2	15.4	9.4
400	4.2	—	—
500	2.3	—	—
600	2.0	—	—
700	1.5	—	—

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.

same level as that of nonmodified conventional pillared montmorillonite (PM; 14.3% conversion). No outstanding increase in the activity with a rise in the calc. 1 temperature until 300 °C was found in these clays, which was the most significant difference from the case of TSM.

The Amount of Ca Fixed in Pillared Clay. Figure 2 shows the residual amounts of Ca in Ca^{2+}–PTSM, Ca^{2+}–PM, and Ca^{2+}–PT after calc. 2 at 300 °C. The amount of Ca is expressed for convenience as the mole ratio of Ca to Si when taking 4.00 for Si, because TSM ideally has a half unit cell formula, $Na^{+}(Mg_{5/2})^{oct.}(Si_4)^{tet.}O_{10}F_2$.

The Ca^{2+}-exchanged TSM before pillaring (Ca^{2+}–TSM) had a Ca amount of 1.03 (left side of Fig. 2), which corresponded to about twice the amount (0.50) calculated from the theoretical CEC (Cation Exchange Capacity) of TSM. Though the reason for this discrepancy is not clear, it is possibly due to an unavoidable hydrolysis of Ca^{2+} to form $Ca(OH)_2$. Reportedly, in cation-exchange process on H^{+}-montmorillonite with Cu^{2+}, Zn^{2+},[17] and La^{3+},[18] montmorillonite can retain these polyvalent cations beyond the CEC under a certain condition (pH, concentration, and the kind of coexisting anions), which is considered to be due to hydroxide precipitation.[17,18] Ca^{2+}-exchanged taeniolite (Ca^{2+}–T) also had excess Ca (0.80), as shown in Fig. 2. Under the present experimental conditions, however, Ca^{2+}-montmorillonite (Ca^{2+}–M) had a nearly equivalent amount (0.20) to the theoretical value (0.23) corresponding to the CEC which was calculated from the chemical formula shown above. Thus, the extensive hydrolysis of Ca^{2+} appears to be related to the layer charge of the clay.

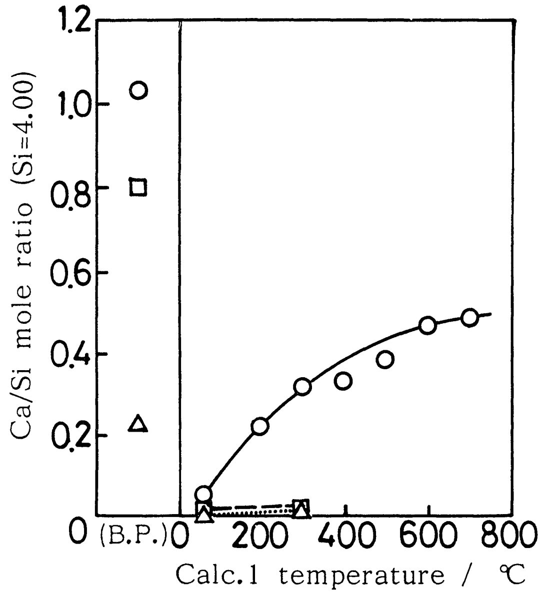


Fig. 2. Effect of the temperature of calc. 1 on the residual amount of Ca in Ca^{2+}-modified pillared clays. (○) TSM, (△) montmorillonite, (□) taeniolite. (B.P.) Ca^{2+}-exchanged clay before pillaring.

When calc. 1 was carried out at 60 °C, most parts of both the exchangeable Ca^{2+} and the above-mentioned excess of Ca incorporated in these clays were released after pillaring manipulation, being replaced by aluminum hydroxy cluster cations. Fortunately, under such circumstances, thermally fixed Ca is clearly quantitatively distinguishable from other types of Ca at higher temperatures of calc. 1. Indeed, the residual amount of Ca in Ca^{2+}–PTSM progressively increased with increasing calc. 1 temperature and reached 0.48 at 700 °C, coming near to a critical amount (0.50) limited by the CEC. This result is direct evidence of thermally induced Ca^{2+} fixation by the TSM layers. On the contrary, the residual Ca^{2+} did not increase at 300 °C at all in montmorillonite and taeniolite, suggesting that fixation did not occur in these clays. The fixation phenomenon well accounts for the change in catalytic activity shown in Fig. 1; that is, the activity of TSM is greatly enhanced with the progress of fixation, though no noticeable changes in the activity (see Table 1) are found in montmorillonite and taeniolite because of the absence of fixation.

The Ca^{2+} fixation by bentonite or montmorillonite, which brings about a reduction of CEC by a heat treatment, was reported by Hofmann and Endell[12] and Kondo.[13] Nevertheless, the fixation of Ca^{2+} by montmorillonite was not observed in the present study. The CEC of clay minerals is usually measured by the use of an aqueous salt solution under neutral conditions,[19] while in this study, the heated Ca^{2+}-montmorillonite was dispersed in a mixed solvent of acetone and water and then Ca^{2+} ions were subjected to exchange with an aqueous solution of aluminum hydroxy cluster cations (pH=4.0). The use of acetone and an acidic cation-exchange condition is possibly related to the difficulty of Ca^{2+} fixation onto the layer surface of montmorillonite. The large dipole moment of the acetone molecule facilitates the solvation of interlayer cations of charge-reduced montmorillonite.[20]

The most important question is what factor influence the ease of Ca^{2+} fixation in the three different clays. For an explanation, some of the known factors[9,10] controlling K^{+} fixation in soils and clay minerals are applicable, since both K^{+} and Ca^{2+} fix onto a silicate-layer surface, partly lodging in the hexagonal holes in a similar way.[3] These factors involve a layer charge as well as a substitution of F for OH in the octahedral sheet.[10] TSM has a much larger layer charge than dose montmorillonite, and can hold any fixed cations firmly. When a clay has an OH at the bottom of a hexagonal hole, the K^{+} ion receives an electrostatic repulsion force from the protonic part of the OH group. The substitution of F for OH removes this repulsion effect and facillitates the fixation of K^{+}.[10] Therefore, the F substitution in TSM must further facilitate the fixation of Ca^{2+} in addition to the effect of a large layer charge. However, these factors cannot account for the difference between TSM and taeniolite. The octahedral vacancies which exist in TSM must play an important role. In the case of K^+ fixation, it is also known that dioctahedral minerals hold K^+ ions more tightly than do trioctahedral minerals.[9] The Ca^{2+} fixation observed in TSM thus suggests the dioctahedral-like character of TSM.

The Amount of Al Incorporated by Pillaring. Figure 3 shows the amount of Al in the three catalysts after calc. 2. These clays had different amounts of Al before pillaring. The amounts of Al in TSM (0.05) and montmorillonite (1.61) determined by the present study agreed very well with the reported values[14,15] shown in the experimental section.

After pillaring, each clay increased in Al amount by intercalation of aluminum hydroxy cluster cations. When the calc. 1 procedure was performed at 60 °C, the amount that increased from the value before pillaring corresponded to the amount of Al incorporated by pillaring in the absence of Ca^{2+} fixation. These amounts of Al in TSM (1.06) and taeniolite (0.95) were greater than that of montmorillonite (0.79), reflecting a difference in the layer charge of native calys. The average positive charge per Al atom incorporated (Q_{Al}) was calculated using the following equation for both montmorillonite and TSM:

$$Q_{Al} = (Q_{layer} - M_{Na} - 2M_{Ca})/M_{Al},$$

where Q_{layer} denotes the layer charge of montmorillonite (0.46) or TSM (1.00) after Ref. 15; M_{Na} and M_{Ca} are the amounts of Na and Ca, respectively, remaining after pillaring, and M_{Al} is the amount of incorporated Al. The calculated values of Q_{Al} for TSM (0.56) and montmorillonite (0.57) were not only in fair agreement with a reported value on montmorillonite (0.56),[21] but were also very close to the Al charge (0.54) calculated from the formula of aluminum hydroxy cluster cation, $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$. This indicates that a direct exchange of Al_{13} cations occurred in these two clays.

The amount of incorporated Al monotonously decreased with increasing calc. 1 temperature in TSM. The decline curve was just upside-down to the rising curve of the Ca^{2+} amount in Fig. 2, suggesting that the layer charge reduction caused by Ca^{2+} fixation led to the decrease in the uptake of Al_{13} polycations. In contrast, no decrease in the Al amount was observed in montmorillonite and taeniolite, which is in harmony with the result that these clays do not fix Ca^{2+} ions.

Residual Amount of Na. The residual amount of Na in Ca^{2+}–PTSM is also plotted in Fig. 4 as a function of the calc. 1 temperature.

Ca^{2+}-exchanged TSM before pillaring had a considerable amount of residual Na (0.41; not shown in Fig. 4). Goto et al. reported that the cation exchange ratio of Na^+–TSM by divalent cations (Ca^{2+}, Mg^{2+}, and Ba^{2+}) was ca. 75%.[14] Ohtsuka et al. also described that 60—80% of Na^+ in TSM could be exchanged by Ni^{2+},[22] Co^{2+},[23] or Fe^{2+}.[24] Moreover, Kitajima et al. stated that 50—65% of the Li^+ ions in Li^+-taeniolite was exchangeable by monovalent cations and 70—85% by divalent cations.[25] The low exchange ratio in these expandable micas must be related to their high layer charges, since Na-type fluor-hectorite with a low layer

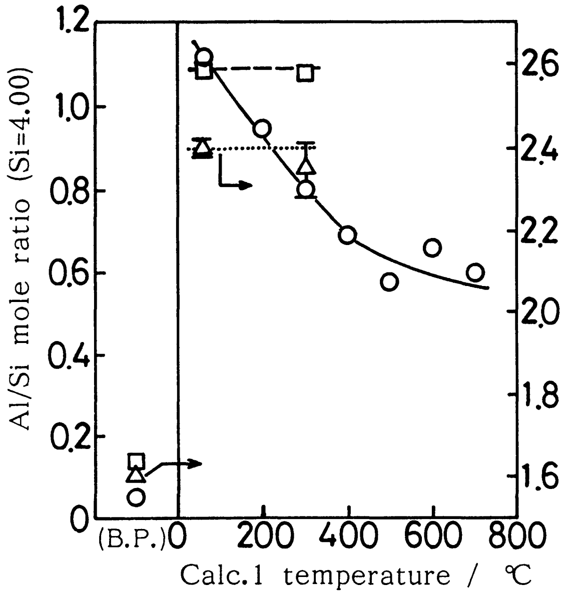


Fig. 3. Effect of the temperature of calc. 1 on the amount of Al in Ca^{2+}-modified pillared clays. (○) TSM, (△) montmorillonite, (□) taeniolite. (B.P.) Ca^{2+}-exchanged clay before pillaring.

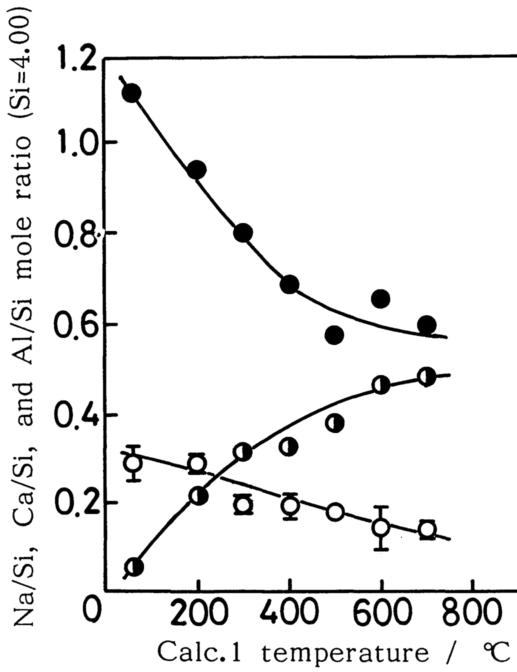


Fig. 4. Effect of the temperature of calc. 1 on the residual amount of Na, Ca, and Al in Ca^{2+}–PTSM. (○) Na, (◑) Ca, (●) Al.

Table 2. Basal Spacing of Each Catalyst

Calc. 1 temp	Basal spacing d_{001}/Å				
	Ca^{2+}–PTSM			Ca^{2+}–PM	Ca^{2+}–PT
	After calc. 1	After pillaring	After calc. 2	After calc. 2	After calc. 2
60	15.4	17.5	17.7	17.8	17.0
200	15.2	17.7	17.8	—	—
300	12.5	17.5	17.8	17.8	17.0
400	12.5	17.7	17.8	—	—
500	12.4/9.6	17.3	17.8	—	—
600	12.5/9.7	17.3	18.4	—	—
700	12.4	17.8	18.4	—	—

charge (1/3 per half unit cell) can exchange cations in a higher ratio than does taeniolite (90—95% of Na^+ are exchangeable by monovalent cations and 95—98% by divalent cations).[25]

The residual Na was decreased from 0.41 ro 0.29 due to a subsequent cation exchange with Al hydroxy cluster cations in a pillaring procedure when calc. 1 was performed at 60 °C. Quite different from the case of Ca, the Na amount was further decreased with a rise in temperature at calc. 1. This implies that a thermally induced fixation of Na never occurs, supporting the classification of the fixation mode already discussed in a preceding paper.[3]

Change in Basal Spacing and Surface Area. Table 2 shows the change in the basal spacing with the temperature in the calc. 1 procedure. Ca^{2+}-exchanged TSM after calc. 1 at 60 or 200 °C had a double-layer hydrated form (d_{001}=15.2—15.4 Å). The spacing decreased to 12.5 Å at 300—400 °C, where the clay is a single-layer hydrated form. In addition to the appearance of an anhydrous phase at 500—600 °C (d_{001}=9.6—9.7 Å), Ca^{2+}–TSM still maintained the single-layer hydrated form, even above 500 °C. This feature was very different from that of La^{3+}–TSM, since only an anhydrous form was observed at 400 °C or above in La^{3+}–TSM. An expansion of the basal spacing to 17—18 Å by pillaring was observed throughout the temperature range 60—700 °C; this spacing was maintained after calc. 2 at 300 °C. The Ca^{2+}–PTSM, thereby, showed a >1.5% cumene cracking conversion, even when the temperature of calc. 1 exceeded 500 °C, whereas La^{3+}–PTSM was almost inactive in toluene alkylation due to a collapsed basal spacing (d=9.7 Å) when treated at 500 °C in calc. 1. This structural difference beween Ca^{2+}–PTSM and La^{3+}–PTSM is possibly ascribed to a difference in the charge of the modification cations. The higher charge of La^{3+} can neutralize the negative charge of TSM layers more effectively than Ca^{2+}, as revealed from the ^{29}Si-MASNMR data.[3] The highly charge-reduced La^{3+} exchanged TSM (above 500 °C of calc. 1 temperature) is too much decreased in swellability to uptake Al polycations between layers in a pillaring manipulation.[2]

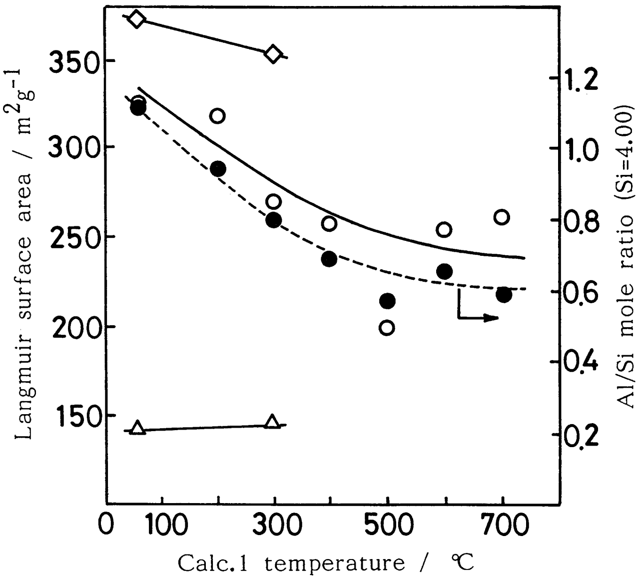


Fig. 5. Effect of the temperature of calc. 1 on the surface area of catalysts. (○) TSM, (◇) montmorillonite, (△) taeniolite. (●) The amount of Al in Ca^{2+}–PTSM.

Table 3. Surface Area of Ca^{2+}–PTSM

		Calc. 1 at 60 °C	Calc. 1 at 300 °C
Surface area[a)]	S_{all}	324	270
	S_{ext}	37.0	41.8
$m^2 g^{-1}$	S_{int}	287	228

a) S_{all}: Total Langmuir surface area, S_{ext}: external surface area, S_{int}: internal surface area.

The formation of a pillared structure with a basal spacing of 17—18 Å was also confirmed both in Ca^{2+}–PM and in Ca^{2+}–PT. No difference in the basal spacing was found when each of them was subjected to a thermal treatment in calc. 1 at temperature of 60 and 300 °C.

Figure 5 shows the change in the surface area. Ca^{2+}–PTSM diminished its surface area with a rise in the calc. 1 temperature. The decreasing curve was similar to that of the change (Fig. 3) in the amount of

Al remaining in the catalyst. On the basis of a pore-size distribution analysis, the surface areas belonging to both the internal micropore (S_{int}) and the exteranl mesopore (S_{ext}) were calculated (Table 3). S_{int} is a measure of the micropores formed between silicate layers by pillaring.[26] When S_{int} and S_{ext} are compared after thermal treatments at between 60 and 300 °C, it is noticed that the reduction of the total surface area (S_{all}) is ascribed to a decrease in the internal micropore surface area (S_{int}). The reduction in the surface area is, thus, based on a reduction in the amount of the Al-pillar, which prop silicate layers according to the progress of Ca^{2+} fixation.

In Ca^{2+}–PT, however, the surface area did not decrease. Though the surface area decreased by 20 $m^2 g^{-1}$ between 60 and 300 °C in Ca^{2+}–PM, the decreasing ratio (5%) was much smaller than that of Ca^{2+}–PTSM (17%). From these data it is concluded that the structural change is little in catalyst systems where cation fixation does not occur.

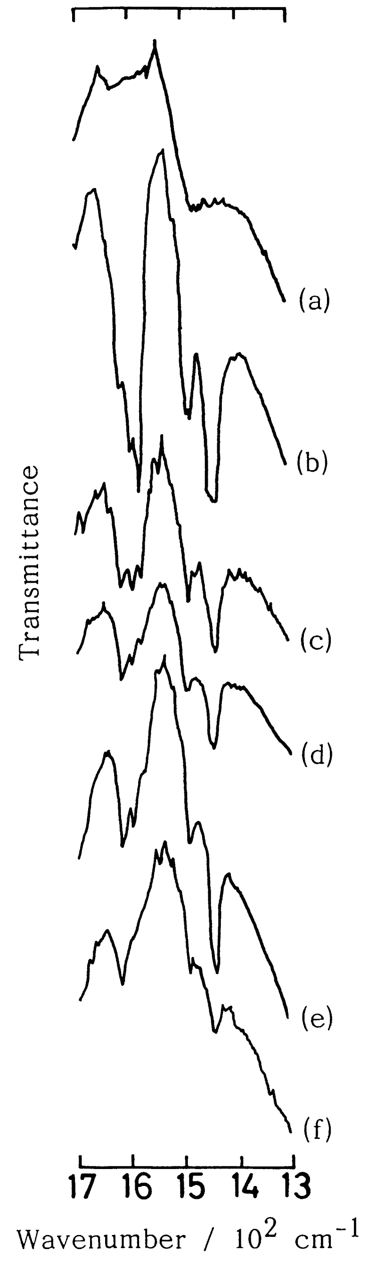


Fig. 6. IR spectra of pyridine adsorbed on Ca^{2+}–PTSM (both calc. 1 and calc. 2 at 300 °C). (a) Back ground spectra, (b) after pyridine adsorption followed by evacuation at 150 °C, (c—e) followed by successive evacuation at 250 °C (c), 350 °C (d) and at 450 °C (e), (f) followed by water vapor adsorption and evacuation at 200 °C.

Change in Acidic Property. Figure 6 shows the IR spectra of the pyridine adsorbed on Ca^{2+}–PTSM treated at 300 °C on the calc. 1 procedure, which exhibited the highest conversion (4.2%) in cumene cracking. The features of the spectra were similar to that of La^{3+}–PTSM, as a whole. This similarity is reasonable, since both cations (Ca^{2+} and La^{3+}) belong to the same group according to the classification given in the preceding paper.[3] After pyridine adsorption at 150 °C, followed by evacuation, both a strong band at 1450 and a weaker band at 1490 cm^{-1} were observed, indicating the Lewis acidic nature of the catalyst. The 1450 cm^{-1} band remained constant, even after successive evacuation at 450 °C. When water adsorbed on this catalyst 200 °C followed by evacuation, the 1550 cm^{-1} band appeared silightly and the genesis of Brønsted acidity was suggested. It is well-known that cumene cracking is catalyzed by Brønsted acidity.[27] The active sites of Ca^{2+}–PTSM must be situated close to fixed Ca, and they must exist as the Brønsted acid sites formed by the reaction of residual water and Ca^{2+}, as already reported.[2]

The above-mentioned Ca^{2+}–PTSM (calc. 1 temp 300 °C), most active for cumene cracking, had an acid amount of 222 $\mu mol\, g^{-1}$, which was estimated from the amount of desorbed ammonia in the TPD spectra shown in Fig. 7. The acid amount slightly increased at 400 °C, and then decreased above this temperature. The change in the acid amount exhibited a good

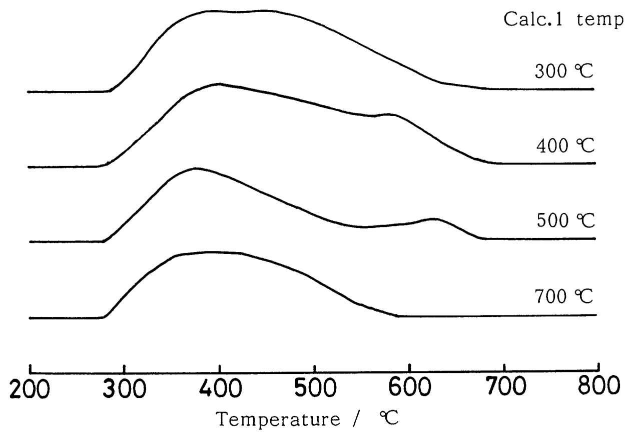


Fig. 7. TPD spectra of adsorbed ammonia on Ca^{2+}–PTSM.

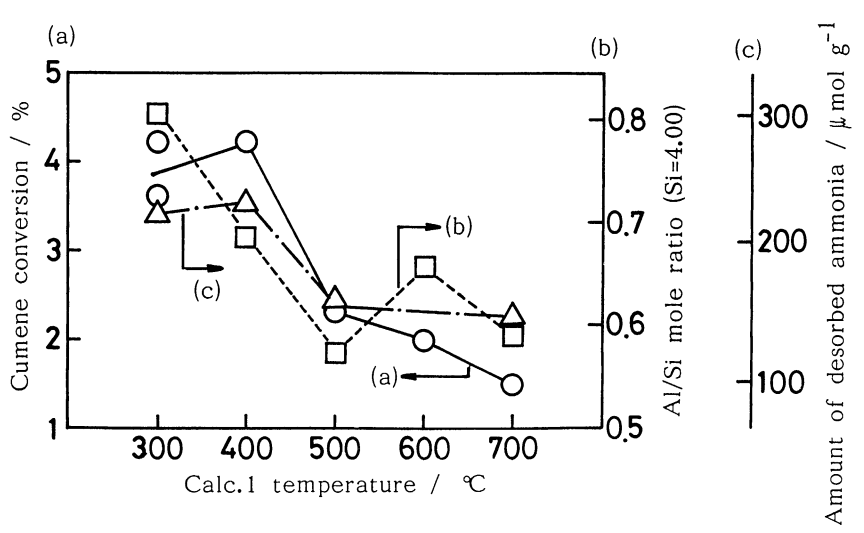


Fig. 8. Cumene cracking activity of Ca^{2+}-PTSM (a), the amount of Al (b), and the amount of desorbed ammonia in TPD (c) as a function of calc. 1 temperature.

correlation with the change in the cracking activity (Fig. 8). A similar relationship between cumene cracking activity, or the measure of Brønsted acidity, and the acid amount estimated from TPD has been ascertained for various-cation fixed pillared TSM catalysts.[3)]

The acid amount further correlated with the residual amount of Al at 400°C or above, which may be associated with the fact that the precursor of pillar (Al hydroxy cluster cation) functions as a proton source, since it releases protons upon calcination. The released protons migrate onto the silicate layers and can form acidic sites near the Ca-fixed sites.

In connection with the acid strength, a decrease in the number of strong acidic sites was observed with an increase in the calc. 1 temperature, which is indicated in Fig. 8 by the gradual decrease in the amount of ammonia desorbed between 400 and 650°C.

Distribution of Fixed Ca Ion on the Surface of Silicate Layer. Figure 9 depicts the basal oxygen plane of the silicate layer of TSM. The open circles represnt the center of hexagonal holes, or the possible sites of fixed Ca ions. When one of these sites is analyzed, it can be seen that there are six nearest-neighbor sites around it. When a fixed Ca is surrounded by several nearest-neighbor Ca ions (*k* in number), the Ca is called a "type n*k* calcium." Thus, seven types of Ca (n0, n1, .., n6) are distinguishable. The proportion of each type, which depends on the total occupancy of hexagonal holes by Ca, can be calculated based on the two following assumptions.

1. Fixed Ca ions are distributed in a completely random fashion.
2. The fixed ions are divided into halves on both surfaces of silicate layers when Al-pillars are inserted between them.

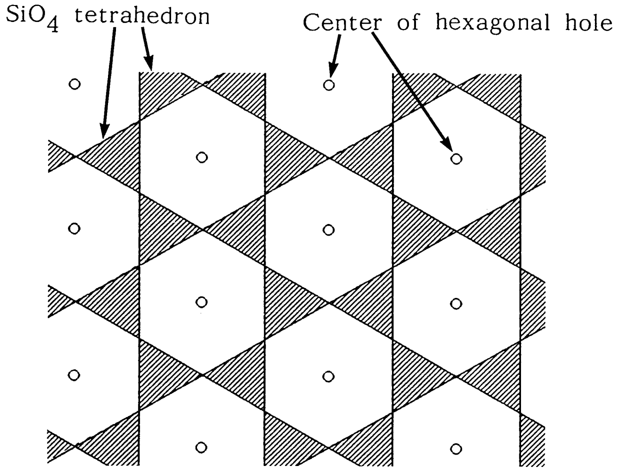


Fig. 9. Basal oxygen plane of layer silicate.

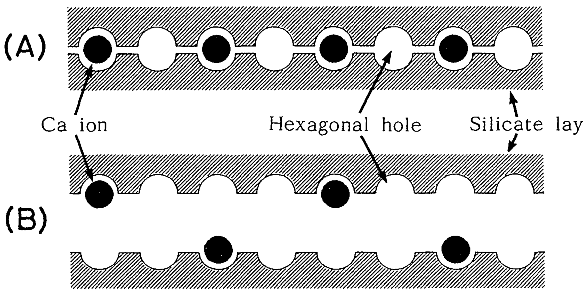


Fig. 10. Schematic diagram of Ca distribution on layer surface. (A) Before pillaring (Ca exchange rate of 100%). (B) After pillaring.

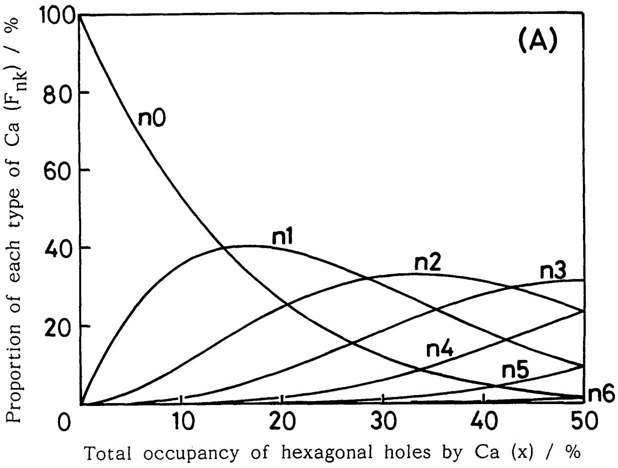
The first assumption is reasonable from the result of ^{29}Si-MASNMR, since the Q^3(0Al) signal in Ca^{2+}–TSM is markedly broadened upon heating, and such broadening is reasonably understood by Ca fixation in a random fashion.[3)] Fig. 10 illustrates the situation regarding the second assumption. At a maximum cation-exchange ratio of 100%, the exchanged Ca^{2+} ions should occupy half the hexagonal holes of TSM, which has a layers charge of 1.00 per Si_4O_{10} unit. Since these Ca ions are divided into halves after pillaring, the occupancy of hexagonal holes by Ca becomes 25% if all of the Ca ions are fixed and remain on the silicate surface.

The distributions were then calculated according to the following binominal equations, which are similar to the equation employed for the calculation of the siting of Si and Al atoms in the faujasite-type zeolite lattice:[28)]

$$F_{nk} = \frac{6!}{k!(6-k)!}x^k(1-x)^{6-k}$$

and

$$N_{nk} = \frac{6!}{k!(6-k)!}x^{k+1}(1-x)^{6-k}.$$



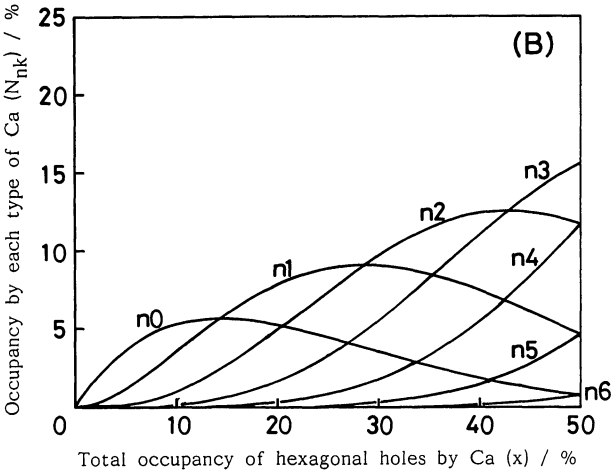


Fig. 11. Distribution of types of Ca atoms in Ca^{2+}–PTSM. (A) Proportion of each type of Ca. (B) Occupancy of hexagonal holes by each type of Ca.

Here, x is the occupancy of hexagonal holes by all types of Ca, F_{nk} the proportion of each type of Ca (type nk, k=0..6), and N_{nk} the occupancy of hexagonal holes by each types of Ca. The result of computing is shown in Figs. 11 (A) and (B). These curves of the Ca distribution are similar to that of Al in the framework of faujasite-type zeolites.[29–31)] Since in zeolites two Al ions can not occupy adjacent tetrahedral sites (Loewenstein's rule), the next nearest-neighbor sites are considered for the calculations. Since zeolite acidity arises from an isomorphous substitution of Al for Si, the distribution state of Al sensitively influences the catalytic activity. Only isolated Al, which has no next nearest-neighbor Al, generates strong acidity.[32)] The catalyst which has such sites in maximum number shows the highest activity in reactions which require strong acidity, such as cracking.[32,33)]

In the case of the Ca^{2+}–PTSM catalysts, the acid strength must depend entirely on the distribution of the fixed Ca. Because neither silicate layers, themselves, nor pillars have acidic sites, the acidic sites are formed on silicate layers by Ca fixation. The obtained Ca distribution on a TSM layer, then, is discussed in connection with the cracking activity. When Ca^{2+}–PTSM is most active for cumene cracking, or when the catalyst is treated at 300—400 °C on calc. 1 procedure (Fig. 1), the fixed amount of Ca is 0.31—0.33 per Si=4 (Fig. 2). This amount corresponds to a total occupancy of 16% under the above-mentioned second assumption. Fig. 11 indicates that the isolated Ca (type n0) is predominant until this Ca content. Moreover, the number of type n0 calcium becomes maximum near this total occupancy (according to the above equation, N_{n0} gives a maximum value at x=0.143), showing good agreement with the maximum catalytic activity. This agreement strongly supports the fixation model in the present study: that the Ca cations fix onto the silicate-layers while lodging in the hexagonal holes and taking charge of the genesis of acidic sites.

Concluding Remarks

When the same procedure for the preparation of Ca^{2+}-modified pillared clays were applied to three different clays (TSM, montmorillonite, and taeniolite), only Ca^{2+}–PTSM showed a notable acidity enhancement by Ca^{2+} fixation. Ca^{2+} was not fixed by the other two clays under the same preparation conditions. The ease of Ca fixation onto the TSM layer must come from the structural characteristics of TSM: a high layer charge and the existence of an octahedral vacancy. The dependence of the catalytic activity of Ca^{2+}–PTSM on the calcination temperature before pillaring was successfully interpreted in terms of the random distribution model for Ca^{2+} fixed on the surface of the TSM layer.

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