

# Non-expanding mica incorporating alumina in the interlayer regions: a new preparation technique of fine particles of alumina

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## Abstract

The fluoro tetrasilic mica intercalating the fine particles of alumina was prepared by hydrolysis of  $\text{Al}^{3+}$  ion in its interlayer regions with moist ammonia gas. The data of XRD and MAS  $^{27}\text{Al}$  NMR measurements indicate that the pillar consists of very thin particles of the alumina. Moreover, the data of ammonia temperature programmed desorption and FTIR spectra of adsorbed pyridine show that the intercalation of the alumina increases significantly in acid sites and possesses Brønsted acid and Lewis acid sites. The vacuum treatment at high temperature gives strong Lewis acid sites and supports the high dispersion of the interlamellar alumina. The dehydration of tertiary-butanol over the catalyst was studied. The intercalation of the alumina appears the dehydration activity of *t*-butanol to 2-methylpropene. The diffusional controlling rate of the dehydration and small interlamellar spaces also support the idea that the interlamellar alumina is fine particles. © 1999 Elsevier Science B.V. All rights reserved.

*Keywords:* Mica; Fine particle; Alumina; Dehydration of alcohol

## 1. Introduction

The interlayer regions have been recently noticed as unique reaction fields for next generation catalysts. Alumina was frequently employed as a pillar to control the interlayer regions of swelling layer compounds [1–11]. We have already reported that the intercalation of alumina in the interlayer regions of montmorillonite increases the surface areas of alumina, and improves significantly dehydration activity

of alcohol [12]. The fine particles of the metal oxides have been often used as catalytic material and support to improve catalytic properties. In the case of alumina pillar, the fine particles are inserted by various chemical means into the interlayer region [13–22], and typically prepared by the intercalation of the macrocations (such as the Keggin ion  $[\text{Al}_{13}\text{O}_4(\text{OH})_{24}(\text{H}_2\text{O})_{12}]^{7+}$ ), in swelling clays [13–20,22]. While the macrocations can not be intercalated in non-expanding layer compounds, because the molecular sizes are larger than their interlamellar spaces. Thus the particle size of alumina depends on that of the used macrocations and a

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matrix available to preparation of fine particles is limited. In addition, it is difficult to control the alumina particles within a specific size range, because some macrocations coexist at equilibrium in an aqueous solution. The alumina size becomes smaller, its catalytic properties may be more improvable. Hence, the development of new technique preparing more fine particles is significant for an improvement of catalytic properties. If an aggregation proceeds to a similar extent in macro, oligomeric, monomer cations, etc., the size of alumina prepared by hydrolysis of intercalated aluminum ions in a small interlamellar space should be more fine particle than that prepared from the macrocations. Furthermore the incorporation of the fine particles of alumina in the non-expanding spaces develops non-swelling layer compounds as catalyst. Potassium form of fluoro tetrasilic mica has non-expanding, thermally stable, and neutral properties. These properties are available to catalytic supports. The chemical formula is  $K^+Mg_{5/2}(Si_4O_{10})F_2$ . We attempted to incorporate the fine particles of alumina in the potassium form of fluoro tetrasilic mica. In this paper, we report: (1) the fine particles of alumina can be prepared by hydrolysis of aluminum ions in the interlayer regions with moist ammonia gas; (2) the mica intercalated the alumina increases significantly acid sites; (3) the mica appears the dehydration activity of *t*-butanol.

## 2. Experimental

### 2.1. Materials

All chemicals were analytical grade commercial materials, and used without further purification. Potassium form of fluoro tetrasilic mica,  $K^+/TSM$ , was kindly supplied by Topy Industries.

### 2.2. Preparation of catalyst, $Al/TSM$

Aluminum nitrate hydrate (2 g) was dissolved in 100 ml of distilled water. The potas-

sium form of fluoro tetrasilic mica (2 g) was dispersed to ion-exchange in the solution. The ion-exchanging mixture was vigorously stirred for 3 h at 60°C with a magnetic stirrer. The resulting product was separated by vacuum filtration, washed four times with 400 ml of distilled water, and dried for 5 h at 100°C. The product,  $Al^{3+}/TSM$ , was then exposed to 101.3 kPa of moist ammonia gas for 60 h at room temperature to hydrolyze aluminum ions in the interlayer regions. The final product was dried for 1 h at 100°C, followed by calcination for 6 h at 450°C in an air stream. The chemical analyses of the catalysts were carried out using an atomic adsorption spectrometry.

### 2.3. MAS $^{27}Al$ NMR measurements

MAS  $^{27}Al$  NMR spectra were recorded on a JEOL-JNM-EX270 spectrometer at 70.2 MHz for single pulse experiments. All sample powders were packed in zirconia rotors and spun at 5–55.5 kHz at the magic angle. All the  $^{27}Al$  spectra were referenced to  $Al(H_2O)_6^{3+}$  (0 ppm). Time intervals between successive accumulations were chosen in order to avoid saturation effects and were 1 s for the  $^{27}Al$  signal. 40,000 scans were collected.

### 2.4. X-ray powder diffraction

XRD patterns of the samples were recorded using a Macscience 18 spectrometer (Ni-filtered  $Cu K_{\alpha}$ , 40 kV–50 mA). The samples were first heated for 1 h at 400°C, and then were contacted with air. They were mounted on sample boards as quickly as possible and the measurements were immediately carried out.

### 2.5. FTIR measurements

FTIR measurements of the catalysts were carried out using a Shimadzu FTIR 8000 spec-

trometer. IR cell and its procedures are the same as described previously [12].

### 2.6. Ammonia temperature programmed desorption

Ammonia TPD was carried out using a conventional apparatus. The sample (0.060–0.070 g) was preheated in vacuo at 400°C, until the sample became a constant weight. The constant value was used as a base weight of no ammonia adsorption. The sample was exposed to ammonia (ca. 0.7 kPa) at 100°C, and allowed to stand until the adsorption reached a state of equilibrium. The sample was evacuated for 1 h at 100°C after ammonia adsorption at equilibrium. The ammonia TPD were carried out in vacuo from 100°C to 400°C with a heating rate of 1.4°C/min. The amount of ammonia adsorbed irreversibly was determined from the difference between the weight of partial deammoniation catalyst and the base weight.

The effects of vacuum treatment temperature on number of strong acidic sites were studied under the pressure less than 0.013 Pa using the same apparatus as described above. The number of the strong acidic sites was determined from the amount of irreversible ammonia adsorption at 350°C, because the vacuum treatment at high temperature gives the strong acidic sites.

### 2.7. Dehydration of tertiary butanol

The *t*-butanol conversions were performed in a pulse microcatalytic reactor at 150–200°C. The catalyst (0.010 g; 80–100 mesh) was sandwiched with quartz wool (0.002 g) in a stainless reaction tube of 1-mm inner diameter. It was confirmed that the contribution of quartz wool (packing materials), and stainless tube was very small under these conditions. The catalyst bed was activated for 2 h at 250°C under helium (10 ml/min). The volume of one butanol pulse was 0.1–0.4  $\mu$ l (10.9–43.7  $\mu$ mole). The reaction products were analyzed using a gas chromatography.

## 3. Results and discussion

The chemical components of the samples are summarized in Table 1. The content of aluminum, potassium and magnesium in the K<sup>+</sup>/TSM agrees well with the corresponding value calculated from the chemical formula. The chemical component of the AL/TSM shows an appearance of aluminum element and a decrease of potassium one after ion-exchanging. One equivalent of Al<sup>3+</sup> ion exchanges with three equivalents of K<sup>+</sup> ion on ion-exchanging. The decrease equivalent of potassium ion is equal to three times of the aluminum one. Hence, the appearance and decrease indicate that aluminum is loaded on the fluoro tetrasilic mica by the ion-exchanging. The ion-exchange extent of the AL/TSM is calculated to be 87% from the potassium decrease and ion-exchange capacity.

High-resolution MAS <sup>27</sup>Al NMR spectra of the AL/TSM are shown in Fig. 1. Two strong and broad peaks of the MAS <sup>27</sup>Al NMR were observed at 67 ppm and –0.7 ppm, and the peak intensity at 67 ppm is stronger than that at –0.7 ppm. In the literature [23,24], the peak of MAS <sup>27</sup>Al NMR at 50–70 ppm is attributed to tetrahedral Al ions, and the central peak at –10–20 ppm to octahedral Al ions. In addition, it is known that the <sup>27</sup>Al NMR spectra for the compounds containing alumina and alumina consist of two principal components, at 70 ppm and 0 ppm [25–27]. The results indicate the presence of aluminum oxide in the AL/TSM. The similar <sup>27</sup>Al NMR patterns have been observed in the amorphous form of aluminosilicate

Table 1  
Chemical composition of the catalysts

Catalyst	Composition [wt.%]		
	Mg	K	Al
K <sup>+</sup> /TSM	15.0	9.4	0.0
	14.8 <sup>a</sup>	9.5 <sup>a</sup>	0.0 <sup>a</sup>
AL/TSM	15.8	1.3	2.0

<sup>a</sup>Value calculated from the formula, K<sup>+</sup> Mg<sub>2.5</sub>(Si<sub>4</sub>O<sub>10</sub>)F<sub>2</sub>.

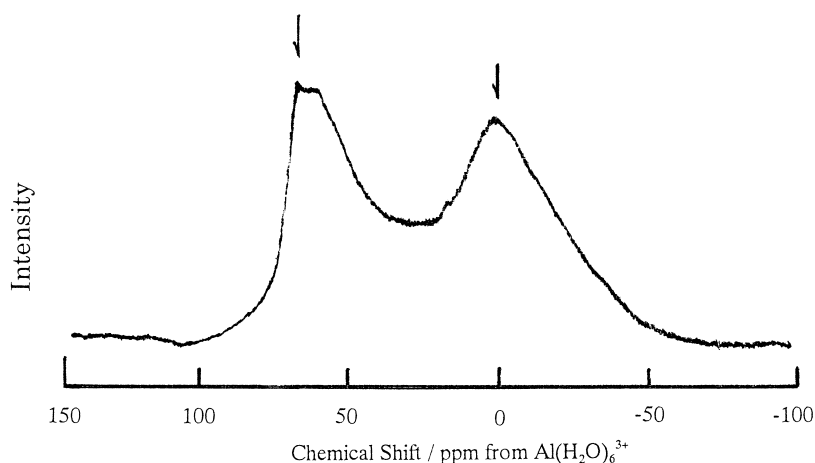


Fig. 1.  $^{27}\text{Al}$  MAS NMR spectra of the AL/TSM.

glass [24]. The intensity ratio of  $\text{AlO}_4$  peak to  $\text{AlO}_6$  peak in the AL/TSM is very different from that in a bulky alumina [24]. The similarity between  $^{27}\text{Al}$  NMR patterns of the AL/TSM and aluminosilicate and the difference in ones of the AL/TSM and bulky alumina suggest that the aluminum oxides are neighboring to the silicate framework of the TSM.

X-ray powder diffraction analyses of the catalysts were measured, and the results are shown in Fig. 2. The space distances,  $d(001)$ , in the  $\text{K}^+$ /TSM and AL/TSM are 0.988 and 1.020 nm, respectively. The space distance of the mica is the sum of layer thickness (0.66 nm) and ion diameter of interlamellar cation, such as potas-

sium ion (0.30–0.33 nm) [28], and aluminum ion (0.11–0.13 nm) [28]. The observed value of 1.02 nm in the AL/TSM is larger than the sum value (0.77–0.79 nm) calculated from the layer thickness and diameter of  $\text{Al}^{3+}$  ions. The interlamellar space height (1.02 – 0.66 = 0.36 nm) is nearly equal to an alumina unit size [29,30]. Therefore, the space distance of 1.02 nm indicates that the thickness of interlamellar aluminum oxides are monomolecular or double layer of an alumina, even if the aluminum oxides aggregate. This fact indicates that the interlamellar alumina are neighboring to the silicate framework of the TSM. In addition, the result means that the pillar consisted of aggregated

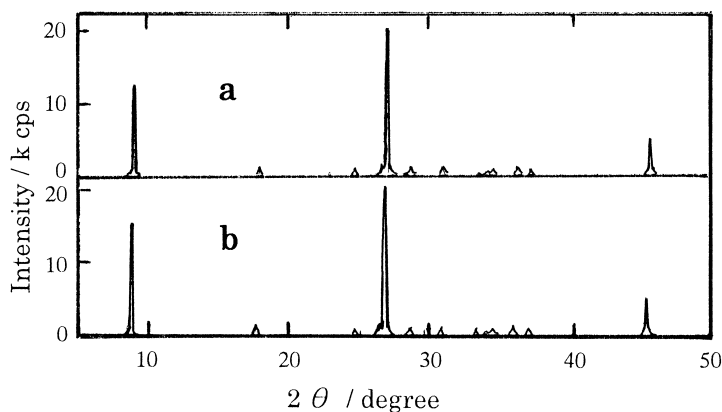


Fig. 2. XRD patterns of the catalysts. (a)  $\text{K}^+$ /TSM, (b) AL/TSM.

large cations such as the Keggin-like ion should have a large diameter and large interlamellar spaces, because 39 unit cells of the TSM possess only one alumina pillar in the case of the Keggin-like ion: In our method, one cation of  $\text{Al}^{3+}$  is exchangeable with three cations of  $\text{K}^+$  which exist in three unit cells of the TSM.

FTIR spectra of catalysts were shown in Fig. 3. In hydrated aluminum ions, no IR bands resulting from coordination water occur in the region between  $1600\text{--}1200\text{ cm}^{-1}$  [31]. In the  $\text{Al}^{3+}$ /TSM, no IR bands have been observed in this region. In contrast with the  $\text{Al}^{3+}$ /TSM, the bands at  $3280$ , and  $1418\text{ cm}^{-1}$  appear in the AL/TSM as a result of the ammonia treatment and calcination. The bands at  $3280$  and  $1418\text{ cm}^{-1}$  can be attributed to OH or  $\text{NH}_2$  stretching and bending vibration, respectively. However, the assignment to  $\text{NH}_2$  stretching and bending one is refused because no ammonia adsorbs on the catalyst at temperature more than  $350^\circ\text{C}$ , as described below, and the catalyst was

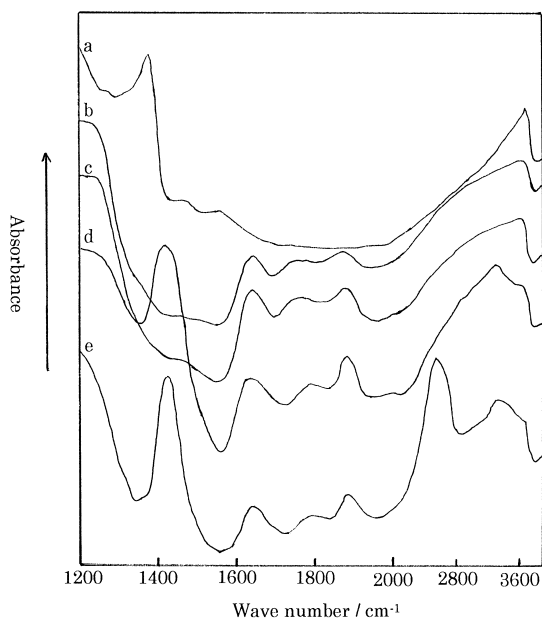


Fig. 3. IR spectra. The samples were preheated in vacuo for 2 h at  $400^\circ\text{C}$ , followed by FTIR measurements: (a)  $\gamma$ -alumina; (b)  $\text{K}^+$ /TSM; (c)  $\text{Al}^{3+}$ /TSM; (d) AL/TSM; (e)  $\text{D}_2\text{O}$  adsorbed for 5 h at  $250^\circ\text{C}$  on the preheated AL/TSM, followed by evacuation for 2 h at  $250^\circ\text{C}$ .

calcined for 6 h at  $450^\circ\text{C}$ . On the other hand, the IR bands have been observed at  $3750$ , ca.  $3650$ , and  $1375\text{ cm}^{-1}$  in  $\gamma$ -alumina. In particular, the band at  $1375\text{ cm}^{-1}$  is very strong. Only both of  $\gamma$ -alumina and the AL/TSM catalyst display the band in the region between  $1600\text{--}1300\text{ cm}^{-1}$ . A similar strong band in the region is observed in some metal oxides such as titania [32], and ceria [33]. In the former literature, Yates [32] reported that the band at  $1360\text{ cm}^{-1}$  might be the OH bending vibration of strongly held water. The intensity of the band at  $1418$  and  $1375\text{ cm}^{-1}$  decreases upon outgassing at temperature more than  $400^\circ\text{C}$ . The band width at  $1418\text{ cm}^{-1}$  decreases as a result of  $\text{D}_2\text{O}$  adsorption as shown in Fig. 3e. The facts strongly suggest that the bands at  $1418$  and  $1375\text{ cm}^{-1}$  are also the OH bending vibration on the alumina surface. The IR-band shift to higher frequency may be due to host–guest interactions in the interlamellar spaces. The adsorption of  $\text{D}_2\text{O}$  on the alumina accomplishes H–D exchange of hydroxyl groups on the alumina surface. The isotope exchanging decreases the intensity of the bands at  $3750$ , ca.  $3650\text{ cm}^{-1}$ , and a band, typical of OD stretching frequency, occurs at ca.  $2660\text{ cm}^{-1}$  [34–38]. It is well known that the OH stretching vibration occurs near at  $3700\text{ cm}^{-1}$  for hydroxyl groups on alumina [34–38] and in the region between  $3300\text{--}3500\text{ cm}^{-1}$  for hydrogen bonding OH groups and adsorbed  $\text{H}_2\text{O}$  molecular on alumina [34–38]. It is concluded that the absorption attributed to the OH stretching vibration occurs at ca.  $3650$  and  $3280\text{ cm}^{-1}$  in the AL/TSM. The similar absorption were also reported for the adsorbed  $\text{H}_2\text{O}$  in zeolite cavities [39–41].

IR spectrum of pyridine adsorbed on the AL/TSM is shown in Fig. 4. In the literature [42–45], the bands at  $1490$  and  $1596\text{ cm}^{-1}$  are attributed to pyridine adsorbed on Brønsted acid sites, and the bands at  $1450$  and  $1610\text{ cm}^{-1}$  to pyridine adsorbed on Lewis acid sites. As shown in Fig. 4, Brønsted acid and Lewis acid sites are present in the AL/TSM which is pretreated in vacuum at  $400^\circ\text{C}$ . Apparently Brønsted acid is

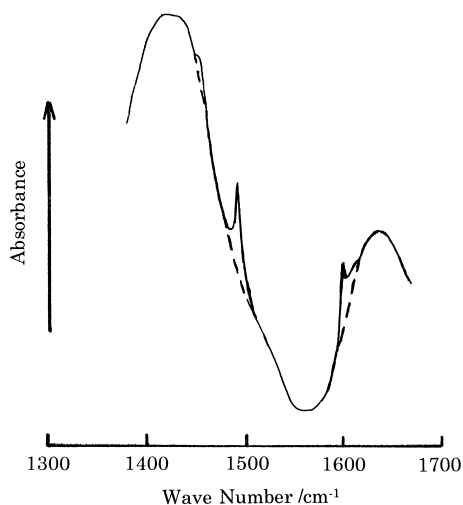


Fig. 4. IR spectra of adsorbed pyridine. The AL/TSM samples were preheated in vacuo for 2 h at 400°C, followed by FTIR measurements. Dotted line: after pretreatment, Solid line: adsorbed pyridine at 200°C under 0.5 kPa of pyridine pressure.

largely favored. While no adsorption band due to adsorbed pyridine species are observed in the  $K^+$ /TSM. Hence this finding indicates that Brønsted acid and Lewis acid sites appear on intercalating the fine particles of alumina in the interlamellar spaces of the TSM. The presence of Brønsted acid strongly suggests that proton formation occurs on calcination of the catalyst at 450°C for 5 h: the formation process of proton neutralizing the charge lost by conversion of  $Al^{3+}$  to alumina is explainable in terms of deammoniation of  $NH_4^+$  or dissociation of interlamellar water; the proton sites are Brønsted acid.

Ammonia TPD data are summarized in Table 2. Ammonia adsorbs irreversibly even at 300°C

Table 2  
Ammonia TPD

Catalyst	Amount of adsorbed $NH_3$ [mg/g]					
	100°C	150°C	200°C	250°C	300°C	350°C
$K^+$ /TSM	0.00	–	–	–	–	–
AL/TSM	0.87	0.72	0.59	0.45	0.18	0.00
$\gamma$ -Alumina	2.97	1.72	0.00	–	–	–

0.87 mg/g is converted into  $1.4 \times 10^{-3}$  mole per 1 g of an alumina; 2.97 mg/g is converted into  $1.7 \times 10^{-4}$  mole per 1 g of  $\gamma$ -alumina.

in the AL/TSM. No ammonia adsorbs on the  $K^+$ /TSM, and so the fact shows that the potassium form of the mica has no acidic sites. The intercalation of the alumina forms acid sites, of which strength is stronger than that of  $\gamma$ -alumina, because no ammonia adsorbs on  $\gamma$ -alumina at temperature more than 200°C. The amount of ammonia adsorbed irreversibly at 100°C is  $1.4 \times 10^{-3}$  and  $0.17 \times 10^{-3}$  mole per 1 g of alumina in the AL/TSM and  $\gamma$ -alumina, respectively. The results indicate that the amount of acid sites per alumina unit is significantly increased by the intercalation.

It is usually agreed that Lewis sites in alumina are Al cations of low coordination. Their number changes dramatically with the temperature of vacuum treatment, and highly dispersed alumina should exhibit higher Lewis acidity and more acid sites. The effects of the temperature of vacuum treatment on the acidity of alumina and number of acid sites were studied and summarized in Table 3. The vacuum treatment of bulky  $\gamma$ -alumina at 600°C significantly increases strong acid sites, and a similar increase in strong acid sites is obtained in AL/TSM treated in vacuo at 500°C. The adsorption of pyridine on the pretreated AL/TSM and  $\gamma$ -alumina appears strong IR bands at 1622 and

Table 3  
Effects of temperature and time of vacuum treatment on irreversible ammonia adsorption

Catalyst	Vacuum treatment time				$NH_3^a$ [mg/g-cat]
	at 400 °C	at 500 °C	at 550 °C	at 600 °C	
AL/TSM	+3 h	–	–	–	none
AL/TSM	+3 h	+3 h	–	–	0.95
AL/TSM	+3 h	+3 h	+2 h	–	–1.0
$\gamma$ -Alumina	+3 h	–	–	–	none
$\gamma$ -Alumina	+3 h	+3 h	–	–	0.62
$\gamma$ -Alumina	+3 h	+3 h	–	+6 h	2.5

<sup>a</sup>Amount of ammonia adsorbed irreversibly at 350°C. The sample was treated at fixed temperature under the pressure less than 0.013 Pa.

The values for AL/TSM, 0.95 and 1.0 mg/g, are converted into 26 and 27 mg per 1 g of the interlamellar alumina, respectively.

1454  $\text{cm}^{-1}$  assigned to pyridine adsorbed on Lewis acid sites. In addition, the vacuum treatment of  $\gamma$ -alumina at 600°C for 6 h remarkably increases the strength of the bands, and gives a blue shift of the bands. The results indicate that the vacuum treatment at 600°C forms strong Lewis acid sites. The number of the strong acid sites per an unit of alumina in AL/TSM is much more than that in the bulky  $\gamma$ -alumina. These facts well explain a high dispersion of alumina in the interlayer regions.

The dehydration of *t*-butanol over AL/TSM and  $\text{K}^+$ /TSM was studied. In the  $\text{K}^+$ /TSM, no activity was observed. The dehydration of *t*-butanol over AL/TSM produces mainly 2-methylpropene. The other products are oligomeric 2-methylpropene. Higher the reaction temperature increases, more the dehydration produces 2-methylpropene. In the literature [46–49], it has been reported that the dehydration of alcohol over solid acid catalysts has generally a direct conversion from alcohol to corresponding olefin and ethers. The dehydration of tertiary alcohol produces corresponding olefin. The intercalation of the alumina enhances significantly the dehydration of *t*-butanol. Effects of the volume of doped *t*-butanol on the 2-methylpropene yield are shown in Fig. 5. The production amount of 2-methyl-

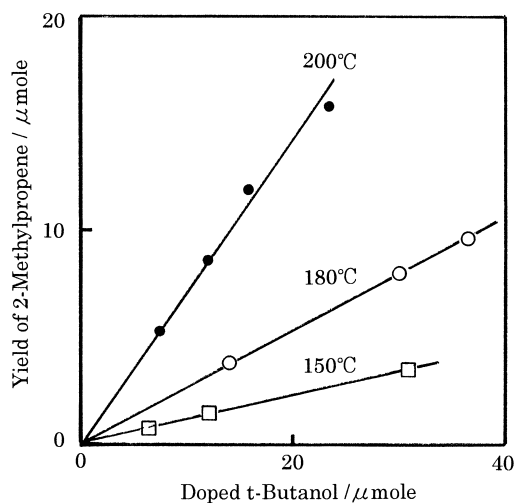


Fig. 5. Dehydration of *t*-Butanol over the AL/TSM.

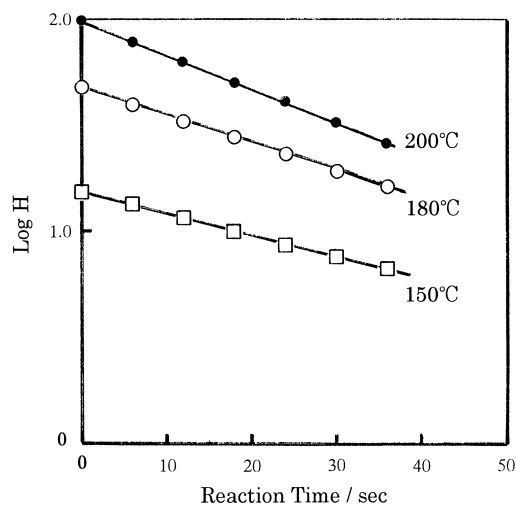


Fig. 6. Change of the height of GC peak tailing slope with passage of reaction time.

propene is proportional to the volume of doped *t*-butanol, that is, the effect of the alcohol concentration on its conversion is little at the fixed temperature. The results indicate that the dehydration rate of *t*-butanol is of first order in the alcohol concentration or that the dehydration is linear reaction [50–55]. The reaction rate constant is determined in the first order or linear reaction using pulse method [50–55]. Fig. 6 shows the change of GC peak tailing slope in the pulse reaction with passage of reaction time. The height exists in a linear relation with the reaction time. The coefficient of the correlation in the relations indicates the rate constant [50–55]. The apparent activation energy is determined to be 4.7 kcal/mole from Arrhenius plots of the rate constant. This small value strongly suggests that the rate controlling step of the dehydration is a diffusion of reactants into the interlamellar spaces, because the dehydration is easy acid-catalyst reaction. The pillar consisted of aggregated alumina should form large interlamellar spaces, whereas the pillar consisted of fine particles and the resulting small interlamellar-spaces are an obstacle to diffuse the reactants. Therefore it is probable that our preparation method gives fine particles of alumina in the interlayer regions of the TSM.

## 4. Conclusion

Fluoro tetrasilic mica intercalating the fine particles of alumina in its non-expanding interlamellar spaces was prepared by the hydrolysis of the interlamellar  $\text{Al}^{3+}$  ions with moist ammonia gas and calcination. On the basis of the data of MAS  $^{27}\text{Al}$  NMR, XRD, FTIR, ammonia-TPD, vacuum treatment, and dehydration of *t*-butanol, it is concluded that the alumina is finely dispersed as fine particles in the interlayer regions of the mica. Therefore, this technique is applicable for a preparation of a clay contained a small interlamellar space and fine particles of alumina. The mica intercalating the alumina increases significantly acid sites, possesses Brønsted acid and Lewis acid, and appears the dehydration activity.

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