# Synthesis of Ga-incorporated SAPO-34s (GaAPSO-34) and their catalytic performance on methanol conversion

Misook Kang *, Chul-Tae Lee

*Department of Chemical Engineering, Dankook University, San 8, Hannam-dong, Youngsan-ku, Seoul 140-714, South Korea*

## Abstract

This study has been focused on the synthesis of GaAPSO-34s substituted gallium for aluminum in order to improve the acidic property in SAPO-34 crystal. As the result, GaAPSO-34s with various Al/Ga ratios (Al/Ga = ∞, 40, 20, 10, 5, and 0) were successfully synthesized. These were characterized by XRD, SEM, ICP, TG-DTA, MAS-NMR, and BET surface areas. The crystallinity identified from the intensity of XRD peak (for angles of 22.5° and 9.7°) and the particle size observed from SEM photographs decreased with an increase in the Ga content incorporated into the SAPO-34 framework. On the other hand, decrease in the acid sites in crystal as a target in this study was confirmed in the Ga-incorporated samples. In particular, a surprising result was that the selectivity to ethylene on methanol conversion increased in catalyst with Al/Ga = 20 compared with pure SAPO-34 catalyst. However, in spite of the decreases in acid sites and particle size in catalyst with much more Ga content, the selectivity to ethylene was not enhanced, rather the methane which related to catalytic deactivation increased in GaAPSO-34 catalysts. This is ascribed to collapses of framework of SAPO-34 with an increase in Ga content. © 1999 Elsevier Science B.V. All rights reserved.

*Keywords:* Ga-incorporated SAPO-34 (GaAPSO-34); Acidic property; Methanol conversion

## 1. Introduction

The isomorphous substitution of $Al^{3+}$ by trivalent metal ions can modify the chemical nature of aluminosilicate zeolites and plays a significant role in designing catalytic and adsorptive properties of zeolite-related molecular sieves. Metal is usually incorporated in zeolites during the hydrothermal synthesis or the post-synthesis step, and it may stay in the framework or in the intra-framework cavities as metal oxides or counter ions. These results showed that new open framework compositions of oxides outside of the known aluminosilicate and silicate zeolites were possible [1–3].

In particular, Union Carbide (UC) developed a new generation of molecular sieves $AlPO_4$-n [4] based on aluminophospates framework, this initial discovery was followed by a number of reports describing partial isomorphous substitutions of aluminum and/or phosphorous by an-

* Corresponding author. Tel.: +82-2-709-2603; Fax: +82-2-790-2558; E-mail: msk1205@chollian.dacom.co.kr

other element such as Si, Sn or Me (Mg, Mn, Fe, Co, and Zn).

Since 1985, a number of gallophosphates with a microporous framework obtained by hydrothermal synthesis were reported [5,6] and some of them are isothermal of aluminophosphate. Although the aluminosilicate modification was reported to act as an acid-catalyst for the reaction of alkanes, gallium was suggested to play the role of dehydrogenation as well as to affect the zeolitic acidity [7,8].

On the other hand, in the catalytic conversion of methanol to hydrocarbons, in particular, the production of light olefins such as ethylene and propylene has a high potential for industrialization. In the early stages of the study, considering the fit to the molecular sizes of light olefins, narrow pore size zeolites such as erionite and chabazite [9], chabazites modified with lanthanide oxides, ZSM-34 or offretite–erionite intergrowth zeolite [10], and offretite were used as the catalysts for this purpose. These catalysts exhibited a rather higher selectivity to ethylene than to propylene in methanol conversion reaction, but the short catalyst life caused by the coke deposits that occurred mainly in the spaces of their large cavities could not be avoided, even after many trials such as moderation of the acidity by basic materials [11] and regulation of crystallite size.

After the innovation in synthesis of aluminophosphate molecular sieves, a trial of methanol conversion had been done using SAPO-34 as the catalyst for methanol conversion [12,13]. However, on these catalysts with pure type, highly selective synthesis of light olefins could not be expected, and a considerable problem of deactivation resulting from strong acidity remained. In order to solve the problem, metal-incorporated types have been investigated [14,15], but it has not been solved yet.

On the other hand, in previous papers [16], we have suggested that iron groups metal-incorporated SAPO-34s scarcely decreased in acid sites, and then, this led to enhancement of the

lower olefin selectivity on methanol to hydrocarbon conversion. Therefore, if the acidity could be adjusted just to fit the target olefin synthesis, quantitative synthesis of the target olefin would become possible.

Since it is so, we have tried to synthesize GaAPSO-34 by substituting the gallium for the aluminum to introduce weak acidity in crystal in this paper. Furthermore, we had expected the enhancement of selectivity to ethylene by reduction of acid sites on methanol conversion.

## 2. Experimental

### 2.1. Catalyst preparation

GaAPSO-34s of six kinds were synthesized by the rapid crystallization method [17] as shown in Fig. 1 and described in Table 1.
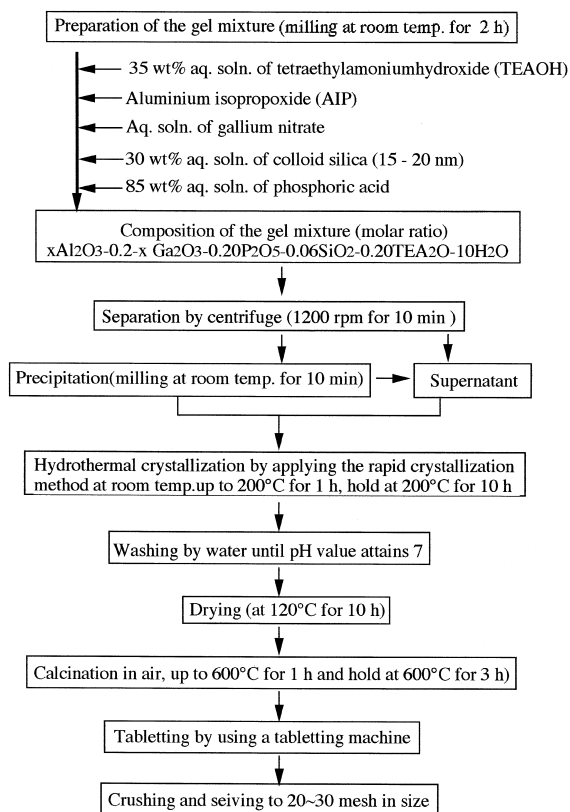
Fig. 1. Preparation procedure of GaAPSO-34 crystals.

Table 1
Comparison of compositions in gel mixture and crystal

| Catalyst | Composition in gel mixture (molar ratio) | Composition in crystal[a] (atomic ratio, Al = 1) |
|---|---|---|
| Al/Ga = ∞ | $0.2(TEA)_2O:0.06SiO_2:0.2Al_2O_3:0.2P_2O_5:10H_2O$ | 0.17Si:0.84P |
| Al/Ga = 40 | $0.2(TEA)_2O:0.06SiO_2:0.195Al_2O_3:0.005Ga_2O_3:0.2P_2O_5:10H_2O$ | 0.050Ga:0.16Si:0.84P |
| Al/Ga = 20 | $0.2(TEA)_2O:0.06SiO_2:0.19Al_2O_3:0.01Ga_2O_3:0.2P_2O_5:10H_2O$ | 0.052Ga:0.15Si:0.86P |
| Al/Ga = 10 | $0.2(TEA)_2O:0.06SiO_2:0.18Al_2O_3:0.02Ga_2O_3:0.2P_2O_5:10H_2O$ | 0.108Ga:0.16Si:0.87P |
| Al/Ga = 5 | $0.2(TEA)_2O:006SiO_2:0.16Al_2O_3:0.04Ga_2O_3:0.2P_2O_5:10H_2O$ | 0.125Ga:0.16Si:0.90P |
| Al/Ga = 0 | $0.2(TEA)_2O:0.06SiO_2:0.2Ga_2O_3:0.2P_2O_5:10H_2O$ | – |

[a] This was attained by ICP.

Reagents used for preparation of the gel mixture were as follows: 35 wt.% aqueous solution of tetraethyl ammonium hydroxide (TEAOH, Aldrich Chemical) was used as the organic template. Aluminum isopropoxide (AIP, Wako), cataloid-30 (30 wt.% $SiO_2$, Kasei Tesque), phosphoric acid (85 wt.% $H_3PO_4$, Nacalai Tesque), and gallium nitrate (($Ga(NO_3)_3$ $6H_2O$, Nacalai Tesque) were used as the starting materials of Al, Si, P, and Ga ingredients of GaAPSO-34, respectively.

### 2.2. Characterization

Synthesized samples were identified by powder X-ray diffraction analysis (XRD), Shimazu XD-DI with Nickel filtered Cu Kα radiation (30 kV, 30 mA) at an angle of $2\theta$ range from 5° to 50°. The scan speed was 1°/min and time constant was 1 s. The diffraction angles of 22.0° and 9.7° were selected to discuss the crystallinity of synthesized samples.

Compositions of elements were analyzed by ICP-AES (inductively coupled plasma atomic emission spectrometry), Shimadzu ICPS-1000III. The result was displayed by atomic ratios.

BET surface areas of crystals were measured by nitrogen gas adsorption with continuous flow method using a gas chromatograph equipped with a TCD detector at the liquid nitrogen temperature in mixing gas of nitrogen and helium flow as the carrier gas with Shimadzu Flow sorbs 2-2300.

Particle size and shape were observed by using Hitachi S-2500CX scanning electron microscope (SEM).

Particle size distribution of samples was obtained after ultrasonic wave treatment with 120 W in water for 10 min. Dynamic light scattering (DLS) spectrophotometer of Photal Otsuka Electronics, ELS-8000SA was used at a 90° angle. The analysis was determined by weight-based distribution.

The coordination state of Al and P in framework was analyzed by magic angle spinning (MAS)-NMR using a JEOL GSX-270 solid state, high resolution spectrometer. The scan times were over 400 while $Al(NO_3)_3$ and $H_3PO_4$ were used as the standard references. High-power decoupling experiments were carried out at 40° with 40.4 MHz for $^{27}Al$ and at 40° with 193 MHz for $^{31}P$.

Acidity of catalyst was estimated by TPD (temperature-programmed desorption) profiles of pre-adsorbed $NH_3$ using a Quadruple Mass Spectrometer (M-QA100F) of BEL Japan. Adsorption of ammonia was done at above 100°C to restrain influence of water. The desorption of $NH_3$ was measured on mass number 16 by Q-Mass detector with a constant heating rate of 10°C/min at the temperature range from 100 to 600°C.

The template decomposition in catalysts before the calcination was measured by temperature-programmed oxidation (TPO) by using a Shimadzu DT-40 thermo-gravimeter at a heating rate of 10°C/min in a 40 ml/min air flow.

The profiles were calculated from the weight loss in a temperature range from room temperature to 800°C.

## 2.3. Reaction method

Each methanol conversion reaction was carried out by using an ordinary continuous flow reactor. A 0.325 g portion (0.35 ml) catalyst was packed into a quartz tubular reactor of 0.5 cm inner diameter, and then it was pretreated with a nitrogen flow at 500°C for 30 min to standardize the catalyst surface state by removal of pre-adsorbed water. The reaction gas composed of 15 mol% methanol and 85 mol% $N_2$ was allowed to flow with a gaseous space velocity (GHSV) of 500 $h^{-1}$ at 425°C of a temperature range of 1–5 h.

The products were analyzed by three gas chromatographs with FID-type detector, Shimadze GC7A, 12A, and 14A. Columns of porapark T, VZ-10, and silicon OV-101 were used to analyze dimethyl ether, $C_1$–$C_4$ hydrocar-

bons, and gasoline range hydrocarbons, respectively.

## 3. Result and discussion

### 3.1. Physical properties

Table 1 depicts the composition in synthesized crystals analyzed by ICP. As shown, the compositions in synthesized crystals almost accorded with those in the gel mixture, and the values of Al + Ga and Si + P were closed to 1.00. From this result, it could be supposed that the Al sites in SAPO-34 framework were substituted by the Ga element.

Obtained GaAPSO-34 crystals are identified by XRD as shown in Fig. 2. The peak intensity (for angles of 22.5° and 9.7°) and BET surface areas decreased with an increase in Ga content in crystal. It is ascribed that ionic diameter of the $Ga^{3+}$ substituted is larger than that of the $Al^{3+}$, and then this resulted in a damage in the
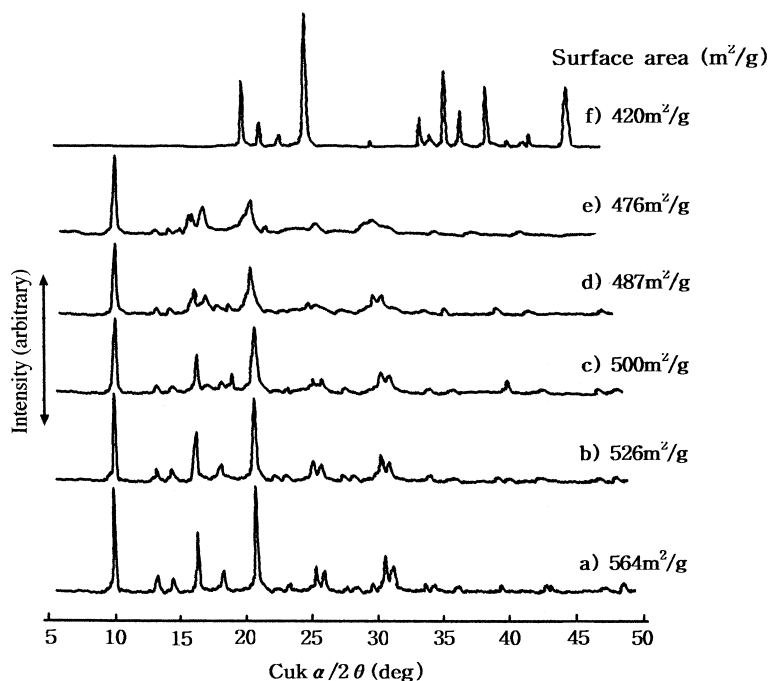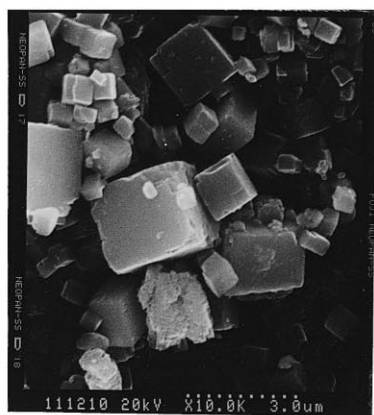


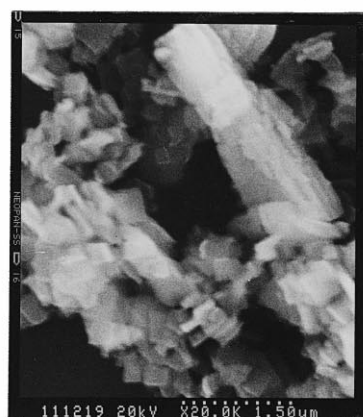Fig. 2. XRD patterns and BET surface areas of GaAPSO-34 crystals. (a) Al/Ga = ∞, (b) Al/Ga = 40, (c) Al/Ga = 20, (d) Al/Ga = 10, (e) Al/Ga = 5, (f) Al/Ga = 0.
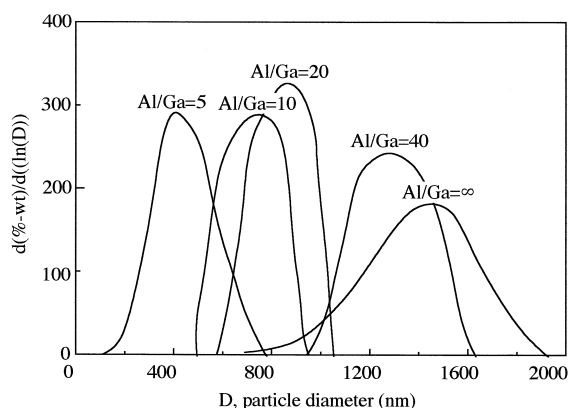
Fig. 3. SEM photographs of GaAPSO-34 crystals.

Fig. 4. Effect of Ga content on distribution of particle size of GaAPSO-34s.

framework. In particular, the uniformity of structure was collapsed and broken when the Al/Ga value was below 10, finally it changed into a different structure type at Al/Ga = 0. This structure was assigned to the $AlPO_4 \cdot \frac{1}{2}H_2O$.

In Fig. 3, the morphologies of GaAPSO-34s observed by SEM are shown. As shown, the shapes of crystals kept on uniform cubic forms above Al/Ga = 10. However, the uniformity collapsed and broke when the value was below 10, and many amorphous parts were observed.
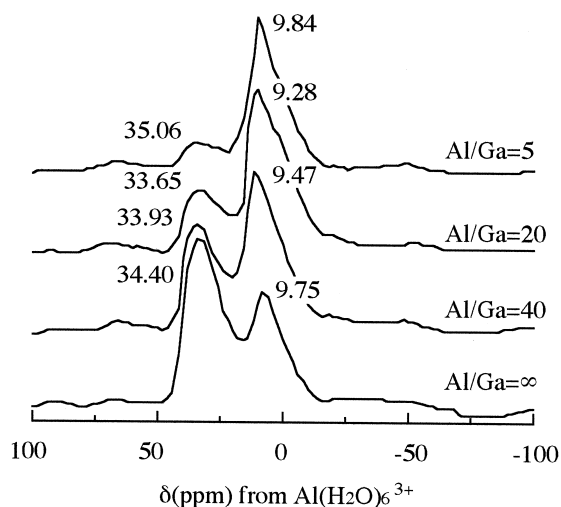
On the other hand, the particle size of catalyst with much Ga was smaller than that of the catalyst with little Ga. From this result, it could be supposed that the gallium element is more related to the increase in the number of the nucleus of the crystal than the crystallinity.

The distribution of particle sizes was attained sharply with an increase in Ga amount in the crystal as shown in Fig. 4. The particle size of the catalyst which contained much Ga was smaller than that of catalyst which contained little Ga. This accorded with the result in Fig. 3.

MAS-NMR spectra of $^{27}$Al and $^{31}$P are shown in (a) and (b) of Fig. 5. The NMR studies are suitable to explain the coordinated environments for the Al and P atoms of GaAPSO-34 crystal. However, the Si and Ga incorporation were insufficient, because it was distributed with asymmetric to framework in small amounts. On the other hand, Blackwell and Patton [18] have shown that the addition of water involves a remarkable change in the spectra. From these results, it is affirmed that the presence of water molecules involved different aluminum environments. In the results of the $^{27}$Al-MAS-NMR spectra of samples as shown in (a), the Al situations with two broad lines, around 9–10



a) $^{27}$Al MAS-NMR
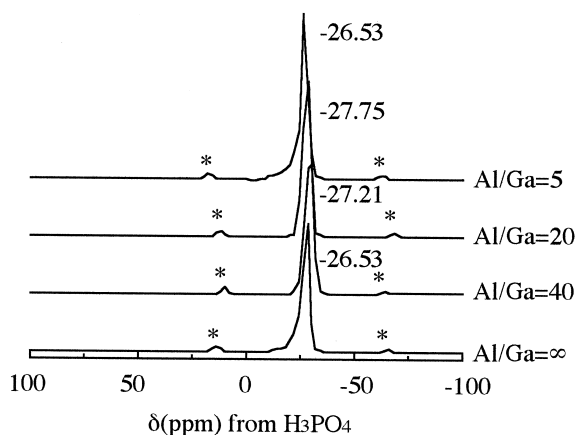
b) $^{31}$P MAS-NMR

Fig. 5. $^{27}$Al and $^{31}$P MAS-NMR spectras of the GaAPSO-34 catalysts after calcination.

ppm as rehydration type (five coordinated situation) and around 35–40 ppm as dehydration type (tetrahedral) are shown. Compared with the other samples, the peak intensity around 35 ppm was strong and the peak intensity around 9 ppm was weak for non-incorporated SAPO. However, the peak around 35 ppm decreased and the peak around 9 ppm rather increased, and these peaks shifted into the left with an increase in Ga amount in crystal. The chemical shift was assumed to come from alternation of the Al nuclear symmetric and distortion of the neighboring framework geometry. Therefore, this result explains that the structure was strongly effected by incorporation of Ga. Judging from (b) in Fig. 5, the peak for P element exhibited one type. The peak shifted into the right and the width was broader when the Ga content increased. This result coincides with the chemical shifts and width for Al peak shown in (a). From these results, it could be reconfirmed that the Al was substituted by the Ga. Consequently, it must have influence on the catalytic activity.

### 3.2. Thermal analysis

In Fig. 6, temperature-programmed oxidation (TPO) profiles in the three catalysts in as-synthesized state, i.e., containing the organic template are compared. The templates of or-ganic base play an important role in directing the formation of specific structure in the synthesis of molecular sieves. Wilson et al. [19] explained these structure-directing effects by the steric and electronic effects of templates. For the molecular sieves to be used as catalyst, absorbents, ion-exchanger, these organic species have to be removed from the channel or cavities in the framework. The organic species used in the synthesis of molecular sieves are generally occluded within the framework structure, and in order for the material to be used as a catalyst, these organic species have to be removed from the channel.

As shown in (a) of Fig. 6, TPO profiles of tetraethylammonium hydroxide (TEAOH) consist of two endothermic peaks around 100°C and 270°C, and an exothermic peak ($\sim$400°C). The TG thermogram shows continuous weight loss as shown in (b) of Fig. 6. The first endothermic peak around 100°C may be attributed to the desorption of water, and the second endothermic peak ($\sim$270°C) may be due to the ethylene from the oxidative decomposition of TEAOH. The temperature was higher in Ga-incorporated samples than SAPO-34. In particular, the temperature was shifted into the lower with an increase in Ga content on framework. Finally, the large and sharp exothermic peak around 400°C may be attributed to the thermal decomposition and oxidation of template. The decom-
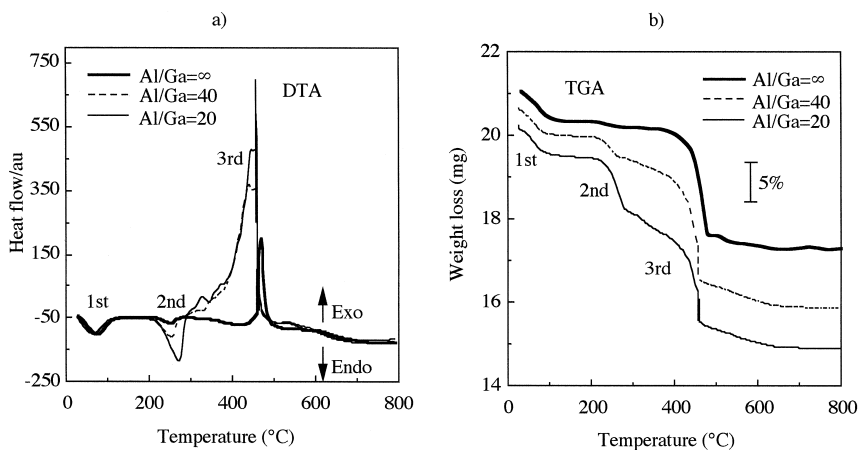


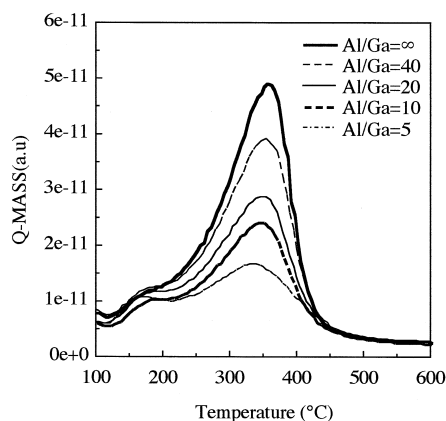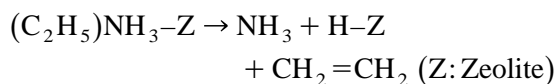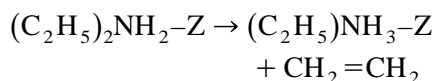Fig. 6. TPO test on templates combustion of GaAPSO-34 crystals.
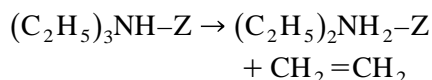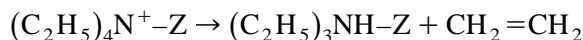
Fig. 7. NH$_3$-TPD profiles for GaAPSO-34s with various Ga contents.

position mechanisms of TEAOH can be suggested as follows [19].

$$(C_2H_5)_4N^+\text{--}Z \rightarrow (C_2H_5)_3NH\text{--}Z + CH_2\text{=}CH_2$$

$$(C_2H_5)_3NH\text{--}Z \rightarrow (C_2H_5)_2NH_2\text{--}Z$$
$$+ CH_2\text{=}CH_2$$

$$(C_2H_5)_2NH_2\text{--}Z \rightarrow (C_2H_5)NH_3\text{--}Z$$
$$+ CH_2\text{=}CH_2$$

$$(C_2H_5)NH_3\text{--}Z \rightarrow NH_3 + H\text{--}Z$$
$$+ CH_2\text{=}CH_2 \; (Z\text{:}\, Zeolite)$$

Scheme. Expectation of decomposition mechanisms for TEAOH

When TEAOH is a counter ion of the framework negative charge, an acid site is formed during Hofmann's ß-elimination reaction [19] on the ethyl chains, giving successive rise to ethylene, lower amine and ammonia. In this scheme, the ethylamines react with the acid site generated by the Hofmann reaction as soon as they are formed, before undergoing further ß-elimination.

## 3.3. Acidity of samples

The NH$_3$-TPD profiles are shown in Fig. 7. Zeolitic materials possess lots of acid sites and certain acidic strengths, attributed to their high Al contents and tetrahedral Al sites, respectively. In general, aluminophosphates (AlPO$_4$-n) are prepared in the presence of cation or neutral amine additives and crystallize with a composition ratio of Al/P of one, resulting in no net charge on the framework. However, as the a result of the addition of silica (SAPO) and/or other metal ions to the structure, it introduced both ion exchange capacity and catalytic acid activity. In particular, in the case of SAPO, the incorporation of silica into the framework dis-
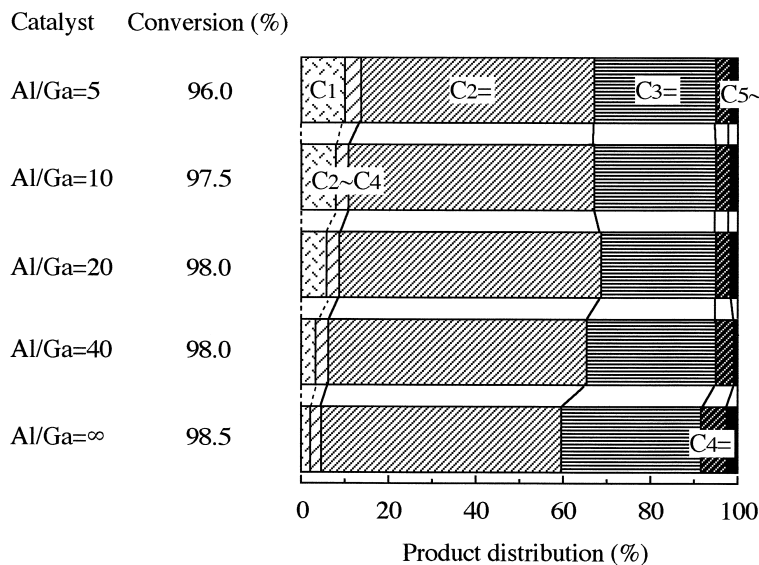


Fig. 8. Product distribution for methanol conversion on GAPSO-34s with various Ga contents.

played Brønsted acid sites. Therefore, in the case of SAPO materials, the amount of acid sites depend on the Si amount. These profiles consist of two peaks: one appears at a low temperature range around 150–180°C and another appears at a high temperature range around 420–470°C. The low and high temperature peaks correspond to the weak and strong acid sites, respectively. When the Al/Ga ratio decreased, the amount of acid site decreased also. The order of the amount of acid sites based on $NH_3$-TPD was as follows: $Al/Ga = \infty > 40 > 20 > 10 > 5$.

### 3.4. Methanol conversion

Fig. 8 shows catalytic performances on methanol conversion for these catalysts. The methanol conversion exhibited 100% for almost catalysts. For GaAPSO-34 crystal (Al/Ga = 20) having a small particle size and a little acid site, methanol was converted selectively to ethylene with high yield. However, when the Ga content increased, the selectivity to ethylene rather decreased. This is ascribed to the collapse of the framework in crystal with much Ga content. A surprising result of the increase in Ga content was the increase in methane yield. This also resulted in a decrease of selectivity to ethylene.
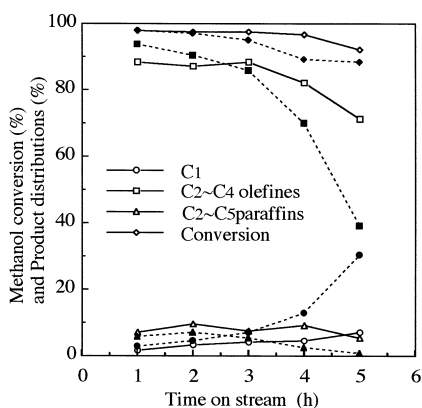


Fig. 9. Effect of time on stream for methanol conversion and product distribution on non-incorporated and Ga-incorporated SAPO-34s. Opened symbol: Al/Si = ∞, closed symbol: Al/Ga = 20.

The selectivity is minor compared with that on catalyst incorporated $Ni^{2+}$ (above 70% [16]).

Results of the duration test are shown in Fig. 9. The ethylene was selectively synthesized in the catalyst with Al/Ga = 20 compared with the catalyst with Al/Ga = ∞ until 2 h. However, the methanol conversion almost coincides with that. On the other hand, the selectivity to ethylene and methanol conversion decreased abruptly after 3 h.

## 4. Conclusion

GaAPSO-34s with various Al/Ga ratios (Al/Ga = ∞, 40, 20, 10, 5, and 0) were successfully synthesized by rapid crystallization. As a characteristic result, the crystallinity and the particle size decreased with an increase in the Ga content incorporated into the framework. The incorporation of Ga into the SAPO framework was confirmed by $^{27}Al$ and $^{31}P$ MAS-NMR. On the other hand the selectivity to ethylene on methanol conversion increased on catalyst with Al/Ga = 20 compared with pure SAPO-34 catalyst. However, in spite of the decreases in acid sites and particle size in catalyst with much more Ga content, the selectivity to ethylene was not enhanced, rather the methane related to catalytic deactivation increased in GaAPSO-34 catalysts. This is supposed to be due to the collapse of the framework of the SAPO-34 with an increase in Ga content. However, the correct cause has not been resolved yet. Consequently, it was confirmed that the Ga incorporation was not suitable as the selective synthesis of ethylene on methanol conversion.

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