1. Introduction

Light olefins such as ethylene and propylene are basic raw materials that are used in the synthesis of various chemicals and are usually produced by steam cracking of naphtha. Production of light olefins from methanol and bio-ethanol using solid catalysts, especially zeolites, has become more important recently because of the increasing concerns about global warming and exhaustion of petroleum resources. Methanol can be produced via synthesis gas (CO/H_2) from various carbon sources such as coal, natural gas, and biomass, and ethanol can be obtained by fermentation of biomass.

The methanol-to-olefins (MTO) and methanol-to-gasoline (MTG) processes have been extensively studied in China and the USA. In Japan, the JGC Corp. and Mitsubishi Chemical Corp. have developed the leading technology for propylene production from dimethyl ether (DTP process) and constructed a demonstration plant. These processes are known as methanol-to-hydrocarbons (MTH) processes and a great deal of effort has been devoted toward their improvement in recent years. The MTO process likely proceeds via a dual-cycle mechanism, commonly called the hydrocarbon pool mechanism, in which both alkenes and aromatics are treated as important hydrocarbon pool compounds and are methylated with methanol (or dimethyl ether) to give larger hydrocarbons that are subsequently cracked or dealkylated to form lighter alkenes. The alkene-based cycle is predominant over TON type zeolite (ZSM-22) catalyst with 1D straight channels, yielding propylene as the main product. In contrast, the aromatic-based cycle prevails over BEA type zeolite catalyst with larger 3D 12-MR channels, yielding ethylene and propylene in nearly equal proportions.

Various ZSM-5 type zeolites containing alkaline earth metals (AE-ZSM-5) were synthesized and catalytic performances in the conversion of methanol to light olefins were investigated. The AE-ZSM-5 showed increased selectivity for light olefins at temperatures above 500 °C. High (C_2H_4 + C_3H_6) yields (>50 C%) were obtained over Mg-ZSM-5, Ca-ZSM-5, and Sr-ZSM-5 with SiO_2/Al_2O_3 ratios of 200-800, 100-800, and 80-300, respectively. Maximum (C_2H_4 + C_3H_6) yield of ca. 65 C% was achieved over Ca-ZSM-5 with SiO_2/Al_2O_3 ratios of 100-300. The strong acid sites of ZSM-5 became weakly acidic after incorporation of alkaline earth metals, which suppressed coking and dealumination, resulting in improved catalyst lifetime. However, part of the incorporated alkaline earth metals underwent leaching from the weak acid sites due to H_2O and CO_2 produced during the reaction, which resulted in the regeneration of the strong acid sites of the zeolite. These strong acid sites promote the formation of carbonaceous deposits that are ultimately responsible for the deactivation of the zeolite catalysts. Investigation of the stabilization of weak acid sites found that the zeolite catalyst lifespan could be greatly extended by modification with alkaline earth metal carbonates. SrCO_3/Sr-ZSM-5 (SiO_2/Al_2O_3 = 100) maintained a (C_2H_4 + C_3H_6) yield of more than 50 C% for 2000 h at 550 °C with only three regeneration cycles. The high catalytic performance of CaCO_3/Ca-ZSM-5 was evaluated by a bench-scale test. Total C_2H_4 and C_3H_6 production was 11.52 kg from a methanol feed of 42.347 kg after 266 h. The conversion of ethanol to light olefins over various ZSM-5 zeolites with different acidity, especially zeolites with isomorphous framework-substitution, was also investigated. The highest propylene yield of ca. 29 C% was obtained over co-modified La/P/ZSM-5(Ga) with P/Ga and La/Ga ratios of 1 and 0.4, respectively. The introduced lanthanum reacts with the pre-introduced phosphorus to regenerate some of the Bronsted acid sites (Si(OH)Ga).

Keywords
ZSM-5, Alkaline earth metal, Phosphorus, Methanol, Ethanol, Light olefin
amounts. Both the aromatic-based and alkene-based cycles may occur over MFI type zeolite (ZSM-5) catalyst with 2D sinusoidal channels crossed with 1D straight channels, which form intersection cavities. Therefore, the catalysts used to produce light olefins such as ethylene and propylene as the main products must be modified to suppress the formation of higher olefins and carbonaceous materials.

Various approaches have been investigated including reduction of the conversion of methanol by decreasing contact time, reaction temperature, or methanol partial pressure\(^{14}\), modification with phosphorus and magnesium\(^{15,16}\), chemical vapor deposition of silicon methoxide\(^{17}\), and the use of zeolites with smaller pore sizes such as SAPO-34, SSZ-13, SAPO-18, SSZ-39, or ZSM-34\(^{18,24}\). In particular, the selectivity for light olefins can be enhanced by using higher reaction temperature, greater SiO\(_2\)/Al\(_2\)O\(_3\) ratio in the zeolite\(^{25}\), or borosilicates\(^{26}\).

We previously developed various zeolite catalysts for the selective synthesis of light olefins from methanol at high temperatures. ZSM-5 type zeolites containing alkaline earth metals catalyze the formation of light olefins in high yields at temperatures higher than 500 °C, and these catalysts have long productive lifetimes\(^{27,28}\). Interestingly, these zeolites also have high catalytic activity for the conversion of ethanol to light olefins\(^{29,31}\). Here, we review our studies on the selective production of light olefins from methanol and ethanol using various MFI type zeolites. We believe that these results are useful for the development of high-performance zeolite catalysts intended for the production of light olefins from alcohols.

2. Methanol-to-olefins

2.1. Conversion of Methanol to Light Olefins over AE-ZSM-5

ZSM-5 type zeolites containing alkaline earth metals (AE-ZSM-5) were synthesized hydrothermally from starting mixtures containing alkaline earth metal salts\(^{27}\). The nomenclature AE-ZSM-5\((X)\) is adopted here where AE and \(X\) refer to the alkaline earth metal and SiO\(_2\)/Al\(_2\)O\(_3\) ratio, respectively. As summarized in Table 1, the AE/Al\(_2\) ratios of some AE-ZSM-5 zeolites were greater than 1. Therefore, the amount of each alkaline earth metal occluded in the AE-ZSM-5 zeolites was greater than that introduced by conventional ion-exchange methods. Under basic conditions, highly siliceous ZSM-5 zeolites exhibit intracrystalline cation exchange capacity of more than the tetrahedral aluminum content of the framework. Occluded silicate ions, trapped OH\(^-\) groups, or SiO\(^-\) groups are considered responsible for the cation exchange regardless of the aluminum content\(^{32,34}\).

<table>
<thead>
<tr>
<th>Zeolite</th>
<th>Chemical composition(^{19})</th>
<th>BET surface area</th>
<th>Particle size</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SiO(_2)/Al(_2)O(_3)</td>
<td>AE/Si</td>
<td>AE/Al(_2)</td>
</tr>
<tr>
<td>Mg-ZSM-5(80)</td>
<td>82</td>
<td>0.0095</td>
<td>0.78</td>
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<tr>
<td>Mg-ZSM-5(100)</td>
<td>101</td>
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<td>0.88</td>
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<tr>
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<td>1.78</td>
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<td>Ba-ZSM-5(3200)</td>
<td>3160</td>
<td>0.0068</td>
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\(^{a}\) After H\(^+\) ion-exchange with 0.6 M HCl.
AE-ZSM-5 at 600 °C plotted against the SiO2/Al2O3 ratio. High (C2H4 + C3H6) yields (> 50 C%) were obtained over Mg-ZSM-5, Ca-ZSM-5, and Sr-ZSM-5 with SiO2/Al2O3 ratios of 200-800, 100-800, and 80-300, respectively. In contrast, unmodified ZSM-5 produced C2H4 and C3H6 in high yields at low reaction temperatures, but rapid deactivation was observed at 550 °C and the (C2H4 + C3H6) yield dropped to zero at 600 °C. The maximum (C2H4 + C3H6) yield was ca. 65 C%, obtained over Ca-ZSM-5 with SiO2/Al2O3 ratios of 100-300.

2.2. Chemical State of Alkaline Earth Metals in AE-ZSM-5

Two well-defined peaks are observed in the diffuse reflectance Fourier transform infrared (FT-IR) spectra of AE-ZSM-5 and ZSM-5, occurring at 3605 cm−1 and in the range 3730-3740 cm−1.36),37) The low frequency peak is assigned to an acidic, bridged OH of the Si(OH)Al units, and the high frequency peak is assigned to either a terminal SiOH or an extra-framework silica unit. In addition, the broad peak near 3500 cm−1 may be assigned to the hydrogen bond between adjacent hydroxyl groups.37) A peak at 3658 cm−1 can also be observed in the spectrum of Ca-ZSM-5. The intensity of the peak at 3605 cm−1 decreases in the following order: ZSM-5 > Mg-ZSM-5 > Ca-ZSM-5 > Sr-ZSM-5 > Ba-ZSM-5. The FT-IR spectra of Ca-ZSM-5(200) with Ca/Al2 ratios ranging from 0 to 3.23 showed decreased intensity of the peak at 3605 cm−1 and increased intensity of the peak at 3658 cm−1 with higher Ca/Al2 ratio. This observation strongly suggests that both Al and Ca contribute to the peak at 3658 cm−1.38).

To better understand the acidic property of the hydroxyl group responsible for the absorption peak at 3658 cm−1, FT-IR spectra of Ca-ZSM-5 were obtained after Na+ ion-exchange and pyridine adsorption. Figure 2 shows the FT-IR spectra of ZSM-5(200) and Ca-ZSM-5(200) before and after Na+ ion-exchange and pyridine adsorption.35),39) The peak at 3605 cm−1 had disappeared after both processes, whereas the absorp-
tion peak for Ca-ZSM-5 at 3658 cm⁻¹ did not change after Na⁺ ion-exchange but disappeared after pyridine adsorption. These observations strongly indicate that the newly generated OH groups, formed as a result of the interaction between Si(OH)Al and Ca, are less acidic than those of unmodified Si(OH)Al. The FT-IR spectrum of Ca²⁺-ZSM-5, prepared by conventional ion-exchange using 1 M calcium chloride solution, showed absorption peaks at 3658, 3605, and 3740 cm⁻¹. The intensity of the peak at 3658 cm⁻¹ increased with greater Ca²⁺-exchange, whereas that of the peak at 3605 cm⁻¹ decreased. Both these peaks disappeared after adsorption of pyridine. These observations suggest that the chemical state of the alkaline earth metals in AE-ZSM-5 is essentially the same as that in the alkaline earth metal ion-exchanged ZSM-5, and the presence of such metals in ZSM-5 reduces the acidity of its acid sites. For ZSM-5 with a high SiO₂/Al₂O₃ ratio, high degree of alkaline earth metal ion-exchange is difficult to attain by conventional ion-exchange methods. Consequently, the addition of alkaline earth metal salts into the starting hydrogel for zeolite synthesis is an effective method for the preparation of ZSM-5 with high alkaline earth metal content.

2.3. Change in Acidity of Ca-ZSM-5 during Methanol Conversion

The changes in product distribution with time-on-stream for Ca-ZSM-5(200) are shown in Fig. 3(A). Yields of C₂H₄, C₃H₆, and C₄H₈ decreased gradually with time-on-stream, whereas yields of C₅H₁₀, C₆⁺ hydrocarbons with C number more than 6), CH₄, and (CO + CO₂) increased, and yields of BTX (benzene + toluene + xylene) and C₂-C₅ paraffins were unchanged. Similar changes in product distribution were observed for other zeolites. Figure 3(B) shows the relationship between contact time (l/(liquid hourly space velocity (LHSV))) and product distribution for methanol conversion at 600 °C over Ca-ZSM-5(200). Yields of C₂H₄, CH₄, and BTX decreased with shorter contact time, whereas yields of C₅H₁₀, C₆⁺ and Ca²⁺ increased, and yields of C₃H₆ were unchanged. Generally, the number of active sites available for reaction decreases with deactivation of the zeolite catalysts caused by accumulation of carbonaceous deposits. Consequently, the product distribution varies with time-on-stream and the product variation resembles that with shorter contact time. Such mechanisms can explain the decrease in the yields of light olefins and the increase in the yields of C₅H₁₀ and C₆⁺ yields with time-on-stream. However, this reasoning cannot explain the absence of change in the yields of BTX and paraffins with time-on-stream. This observation suggests that strong acid sites are regenerated with time-on-stream, because formation of BTX and paraffins apparently occurs at strong acid sites.

Water is a by-product of methanol conversion, so the zeolite catalysts are exposed to a moisture-rich atmosphere during the reaction. Since deactivation of zeolites by steam dealumination is known to occur readily at high temperatures, the stability of acidic sites in Ca-ZSM-5(200) was investigated under these conditions. Conversion of methanol during the first run was carried out at slowly increasing temperatures between 400 °C and 600 °C and subsequently, at 600 °C for 50 h. After the first run, the carbonaceous deposits formed on the deactivated catalyst were burned off under a flow of air, and a second run was performed on the regenerated
catalyst to compare the catalyst stability. Figure 4 shows the relationship between \((\text{C}_2\text{H}_4 + \text{C}_3\text{H}_6)\) selectivity and methanol conversion to hydrocarbons [effective conversion (\%) = 100 − (\text{MeOH} + \text{DME}) yield] at temperatures ranging from 400 to 600 °C. Once effective conversion reached 100 %, the selectivity was plotted against the time-on-stream. The effective conversion values for the first and second runs at 400 °C were strikingly different at 7 % and 100 %, respectively.

To clarify the reason for the increase in catalytic activity during the second run, Ca-ZSM-5 was characterized by FT-IR spectroscopy, K\(^+\) ion-exchange, and X-ray photoelectron spectroscopy (XPS) before and after the reaction. The FT-IR spectrum of Ca-ZSM-5 after the reaction (Fig. 5) showed a remarkable increase in the intensity of the peak at 3605 cm\(^{-1}\), which is assigned to strong acid sites. This peak disappeared after K\(^+\) ion-exchange. In contrast, the intensity of the peak at 3658 cm\(^{-1}\) decreased after the reaction, indicating that some calcium ions that had modified the strong acid sites were released from these sites during the course of testing. This result is supported by the findings of K\(^+\) ion-exchange experiments, as summarized in Table 2. The K/Al ratio of the regenerated catalyst was 0.47, whereas that of the fresh catalyst was only 0.05. This ratio reflects the numbers of strong Brønsted acid sites in the zeolite, as K\(^+\) ions exchange predominantly with H\(^+\) cations. Furthermore, Table 2 shows that the bulk Ca/Al\(_2\) ratio of the regenerated catalyst was similar to that of the fresh catalyst, but decreased on K\(^+\) ion-exchange. The latter observation suggests that Ca ions were released from the strong acid sites and migrated to the external surface of the zeolite crystals, where they were readily dissolved in the aqueous solution during K\(^+\) ion-exchange. Migration of Ca ions to the outer surface was also confirmed by XPS data; the Ca/Si ratio of the external surface increased after the lifetime test. Thus, the number of strong acid sites clearly increased due to the gradual release of Ca ions from these sites during the lifetime tests.

![Figure 4](image1.png) Methanol Conversion over Ca-ZSM-5(200)

![Figure 5](image2.png) FT-IR Spectra of Ca-ZSM-5(200)

<table>
<thead>
<tr>
<th>Table 2</th>
<th>Elemental Analysis of Ca-ZSM-5</th>
</tr>
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<tr>
<td>Molar and atomic ratios</td>
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</tr>
<tr>
<td>H(^-)-form (before K(^+) ion-exchange)</td>
<td></td>
</tr>
<tr>
<td>Fresh zeolite</td>
<td></td>
</tr>
<tr>
<td>After reaction(^c)</td>
<td></td>
</tr>
</tbody>
</table>

\(a\) K\(^+\) ion-exchange was performed using a 1 M KCl solution at 80 °C for 8 h.

\(b\) Ca\(_{2p}\)Si\(_{2p}\) peak intensity ratio was determined from XPS.

\(c\) Methanol conversion was carried out using Ca-ZSM-5 at 600 °C and LHSV of 2.3 h\(^{-1}\) (MeOH/Ar = 1) for 50 h, and the catalyst was subsequently regenerated in air.

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Therefore, modification of the zeolite strong acid sites by Ca ions effectively reduces the formation of carbonaceous deposits and prolongs the catalyst lifetime. However, the beneficial effects due to incorporation of Ca ions are lost with time-on-stream because the Ca ions are released from these sites during methanol conversion.

In addition to H₂O, CO₂ is also produced during methanol conversion. Consequently, the alkaline earth metal species are probably transformed into their carbonates in the presence of CO₂. Therefore, the catalytic activity of AE-ZSM-5 is likely influenced by the addition of CO₂ to the feedstock. Methanol conversion over ZSM-5(200), Ca-ZSM-5(200), and Sr-ZSM-5(200) was carried out using either N₂ or CO₂ as the carrier gas and showed that the (C₂H₄ + C₃H₆) selectivity over AE-ZSM-5 was lower with CO₂ carrier gas than with N₂. In particular, the selectivity of these products over Sr-ZSM-5 was 47.6 % with CO₂ but 51.9 % with N₂. In contrast, the activity and the selectivity over unmodified ZSM-5 were the same with CO₂ and N₂ carrier gases. However, the selectivity for BTX over Sr-ZSM-5 increased markedly from 1.5 C% using N₂ to 4.1 C% using CO₂. Both Ca-ZSM-5 and Sr-ZSM-5 developed many carbonaceous deposits in the presence of CO₂, whereas ZSM-5 showed no difference in the amount of carbonaceous deposits formed with N₂ and CO₂ carrier gases. Based on the observation that deactivation of the catalysts occurred readily in the presence of CO₂, Ca (or Sr)-modified acidic sites presumably reacted with CO₂ to form CaCO₃ (or SrCO₃), resulting in the release of Ca ions from the acidic sites. The loss of Ca during methanol conversion leads to the regeneration of strong acid sites and the production of BTX. Consequently, the formation of carbonaceous deposits is accelerated, which results in rapid catalyst deactivation.

The 100 % steam dealumination rates of AE-ZSM-5 (200) and ZSM-5(200) were also systematically investigated using solid state ²⁷Al MAS nuclear magnetic resonance (NMR). The dealumination rate followed Eq. (1), i.e., there is a second-order dependence on the amount of tetrahedrally coordinated Al of the zeolite.

\[ -dA/dt = k_2 \cdot A^2 \]  

(1)

where A, t, and k₂ refer to the amount of tetrahedrally coordinated Al, steaming time, and second-order rate constant, respectively. Equation (2) was obtained by integration of Eq. (1).

\[ \left( A_0/A \right) - 1 = A_0 \cdot k_2 \cdot t \]

(2)

where A₀ is the initial amount of the tetrahedrally coordinated Al.

The rate constants of A₀ \( \cdot k₂ \) (day⁻¹) calculated using ²⁷Al MAS NMR data were as follows: 4.0 for ZSM-5, 4 \( \times 10^{-2} \) for Mg-ZSM-5, 1.9 \( \times 10^{-1} \) for Ca-ZSM-5, 2.6 \( \times 10^{-2} \) for Sr-ZSM-5, and 1.9 \( \times 10^{-2} \) for Ba-ZSM-5. These values suggest that dealumination of ZSM-5 is suppressed by modification with alkaline earth metals.

2.4. Improvement of the Catalyst Life of AE-ZSM-5

Figure 6 shows the relationship between the Ca/Al₂ ratio of Ca-ZSM-5 and the yields of (C₂H₄ + C₃H₆), C₁-C₃ paraffins, and BTX in the initial stages of methanol conversion (58). (C₂H₄ + C₃H₆) yield markedly increased with higher Ca/Al₂ ratios of less than two, whereas the yields of C₁-C₃ paraffins and BTX decreased. Carbonaceous deposition over Ca-ZSM-5 was lower, possibly because of the reduction in BTX formation ( coke precursors) by zeolite modification with alkaline earth metals. The catalyst lifetime, or time-on-stream until dimethyl ether (DME) was detected in the effluent gas, was extended greatly at Ca/Al₂ ratios greater than three, although the product yield remained constant at Ca/Al₂ ratios greater than two. This observation suggests that the acidic properties of zeolites do not change significantly in this region, and that further incorporation of alkaline earth metals into the zeolite tends to extend the catalyst life. Therefore, AE-ZSM-5 was modified with various alkaline earth metal salts using a well-known impregnation method, and long-term lifetime tests were carried out for methanol conversion.

BTX selectivity decreased to less than one-fifth of that of the parent zeolite, and the catalytic lifespan was improved by about four times. In contrast, (C₂H₄ + C₃H₆) selectivity remained unchanged. Similar results were obtained by employing a mechanical mixing technique for zeolite modification instead of the impregnation technique. Table 3 lists the results of methanol conversion.
Long-term Lifetime Tests for AE-ZSM-5

Migration of the calcium ions from the acidic sites.

The lifetime test for Sr-ZSM-5 was carried out for 1000 h. The catalyst was regenerated twelve times at intervals of 74-79 h, and the methanol conversion was maintained at a constant level (ca. 100%). The total yield of \( \text{C}_2\text{H}_4 + \text{C}_3\text{H}_6 + \text{C}_4\text{H}_8 + \text{C}_5\text{H}_{10} \) reached a maximum of 80-83 C%. Total yield decreased with time-on-stream, but could be almost completely recovered by catalyst regeneration.

In contrast, the long-term lifetime test for Mg-ZSM-5 was carried out for 660 h, and showed that regeneration was required after much shorter intervals because this catalyst was more easily deactivated. The maximum total yield of \( \text{C}_2\text{H}_4 + \text{C}_3\text{H}_6 + \text{C}_4\text{H}_8 + \text{C}_5\text{H}_{10} \) during the regeneration interval ranged from 68 to 77 C% in the first 400 h of time-on-stream and subsequently decreased slightly. The lifetime test for Ca-ZSM-5 was also carried out for 1000 h. The total yield of \( \text{C}_2\text{H}_4 + \text{C}_3\text{H}_6 + \text{C}_4\text{H}_8 + \text{C}_5\text{H}_{10} \) varied similarly to Sr-ZSM-5. Ca-ZSM-5 required regeneration about ten times, which was less than for Sr-ZSM-5. The maximum total yield of \( \text{C}_2\text{H}_4 + \text{C}_3\text{H}_6 + \text{C}_4\text{H}_8 + \text{C}_5\text{H}_{10} \) ranged from 83 to 86 C% over Ca-based zeolite, higher than that obtained using Sr-ZSM-5. However, the regeneration interval for the former needed to be gradually shortened from 120 to 75 h with increasing time-on-stream. Therefore, the Sr-ZSM-5 catalyst is more stable and has a longer lifetime than both Mg-ZSM-5 and Ca-ZSM-5.

The degrees of dealumination and the intensity ratios (i.e., the value observed for the used catalysts to that of the corresponding fresh catalyst) of the peaks at 3 ppm assigned to tetrahedrally coordinated aluminum of the three catalysts were determined using \(^{27}\text{Al}\) MAS NMR. The intensity ratio for Sr-ZSM-5 was 94 %, distinctly higher than that observed for both Mg-ZSM-5 (18-19 %) and Ca-ZSM-5 (32-56 %). Therefore, Sr-ZSM-5 has a higher resistance against dealumination. We consider that as the acidity of zeolites originates from the dealumination of the Cr-ZSM-5 sample, the long catalyst lifespan of Sr-ZSM-5 can be attributed to the greater resistance against dealumination of this aluminosilicate framework.

The diffuse reflectance FT-IR spectra for the three catalysts before and after the lifetime tests were also measured to study the changes in the peaks corresponding to hydroxyl groups. The peak at 3605 cm\(^{-1}\) observed in the spectrum of the fresh Mg-ZSM-5 catalyst disappeared completely after testing for 660 h. This observation is consistent with the release of a large number of aluminum atoms from the framework. The peak at 3605 cm\(^{-1}\) had very low intensity for fresh Ca-ZSM-5. The strong acid sites of Ca-ZSM-5 correspond to the peak at 3605 cm\(^{-1}\), as discussed previously, and the peak gradually increased in intensity with the time-on-stream during methanol conversion because of migration of the calcium ions from the initially weak acid sites to the surface of the crystalline zeolite.
intensity of the peak at 3605 cm⁻¹ of the catalyst sample withdrawn from the upper layer of the reactor after the lifetime test was very low compared to that of the fresh catalyst. In contrast, the intensity of this same peak for the sample obtained from the lower layer had increased. Possibly the deterioration of the catalyst due to dealumination is greater within the upper layers of the catalyst because methanol was fed from the top of the reactor. The ²⁷Al MAS NMR results clearly support this possibility. The relative intensity of the peak at 53 ppm was lower for the catalyst sample from the upper layer (32 %) than for the catalyst in the lower layer (56 %). On the other hand, the peak at 3605 cm⁻¹ was not observed for either fresh or used Sr-ZSM-5 catalyst. These observations of FT-IR and ²⁷Al MAS NMR indicate that Sr-ZSM-5 is a remarkably stable catalyst for the conversion of methanol to light olefins. Therefore, Sr-ZSM-5 catalyst offers the best yield of light olefins and catalyst lifetime among the various AE-ZSM-5 catalysts studied.

Figure 7 shows the result of the long-term catalyst lifetime test performed at 550 °C with SrCO₃/Sr-ZSM-5(100) (SrCO₃/Sr-ZSM-5 = 1/2, weight ratio). The catalyst lifetime for a (C₂H₄ + C₃H₆) yield of more than 50 C% was 2000 h achieved with only three regeneration cycles. The characteristics of the SrCO₃/Sr-ZSM-5 catalyst after the lifetime test were evaluated by ²⁷Al MAS NMR and X-ray diffraction. In addition, the intensity ratio of the NMR peak at 53 ppm was 44 % and 56 % for the upper and lower layers of the catalyst, respectively, after the catalyst lifetime test. About 50 % aluminum was found to have remained in the zeolite framework after testing for 2000 h.

2.6. Bench-scale Test over CaCO₃/Ca-ZSM-5

A bench-scale apparatus consisting of two fixed-bed reactors in series was constructed, with the production capacity of 1 kg/day of ethylene and propylene. The fixed-bed reactors were pseudo-isothermal and the reactor tubes were made of SUS-321, with dimensions of 37.1 mm × 2400 mm (Reactor I) and 65.7 mm × 1400 mm (Reactor II) as diameter × length. The pellets of CaCO₃/Ca-ZSM-5(200) (CaCO₃/Ca-ZSM-5 = 1/2, weight ratio) were molded either by an extruder (CC-E-type catalyst) or by a tablet machine (CC-T-type catalyst). The pellet size of the CC-E-type catalyst molded with alumina binder was 3 mm × 5 mm, and that of the CC-T-type catalyst without a binder was 4 mm × 2 mm (diameter × length). The performances of the two types of pellet catalysts were estimated in Reactor I. The selectivities for (C₂H₄ + C₃H₆) at 100 % methanol conversion of the CC-E-type catalyst were 59.6, 61.8, and 65.5 C% at 550, 570, and 600 °C, respectively, and the selectivities for the CC-T-type catalyst were 61.7, 65.3, and 68.5 C%, respectively, at these temperatures. Therefore, the selectivity for (C₂H₄ + C₃H₆) product mixture was slightly higher for the CC-T-type catalyst than for the CC-E-type catalyst.

A long-term lifetime test was performed continuously for the CC-T-type catalyst for a total of 421 h (after 278 h of time-on-stream, the reaction was stopped once for decoking) under the following conditions: CC-T-type catalyst = 143 cm³, LHSV = 1.4 h⁻¹, N₂/MeOH ratio = 3, temperature = 550-570 °C, pressure = 1.5 atm, in Reactor I. The selectivities for C₂H₄, C₃H₆, and C₅H₁₀ were found to change with time-on-stream (Fig. 8). The selectivity for C₂H₄ decreased with...
time, but recovered at higher reaction temperature. In contrast, the reverse of the C2H4 trend was observed for C5H10. Furthermore, the selectivity for C3H6 was independent of the reaction temperature. The selectivity for aromatics increased slowly with time, reaching the maximum yield after about 200 h. The yield of hydrogen and the selectivities for CO and CH4 increased significantly with time. Total C2H4 and C3H6 production was 11.52 kg from a methanol feed of 42.347 kg after 266 h.

3. Conversion of Ethanol to Olefins

3.1. Effect of Acidity of ZSM-5 on Conversion of Ethanol to Propylene

Conversion of ethanol to light olefins over AE-ZSM-5 was also investigated, finding that Sr-ZSM-5 gave a high propylene yield of ca. 32 C% and also exhibited high catalytic stability (4). Previous and the present results indicate that the product distribution in the zeolitic ethanol conversion process depends strongly on the acidity and the channel structure of the zeolites. Therefore, several attempts have been made to control the acidity of the zeolites by modifying them with various metals including Zr, La, and Sr (45–47). However, ethanol conversion has not been investigated over zeolites with different acid strengths determined by isomorphous substitution of their frameworks.

Therefore, the influence of the acidity of the zeolite catalyst on the ethanol conversion process was investigated using ZSM-5 zeolites with isomorphous substitution (ZSM-5(M), M = Al, Ga, and Fe) and different oxide ratios (SiO2/M2O3) in the conversion of ethanol to propylene.

The acidic properties of ZSM-5(M) were evaluated by FT-IR and NH3-temperature programmed desorption (TPD). The IR spectrum of ZSM-5(Al) with a SiO2/Al2O3 ratio of 74 showed two sharp peaks at ~3740 cm–1 assigned to the isolated silanol group, and 3610 cm–1 assigned to an acidic, bridging OH group of Si(OH)Al, i.e., a Brønsted acid site. The broad peak near 3500 cm–1 corresponds to hydrogen-bonded adjacent hydroxyl groups (48). The IR spectra of ZSM-5(Ga) with SiO2/Ga2O3 ratio of 70 and ZSM-5(Fe) with SiO2/Fe2O3 ratio of 78 were also characterized by two sharp peaks. The peak at ~3740 cm–1 was similar to that of ZSM-5(Al). However, the second OH peak was shifted toward higher frequencies (3620 cm–1 and 3630 cm–1 for ZSM-5(Ga) and ZSM-5(Fe), respectively) compared to ZSM-5(Al) at 3610 cm–1, as a consequence of frequency dependence on acid strength. Therefore, the Brønsted acidity increased in the following order: Si(OH)Fe < Si(OH)Ga < Si(OH)Al (49). Figure 9 shows typical NH3-TPD curves for ZSM-5(SiO2/Al2O3 = 74), ZSM-5(SiO2/Ga2O3 = 70), and ZSM-5(SiO2/Fe2O3 = 78). Peaks observed above 200 °C can be attributed to NH3 desorption from the Brønsted acid sites. If the zeolite sample has almost the same amount of acid sites, the position of the temperature maximum in the TPD curves is a qualitative indication of the relative acid strength. The temperature maxima were 280, 300, and 330 °C for ZSM-5(Fe), ZSM-5(Ga), and ZSM-5(Al), respectively. Therefore, the order of relative acid strength deduced from the maximum temperature values agreed with that of the IR data.

BTX = benzene + toluene + xylene.

Fig. 9  NH3-TPD Curves of (a) ZSM-5(Al), (b) ZSM-5(Ga), and (c) ZSM-5(Fe)
The catalytic performance of ZSM-5(M) for ethanol conversion was investigated using various parameters. Figure 10 shows the relationship between the W/F value and the propylene yield for ZSM-5(M) with different SiO2/M2O3 ratios at the reaction temperature of 500 °C. Conversion of ethanol was 100 % for all zeolites. The propylene yield strongly depended on the SiO2/M2O3 ratio and the W/F value. High propylene yields in excess of 25 C% were obtained over ZSM-5(Al) and ZSM-5(Ga) by optimizing both the SiO2/M2O3 ratio and the W/F value. On the other hand, ZSM-5(Fe) yielded ethylene instead of propylene under all conditions. These results suggest that selective zeolitic production of propylene from ethanol requires ZSM-5 zeolite catalysts with acid strength that greater than that of ZSM-5(Ga), and that the W/F value is related to the SiO2/M2O3 ratio of the ZSM-5(M) catalyst. Analysis of the product distributions obtained over ZSM-5(Al) with SiO2/Al2O3 ratio of 74 and ZSM-5(Ga) with SiO2/Ga2O3 ratio of 70 showed that the yields of the C2-C4 paraffins, C5+ fraction (hydrocarbons with C number more than 5), and aromatics were lower using ZSM-5(Ga) than using ZSM-5(Al). Suppression of the formation of C2-C4 paraffins and C5+ species over ZSM-5(Ga) was probably due to the presence of weak acid sites in this zeolite.

3.2. Conversion of Ethanol to Propylene over ZSM-5(Ga) Co-modified with Lanthanum and Phosphorus

Modification of ZSM-5(Al) with phosphorus is a very effective means of improving its catalytic activity and stability by reducing the number of strong acid sites50,51. Phosphorus-modified ZSM-5(Al) with SiO2/Al2O3 and P/Al ratios of 80 and 0.5, respectively, achieved high propylene yield of 32 C% in ethanol conversion52. The influence of phosphorus modification on the catalytic performance of ZSM-5(Ga) was also investigated. Phosphorus-modified ZSM-5(Ga), here called P/ZSM-5(Ga), yielded ca. 28 C% of propylene at 500 °C and displayed good catalytic stability because of the suppression of both carbonaceous deposition and release of gallium from the zeolite framework.

To further enhance the catalytic performance of P/ZSM-5(Ga), several co-modified ZSM-5(Ga), here called M/P/ZSM-5(Ga), were prepared from P/ZSM-5(Ga) by adding different metal cations and their ethanol conversion efficiency was studied53. Figure 11 shows the relationship between the M/Ga ratio and the ethylene and propylene yields. Conversion of ethanol was 100 % for all tested zeolites. The ethylene yields decreased remarkably with increasing M/Ga ratios, whereas the propylene yields increased and reached the maximum values of ca. 26 for Zr/P/ZSM-5(Ga) with a Zr/Ga ratio of 0.25, and 29 C% for La/P/ZSM-5(Ga) with a La/Ga ratio of 0.4. The propylene yields were ca. 22 C% for Mg/P/ZSM-5(Ga) with Mg/Ga ratio of 0.7 and 23 C% for Ca/P/ZSM-5(Ga) with Ca/Ga ratio of 0.7.

It is generally accepted that ethanol is first converted to ethylene and subsequently to higher hydrocarbons. The initial ethylene and propylene yields are believed to be related to the oligomerization capacity of the zeolite. Therefore, the effect of ethylene consumption on the propylene yield was investigated for ZSM-5(Ga) and M/P/ZSM-5(Ga). The propylene yields were plotted against the ethylene consumption ratio (C%, 100 – yield of ethylene) as shown in Fig. 1253. The propylene yields over both ZSM-5(Ga) and M/P/ZSM-5(Ga) increased with increasing ethylene consumption ratio and reached the maximum at the same ethylene consumption ratio of ca. 70 C%. This observation indicates that there is no difference in the acidities of ZSM-5(Ga) and M/P/ZSM-5(Ga).

To obtain further information about the oligomerization capacity, the initial product distributions after 0.5 h of time-on-stream over various M/P/ZSM-5(Ga) zeo-
lites with the same acidities were determined as summarized in Table 4. Clearly the product distribution differed greatly between the co-modified zeolites. As these catalysts have the same acid strength and number of acid sites\(^{30,53}\), the variation in product distribution might be explained by differences in the local distribution of the Brønsted acid sites. Aluminum distribution in the framework of ZSM-5(Al) affects the product composition during 1-butene cracking, as the close proximity of the aluminum atoms enhances the hydrogen transfer reaction, leading to the formation of aromatics\(^{30}\). Therefore, the enhanced oligomerization activity of these co-modified zeolites is likely due to the regeneration of native strong acid sites.

### 3.3. Regeneration of Brønsted Acid Sites

Figure 13 shows the typical NH\(_3\)-TPD curves for P/ZSM-5(Ga), Mg/P/ZSM-5(Ga), Ca/P/ZSM-5(Ga), La/P/ZSM-5(Ga), and Zr/P/ZSM-5(Ga)\(^{53}\). For reference, the NH\(_3\)-TPD curve for ZSM-5(Ga) is also shown. A peak was observed at \(\text{ca. } 320^\circ C\) for all zeolite samples, which is attributed to desorption of NH\(_3\) from the strong

Table 4  Initial Product Distribution after 0.5 h of Time-on-stream of Ethanol Conversion over M/P/ZSM-5(Ga)

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>P/Ga</th>
<th>M/Ga</th>
<th>Acid amount(^a) [mmol/g]</th>
<th>(%) C(_2)H(_4)</th>
<th>C(_2)H(_6)</th>
<th>C(_3)H(_6)</th>
<th>C(_2)-C(_4) paraffins</th>
<th>C(_5^+)b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg/P/HZSM-5(Ga)</td>
<td>1.0</td>
<td>0.6</td>
<td>0.25</td>
<td>46.9</td>
<td>22.8</td>
<td>13.4</td>
<td>3.5</td>
<td>13.4</td>
</tr>
<tr>
<td>Ca/P/HZSM-5(Ga)</td>
<td>1.0</td>
<td>0.4</td>
<td>0.23</td>
<td>50.0</td>
<td>22.7</td>
<td>13.6</td>
<td>3.3</td>
<td>10.5</td>
</tr>
<tr>
<td>La/P/HZSM-5(Ga)</td>
<td>1.0</td>
<td>0.4</td>
<td>0.26</td>
<td>31.2</td>
<td>28.7</td>
<td>18.0</td>
<td>7.9</td>
<td>14.2</td>
</tr>
<tr>
<td>Zr/P/HZSM-5(Ga)</td>
<td>1.0</td>
<td>0.25</td>
<td>0.24</td>
<td>40.7</td>
<td>26.2</td>
<td>16.3</td>
<td>6.7</td>
<td>10.0</td>
</tr>
</tbody>
</table>

\(a\) Determined by NH\(_3\)-TPD.

\(b\) C\(_5^+\) = hydrocarbons with C number more than 5.
Brønsted acid sites. The curve for P/ZSM-5(Ga) also showed a shoulder peak at ca. 220 °C, probably due to NH₃ desorption from the phosphorus-modified weak acid sites. The intensity of the shoulder peak was markedly decreased for M/P/ZSM-5(Ga), whereas the intensity of the peak at ca. 320 °C increased. This finding suggests that regeneration of the strong acid sites occurs. The introduced metal cations Mg, Ca, La, and Zr react with the pre-introduced phosphorus to generate phosphorus species such as $M_x(PO_4)_y$, resulting in regeneration of some native Brønsted acid sites (Si(OH)Ga) as follows:

$$\text{Si Ga P O Si Ga P O Si Ga P O}$$

$$\xrightarrow{\text{M/Mg, Ca, La or Zr introduction}} \text{Si Ga P O Si Ga P O Si Ga P O} + M_x(PO_4)_y$$

The curves of ZSM-5(Ga) and M/P/ZSM-5(Ga) showed nearly the same temperature maxima. If zeolites have almost the same numbers of acid sites, the position of the temperature maximum is a qualitative indication of relative acid strength. Therefore, ZSM-5(Ga) and M/P/ZSM-5(Ga) may have no difference in the acid strength, as homogeneous Brønsted acid sites are recreated by doping with various metal cations. Figure 14 shows the relationship between the M/Ga ratio and the increase in the amount of NH₃ desorbed after co-modification, i.e., $\text{NH}_3[M/P/ZSM-5(Ga)] - \text{NH}_3[P/ZSM-5(Ga)]$.

### 4. Conclusions

ZSM-5 type zeolites containing alkaline earth metals (AE-ZSM-5) with SiO₂/Al₂O₃ ratios between 70 and 3700 were synthesized and catalytic performances for the conversion of methanol to light olefins were investigated at temperatures between 400 °C and 600 °C. AE-ZSM-5 zeolites were selective for light olefin generation at temperatures higher than 500 °C and the yield of (C₂H₄ + C₃H₆) was greater than 50 C%. The highest (C₂H₄ + C₃H₆) yield (ca. 65 C%) was obtained for Ca-ZSM-5 with SiO₂/Al₂O₃ ratios of 100-300. This high catalytic performance could be attributed to the incorporation of alkaline earth metals in the zeolite, which reduced the acidity of its strong acid sites. However, the incorporated alkaline earth metals were released during methanol conversion, resulting in regeneration of the strong acid sites. These strong acid sites promote coke deposition, which deactivates the catalyst.
Therefore, the weak acid sites were stabilized by adding alkaline earth metal carbonates, which markedly extended the catalyst lifetime. The productive catalyst lifetime of SrCO₃/Sr-ZSM-5 was 2000 h at 550 °C, requiring only three regeneration cycles.

The conversion of ethanol to propylene was also carried out over ZSM-5(Ga) co-modified with lanthanum and phosphorous (La/P/ZSM-5(Ga)). The catalytic stability and activity of ZSM-5(Ga) was effectively enhanced by co-modification because of the suppression of carbonaceous deposition and elimination of gallium from the zeolite framework. The yields of propylene were strongly dependent on both the La/Ga and P/Ga ratios, and the highest value of ca. 29 C% was obtained at P/Ga and La/Ga ratios of 1 and 0.4, respectively. FT-IR, ³¹P MAS NMR, and ⁷¹Ga MAS NMR investigations showed that the introduced lanthanum reacted with the pre-introduced phosphorus to regenerate some of the Brønsted acid sites (Si(OH)Ga), and these latter sites were homogeneously distributed within the zeolite framework.

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ZSM-5型ゼオライト触媒によるメタノールおよびエタノールからの低級オレフィン合成

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SiO2/Al2O3 比 70 〜 3700 のアルカリ土類金属含有 ZSM-5 型ゼオライト触媒を合成し、そのメタノール転化性能を調べた。500 ℃ を超える高温で高い低級オレフィン選択性を示した。特に、SiO2/Al2O3 比 100 〜 300 の Ca-ZSM-5 では（エチレン+プロピレン）収率は 65 C% にも達した。この高い低級オレフィン選択性は、導入されたアルカリ土類金属が ZSM-5 ゼオライトの弱酸点を弱酸点に変え、コーチ質の生成および脱アルミニウムを抑制していることに起因している。しかし、メタノール転化反応中に副生する水および二酸化炭素によって、弱酸点からのアルカリ土類金属の脱離が起こり、弱酸点が再生することが明らかとなった。弱酸点の再生はゼオライト触媒の失活の原因であるコーク質の生成および脱アルミニウムを促進するため、弱酸点をいかに安定させるかをさらに検討した。その結果、アルカリ土類金属炭酸塩による修飾が弱酸点の安定化に有効であり、触媒寿命はさらに向上した。特に、SrCO3 修飾 Sr-ZSM-5 は 2000 時間の触媒寿命を示した。また、酸性質の異なる種々の ZSM-5 型ゼオライトを用いてエタノール転化反応も行った。

Al を Ga で同型置換した ZSM-5(Ga) を P および La で共修飾 La/P/ZSM-5(Ga) では La/Ga 比の増大とともにプロピレン収率は増大し、P/Ga 比 1, La/Ga 比 0.4 で約 29 C% の最大プロピレン収率が得られた。さらに、La 添加により強酸点を修飾していた P 種が LaPO4 として脱離することにより、プロピレン生成に有効な強酸点が再生することを明らかにした。