

## [Review Paper]

# Synthesis of Light Olefins from Methanol Using ZSM-5 Type Zeolite Catalysts

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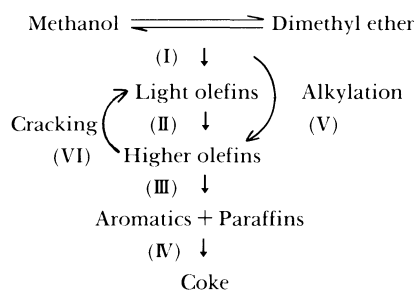
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HZSM-5 type zeolites containing alkaline earth metals (M-HZSM-5) showed an increased selectivity to light olefins at temperatures above 500°C where ethylene and propylene were produced in yields greater than 50%. Part of the alkaline earth metals incorporated changed the strong acid sites of HZSM-5 to weak ones, resulting in the improvement of catalyst life by suppressing both coking and dealumination. However, it was suggested that the release of alkaline earth metals from the weak acid sites by the H<sub>2</sub>O and CO<sub>2</sub> produced took place during the methanol conversion, resulting in the regeneration of strong acid sites. As these acid sites promote the formation of coke deposits that are responsible for deactivation of the zeolites, some means to stabilize the weak acid sites were investigated. It was found that modifying with alkaline earth metal carbonates was effective for stabilizing the weak acid sites, and for extending the catalyst life. Micro-crystalline HZSM-5 modified with calcium phosphate also showed an excellent catalyst performance for the methanol conversion to light olefins. Moreover, these catalysts had a long catalyst life. This was confirmed by the long-term life test run of over 2,000 h.

## 1. Introduction

Methanol conversion to light olefins and gasoline over various zeolite catalysts was extensively studied since the innovation of high siliceous zeolite of ZSM-5 by the Mobil Oil Co. As shown in the following reaction path of methanol to hydrocarbons, methanol first converts to dimethyl ether (DME), maintaining equilibrium with DME, and then yields light and higher olefins, followed by conversion to paraffins and aromatic hydrocarbons<sup>1)~4)</sup>.



Reaction path of methanol conversion to hydrocarbons

Therefore, it is essential for the catalysts synthesizing light olefins such as ethylene and propylene as the main products to suppress reaction steps (III) and (IV). From this standpoint, various approaches were made in an effort to enhance the

yields of light olefins. The approaches include lowering the methanol conversion by decreasing contact time, and/or reaction temperature, and/or methanol partial pressure<sup>5)</sup>; modifying ZSM-5 with phosphorus and magnesium<sup>6)~8)</sup>; chemical vapor depositing of silicon methoxide<sup>9)</sup>; using smaller pore zeolites such as erionite, chabasite or ZSM-34<sup>10)</sup>; increasing the reaction temperature and the SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio of the zeolite<sup>11), 12)</sup>; adding basic compounds to the methanol feed<sup>13), 14)</sup>; and using borosilicates<sup>15)</sup> or ferrosilicates<sup>16)</sup>.

We also made great efforts to develop selective zeolite catalysts for the synthesis of light olefins from methanol. Considering that high reaction temperatures above 500°C are favorable for the synthesis of light olefins, and that experiments using C<sub>2</sub>—C<sub>8</sub> olefins as the feed instead of methanol showed cracking of the olefins to be predominant and aromatization of the olefins to be suppressed at high temperatures, we tried to develop zeolite catalysts which are capable of operating at high temperatures. Since deactivation of zeolite catalysts by steam dealumination occurs easily at high temperatures<sup>17), 18)</sup>, the steam stability of zeolite must be improved. In this paper, we shall describe two kinds of effective catalysts we have developed, that is, HZSM-5 type zeolites modified with alkaline earth metals and calcium phosphate.

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Table 1 Characteristics of Various Zeolites

Zeolite	Chemical analysis <sup>a)</sup>			BET surface area [m <sup>2</sup> /g]	Particle size [μm]
	SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>	M/Si	M/Al <sub>2</sub>		
Mg-HZSM-5 (80)	82	0.0095	0.78	347	3-7
Mg-HZSM-5 (100)	101	0.0087	0.88	347	4-5
Mg-HZSM-5 (200)	215	0.0041	0.87	351	3-6
Mg-HZSM-5 (300)	325	0.0050	1.63	354	4-6
Mg-HZSM-5 (800)	783	0.0023	1.78	354	6-10
Mg-silicalite	3,610	0.0026	—	366	6-9
Ca-HZSM-5 (80)	81	0.0141	1.14	312	<1.5
Ca-HZSM-5 (100)	103	0.0141	1.45	311	1-2
Ca-HZSM-5 (200)	211	0.0153	3.23	315	3-6
Ca-HZSM-5 (300)	309	0.0127	3.94	334	3-5
Ca-HZSM-5 (800)	797	0.0106	8.45	346	5-9
Ca-silicalite	3,710	0.0098	—	379	10-13
Sr-HZSM-5 (70)	73	0.0134	0.98	307	1-2
Sr-HZSM-5 (80)	83	0.0144	1.18	309	2-4
Sr-HZSM-5 (100)	108	0.0176	1.90	300	3-5
Sr-HZSM-5 (200)	206	0.0175	3.61	316	3-8
Sr-HZSM-5 (300)	290	0.0154	4.46	323	7-9
Sr-silicalite	3,710	0.0082	—	350	9-15
Ba-HZSM-5 (70)	72	0.0141	1.02	304	2-4
Ba-HZSM-5 (80)	84	0.0147	1.24	311	2-4
Ba-HZSM-5 (100)	102	0.0188	1.92	307	2-4
Ba-HZSM-5 (200)	203	0.0141	2.87	315	3-8
Ba-silicalite	3,160	0.0068	—	344	8-12

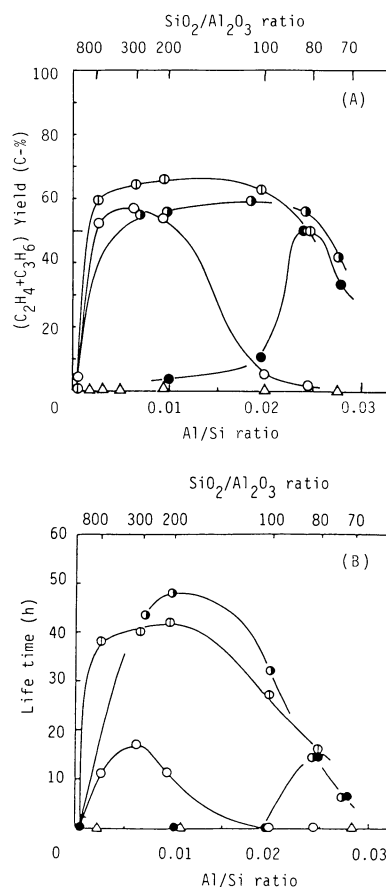
a) After H<sup>+</sup> ion-exchange with 0.6N-HCl.

## 2. HZSM-5 Type Zeolites Containing Alkaline Earth Metals

HZSM-5 type zeolites containing alkaline earth metals (M-HZSM-5, M: alkaline earth metal) were hydrothermally synthesized from synthesis mixtures containing alkaline earth metal salts. As shown in Table 1, the amount of alkaline earth metals occluded in M-HZSM-5 was more than that of the alkaline earth metals introduced by the conventional ion-exchange method. Presumably, the incorporation of excess alkaline earth metals into the zeolite is achieved by the presence of occluded silicate ions or trapped OH<sup>-</sup> groups which are responsible for the cation exchange in excess of that equivalent to the aluminium content<sup>19)~21)</sup>.

### 2.1 Light Olefin Yield and Catalyst Life

The yield of (C<sub>2</sub>H<sub>4</sub>+C<sub>3</sub>H<sub>6</sub>) over M-HZSM-5 and the life time of M-HZSM-5 at 600°C are plotted against the Al/Si ratio in Figs. 1(A) and (B)<sup>22)~24)</sup>. Life time is defined as the time during which methanol conversion is 100% with no residual dimethyl ether. In the case of HZSM-5 zeolites with SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratios between 70 and 1,100 and the crystal size of more than 1 μm, both the (C<sub>2</sub>H<sub>4</sub>+C<sub>3</sub>H<sub>6</sub>) yield and the catalyst life were apparently zero because of deactivation by coking. In the case of M-HZSM-5, high (C<sub>2</sub>H<sub>4</sub>+C<sub>3</sub>H<sub>6</sub>) yields of more than 50% were obtained for Ca-HZSM-5 with SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratios between 100 and 800, and Sr-HZSM-5 with SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratios between 80 and 300. The longest catalyst life was obtained for Ca-HZSM-5 and Sr-HZSM-5 with the SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio of 200. The amount of coke deposit on the



Reaction conditions: Temp.=600°C, LHSV=2.3 h<sup>-1</sup>, MeOH/Ar=1/1.

○: Mg-HZSM-5, □: Ca-HZSM-5, ●: Sr-HZSM-5, ●: Ba-HZSM-5, △: HZSM-5.

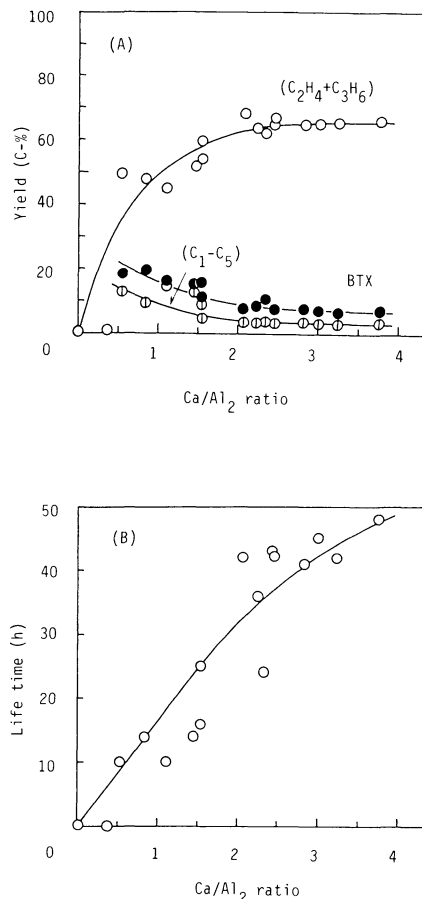
Fig. 1 Effects of Al/Si Ratio of Zeolite on (A) (C<sub>2</sub>H<sub>4</sub>+C<sub>3</sub>H<sub>6</sub>) Yield and on (B) Catalyst Life Time

M-HZSM-5 after 4 h of methanol conversion was less than that on HZSM-5 with the same  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio, particularly for Ca-HZSM-5, Sr-HZSM-5, and Ba-HZSM-5. **Figure 2(A)** shows the correlations between the  $\text{Ca}/\text{Al}_2$  ratio of Ca-HZSM-5 and the yield of  $(\text{C}_2\text{H}_4+\text{C}_3\text{H}_6)$ ,  $(\text{C}_1-\text{C}_5)$ , and BTX at the initial stage of the methanol conversion<sup>25</sup>. In the region of  $\text{Ca}/\text{Al}_2$  ratio below 2, the  $(\text{C}_2\text{H}_4+\text{C}_3\text{H}_6)$  yield increased markedly with  $\text{Ca}/\text{Al}_2$  ratio, while  $(\text{C}_1-\text{C}_5)$  and BTX yields decreased. The less coke deposition over M-HZSM-5 seems to be attributable to the depression of the formation of BTX, *i.e.*, the precursors of coking, by modification with the alkaline earth metals. **Figure 2(B)** illustrates the relationship between  $\text{Ca}/\text{Al}_2$  ratio and catalyst life<sup>25</sup>. The catalyst life is extended much longer in the region of  $\text{Ca}/\text{Al}_2$  ratio over 3, even though the product distribution maintains constant in the region of  $\text{Ca}/\text{Al}_2$  ratio over 2, suggesting that the acidic properties of zeolites hardly changed in this region. These results demonstrate that further incorporation of the alkaline earth metals into the zeolite tends to extend the catalyst life.

## 2.2 Chemical State of Alkaline Earth Metal

**Figure 3** shows the diffuse reflectance FT-IR spectra of hydroxyl groups of M-HZSM-5 with  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio of 200 (M-HZSM-5 (200))<sup>26,27</sup>. The spectrum of HZSM-5 was characterized by two well-defined peaks at 3,605 and 3,730–3,740  $\text{cm}^{-1}$ . The low-frequency hydroxyl has been assigned to the acidic bridged OH of  $\text{Si}(\text{OH})\text{Al}$ , while the high-frequency hydroxyl to the terminal  $\text{SiOH}$  or extraframework silica gel. The broad peak at near 3,500  $\text{cm}^{-1}$  is attributable to hydrogen bonding between adjacent hydroxyl groups. Except for Mg-HZSM-5, intensities of all of these peaks for M-HZSM-5 were very weak as compared with those for HZSM-5. New peaks were observed at 3,674 and 3,658  $\text{cm}^{-1}$  for Mg-HZSM-5 and Ca-HZSM-5, respectively. A peak at 3,676  $\text{cm}^{-1}$  was observed for Mg-silicalite, while a peak at 3,685  $\text{cm}^{-1}$  for the other silicalites containing Ca, Sr, and Ba<sup>23,25</sup>. The intensity of the peak at 3,658  $\text{cm}^{-1}$  in the spectra of Ca-HZSM-5 increased with a decrease in the  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio and an increase in the  $\text{Ca}/\text{Al}$  ratio. The results indicate that both aluminium and calcium have contributed to the peak at 3,658  $\text{cm}^{-1}$ .

In order to get a better understanding of the acidic properties of the hydroxyl groups giving a new peak at 3,658  $\text{cm}^{-1}$ , the FT-IR spectra of Ca-HZSM-5 were measured after  $\text{Na}^+$  ion-exchange and pyridine adsorption. **Figure 4** shows the FT-IR spectra of hydroxyl groups of HZSM-5, Ca-HZSM-5, and Ca-silicalite before and after  $\text{Na}^+$



Reaction conditions: Temp.=600°C, LHSV=2.3 h<sup>-1</sup>, MeOH/Ar=1/1.

Fig. 2 Effects of  $\text{Ca}/\text{Al}_2$  Ratio of Zeolite on (A) Product Distribution and on (B) Catalyst Life Time

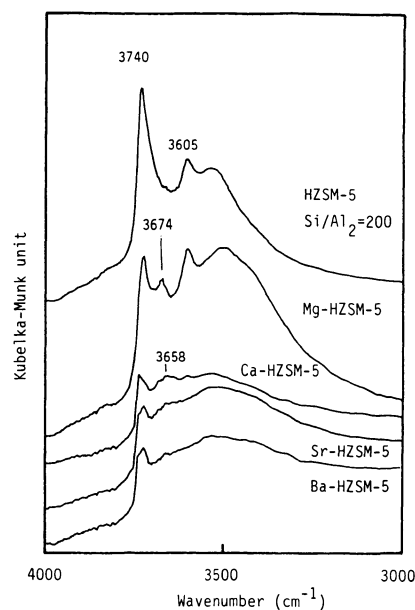
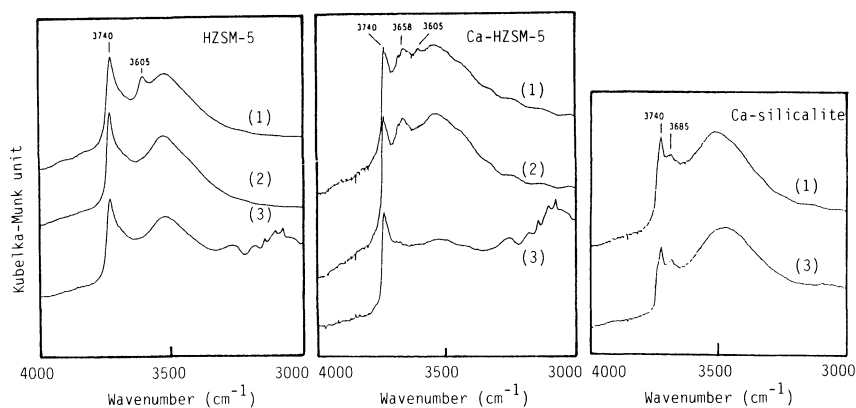


Fig. 3 FT-IR Spectra of Various Zeolites ( $\text{SiO}_2/\text{Al}_2\text{O}_3=200$ )



(1) Fresh, (2) After Na<sup>+</sup> ion-exchange, (3) After pyridine adsorption.

Fig. 4 FT-IR Spectra of Zeolites ( $\text{SiO}_2/\text{Al}_2\text{O}_3=200$ ) after Na<sup>+</sup> Ion-exchange and Pyridine Adsorption

ion-exchange and pyridine adsorption<sup>23), 27)</sup>. As shown in Fig. 4, the peak at  $3,605\text{ cm}^{-1}$  disappeared after these treatments, while the peak observed for Ca-HZSM-5 at  $3,658\text{ cm}^{-1}$  did not change at all after the Na<sup>+</sup> ion-exchange but disappeared after the pyridine adsorption. The facts suggest that the acid strength of the new OH group generated by the interaction between Si(OH)Al and Ca is weaker than that of unmodified Si(OH)Al.

The spectra of adsorbed pyridine taken after evacuation at  $250^\circ\text{C}$  are shown in Fig. 5<sup>27)</sup>. With the disappearance of the hydroxyl band, the characteristic peaks of pyridinium ion (adsorbed on Brønsted acid site) and pyridine coordinated to Al(Lewis acid site) appeared at  $1,546$  and  $1,457\text{ cm}^{-1}$ , respectively. The peak intensity at  $1,546\text{ cm}^{-1}$  decreased in the order: HZSM-5  $\approx$  Mg-HZSM-5  $\gg$  Ca-HZSM-5  $>$  Sr-HZSM-5  $\approx$  Ba-HZSM-5, indicating low concentrations of Brønsted acid sites in Ca-, Sr-, and Ba-HZSM-5. The strong peak at  $1,447\text{ cm}^{-1}$  assigned to the hydrogen-bonded pyridine appeared in the spectra of Ca-, Sr-, and Ba-HZSM-5. From the fact that the peak at  $1,447\text{ cm}^{-1}$  was observed for Ca-silicalite, it seemed that the peak at  $1,447\text{ cm}^{-1}$  had originated from the pyridine coordinated to Lewis acid sites, probably Ca, Sr, and Ba ions. The spectra of the hydroxyl groups of Ca<sup>2+</sup>-ZSM-5 prepared by the conventional ion-exchange method using a 1 N calcium chloride solution showed a peak at  $3,658\text{ cm}^{-1}$  as well as peaks at  $3,605$  and  $3,740\text{ cm}^{-1}$ . The intensity of  $3,658\text{ cm}^{-1}$  peak increased with the degree of Ca<sup>2+</sup>-exchange, while the peak at  $3,605\text{ cm}^{-1}$  decreased with it. Both peaks disappeared after pyridine adsorption. From the results, we concluded that the chemical state of the alkaline earth metals in M-HZSM-5 was essentially the same as

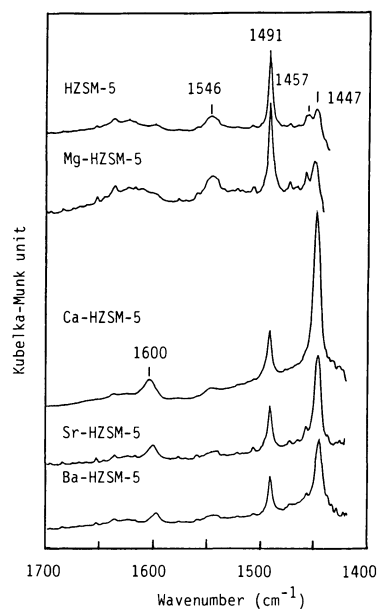


Fig. 5 FT-IR Spectra of Pyridine Adsorbed on Various Zeolites ( $\text{SiO}_2/\text{Al}_2\text{O}_3=200$ )

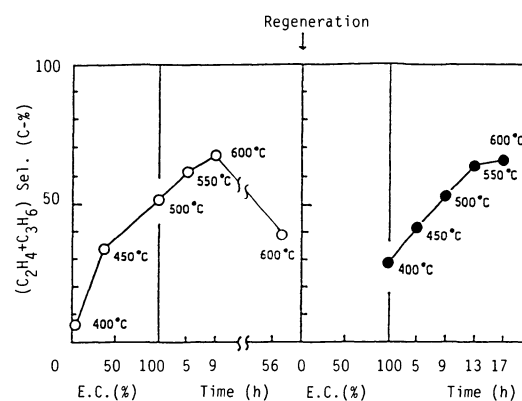
that in the alkaline earth metal ion-exchanged ZSM-5, and that the alkaline earth metals changed the strong acid sites of HZSM-5 to weak ones<sup>27)</sup>.

### 2.3 Stability of Acid Sites

As water is produced in the methanol conversion, the zeolite catalysts are exposed to a moisture-rich atmosphere during the reaction. Since the deactivation of zeolite by steam dealumination occurs readily at high temperatures, the stability of acid sites in M-HZSM-5 was studied. The methanol conversion for the first run was carried out at temperatures raised step by step from  $400$  to  $600^\circ\text{C}$  and then continued at  $600^\circ\text{C}$  for 50 h. After the first run, the carbonaceous deposit on the de-

activated catalyst was burned off in a flow of air, and the second run was performed on the regenerated catalyst in order to compare the catalyst stability. **Figure 6** shows the relationships between  $(C_2H_4+C_3H_6)$  selectivity and methanol conversion to hydrocarbons [E.C. (%)=100-(MeOH+DME) Yield] in a range of temperature 400–600°C<sup>28)</sup>. After the value of E.C. reached 100%, the selectivity was plotted against the time on stream. The E.C. at 400°C were 7 and 100% for the first and the second run, respectively. In order to clarify the reason for the increase in the catalytic activity in the second run, Ca-HZSM-5 before and after the reaction was characterized by FT-IR,  $K^+$  ion-exchange and XPS. In the FT-IR spectrum of Ca-HZSM-5 after the reaction (**Fig. 7**)<sup>28)</sup>, a remarkable increase in the intensity of 3,605  $cm^{-1}$  peak assigned to the strong acid sites was observed and the peak disappeared after  $K^+$  ion-exchange. On the other hand, the intensity of the peak at 3,658  $cm^{-1}$  decreased after the reaction. The results of the  $K^+$  ion-exchange of Ca-HZSM-5 before and after the reaction are shown in **Table 2**<sup>28)</sup>. After  $K^+$  ion-exchange, the K/Al ratio in Ca-HZSM-5 was 0.47 after the reaction, while that in the fresh Ca-HZSM-5 was only 0.05. The XPS data showed an increase in the Ca/Si ratio at the external surface of zeolite after the reaction. As the catalytic activity and K/Al and Ca/Si ratios were not increased by heat but by steam treatment, the above results indicate that the alkaline earth metals interact with the steam produced during the methanol conversion and migrate from the weak acid sites to the outer surfaces of zeolite crystals, resulting in the regeneration of the strong acid sites. That tend to promote the formation of carbonaceous deposits, which are responsible for deactivation of zeolites. Therefore, the release of alkaline earth metals from the weak acid sites is undesirable.

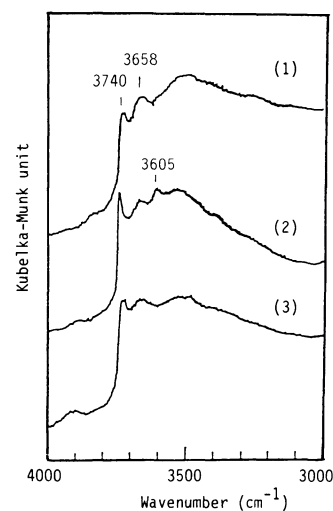
As it is also well known that  $CO_2$  is produced in the methanol conversion and that alkaline earth metal oxides are transformed into the carbonates in the presence of  $CO_2$ , it is predicted that the catalytic activity of M-HZSM-5 would be influenced by



Reaction conditions: Temp.=400–600°C, LHSV=2.3 h<sup>-1</sup>, MeOH/Ar=1/1.

○: Fresh, ●: Regenerated, E.C.(%)=100-(MeOH+DME)Yield.

Fig. 6 Methanol Conversion to Light Olefins over Fresh and Regenerated Ca-HZSM-5(200)



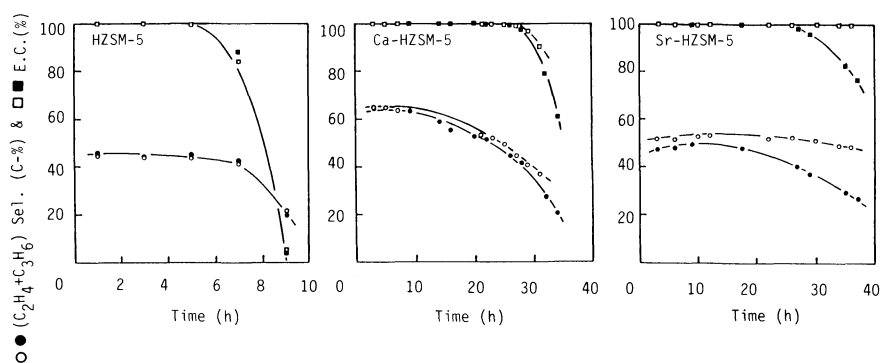
(1) Fresh, (2) After methanol conversion at 600°C for 50 h, and then regenerated, (3) After  $K^+$  ion-exchange of regenerated zeolite.

Fig. 7 FT-IR Spectra of Ca-HZSM-5(200)

Table 2 Elemental Analysis of Ca-HZSM-5

	Molar and atomic ratios					
	Hydrogen form			After $K^+$ ion-exchange <sup>a)</sup>		
	SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>	Ca/Al <sub>2</sub>	Ca2p/Si2p <sup>b)</sup>	SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>	Ca/Al <sub>2</sub>	K/Al
Fresh zeolite	200	2.63	$2 \times 10^{-2}$	198	2.11	0.05
After reaction <sup>c)</sup>	201	2.65	$5 \times 10^{-2}$	198	1.07	0.47
After steaming <sup>d)</sup>	201	2.65	$3 \times 10^{-2}$	200	1.42	0.50

a)  $K^+$  ion-exchange was performed with a 1 N KCl solution at 80°C for 8 h. b) The Ca2p/Si2p peak intensity ratio in XPS. c) Ca-HZSM-5 was used at 600°C and LHSV of 2.3 h<sup>-1</sup> (MeOH/Ar=1) for 50 h, and then regenerated in air. d) The steaming was carried out at 600°C and LHSV=1.2 h<sup>-1</sup> ( $H_2O/Ar=0.67$ ) for 7 h.



Reaction conditions: Temp.=600°C(HZSM-5(200), 500°C), LHSV=1 h<sup>-1</sup>, MeOH/CO<sub>2</sub>(N<sub>2</sub>)=1/1.

Carrier gas: ○ □: N<sub>2</sub>, ● ■: CO<sub>2</sub>.

Fig. 8. Effects of Carrier Gas on Methanol Conversion over HZSM-5(200), Ca-HZSM-5(200) and Sr-HZSM-5(200)

Table 3 Effect of CO<sub>2</sub> on Initial Product Distribution

Zeolite	Carrier gas	Initial product distribution [C-%] <sup>a)</sup>										Coke [wt%]	Reaction time [h]
		C <sub>2</sub> H <sub>4</sub>	C <sub>3</sub> H <sub>6</sub>	C <sub>4</sub> H <sub>8</sub>	C <sub>5</sub> H <sub>10</sub>	CH <sub>4</sub>	(C <sub>2</sub> -C <sub>6</sub> )	BTX	CO	CO <sub>2</sub>	C <sub>6</sub> <sup>+</sup>		
HZSM-5 (200) <sup>b)</sup>	N <sub>2</sub>	15.9	28.9	16.7	5.1	2.5	12.6	11.9	0.1	0.0	6.3	11.4	14
HZSM-5 (200) <sup>b)</sup>	CO <sub>2</sub>	16.1	29.8	17.1	5.4	2.2	12.0	11.8	0.1	—	5.5	11.4	14
Ca-HZSM-5 (200)	N <sub>2</sub>	17.5	47.6	20.9	4.4	0.9	1.8	3.7	0.3	0.1	2.8	9.1	38
Ca-HZSM-5 (200)	CO <sub>2</sub>	16.9	47.3	20.7	3.6	1.0	1.9	4.9	0.7	—	3.0	13.7	37
Sr-HZSM-5 (200)	N <sub>2</sub>	8.3	43.6	21.5	11.4	1.9	1.6	1.5	4.3	0.9	5.0	3.7	39
Sr-HZSM-5 (200)	CO <sub>2</sub>	7.9	39.7	19.8	12.1	2.3	1.1	4.1	6.0	—	7.0	7.4	39

a) After 3 h. b) After 1 h.

addition of CO<sub>2</sub> in the feed. **Figure 8** shows the results of methanol conversion over HZSM-5, Ca-HZSM-5, and Sr-HZSM-5 using N<sub>2</sub> or CO<sub>2</sub> as the carrier gas<sup>29</sup>. The (C<sub>2</sub>H<sub>4</sub>+C<sub>3</sub>H<sub>6</sub>) selectivity on M-HZSM-5 with CO<sub>2</sub> carrier gas was lower than that with N<sub>2</sub>, especially on Sr-HZSM-5. In the case of HZSM-5, the activity and the selectivity with CO<sub>2</sub> were the same as those with N<sub>2</sub>. **Table 3** shows the initial product distribution with N<sub>2</sub> and CO<sub>2</sub> carrier gases<sup>29</sup>. For Sr-HZSM-5, the selectivity to BTX increased markedly by changing the carrier gas from N<sub>2</sub> to CO<sub>2</sub>. As is reported<sup>22</sup>, the aromatics formed by cyclization and dehydrogenation or by hydrogen-transfer reactions of C<sub>6</sub><sup>+</sup> olefins are the intermediates in the formation of carbonaceous species. Both Ca-HZSM-5 and Sr-HZSM-5 formed large amounts of carbonaceous deposits in the presence of CO<sub>2</sub>, while there was no difference in the amount of carbonaceous deposits between the results obtained with N<sub>2</sub> and CO<sub>2</sub> carrier gases over HZSM-5. These results imply that the release of alkaline earth metals from the weak acid sites is promoted by the presence of CO<sub>2</sub> which brings about the regeneration of the strong acid sites.

Deactivation caused by steam dealumination of M-HZSM-5 (200) was investigated. **Figure 9** shows

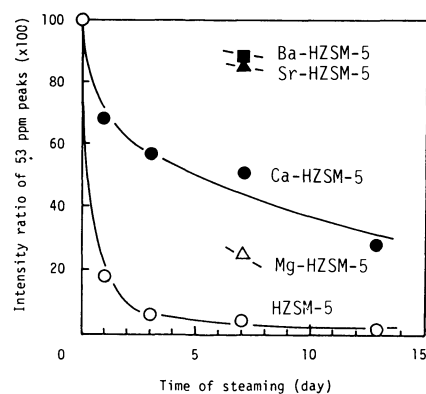


Fig. 9. Relationship between Steaming Time and Intensity Ratio of 53 ppm Peak in <sup>27</sup>Al-MAS-NMR Spectra

the relationship between the time of steaming and the intensity ratio (the value observed for the steamed to that for unsteamed zeolite) of the 53 ppm peaks in the <sup>27</sup>Al-MAS-NMR spectra. The intensity ratio corresponds to the fraction of Al remaining in the zeolite framework (tetrahedrally coordinated Al) after steaming<sup>30</sup>. A rapid decay curve was obtained for HZSM-5,

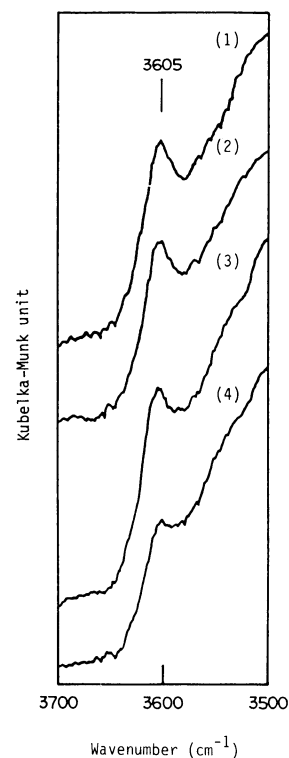
whereas a slow decay curve for Ca-HZSM-5. The order of the intensity ratio of M-HZSM-5 at the steaming time of 7 days was Ba-HZSM-5>Sr-HZSM-5>Ca-HZSM-5>Mg-HZSM-5>HZSM-5, indicating greater stability of Ba-, Sr- and Ca-HZSM-5 against steaming.

### 3. Improvement in Catalyst Life of M-HZSM-5

#### 3.1 Modification with Alkaline Earth Metal Carbonate

Figure 10 shows the FT-IR spectra of hydroxyl groups of HZSM-5 with  $\text{SiO}_2/\text{Al}_2\text{O}_3=200$  and a mechanical mixture of  $\text{BaCO}_3$  and HZSM-5 ( $\text{BaCO}_3/\text{HZSM-5}=1/2$ , weight ratio) before and after calcining at  $600^\circ\text{C}$  for 18 h<sup>31)</sup>. For HZSM-5, the calcination does not affect the intensity of  $3,605\text{ cm}^{-1}$  peak assigned to the acidic OH of  $\text{Si}(\text{OH})\text{Al}$ . For the mechanical mixture of  $\text{BaCO}_3/\text{HZSM-5}$ , however, the intensity of the corresponding peak was decreased to some extent by the calcination. Table 4 shows the chemical compositions of both  $\text{BaCO}_3/\text{HZSM-5}$  and  $\text{BaCO}_3/\text{silicalite}$  after calcining or steaming<sup>31)</sup>. The  $\text{BaCO}_3/\text{zeolites}$  after calcining or steaming were treated with a HCl solution in order to remove free  $\text{BaCO}_3$  from the mixture. The Ba/Si and Ba/Al<sub>2</sub> ratios of  $\text{BaCO}_3/\text{HZSM-5}$  increased both by calcination and steam treatment. On the other hand, the Ba/Si ratios of  $\text{BaCO}_3/\text{silicalite}$  were zero. This indicates that the migration of barium into zeolite channels from the outer surfaces of zeolite crystals occurs by calcining or by steaming and that barium is occluded in the zeolite, presumably, through the interaction with the strong acid sites, since such sites are present on HZSM-5 but not on silicalite.

From the above results, it is expected that regeneration of the strong acid sites due to the release of the alkaline earth metal from the weak acid sites in M-HZSM-5 is apparently depressed when M-HZSM-5 is mixed with an alkaline earth metal salt, resulting in the stabilization of the weak acid sites. We modified M-HZSM-5 with various



- (1) HZSM-5(200) before calcining.  
 (2) HZSM-5(200) after calcining.  
 (3)  $\text{BaCO}_3/\text{HZSM-5}(200)$  before calcining.  
 (4)  $\text{BaCO}_3/\text{HZSM-5}(200)$  after calcining.  
 Calcining conditions: Temp.= $600^\circ\text{C}$ , Time=18 h.

Fig. 10 FT-IR Spectra of HZSM-5(200) and  $\text{BaCO}_3/\text{HZSM-5}(200)$  before and after Calcining

alkaline earth metal salts using a well known impregnation method and carried out long-term life tests in the methanol conversion<sup>32)</sup>. It was found that BTX selectivity decreases to less than one fifth of that of the parent zeolite, and also that the catalytic life is improved by about four times that of the parent zeolite while ( $\text{C}_2\text{H}_4+\text{C}_3\text{H}_6$ ) selectivity remained unchanged by such modification. A mechanical mixing technique for modification

Table 4 Characteristics of Various  $\text{BaCO}_3$ -Mixed Zeolites<sup>a)</sup>

	Time of treatment [h]		Molar and atomic ratio after HCl treatment <sup>d)</sup>		
	Calcining <sup>b)</sup>	Steaming <sup>c)</sup>	$\text{SiO}_2/\text{Al}_2\text{O}_3$	Ba/Si	Ba/Al <sub>2</sub>
$\text{BaCO}_3/\text{HZSM-5}$	7		202	0.0008	0.16
	18		203	0.0015	0.31
	40		204	0.0016	0.33
$\text{BaCO}_3/\text{Silicalite}$		7	212	0.0013	0.27
	18		3,300	0.0000	
	96		3,400	0.0000	
		7	3,300	0.0000	
		40	3,500	0.0008	

a) 1 g of the zeolite was mechanically mixed with 0.5 g of  $\text{BaCO}_3$ . b) Temp.= $600^\circ\text{C}$  in air. c) Temp.= $600^\circ\text{C}$ , LHSV of  $\text{H}_2\text{O}=1.2\text{ h}^{-1}$ ,  $\text{H}_2\text{O}/\text{Ar}=0.67$ . d) The treatment of HCl was performed with a 0.6 N HCl solution at room temperature for 18 h.

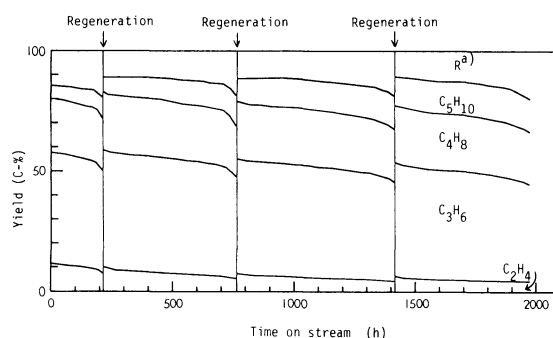
Table 5 Life Test in Methanol Conversion over Various Alkaline Earth Metal Carbonate-mixed Ca-HZSM-5 (200)<sup>a)</sup>

No.	Alkaline earth metal carbonate mixed [g/g zeol.]	Yield [C-%] after 1 h <sup>b)</sup>									Life time <sup>c)</sup> [h]
		C <sub>2</sub> H <sub>4</sub>	C <sub>3</sub> H <sub>6</sub>	C <sub>4</sub> H <sub>8</sub>	C <sub>5</sub> H <sub>10</sub>	C <sub>2</sub> —C <sub>5</sub>	CH <sub>4</sub>	BTX	C <sub>6</sub> <sup>+</sup>	CO+CO <sub>2</sub>	
1	—	16.0	44.4	19.9	4.3	1.2	1.1	4.1	8.0	1.0	22
2	MgO (0.5)	14.6	45.6	21.1	5.4	1.2	1.0	1.1	7.4	2.6	22
3	CaCO <sub>3</sub> (0.3)	14.2	46.3	21.9	5.1	1.2	0.9	0.3	6.5	3.6	122
4	CaCO <sub>3</sub> (0.5)	13.3	45.7	21.9	6.1	1.2	0.9	0.2	5.8	4.9	150
5	CaCO <sub>3</sub> (1.0)	11.4	44.0	21.5	7.7	1.1	1.0	0.1	6.4	6.8	126
6	SrCO <sub>3</sub> (0.3)	13.6	46.4	22.0	6.1	1.2	0.9	0.5	6.3	3.0	105
7	SrCO <sub>3</sub> (0.5)	13.3	46.4	22.2	6.5	1.2	0.9	0.3	5.2	4.0	125
8	SrCO <sub>3</sub> (1.0)	12.0	46.6	22.5	7.4	1.0	1.1	0.2	4.3	4.9	113
9	BaCO <sub>3</sub> (0.3)	14.8	48.3	22.5	5.1	1.3	1.0	0.7	3.0	3.3	79
10	BaCO <sub>3</sub> (0.5)	13.1	47.2	22.5	6.4	1.1	1.0	0.3	3.7	4.7	92
11	BaCO <sub>3</sub> (1.0)	11.6	45.1	21.9	7.5	1.1	1.1	0.2	5.9	5.6	75
12	Silicalite (0.5)	13.4	43.1	19.9	5.9	1.1	1.5	4.6	9.2	1.3	15

a) Alkaline earth metal acetates were calcined in the air at 500°C for 18 h to obtain MgO, CaCO<sub>3</sub>, SrCO<sub>3</sub> and BaCO<sub>3</sub>. Silicalite: SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>=3,300. b) Reaction conditions: LHSV=4.6 h<sup>-1</sup> (MeOH/Ar=1.1), Temp.=600°C. c) Life time=Time on stream until dimethyl ether was detected in the effluent gas.

instead of the impregnation technique gave almost the same effects. **Table 5** shows the results of methanol conversion over Ca-HZSM-5 (200) modified with various alkaline earth metal carbonates<sup>33)</sup>. The catalyst life of Ca-HZSM-5 was 22 h, and it barely changed by mixing with MgO or silicalite. On the other hand, treatment by mixing with carbonates of Ca, Sr, and Ba remarkably improved the catalyst life, up to 75–150 h, demonstrating that alkaline earth metal salts exhibit a striking effect on the catalyst life for methanol conversion. **Figure 11** shows the results of the long-term catalyst life test with SrCO<sub>3</sub>/Sr-HZSM-5 (100) (SrCO<sub>3</sub>/Sr-HZSM-5=1/2, weight ratio). The catalyst life with (C<sub>2</sub>H<sub>4</sub>+C<sub>3</sub>H<sub>6</sub>) yield of more than 50% attained 2,000 h only by repeating regeneration operation three times. **Table 6** illustrates the characteristics of SrCO<sub>3</sub>/Sr-HZSM-5 after the life test. About 50% of aluminium existed in the zeolite framework even after the 2,000 h catalyst life test.

In order to clarify the working state of alkaline earth metal carbonates, the catalyst stability of CaCO<sub>3</sub>/Ca-HZSM-5, CaO/Ca-HZSM-5, Ca-HZSM-5, and HZSM-5 in a long-term methanol conversion test was compared with the changes in the conversion to hydrocarbons and (C<sub>2</sub>H<sub>4</sub>+C<sub>3</sub>H<sub>6</sub>) selectivity as shown in **Fig. 12**<sup>32)</sup>. In the case of CaCO<sub>3</sub>/Ca-HZSM-5 and CaO/Ca-HZSM-5, with N<sub>2</sub> as a carrier gas, about 100% conversion was maintained even after 160 h, and it was observed that the selectivity decayed very slowly. On the other hand, both conversion and selectivity de-



a) R is composed of CH<sub>4</sub>, C<sub>2</sub>—C<sub>5</sub> paraffins, BTX, CO, CO<sub>2</sub>, and C<sub>6</sub><sup>+</sup>.

Fig. 11. Long-term Catalyst Life Test over SrCO<sub>3</sub>/Sr-HZSM-5(100)

cayed rapidly for CaCO<sub>3</sub>/Ca-HZSM-5 by using CO<sub>2</sub> as a carrier gas. The decay curve was the same as that of Ca-HZSM-5 with CO<sub>2</sub> or N<sub>2</sub> carrier gas. As it is well known that CaCO<sub>3</sub> is pyrolyzed to CaO with evolution of CO<sub>2</sub> and that the pyrolysis is inhibited in the presence of CO<sub>2</sub>, it is clearly understandable that basic compounds such as CaO and Ca(OH)<sub>2</sub> formed by the reaction of CaO with the water produced poison the acidic sites on the external surfaces of zeolite crystals and stabilize the weak acid sites formed by the interaction between Si(OH)Al and Ca.

### 3.2 Control of Crystal Size of M-HZSM-5

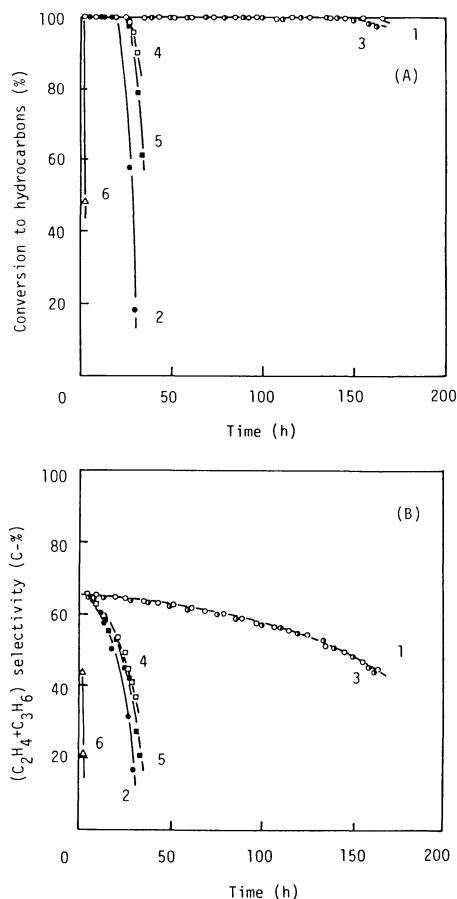
At high temperatures, the diffusion rate of molecules in the zeolite channel is very slow compared with the reaction rate. This indicates that only

Table 6 Characteristics of SrCO<sub>3</sub>/Sr-HZSM-5 (100) after Long Catalyst Life Test

Zeolite	Intensity ratio of 53 ppm peak <sup>a)</sup>	Ratio of residual SrCO <sub>3</sub> <sup>b)</sup>
	[%]	[%]
Upper layer	44	37
Lower layer	56	48

a) Determined by <sup>27</sup>Al-MAS-NMR. b) Determined by XRD.





Reaction conditions: Temp.=600°C, LHSV=4 h<sup>-1</sup>,  
MeOH/N<sub>2</sub>(CO<sub>2</sub>)=1/1.

1,2 : CaCO<sub>3</sub>/Ca-HZSM-5(200).

3 : CaO/Ca-HZSM-5(200).

4,5 : Ca-HZSM-5(200).

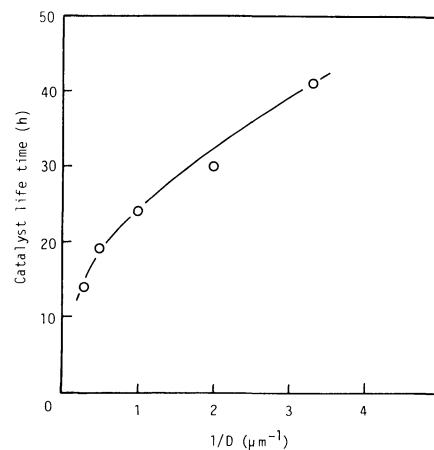
6 : HZSM-5(200).

Carrier gas : 1, 3, 4, 6; N<sub>2</sub>.

2,5; CO<sub>2</sub>.

Fig. 12 Changes in (A) Conversion to Hydrocarbons and in (B) (C<sub>2</sub>H<sub>4</sub>+C<sub>3</sub>H<sub>6</sub>) Selectivity with Time on Stream over Various Zeolites

part of zeolite crystals in the vicinity of the pore entrance is effective for the reaction, that is to say, the reaction hardly takes place in the inner part of zeolite crystals. Therefore, the selectivity to light olefins is not affected appreciably by the crystallinity of zeolite, and the zeolite with high external surface areas (small crystal size) is desirable to realize a long-period sufficient catalytic activity. We attempted to control the crystal size of M-HZSM-5. We found that zeolite crystal size became smaller by adding an adequate amount of boric acid, and the crystal size of Ca-HZSM-5(Ca/Al<sub>2</sub>=3.29) thus obtained was below 1 μm. The initial product distribution with the micro-crystalline Ca-HZSM-5 synthesized in the pres-



Reaction conditions: Temp.=600°C, LHSV=4 h<sup>-1</sup>,  
MeOH/Ar=1/1.

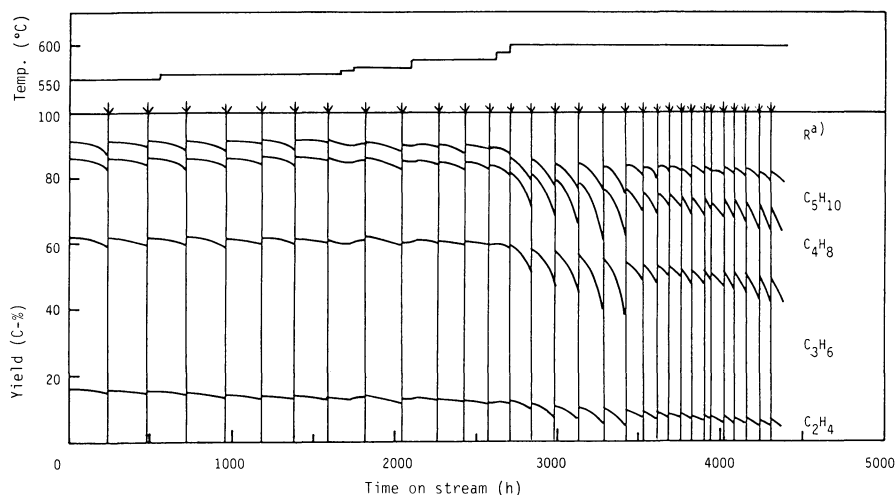
a) The catalyst life time is defined as the time during which methanol conversion is 100% with no residual dimethyl ether and with a yield for (C<sub>2</sub>H<sub>4</sub>+C<sub>3</sub>H<sub>6</sub>) of >50%.

Fig. 13 Effect of Average Crystal Diameter (*D*) of Ca-HZSM-5(200) on Catalyst Life<sup>a)</sup>

ence of boric acid was similar to that with Ca-HZSM-5 synthesized in its absence, indicating that the acidic properties of the zeolite hardly changed by the synthesis with boric acid. **Figure 13** shows the relationship between average crystal diameter of zeolite (*D*) and catalyst life time with (C<sub>2</sub>H<sub>4</sub>+C<sub>3</sub>H<sub>6</sub>) yields of more than 50%. The catalyst life time of the micro-crystalline Ca-HZSM-5 prepared in boric acid (the average crystal diameter of 0.3 μm, 1/*D*=3.3 μm<sup>-1</sup>) was approximately 40 h, which was 3 times that of the zeolite prepared without the acid<sup>35</sup>. A long-term catalyst life test of the micro-crystalline Ca-HZSM-5 modified with SrCO<sub>3</sub> (SrCO<sub>3</sub>/Ca-HZSM-5=1/2, weight ratio) was carried out using dimethyl ether instead of methanol (**Fig. 14**)<sup>36</sup>. The catalyst life with (C<sub>2</sub>H<sub>4</sub>+C<sub>3</sub>H<sub>6</sub>) yields higher than 60% was about 2,600 h.

#### 4. Micro-crystalline HZSM-5 Modified with α-Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>

We investigated in detail various effects of hydrothermal synthetic conditions of ZSM-5 zeolite, especially the effects of H<sub>2</sub>O/SiO<sub>2</sub> ratio, SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio, and crystallization time of zeolite, upon the catalytic activity for the synthesis of light olefins from methanol<sup>37,38</sup>. The average diameter of zeolite crystal decreased with a decrease in the H<sub>2</sub>O/SiO<sub>2</sub> ratio of the synthesis mixture. In the case of H<sub>2</sub>O/SiO<sub>2</sub> ratios of less than 20, the average crystal diameters of zeolites synthesized were below 1 μm. The catalyst life times of the micro-crystal-



Reaction conditions: GHSV=1,100 h<sup>-1</sup>, DME/Ar=1/2.

a) R is composed of CH<sub>4</sub>, C<sub>2</sub>–C<sub>5</sub> paraffins, BTX, CO, CO<sub>2</sub>, and C<sub>6</sub><sup>+</sup>.

An arrow denotes regeneration process (600°C, Air/Ar=4/5).

Fig. 14 Long-term Catalyst Life Test over SrCO<sub>3</sub>/micro-crystalline Ca-HZSM-5(200) Using DME

line zeolites synthesized with H<sub>2</sub>O/SiO<sub>2</sub> ratios of less than 20 were about four times those of the zeolites (the average crystal diameter: 2–5 μm) with H<sub>2</sub>O/SiO<sub>2</sub> ratios between 40 and 80. Considering that SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratios in the bulk composition are almost constant regardless of the H<sub>2</sub>O/SiO<sub>2</sub> ratios and that the aluminium concentration of the outer surface of the zeolite crystals becomes lower with a decrease in the H<sub>2</sub>O/SiO<sub>2</sub> ratio (Fig. 15), the effect of the outer surface aluminium concentration on catalyst life should be also considered.

We then tried to improve the catalyst performance of the micro-crystalline HZSM-5 by modifying with calcium phosphate (CP)<sup>39,40</sup>. The CP-modified HZSM-5 zeolite was prepared by co-milling α-Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> (α-TCP) and HZSM-5, and the product was then hydrothermally treated in HPO<sub>4</sub><sup>2-</sup> solution. In Fig. 16, the results of catalyst life of hydrothermally treated (HZSM-5/α-TCP/HPO<sub>4</sub><sup>2-</sup>) and untreated (HZSM-5/α-TCP) catalysts are plotted against the amount of α-TCP added. The result indicates that the maximum catalyst life is achieved by addition of ca. 10% of α-TCP for the treated catalyst, but slightly more for the untreated. The (C<sub>2</sub>H<sub>4</sub>+C<sub>3</sub>H<sub>6</sub>) selectivity tends to become slightly higher with an increase in the amount of α-TCP. In the long-term catalyst life of HZSM-5/α-TCP/HPO<sub>4</sub><sup>2-</sup> using DME, the catalyst life attained was about 3,000 h.

As described above, the observed rapid deactivation of HZSM-5 is attributed to coke deposition, in

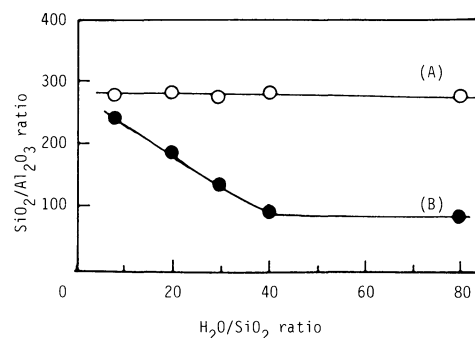
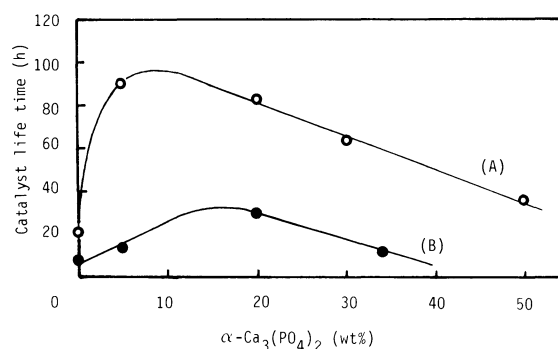


Fig. 15 Effects of H<sub>2</sub>O/SiO<sub>2</sub> Ratio of Synthesis Mixture on SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> Ratio of (A) Bulk and (B) Outer Surface of Zeolite



(A) HZSM-5/α-TCP/HPO<sub>4</sub><sup>2-</sup>, (B) HZSM-5/α-TCP.

Fig. 16 Relationship between Catalyst Life and Amount of α-TCP Added

particular, on the external surface of the micro-crystalline zeolite. We speculated that by grinding HZSM-5 together with  $\alpha$ -TCP, the amount of acid sites of zeolite would reduce according to the following equation;



If this reaction actually occurs,  $\text{Ca}_2\text{P}_2\text{O}_7$ , which is formed by calcination of  $\text{CaHPO}_4$  at  $500^\circ\text{C}$ , should be identified by XRD analysis of the zeolites ground with  $\alpha$ -TCP. However,  $\text{Ca}_2\text{P}_2\text{O}_7$  was not detected in the XRD pattern of HZSM-5/ $\alpha$ -TCP/ $\text{HPO}_4^{2-}$  calcined at  $900^\circ\text{C}$ . Considering that a low-intensity peak assigned to  $\beta$ - $\text{Ca}_2\text{P}_2\text{O}_7$  was observed for HY zeolite ( $\text{Si}/\text{Al}=2.6$ )/ $\alpha$ -TCP/ $\text{HPO}_4^{2-}$ , no diffraction lines of  $\text{Ca}_2\text{P}_2\text{O}_7$  for HZSM-5/ $\alpha$ -TCP/ $\text{HPO}_4^{2-}$  seem to be attributed to a low concentration of aluminium (acid sites). In addition to the direct interaction of  $\alpha$ -TCP with the acid sites, the role of nonstoichiometric hydroxyapatite transformed from  $\alpha$ -TCP and/or that of  $\text{HPO}_4^{2-}$  supplied from the nonstoichiometric hydroxyapatite should be considered. Modification of HZSM-5 by other phosphorous compounds has already been reported in the literature<sup>6),7)</sup>.

We also studied the direct synthesis of light olefins from synthesis gas over a composite catalyst consisting of a methanol synthesis catalyst (Zn-Cr oxides) and a zeolite catalyst<sup>41)~46)</sup>. The combination of Zn-Cr oxides and HZSM-5 resulted in the selective formation of paraffins in the conversion of synthesis gas to hydrocarbons. In contrast, a higher ( $\text{C}_2\text{H}_4 + \text{C}_3\text{H}_6$ ) selectivity of more than 50% was achieved by using M-HZSM-5 modified with alkaline earth carbonates, whose hydrogenation ability was considerably lower than that of HZSM-5. When  $\text{SrCO}_3/\text{Ca}$ -HZSM-5 was used as the zeolite component, a high ( $\text{C}_2\text{H}_4 + \text{C}_3\text{H}_6$ ) selectivity of above 60% was obtained.

## 5. Conclusion

It was found that HZSM-5 type zeolites containing alkaline earth metals showed a high selectivity to light olefins at temperatures above  $500^\circ\text{C}$ , where ethylene and propylene were produced in yields greater than 50%. The catalyst life of these catalysts could be greatly extended by modifying with alkaline earth metal carbonates to suppress coking and dealumination. It was also found that calcium phosphate modified micro-crystalline HZSM-5 synthesized from the synthesis mixtures with low  $\text{H}_2\text{O}/\text{SiO}_2$  ratios showed an excellent catalyst performance.

Recently, Inui *et al.* have reported that Ni-containing SAPO-34 produced ethylene with

selectivity of 90% at 100% methanol conversion<sup>45)</sup>. This indicates that selective synthesis of light olefins from methanol is accomplished by controlling the pore structure and the acidic properties of microporous materials.

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## 要 旨

### ZSM-5 型ゼオライト触媒を用いるメタノールからの低級オレフィン合成

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アルカリ土類金属含有 HZSM-5 型ゼオライト (M-HZSM-5) は, 500 °C を越える高温で高い低級オレフィン選択性を示した。このときの (エチレン+プロピレン) 収率は 50 % 以上であった。導入されたアルカリ土類金属の一部は HZSM-5 の強酸点を弱酸点に変えており, その結果コーク質の生成および脱アルミニウムが抑制された。しかし, メタノール転化反応中に副生する水および CO<sub>2</sub> によって弱酸点からのアルカリ土類金属の離脱が起り, 強酸点が再生することが示

唆された。強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を促進するため, 弱酸点をいかに安定させるかについて次に検討した。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, 触媒寿命がさらに向上することが明らかになった。リン酸カルシウム修飾微結晶 HZSM-5 もメタノールからの低級オレフィン合成に高性能を示した。これらの触媒の触媒寿命の長さは 2,000 時間を越える寿命試験において確認された。

## Keywords

ZSM-5, Alkaline earth metal, Light olefin, Calcium phosphate, Catalyst life