CHAPTER V

RESULTS AND DISCUSSION

In this research, the aromatization of liquefied petroleum gas (LPG) was carried out in a quartz tubular reactor as described in chapter 4. The results were categorized into 13 parts as follow.

5.1 Catalyst Characterization

5.2 Propane Aromatization over Various Metal Ion-exchanged ZSM-5 Catalysts

5.3 Effect of Zinc Loading Amount in NH_4-ZSM-5 Catalysts.

5.4 Effect of Gallium Loading Amount in H-ZSM-5 Catalysts.

5.5 Effect of Zinc Introduction By Incorporation and Ion-exchange Method.

5.6 Effect of Gallium Introduction By Incorporation and Ion-exchange Method.

5.7 Catalyst Performance of Zn.Al-silicate Catalysts.

5.8 Catalyst Performance of Ga.Al-silicate Catalysts.

5.9 Effect of Reaction Temperature on the Product Distribution of Propane Aromatization.

5.10 Effect of GHSV on the Product Distribution of Propane Aromatization.

5.11 Effect of Feed Composition on the Aromatization Reaction.

5.12 Effect of Time on Stream on Product Distribution of the Optimum Catalysts.

5.13 Effect of Platinum Loading on NH_4-Zn.Al-silicate and H-Ga.Al-silicate.

5.1 Catalyst Characterization

5.1.1 X-ray Diffraction Patterns

X-ray diffraction patterns for the catalysts prepared and those of H-ZSM-5 of from the patent literature [65] are shown in Figure 5.1. All the XRD patterns of the catalysts prepared in this laboratory by rapid crystallization method were similar to those of the H-ZSM-5 . This indicates that all the catalysts have the same pentasil pore-opening structure as ZSM-5.

5.1.2 Morphology

Scanning electron microscope photographs of the metallosilicate catalysts are shown in Figure 5.2. As shown, the morphology was greatly affected by the kinds of metal : gallium incorporated catalysts were composed of small crystal of non-uniform size distribution (1-2 μm). Zinc incorporated catalyst was well-crystallized spherical particle of uniform size distribution (5-7 μm).

5.1.3 BET Surface Area

BET surface areas of the crystals are shown in Table 5.1. The surface areas of all metal ion-exchanged ZSM-5, zinc incorporated and gallium incorporated catalysts were almost as large as that of H-ZSM-5. This is consistent with the above-mentioned result that the XRD patterns and the morphology of the catalysts were almost the same as that of H-ZSM-5.
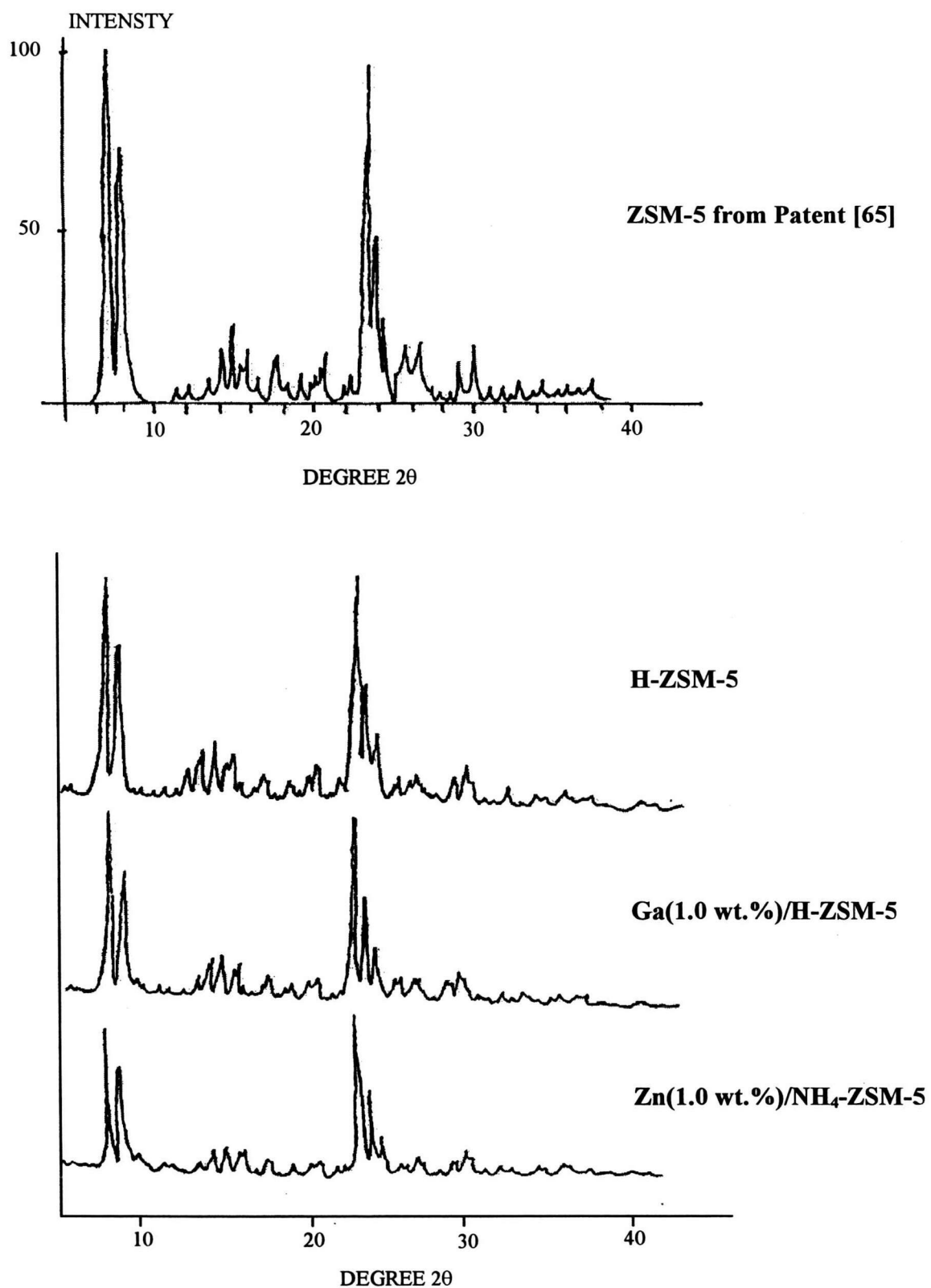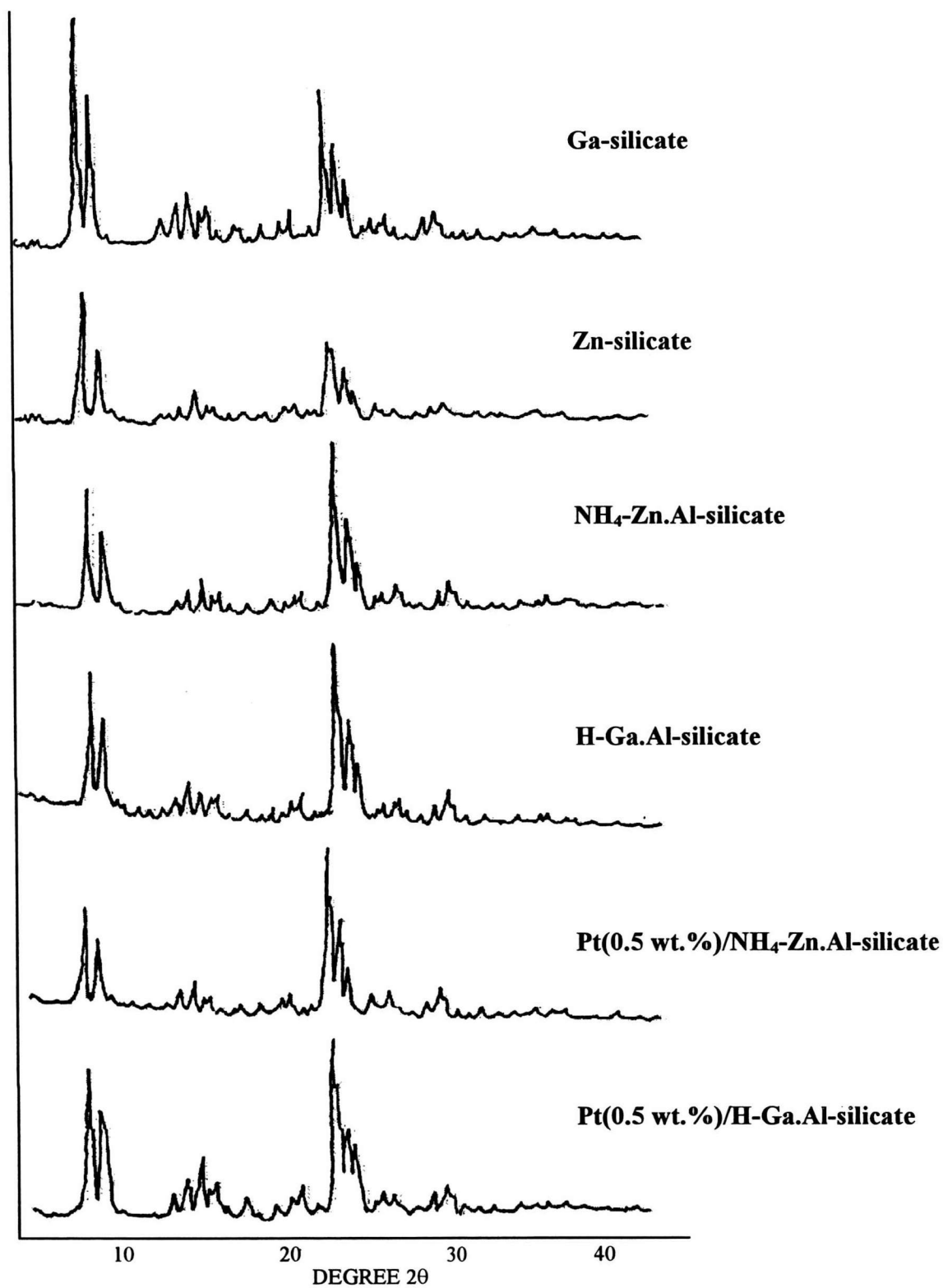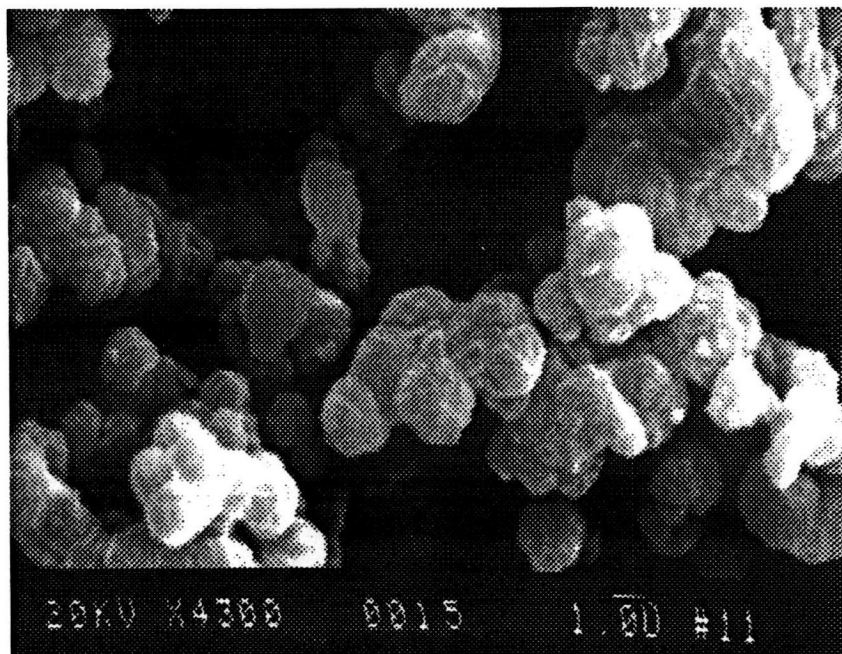
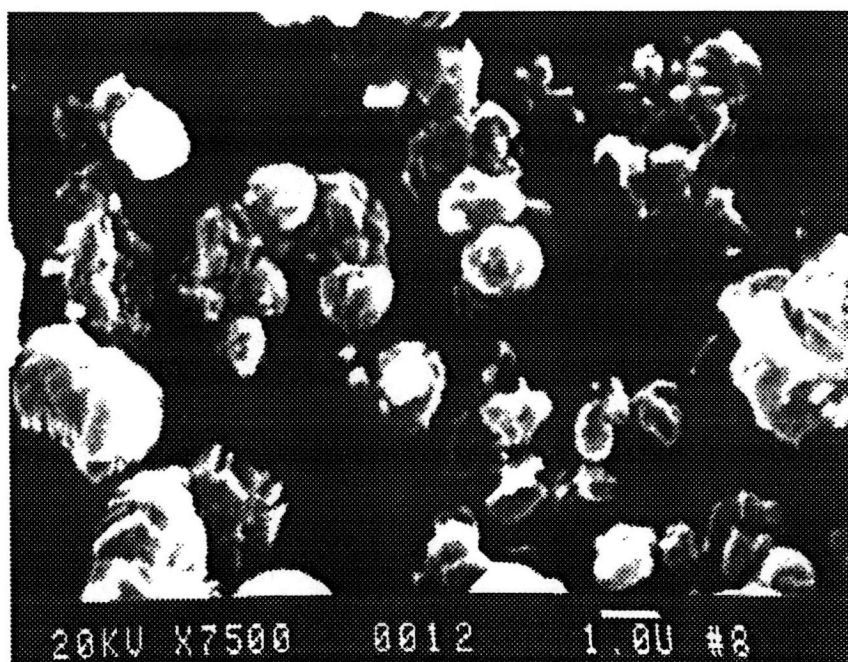Figure 5.1 X-ray diffraction patterns of the catalysts

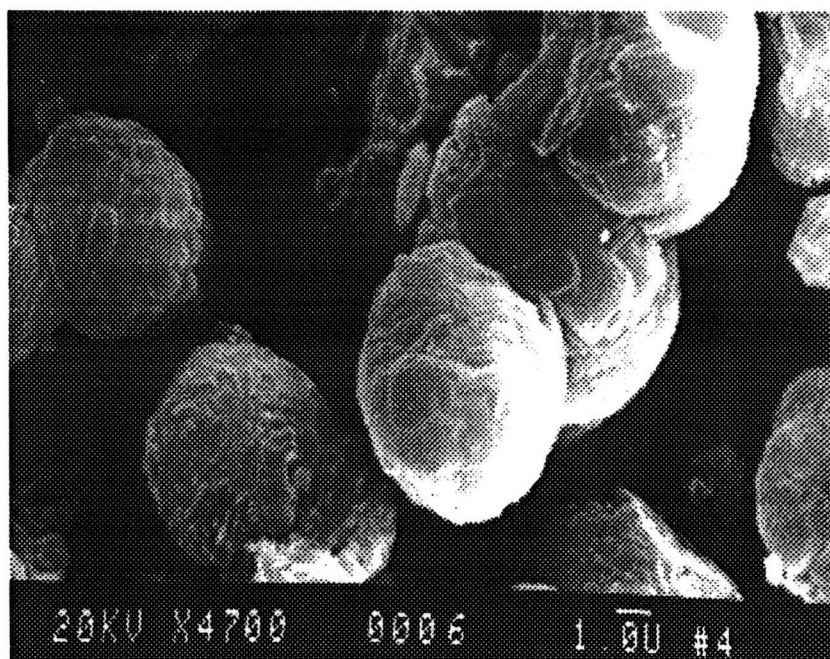Figure 5.1 X-ray diffraction patterns of the catalysts (continued)
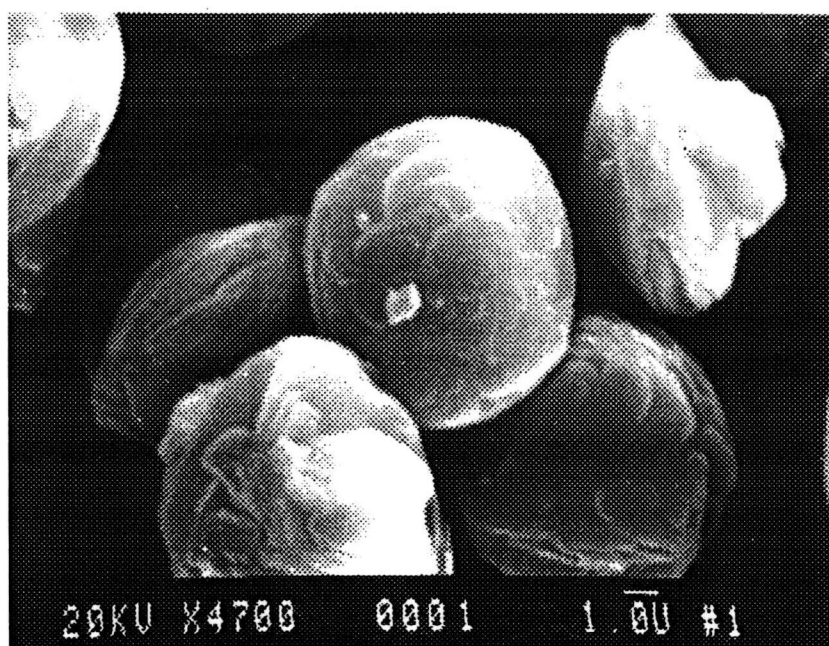
a) H-ZSM-5

b) Ga(1.0 wt.%)/H-ZSM-5

Figure 5.2 SEM photographs of the catalysts.

c) Zn(0.7 wt.%)/NH$_4$-ZSM-5

d) Zn-silicate

Figure 5.2 SEM photographs of the catalysts. (continued)
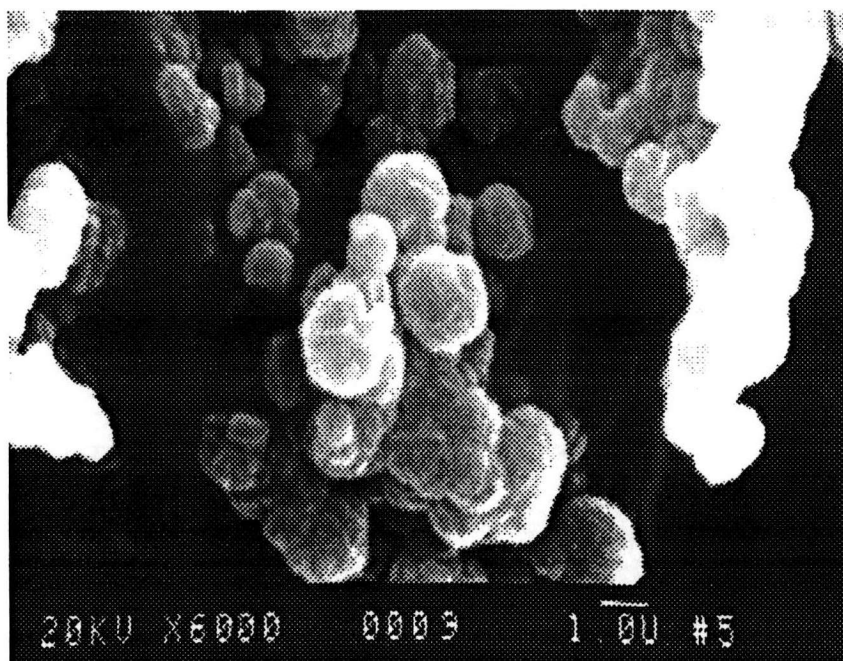
e) Ga-silicate

f) Zn.Al-silicate (Si/Zn = 150, Si/Al = 40)

Figure 5.2 SEM photographs of the catalysts. (continued)

g) Ga.Al-silicate (Si/Ga = 155, Si/Al = 40)

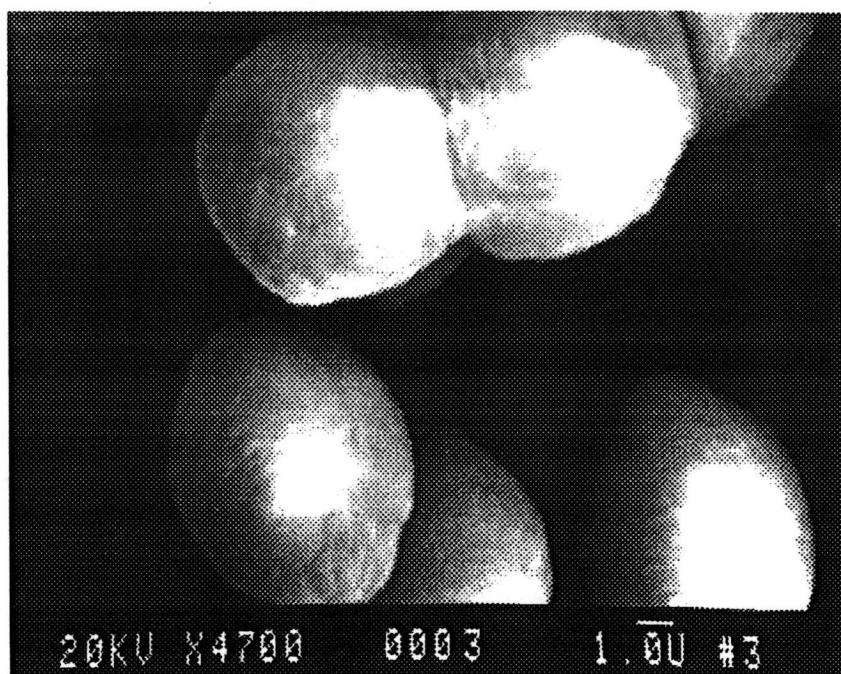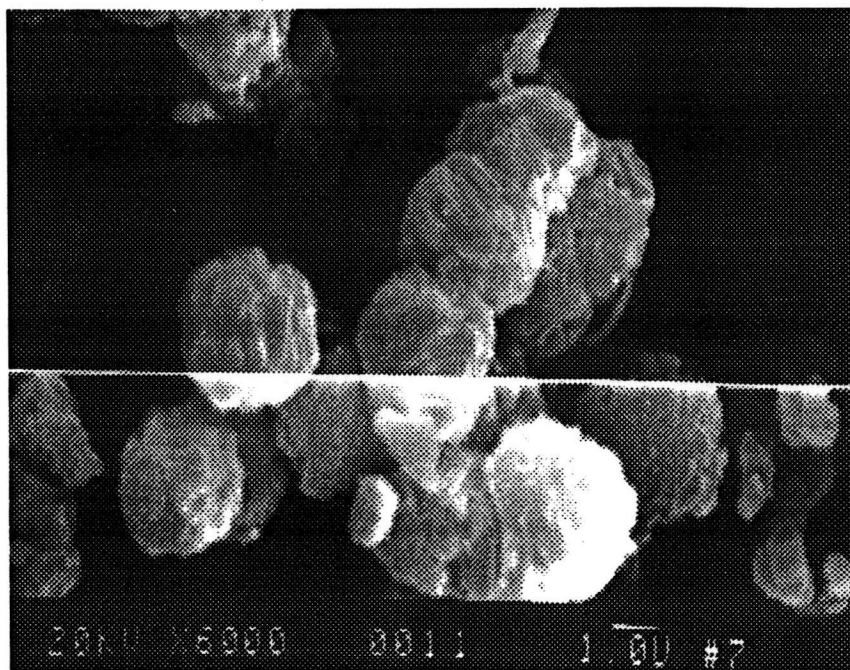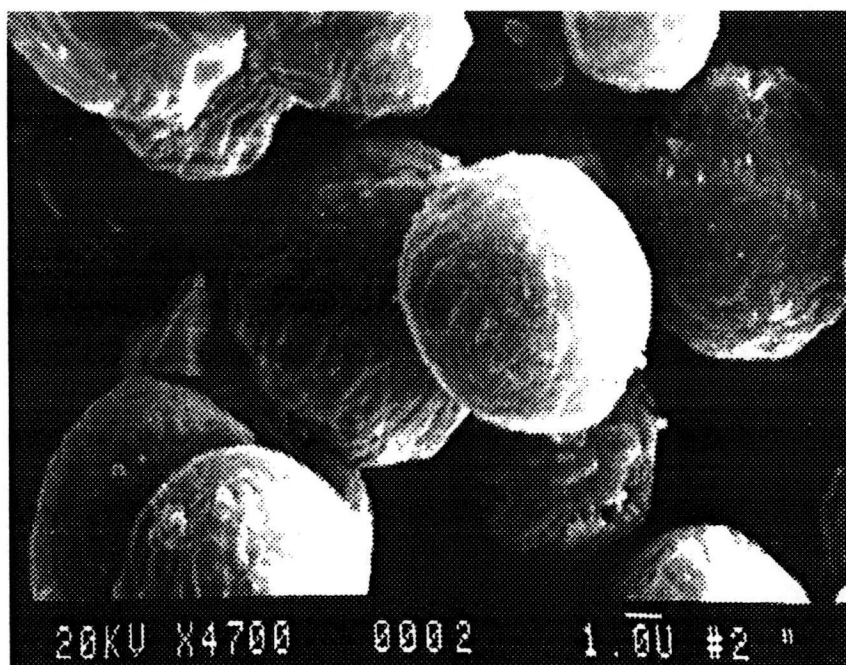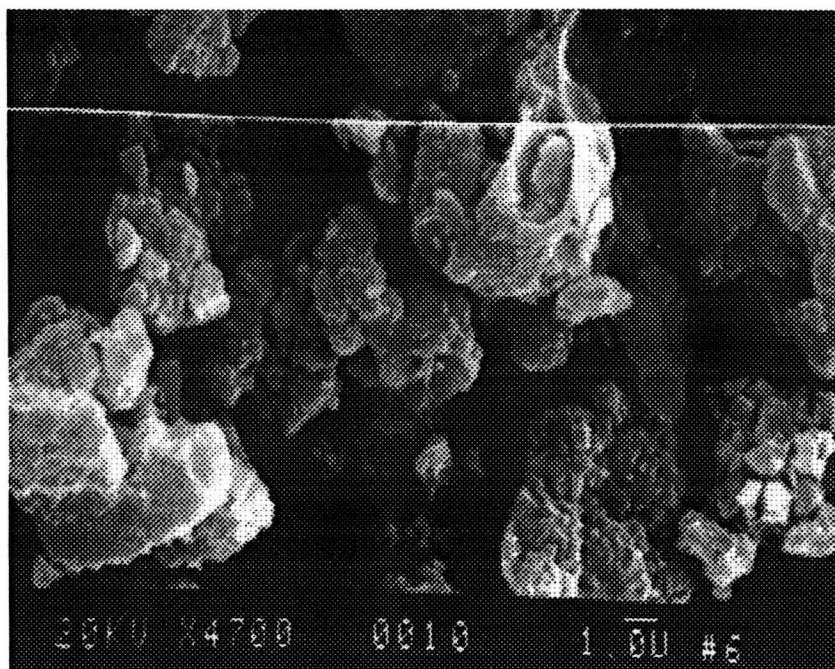h) Pt(0.5 wt.%)/NH$_4$-Zn.Al-silicate

Figure 5.2 SEM photographs of the catalysts. (continued)

i) Pt(0.5 wt.%)/H-Ga.Al-silicate

Figure 5.2 SEM photographs of the catalysts.(continued)

Table 5.1 BET surface areas of the catalysts.

Catalysts	BET surface areas (m²/g of catalyst)
H-ZSM-5	380.59
Zn(0.5 wt.%)/NH$_4$-ZSM-5	378.67
Ga(0.5 wt.%)/H-ZSM-5	398.31
H-Zn-silicate	234.24
H-Ga-silicate	362.53
NH$_4$-Zn.Al-silicate	326.07
H-GA.Al-silicate	370.07
Pt(0.5 wt.%)/NH$_4$-Zn.Al-silicate	341.17
Pt(0.5 wt.%)/H-Ga.Al-silicate	357.48

5.1.4 Chemical Composition

Table 5.2 shows the results of quantitative analysis of gallium, zinc and platinum ingredients in the synthesized crystals. The observed gallium oxide and zinc oxide concentration was almost equal to the charged concentration. This indicates that amounts of various metals can be incorporated in the crystal by changing the charged metal amounts at the stage of gel formation and almost all of the charged metal is incorporated in the crystal. If the interaction of metal with zeolite crystal is not strong enough, the metal may be removed into supernatant liquid and/or washing water [66,67].

Table 5.2 The metal contents of various catalysts which were measured by atomic absorption spectrometry method.

Catalyst	Gallium content (wt.%)	Zinc content (wt.%)	Platinum content (wt.%)
NH$_4$-Zn.Al-silicate Si/Zn=150, Si/Al=40	-	0.9448	-
H-Ga.Al-silicate Si/Ga=155, Si/Al=40	0.9890	-	-
Pt/NH$_4$-Zn.Al-silicate	-	0.9049	0.2274
Pt/H-Ga.Al-silicate	0.9007	-	0.3583

5.1.5 Acidity

The TPD profiles of desorbed ammonia from H-ZSM-5(Si/Al =40), NH$_4$-Zn.Al-silicate, H-Zn.Al-silicate (Si/Zn =150 and Si/Al =40), and H-Ga.Al-silicate (Si/Ga =155 and Si/Al =40) are shown in Figure 5.3. The profile is composed of two peaks, i.e., a high temperature peak of the strong acid sites and a low temperature peak of the weak acid sites [68-71,77]. The peak temperature is a reflection of the acid strength. In the acid-catalyzed reaction, i.e. aromatization reaction, the strong acid sites play the important role for active sites mainly [72, 77]. As shown in Figure 5.3, the peak temperature of strong acid sites for NH$_4$-Zn.Al-, H-Zn.Al-,and H-Ga.Al-silicates were found at around 400 °C. These temperatures were higher than that of H-ZSM-5 (around 350 °C). Therefore, the acid strength for Zn or Ga incorporated in the aluminosilicate was higher than that for H-ZSM-5. Of all the catalysts, H-Ga.Al-silicate showed the maximum amount of strong acid sites.
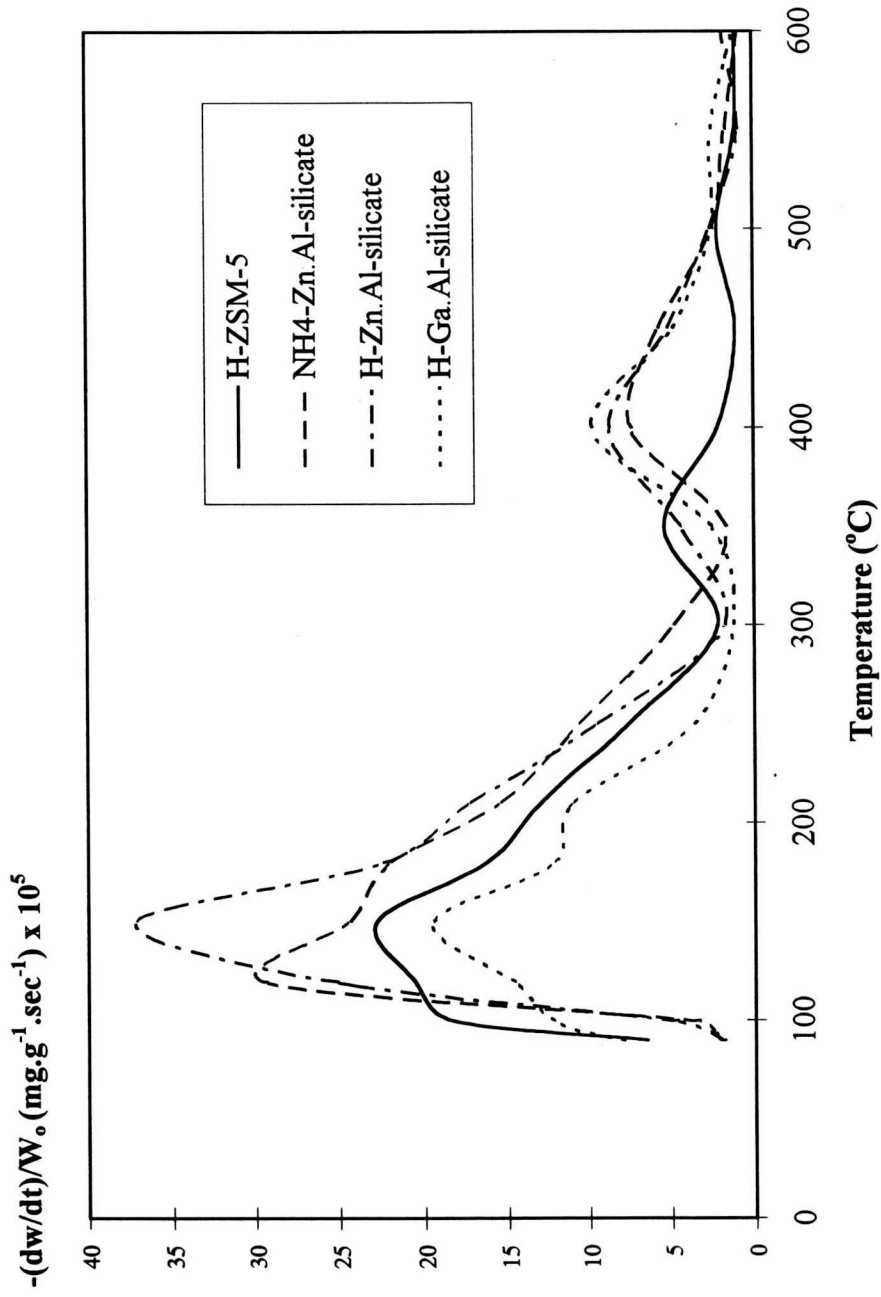
Figure 5.3 TPD profile of desorbed NH_3 from the catalysts

5.2 Aromatization of Propane over Various Metal Ion-exchanged ZSM-5.

Distribution of hydrocarbons produced on various metal ion-exchanged ZSM-5 catalyst are shown in Table 5.3, for NH4-ZSM-5, and Table 5.4, for H-ZSM-5. The reaction was carried out at the reaction temperature of 600 °C, 20% propane and 80% nitrogen, GHSV 2,000 h^{-1} and 1 hour on stream. The concentration of metal was set at 0.5 wt.% and ZSM-5 having Si/Al atomic ratio of 40.

5.2.1 Effect of Various Metal Ion-exchanged NH4-ZSM-5 on Aromatization of Propane.

Table 5.3 Performance of various metal ion-exchanged NH4-ZSM-5 for propane conversion.

Ion-exchanged metal	Conversion [%]	Product distribution [C-wt.%]					
		C_1	C_2	$C_2^=$	$C_3^=$	C_4^+	Aroma.
NH4[a]	78.44	23.51	6.49	33.32	19.23	6.43	11.01
Mo	75.53	24.69	6.89	31.92	18.67	6.28	11.56
Fe	36.56	21.59	3.92	36.48	19.31	4.85	13.85
V	46.23	24.44	4.48	41.89	20.79	4.95	3.45
Zr	45.51	24.52	3.62	41.13	20.87	6.37	3.62
Ni	40.50	23.24	3.46	32.50	13.70	0.90	21.58
Mn	27.80	24.91	2.84	45.33	22.07	1.15	1.01
Cu	48.88	21.25	2.88	32.18	13.44	2.18	27.93
Co	70.35	14.03	9.72	16.93	16.30	2.21	40.56
Cr	46.25	24.49	4.98	38.21	19.02	4.48	8.67
Ga	81.69	22.47	7.32	22.17	12.69	2.04	35.25
Zn	84.06	15.47	7.62	13.87	9.52	1.05	52.45

a) Nonion exchanged, NH4-ZSM-5

The effect of various metals ion-exchanged NH₄-ZSM-5 on propane aromatization, is shown in Table 5.3. NH₄-ZSM-5, Ga/NH₄-ZSM-5 and Zn/NH₄-ZSM-5 were effective for conversion of propane to aromatics, while Co/NH₄-ZSM-5, Ga/NH₄-ZSM-5 and Zn/NH₄-ZSM-5 converted propane to aromatics much higher than parent catalysts, NH₄-ZSM-5. The selectivity to aromatics is highest for Zn/NH₄-ZSM-5.

5.2.2 Effect of Various Metal Ion-exchanged H-ZSM-5 on Aromatization of Propane.

Table 5.4 Performance of various metal ion-exchanged H-ZSM-5 for propane conversion.

Ion-ex-changed metal	Conver-sion [%]	Product distribution [C-wt.%]					
		C_1	C_2	$C_2^=$	$C_3^=$	C_4^+	Aroma.
H[a]	75.54	25.04	6.31	31.83	16.42	5.07	15.31
Mo	77.71	24.73	7.22	28.94	15.57	4.80	18.75
Fe	7.67	15.96	1.52	30.08	50.08	1.02	0.61
V	9.96	20.15	1.82	37.92	38.83	1.28	0.18
Zr	14.54	21.40	1.35	41.61	33.02	2.39	0.24
Ni	17.05	20.91	1.40	39.63	33.72	1.16	5.00
Mn	10.88	22.16	1.60	44.85	29.95	2.94	0.51
Cu	22.40	20.43	2.31	38.45	30.37	1.66	6.68
Co	12.45	7.69	0.74	14.12	75.97	0.51	1.03
Cr	12.00	19.19	2.78	35.80	41.08	0.87	0.56
Ga	86.70	11.53	3.30	13.95	10.00	1.35	59.75
Zn	74.32	23.22	6.17	28.41	12.48	2.68	26.52

a) Nonion exchanged, H-ZSM-5.

Table 5.4 shows the results of propane conversion on various metal ion-exchanged H-ZSM-5 catalysts. Except Ga, Zn and Mo, the ion-exchanged metals reduced the propane conversion activity to the same extent; Fe, V, Zr, Ni, Mn, Cu, Co and Cr exchanged H-ZSM-5 were not selective for the aromatization. On the other hand, Ga/H-ZSM-5 was the most selective catalyst for the aromatization of propane, which is in accordance with the previous investigations [6,73].

5.3 Effect of Zn Loading Amount in NH₄-ZSM-5 Catalyst.

From section 5.2.1 we found that Zn exchanged NH₄-ZSM-5 exhibited the highest activity for propane conversion to aromatic hydrocarbons. So the Zn-exchanged NH₄-ZSM-5 was selected to study the performance of propane aromatization.

The hydrocarbon distributions on Zn exchanged NH₄-ZSM-5 zeolite catalyst with various amount of Zn; 0.30, 0.50, 0.70, 1.00 and 2.00 wt.% (the calculation see appendix A-2) are shown in Figure 5.4. When the amount of Zn increased the selectivity to aromatics was also increased. On the other hand, the selectivity to C_4^+ and olefins decreased with the increasing amount of Zn loading. These results suggested that propane was converted to olefins on Zn by dehydrogenation reaction. The olefins, which occurred on Zn, were transferred and converted to aromatics and lower hydrocarbons on strong acid site of NH₄-ZSM-5. This role of Zn may lead Zn exchanged NH₄-ZSM-5 to the higher selectivity to aromatics.

Zn exchanged NH₄-ZSM-5 with 0.7 wt.% Zn loading exhibited the highest amount of aromatic hydrocarbons (53.45 %). When the Zn loading was increased the activity for aromatics declined slightly probably due to less Zn dispersion caused by sintering of its excessive amount.
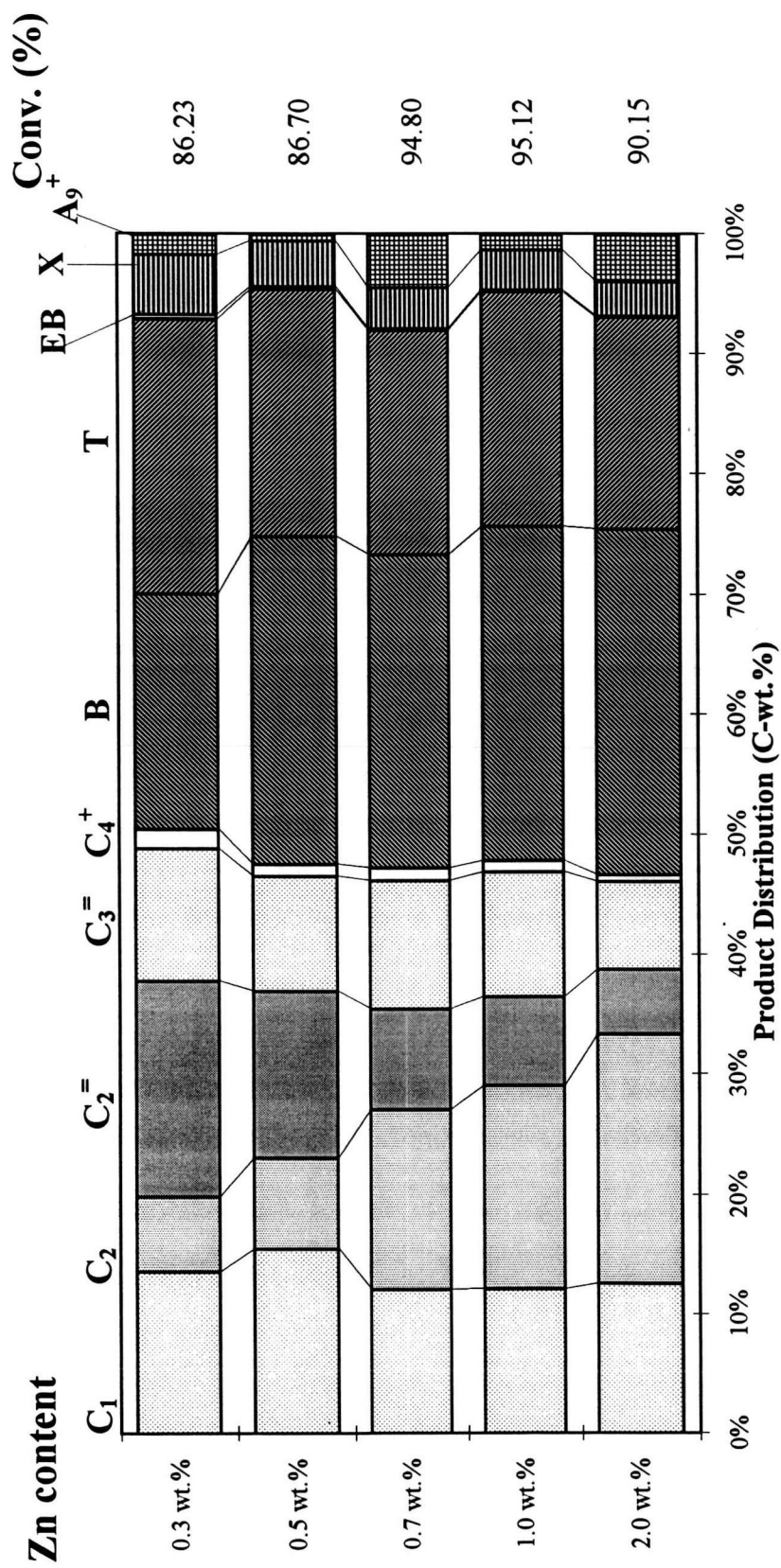
Figure 5.4 Propane aromatization on Zn/NH$_4$-ZSM-5 catalysts with various Zn loading content.

5.4 Effect of Ga Loading Amount in H-ZSM-5 Catalyst.

For metal ion-exchanged H-ZSM-5 (from section 5.2.2), we found Ga is the suitable metal for propane aromatization. Figure 5.5 shows the catalytic performance of propane aromatization on Ga-exchanged H-ZSM-5 (Ga/H-ZSM-5) catalysts having different amounts of Ga loading. The loading amount of Ga used was 0.30, 0.50, 0.70, 1.00 and 2.00 wt.%. The catalyst activity and selectivity for aromatic increased with the increasing amount of Ga loading and the selectivity to C_4^+ and olefins decreased. This indicates that Ga played the role on propane dehydrogenation to aromatics as same as Zn on NH_4-ZSM-5.

Ga/H-ZSM-5 with 1 wt.% Ga loading exhibited approximately 62.5 % of BTX. When the Ga loading was increased to 2 %, the activity and the selectivity for aromatics declined slightly as same as Zn . Therefore, 1.0 wt.% Ga/H-ZSM-5 was the optimum amount on giving high aromatic hydrocarbons.

5.5 Effect of Zinc Introduction by Incorporation and Ion-Exchange Method.

The results of propane aromatization on Zn/NH_4-ZSM-5 with Zn-loading content of 0.7 wt.%, NH_4-Zn-silicate and H-Zn-silicate with Si/Zn ratio of 40, which was equivalent to 3.28 wt.% of zinc are shown in Figure 5.6. The result of NH_4-ZSM-5 and H-ZSM-5 was also shown for comparison. For Zn-silicate (both H-form and NH_4-form) exhibited worse conversion and selectivity than ZSM-5 (both NH_4-form and H-form). But when ZSM-5 contain zinc, even with less zinc loading content, Zn- exchanged NH_4-ZSM-5 gave higher activity and selectivity than Zn-silicate and ZSM-5.

Zn/NH_4-ZSM-5 was different from ZSM-5 and Zn-silicate in that Zn/NH_4-ZSM-5 have both zinc and aluminium metal in the catalyst. This result may be referred to the previous investigation that zinc played the role for dehydrogenation of paraffins
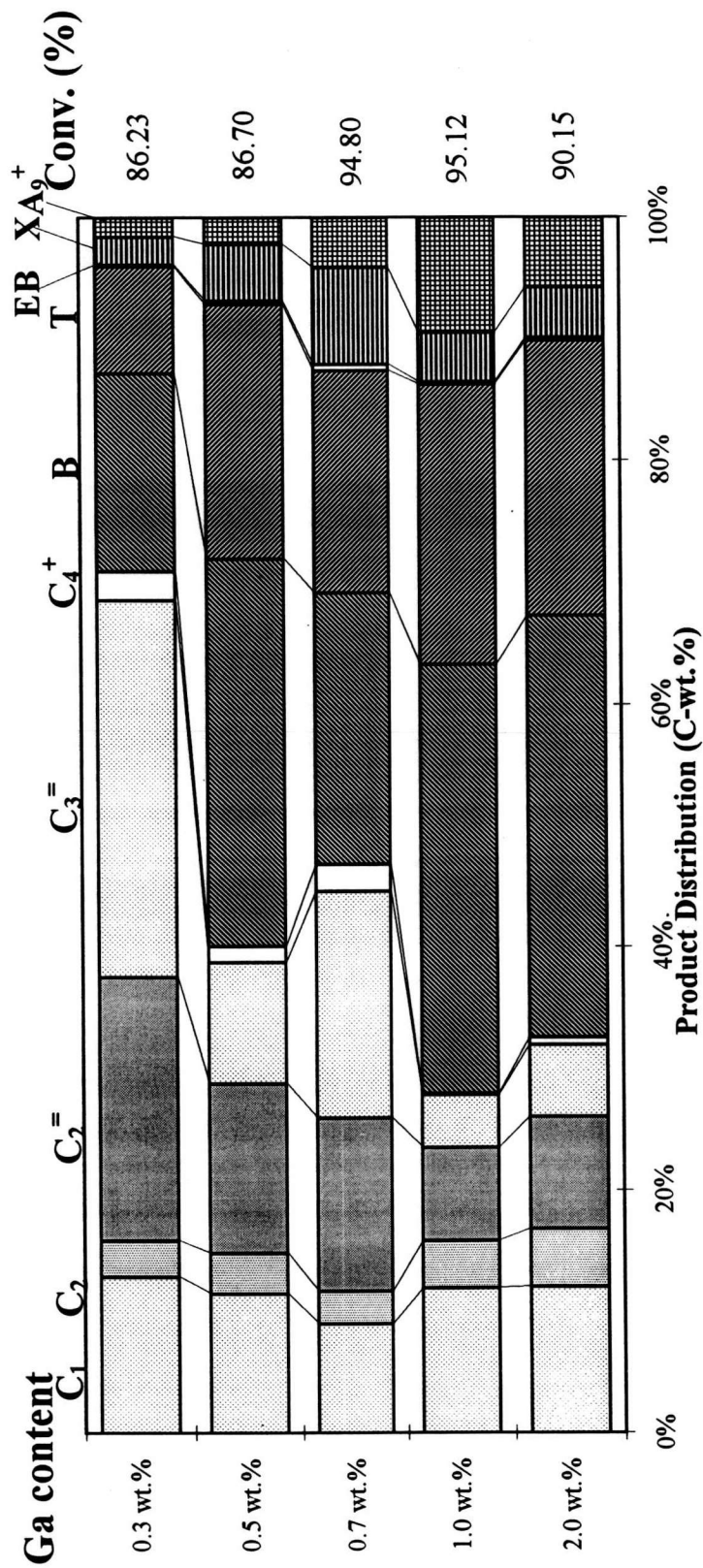
Figure 5.5 Propane aromatization on Ga/H-ZSM-5 catalysts with various Ga loading content.
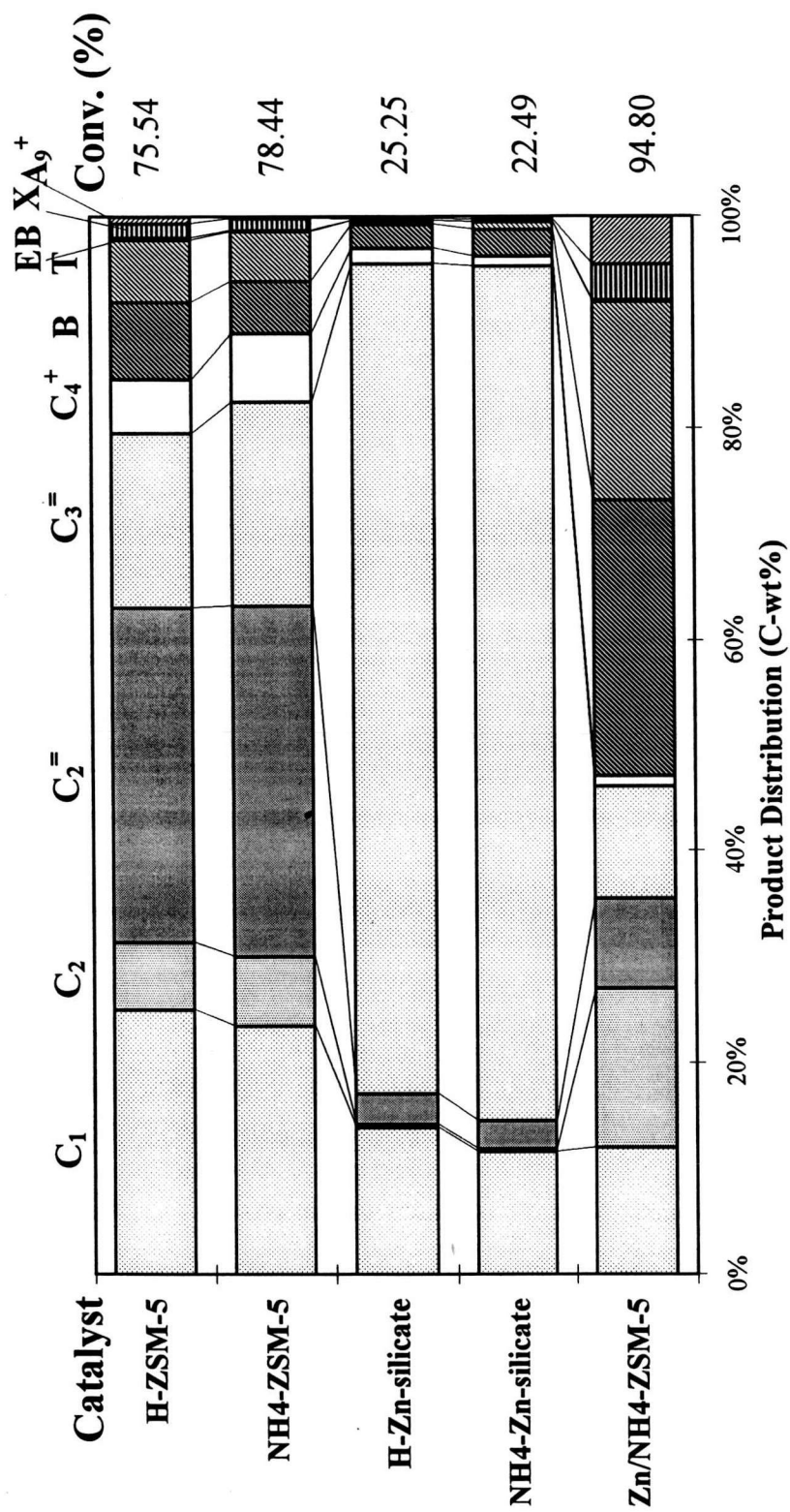
Figure 5.6 Propane aromatization on ZSM-5 and Zn-containing MFI catalysts

[78,79]. The strong acid sites for olefin aromatization are derived from aluminium [78].

5.6 Effect of Gallium Introduction by Incorporation and Ion-exchanged Method.

In the section 5.4, it is observed that Ga exchanged H-ZSM-5 with gallium loading content 1.0 wt.% exhibited the highest amount of aromatic hydrocarbons.

In this study , Ga-silicate was prepared by incorporating gallium metal in place of aluminium metal in the zeolite framework. The catalytic performances on propane aromatization of 1.0 wt.% Ga-exchanged H-ZSM-5 and H-Ga-silicate with Si/Ga ratio of 40 which was equivalent to approximately 3.78 wt.% gallium were compared. The result is shown in Figure 5.7 with result of H-ZSM-5 for comparison. The catalyst containing gallium metal exhibited much higher activity and selectivity than those of H-ZSM-5. Even with less gallium loading content, Ga/H-ZSM-5 gave better catalytic performance than H-Ga-silicate.

The reason of which should be ascribed to the effect of the presence of aluminium in zeolite framework on increasing the catalyst acidity.

5.7 Catalyst Performance of Zn.Al-silicate Catalyst.

From the section 5.5 it is observed that the catalyst containing both zinc and aluminium gave high catalytic performance.

In this study, effect of zinc and aluminium of catalyst prepared by incorporation with various form of catalyst on propane conversion were investigated. First, Si/Al ratio was fixed at 40 and zinc incorporation was varied from Si/Zn ratio of 400 to 40.
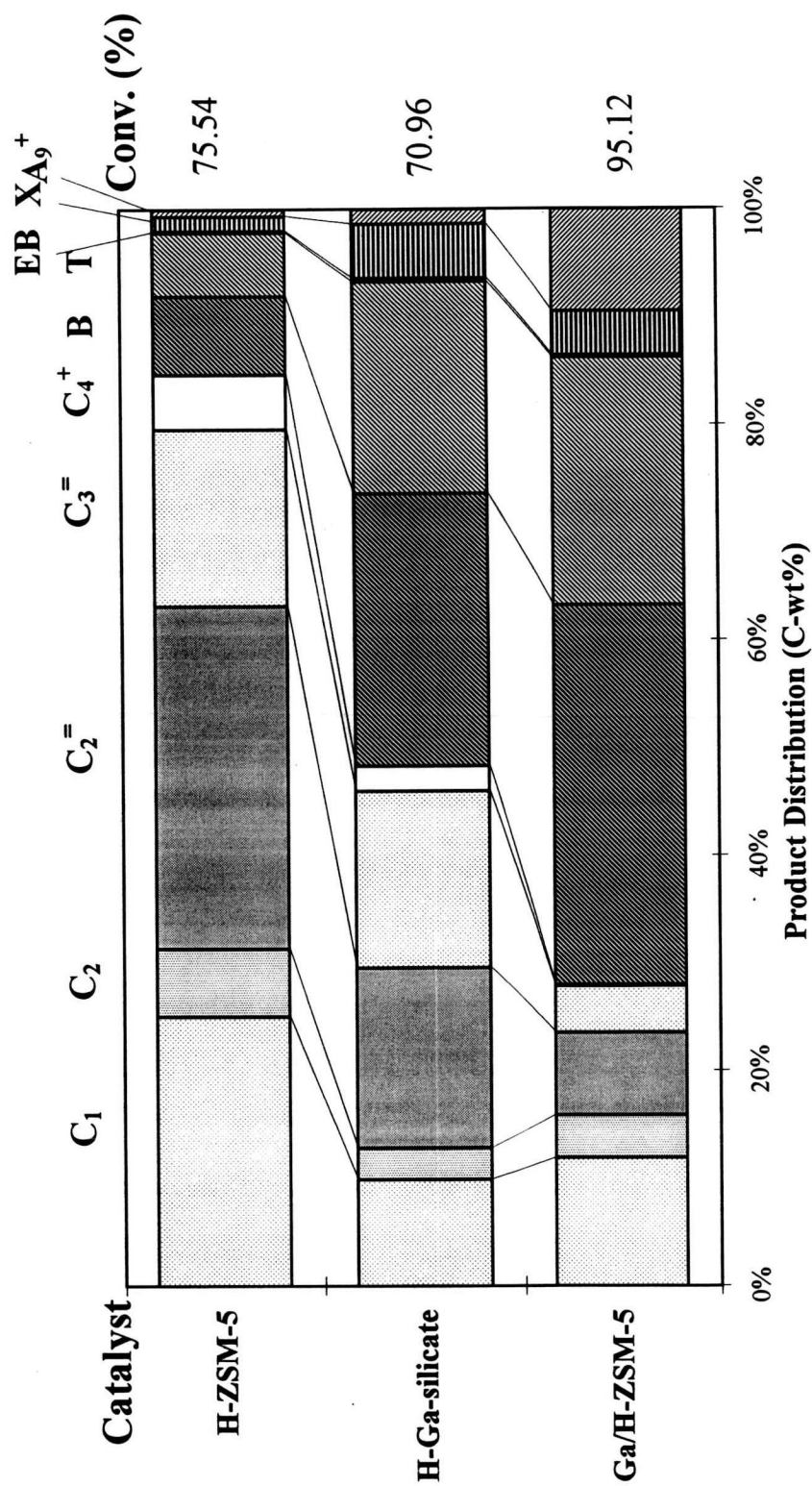
Figure 5.7 Propane aromatization on H-ZSM-5 and Ga-containing MFI catalysts

Figure 5.8 shows the catalytic performance on propane aromatization of Zn.Al-silicate . The activity and selectivity for aromatics increased with the higher amount of zinc (or decreasing Si/Zn ratio), and NH$_4$-Zn.Al-silicate with Si/Zn ratio of 150 (0.9 wt.% Zn incorporated) exhibited approximately 53.4 % of aromatic hydrocarbons. Further increase of zinc incorporation (Si/Zn ratio of 40, 3.28 wt.% of zinc) did not enhance the catalyst activity, and thus Si/Zn ratio of 150 was considered to be optimum. The NH$_4$-Zn.Al-silicate with Si/Zn ratio of 150 and Si/Al ratio of 40 was found to be the optimum catalyst for propane conversion with high aromatics selectivity.

As shown in Figure 5.9, the effect of aluminium content in the catalyst was investigated. When catalysts having Si/Al ratio other than 40, i.e. Si/Al ratio of 2000 and 20, with the optimum Si/Zn ratio of 150 were prepared and their catalytic performances were observed, it has been found that the low aluminium content catalyst (Si/Al ratio of 2000) showed low activity and selectivity to aromatics and so did the high aluminium content catalyst (Si/Al ratio of 20). It has clearly been shown that a certain amount of aluminium was necessary to provide enough acidity required for the aromatization of propane.

5.8 Catalyst Performance of Ga.Al-silicate Catalyst.

In the section 5.6, it was observed that 1 wt.% gallium-exchanged H-ZSM-5 exhibited the high activity and selectivity for aromatization of propane.

In this study, Ga.Al-silicate was prepared by incorporation of gallium and aluminium in the zeolite framework. The catalytic performance on propane aromatization of H-Ga.Al-silicate with various Si/Ga ratio is shown in Figure 5.10. As same with the previous section, Si/Al ratio was fixed at 40 and gallium incorporation was varied from Si/Ga ratio of 520 to 40. When the amount of gallium was increased (or decreasing Si/Ga ratio), the aromatics selectivity increased and H-Ga.Al-silicate
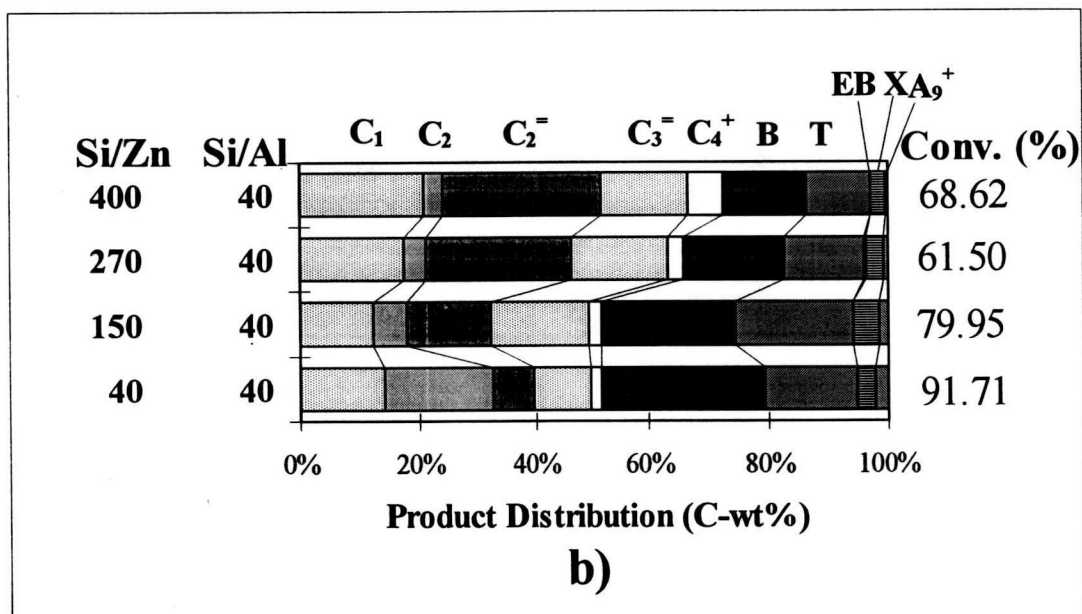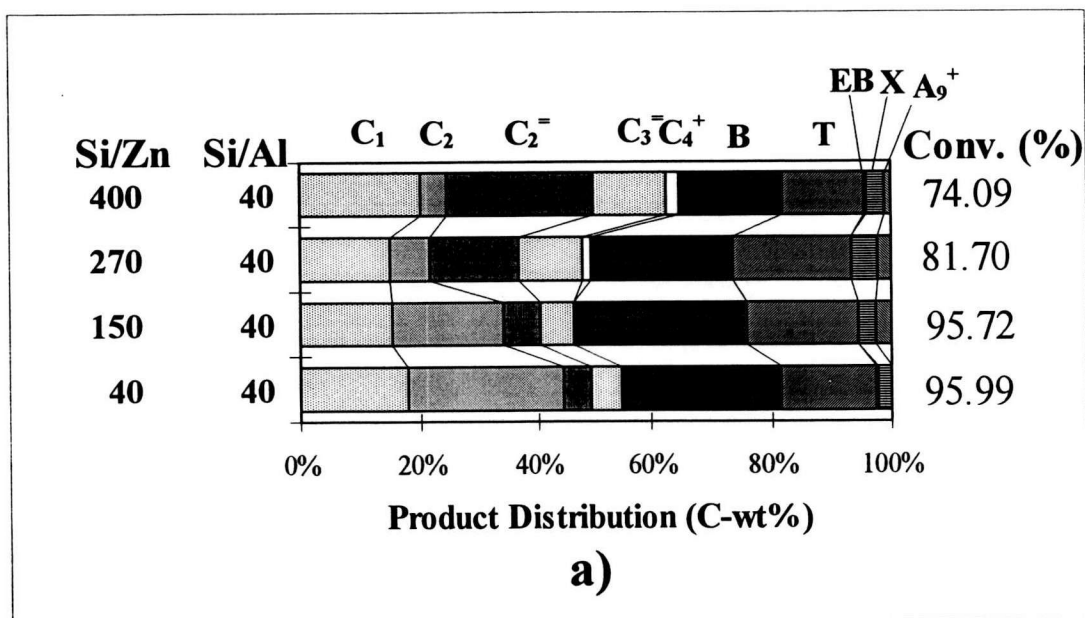
Figure 5.8 Propane aromatization on

    a) NH_4-Zn.Al-silicate catalysts
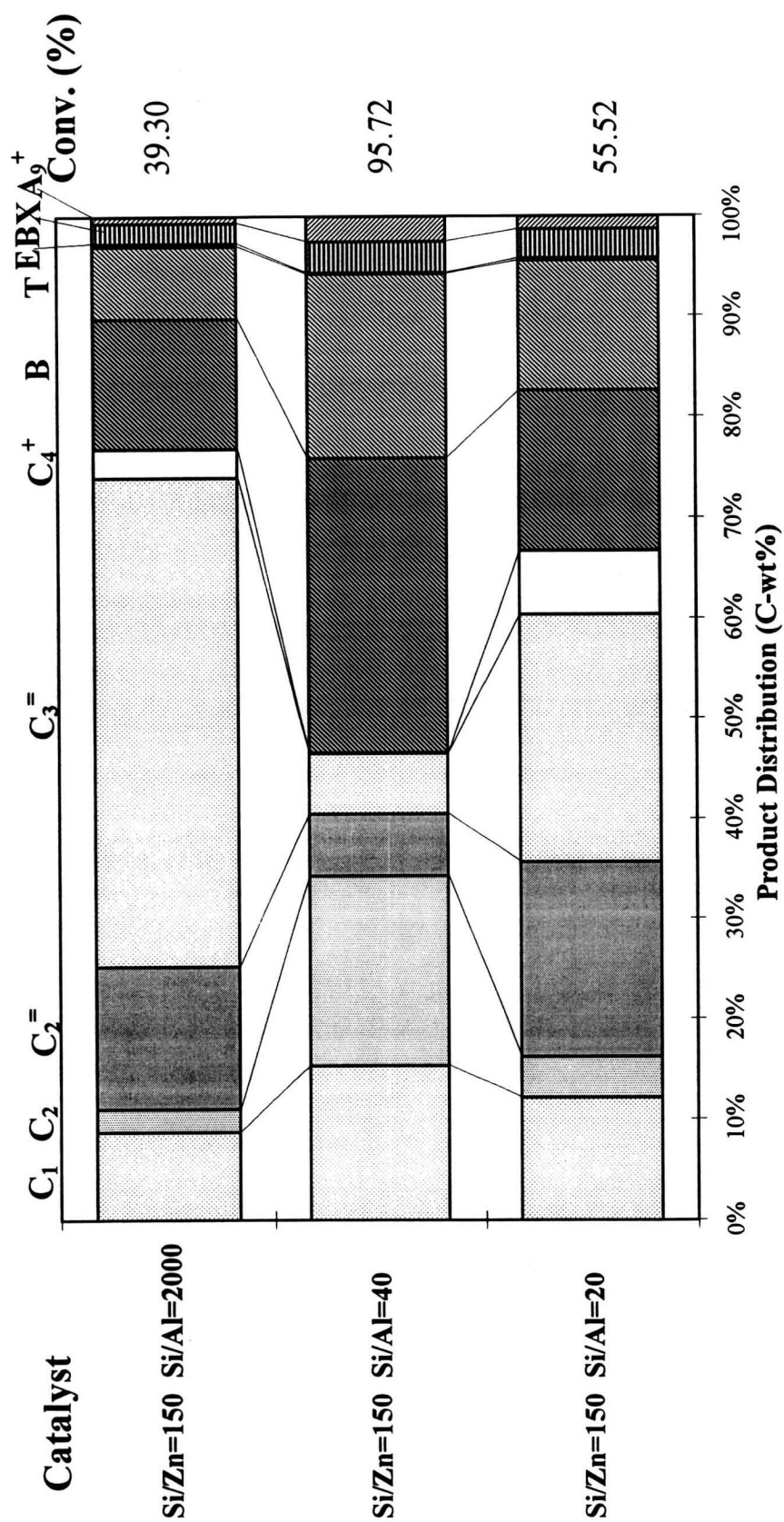
    b) H-Zn.Al-silicate catalysts.

Catalyst

Conv. (%)

Si/Zn=150 Si/Al=2000 — 39.30

Si/Zn=150 Si/Al=40 — 95.72

Si/Zn=150 Si/Al=20 — 55.52

C_1 C_2 $C_2^=$ $C_3^=$ C_4^+ B T EB X A_9^+

Product Distribution (C-wt%)

0% 10% 20% 30% 40% 50% 60% 70% 80% 90% 100%

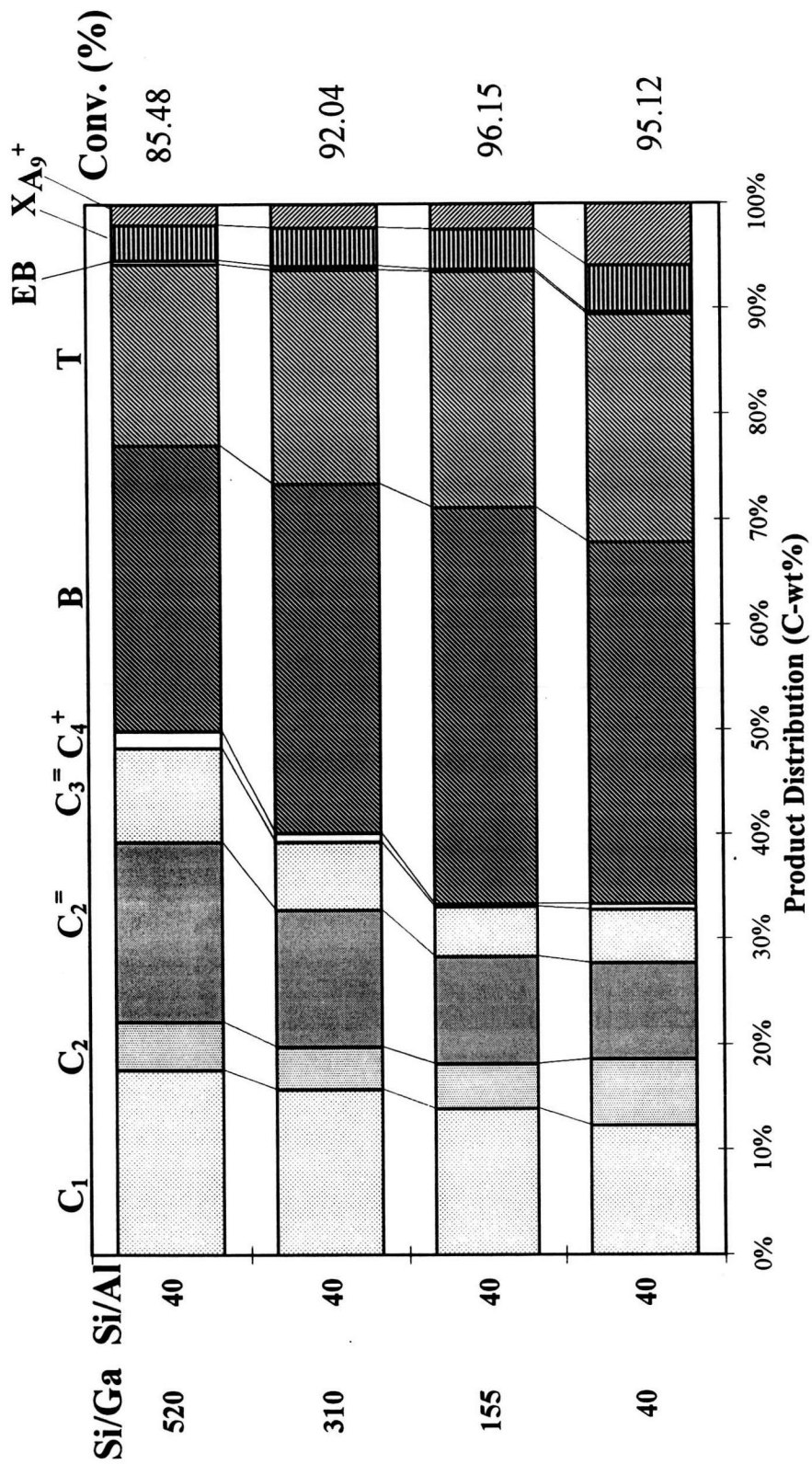Figure 5.9 Effect of Al in propane aromatization on NH_4-Zn.Al-silicate catalysts

Figure 5.10 Propane aromatization on H-Ga.Al-silicate catalysts

with Si/Ga ratio of 155 exerted as high as 64 % of BTX. It should be noted that Si/Ga ratio of 155 is equivalent to 1 wt.% gallium loading in Ga-exchanged H-ZSM-5 and the catalytic performance of both catalysts were roughly comparable. Further increase of gallium incorporation (Si/Ga ratio of 40) did not enhance the catalyst activity and selectivity, and thus Si/Ga ratio of 155 was considered to be optimum.

For the study of effect of aluminium, the result is shown in Figure 5.11. The catalysts having Si/Al ratio other than 40, i.e. Si/Al ratio of 2000 and 20, with the optimum Si/Ga ratio of 155 were prepared and their catalytic performances were observed. It has been shown that a certain amount of Al was necessary to provide enough acidity required for the propane aromatization. Finally, H-Ga.Al-silicate with Si/Ga ratio of 155 and Si/Al ratio of 40 was selected with economic concern.

5.9 Effect of Reaction Temperature on Product Distribution of Propane Aromatization.

The reaction temperature for propane conversion was varied ranging from 450 to 600 °C. The reaction was carried out at GHSV 2000 h^{-1}, by using feed gas mixture of 20 % propane and 80 % nitrogen gas for 1 hour on stream.

The product distributions of propane aromatization over the optimum NH_4-Zn.Al-silicate (Si/Zn ratio of 150 and Si/Al ratio of 40) and the optimum H-Ga.Al-silicate (Si/Ga ratio of 155 and Si/Al ratio of 40) at various reaction temperatures are shown in Figures 5.12 and 5.13, respectively. For both of the catalysts, propane conversion decreased with the decreasing temperature and so did the aromatics selectivity, but selectivity to olefins increased. This indicates olefins can not aromatize well under the low temperature. It was understood that the reaction temperature range of 550-600 °C was required to achieve considerably high aromatization of propane.
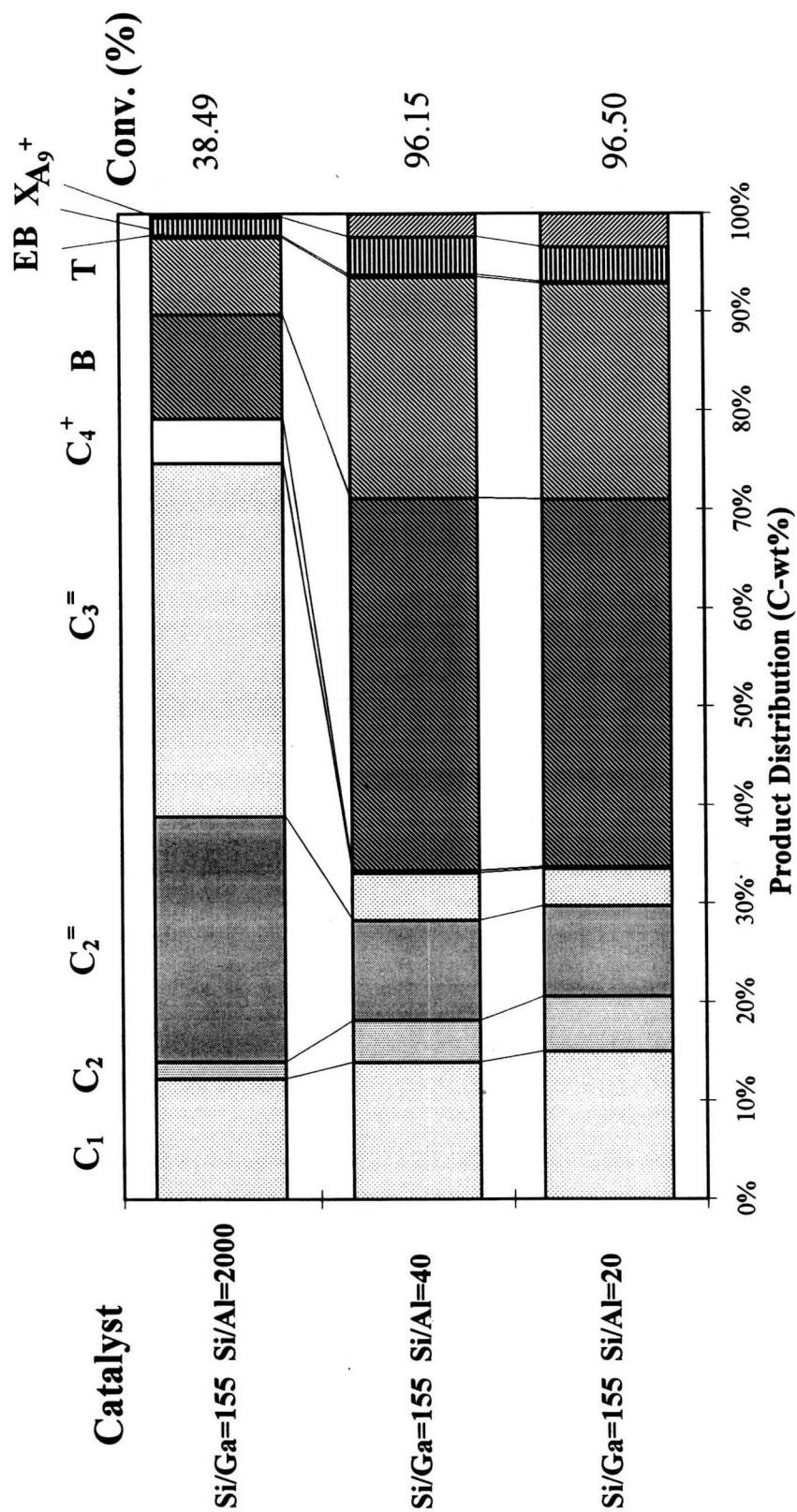
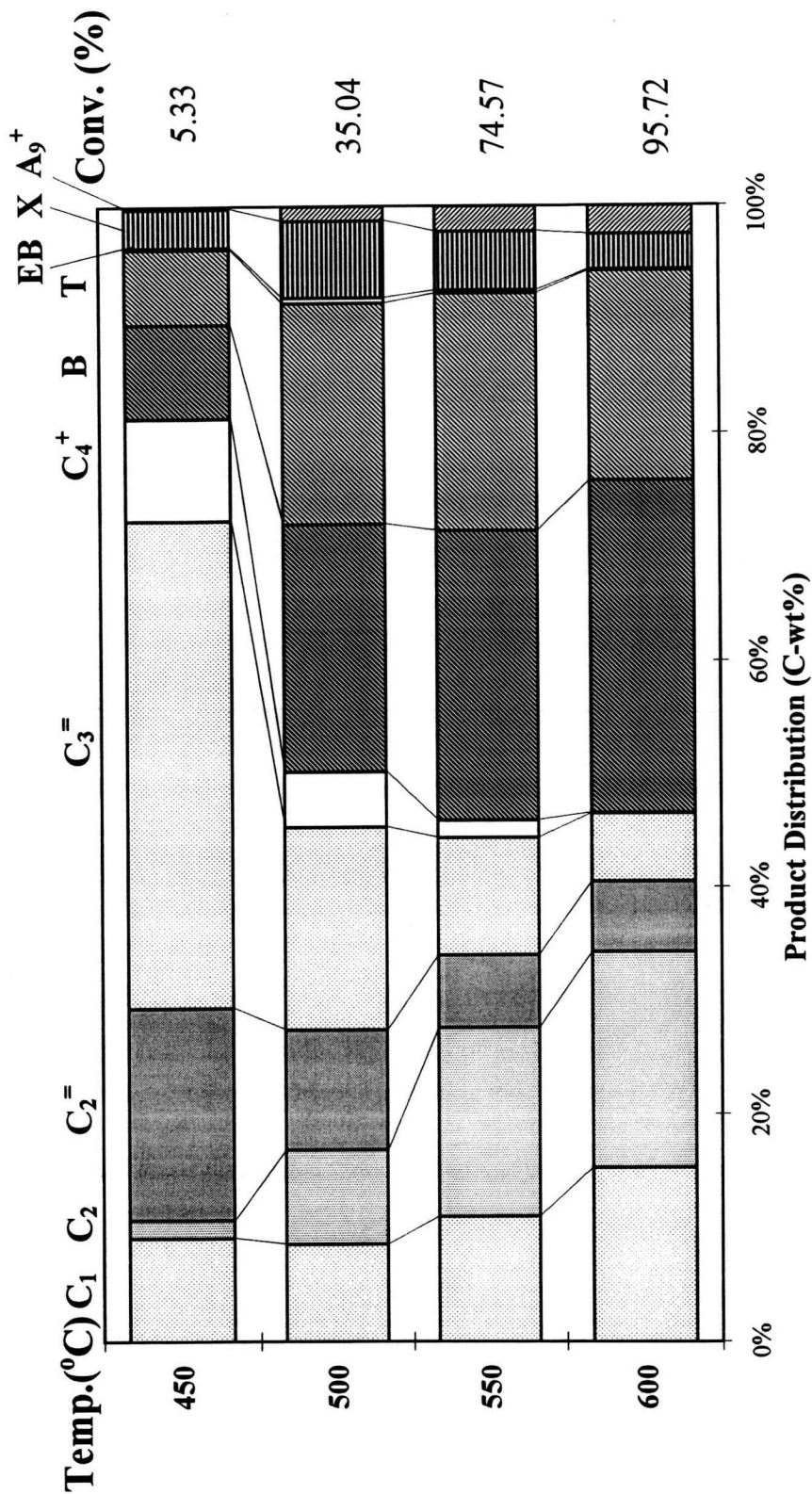Figure 5.11 Effect of Al in propane aromatization on H-Ga.Al-silicate catalysts

Figure 5.12 Propane aromatization on NH_4-Zn.Al-silicate catalyst (Si/Zn =150, Si/Al=40) at various reaction temperatures
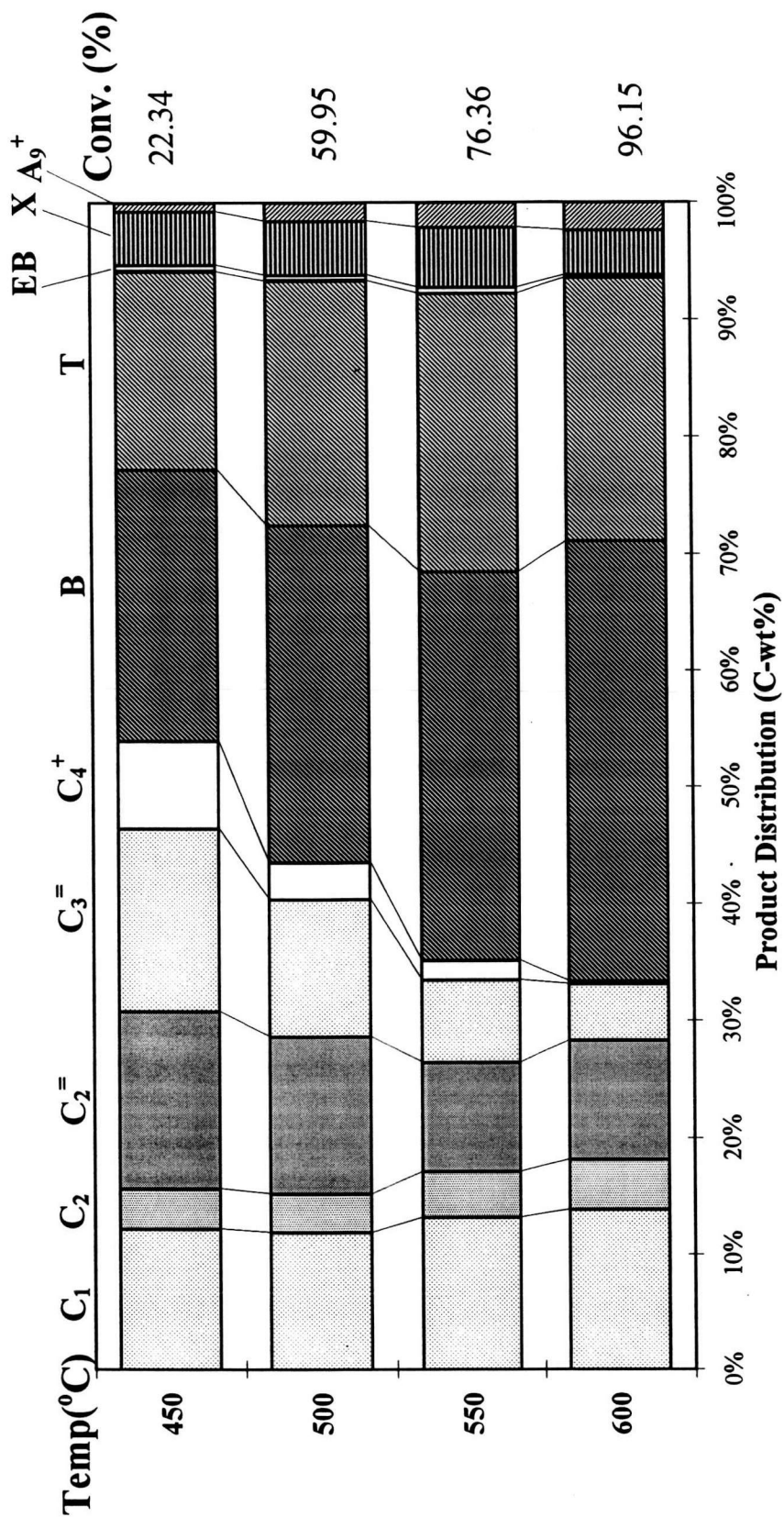
Figure 5.13 Propane aromatization on H-Ga.Al-silicate catalyst(Si/Ga=155, Si/Al=40) at various reaction temperatures

5.10 Effect of GHSV on Product Distribution of Propane Aromatization.

Figures 5.14 and 5.15 show the product distribution of propane aromatization over the optimum NH$_4$-Zn.Al-silicate and the optimum H-Ga.Al-silicate, respectively. The space velocities for propane conversion were varied ranging from 2000 to 8000 h^{-1}. The light olefins fraction such as ethylene and propylene gradually increased with the increasing GHSV and thus aromatics selectivity decreased. This should be ascribed to the short contact time at high GHSV.

5.11 Effect of Feed Composition on the Aromatization Reaction.

The catalyst performances of the optimum H-Ga.Al-silicate and the optimum NH$_4$-Zn.Al-silicate were extensively investigated by using feed composed of propane only, butane only and their mixtures. As shows in Figures 5.16 and 5.17, both of NH$_4$-Zn.Al-silicate and H-Ga.Al-silicate catalysts exhibited the steadily high activity and selectivity for aromatic hydrocarbons irrespective of the feed composition. Therefore it should be noted that both NH$_4$-Zn.Al-silicate and H-Ga.Al-silicate can be effectively employed with the liquefied petroleum gas aromatization as well.

5.12 Effect of Time on Stream on Product Distribution of the Optimum Catalysts.

The stabilities of the optimum NH$_4$-Zn.Al-silicate and the optimum H-Ga.Al-silicate on propane conversion at 600 °C, GHSV 2000 h^{-1} are shown in Figures 5.18 and 5.19, respectively.

Figure 5.18 shows the prolonged operation of the optimum NH$_4$-Zn.Al-silicate. The catalyst deactivation occurred rapidly comparing with that of H-Ga.Al-Silicate. In the section 5.3 and 5.7, when the amount of zinc loading increased ethylene hydrogenation to ethane increased too. This result indicates that hydrogen on the
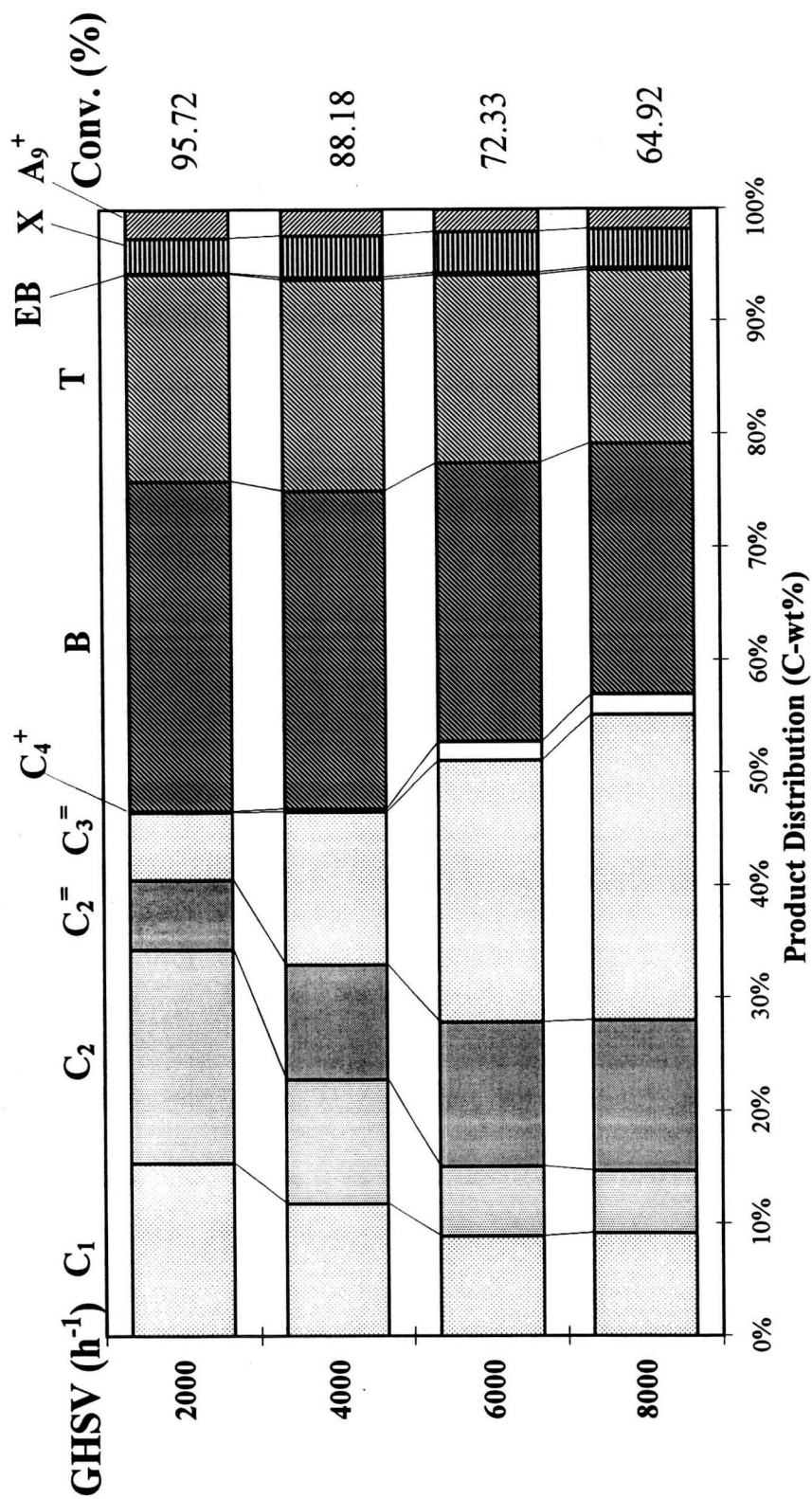
Figure 5.14 Propane aromatization on NH$_4$-Zn.Al-silicate catalyst (Si/Zn =150, Si/Al=40) at various space velocities
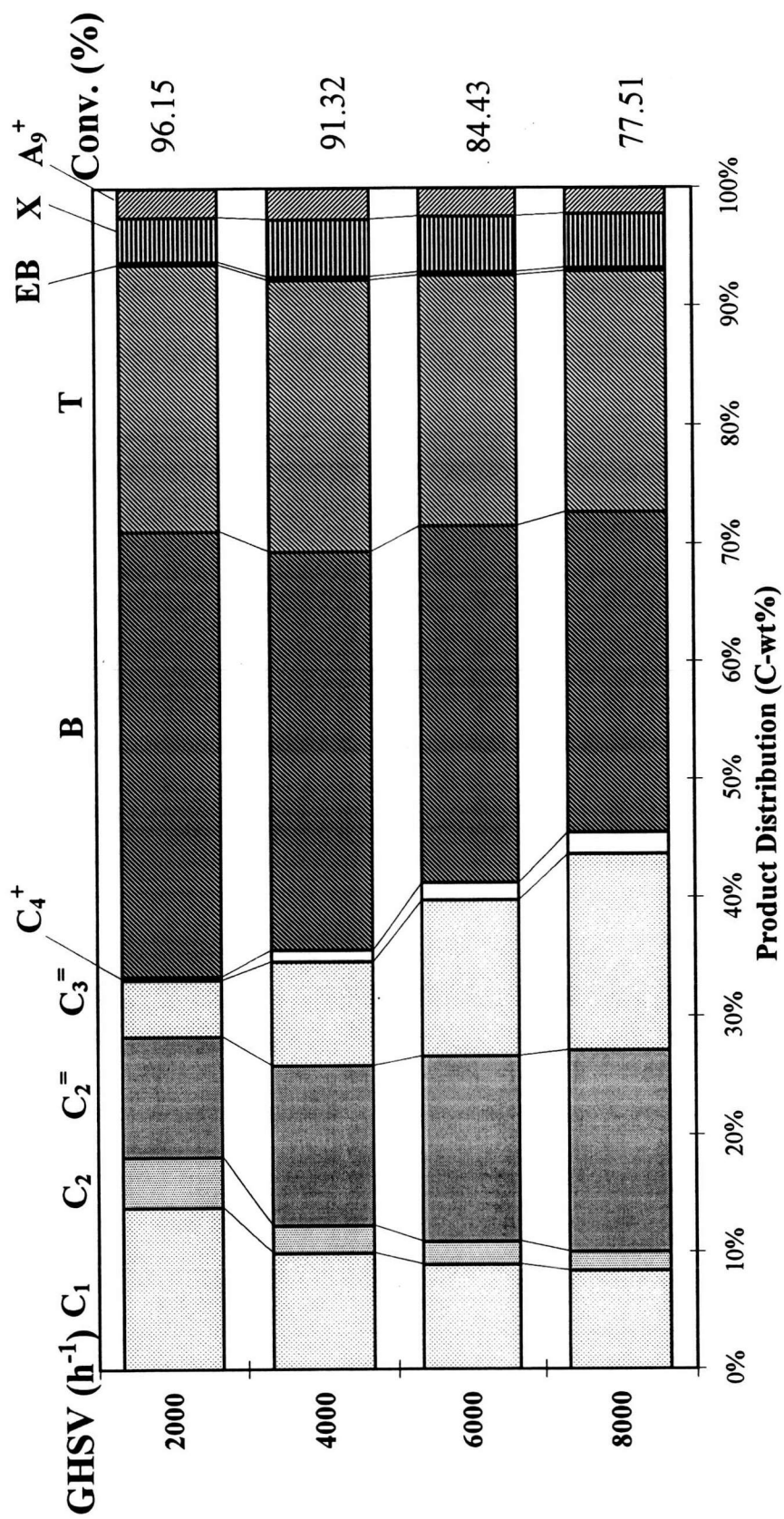
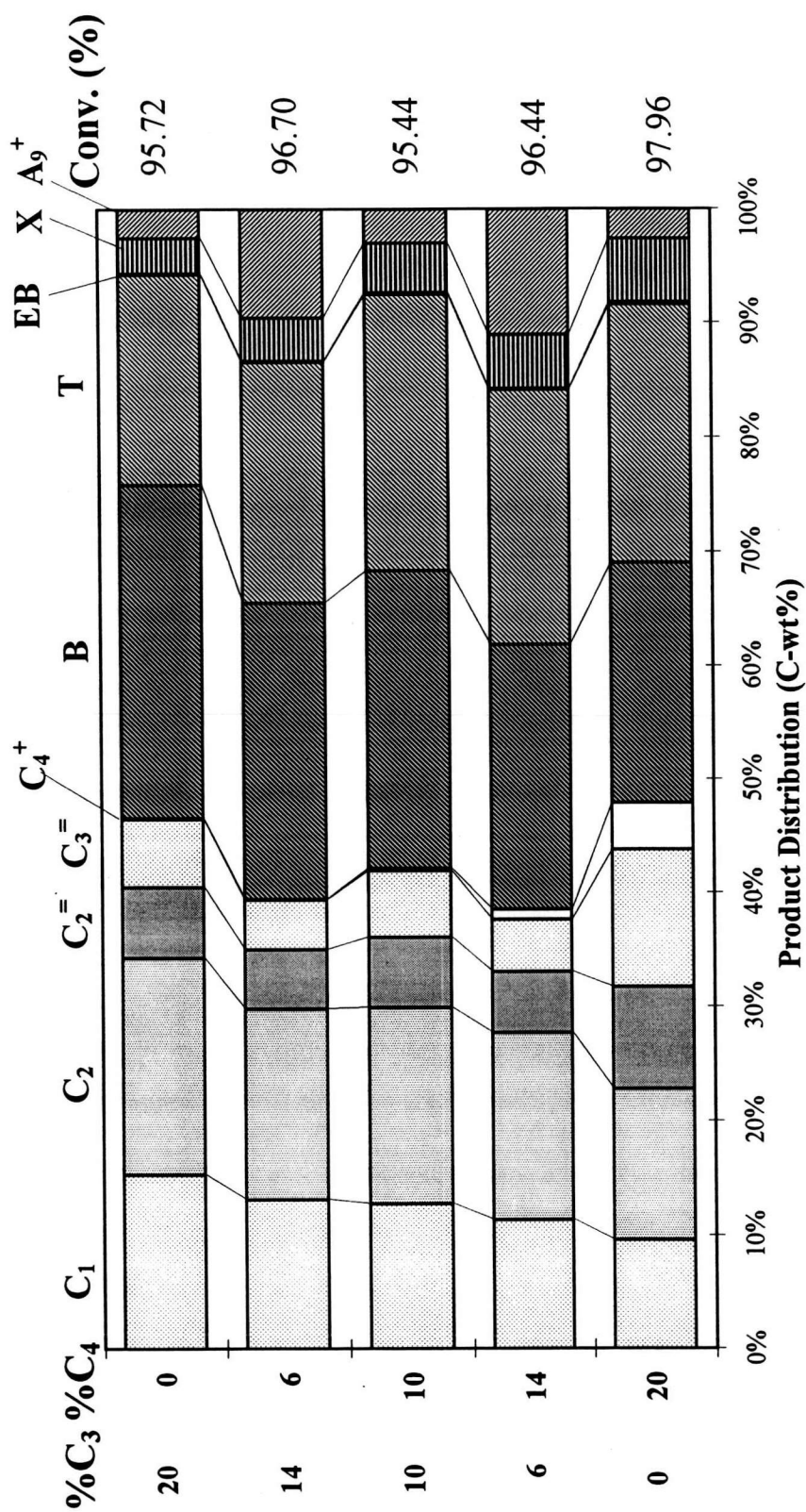Figure 5.15 Propane aromatization on H-Ga.Al-silicate catalyst(Si/Ga=155, Si/Al=40) at various space velocities

Figure 5.16 Aromatization of propane, butane, and their mixtures on NH₄-Zn.Al-silicate catalyst (Si/Zn=150, Si/Al=40)
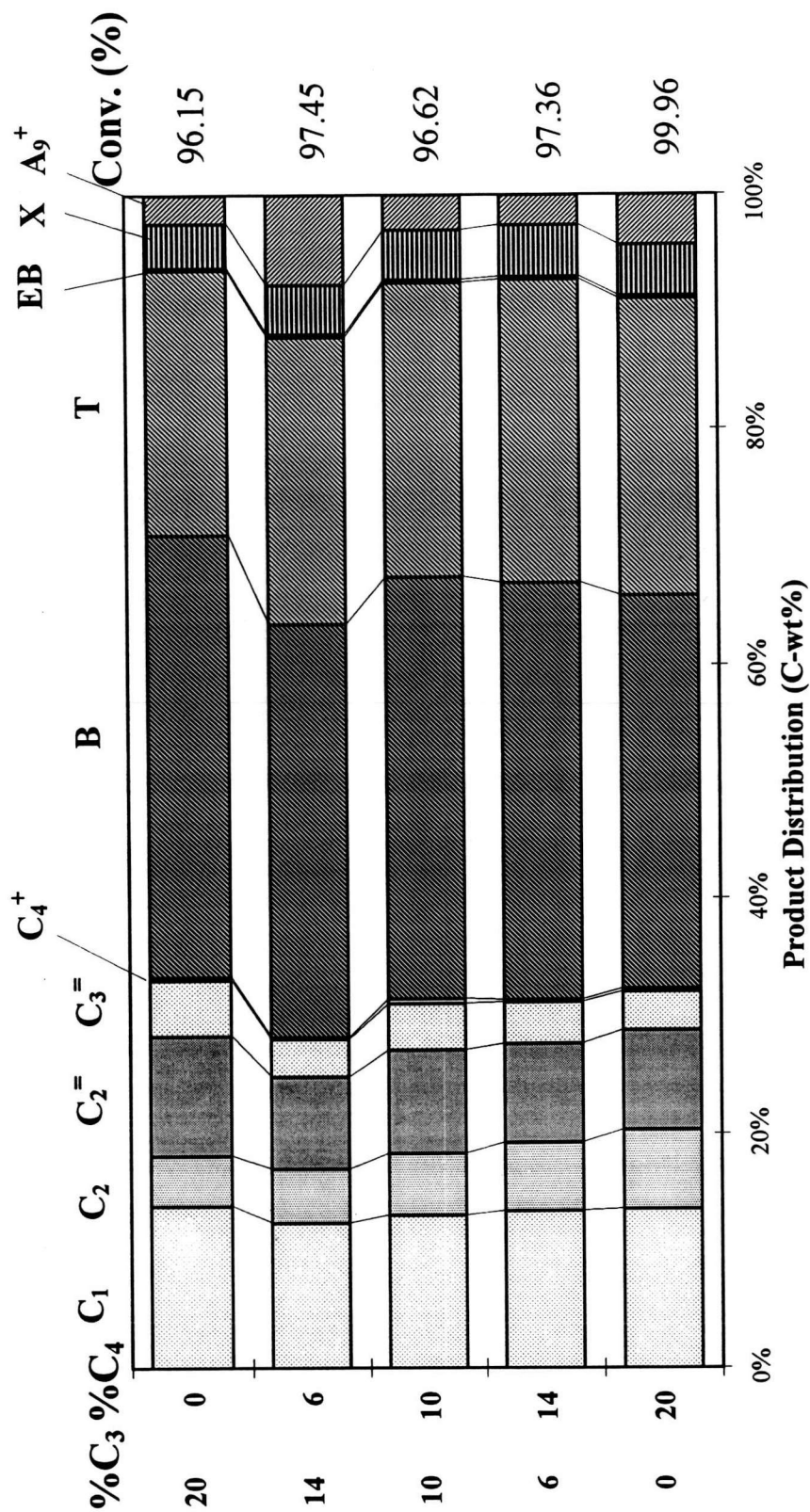
Figure 5.17 Aromatization of propane, butane, and their mixtures on H-Ga. Al-silicate catalyst (Si/Ga=155, Si/Al=40)

catalyst surface was consumed for ethylene hydrogenation, before being used for the combustion of deposited coke. The disadvantageous role of zinc on accelerating the coke formation caused the shorter catalyst life of NH_4-Zn.Al-silicate than H-Ga.Al-silicate. This is consistent with the discussion of Kanai and Kawata [76,44] suggesting that gallium species in galloaluminosilicate have a lower hydrogenation or hydrogenolysis activity than zinc species in ZnO/H-ZSM-5. The yield of aromatic markedly decreased and the yield of ethylene and propylene increased indicating that the strong acid sites, which are responsible for aromatization of light olefins, are selectively decreased by covering with the deposited coke.

After 9 hours, NH_4-Zn.Al-silicate was regenerated by burning the deposited coke with air at 550 °C for 1 hour. In Figure 5.18, the same activity and selectivity of regenerated NH_4-Zn.Al-silicate as those of the fresh one was obtained. This result suggested the stability of the catalyst structure and NH_4-Zn.Al-silicate did not decompose to H-Zn.Al-silicate, whose activity and selectivity to the aromatization of propane were lower than NH_4-Zn.Al-silicate (in Figure 5.8 b); H-Zn.Al-silicate have conversion of 79.95 % and 47.99 % selectivity to aromatics.

For H-Ga.Al-silicate, the propane conversion did not decrease substantially. The selectivity to aromatic hydrocarbons decreased and the selectivity of olefins, the reaction intermediates to aromatic hydrocarbons, increased as time went by. It indicates that the strong acid sites, which are responsible for aromatization of light olefins, are selectively decreased by covering with the deposited coke.

Because of the catalyst deactivation, regeneration of decayed catalyst is necessary for the prolonged operation. As shown in Figure 5.19, the activity of the decayed H-Ga.Al-silicate is completely recovered by regenerating with air at 550 °C for 1 hour. The recoverable activity and selectivity after regeneration suggested the good stability of this catalyst.

Figure 5.18 Propane aromatization on NH₄-
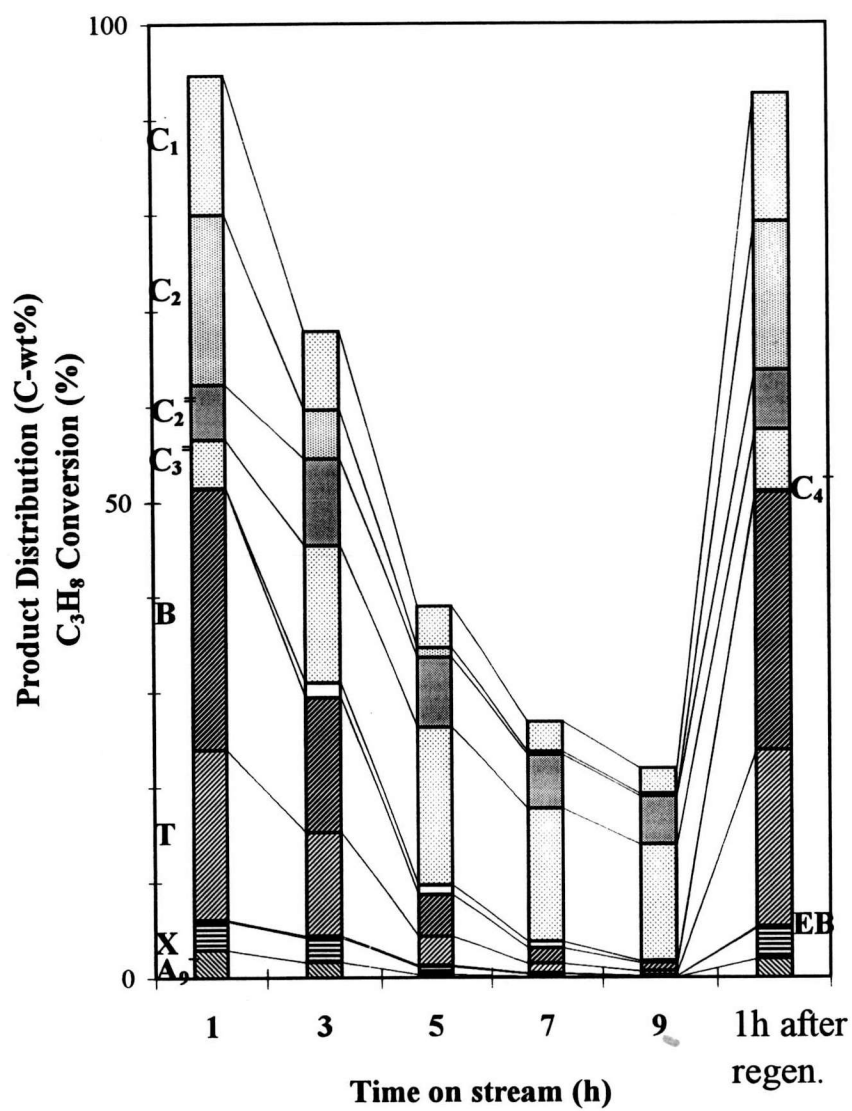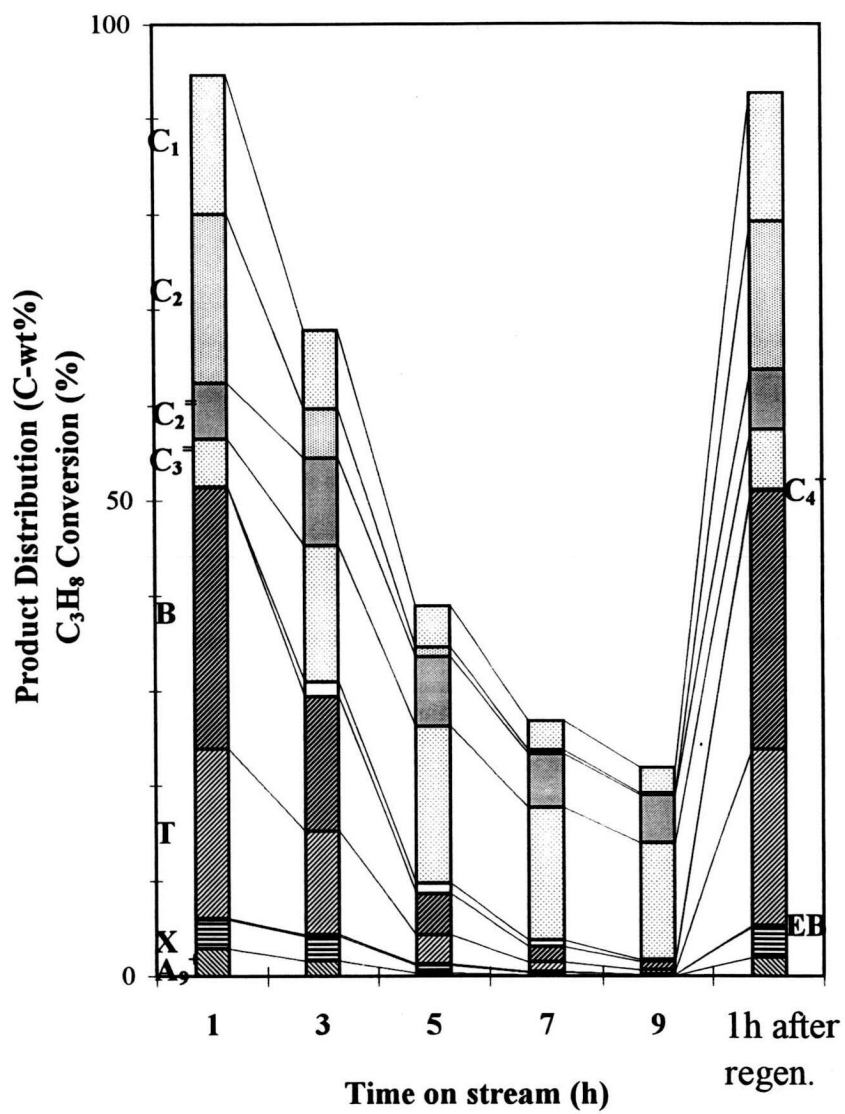Zn.Al-silicate catalyst

Figure 5.18 Propane aromatization on NH₄-
Zn.Al-silicate catalyst

5.13 Effect of Platinum Loading on NH₄-Zn.Al-silicate and H-Ga.Al-silicate.

The optimum catalyst of NH₄-Zn.Al-silicate and H-Ga.Al-silicate were modified with 0.5 wt.% platinum, and the results of propane aromatization on the prolonged operation of these catalysts are shown in Figure 5.20 and 5.21 respectively.

The results of propane conversion on Pt/NH₄-Zn.Al-silicate, Pt-loaded catalyst, is shown in Figure 5.20. Comparing with Pt-non loaded catalyst ,NH₄-Zn.Al-silicate in Figure 5.18, it has been shown that platinum enhance the propane conversion and the selectivity to aromatics is slightly higher than in Pt-non loaded catalyst. The selectivity to methane, ethylene and propane are lower but selectivity to ethane is higher than in Pt-non loaded catalyst. It is clear that the role of platinum as the function of catalyst is the strong dehydrogenation and hydrogenation reaction. Platinum is stronger olefin dehydrogenation than zinc. In Pt-loaded catalyst intermediate, i.e.: propylene, occurred in larger amount than in the Pt-non loaded catalyst. This reason lead to better selectivity to aromatic hydrocarbons. But platinum also have hydrogenation properties causing the higher yield of ethane than Pt non loaded catalyst.

There are many researchers who studied on the deactivation of Pt loaded and Pt non loaded catalyst on propane, n-hexane and n-octane[77, 78]. They found that platinum give a good reaction because it can increase activity of catalyst and prevent coke formation. Inui et al. described the reaction by modeling the reaction scheme of the light paraffins conversion on Pt/H-Ga-silicate[74]. The reaction scheme proposed by Inui et al. explained the role of platinum as follow:

(a) Dehydrogenation of paraffins to olefins.
(b) Porthole for hydrogen spillover which prevents the coke formation.

However, in this research the catalysts studied were NH₄-Zn.Al-silicate and H-Ga.Al-silicate, both having Al in their zeolite framework. For NH₄-Zn.Al-silicate with
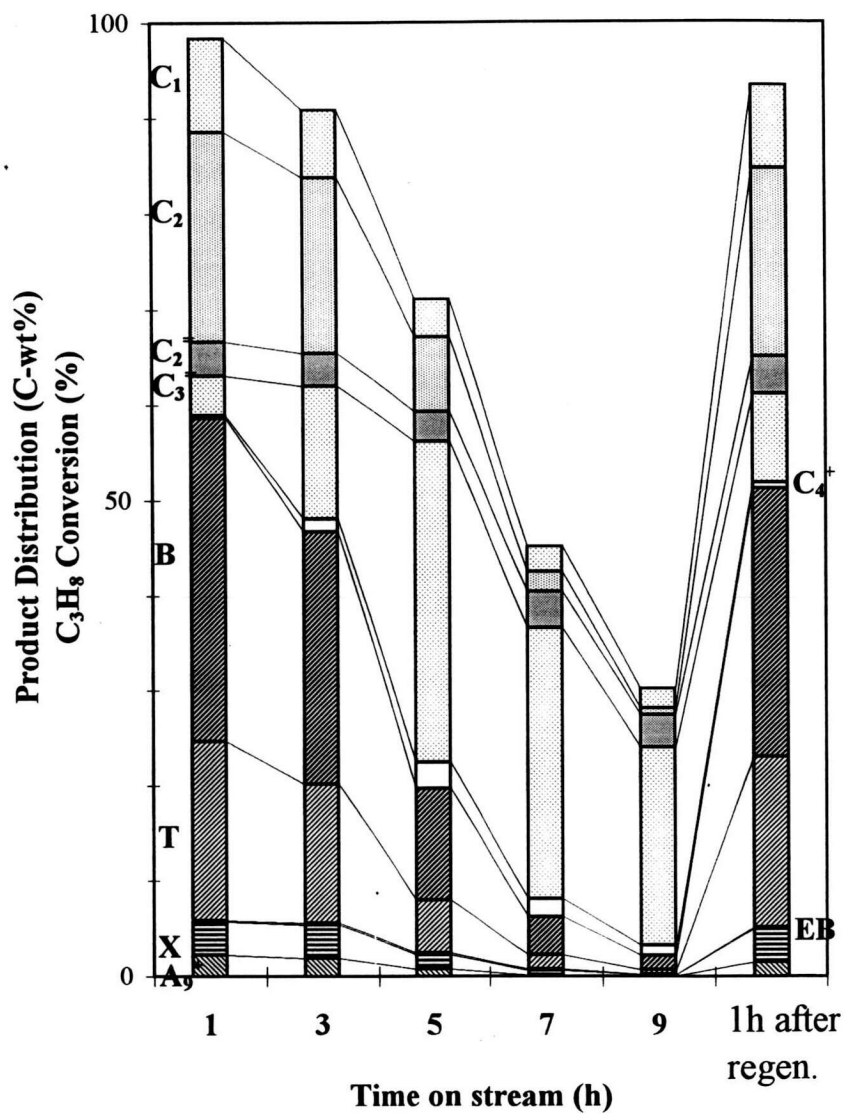
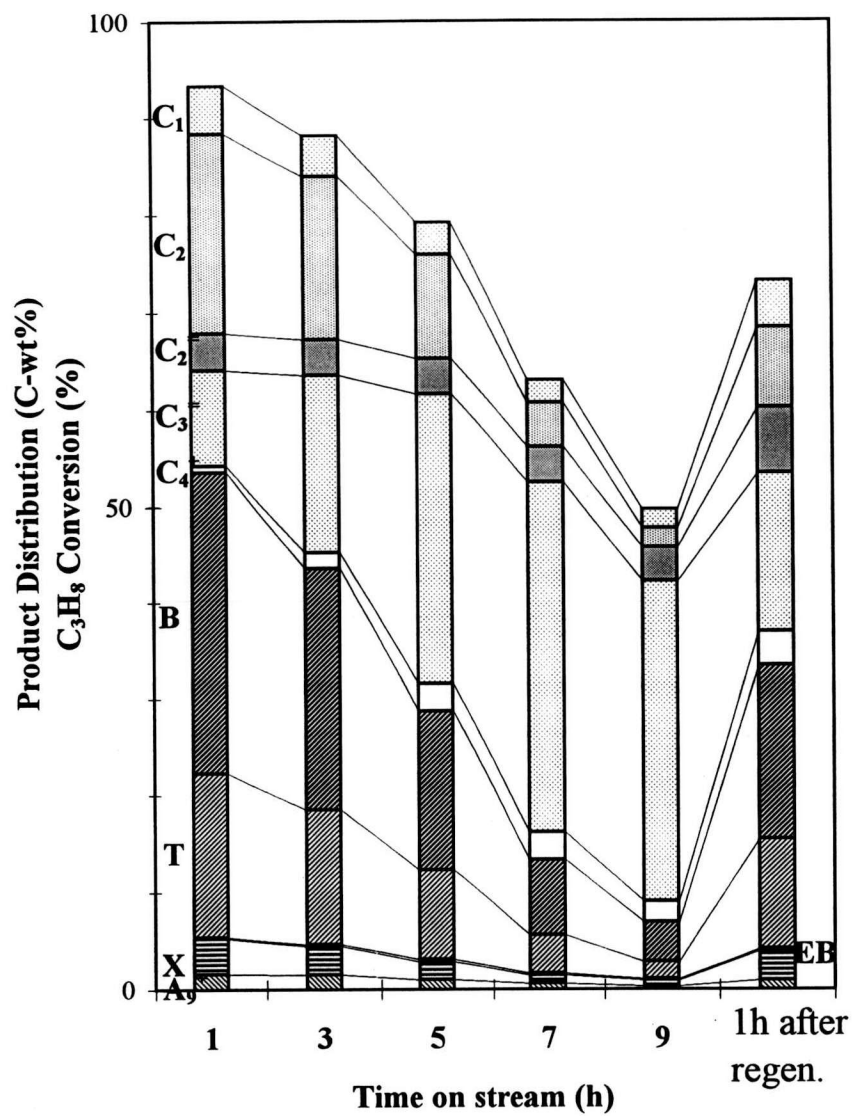Figure 5.20 Propane aromatization on Pt/NH₄-
Zn.Al-silicate catalyst

Figure 5.21 Propane aromatization on Pt/H-
Ga.Al-silicate catalyst

and without platinum as shown in Figure 5.18 and 5.20 respectively, Pt/NH$_4$-Zn.Al-silicate showed no significant improvement in catalyst life, though such effect was found in Pt/H-Ga-silicate by Inui et al. [74]. The presence of Al may cause hydrogen attraction and subsequently hydrogen transfer to the adsorbate species on the catalyst surface. In other words, Al may already have the same function as Pt for hydrogen porthole, thus despite of Pt loading no significant improvement in coke prevention was observed. As it has been found that Zn also played the major role on olefins hydrogenation, the competitive reactions between olefins hydrogenation and the hydrogen addition to aromatics or polyaromatics which are the coke precursor can take place. Such effect was believed to adversely affect the promoting role of Pt on coke prevention.

As for H-Ga.Al-silicate with and without Pt as shown in Figure 5.19 and 5.21 respectively, the above-mentioned postulation has been confirmed. Since Ga was reported to have the strong H$_2$ attraction effect [79], H-Ga.Al-silicate without Pt loading already exhibited the considerably good stability. With Pt loading by ion-exchange, neither improvements in catalyst life nor activity and selectivity on propane aromatization were found for Pt/H-Ga.Al-silicate. Interestingly enough, H-Ga.Al-silicate without Pt loading exerted better catalytic performances than Pt loading one. Ga in combination with Al should facilitate the hydrogen transfer to the carbonaceous adsorbates, or coke precursors, on the catalyst surface and thus preventing the coke formation substantially. Such effect of Ga in combination with Al should be even better than Pt and thus Pt is of no use in this catalyst.