CHAPTER V

RESULTS AND DISCUSSIONS

This thesis deals with studies on the selective dehydrogenation of propane to propylene over NH_4-Zn,Al-silicate and Zn/NH_4-MFI catalysts. The results and discussions are as follows.

5.1 Characterization of the Catalysts

5.1.1 X-ray Diffraction Patterns

The X-ray diffraction patterns for the prepared catalysts such as NH_4-MFI, NH_4-Zn-silicate, NH_4-Zn,Al-silicate and Zn/NH_4-MFI and that of H-MFI of Mobil Oil Corporation are shown in **Figure 5.1**. It was found that the catalysts prepared in this laboratory by rapid crystallization method had the same XRD patterns and almost similar to that of MFI of Mobil Oil Corporation [53]. This indicates that a little amount of other metals added into the framework of catalysts did not change the main structure. Thus the XRD patterns were not changed.

5.1.2 BET Surface Area

BET surface areas of the catalysts are shown in **Figure 5.2**. The surface areas of NH_4-MFI and Zn/NH_4-MFI were larger than NH_4-Zn-silicate and NH_4-Zn,Al-silicate.

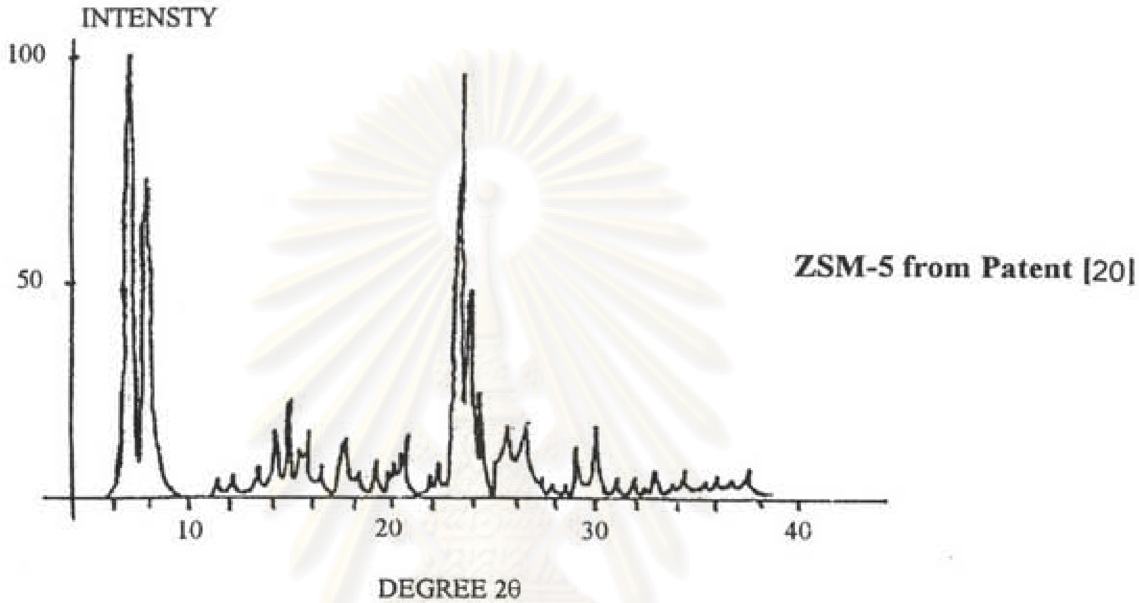


Figure 5.1 X-ray diffraction patterns of the catalysts.

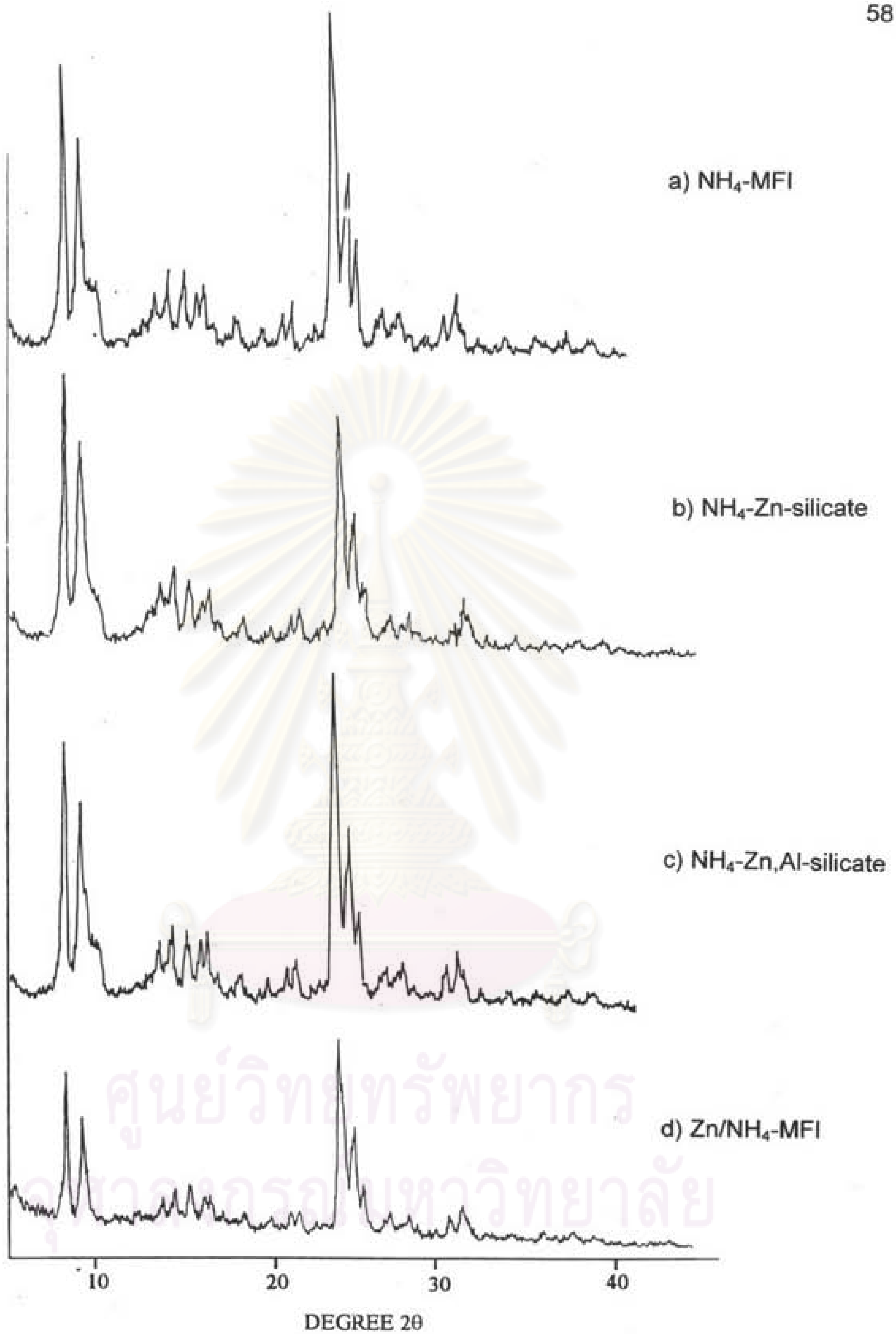


Figure 5.1 X-ray diffraction patterns of the catalysts (continued).

Figure 5.3 shows the pore size distribution of the crystals. It was found that the pore size distribution of all the catalysts were almost the same. Most of the catalysts had the pore diameter within the range of approximately 4-5 A°. The prepared catalysts have different pore size curves though but they have the same XRD patterns. This is dues to the changing size of the metal cation in the framework. Thus the size of the unit cell was changed and the pore size was changed too.

5.1.3 Morphology

SEM (Scanning Electron Microscope) photographs of the prepared catalysts are shown in **Figure 5.4**. As shown, all the catalysts were composed of roughly crystallized spherical particles. It was observed that the morphology of NH_4-MFI, NH_4-Zn-silicate, NH_4-Zn,Al-silicate and Zn/NH_4-MFI catalysts were similar. This indicates that metal loading does not significantly affect the shape of crystals.

5.1.4 Chemical Composition

The results of quantitative analysis of zinc in the synthesized crystals are shown in **Table 5.1** and **Table 5.2**. The observed zinc oxide concentration was almost equal to the charged concentration.

Table 5.1 Zinc content in NH_4-Zn,Al-silicate.

Si/Zn weight ratio of NH_4-Zn,Al-silicate	Zn observed (wt.%)
20	3.20
40	2.14
100	1.02
270	0.33
400	0.28
∞	0

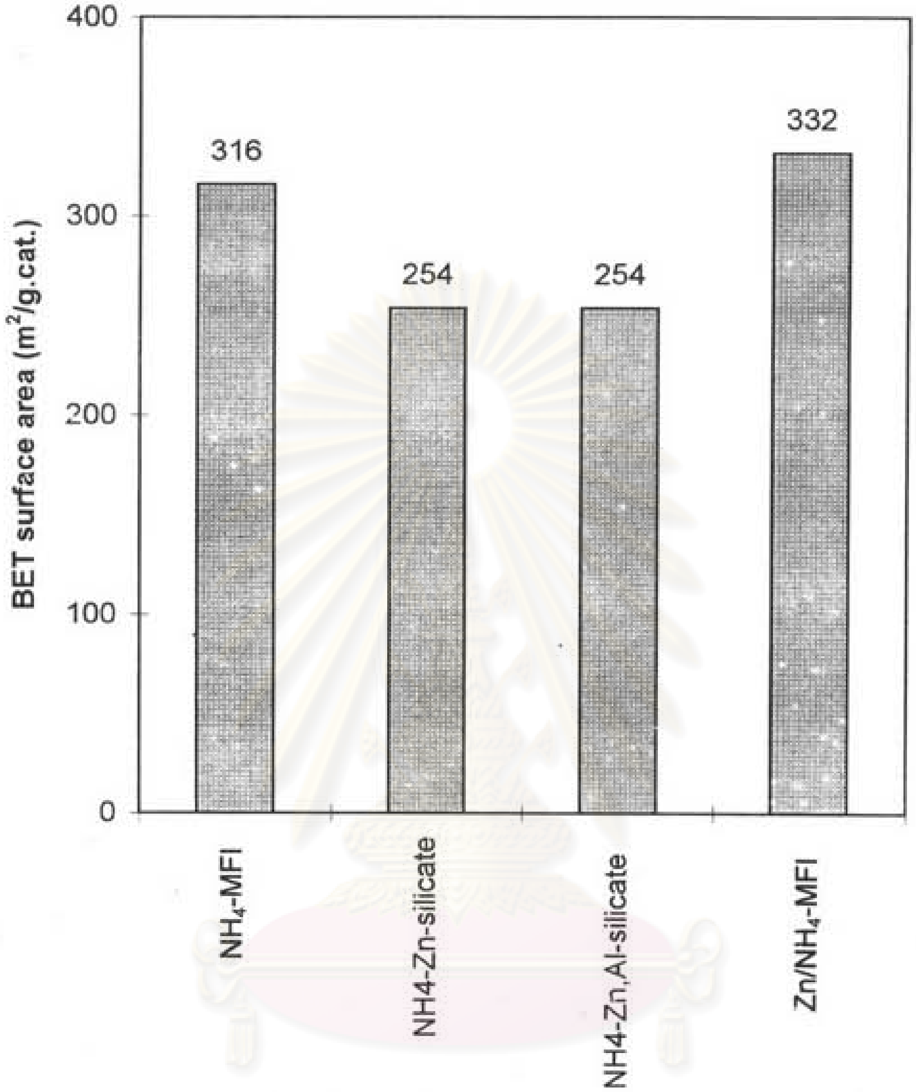


Figure 5.2 BET surface areas of the catalysts.

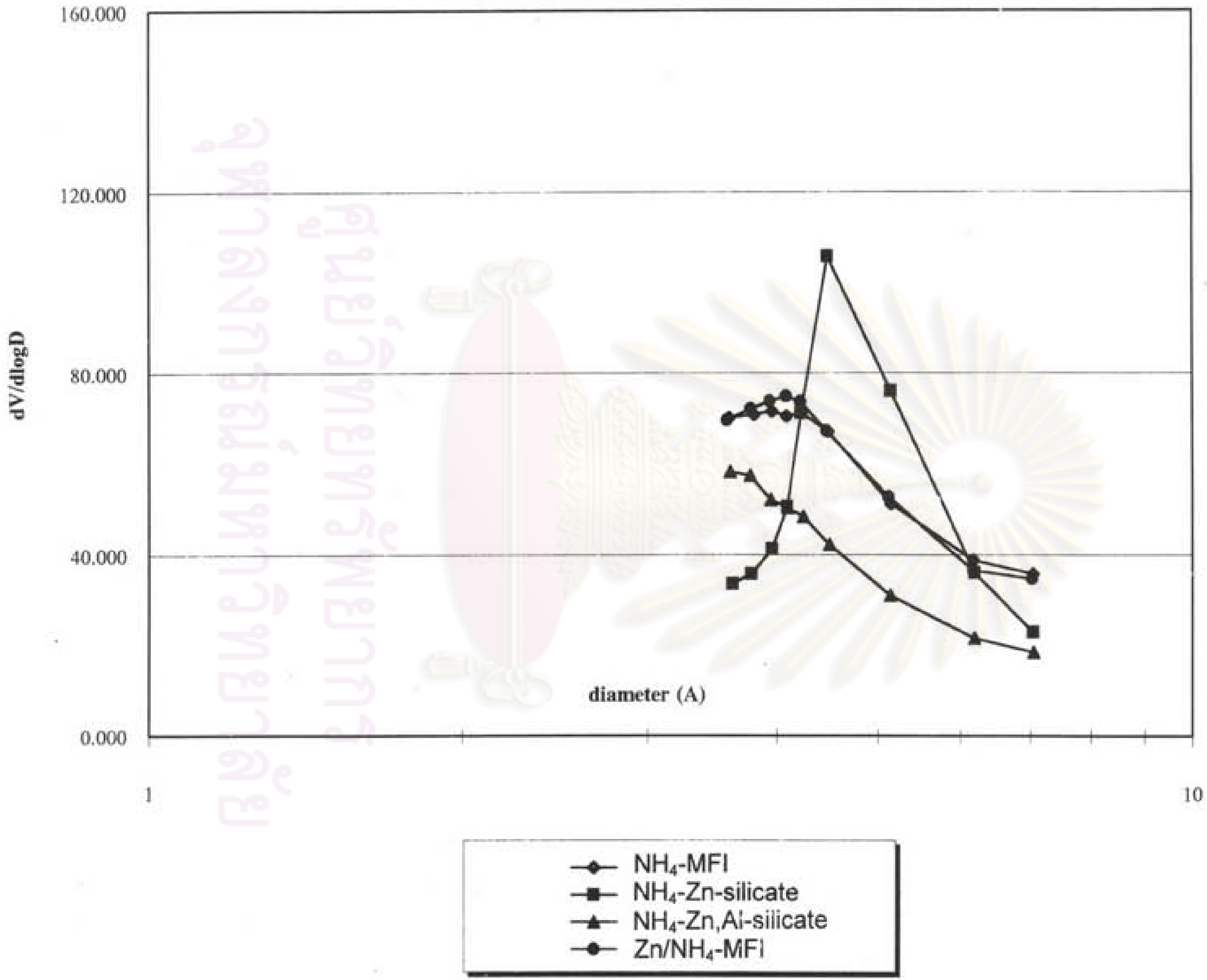
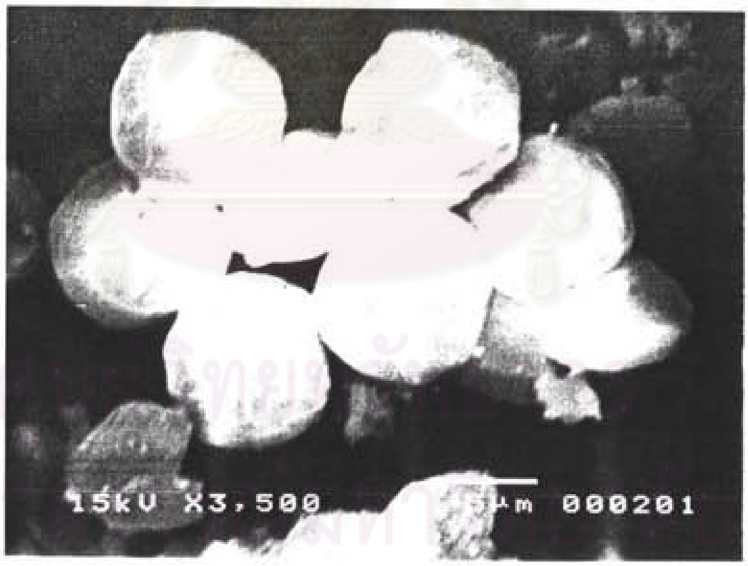


Figure 5.3 Pore size distribution of the catalysts.

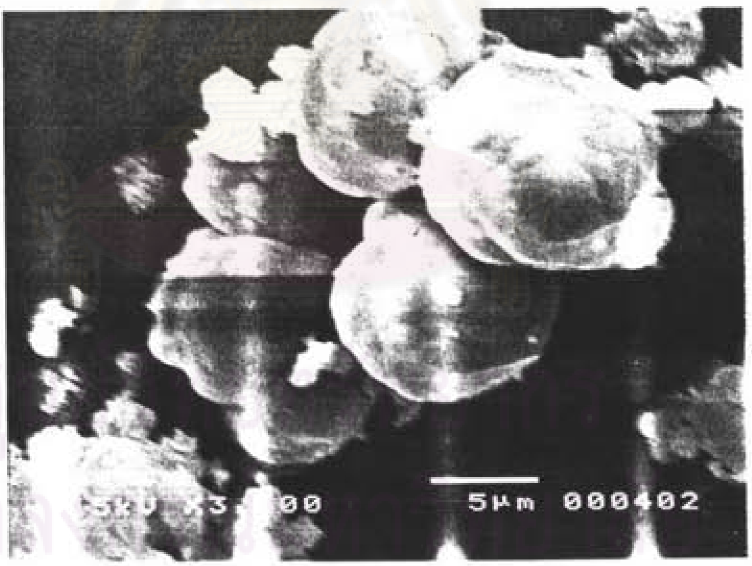
a) NH_4-MFI



b) NH_4-Zn-silicate

Figure 5.4 SEM photographs of the catalysts.

c) NH_4-Zn,Al-silicate



d) Zn/NH_4-MFI

Figure 5.4 SEM photographs of the catalysts (continued).

Table 5.2 Zinc content in Zn/NH_4-MFI.

% Zn loading (wt.%)	% Zn obsreved (wt.%)
0.30	0.22
0.70	0.50
1.40	0.75
2.50	2.01
3.00	2.61
5.00	4.30

5.1.5 Acidity

The TPD profiles of desorbed ammonia from NH_4-MFI (Si/Al = 40), NH_4-Zn-silicate (Si/Zn = 150), NH4-Zn,Al-silicate (Si/Zn = 40 and Si/Ai = 40) and Zn/NH_4-MFI (Zn = 2.61 % and Si/Al = 40) are shown in **Figure 5.5**. The profile is composed of two main peak. The low temperature peak representing the weak acid site was found at around 130-170 °C and the high temperature peak representing the strong acid site was found at around 380 °C. The strong acid sites play the important role in the aromatization reaction mainly [54,55].

5.2 Comparison of Zn-silicate and Pt-Sn/Alumina

The hydrocarbon distribution produced on NH_4-Zn-silicate, H-Zn-silicate and Pt-Sn/Al_2O_3 catalysts are shown in **Figure 5.6**. The reaction was carried out at the reaction temperature of 600 °C with 20 % propane and 80 % nitrogen, GHSV 2000 h^{-1} and 1 hour on stream. The weight ratio of Si/Zn was 150 and the concentration of Pt was 0.3 wt.%. From **Figure 5.6** the propane conversion and the selectivity to propylene was little difference on NH_4-Zn-silicate and Pt-Sn/Al_2O_3. ; however, the conversion on H-Zn-silicate was lower than did NH_4-Zn-silicate and Pt-Sn/Al_2O_3. As

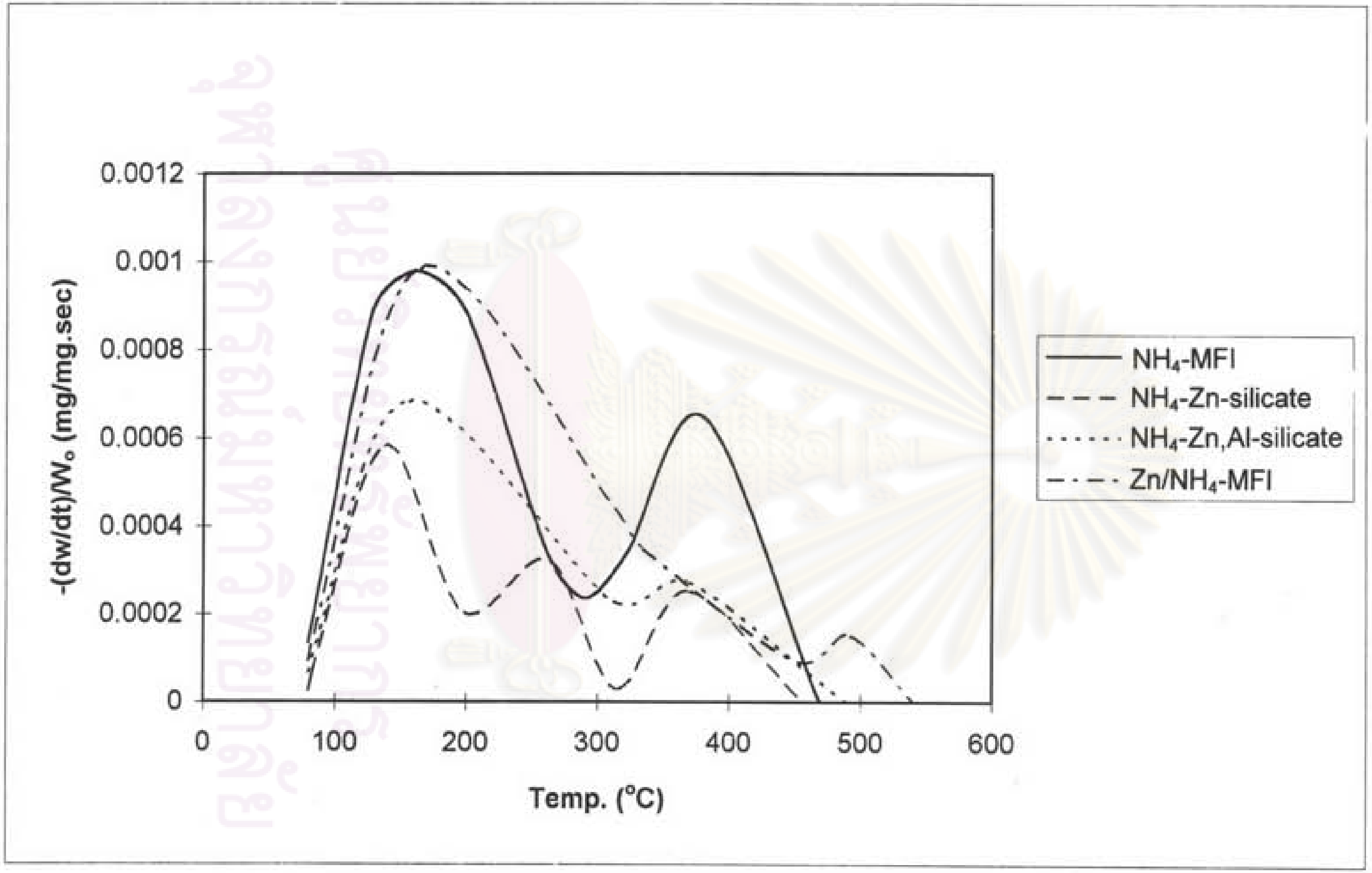


Figure 5.5 TPD profile of desorbed NH_3 from the catalysts

shown in Figure 5.7, at GHSV of 10000 h^{-1} it was found that the propane conversion on NH_4-Zn-Al-silicate was higher than did Pt-Sn-Na/Al_2O_3 at nearly the same selectivity. Pt-Sn/Al_2O_3 and Pt-Sn-Na/Al_2O_3 catalyst have been supplied by the oxidation group, petrochemical laboratory. The weight percent of Pt and Sn in Pt-Sn/Al_2O_3 were both 0.3. And The weight percent of Pt, Sn and Na in Pt-Sn-Na/Al_2O_3 were 0.3, 0.3 and 0.6 respectively. Thus, NH_4-Zn-silicate which gave the higher yield per pass (YPP) was selected to study further by varying amount of metal loading (Zn and Al).

5.3 Effect of Al loading amount in NH_4-Zn,Al-silicate

From **Figure 5.6** it has been found that NH_4-Zn-silicate exhibited the low activity for propane conversion. So further attempt to increase the activity has been made by co-adding Al in the structure of Zn-silicate. Inui et al [51] reported that Al in the structure of Zn-silicate will increase the strong acid site that responsible for the higher activity of propane conversion.

Therefore in this study, NH_4-Zn,Al-silicate was prepared by incorporating both zinc and aluminum in the zeolite framework of which Si/Zn was 100 and the Si/Al ratio was varied between 40 and 2000. From **Figure 5.8**, at GHSV 2000 and 10000 h^{-1}, it has been found that the conversion of propane increased with the increasing amount of aluminum loading (decreasing Si/Al ratio) but the selectivity to propylene decreased. These results suggested that the activity of propane dehydrogenation depends on the acid strength of the catalyst which increases with the increasing amount of aluminum loading. However, the high acid strength can readily convert the propylene formed to aromatics implying that the proper control of catalyst acidity is necessary for the selective conversion of propane to propylene.

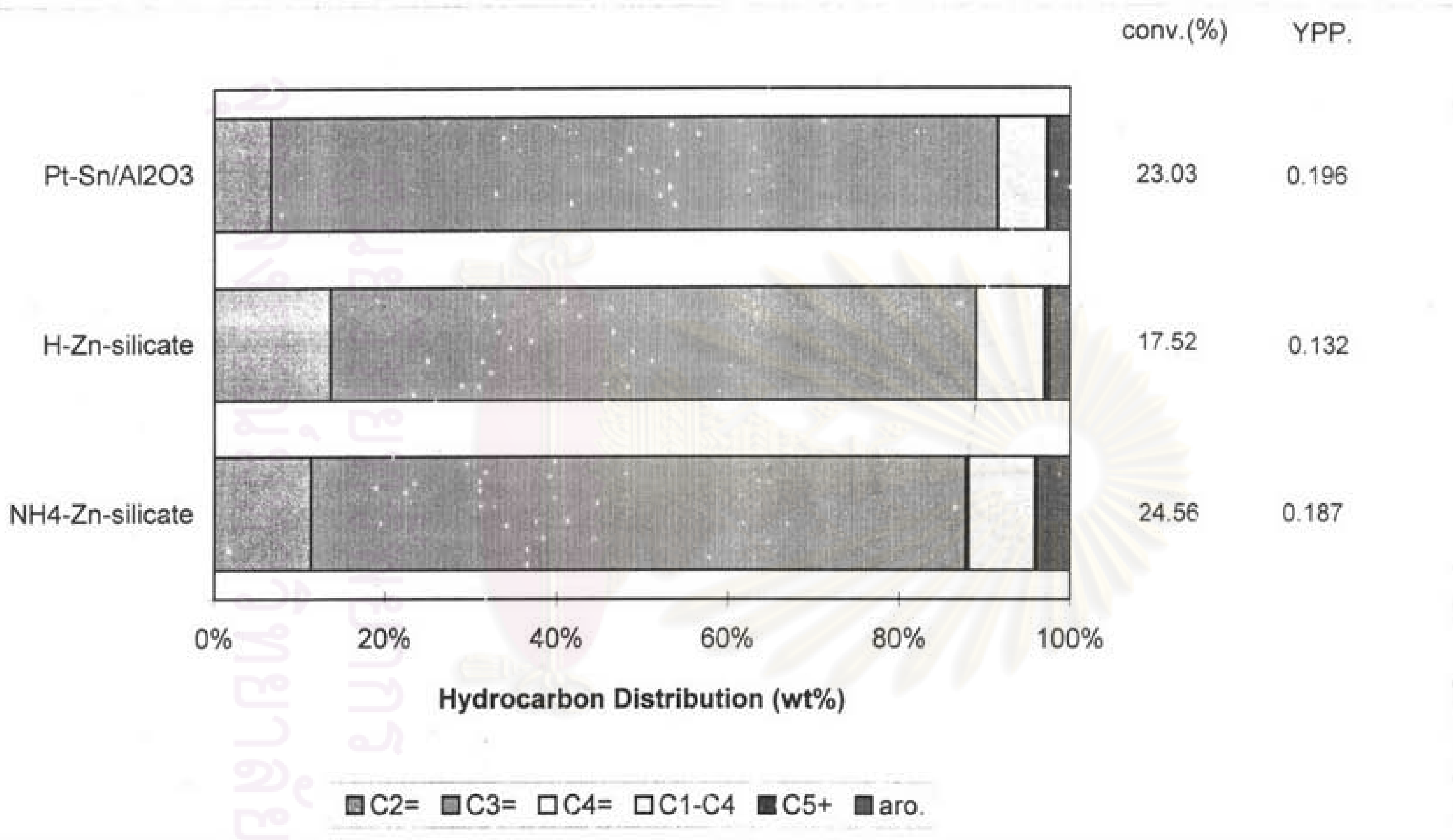


Figure 5.6 Propane dehydrogenation on the catalysts at 600 °C GHSV 2000 h^{-1}

20 % propane in nitrogen.

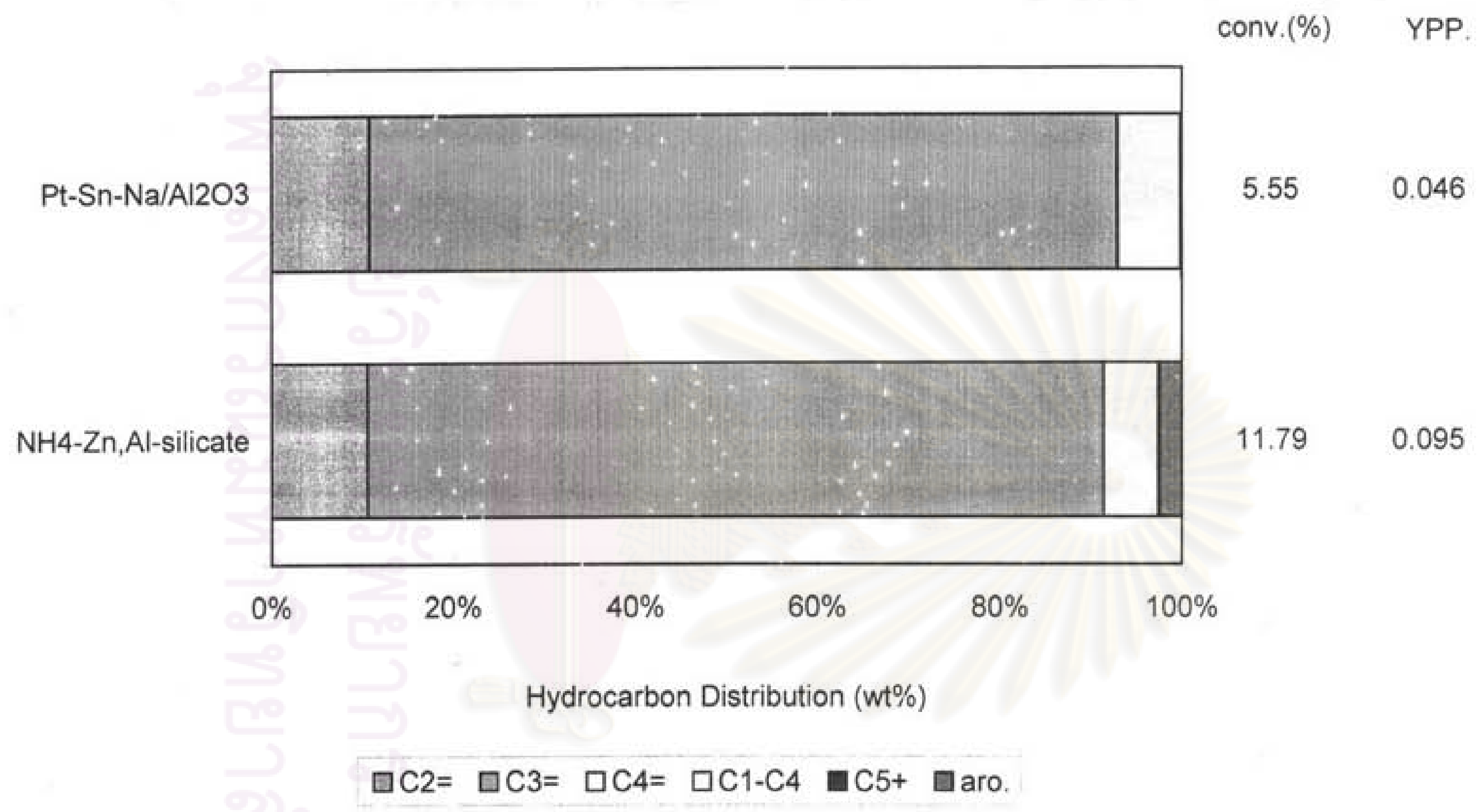


Figure 5.7 Propane dehydrogenation on the catalysts at 600 °C GHSV 10000 h^{-1}

20 % propane in nitrogen.

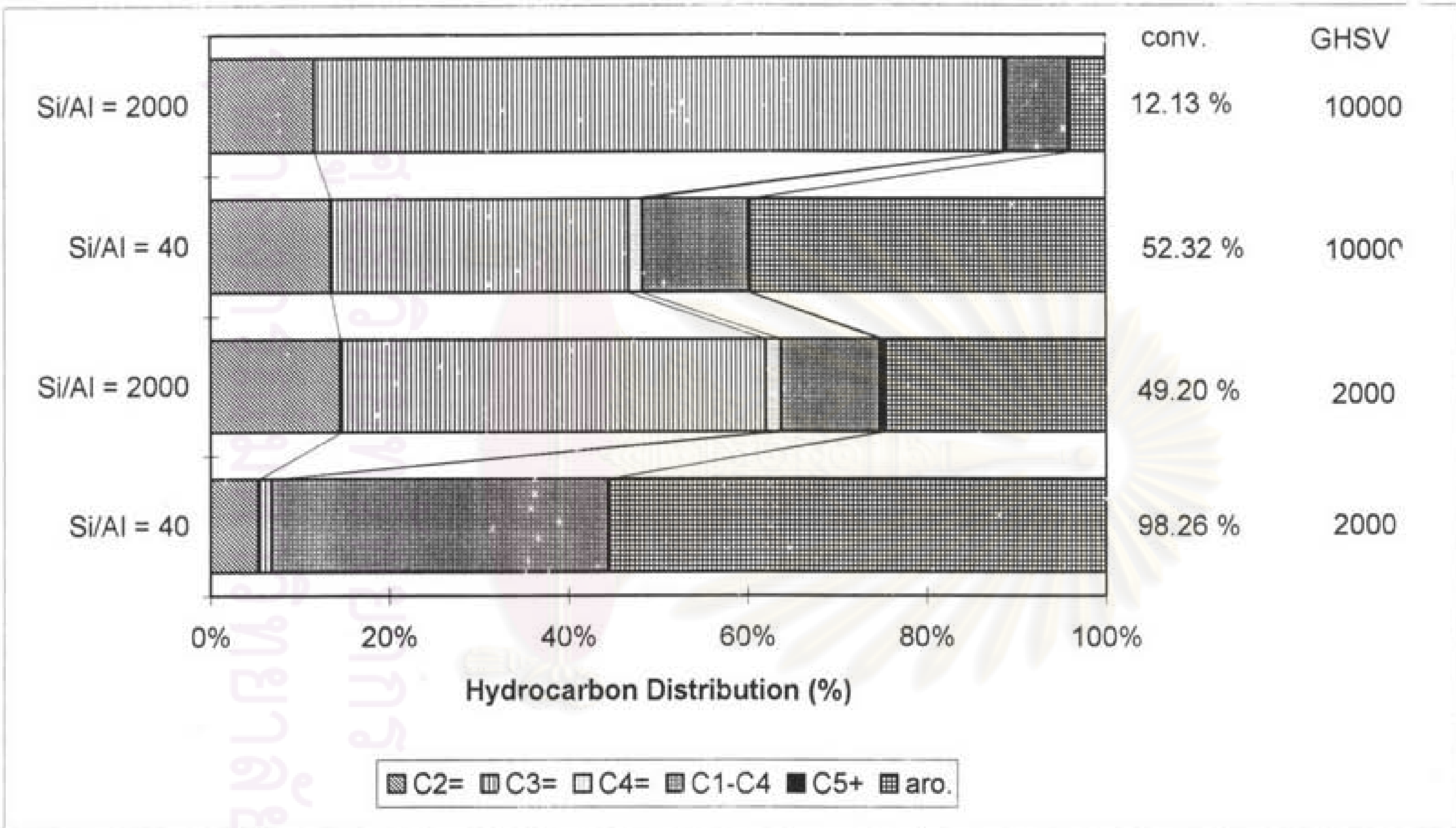


Figure 5.8 Propane dehydrogenation on NH_4-Zn,Al-silicate (Si/Al = 40 and 2000, Si/Zn = 100) GHSV 2000 and 10000 h^{-1} temp. 600 °C.

5.4 Effect of Zn loading amount by incorporation

From section 5.3 it has been found that NH_4-Zn,Al-silicate which Si/Al ratio of 40 exhibited the highest activity for propane conversion to propylene; thus it was selected to observe the optimum amount of zinc by incorporation in the structure of NH_4-MFI.

The ratio of Si/Zn in NH_4-Zn,Al-silicate was changed from 20 to ∞ which the zinc content was measured by AAs as shown in **Table 5.1**. **Figure 5.9** shows the hydrocarbon distribution on NH_4-Zn,Al-silicate. It has been found that when the amount of Zn loading increased the conversion of propane and selectivity to propylene was also increased. In addition, the yield of propylene increased with the amount of Zn loading too. These results suggested that Zn plays the active role for the dehydrogenation of propane to propylene, NH_4-Zn,Al-silicate with Si/Zn ratio 40 and Si/Al ratio 40 exhibited the highest propylene yield (ca. 0.21).

5.5 Effect of Zn loading amount by Ion-exchange with MFI type catalyst

The hydrocarbon distribution on Zn ion-exchange with NH_4-MFI zeolite catalyst with various amount of Zn ; 0, 0.22, 0.50, 0.75, 2.01, 2.61 and 4.30 wt.% (measuring by AAs) are shown in **Figure 5.10**. The conversion of propane increased when the amount of Zn loading was increased but the selectivity to propylene decreased with the increasing amount of Zn loading. Meanwhile the aromatics formed was also increased reflecting that the catalysts contain the acidity high enough to convert the propylene to aromatics upon the increasing amount of Zn loading. However, when taken into consideration the yield per pass, it increased with the amount of Zn and the optimum amount of Zn observed was 2.61 %.

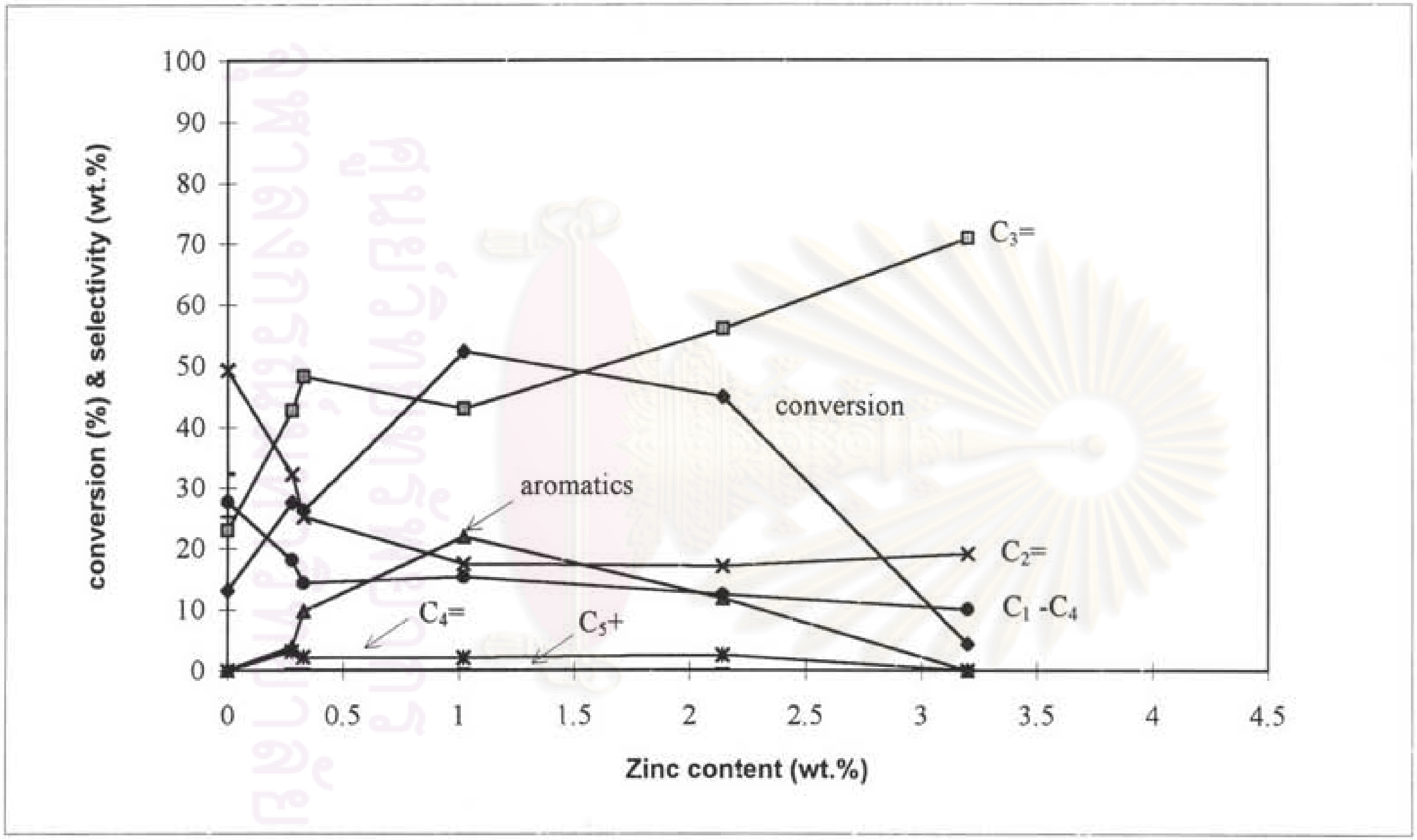


Figure 5.9 Propane dehydrogenation on NH_4-Zn,Al-silicate (Si/Al = 40, Si/Zn = 20 to ∞)

GHSV 10000 h^{-1} temp. 600 °C.

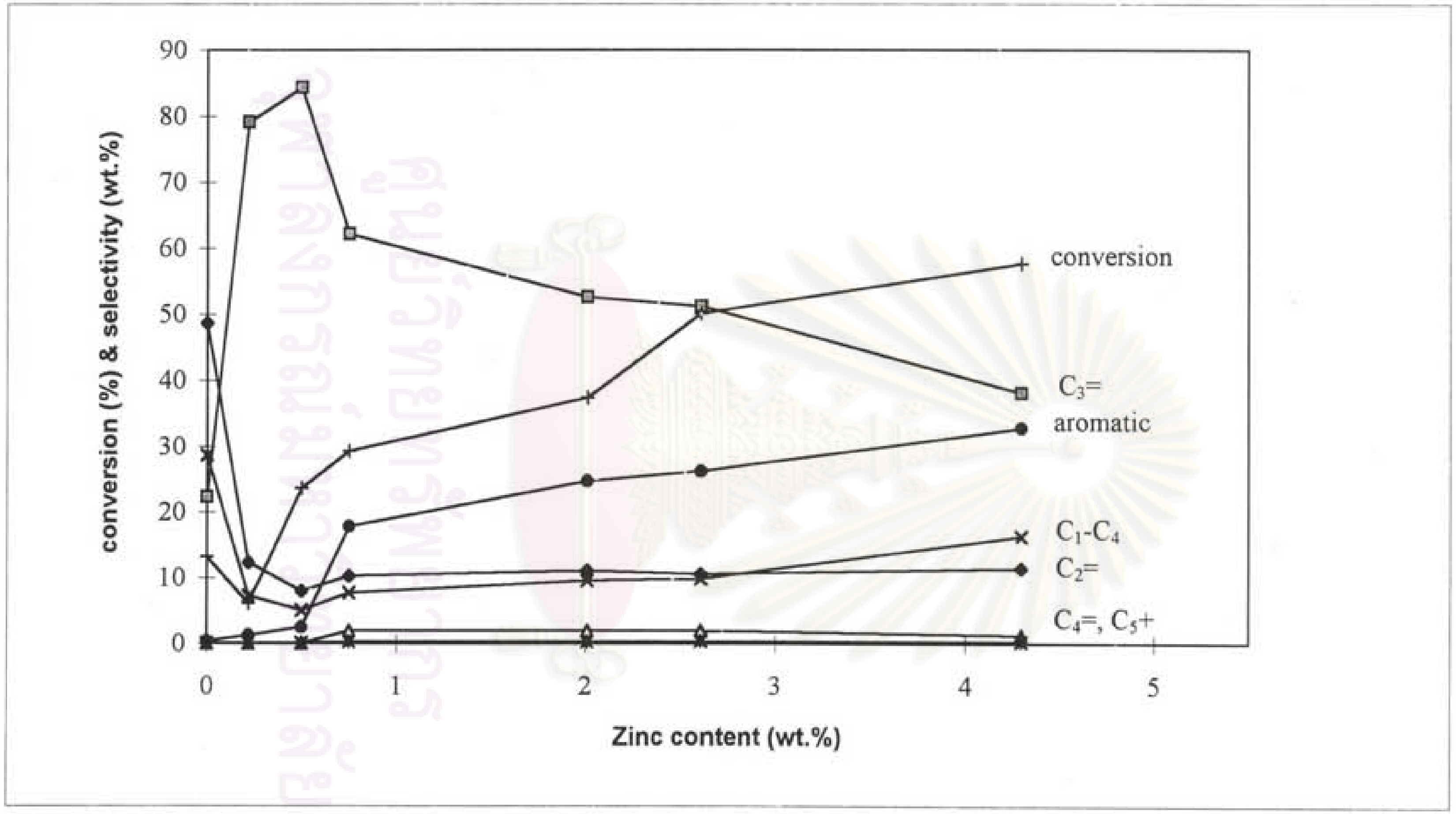


Figure 5.10 Propane dehydrogenation on Zn/NH_4-MFI (Si/Al = 40, Zn = 0 to 4.30 %)

GHSV 10000 h^{-1} temp. 600 °C.

5.6 Comparison of NH_4-Zn,Al-silicate with NH_4-Zn/MFI

From **Figures 5.9** and **5.10**, the hydrocarbon distribution was compared between using NH_4-Zn,Al-silicate and Zn/NH_4-MFI as the catalyst for propane dehydrogenation at nearly the same amount of Zn loading. It has been found that the Zn/NH_4-MFI with approximately 2.6 % Zn gave higher propane conversion than NH_4-Zn,Al-silicate with nearly the same amount of Zn (Si/Al 40) and so did the YPP as shown in **Figure 5.11**. Thus the results reflect the different location of Zn in the catalyst obtained by incorporation and ion-exchange does affect the catalyst activity and selectivity for propane dehydrogenation to propylene.

5.7 Effect of reaction temperature on the product distribution of propane dehydrogenation

The reaction temperature for propane conversion was observed at 550 and 600 °C. The reaction was carried out over NH_4-Zn,Al-silicate (Si/Zn ratio of 40 and Si/Al ratio of 40) at GHSV 10000 h^{-1} by using feed gas mixture of 20 % propane and 80 % nitrogen gas for 1 hour on stream.

The product distributions are shown in **Figure 5.12**. It has been found that the reaction temperature of 600 °C was necessary to dehydrogenate propane to propylene with high activity.

5.8 Effect of GHSV on the product distribution of propane dehydrogenation

Figure 5.13 shows the product distribution of propane dehydrogenation over NH_4-Zn,Al-silicate which space velocities were varied from 2000 to 10000 h^{-1}. At

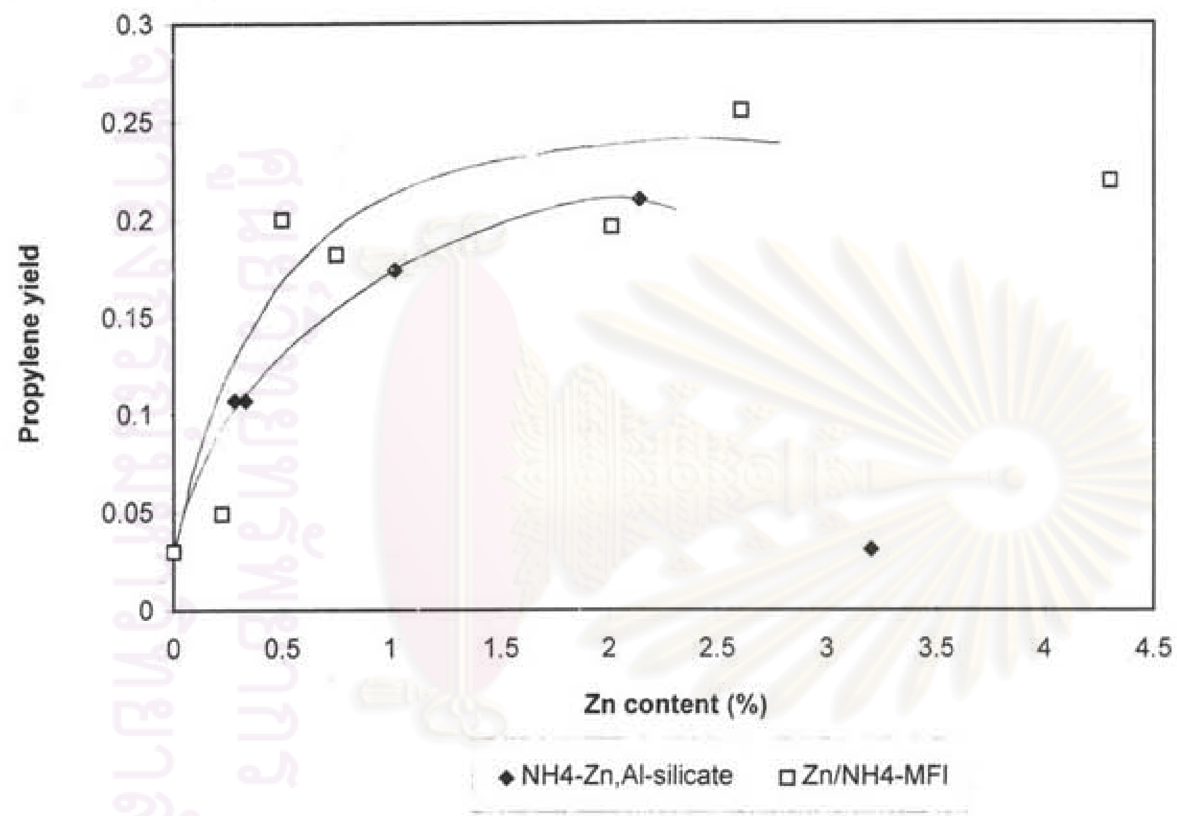


Figure 5.11 Propylene yield of propane dehydrogenation on NH_4-Zn,Al-silicate

Zn/NH_4-MFI at the various zinc content.

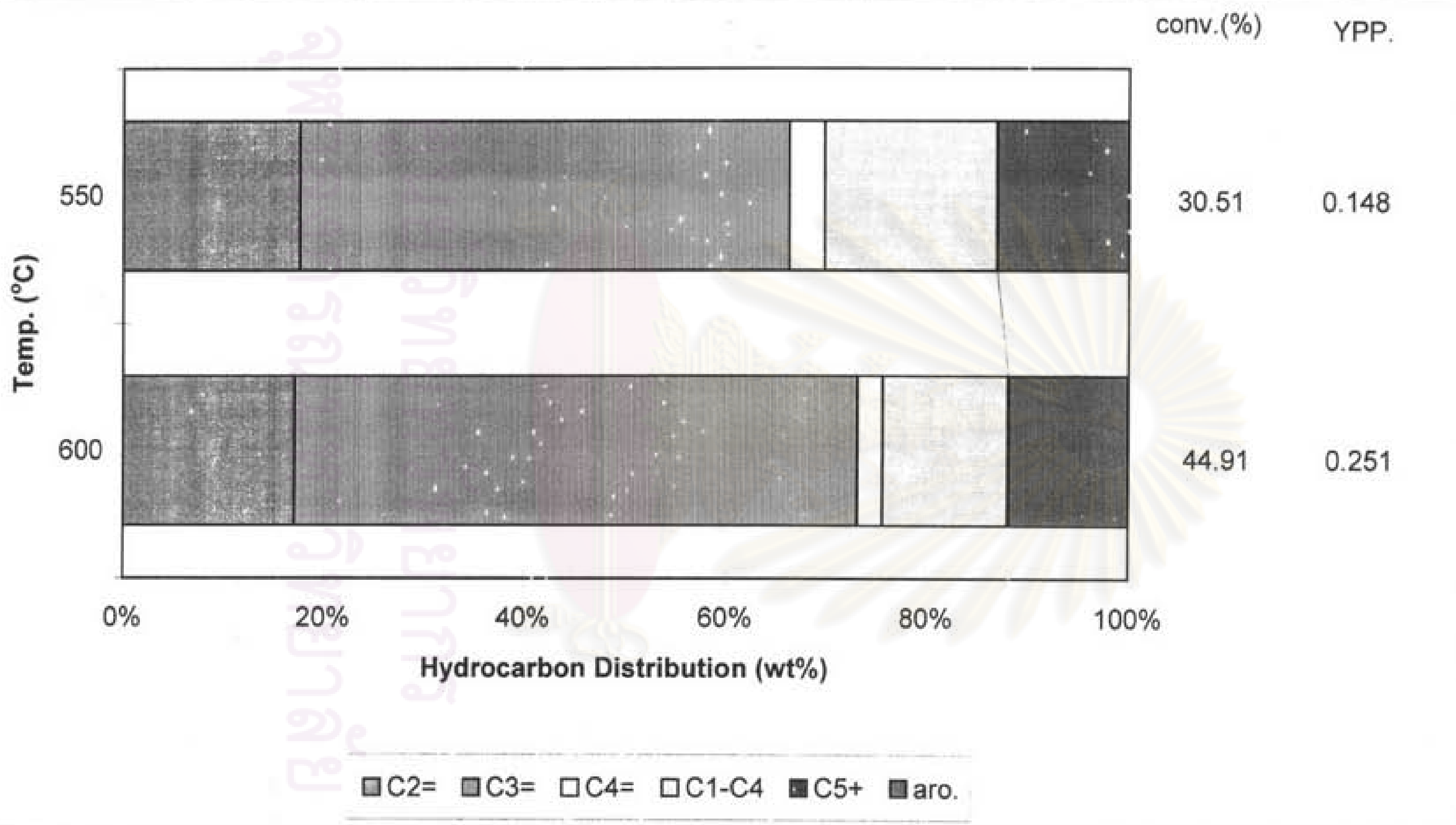
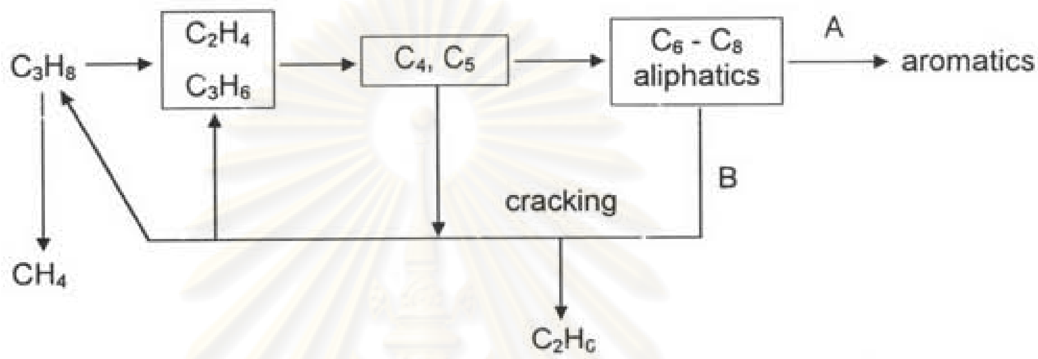


Figure 5.12 Propane dehydrogenation on NH_4-Zn,Al-silicate (Si/Al = 40, Si/Zn = 40) GHSV 10000 h^{-1} temp 550 and 600 °C.

higher GHSV the contact time between propane and catalyst was shortened and thus the conversion decreased ; however, the amount of aromatics was also decreased. Therefore, there has been a tradeoff between propane conversion and propylene selectivity at high GHSV and thus the YPP was not significantly affected. The main reaction pathway may be summarized as follows [13].



5.9 Comparison of the catalyst stability

The prolonged dehydrogenation of propane on NH_4-Zn,Al-silicate (Si/Zn ratio 40, Si/Al ratio 40) and Zn/NH_4-MFI (2.61 % Zn, Si/Al ratio 40) are shown in **Figures 5.14** and **5.15**, respectively. The Zn/NH_4-MFI exhibited higher stability than did NH_4-Zn,Al-silicate. When the product distributions of both catalysts were compared at 5 min on stream as shown in **Table 5.3**, it has been found that Zn/NH_4-MFI gave less aromatics, the precursor of coke, and higher propylene selectivity than did NH_4-Zn,Al-silicate. When the NH_3-TPD profiles of Zn/NH_4-MFI and NH_4-Zn,Al-silicate were taken into consideration, it has been found that less aromatics were produced on the former catalyst having rather higher acidity than the latter one. This unusual results were postulated to be due to the different position of Zn in each catalyst. The amount of ethane formed on Zn/NH_4-MFI was lower than that on NH_4-Zn,Al-silicate. This means Zn in Zn/NH_4-MFI can prevent the hydrogenation of light olefins to light

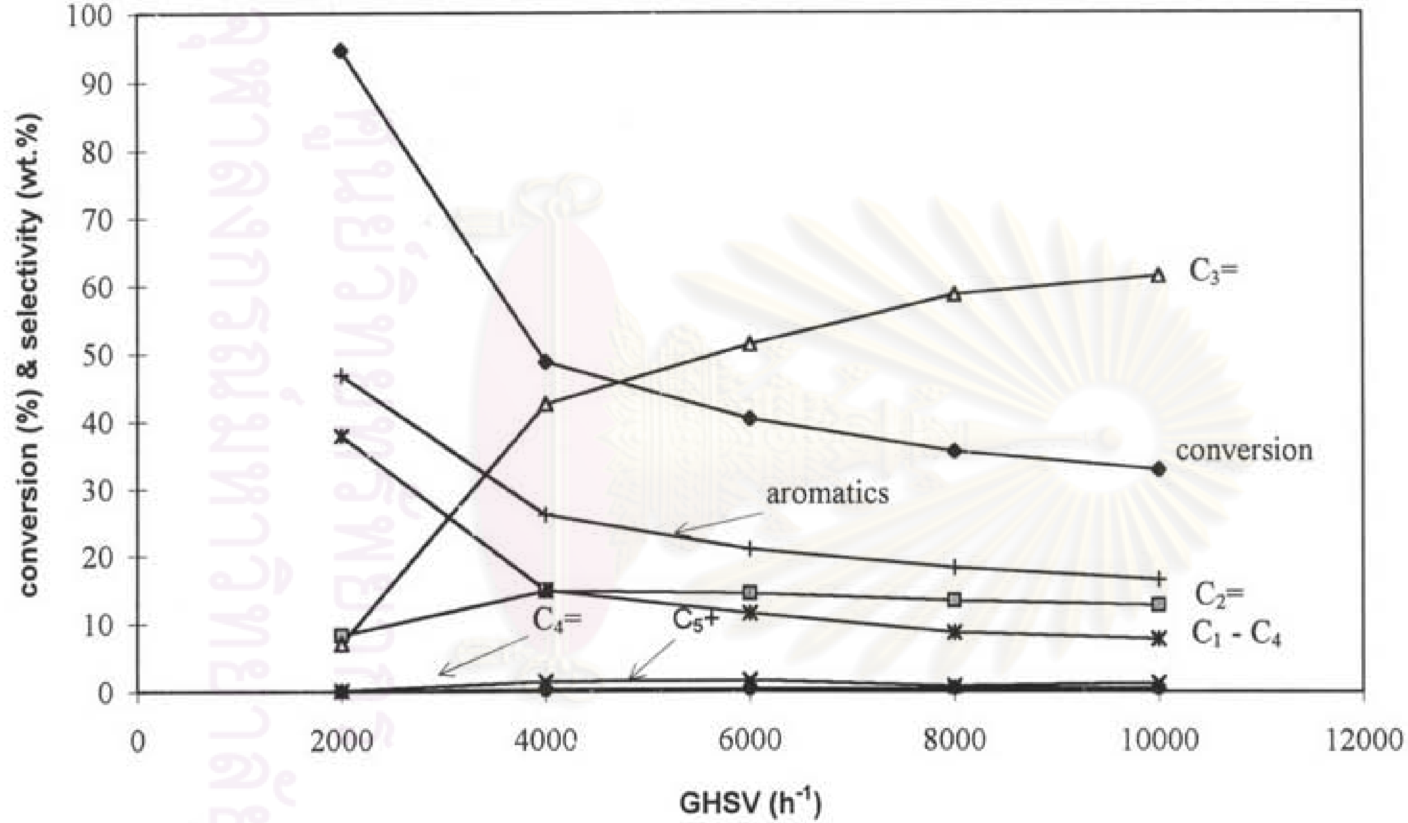


Figure 5.13 Propane dehydrogenation on NH_4-Zn,Al-silicate (Si/Al = 40, Si/Zn = 40)

GHSV 2000 - 10000 h^{-1} temp. 600 °C.

paraffins such as ethane better than did NH_4-Zn,Al-silicate. The less hydrogenation of light olefins to light paraffins means the better hydrogen conserved for the transfer of hydrogen to the carbonaceous deposit on the catalyst surface that responsible for the long catalyst life. In addition Zn/NH_4-MFI also contained higher BET surface area than NH_4-Zn,Al-silicate, thus the available active site at any time of Zn/NH_4-MFI should be kept higher.

Table 5.3 Propane dehydrogenation on NH_4-Zn,Al-silicate (Si/Al = 40, Si/Zn = 40) and Zn/NH_4-MFI (Si/Al = 40, Zn = 2.61) at time on stream 5 min. Temp. 600 °C GHSV 10000 h^{-1}.

	propane conversion and product distribution (%)	
	NH_4-Zn,Al-silicate	Zn/NH_4-MFI
Propane conversion	69.53	47.25
C_1	11.48	7.68
C_2	12.20	5.24
C_2=	7.95	11.08
C_3=	14.22	43.86
C_4	0.15	0.14
C_4=	0.74	1.43
C_5+	0.09	0.09
aromatics	45.17	30.49

5.10 Effect of platinum loading on NH_4-Zn,Al-silicate

To investigate the effect of Pt on catalyst activity and/or stability, Pt was introduced into NH_4-Zn,Al-silicate by ion-exchange. The amount of Pt was varied between 0.1 and 0.3 wt%. The hydrocarbon distributions on Pt/NH_4-Zn,Al-silicate are shown in **Figure 5.16**. When compared with the NH_4-Zn,Al-silicate without Pt loading in **Figure 5.9**, neither conversion nor YPP was improved with the presence of Pt. As for the catalyst stability as shown in **Figure 5.17**, no significant

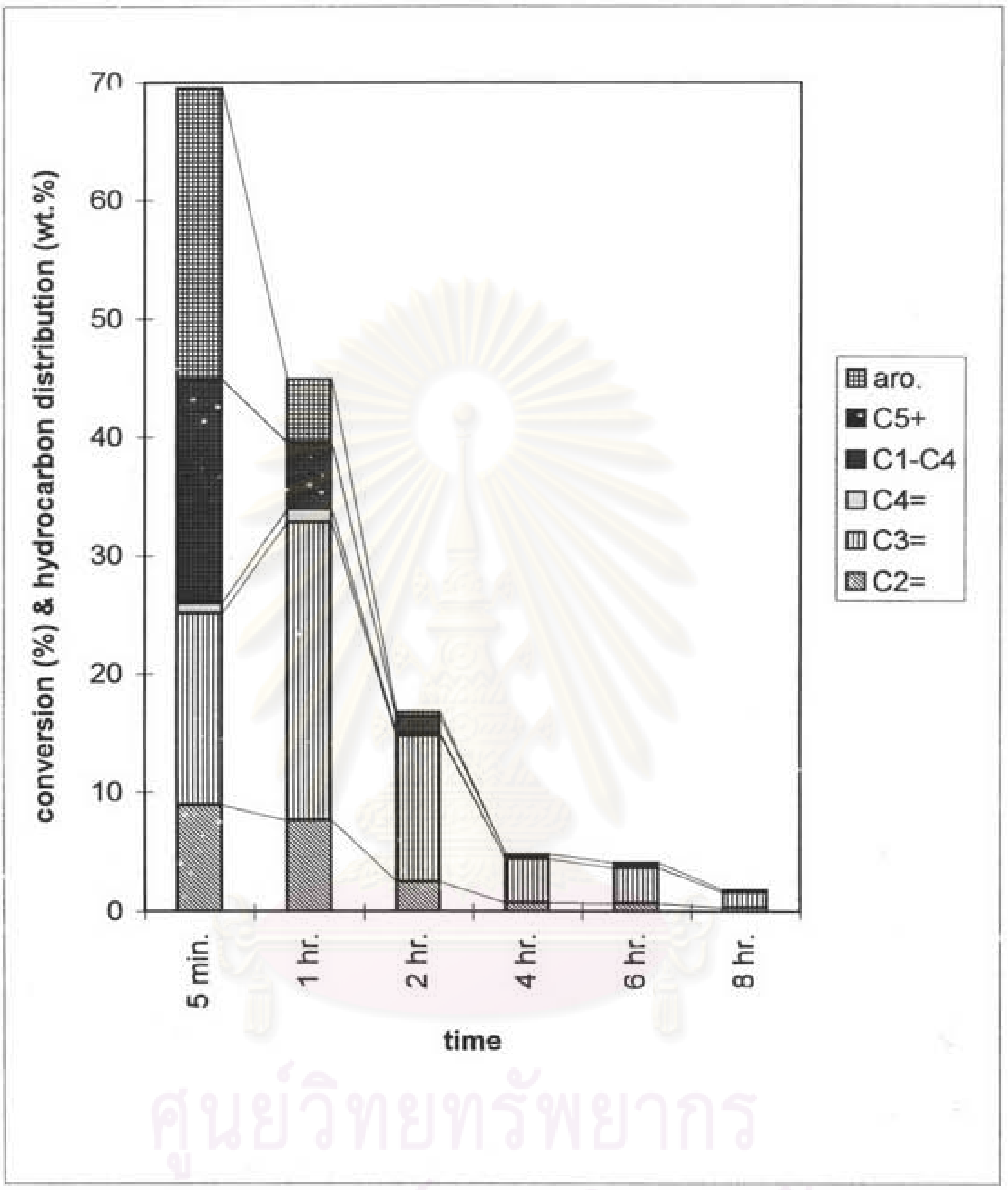


Figure 5.14 Propane dehydrogenation on NH_4-Zn,Al-silicate (Si/Al = 40, Si/Zn = 40)

GHSV 10000 h^{-1} temp. 600 °C.

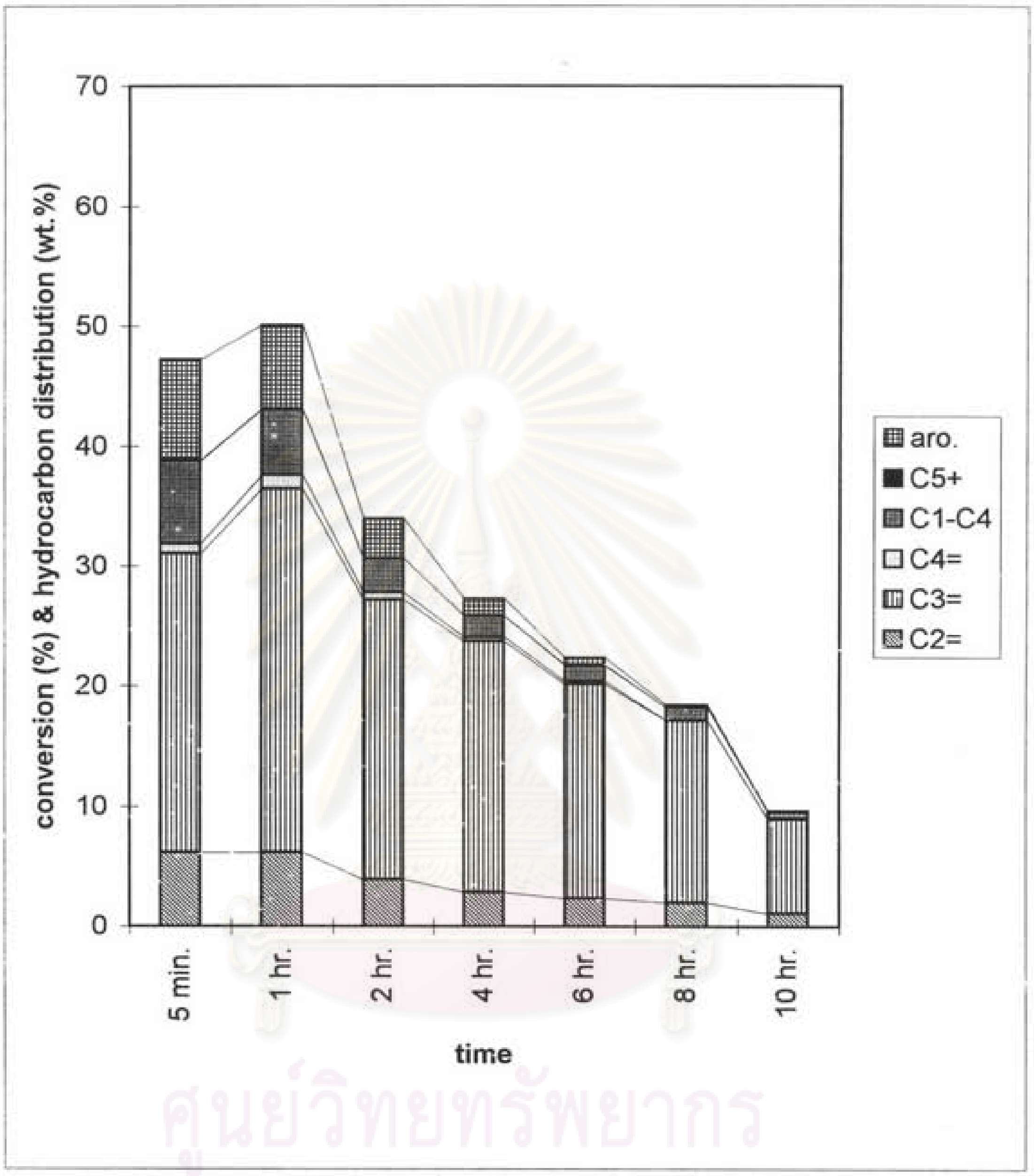


Figure 5.15 Propane dehydrogenation on Zn/NH_4-MFI (Si/Al = 40, Zn = 2.61 %)

GHSV 10000 h^{-1} temp. 600 °C.

improvement on catalyst stability gas been made on Pt/NH_4-Zn,Al-silicate. Aluminum may already have the same function as Pt for hydrogen transfer which Al may cause hydrogen attraction and subsequently hydrogen transfer to the adsorbate species on the catalyst surface.

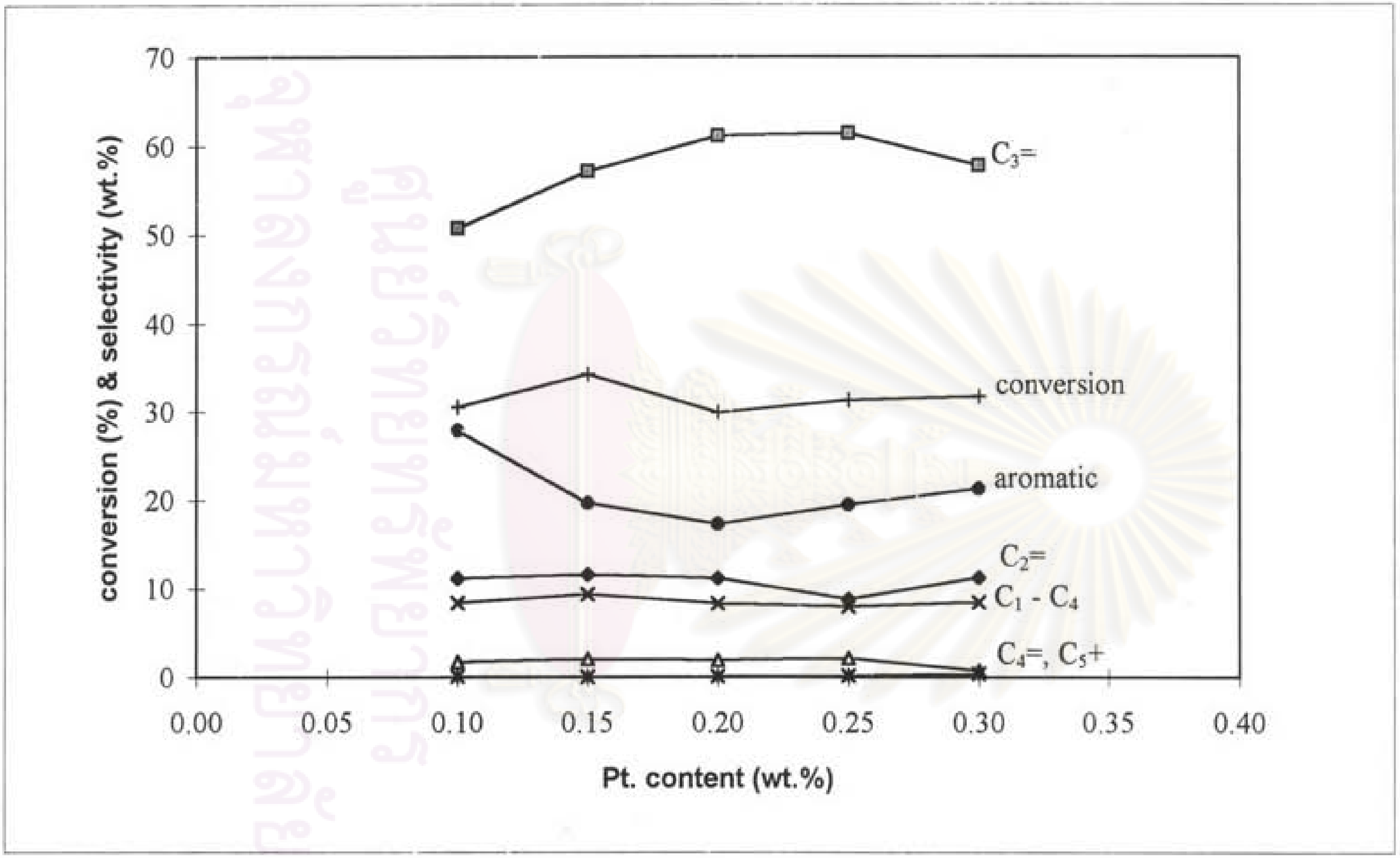


Figure 5.16 Propane dehydrogenation on Pt/NH_4-Zn,Al-silicate (Si/Al = 40, Si/Zn = 40)

Pt = 0.1 - 0.3 % GHSV 10000 h^{-1} temp. 600 °C.

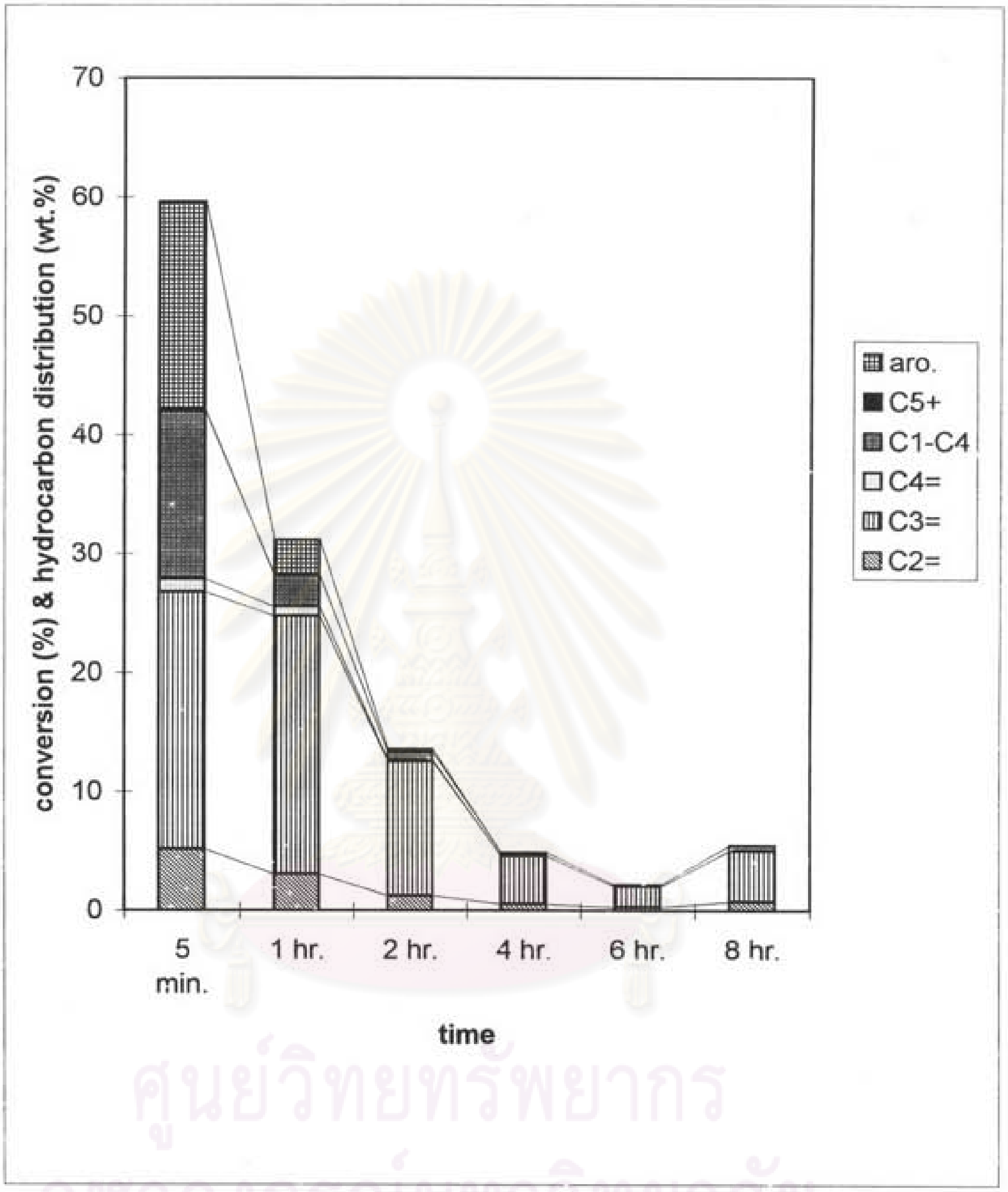


Figure 5.17 Propane dehydrogenation on Pt/NH_4-Zn,Al-silicate (Si/Al = 40, Si/Zn = 40)

Pt = 0.25 % GHSV 10000 h^{-1} temp. 600 °C.