CHAPTER 5

RESULTS AND DISCUSSION

5.1 Reaction Engineering Tests

5.1.1 Influence of Si/V Charged Ratios on the Activity and Selectivity of Vanadosilicate Catalysts

For the MTG reaction, catalysts of Si/V (charged ratios, ∞ ,3200 1600, 400, 200, 90 and 40) have been examined at conditions SV = 2000 h^{-1} 300 °C and 20 % MeOH diluted with N_2. As can be seen from Table 5.1, methanol was completely converted to hydrocarbons over catalysts of Si/V charged ratios ranging from ∞ to 200. For the Si/V ratios less than 200, i.e. 90 and 40, MeOH conversion decreased to 84.0, 33.6 % and hydrocarbon products decreased from 100 % to 74.3 and 68.7 %, respectively. In this range (90, 40) MeOH was also converted to dimethylethe (DME) 25.7 and 31.3 %, respectively. Figure 5.1, shows the effect of Si/V charged ratios on the distribution of hydrocarbons. Hydrocarbon distribution profiles were nearly constant for catalysts of Si/V ratios of more than 400. However, for the Si/V ratios less than 400, hydrocarbon distribution profiles began to decrease in C_5^+ and aromatics, and increase in C_2-C_4 olefins. For Si/V ratios of less than 200,C_5^+ and aromatics decreased sharply and C_2-C_4 olefins first increased showing the maximum at the Si/V ratio 90, and then decreased sharply at Si/V ratio 40. Table 5.2 shows the effect of the Si/V charged ratio on activity and selectivity of metallosilicate catalysts at a higher reaction

TABLE 5.1 Influence of the Si/V charged ratio on the activity and selectivity of metallosilicate catalysts

Si/V (charged ratio)	:	∞	3200[a]	1600	400	200	90	40
MeOH conv. (%)	:	99.2	100.0	100.0	100.0	100.0	84.0	33.6
Conv. to H.C (%)	:	99.9	100.0	100.0	100.0	100.0	74.3	68.7
c-wt% C_2-C_4 (olefins)	:	29.8	24.7	27.1	23.8	33.0	65.7	19.3
C_5^+	:	39.5	39.7	39.8	36.2	37.0	18.2	0.3
Aromatics	:	17.6	21.9	19.8	23.1	17.8	9.4	-

a : data from Inui, T., et al, 52th CSS meeting, 1983, preprint p. 218

(Reaction condition: SV = 2000 h^{-1}, T = 300 °C, 80% N_2, 20% MeOH, 1 h on stream)

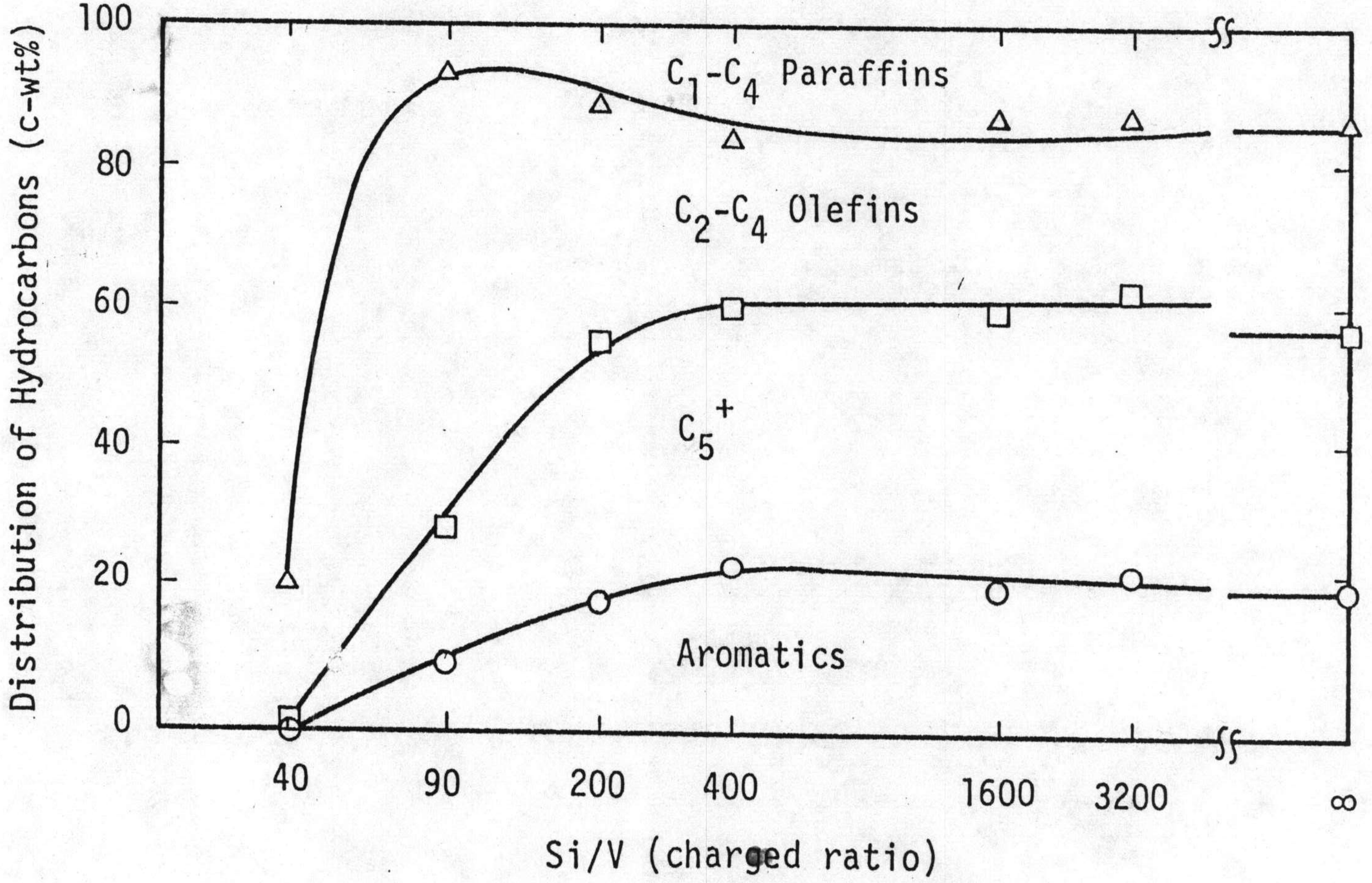

FIGURE 5.1 Effect of Si/V charged ratio on hydrocarbons distribution (c-wt%) (Reaction condition: SV = 2000 h^{-1}, T = 300 °C, 80% N_2, 20% MeOH)

temperature (360 °C). MeOH was complet1y converted to hydrocarbons over catalysts of Si/V ∞ to 90. For the Si/V charged ratio 40, MeOH conversion decreased to 44.8 % and hydrocarbon products decreased to 85.7 %. MeOH was converted to DME 14.3 %. Figure 5.2 shows the effect of the Si/V ratio on the distribution of hydrocarbons at reaction temperature 360 °C. The hydrocarbons distribution profiles show the same patterns as in Figure 5.1. However, at the higher temperature the activity of the vanadosilicate catalysts for MeOH conversion increased. At higher temperature the selectivity of hydrocarbons changed, whereas those increased in C_2-C_4 olefins and decreased in C_5^+ and aromatics. The amount of C_2-C_4 olefins + C_5^+ + aromatics of Figure 5.1 and 5.2 are nearly equal for each Si/V ratios catalysts. Then, Figure 5.1 and 5.2 indicated that when the amount of vanadium charge is too much, the activity and selectivity for MTG reaction decreases, this effect is in contrast with others zeolite catalysts. However, the selectivity of C_2-C_4 olefins began to increase at Si/V ratios less than 400, especially at Si/V ratio 90 gave the highest yields of C_2-C_4 olefins. Therefore, the influence of vanadium charged in metallosilicate may be shown through the effect of catalytic cracking of C_5^+ hydrocarbons and/ or aromatics to low molecular weight olefin hydrocarbons.

5.1.2 Effect of Space Velocity

From Figure 5.1, the interesting range of Si/V charged ratio is between 200 to ∞ . Therefore, to study the effect of space velocity an activity and selectivity, for MTG reaction, catalyst Si/V ratios 200, 400 and ∞ were chosen for the reaction condition : a reaction temperature of 300 °C and 20 % MeOH diluted with N_2. Table 5.3

TABLE 5.2 Influence of the Si/V charged ratio on the activity and selectivity of metallosilicate catalysts

Si/V (charged ratio)		∞	1600	400	200	90	40
MeOH conv. (%)		100.0	100.0	100.0	100.0	100.0	44.8
Conv. to H.C (%)		100.0	100.0	100.0	100.0	100.0	85.7
c-wt%	C_2-C_4 (olefins)	45.4	38.5	42.9	48.7	51.2	18.6
	C_5^+	24.7	28.0	23.9	24.3	23.2	10.8
	Aromatics	17.1	19.0	19.1	15.2	15.6	0.1

(Reaction condition: SV = 2000 h^{-1}, T = 360 °C, 80% N_2, 20% MeOH, 1 h on stream)

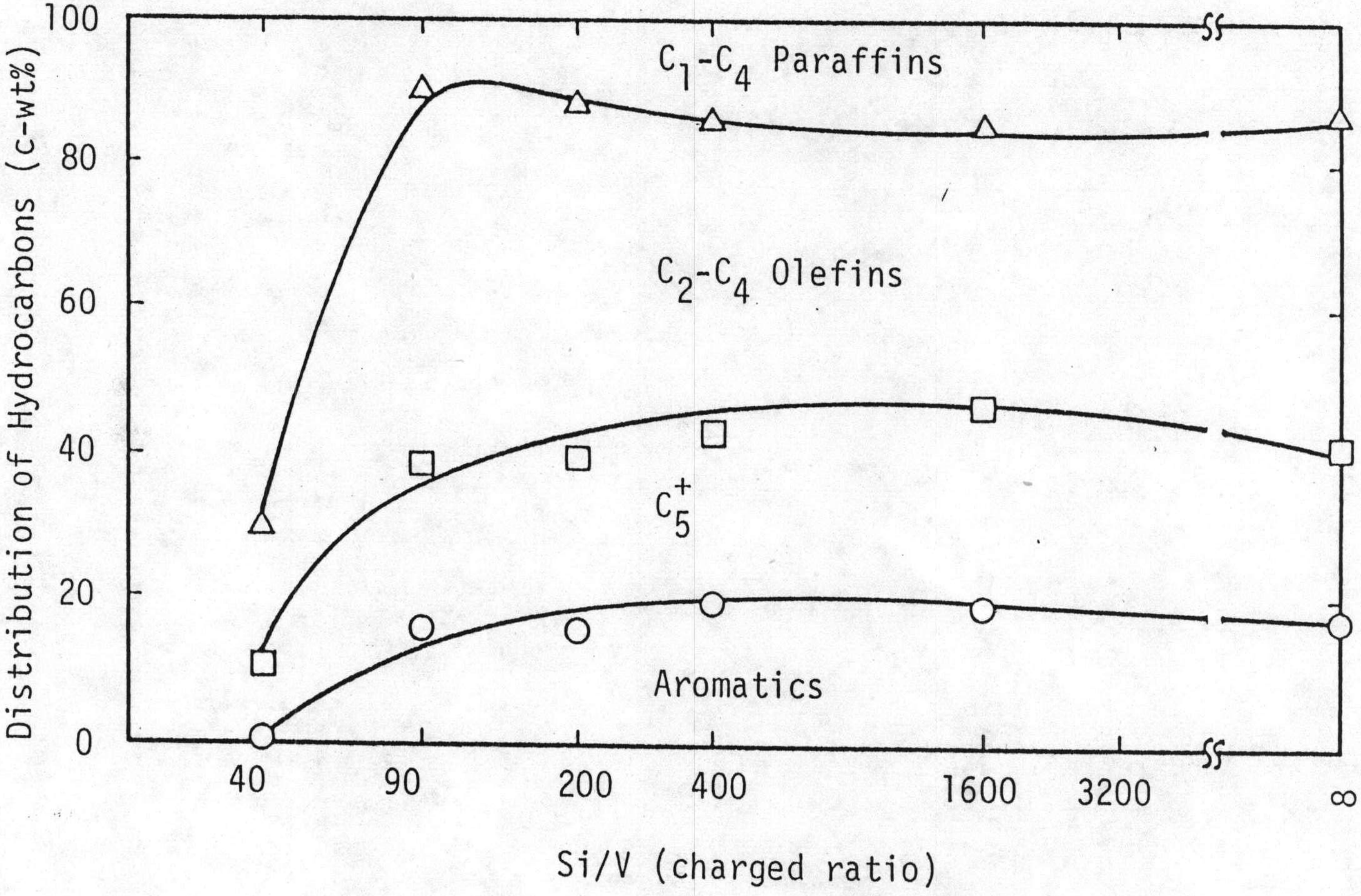

Figure 5.2 Effect of Si/V charged ratio on hydrocarbons distribution (c-wt%) (Reaction condition: SV = 2000 h^{-1}, T = 360 °C, 80% N_2, 20% MeOH)

TABLE 5.3 The effect of space velocity on activity and selectivity of catalysts H-Si-V(∞, 400, 200)

SV, h^{-1}	500		1000			2000			4000			8000		
Si/V(charged ratio)	∞	400	∞	400	200	∞	400	200	∞	400	200	∞	400	200
MeOH conv. (%)	100.0	100.0	100.0	100.0	100.0	99.2	100.0	100.0	98.5	99.7	97.6	90.3	94.7	90.2
Conv. to H.C (%)	100.0	100.0	100.0	100.0	100.0	99.9	100.0	100.0	99.9	100.0	99.4	92.9	96.6	91.7
c-wt% C_2-C_4 (o)	20.6	16.0	18.8	16.1	24.3	29.8	23.8	33.0	34.9	27.4	36.8	45.0	35.8	49.6
C_5^+	32.3	32.7	37.0	36.1	34.6	39.5	36.2	37.0	40.6	38.5	37.7	33.3	35.4	30.0
Aromatics	30.7	30.4	24.8	28.9	24.3	17.6	23.1	17.8	13.6	19.6	14.6	11.2	15.6	10.8

(Reaction condition: T = 300 °C, 80% N_2, 20% MeOH, 1 h on stream)

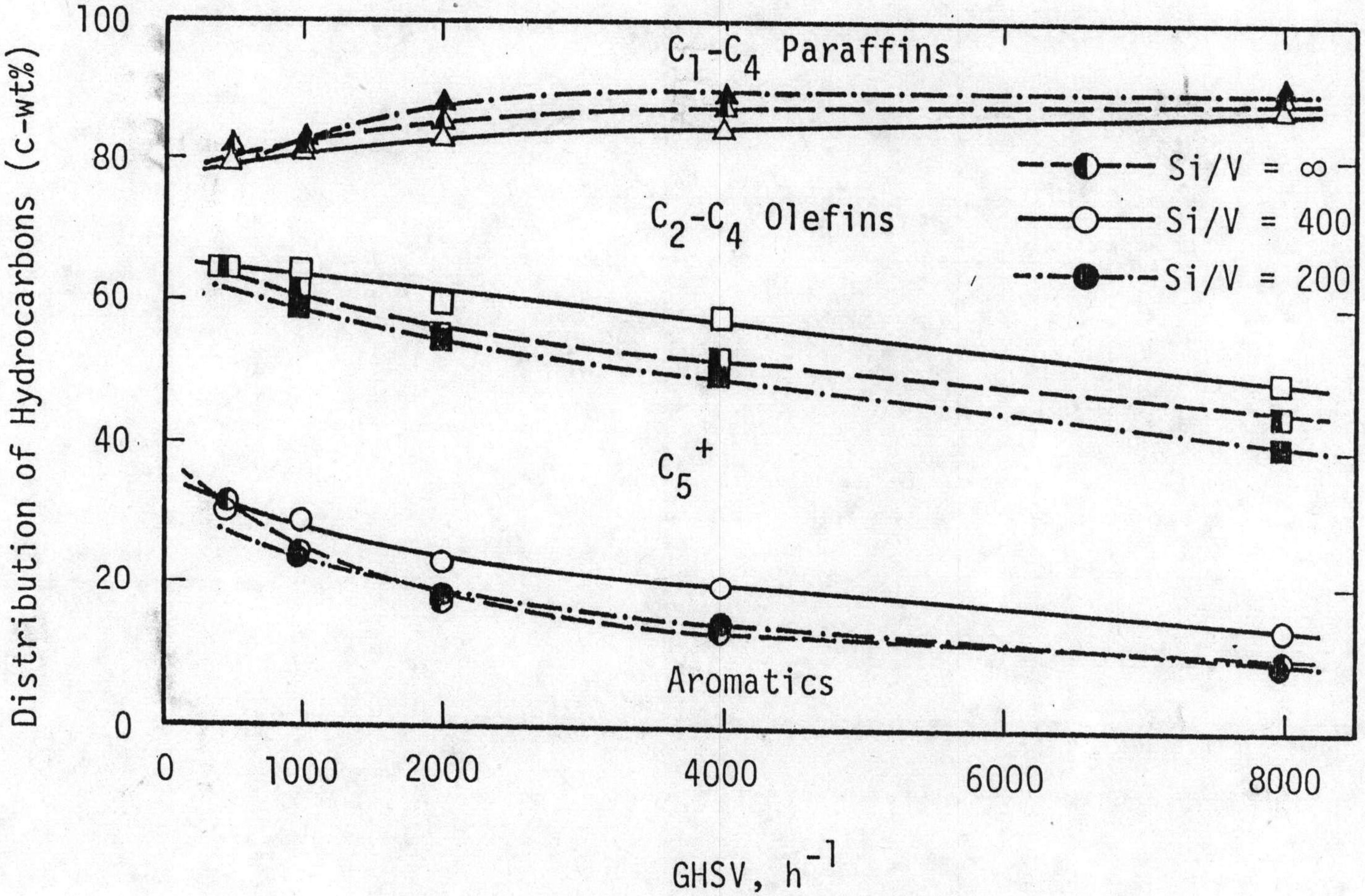

FIGURE 5.3 The effect of space velocity on hydrocarbons distribution
(Reaction condition: T = 300 °C, 80% N_2, 20% MeOH, 1 h on stream)

shows a summary of the effect of SV on catalysts of Si/V ratios 200, 400 and ∞. Methanol conversion on these catalysts were about 100% at SV ranging from 500 to 2000 h^{-1}, and completely converted to hydrocarbons. At SV ranging from 4000 h^{-1}, the conversion decreased and the DME products increased, whereas the hydrocarbon products were decreased. Nevertheless, these catalysts had high activity for MTG reaction even though increasing in SV. Hydrocarbons distribution in Figure 5.3 shows that the olefins of C_2-C_4 increased with increasing in SV, but for aromatics, they decreased gradually. Therefore, gasoline fraction (C_5^+ + aromatics) decreased eventhough C_5^+ increased for ranges of SV between 1000 h^{-1} to 4000 h^{-1} of SV. Then it was expected that space velocity had an effect on the aromatics and C_5^+ formation the reason of this result may be because of the probability the prolongation reaction was decreased by the high space velocity since the contact time of low hydrocarbon molecules on the active site in the pores and cavity channels were reduced.

5.1.3 Effect of Reaction Temperature

The catalyst of Si/V = 1600 and 90 were used for this study at the reaction conditions of SV = 2000 h^{-1}, 80% N_2, 20% MeOH, 1 and 3 h time on stream. From Table 5.4, for catalyst H-Si-V(1600), at 260°C, MeOH conversion was 86.7% in which the main product was DME (74.2%). When the reaction temperature was raised to 280°C, MeOH conversion increased to 98.0% and DME product was about 1.0%, whereas those main products were hydrocarbons. At a temperature ranging from 300 to 370°C, MeOH conversion increased to 100% and MeOH were completely converted to hydrocarbons. Therefore, from the effect of

TABLE 5.4 The effect of temperature on activity and selectivity of catalyst H-Si-V(1600)

Temp., °C	:	260	280	300	330	370
MeOH conv. (%)	:	86.7	98.0	100.0	100.0	100.0
Conv. to H.C (%)	:	25.8	99.2	100.0	100.0	100.0
c-wt% C_2-C_4 (o)	:	92.5	28.0	27.1	32.9	41.1
C_5^+	:	0.2	39.6	39.2	33.2	25.3
Aromatics	:	0.2	18.9	19.8	19.1	18.9

(Reaction condition: SV = 2000 h^{-1}, 80% N_2, 20% MeOH)

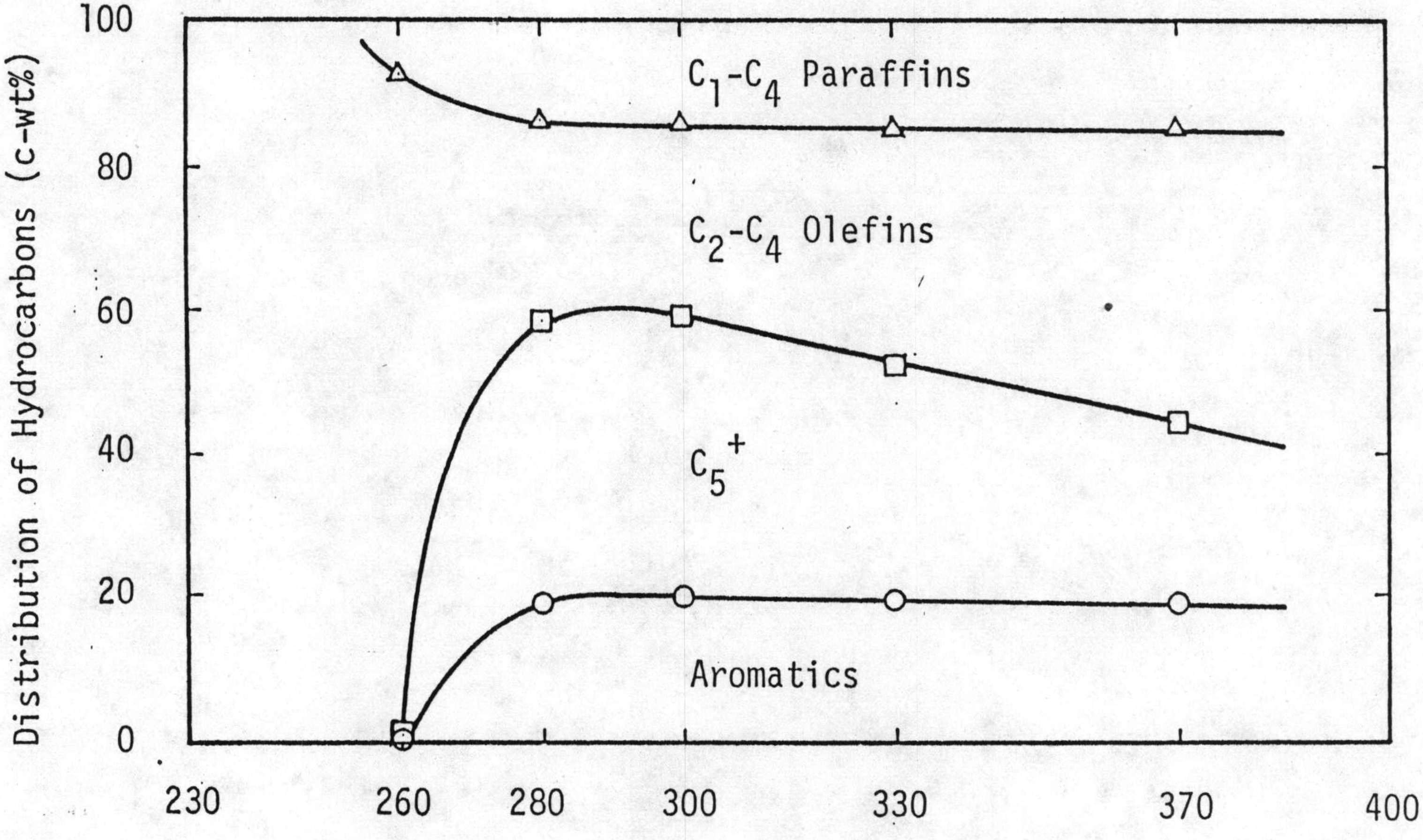

FIGURE 5.4 Effect of temperature on hydrocarbons distribution of the catalyst H-Si-V(1600)
(Reaction condition: SV = 2000 h^{-1}, 80% N_2, 20% MeOH)

reaction temperature, it was also expected that at higher temperature DME was converted to hydrocarbons through the following equation :

$$x\ CH_3OCH_3 \xrightarrow[\text{H-Si-V(200 to } \infty \text{)}]{280^{o}C} 2\ (CH_2)_x \quad + \quad x\ H_2O \qquad (5.1)$$

Figure 5.4 shows that, at a temperature between 300 to 370° C, the selectivity of C_5^+ decreased and that of C_2-C_4 (olefins) increased with increasing temperature. At this temperature range, selectivity of aromatics was maintained at a constant level. Furthermore, C_2-C_4 (olefins) + C_5^+ seemed to be constant. This results shows that there is a relation between decrease of C_5^+ and increase of C_2-C_4 (olefins), i.e. when the reaction temperature was raised C_5^+ were broken to C_2-C_4 (olefin).

From table 5.5, for H-Si-V (90) catalyst, it is shown that at 330° C. MeOH conversion increased from 84.0 to 99.5% and the hydrocarbon products increased from 74.3 to 100.0%. At a temperature range of 360 °C to 420°C, MeOH conversion was 100.0 % and was completely converted to hydrocarbons. Figure 5.5 shows that, at a temperature range from 330°C to 420°C, the selectivity of C_5^+ decreased and that of C_2-C_4 (olefins) and aromatics increased with increasing temperature. For H-Si-V(90), it shows the optimum point of C_2-C_4 (olefins) selectivity at 390°C and for gasoline products at 330°C. Therefore, it should be noted that this catalyst may be suitable to use for low molecular weight olefins synthesis.

5.1.4 Effect of MeOH Concentration

H-Si-V(1600) was used under the conditions of SV = 2000 h^{-1} and 300°C. The effect of MeOH concentration on MeOH conversion was

TABLE 5.5 The effect of temperature on activity and selectivity of catalyst H-Si-V(90)

Temp., :C	300	330	360	390	420
MeOH conv. (%) :	84.0	99.5	100.0	100.0	100.0
Conv. to H.C (%):	74.3	100.0	100.0	100.0	100.0
c-wt% C_2-C_4 (o) :	65.7	43.0	51.2	59.2	53.4
C_5^+ :	18.2	31.2	23.2	14.6	8.6
Aromatics :	9.4	15.4	15.6	17.9	26.9

(Reaction condition: SV = 2000 h^{-1}, 80% N_2, 20% MeOH)

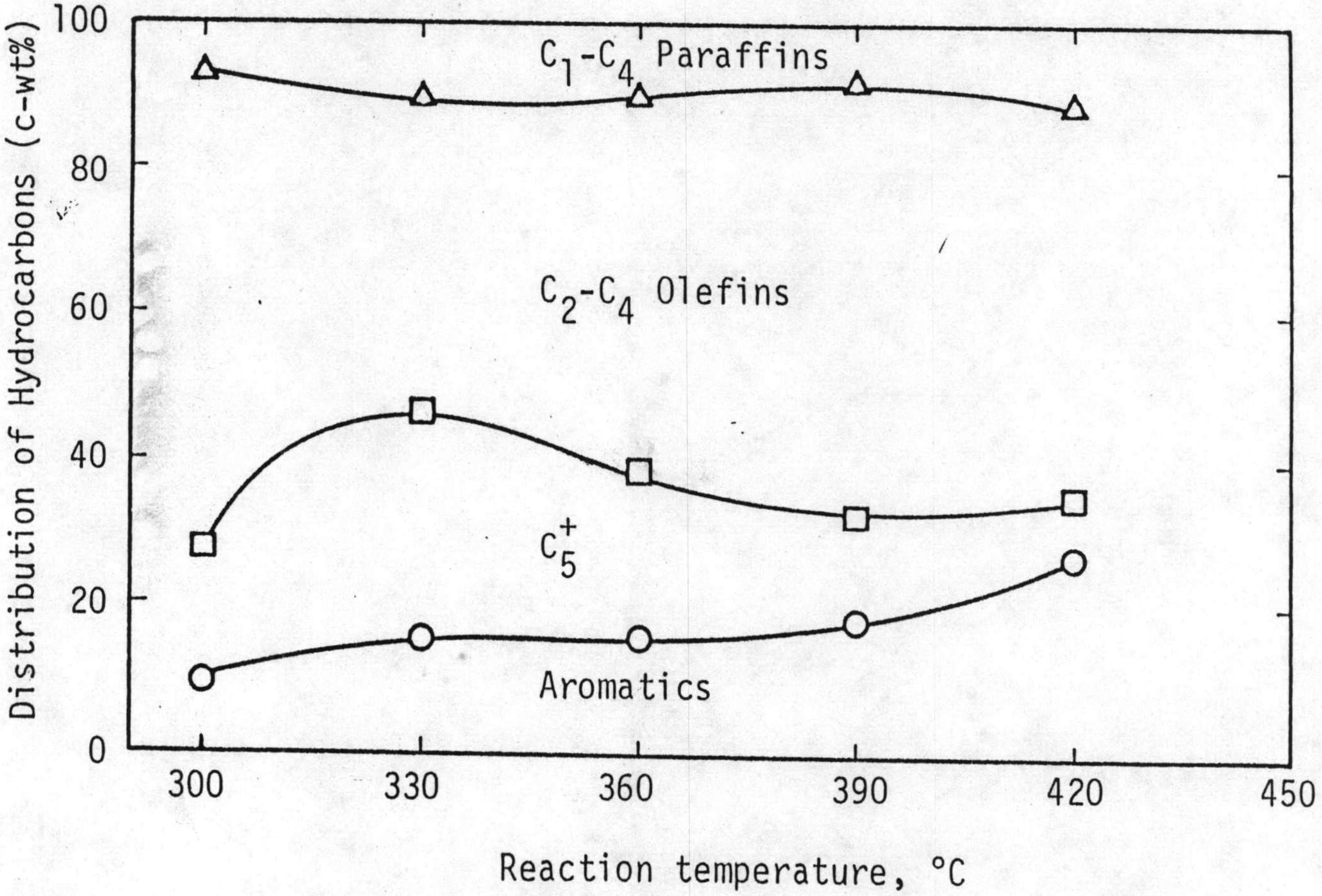

Figure 5.5 Effect of temperature on hydrocarbons distribution of the catalyst H-Si-V(90)
(Reaction condition: SV = 2000 h^{-1}, 80% N_2, 20% MeOH)

TABLE 5.6 The effect of MeOH concentration on activity and selectivity of catalyst H-Si-V(1600)

MeOH conc., % :	5	10	20	40	100
MeOH conv. (%) :	100.0	100.0	100.0	98.2	96.9
Conv. to H.C (%):	100.0	100.0	100.0	99.3	90.9
c-wt% C_2-C_4 (o) :	30.6	26.2	27.1	29.1	32.5
C_5^+ :	33.7	35.9	39.2	39.0	33.2
Aromatics :	20.8	21.8	19.8	18.6	12.8

(Reaction condition: SV = 2000 h^{-1}, T = 300 °C, 80% N_2, 20% MeOH)

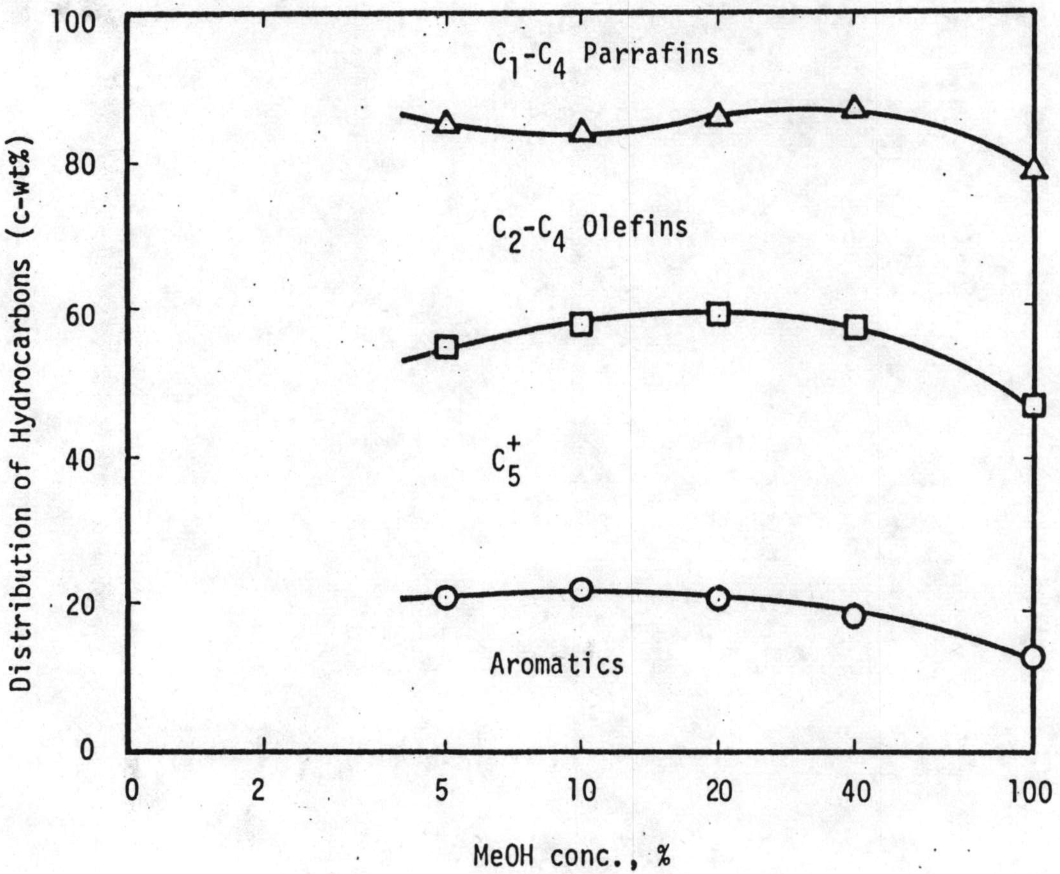

FIGURE 5.6 The effect of MeOH conc. on hydrocarbons distribution of the catalyst H-Si-V(1600)
(Reaction condition: SV = 2000 h^{-1}, T = 300 °C)

not so significant, because with MeOH concentration ranging 5 to 100% Table 5.6, the MeOH conversion were about 97 to 100%. At a MeOH concentration ranging from 5 to 40%, MeOH was see to be completely converted to hydrocarbon products, but for 100% MeOH concentration, hydrocarbon products decreased to 91.0 %. For distribution of hydrocarbons, Figure 5.6, shows that MeOH concentration has a slight effect on the selectivity of C_2-C_4 (olefins). However, the selectivity of aromatics decreased from 18.6% to 12.8% when MeOH concentration increased from 40% to 100%.

5.2 Results of Physical Properties

5.2.1 BET surface area

BET surface area of the catalyst was measured by N_2 adsorption with continuous flow at liquid-nitrogen temperature range by using He as a dilute gas. Table 5.7 shows that BET surface area of H-forms are higher than Na-form through the effect of ion-size, i.e; size of Na ion is bigger than H-ion, then, the pore size, cavities and channel dimentions of catalyst are small in the case of Na-form. THerefore, BET surface area is decreased. A comparison of the results of Table 5.1 and Table 5.7, they show that, for H-form, BET surface area seem to be have an effect on the activity and selectivity of catalyst. Nevertheless, it was found that even Na-form of high Si/V charged ratios,i.e, ∞ to 90, have high BET valve, but the activity of Na-form lower than H-form. Although H-Si-V (∞) and H-Si-V (200) have BET valve higher than H-Si-V (3200, 1600 and 400), but the activity are lower than H-Si-V (3200, 1600 and 400), see also Table 5.3. This means that BET surface area may not be directly related to the activity of the catalyst.

TABLE 5.7 BET surface area of Na-form and H-form of vanadosilicate catalysts

catalysts	BET surface area (m^2/g)
Na-Si-V(∞)	338.4
H-Si-V(∞)	408.8
H-Si-V(3200)	366.3
H-Si-V(1600)	361.4
Na-Si-V(400)	367.6
H-Si-V(400)	399.4
Na-Si-V(200)	331.0
H-Si-V(200)	405.6
Na-Si-V(90)	296.1
H-Si-V(90)	346.3
Na-Si-V(40)	155.3
H-Si-V(40)	171.8

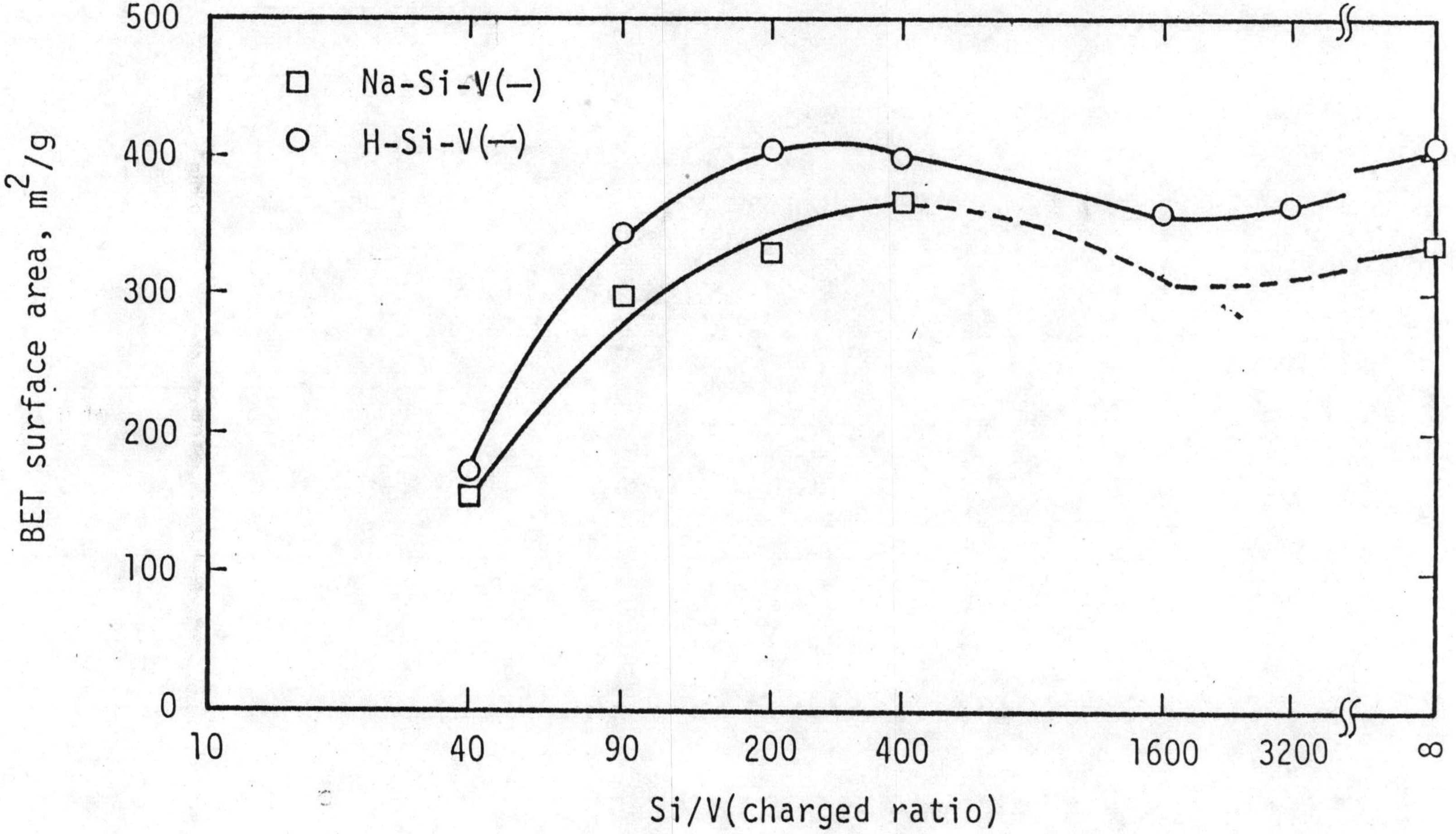

FIGURE 5.7 BET surface area curve of Na-form and H-form of vanadosilicate catalysts

The effect of Si/V charged ratios on BET surface area are not clear at range from ∞ to 200, for a range of Si/V charged ratios less than 200, i.e., 90 and 40, BET surface area decreased since Si/V charged ratio decreased, Figure 5.7.

5.2.2 Atomic Absorption Analysis

The chemical composition of prepared catalysts were analysted by using an atomic absorption equipment. Table 5.8 shows the observed Si/V charged ratios and theoretical Si/V charged ratios. The amount of vanadium in the catalysts are less than the expected value particularly at much high Si/V charged ratio, indicating that vanadium may have been lost in the preparation step of the decant solution and gel formation.

TABLE 5.8 Atomic absorption analysis of vanadosilicate catalysts

Si/V charged ratio	
Theoretical ratio	observed ratio
40	73.7
90	177.7
200	613.0
400	3083.5
1600	trace
3200	trace
∞	∞

5.2.3 X-ray Diffraction

From Figure 5.9, for Si/V charged ratio 40 shows the different

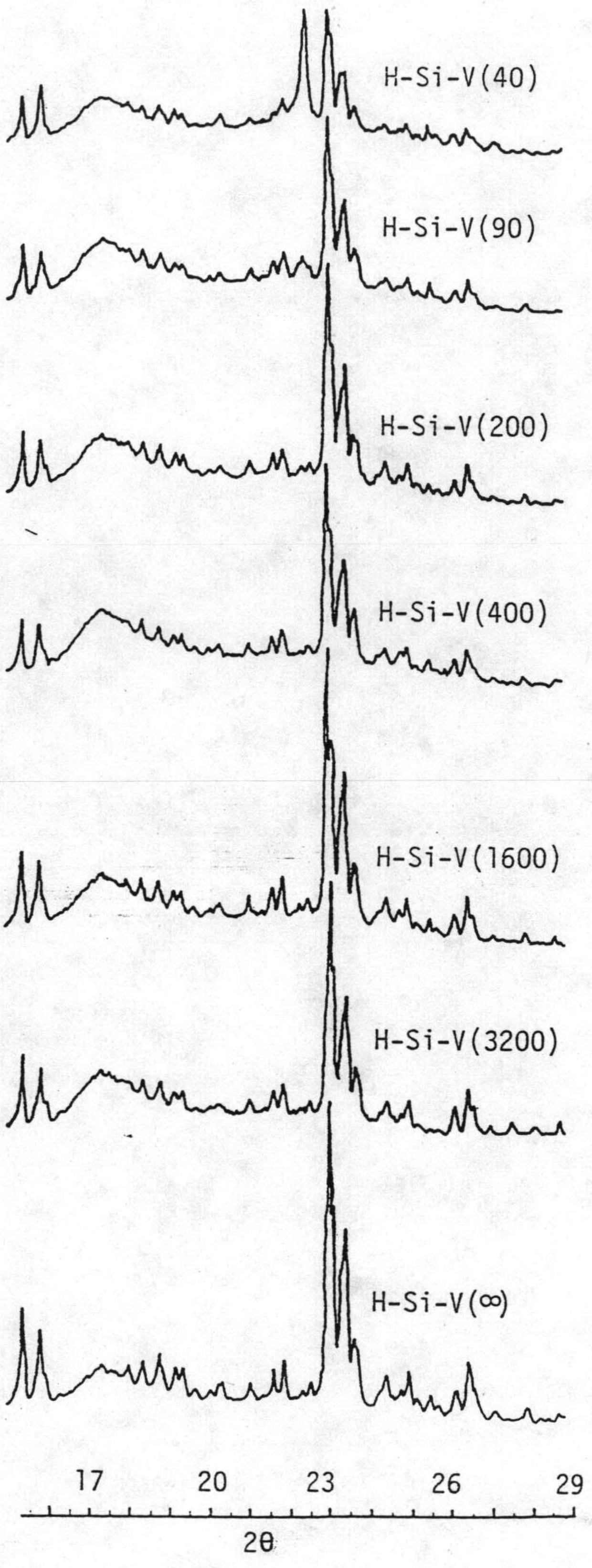

FIGURE 5.9 XRD pattern of vanadosilicate catalysts

principle peak at $2\theta = 23^{\circ}$ from the others Si/V charged ratio, this peak was expected to be the vanadium oxide peak. For Si/V charged ratio ranging from 90 to ∞ , we had a similarity in XRD pattern. Therefore, it was expected that at a range of Si/V charged ratio Higher than 40, i.e, from 90 to nearly ∞ , vanadium ion plays a role with silicon ion to form the crystals. Hence, at suitable amount of vanadium, it can be shown that the MTG reaction can be improved, i.e. activity and selectivity. It is necessary to remark that for Si/V charged ratio range of 200 to 40, after the ion-exchange from Na-from to H-form, the colour of catalysts become different from the others Si/V charged ratio and others zeolite type catalysts, where it has pale yellow colour for Si/V 90 and deep yellow for 40, which is different from the white colour for the other charged ratio and zeolite types catalysts. Of course, this phenomena might play a relative effect on activity, and others physical properties of catalyst.

5.2.4 Acidity of Catalysts

From Figure 5.10, at range of temperature from 300 to 600 °C, it can be shown that Si/V charged ratio ranging from ∞ to 200 have desorption areas of NH_3 which are greater than Si/V charged ratio 90 and 40, i.e. at this temperature range, Si/V charged ratio from ∞ to 200 have higher acidity than Si/V charged ratio 90 and 40. Therefore, it can be shown that an increase in acidity property of vanadosilicate catalyst result to increase in catalyst activity.

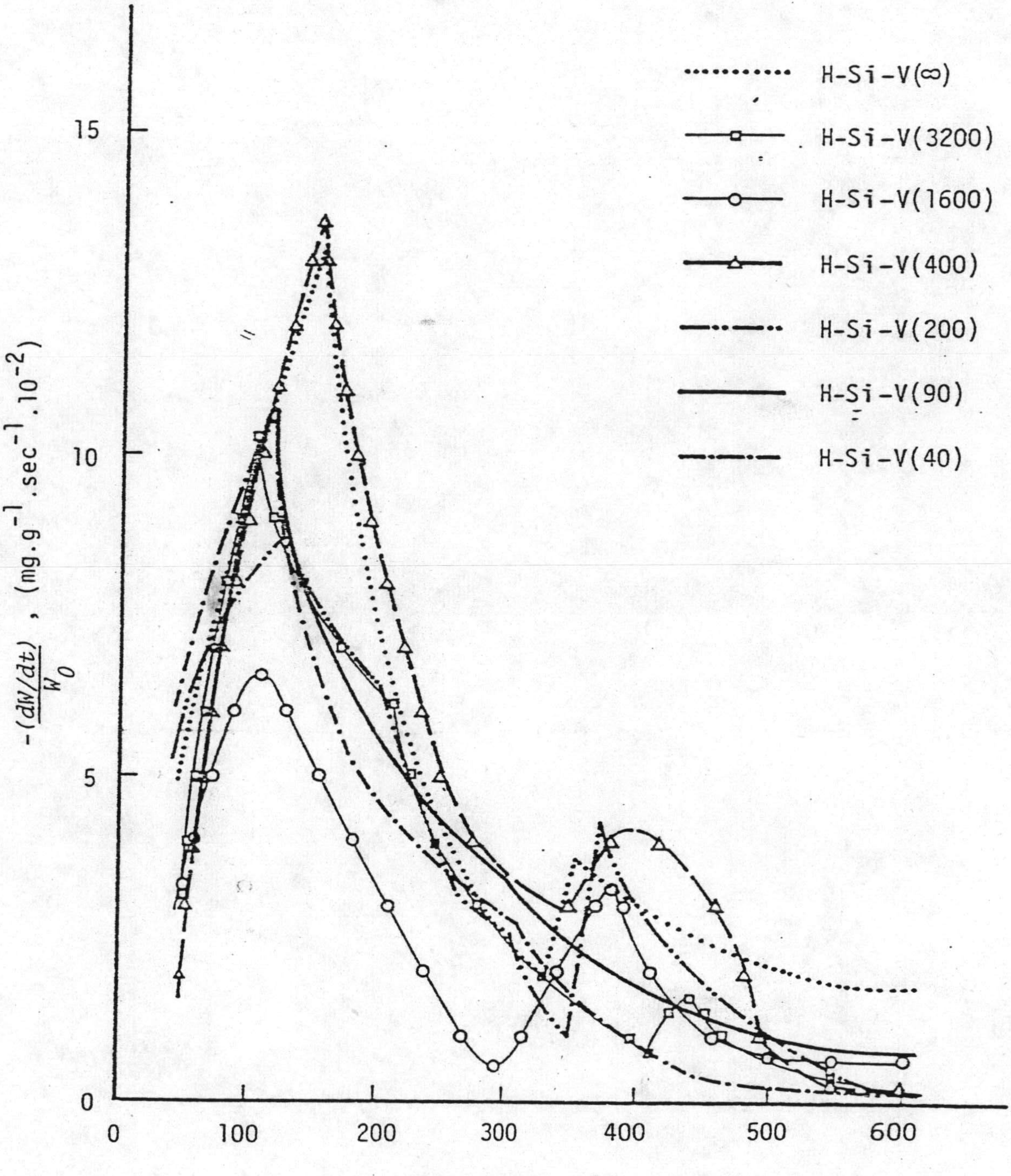

FIGURE 5.10 TPD(NH_3) curve of vanadosilicate catalysts

5.2.5 Scanning Electron Microscope (SEM)

Figure 5.11 Scanning electron micrographs for the Si/V charged ratio ∞ at magnifications from 3,000 to 10,000

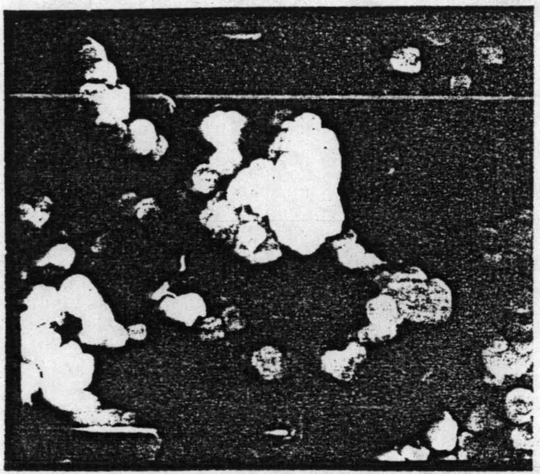
1x3,000

Figure 5.11-1

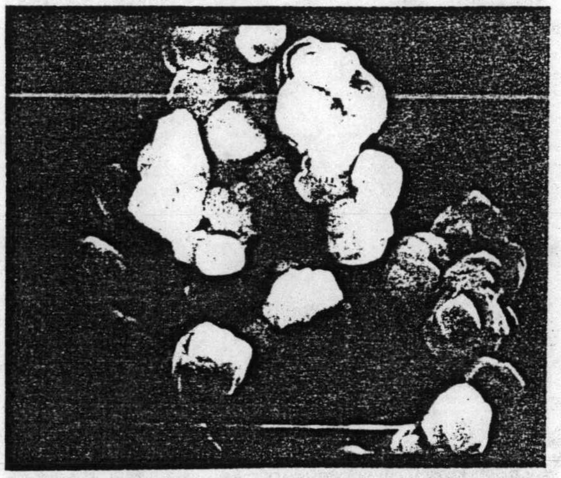
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Figure 5.11-2

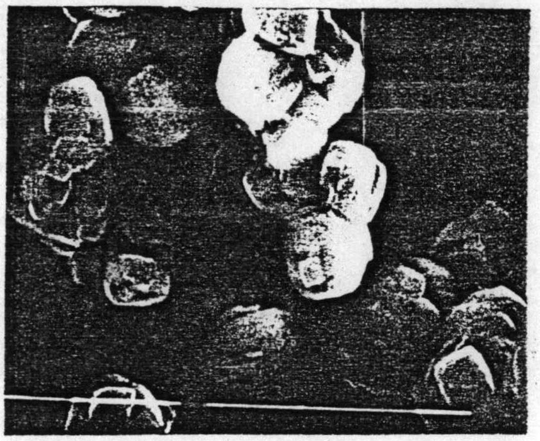
1x7,000

Figure 5.11-3


1x10,000

Figure 5.11-4

Figure 5.12 Scanning electron micrographs for the Si/V charged ratio 200 at magnifications from 500 to 7,000

1x500

Figure 5.12-1

1x3,000

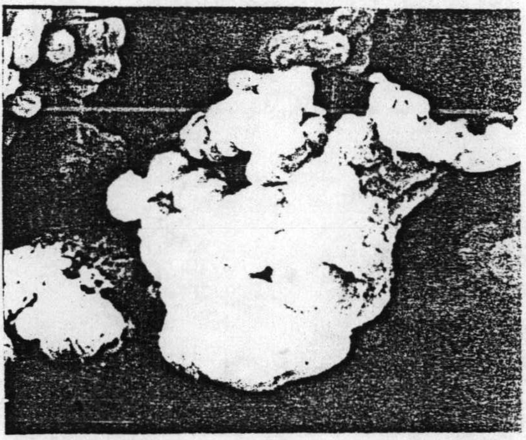

Figure 5.12-2

1x7,000

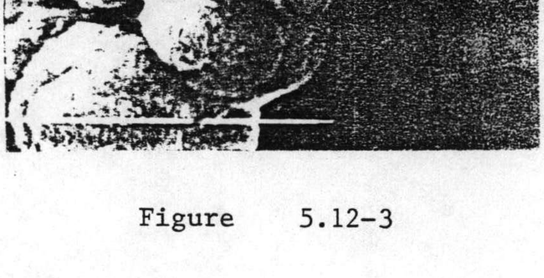

Figure 5.12-3

Figure 5.13 Scanning electron micrographs for the Si/V charged ratio 90 at magnifications from 5,000 to 10,000

1x5,000

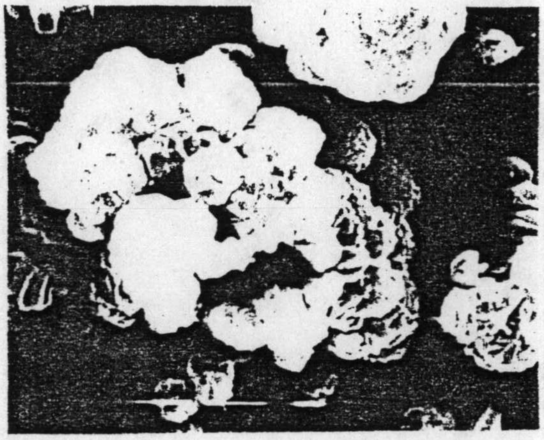

Figure 5.13-1

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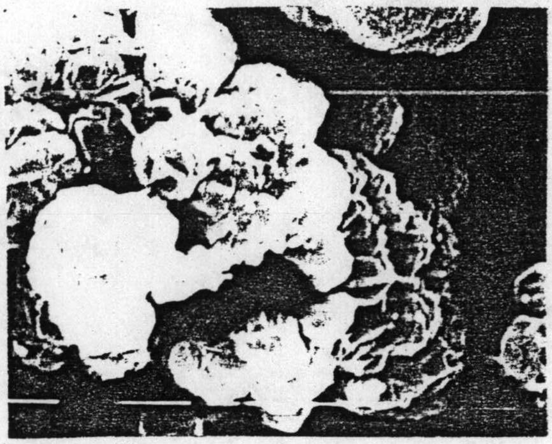

Figure 5.13-2

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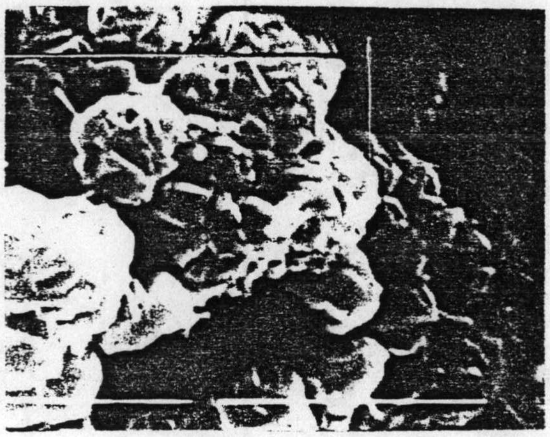

Figure 5.13-3

Figure 5.14 Scanning electron micrographs for the Si/V charged ratio 40 at magnifications from 3,000 to 10,000

1x3,000 1x5,000

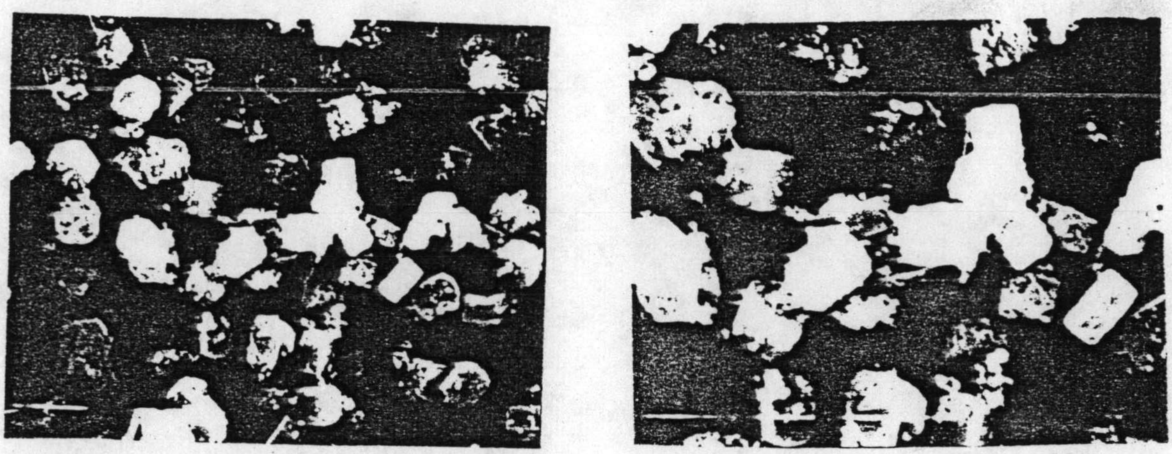

Figure 5.14-1 Figure 5.14-2

1x7,000 1x10,000

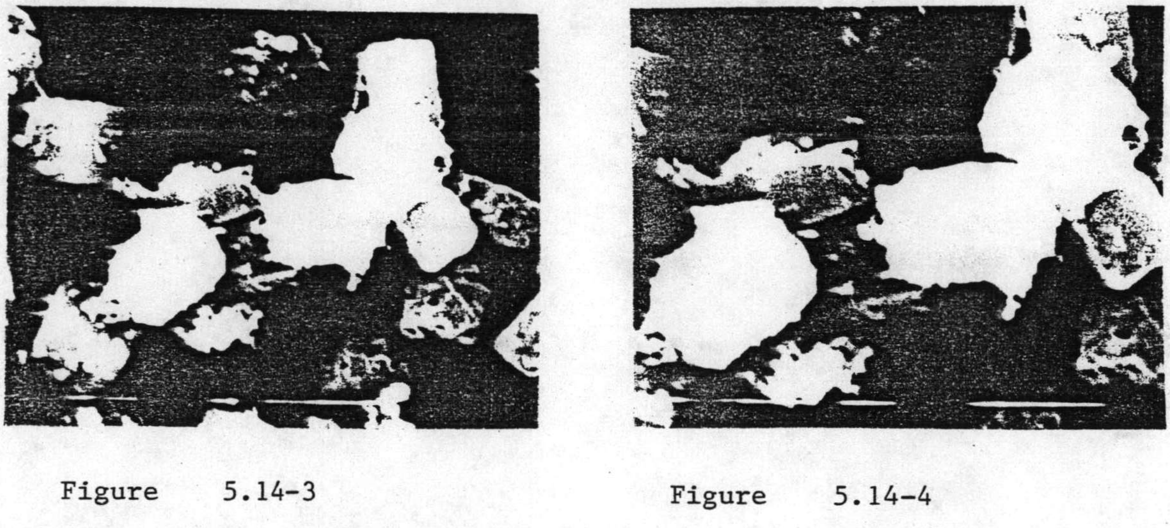

Figure 5.14-3 Figure 5.14-4

Figures 5.11, 5.12, 5.13 and 5.14, show that the Si/V charged ratios ∞ , 200 and 90 give only slightly different outer shapes and characters, where as those for the Si/V charged ratio of 40 are extremely different from the former, having crystals with a cubic-hexagonal shape. The crystals are not agglomerated when compared with the Si/V charged ratios ∞ , 200 and 90. Therefore, the pore sizes, cavities and channel dimensions of this catalyst may be the reason for its very low activity and unsuitibility for the MTG reaction.