

## **CHAPTER V**

### **RESULTS AND DISCUSSIONS**

This thesis deals with studies on isomerization of n-hexane over Beta zeolite. The results and discussions are as follows.

#### **5.1 Characterization of the Catalysts.**

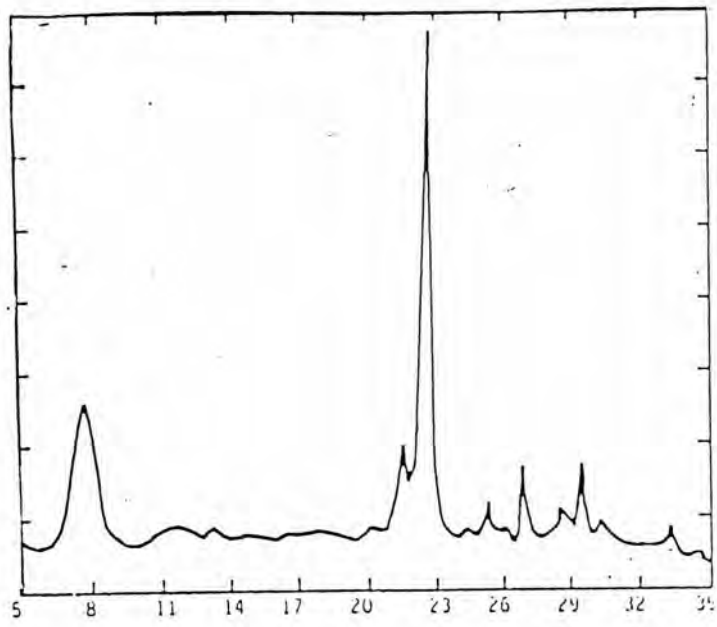
The catalysts were characterized by XRD patterns, BET surface area, morphology, chemical composition, and acidity.

##### **5.1.1 X-Ray Diffraction Patterns**

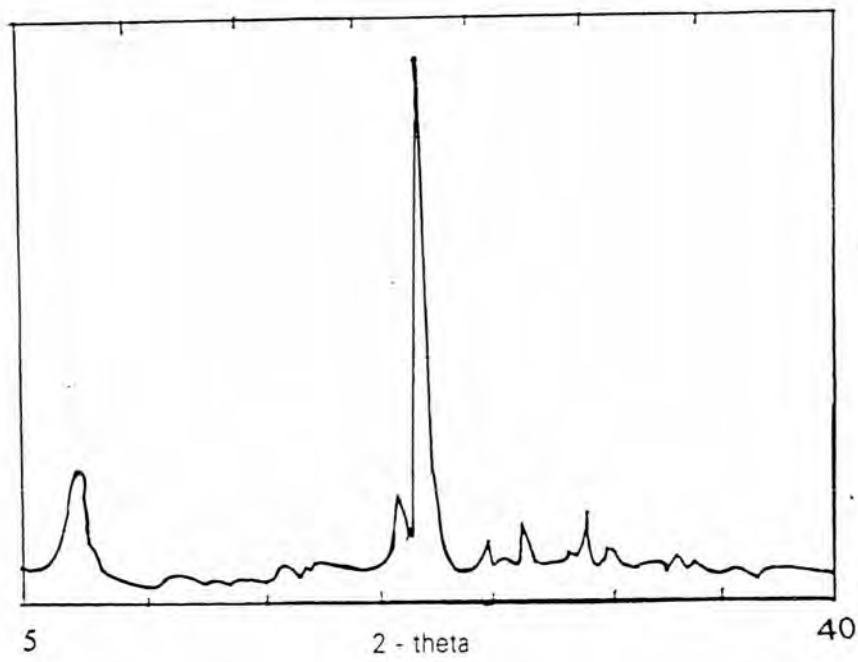
The X-ray diffraction patterns for the catalysts prepared are shown in Figure 5.1. The patterns of catalysts, prepared in this laboratory, were corresponding well with those reported in the literature [22,52]. This indicates that all the prepared catalysts have the same structure as Beta zeolite. It shows that a little amount of other metals added into the framework of catalysts does not significantly change the main structure of these zeolites.

##### **5.1.2 BET Surface Area**

BET Surface areas of the catalysts are shown in Table 5.1. Beta zeolite in different form of Na, NH<sub>4</sub>, and H-form had BET surface area in approximately the

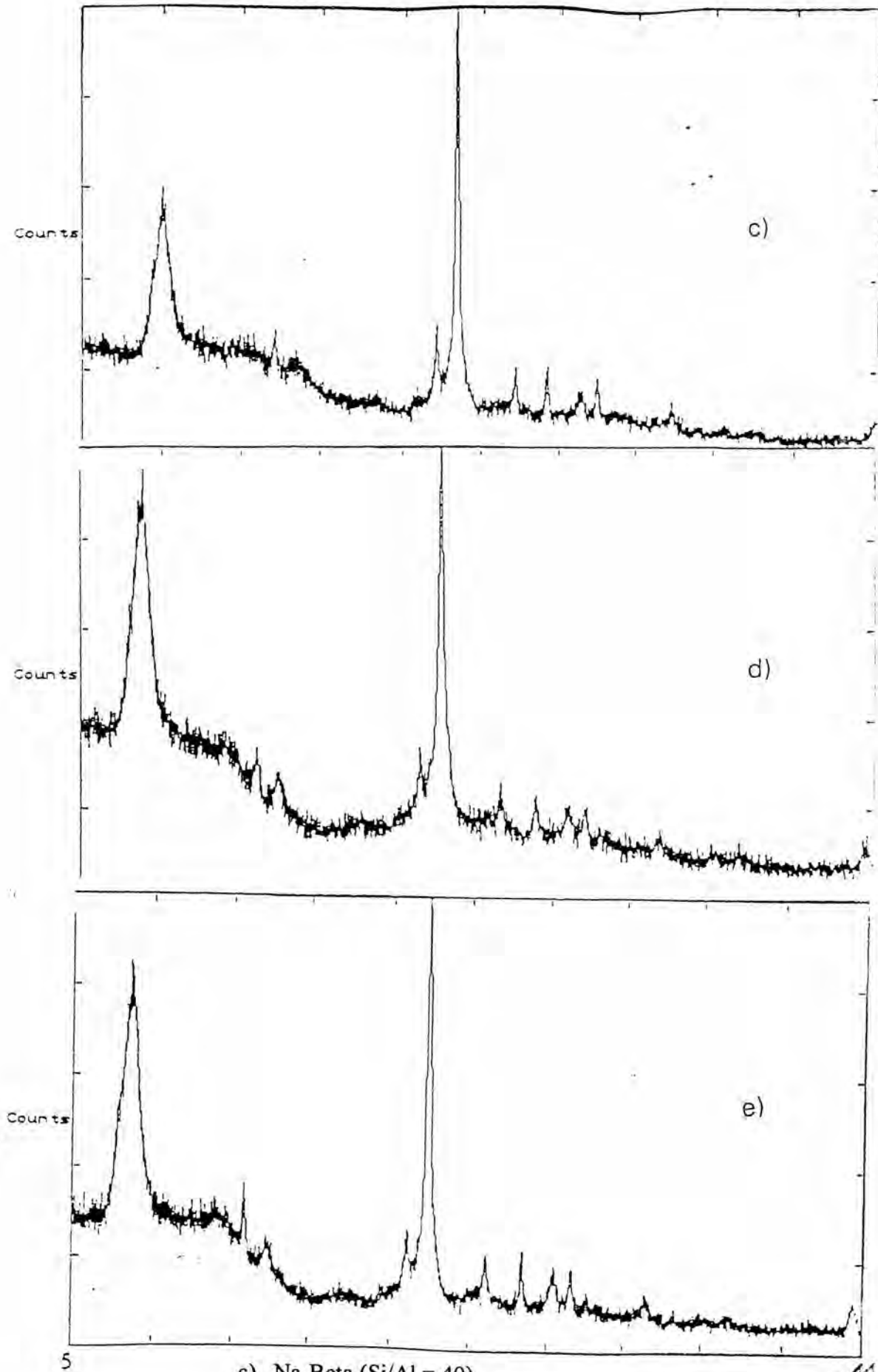


a) Beta zeolite [22]



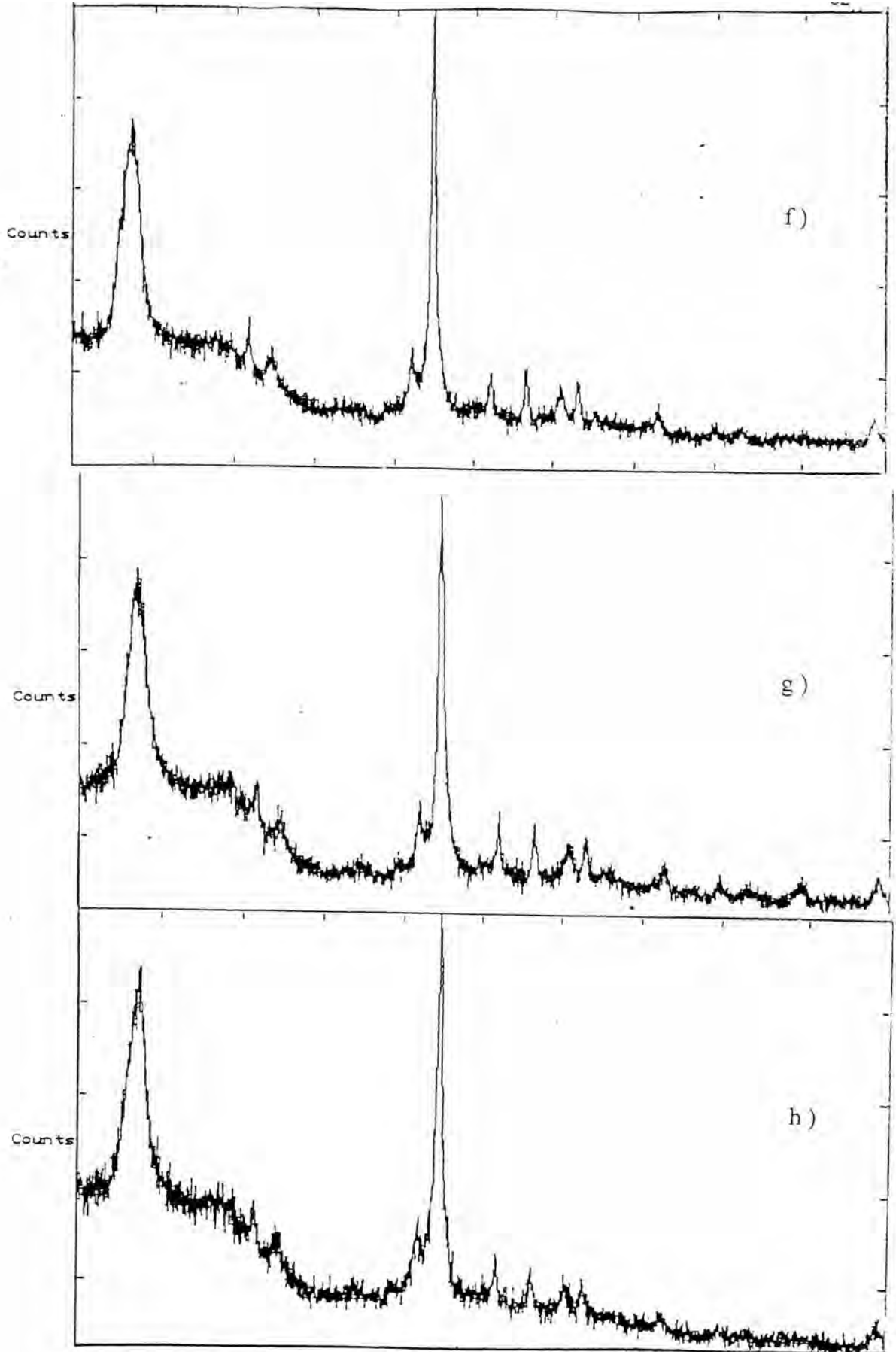
b) Beta zeolite [52]

Figure 5.1 X-ray diffraction patterns of the catalysts.



- c) Na-Beta (Si/Al = 40)
- d) NH<sub>4</sub>-Beta (Si/Al = 40)
- e) H-Beta (Si/Al = 40)

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

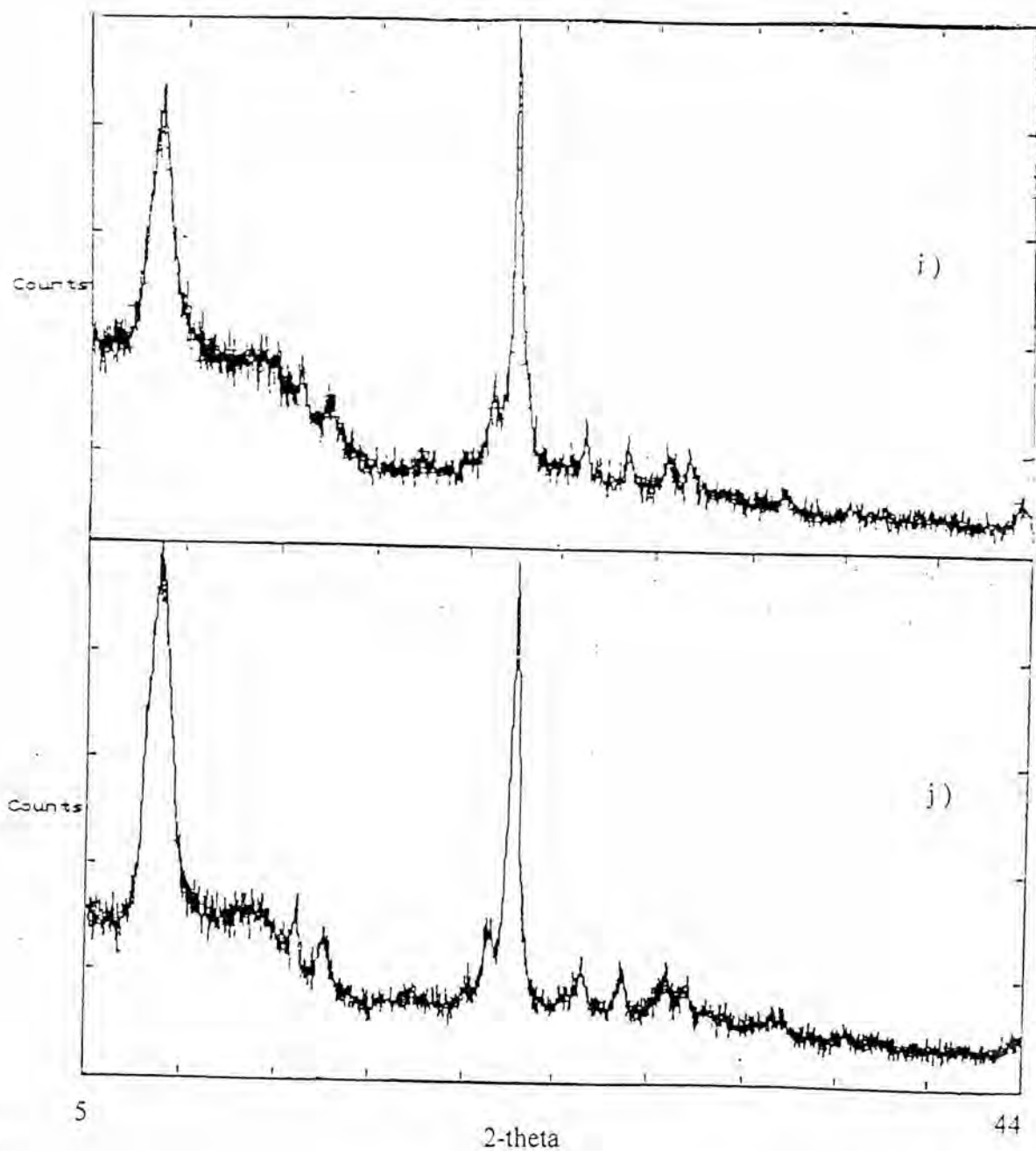


5 f) Pt/H-Beta (Si/Al = 25, 0.6%wt Pt by ion exchange)

g) Pt/H-Beta (Si/Al = 40, 0.6%wt Pt by ion exchange)

h) Pt/H-Beta (Si/Al = 50, 0.6%wt Pt by ion exchange)

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



i) Pt/H-Beta (Si/Al = 40, 0.1%wt Pt by ion exchange)  
j) Pt/H-Beta (Si/Al = 40, 1.0%wt Pt by ion exchange)  
**Figure 5.1** X-ray diffraction patterns of the catalysts (continued).

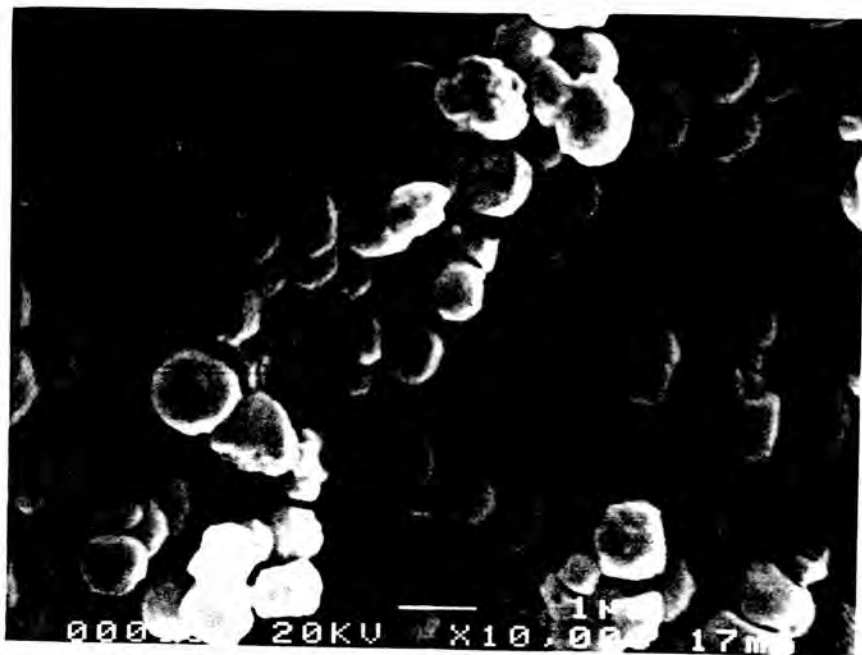
same range. However, it has been found that further modification of Beta zeolite by Pt ion-exchange caused slightly less BET surface area.

**Table 5.1** BET surface area of the catalysts.

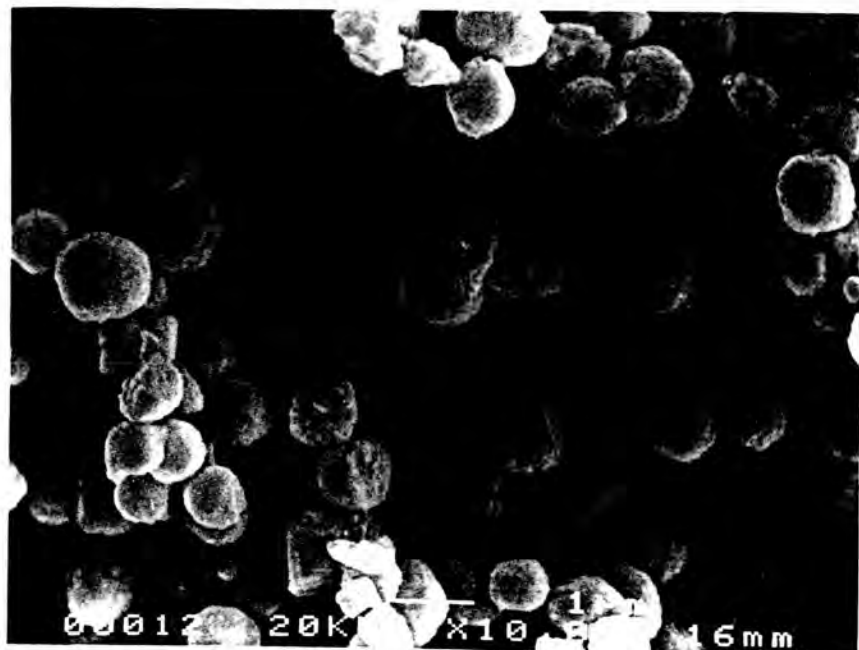
Catalyst	BET surface areas (m <sup>2</sup> /g of catalyst)
1. Na-Beta (Si/Al = 40)	614.0
2. NH <sub>4</sub> -Beta (Si/Al = 40)	610.3
3. H-Beta (Si/Al = 40)	605.7
4. Pt/H-Beta (Si/Al = 25, 0.6 wt%Pt, by ionexchange)	516.6
5. Pt/H-Beta (Si/Al = 40, 0.1 wt%Pt, by ionexchange)	568.3
6. Pt/H-Beta (Si/Al = 40, 0.6 wt%Pt, by ionexchange)	575.2
7. Pt/H-Beta (Si/Al = 40, 1.0 wt%Pt, by ionexchange)	581.4
8. Pt/H-Beta (Si/Al = 50, 0.6 wt%Pt, by ionexchange)	498.2

### 5.1.3 Morphology

Scanning Electron Microscope (SEM) photographs of the prepared catalysts are shown in Figure 5.2. As shown, all the catalysts were composed of roughly crystallized spherical particles. It was observed that the size of the catalyst crystal depends on the Si/Al molar ratio in the zeolite composition. The smaller size of crystal was obtained for the higher of Si/Al molar ratio in zeolite. And this indicates that metal loading does not significantly affect the shape of crystals.

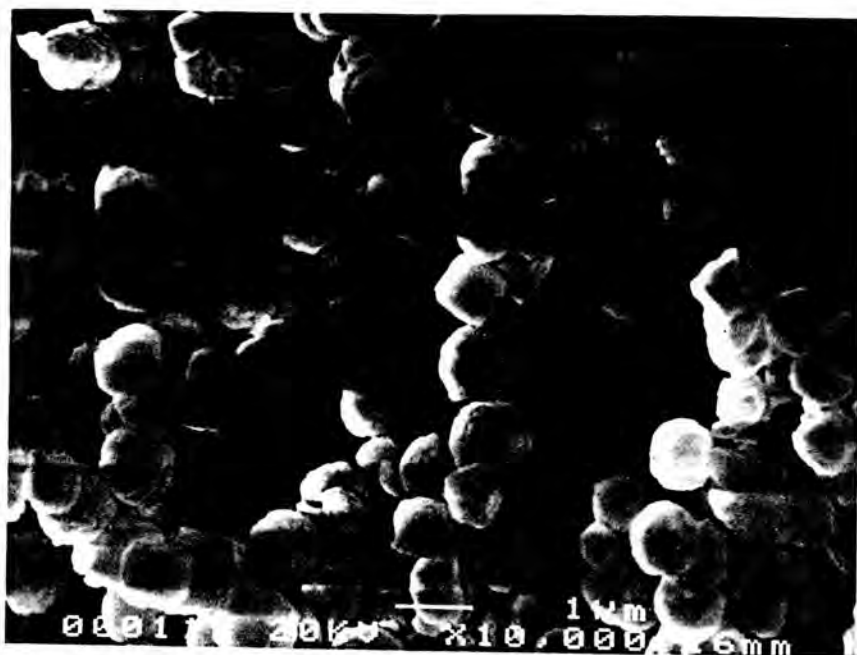


a) Na-Beta (Si/Al = 40)

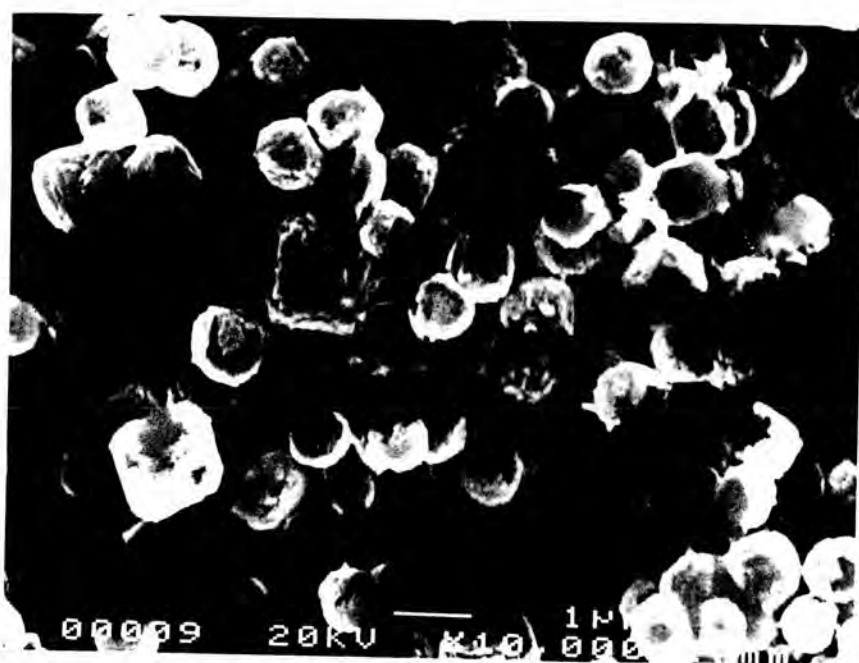


b) NH<sub>4</sub>-Beta (Si/Al = 40)

**Figure 5.2** SEM photographs of the catalysts.



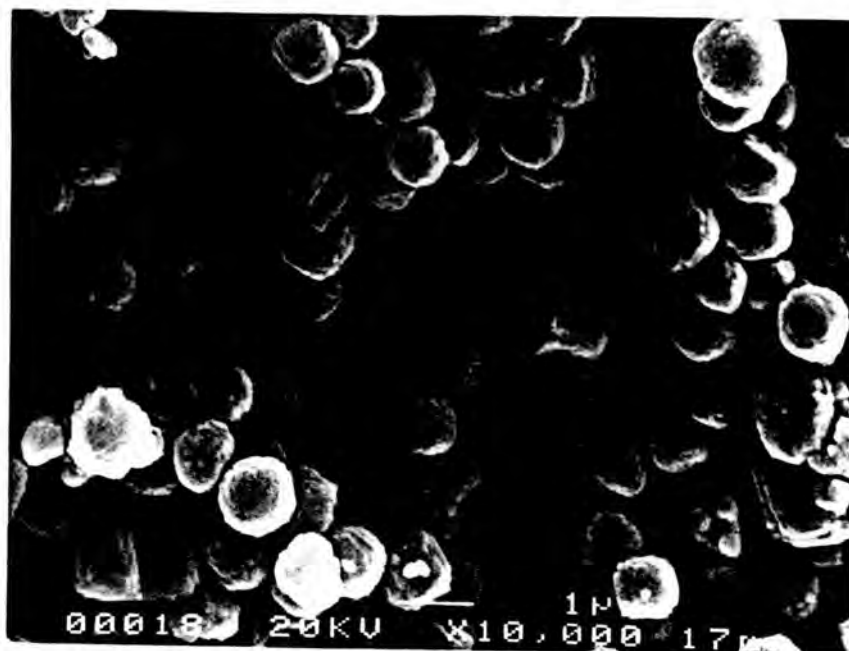
c) H-Beta (Si/Al = 40)



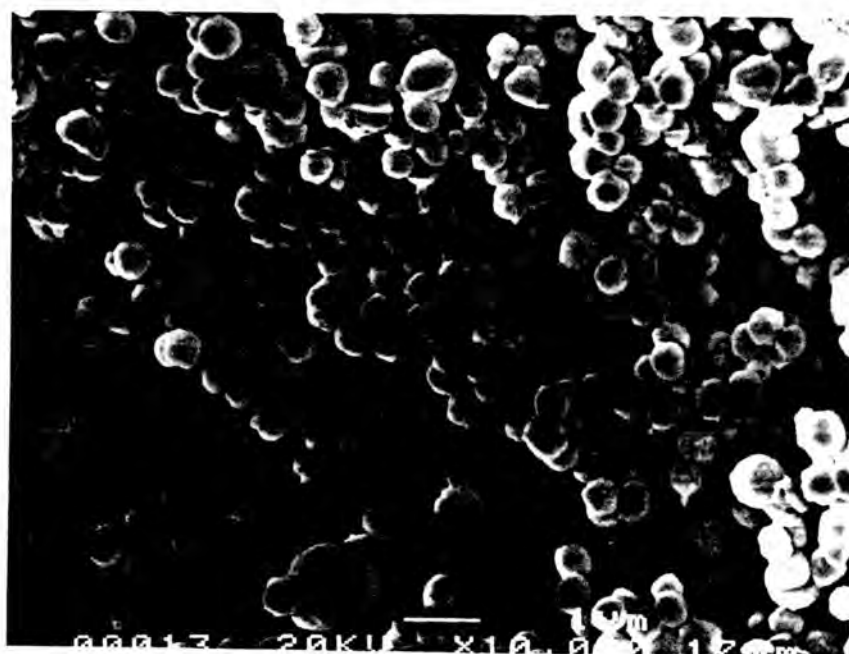
d) Pt/H-Beta (Si/Al = 25, 0.6%wt Pt by ion exchange)

**Figure 5.2** SEM photographs of the catalysts(continued).



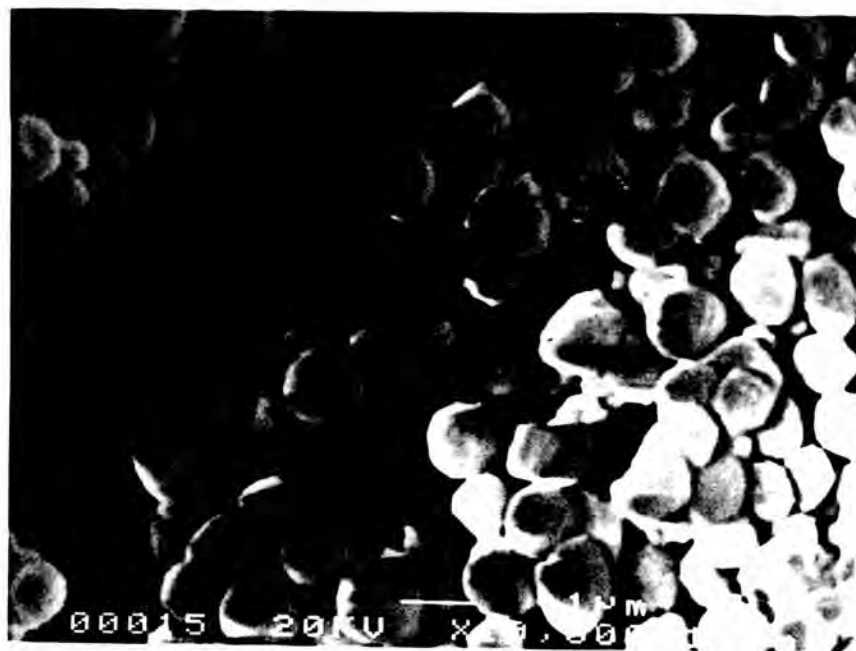


e) Pt/H-Beta (Si/Al = 40, 0.6%wt Pt by ion exchange)

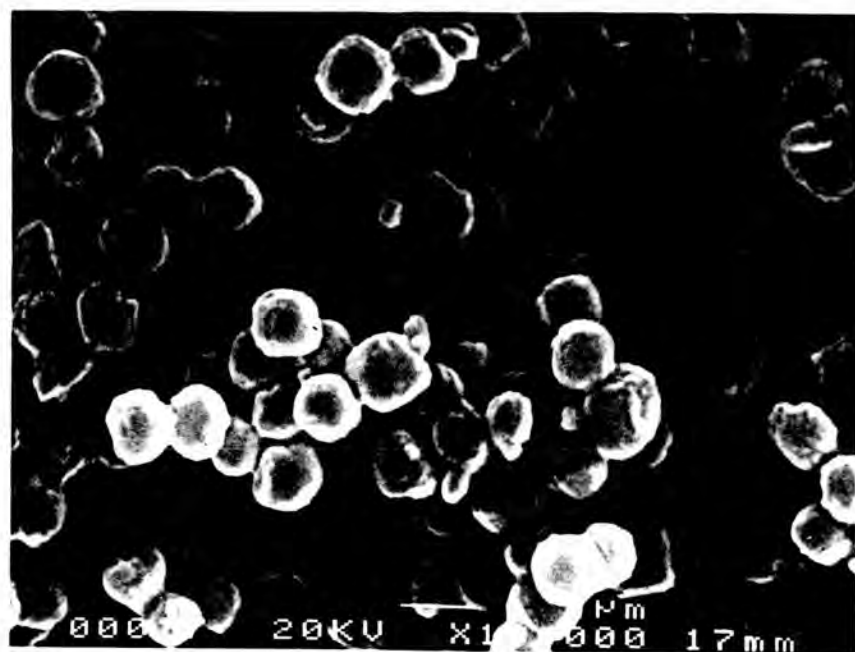


f) Pt/H-Beta (Si/Al = 50, 0.6%wt Pt by ion exchange)

**Figure 5.2** SEM photographs of the catalysts(continued).



g) Pt/H-Beta (Si/Al = 40, 0.1%wt Pt by ion exchange)



h) Pt/H-Beta (Si/Al = 40, 1.0%wt Pt by ion exchange)

**Figure 5.2** SEM photographs of the catalysts(continued).

#### 5.1.4 Chemical Composition

The results of quantitative analysis by XRF of silicon and aluminium in the synthesized crystals are shown in Table 5.2.

**Table 5.2** Si/Al content in catalysts.

Si/Al molar ratio of Pt/H-Beta	Si/Al molar ratio observed
30	24.27
50	38.00
80	47.58

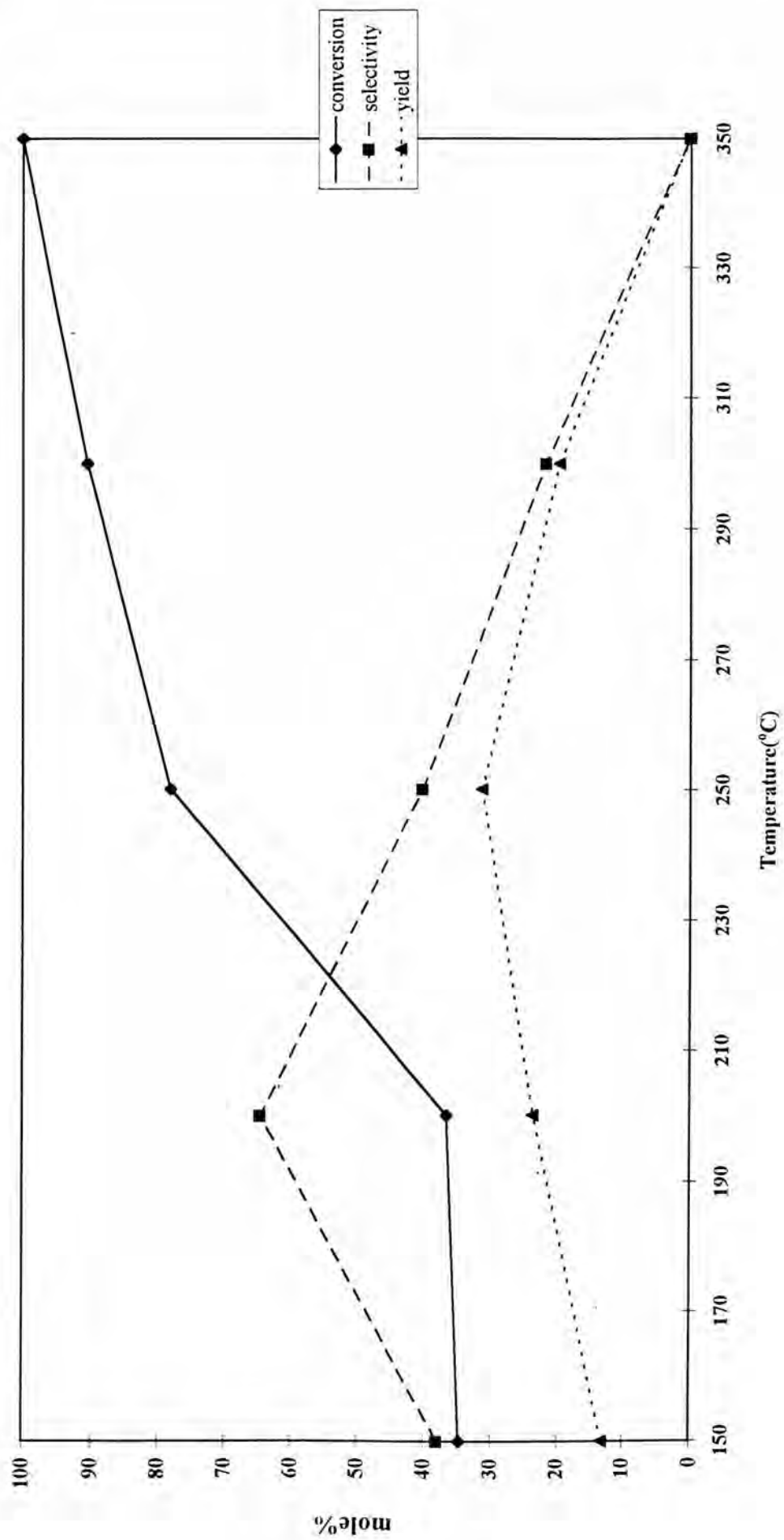
#### 5.1.5 Acidity

The TPD profiles of desorbed ammonia from the prepared catalysts are shown in Figure 5.3. The profile is composed of two main peaks. The low temperature peak representing the weak acid sites was found around 110-300°C and the high temperature peak representing the strong acid sites was found around 350-480°C. It has been found that Pt/H-Beta (40), loaded by ion exchange, contained the highest amount of strong acid sites with moderate weak acid sites.

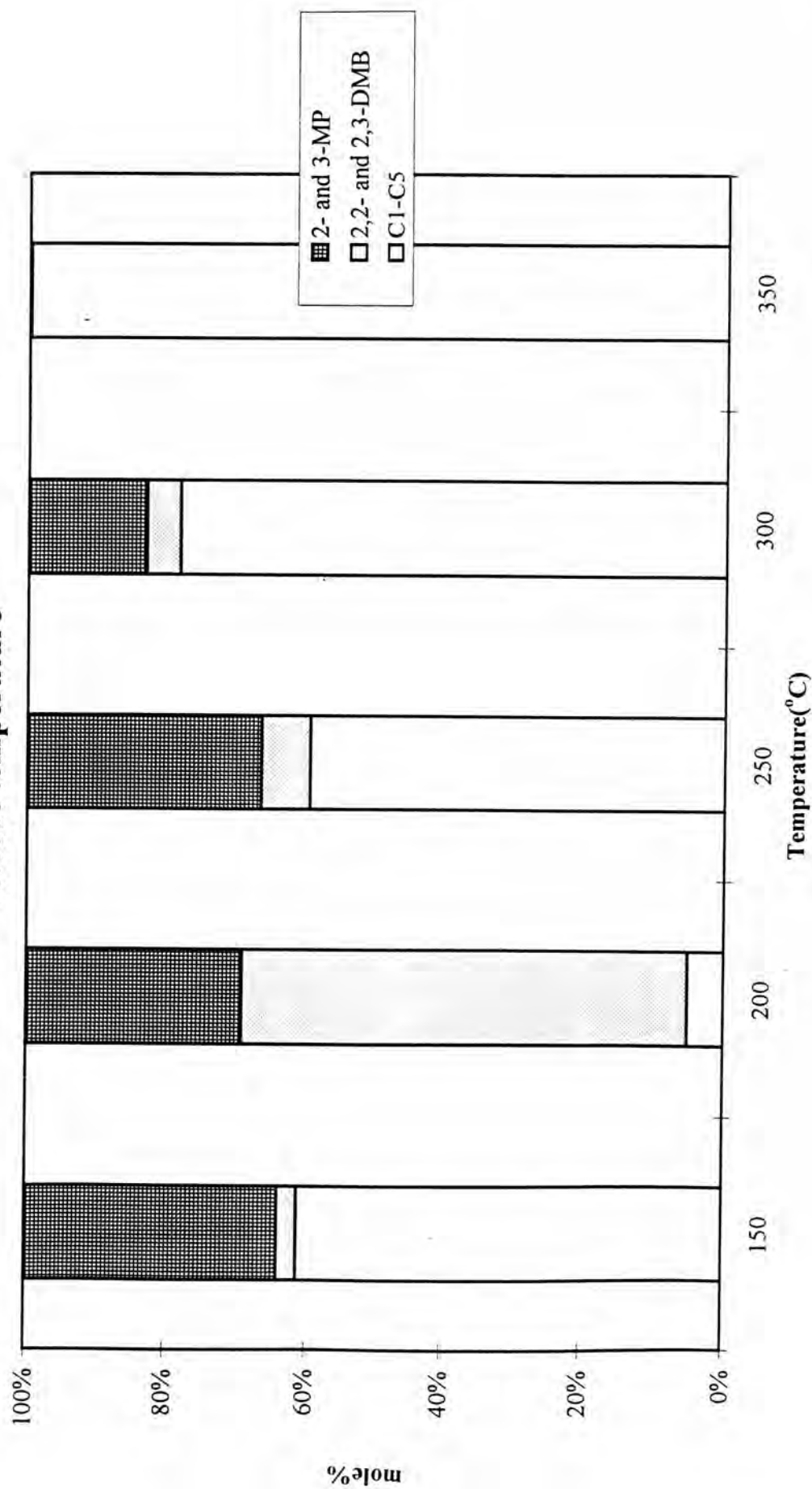
#### 5.2 Effect of reaction temperature on the conversion and product selectivity of n-hexane isomerization.

The reaction temperatures for n-hexane conversion were 150, 200, 250, 300 and 350°C. The reaction was carried out over Pt/H-Beta (Si/Al = 40, 0.6% wt Pt

**Figure 5.4** n-Hexaneisomerization on Pt/H-Beta(Si/Al = 40, 0.6%wt Pt by ion exchange) at GHSV 650 h<sup>-1</sup>, and TOS 20 min with various temperature



**Figure 5.5 Product distribution of n-hexane isomerization on Pt/H-Beta (Si/Al = 40, 0.6%wt Pt by ion exchange) at GHSV 650 h-1, and TOS 20 min with various temperature**



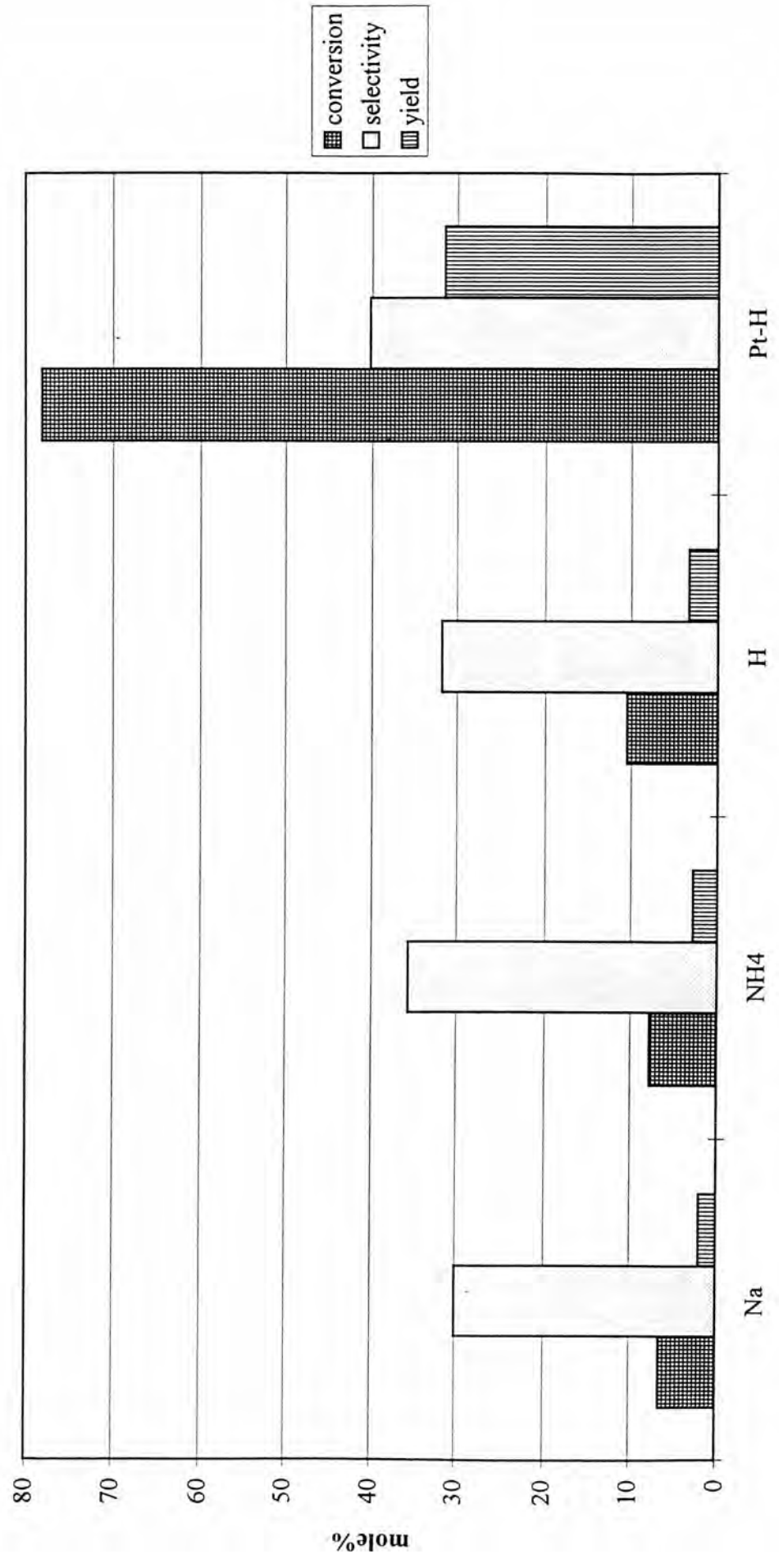
loaded by ion exchange) at GHSV of  $650 \text{ h}^{-1}$  for 20 min on stream by using hydrogen as carrier gas.

The conversion and selectivity of n-hexane isomerization are shown in Figures 5.4 and 5.5. It has been found that the hexane conversion increased with the increasing temperature and as high as 99.98% conversion was obtained at  $350^\circ\text{C}$ . The isomers selectivity(2,2-DMB, 2,3-DMB, 2-MP, 3-MP) was high at the reaction temperature of  $200\text{-}250^\circ\text{C}$ . Concerning both the conversion and selectivity, the maximum yield was obtained at reaction temperature of  $250^\circ\text{C}$ . At temperature higher than  $250^\circ\text{C}$ , much  $\text{C}_1\text{-C}_5$  amount was formed probably due to the catalytic cracking.

### **5.3 Effect of form of catalysts on the conversion and selectivity of n-hexane isomerization.**

From Figure 5.6, the conversion and selectivity are compared when using Beta zeolite in different form as the catalysts for hexane isomerization. The reaction was carried out at  $250^\circ\text{C}$ , GHSV  $650 \text{ h}^{-1}$  by using hydrogen as carrier gas. It has been found that Beta zeolite without Pt showed considerably low activity, though H-Beta gave the relatively highest yield. With the presence of Pt loaded by ion exchange, Pt/H-Beta exhibited much higher conversion and selectivity and yield of desired products was greatly enhanced. The result revealed that platinum plays an active role on the catalyst activity of hexane isomerization[2, 22, 53]. The effect of platinum will be discussed in detail later.

Figure 5.6 n-Hexane isomerization on catalysts at 250 °C, GHSV 650 h<sup>-1</sup>, and TOS 20 min



#### **5.4 Effect of GHSV on the conversion and selectivity of n-hexane isomerization.**

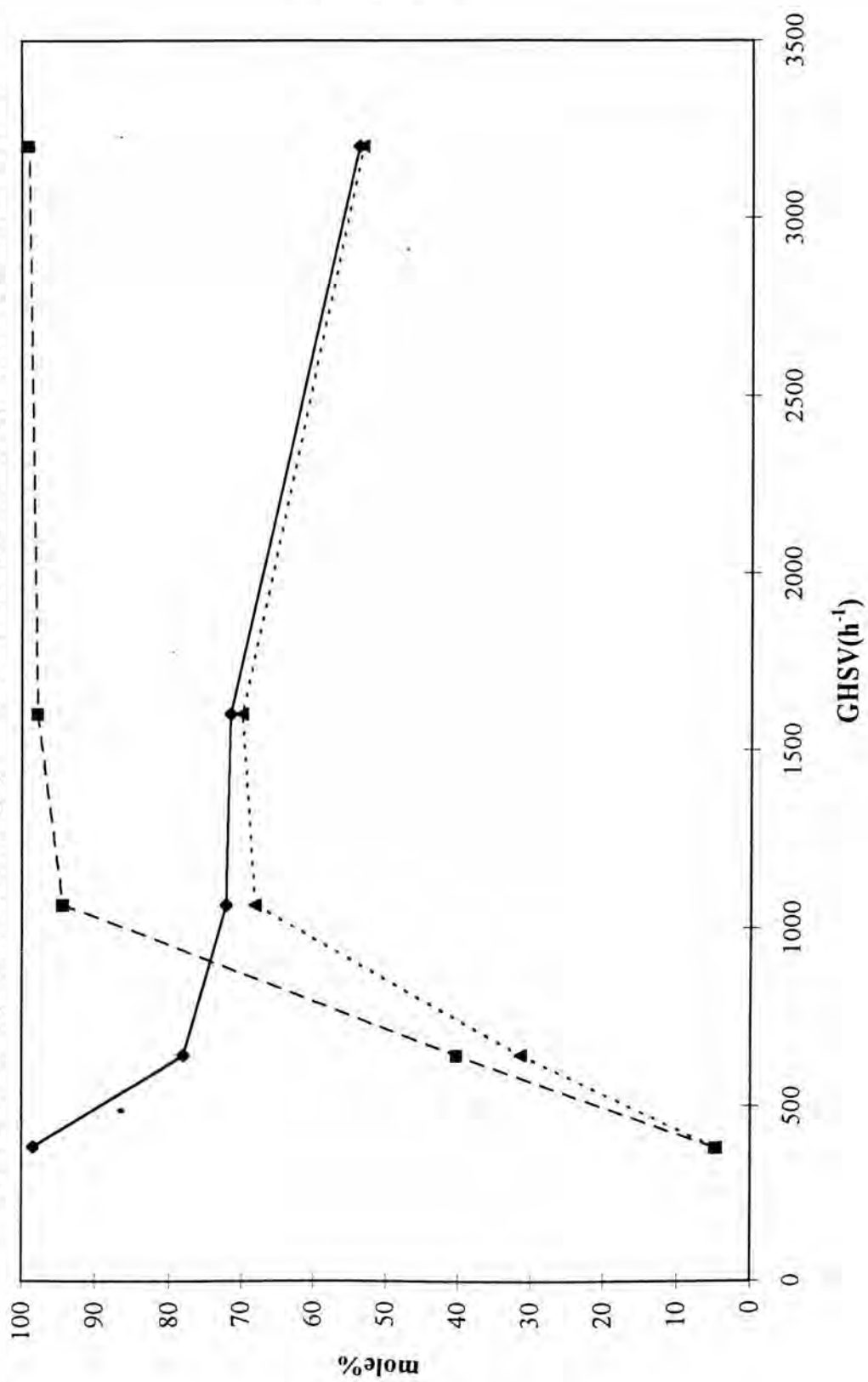
Figure 5.7 shows the conversion and selectivity of n-hexane isomerization over Pt/H-Beta (Si/Al = 40, 0.6% wt Pt loaded by ion exchange) which space velocities (GHSV) varying from 400 to 3200 h<sup>-1</sup>. The reaction was carried out at 250°C for 20 minutes on stream by using hydrogen as carrier gas. At higher GHSV the contact time between hexane and catalyst was shortened and thus the conversion decreased, however the amount of C<sub>6</sub> isomers (2,2-DMB, 2,3-DMB, 2-MP, 3-MP) were markedly increased. It should be noted that at low GHSV especially 380h<sup>-1</sup>, the main product was C<sub>1</sub>-C<sub>5</sub> fraction. It has been suggested that C<sub>1</sub>-C<sub>5</sub> should be formed through catalytic cracking of C<sub>6</sub> isomer during the long contact time. Therefore at high GHSV, the formation of C<sub>1</sub>-C<sub>5</sub> was substantially prevented and thus high yield of isomer products was obtained.

#### **5.5 Effect of carrier gas on the conversion and selectivity of n-hexane isomerization.**

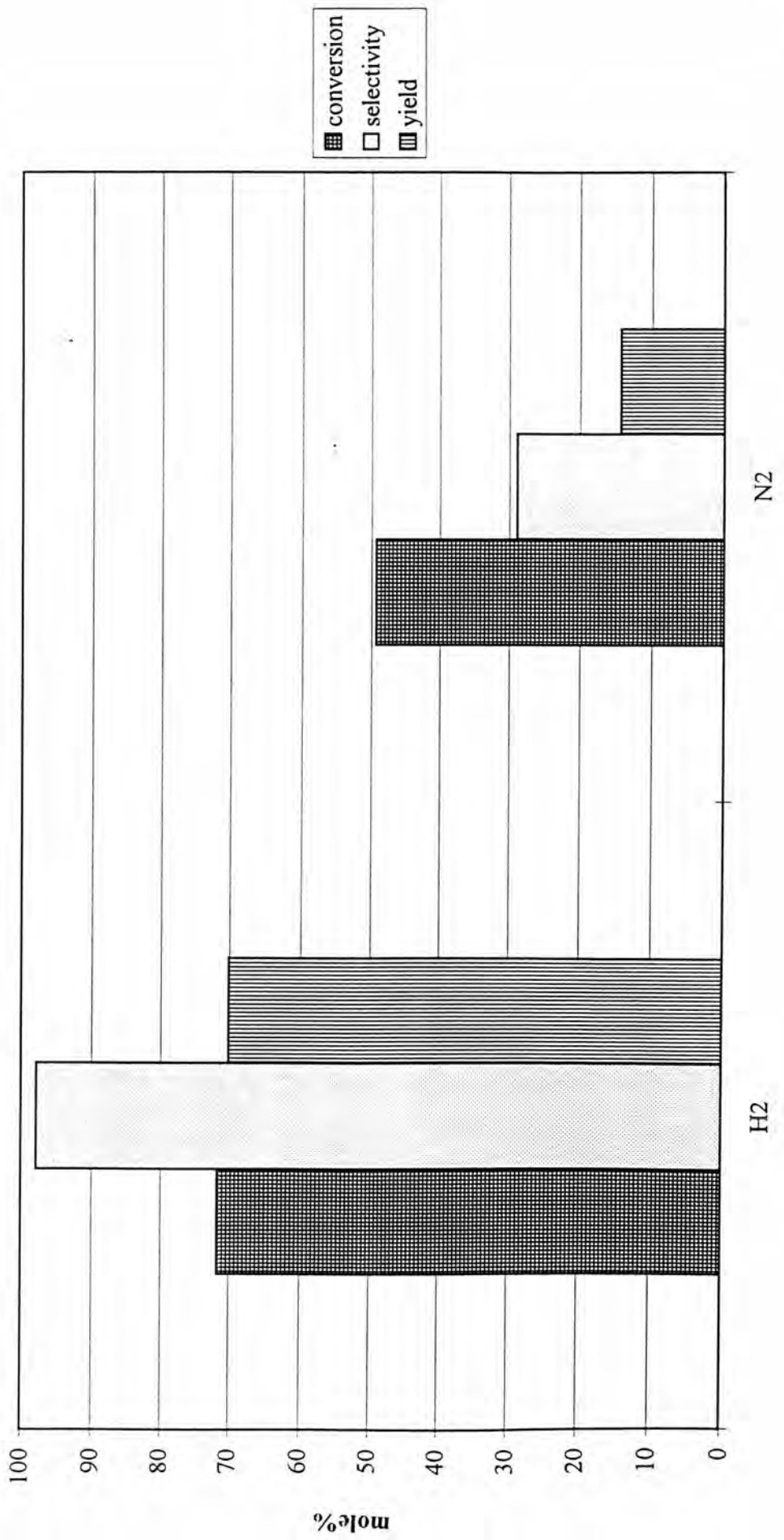
The conversion and selectivity of n-hexane isomerization at 250 °C, GHSV 1600 h<sup>-1</sup> with different carrier gas, N<sub>2</sub> and H<sub>2</sub>, are shown in Figure 5.8. Pt/H-Beta (Si/Al = 40, 0.6 wt%Pt loaded by ion exchange) was used as the catalyst with time on stream of 20 minutes. As for the effect of H<sub>2</sub> in feed stream, it has been suggested that H<sub>2</sub> may be absorbed with dissociation and thus promoting the proton transfer to the acid site of the catalyst [2,22,53]. In addition it has been also accepted



**Figure 5.7 n-Hexane isomerization on Pt/H-Beta(Si/Al =40, 0.6%wt Pt by ion exchange) at 250 °C, TOS 20 min, and difference GHSV**



**Figure 5.8 n-Hexane isomerization on Pt/H Beta (Si/Al = 40, 0.6%wt Pt) at 250 °C, GHSV 1600 h, and TOS 20 min with H<sub>2</sub> and N<sub>2</sub>**



that Pt can play an active role of hydrogen transfer to the carbonaceous adsorbate on catalyst surface and thus suppressing the coke formation. The promoting effect of H<sub>2</sub> for n-hexane isomerization was recommended for further study. Therefore, the presence of hydrogen as carrier gas greatly contributed to the high conversion and selectivity to C<sub>6</sub> isomers.

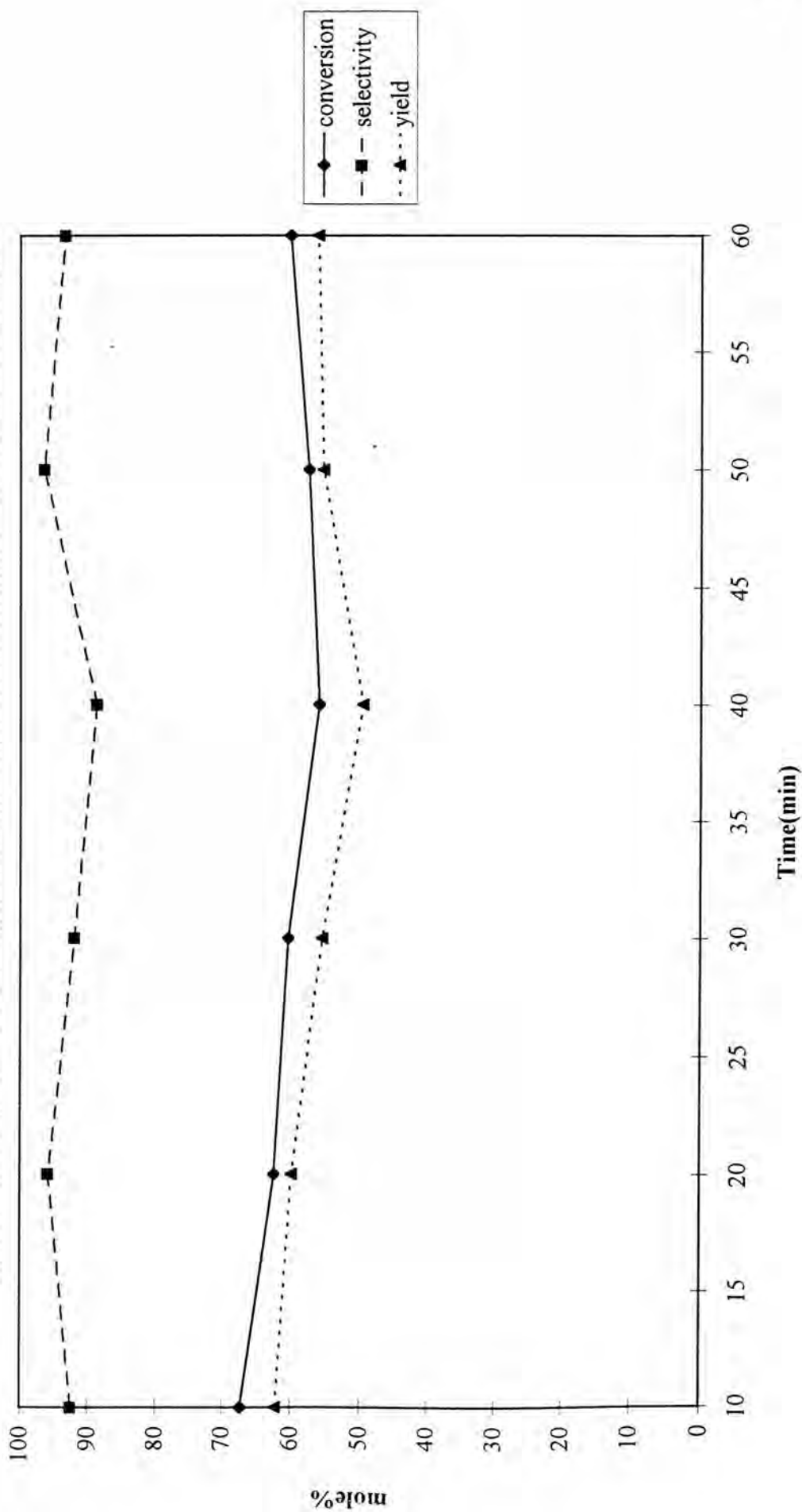
### **5.6 Effect of Time on Stream (TOS) on the conversion and selectivity of hexane isomerization.**

The effect of Time on Stream (TOS) was investigated to select the optimum period of chromatographic analysis. As shown in Figure 5.9, the conversion and selectivity of hexane isomerization were not significantly changed within 60 minutes. Therefore, the product sampling was made at 20 min on stream for convenience reason.

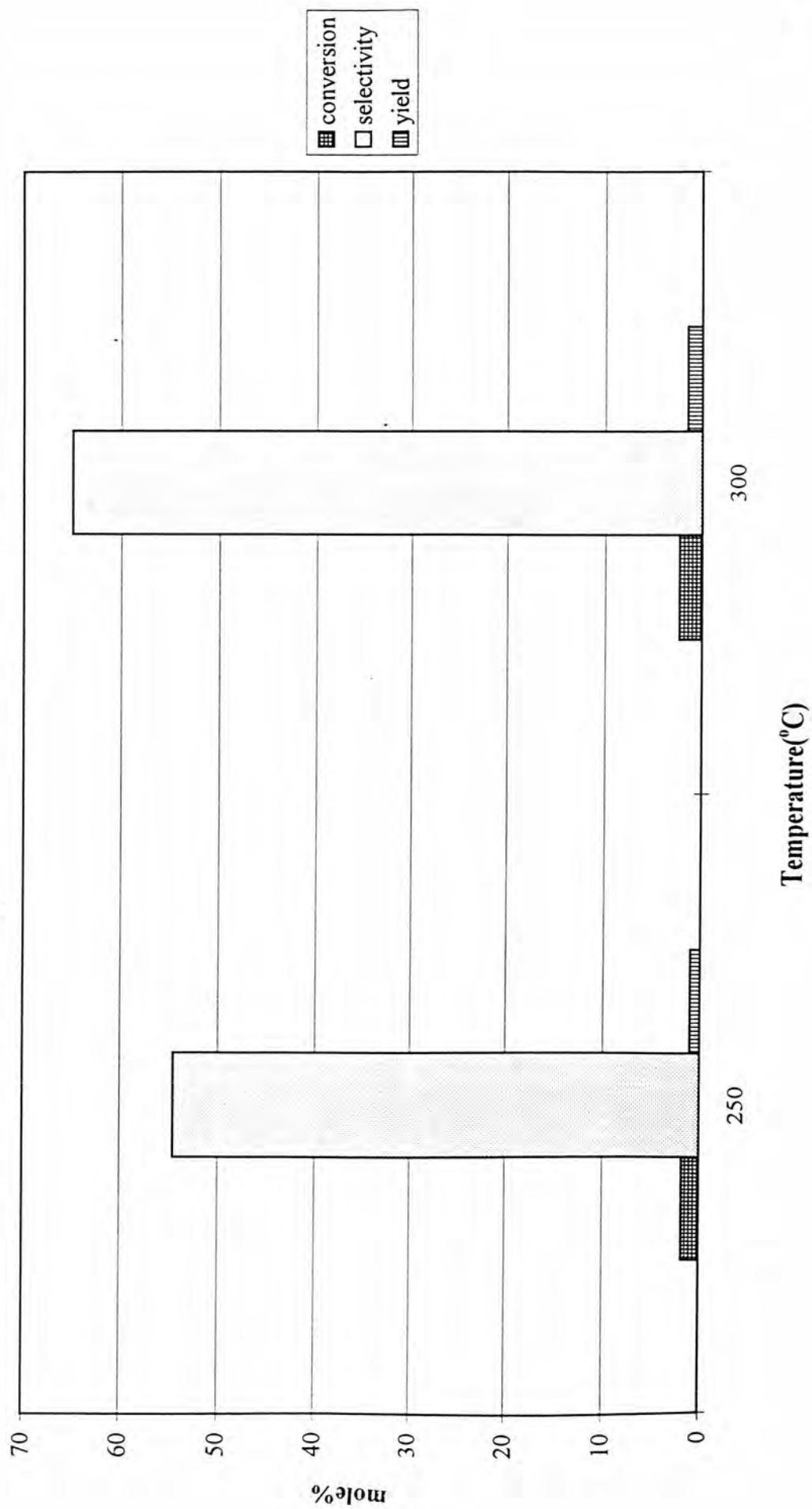
### **5.7 Blank test of n-hexane isomerization**

The hexane isomerization was conducted without catalyst to observe the thermal effect at 250 and 300°C. As shown in Figure 5.10 only few amount of C<sub>6</sub> isomers was formed at either temperature. Therefore, the thermal effect could be negligible.

**Figure 5.9 n-Hexane isomerization on Pt/H Beta (Si/Al = 40, 0.6%wt Pt by ion exchange) at 250 °C, GHSV 1600 h<sup>-1</sup> with various TOS**



**Figure 5.10 Blank test of n-hexane isomerization at 250 and 300 °C**



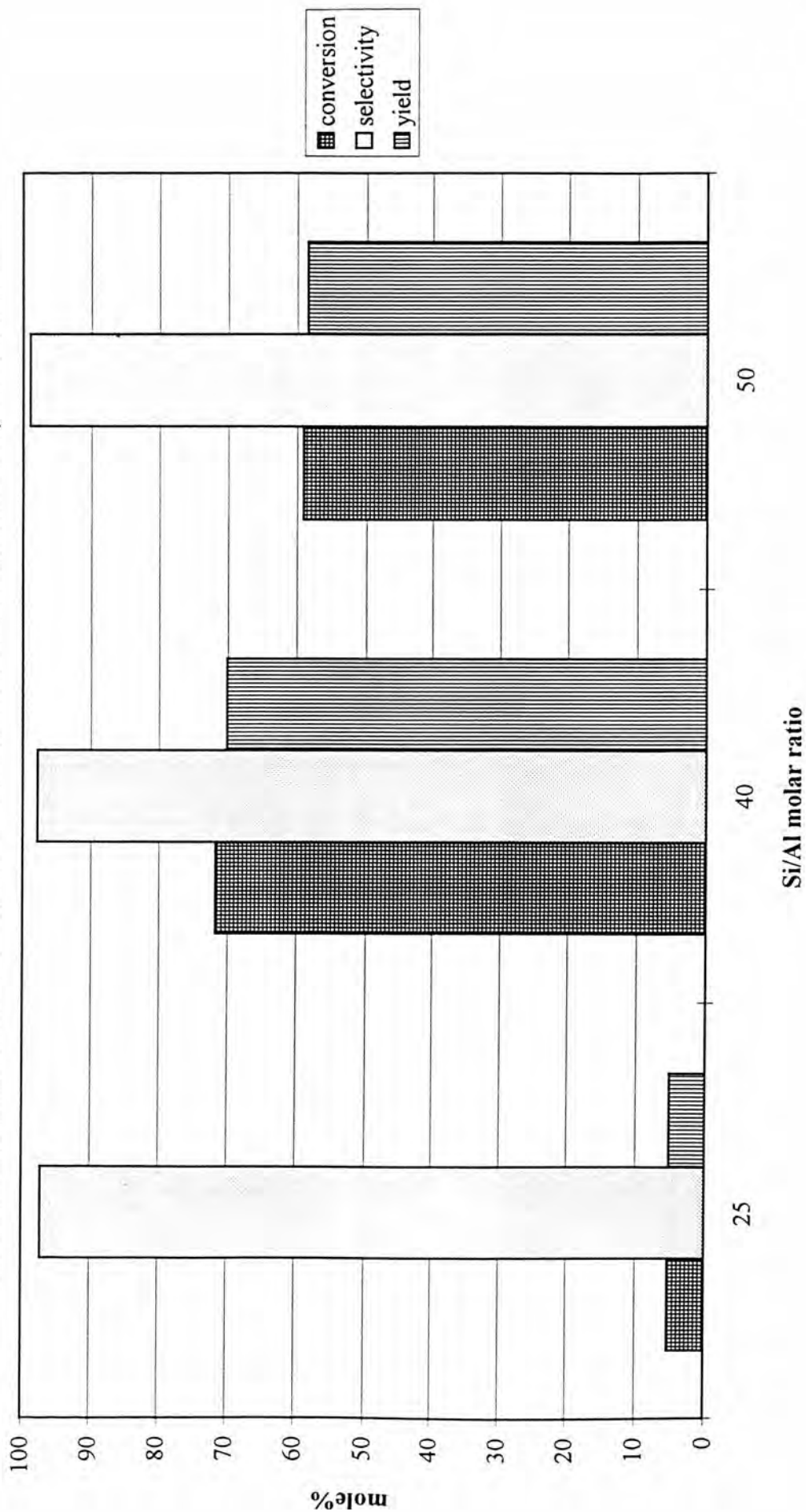
### **5.8 Effect of Si/Al ratios on the conversion and selectivity of hexane isomerization**

Figure 5.11 shows the conversion and selectivity of n-hexane isomerization over Pt/H-Beta (0.6% wt. Pt loaded by ion exchange) having different Si/Al molar ratios (25, 40 and 50). The reaction temperature was 250°C and H<sub>2</sub> was used as carrier gas. It has been found that at Pt/H-Beta with Si/Al ratio of 40 gave the highest n-hexane conversion among all the catalyst compared. In consistent with the NH<sub>3</sub>-TPD results, the Pt/H-Beta catalyst having higher amount of strong acid sites could be in order of Pt/H-Beta (40) > Pt/H-Beta (50) > Pt/H-Beta (25). Therefore, it has been suggested that strong acid sites play an important role on the high catalyst activity.

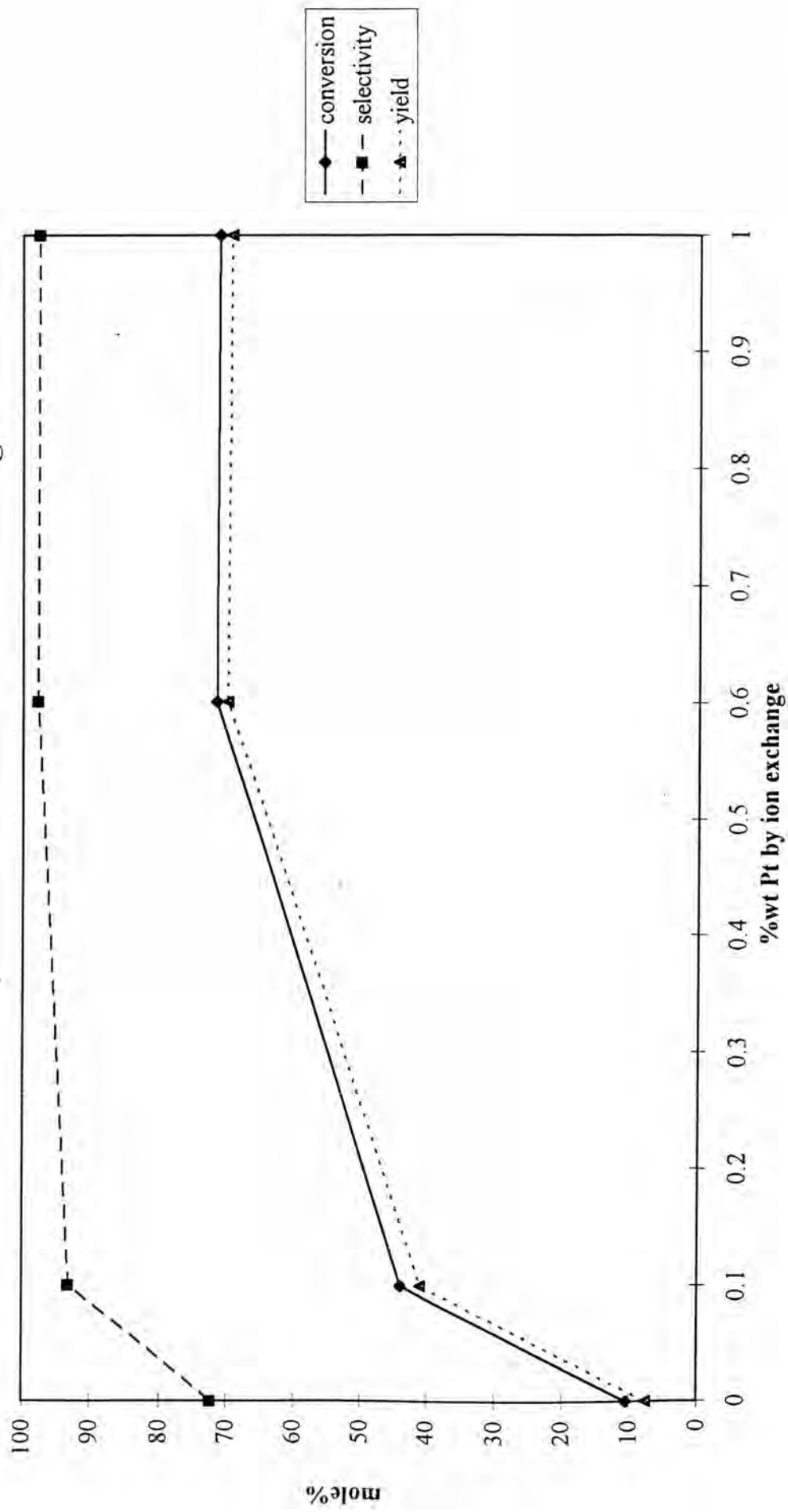
### **5.9 Effect of amount of Platinum loading on the conversion and selectivity of hexane isomerization.**

The hexane conversion and selectivity on Pt/H-Beta with several amount of Pt loaded by ion exchange is shown in figure 5.12. The reaction conditions were: temperature 250°C, GHSV 1600 h<sup>-1</sup> with the presence of H<sub>2</sub> as carrier gas. It has been found that the conversion of n-hexane and selectivity to methylpentanes and dimethylbutanes were also increased with increasing platinum content up to a maximum value at about 0.6 wt.% platinum. Pt should have an important role on dehydrogenation of n-hexane to hexene which will be much more readily converted to C<sub>6</sub> isomers than the condition in absence of Pt. Furthermore, there have been some

**Figure 5.11 n-Hexane isomerization on Pt/H Beta (0.6%wt Pt by ion exchange) at 250 °C, GHSV 1600 h<sup>-1</sup>, and TOS 20 min with Si/Al = 25, 40 and 50**



**Figure 5.12 n-Hexane isomerization on Pt/H-Beta (Si/Al =40) at 250 °C,  
GHSV 1600 h<sup>-1</sup>, TOS 20 min with various Pt loading content**





suggestion that for low metal contents, the hydrogenation and dehydrogenation reactions are the limiting step, the isomerization activity being proportional to the metal content. If the hydrogenating activity was high, which happened for higher metal content, the limiting step would be the skeletal isomerization of olefins on acid sites and the activity depended only on the acidity of the zeolitic catalysts[48].

### **5.10 Comparison of ion exchange and wet impregnation of Platinum.**

The comparison of conversion and selectivity of n-hexane isomerization between Platinum ion-exchange and Platinum wet impregnation over Zeolite H-Beta at the same amount of Platinum loading (0.6 wt.%) are shown in Figure 5.13. The Pt/H-Beta prepared by ion exchange exhibited higher conversion than Pt/H-Beta prepared by wet impregnation while the product selectivities were almost in the same level. It has been suggested that the accessibility of Pt loaded by ion exchange and wet impregnation to Beta zeolite may be different or platinum ion exchange over H-Beta has higher metal dispersion and homogeneous macroscopic distribution of metal into the zeolite structure than wet impregnation catalyst [53].

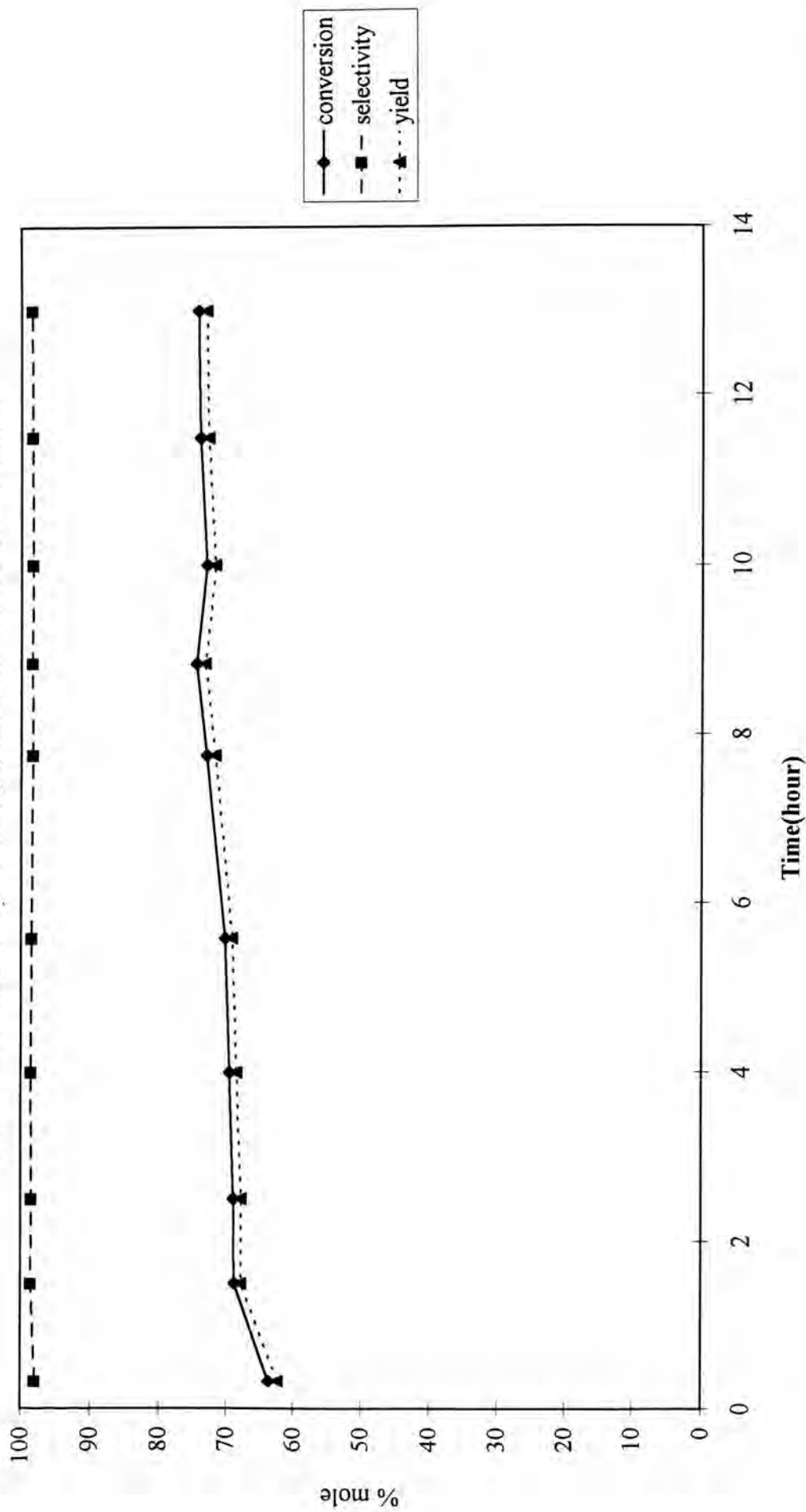
### **5.11 The catalyst stability.**

The catalyst stability was tested by prolonged operation at 250°C and GHSV 1600 h<sup>-1</sup> for 13 h according to Figure 5.14. The conversion and selectivity of n-hexane isomerization were almost constant. It has been suggested that hydrogen in gas stream should suppress the coke formation. In addition, it has been generally

**Figure 5.13 n-Hexane isomerization on Pt/H-Beta (Si/Al =40, 0.6%wt Pt) by ion exchange and wet impregnateat 250°C, GHSV 1600 h<sup>-1</sup>, TOS 20min**



**Figure 5.14 n-Hexane isomerization on Pt/H Beta (Si/Al = 40,  
0.6%wt Pt by ion exchange) at 250 °C, GHSV 1600 h<sup>-1</sup>**

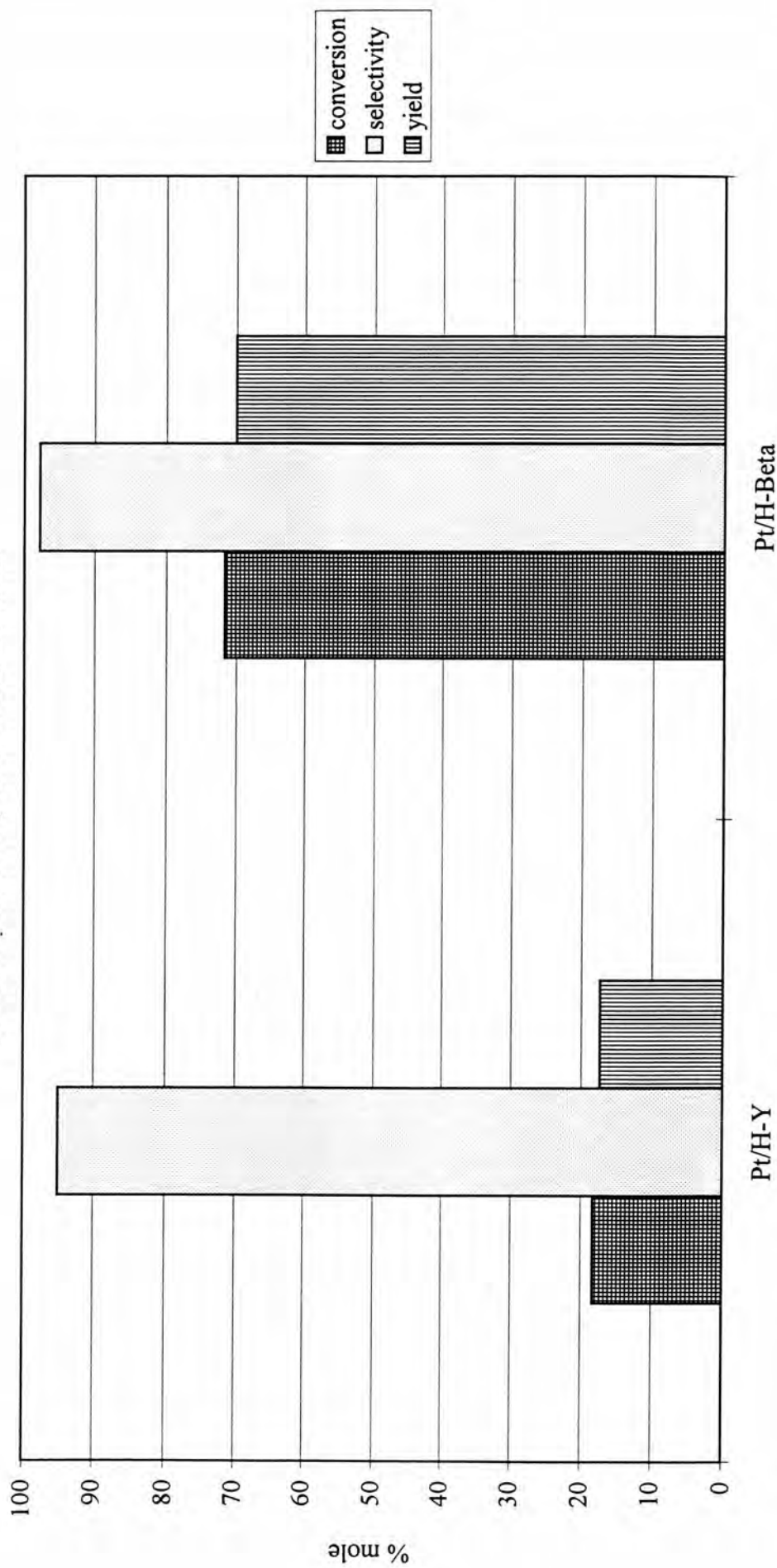


accepted that Pt on the catalyst has the function for hydrogen attraction and subsequently hydrogen transfer to the absorbate species on the catalyst surface. Furthermore, substantially no aromatics was obtained from this reaction. Therefore Pt/H-Beta catalyst was found to be one of the good catalyst for n-hexane isomerization.

### 5.12 Comparison of Pt/H-Beta and Pt/H-Y

From Figures 5.15 and 5.16, the conversion and selectivity of n-hexane isomerization was compared between using Pt/H-Beta and Pt/H-Y as the catalysts with the same amount of platinum loading (0.6% wt. loaded by ion exchange). It has been found that the Pt/H-Beta (Si/Al =40) gave much higher conversion than did Pt/H-Y zeolite. It was suggested that Pt/H-Beta and Pt/H-Y had substantially similar pore size and shape [22,39], which corresponded to the result of average pore diameter of both catalysts; Pt/H-Beta = 15.69 Å<sup>0</sup>, Pt/H-Y =15.57 Å<sup>0</sup>. Therefore, the product selectivities of C<sub>6</sub> isomers obtained on both catalysts were almost the same. However, the higher amount of strong acid sites possessed by Pt/H-Beta should be responsible for the higher n-hexane conversion.

**Figure 5.15 n-Hexane isomerization on catalysts at 250 °C,  
GHSV 1600 h<sup>-1</sup>, and TOS 20 min**



**Figure 5.16 Product distribution of n-hexane isomerization on catalysts at 250 °C, GHSV 1600 h<sup>-1</sup>, and TOS 20 min**

