CHAPTER IV
RESULTS AND DISCUSSION

4.1 Effect of Various Supports on n-Octane Aromatization

In this section, the study of the effect of supports was divided into 3 parts: (I) Ion exchange step, (II) Catalytic activity measurement and (III) Catalyst characterization. The supports used in this study were Beta, L, Omega, Y zeolites and SiO_2.

4.1.1 Ion Exchange Step

After acid zeolites were ion-exchanged by Potassium Nitrate (KNO_3) at 80 °C for 9 hours under stirring condition, the compositions of unit cell were checked by Atomic Absorption Spectrometer (AAS). For successful exchange steps, all Na ions should be totally eliminated. The results were shown in Table 4.1 by comparing the theoretical results with the experimental results.

Table 4.1 AAS results of zeolite composition after ion-exchange.

Catalyst	K/Al		Na
	Theory	Measured	Measured
KBeta	1.00	1.26	nil
KL	1.00	0.86	nil
KOmega	1.00	0.62	nil
KY	1.00	0.97	nil

From Table 4.1, Na ions could not be detected in ion-exchanged supports. These results confirmed that all Na ions in each support were completely exchanged by Potassium ions. In addition, from K/Al results, it is noteworthy that for Beta, L and Y supports were transformed into K-form supports. However, for Omega support, the exchange level was less than unity, which inferred to unsuccessful exchange step.

Furthermore, the stability of exchanged zeolite was investigated by X-ray diffractometer (XRD) in 3 conditions as: fresh, exchanged and calcined exchanged supports.

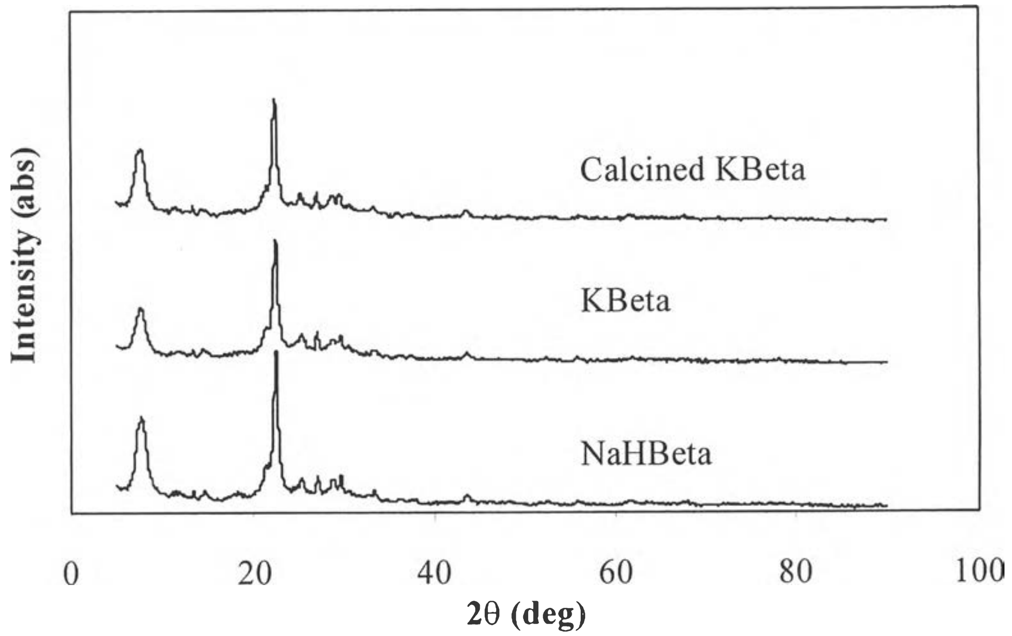

Figure 4.1 The XRD patterns of NaHBeta (before ion-exchange), KBeta (after ion-exchange) and calcined KBeta (after calcination)

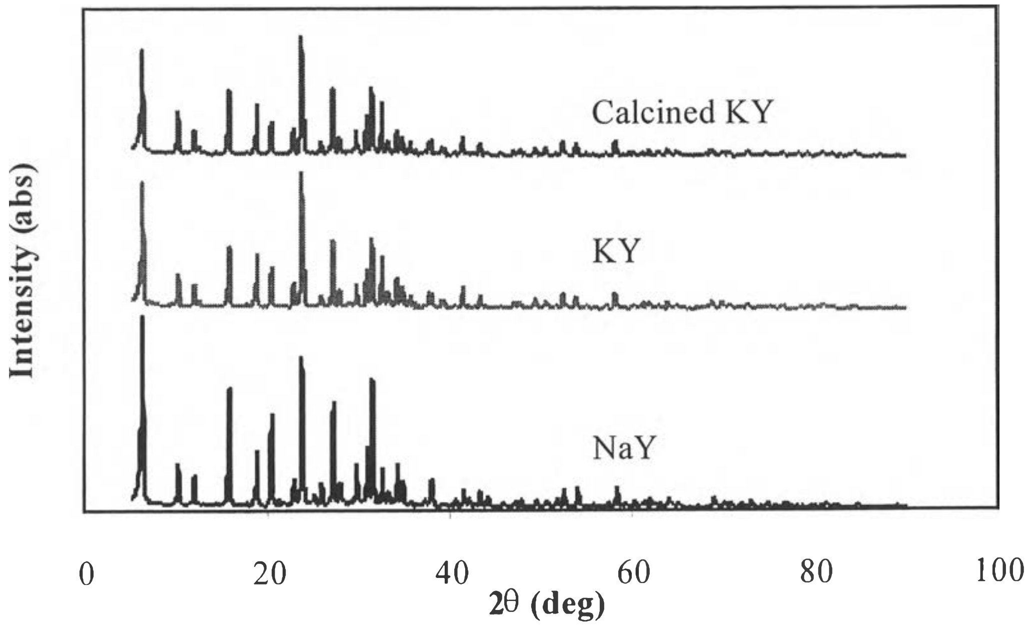

Figure 4.2 The XRD patterns of NaY (before ion-exchange), KY (after ion-exchange) and calcined KY (after calcination)

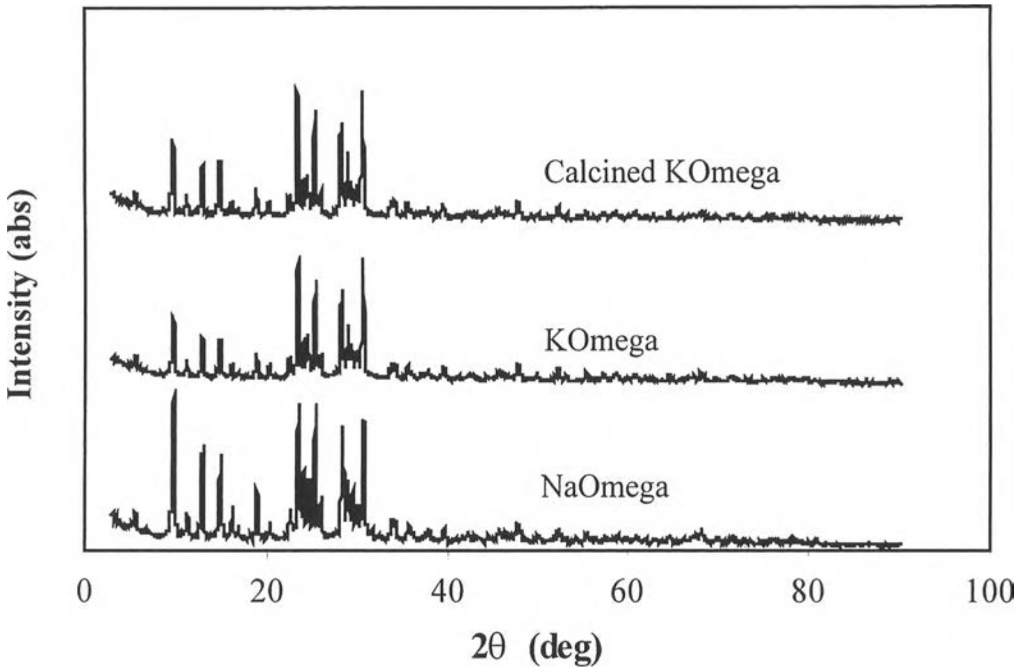

Figure 4.3 The XRD patterns of NaOmega (before ion-exchange), KOmega (after ion-exchange) and calcined KOmega (after calcination).

XRD patterns were used to confirm that all structure of support did not change during ion-exchange and calcination steps. The XRD patterns of Beta, Y and Omega supports are shown in Figures 4.1, 4.2 and 4.3, respectively. All the exchanged supports retained their original structures, and no evidence of the presence of any generated phase was observed. It can be concluded that ion-exchange and calcination steps did not destroy the structure of support.

4.1.2 *BET Results*

BET was used to study surface area and pore volume of the catalysts. The results were shown in table 4.2

Table 4.2 BET results of various supports

Catalyst	Surface area (m^2/g)	Pore volume (cc/g)
KL	473.3	0.1894
Pt/KL	423.4	0.1687
NaHBeta	661.7	0.2065
Pt/KBeta	474.4	0.2144
HOmega	82.5	0.0329
Pt/KOmega	47.01	0.0181
NaY	872.5	0.3490
Pt/KY	607.3	0.0243

The surface area of each support are shown in Table 4.2, It was found that after loading platinum on support, the surface area was decreased. This caused by platinum atoms deposited on the catalyst surface.

4.1.3 Catalytic Activity Measurement

Several activity tests were conducted over VPI prepared catalysts by using n-octane as a feed, in the flow reactor at 500 °C keeping H_2:n-octane (molar) feed ratio at 6 and weight hourly space velocity (WHSV) at 5 h^{-1}. The activity of all catalysts was determined as a function of conversion (pool conversion), total aromatics, and total aromatics yield.

The effect of various supports on n-octane conversion, total aromatics selectivity and total aromatics yield are shown in Figures 4.4, 4.5, and 4.6, respectively. For all catalysts, the conversion, total aromatics and total aromatics yield were slightly decreased with time on stream. From the comparison, Pt/SiO_2 and Pt/KL showed the highest n-octane aromatization activity (total aromatic selectivity: 80-90%) while Pt/KY and Pt/KOmega showed the lowest activity (total aromatic selectivity: 20-30%). It was not surprising because from Temperature Programmed Desorption (TPD) results (Jongpatiwut, 2002), KL and SiO_2 had the lowest acid sites when compared with other supports. As mentioned in the literature survey (Davis, 1994), the higher the acid site, the lower the aromatics selectivity. As a result KL and SiO_2 which had lower acid sites gave the highest aromatics selectivity.

Therefore, the two best supports, KL and SiO_2 were selected to study further on the effect of the percentage of Pt loading.

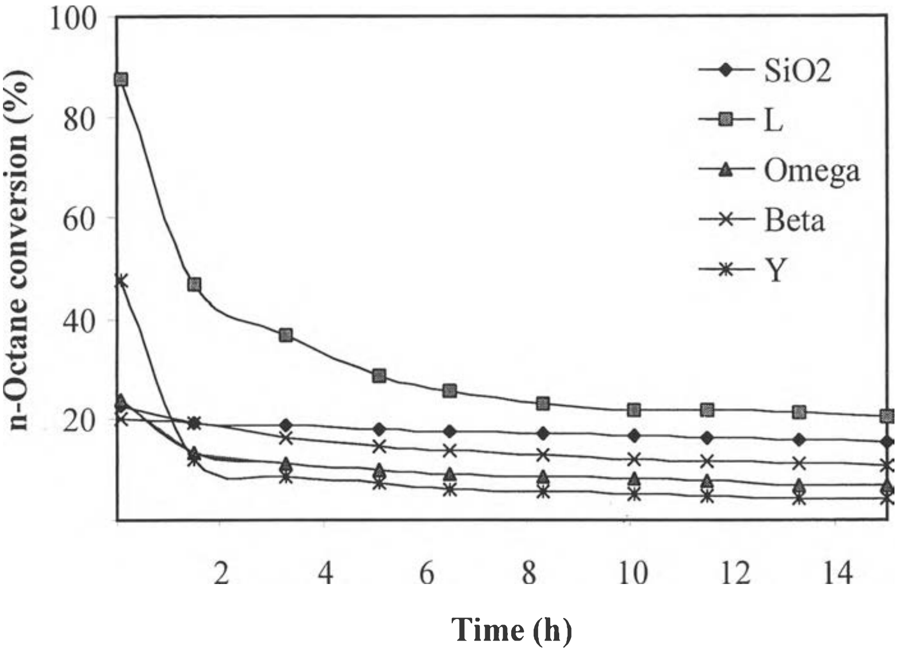

Figure 4.4 The variation of n-octane conversion with time on stream of various support catalysts prepared by VPI method on n-octane aromatization; operated at temperature = 500 °C, WHSV = 5 h^{-1}.

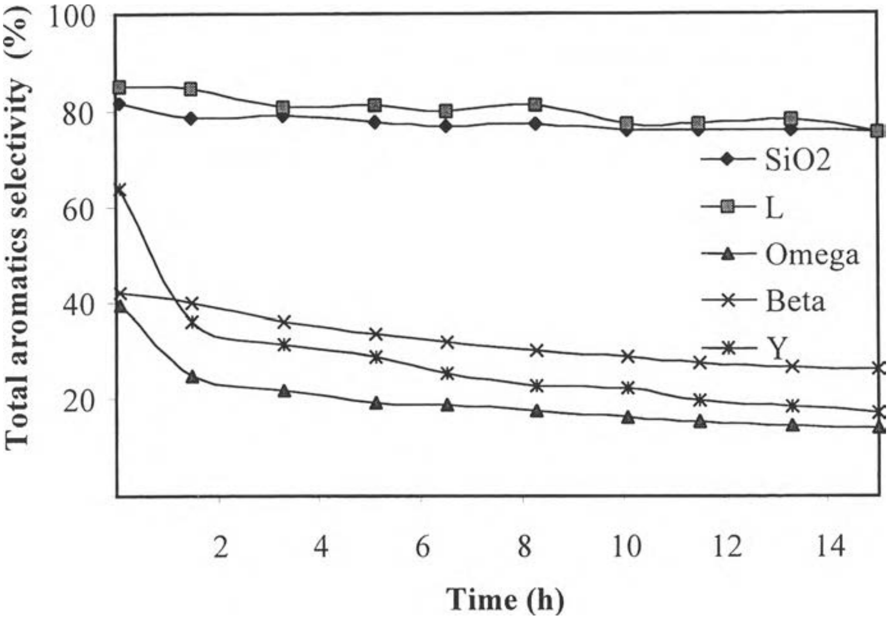

Figure 4.5 The variation of total aromatics selectivity with time on stream of various support catalysts prepared by VPI method on n-octane aromatization; operated at temperature = 500 °C, WHSV = 5 h^{-1}.

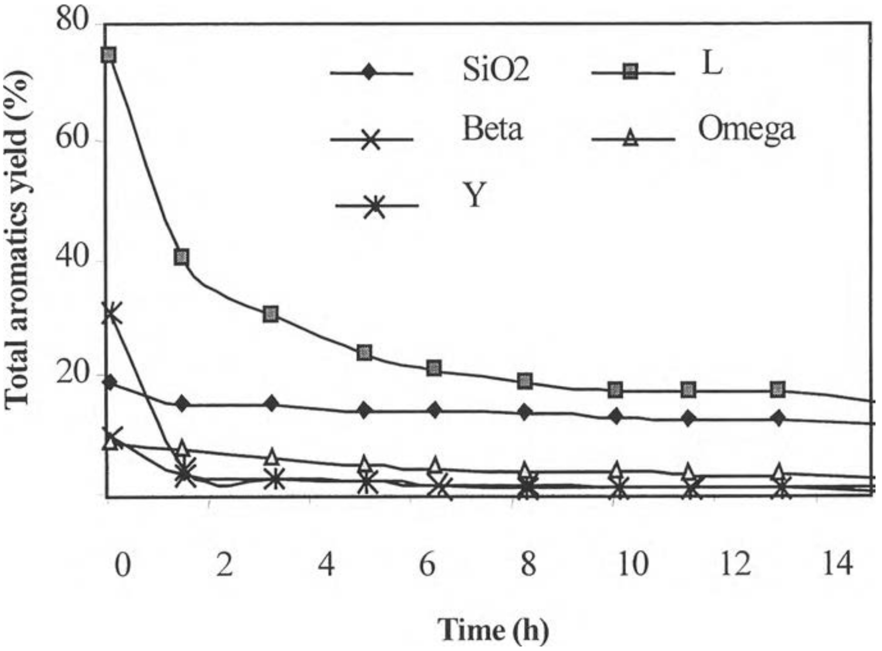

Figure 4.6 The variation of total aromatics yield with time on stream of various support catalysts prepared by VPI method on n-octane aromatization; operated at temperature = 500 °C, WHSV = 5 h^{-1}.

4.1.4 Catalyst Characterizations

4.1.4.1 *FT-IR adsorbed CO*

Fresh and spent catalysts were characterized by FT-IR of adsorbed CO to determine the morphology and location of Pt clusters on the catalysts.

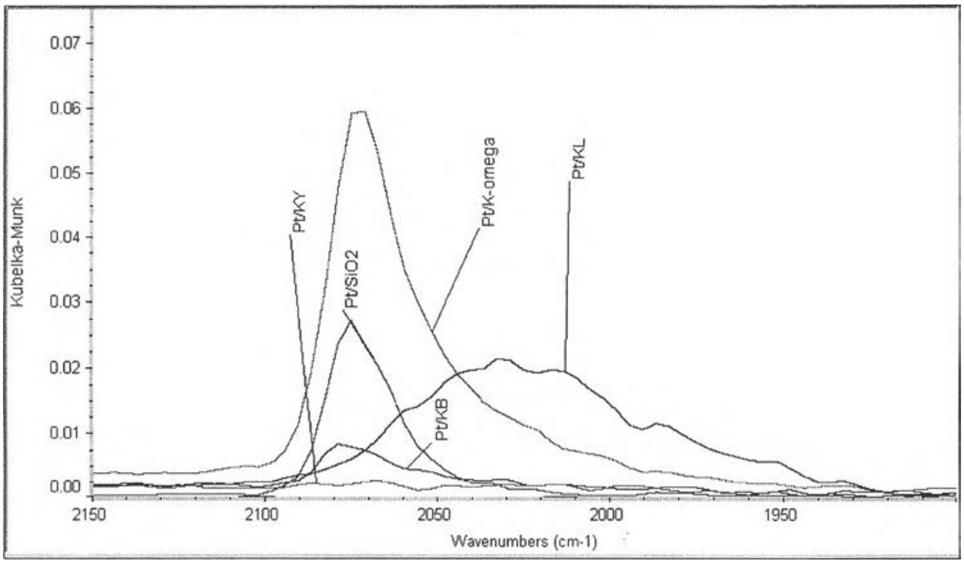

Figure 4.7 FT-IR adsorbed CO spectra of various support catalysts: Pt/KBeta, Pt/KL, Pt/KOmega, Pt/KY and Pt/SiO_2. All these catalysts were prepared by Vapor-Phase Impregnation method (VPI) with 1% Pt loading

FT-IR spectra of various supports Pt catalysts are shown in Figure 4.7. For the KL catalyst, It has been proposed that the different regions of wavenumbers correspond to the variation of the morphology of Pt cluster (Jacob *et al.*, 1999). At low wavenumber (band at 2050-1930 cm^{-1}), the peaks are assigned to Pt-carbonyl species from the small clusters inside the channel of zeolite. The bands between 2050-2075 cm^{-1} are associated with larger Pt clusters in the surface region of catalyst. And, the band at above 2050 cm^{-1} refers to Pt clusters located in the external of zeolite. However, for the other supports, the peak presentsin different active wavenumber (2080 cm^{-1}). Corresponding to Zheng *et al.* (1996) work, CO species which adsorb on small Pt cluster presented in linear form and appeared at 1900-2150 cm^{-1}.

The comparison between fresh and spent catalysts was made. FT-IR of adsorbed CO spectra of fresh and spent Pt/KBeta, Pt/KL, Pt/KOmega, Pt/KY and Pt/SiO_2 are shown in Figures 4.8-4.12, respectively. The spent catalysts show the decreasing of active Pt peak, except Pt/SiO_2 and Pt/KL which are not affected much by the reaction. This result implies that these two supports are more stable when comparing with other supports. The coke formation, one of the major cause of catalyst deactivation, were tested in next characterization technique, Temperature programmed Oxidation.

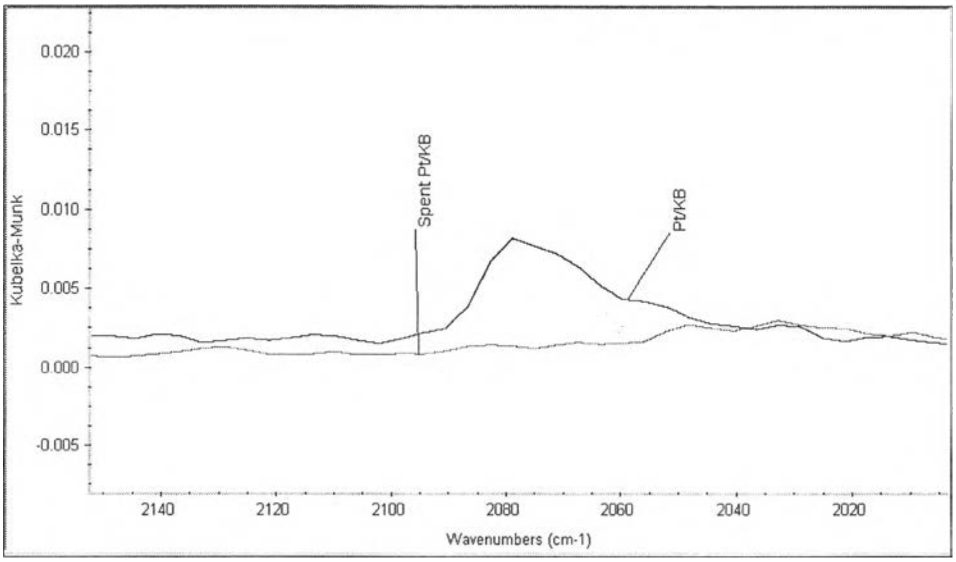

Figure 4.8 FT-IR adsorbed CO spectra of fresh and spent Pt/KBeta catalysts prepared by Vapor-Phase Impregnation method (VPI) with 1% Pt loading.

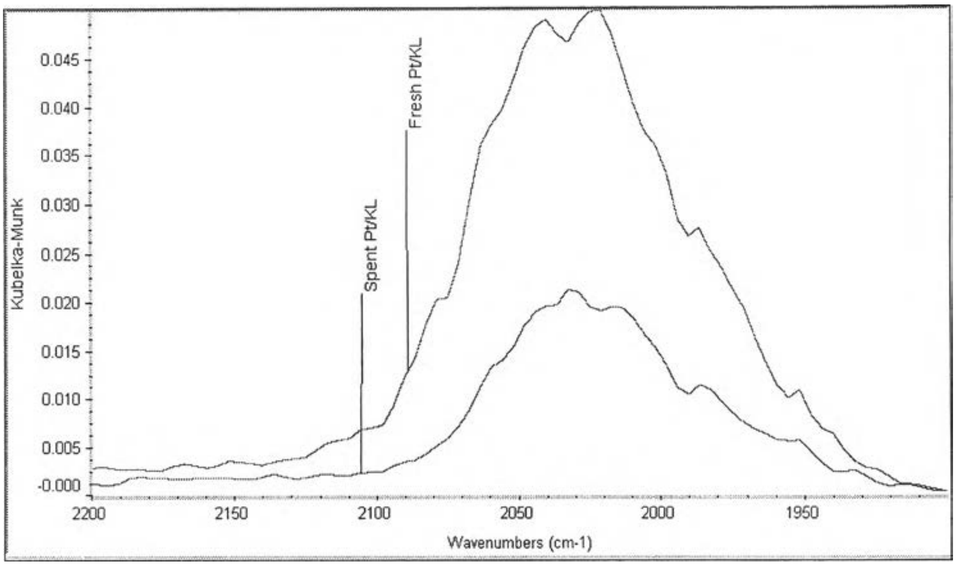

Figure 4.9 FT-IR adsorbed CO spectra of fresh and spent Pt/KL catalysts prepared by Vapor-Phase Impregnation method (VPI) with 1% Pt loading.

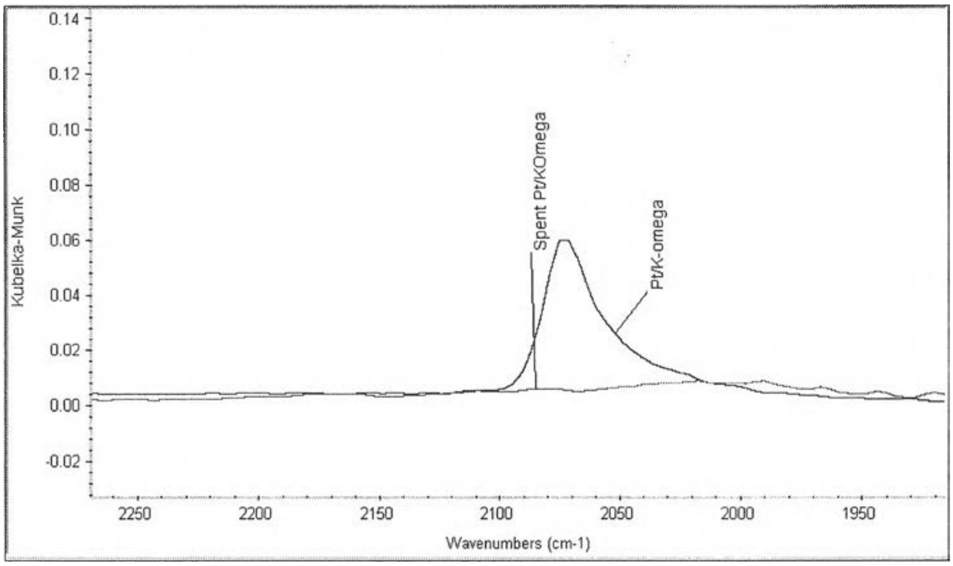

Figure 4.10 FT-IR adsorbed CO spectra of fresh and spent Pt/KOmega catalysts prepared by Vapor-Phase Impregnation method (VPI) with 1% Pt loading.

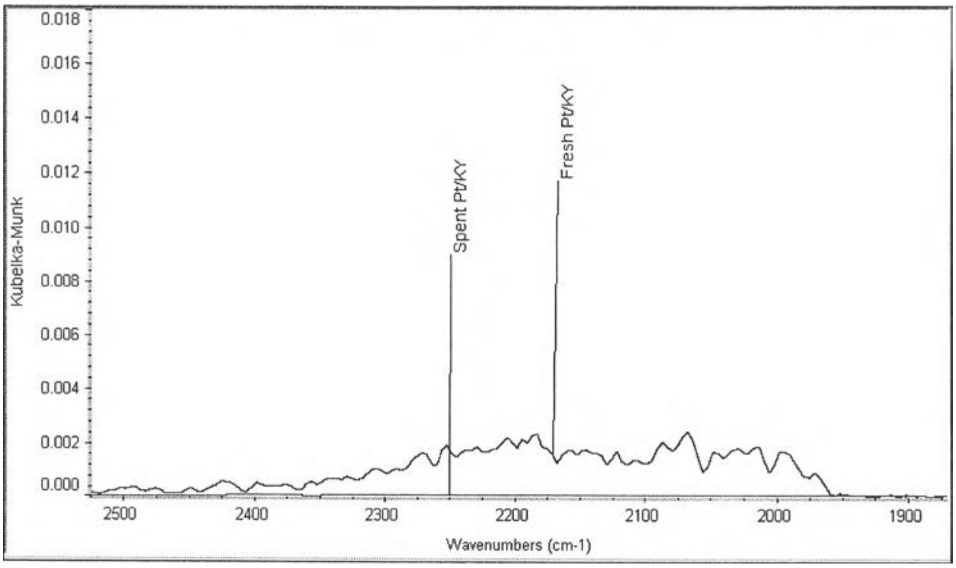

Figure 4.11 FT-IR adsorbed CO spectra of fresh and spent Pt/KY catalysts prepared by Vapor-Phase Impregnation method (VPI) with 1% Pt loading.

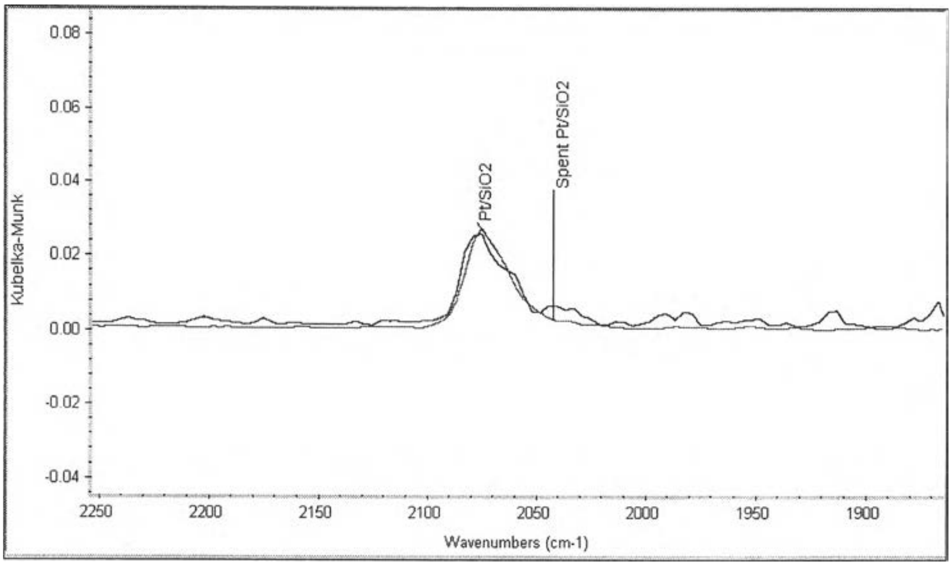

Figure 4.12 FT-IR adsorbed CO spectra of fresh and spent Pt/SiO2 catalysts prepared by Vapor-Phase Impregnation method (VPI) with 1% Pt loading.

4.1.4.2 *Temperature Programmed Oxidation (TPO)*

Temperature Programmed Oxidation was performed to investigate amount of coke formation that occurred in each catalyst after spending 20 hours on stream on n-octane aromatization.

The TPO profiles of spent Pt/KBeta, Pt/KL, Pt/KOmega, Pt/KY and Pt/SiO_2 are showed in Figures 4.13 - 4.17, respectively. For spent Pt/KBeta, Pt/KY and Pt/SiO_2, TPO profiles showed dominant peak at relatively low temperature (200-500 °C) while for other supports showed dominant peak at relatively high temperature. It can indicate that coke which formed on Pt/KBeta, Pt/KY and Pt/SiO_2 were easily to oxidize than coke on other supports. Furthermore, when considered on the amount of coke formation. It was found that the amount of coke deposit on each catalyst was very small. It can propose that all these catalysts had high stability to coke formation.

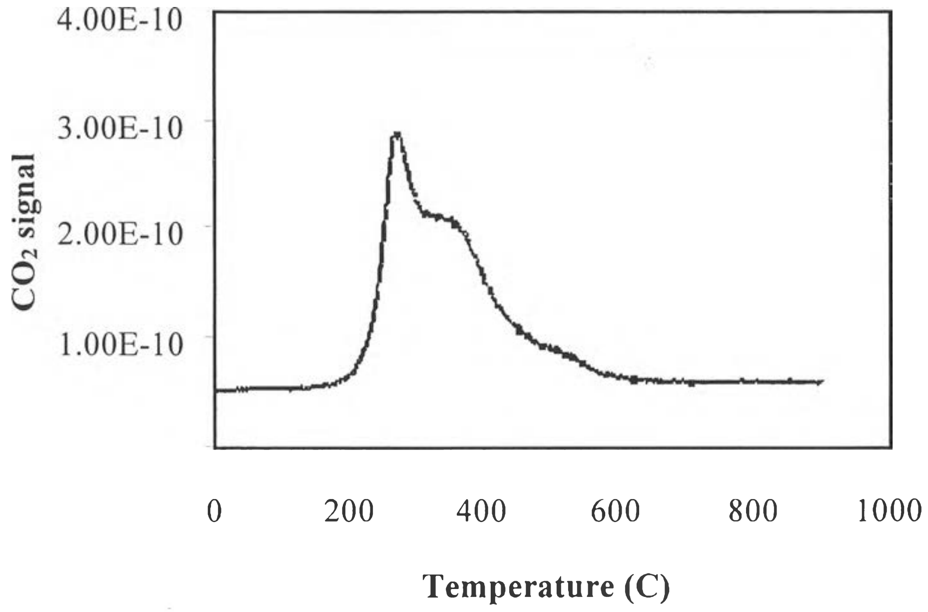

Figure 4.13 TPO profile for the 1% Pt/KBeta catalyst after used in n-octane aromatization for 20 hours on stream

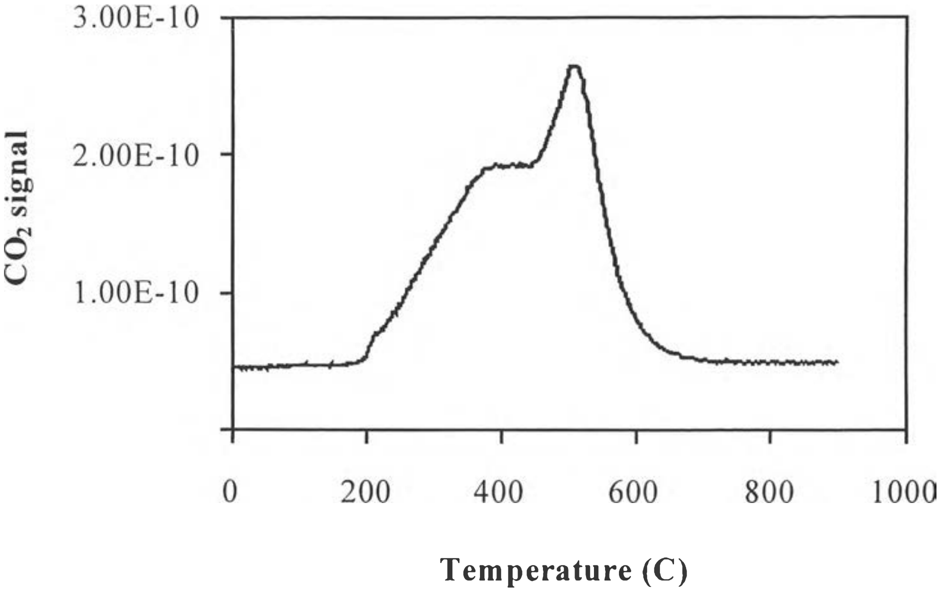

Figure 4.14 TPO profile for the 1% Pt/KL catalyst after used in n-octane aromatization for 20 hours on stream

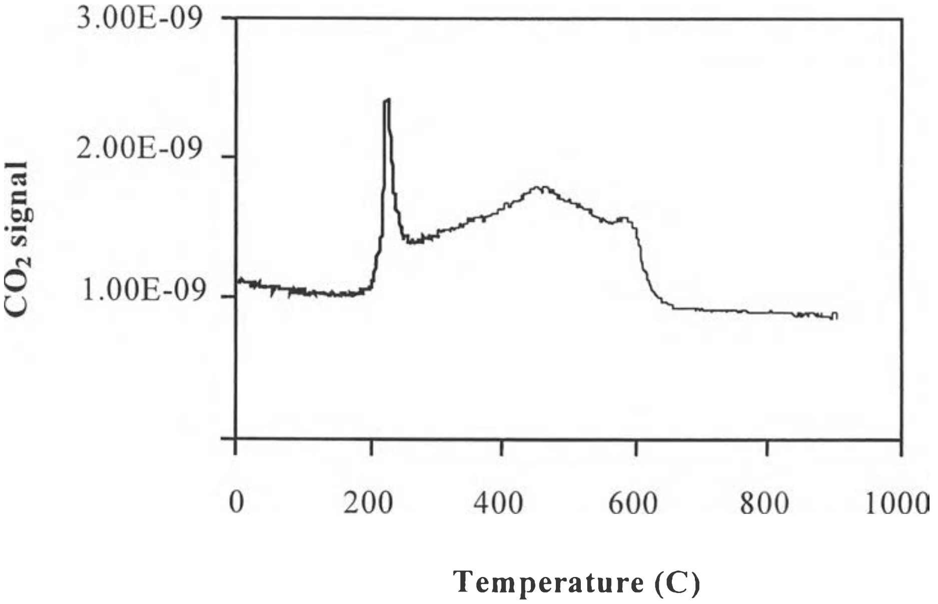

Figure 4.15 TPO profile for the 1% Pt/KOmega catalyst after used in n-octane aromatization for 20 hours on stream

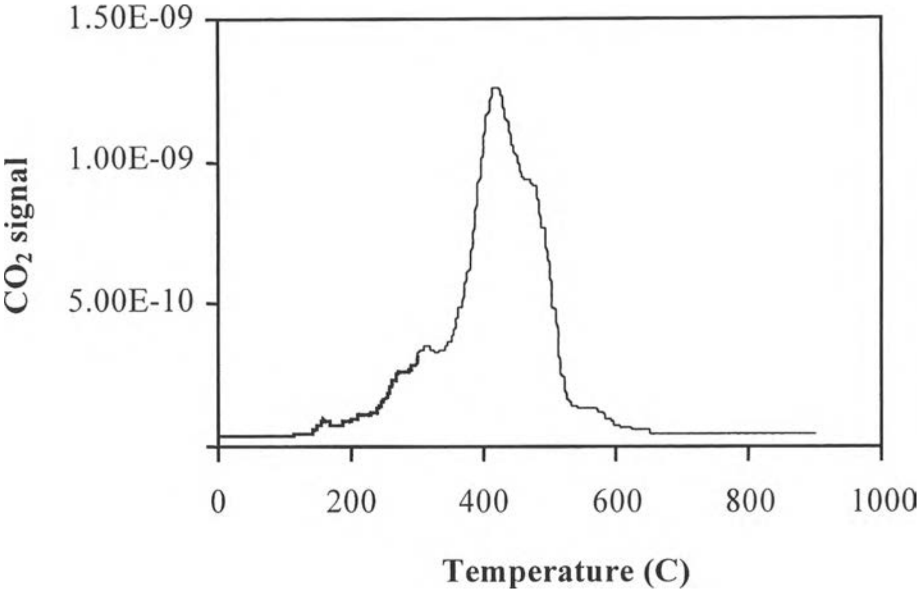

Figure 4.16 TPO profile for the 1% Pt/KY catalyst after used in n-octane aromatization for 20 hours on stream

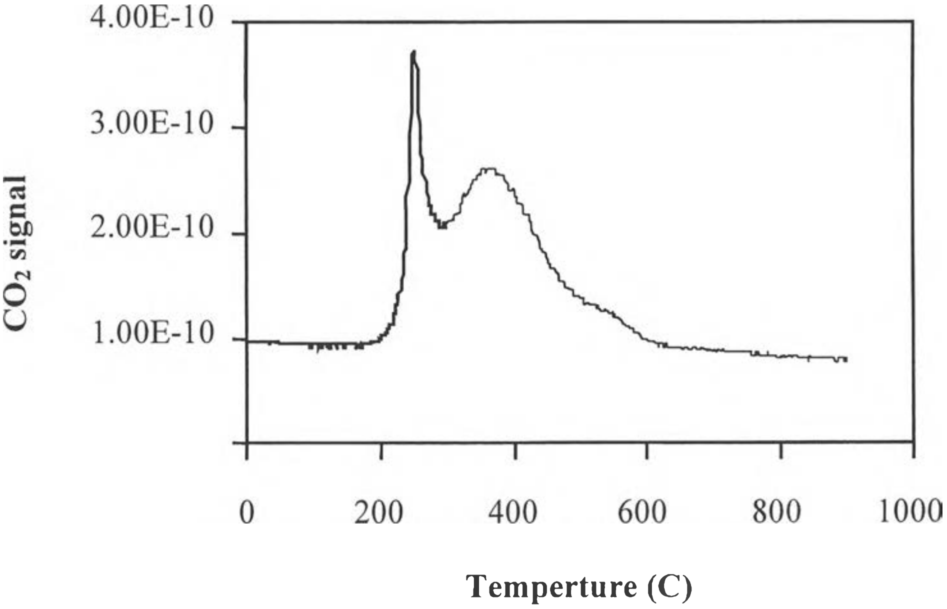

Figure 4.17 TPO profile for the 1% Pt/SiO_2 catalyst after used in n-octane aromatization for 20 hours on stream

4.2 Effect of the Percentage of Pt Loading

Pt/SiO_2 and Pt/KL were studied on the effect of the percentage of Pt loading by varying in the following ratios: 0.5, 1 and 1.5% Pt loading

This section was divided into two parts by the types of catalysts. The first part will be discussed about Pt/KL and followed by Pt/SiO_2 in the second part. All these two series of catalysts were prepared by VPI method and used in n-octane aromatization with the same condition as previously mentioned. The explanation will be discussed in 2 sections: (I) Catalytic activity measurement, and (II) Catalyst characterization.

4.2.1 Pt/KL Study

4.2.1.1 *Catalytic activity measurement*

The aromatization of n-octane was conducted in the flow reactor at 500 °C, at the constant H_2:n-octane ratio of 6 and the weight hourly space velocity (WHSV) of 5 h^{-1} over Pt/KL VPI catalysts by varying Pt loading at 0.5,1 and 1.5 %. The activity was reported in terms of n-octane conversion, total aromatics selectivity, and total aromatics yield.

The catalytic measurement of the various percentage of Pt loading on Pt/KL are shown in terms of n-octane conversion, total aromatics selectivity and total aromatics yield in Figures 4.18-4.20, respectively. It was shown that the higher %Pt loading gave the higher n-octane conversion while aromatics selectivity was optimize at 1%. It was corresponded to the predicted results that the amount of Pt site affected the conversion, while the size of Pt cluster affected the selectivity. From these results, it inferred that the proper amount loading for Pt/KL was 1%, (at this point 1% Pt/KL catalyst exhibited n-octane conversion at 30%, total aromatics selectivity at 80%, total aromatics yield at 25%).

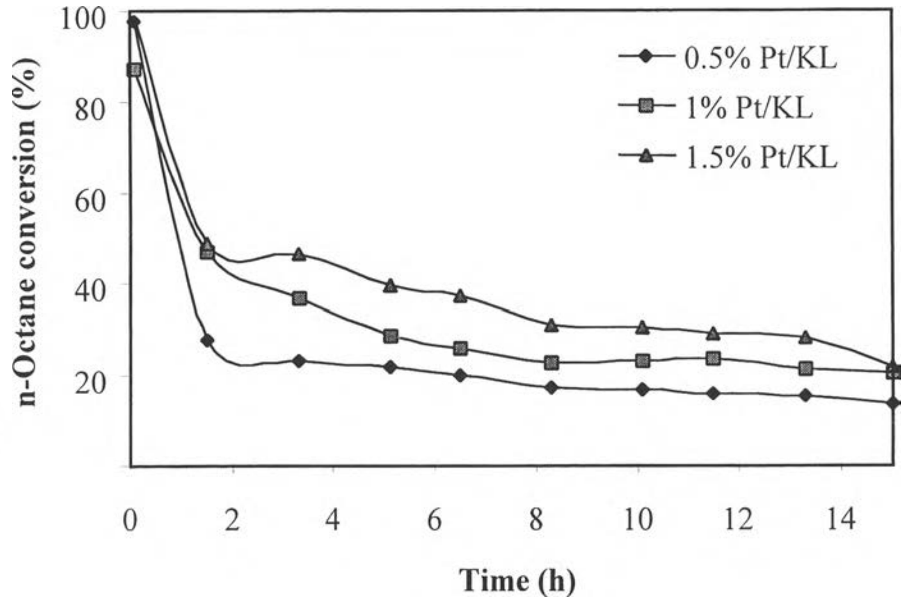

Figure 4.18 The variation of n-octane conversion with time on stream of Pt/KL VPI catalysts with varying % Pt loading on n-octane aromatization, operated at temperature = 500 °C, WHSV = 5 h^{-1}.

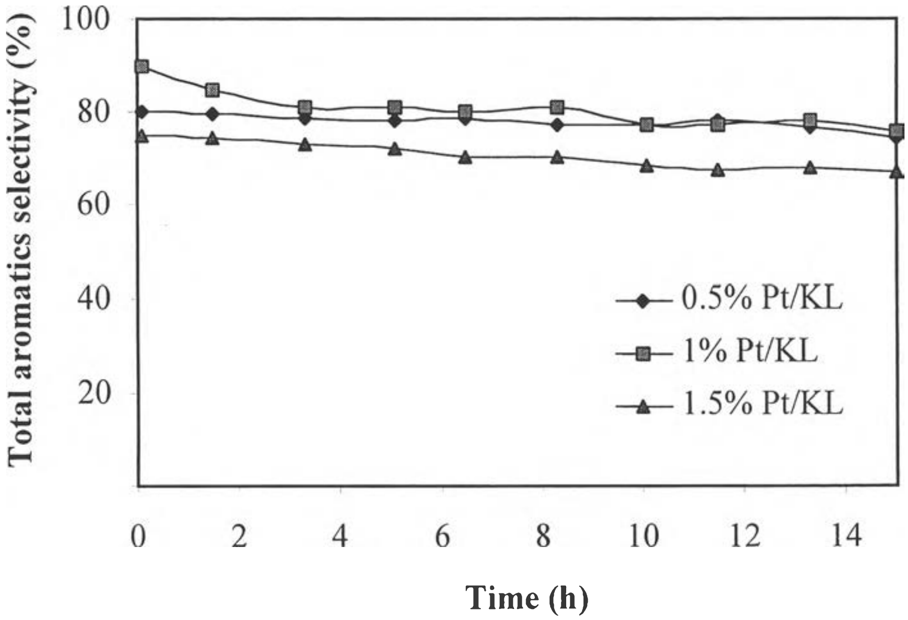

Figure 4.19 The variation of total aromatics selectivity with time on stream Pt/KL VPI catalysts with varying % Pt loading on n-octane aromatization, operated at temperature = 500 °C, WHSV = 5 h^{-1}.

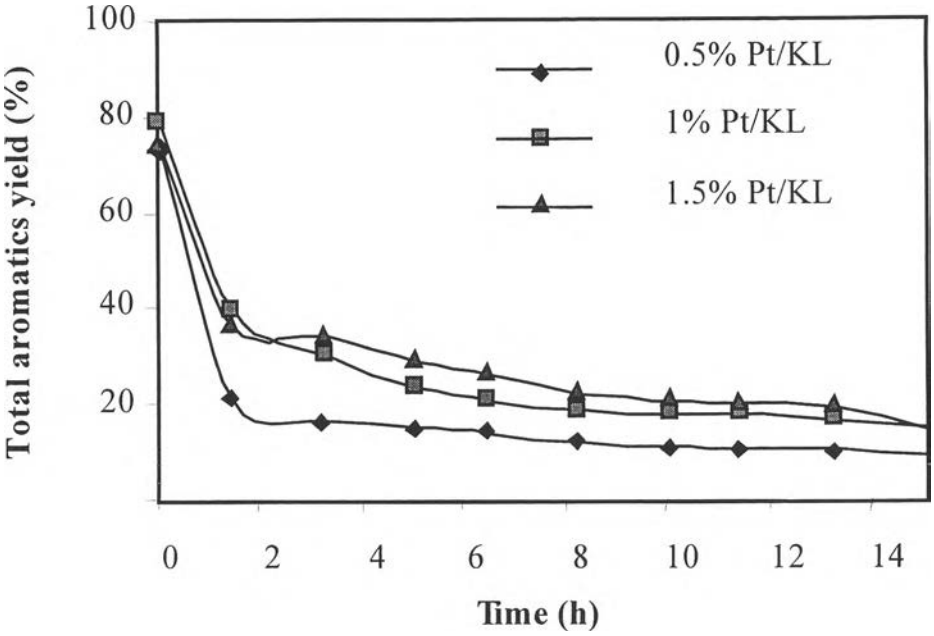

Figure 4.20 The variation of total aromatics yield with time on stream Pt/KL VPI catalysts with varying % Pt loading on n-octane aromatization, operated at temperature = 500 °C, WHSV = 5 h^{-1}.

4.2.1.2 *Catalyst characterizations*

4.2.1.2.1 FT-IR adsorbed CO

Pt/KL VPI catalysts with varying %Pt loading were characterized by FT-IR of adsorbed CO to determine the morphology and the location of Pt clusters on the catalysts.

FT-IR spectra of various percentages of Pt loading on Pt/KL are shown in Figure 4.21. As mentioned, for KL catalyst, low wavenumber (band at 2050-1930 cm^{-1}) bands were assigned to Pt-carbonyl species from the small cluster inside the channel of zeolite. And, bands at above 2050 cm^{-1} referred to Pt cluster located in the external of zeolite. The location of Pt cluster can infer to the aromatic selectivity, that is the internal Pt cluster is desirable according to research of Jacob *et al.* (1999). At low percentages of Pt loading, all Pt clusters presented in an internal site form. Interestingly, at 1.5% Pt loading showed the presence of external Pt cluster site, which is ineffective to aromatization. This result corresponded with catalytic activity test, through at 1.5% Pt loading showed the highest conversion, it has the lowest aromatic selectivity. Therefore, the proper amount of Pt loading for Pt/KL was 1%.

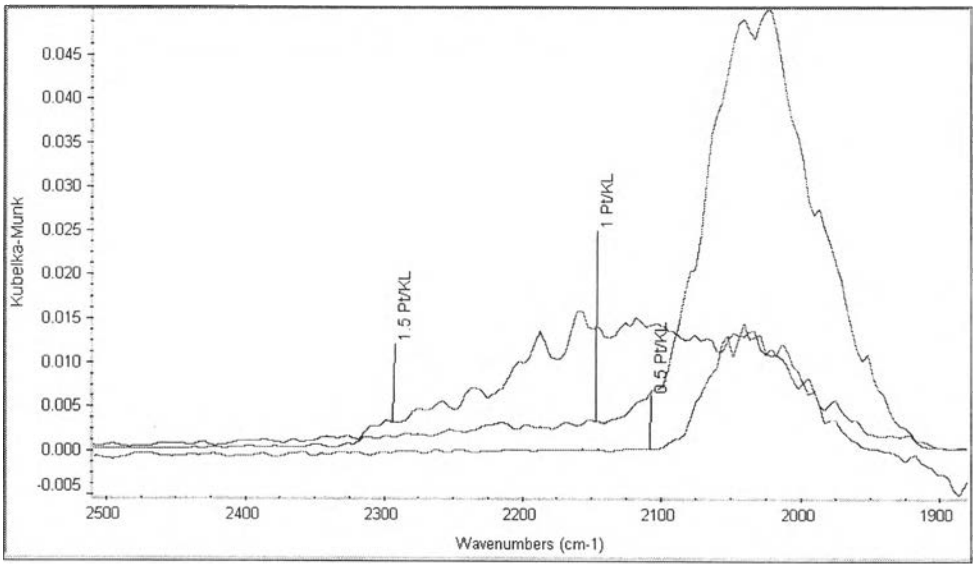

Figure 4.21 FT-IR adsorbed CO spectra of Pt/KL prepared by Vapor-Phase Impregnation method (VPI) with varying % Pt loading at: 0.5, 1 and 1.5%

4.2.1.2.2 *Temperature Programmed Oxidation (TPO)*

Temperature Programmed Oxidation was performed to investigate coke formation occurring after 20 hours on stream. TPO profiles of 0.5, 1 and 1.5% Pt loading catalyst are shown in Figures 4.22-4.24, respectively. Location and profile of TPO can infer to the strength and number of coke site. The peak at higher temperature is assigned to the stronger coke site, because it is difficult to oxidize carbon compound on the catalyst. It was observed that there were no differences of TPO profiles, so these inferred that %Pt loading in the examined range did not affect to the strength of coke site. In addition, the amount of coke formation on each catalyst was almost the same. Consequently, the percentage of Pt loading in the examined range did not affect to the amount and the strength of coke formation.

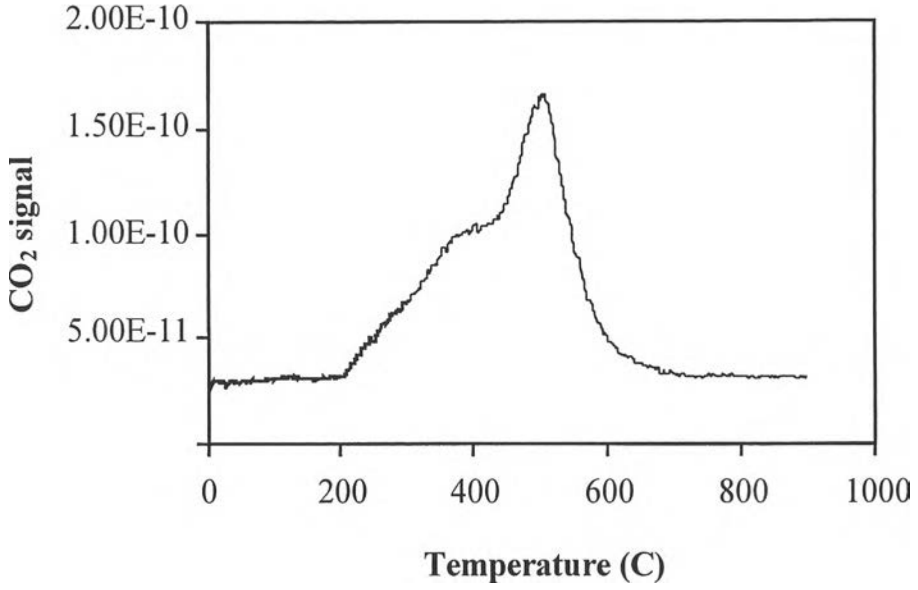

Figure 4.22 TPO profile for the 0.5% Pt/KL catalyst after spent in n-octane aromatization for 20 hours on stream

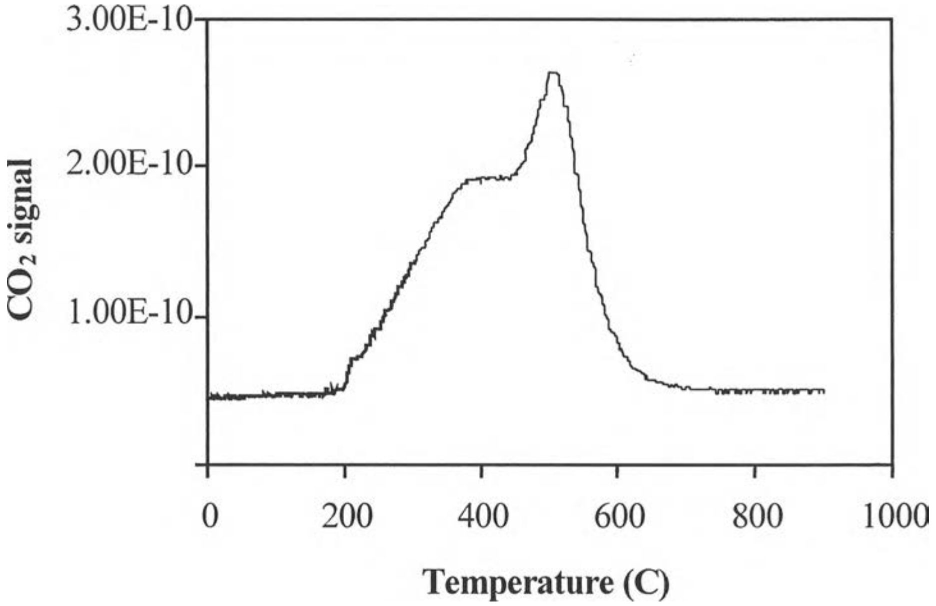

Figure 4.23 TPO profile for the 1% Pt/KL catalyst after spent in n-octane aromatization for 20 hours on stream

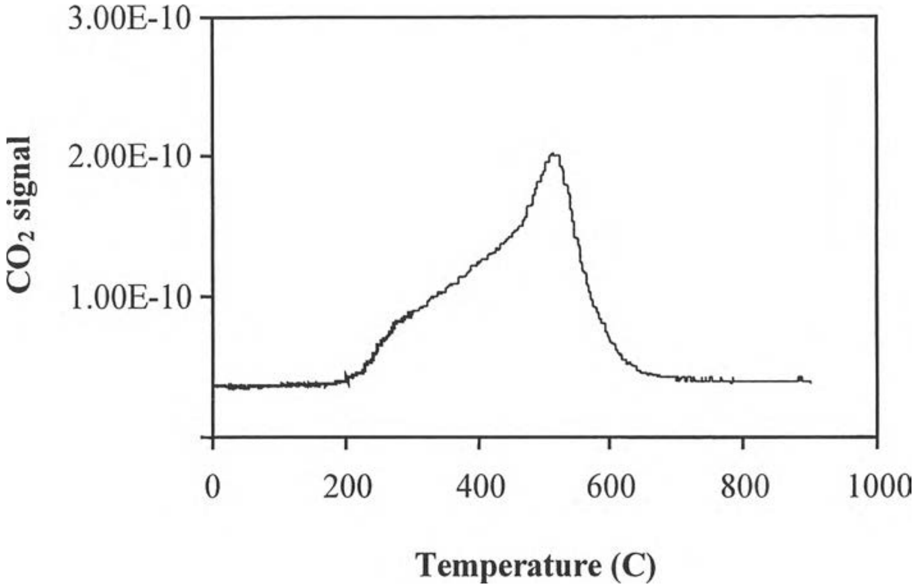

Figure 4.24 TPO profile for the 1.5% Pt/KL catalyst after spent in n-octane aromatization for 20 hours on stream

4.2.2 Pt/SiO$_2$ Study

4.2.2.1 *Catalytic activity measurement*

The aromatization of n-octane was conducted in the flow reactor at 500 °C, at the constant ratio of H_2:n-octane of 6 and weight hourly space velocity (WHSV) of 5 h^{-1} over Pt/SiO$_2$ VPI catalysts by varying the percentage of Pt loading at 0.5,1 and 1.5. The activity was reported in form of conversion, total aromatics selectivity and total aromatics yield.

The catalytic measurements of the various of the percentage of Pt loading on Pt/SiO$_2$ are shown in term of n-octane conversion, total aromatics selectivity and total aromatics yield in Figures 4.25-4.27, respectively. It was shown that the higher %Pt loading gave the higher conversion while aromatics selectivity was optimize at 1%. Corresponding with the Pt/KL study that the higher Pt loading gave the higher conversion, while selectivity had an optimum value. From these results, it presented that the proper amount loading for Pt/SiO$_2$ was also 1%, at this point 1% Pt/SiO$_2$ exhibited conversion at 20%, total aromatics selectivity at 90% and total aromatics yield at 20%.

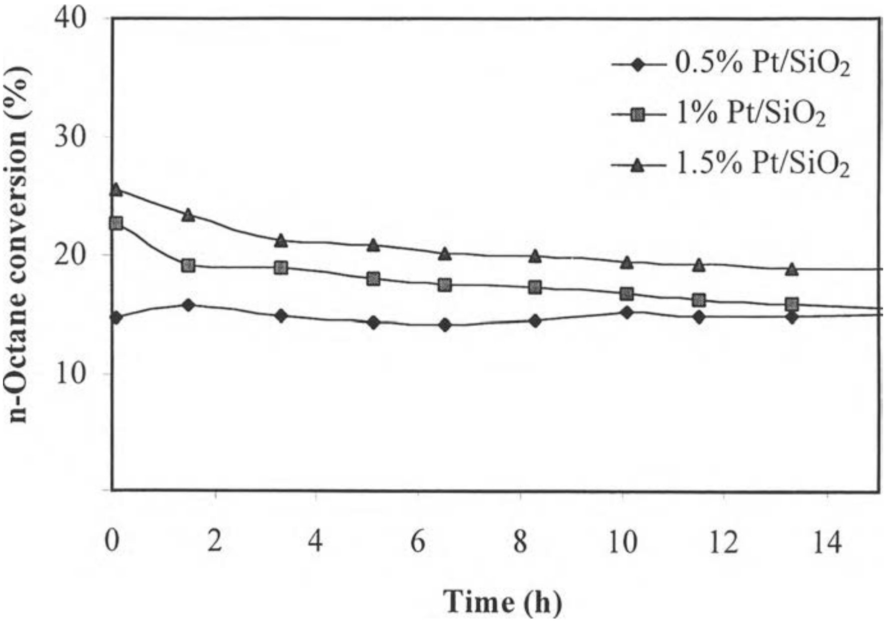

Figure 4.25 The variation of n-octane conversion with time on stream of Pt/SiO$_2$ VPI catalysts with varying %Pt loading on n-octane aromatization; operated at temperature = 500 °C, WHSV = 5 h^{-1}.

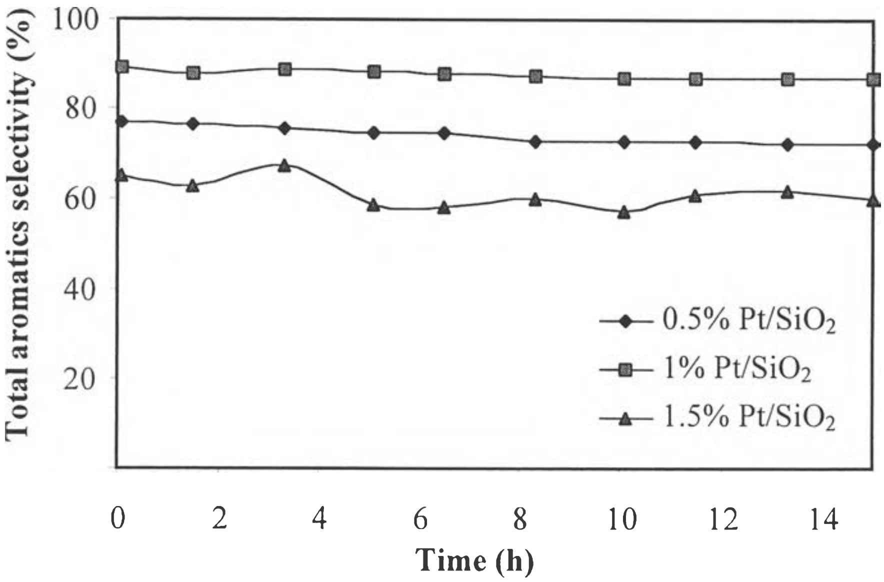

Figure 4.26 The variation of total aromatics selectivity with time on stream of Pt/SiO$_2$ VPI catalysts with varying %Pt loading on n-octane aromatization; operated at temperature = 500 °C, WHSV = 5 h^{-1}.

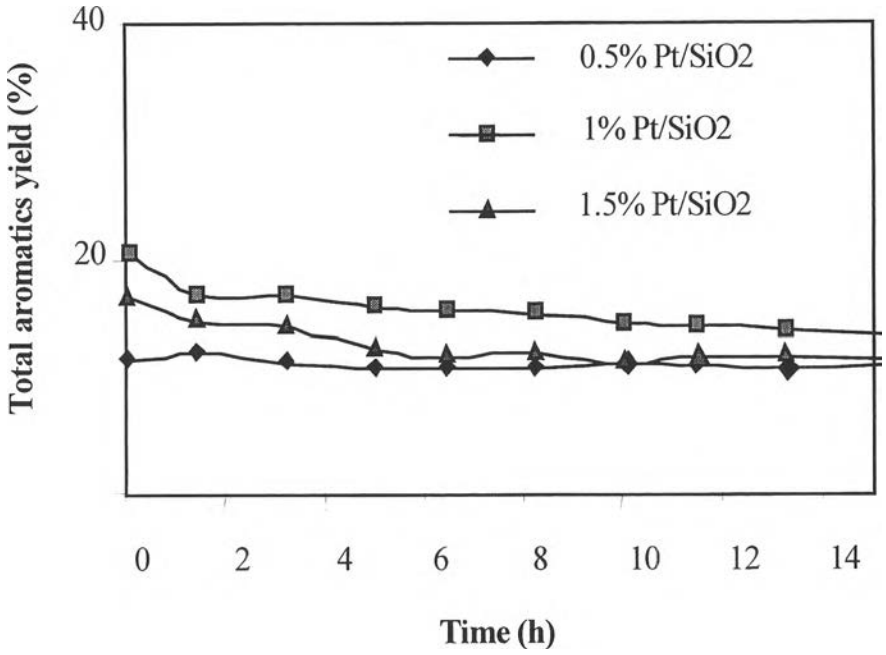

Figure 4.27 The variation of total aromatics yield with time on stream of Pt/SiO$_2$ VPI catalysts with varying %Pt loading on n-octane aromatization; operated at temperature = 500 °C, WHSV = 5 h^{-1}.

4.2.2.2 *Catalyst characterizations*

4.2.2.2.1 <u>FT-IR adsorbed CO</u>

Various percentage of Pt loading catalyst on Pt/SiO$_2$ was characterized by FT-IR of adsorbed CO to determine the morphology and location of Pt clusters on the catalysts.

FT-IR spectra of various percentage of Pt loading on Pt/SiO$_2$ are shown in Figure 4.28. As mentioned, for Pt/SiO$_2$ catalyst the active Pt site presented at 2080 cm^{-1}. The spectra referred that all Pt clusters appeared to be the active form. FT-IR adsorbed CO spectra showed that the higher %Pt loading, the higher amount active Pt sites are created.

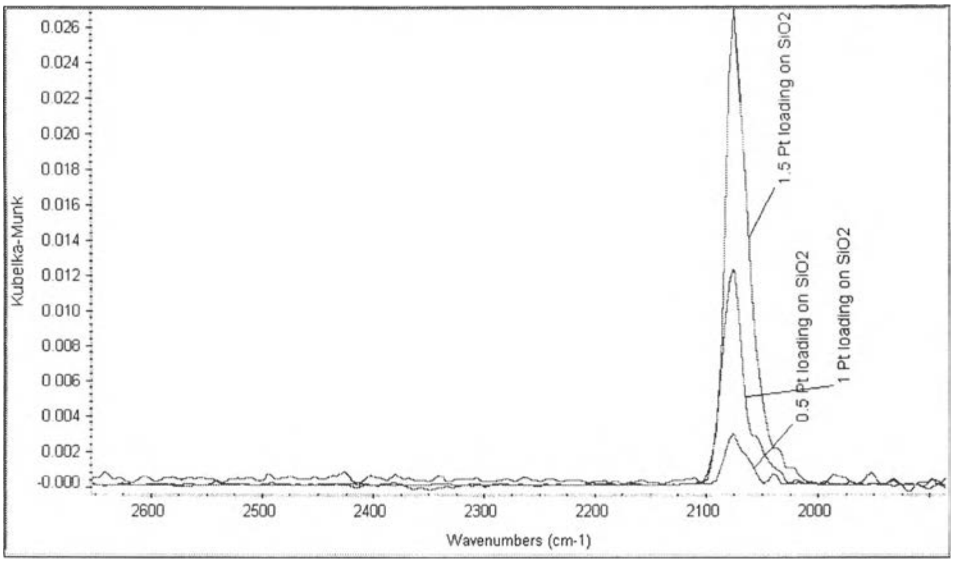

Figure 4.28 FT-IR adsorbed CO spectra of Pt/SiO_2 prepared by Vapor-Phase Impregnation method (VPI) with varying % Pt loading at: 0.5, 1 and 1.5%

4.2.2.2.2 *Temperature Programmed Oxidation (TPO)*

Temperature Programmed Oxidation was performed to investigate coke formation occurred in Pt/SiO_2 catalyst. TPO profiles of 0.5, 1 and 1.5% Pt loadings on SiO_2 are shown in Figures 4.30-4.32, respectively. As mentioned, location and profile of TPO infer to the strength of coke site. It was observed that 0.5 and 1% Pt loading had similar TPO profile, while 1.5% Pt loading had one additional stronger coke site at 600 °C and one additional weaker coke sites at 200 °C.

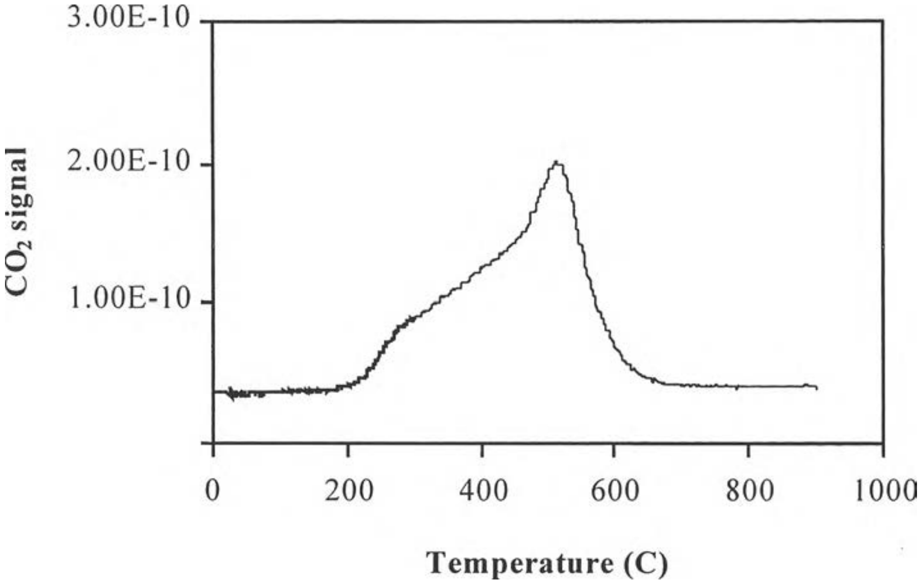

Figure 4.29 TPO profile for the 0.5% Pt/SiO_2 catalyst after spent in n-octane aromatization for 20 hours on stream

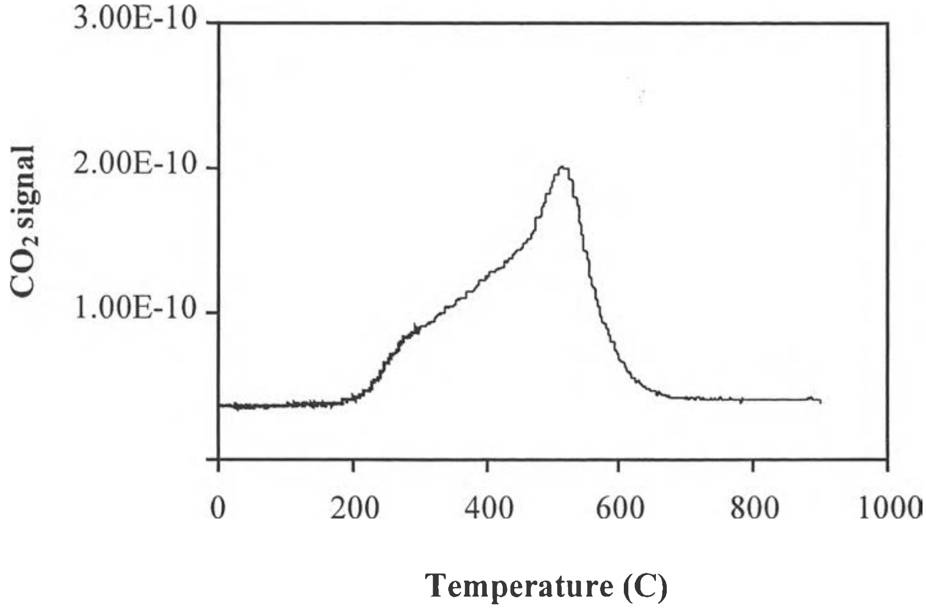

Figure 4.30 TPO profile for the 1% Pt/SiO_2 catalyst after spent in n-octane aromatization for 20 hours on stream

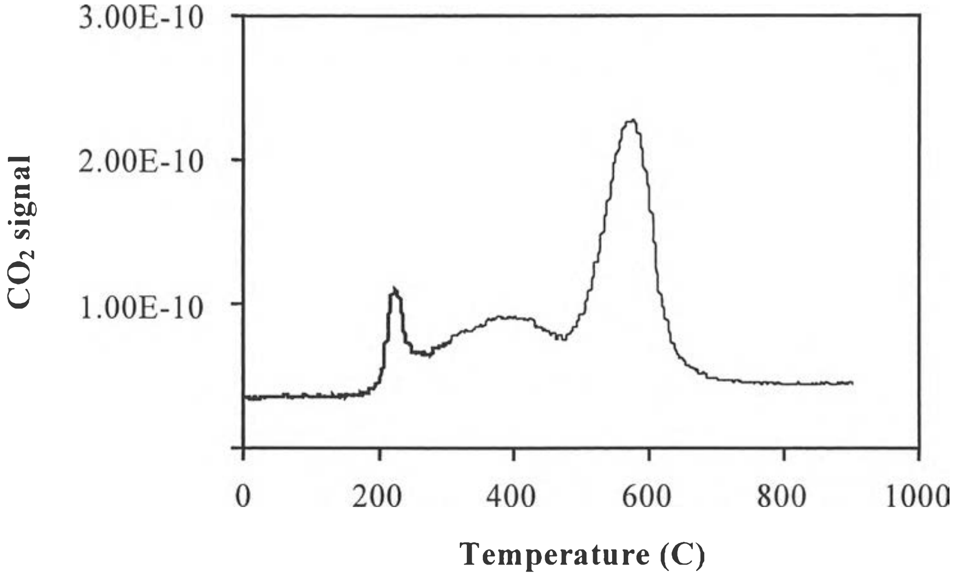

Figure 4.31 TPO profile for the 1.5% Pt/SiO_2 catalyst after spent in n-octane aromatization for 20 hours on stream