

CHAPTER IV

RESULTS AND DISCUSSION

4.1 The Aromatization of n-Hexane

4.1.1 Catalytic Activity Measurement

The aromatization of n-hexane was conducted in the flow reactor at 500°C, keeping a H₂/n-hexane (molar) feed ratio of 6 and weight hourly space velocity (WHSV) of 5 h⁻¹ over the IWI, VPI, and rare-earth (Ce) promoted catalyst. The activity of all catalysts was measured as function of conversion, benzene selectivity and time. In this section, the results and discussion be divided into 4 parts: (I) Effect of preparation method, (II) Effect of sulfur in the feed, (III) Effect of rare earth promoter and (IV) Effect of water.

4.1.1.1 Effect of Preparation Method

To study the effect of preparation method, the reaction testing was done as shown in Figure 4.1. It was seen clearly that the Pt/KL catalysts, which prepared by vapor-phase impregnation (VPI) method gave significantly higher in both conversion and benzene selectivity than those of incipient wetness impregnation (IWI) catalysts. This result agreed with the observation (Jacobs *et al.*, 1999) that the different methods of preparation caused the different Pt clusters distribution, by the various characterization techniques revealed that both IWI and VPI preparation methods gave Pt clusters, which have a very small size located inside the L zeolite channels. However, it was demonstrated that the VPI catalysts lead the formation of very small Pt particles interaction with the zeolite walls than those of the IWI catalysts. Therefore the VPI catalysts were better than the IWI catalysts for n-hexane aromatization.

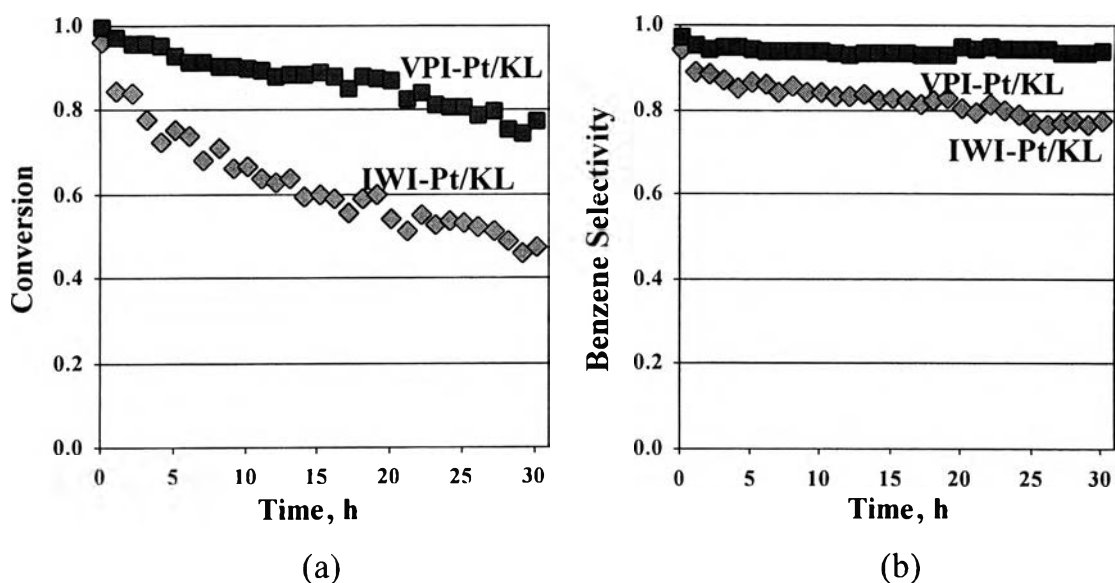


Figure 4.1 The variation of conversion and benzene selectivity with time on stream of Pt/KL catalysts prepared by IWI and VPI method, at 500°C, WHSV = 5 h⁻¹.

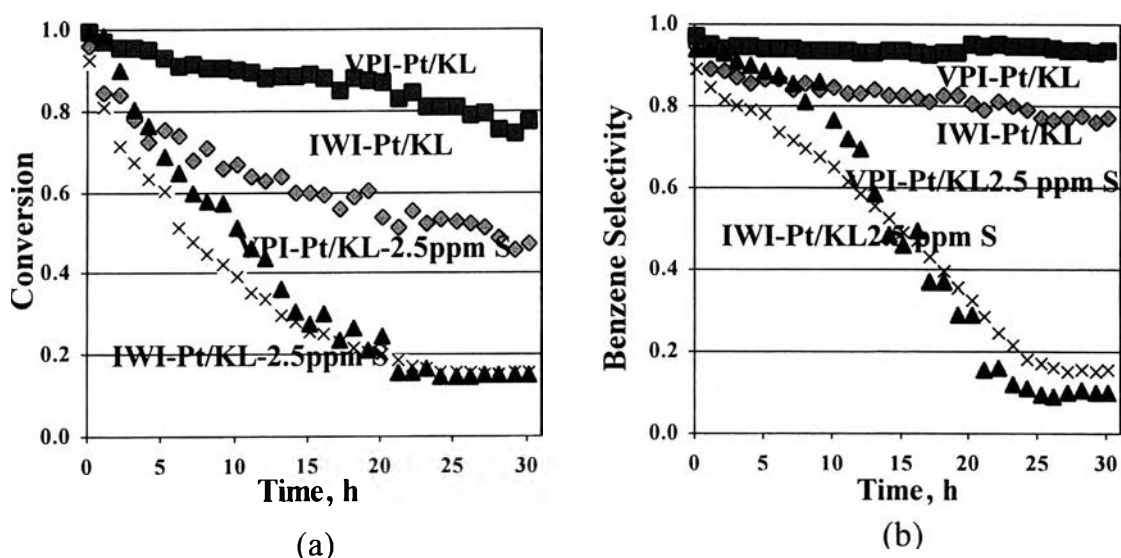


Figure 4.2 The variation of conversion and benzene selectivity with time on stream of Pt/KL catalysts in clean condition and in the presence of 2.5 ppm sulfur at 500°C, WHSV = 5 h⁻¹.

4.1.1.2 Effect of Sulfur in the Feed

Figure 4.2 shows the comparison of both the IWI and VPI catalysts in sulfur-free and 2.5 ppm sulfur-poisoned condition. It was observed that the presence of sulfur in the feed caused the dramatic decrease in conversion and selectivity for both IWI and VPI catalysts. As previously reported (Vaarkamp *et al.*, 1992), the deactivation of Pt/KL catalysts for the aromatization resulting from the Pt agglomeration after exposed to sulfur especially the agglomeration occurred near the pore mouth that caused the block of zeolite channel. Moreover, in the 2.5 ppm sulfur-poisoned condition the Pt/KL prepared by VPI method shows a little better catalytic performance than those IWI catalysts.

4.1.1.3 Effect of Rare Earth Promoter

In clean condition, the study of effect of rare earth promoters was done as illustrated in Figure 4.3 by using the same preparation method, VPI, for both unpromoted and promoted Pt/KL catalysts. It can be seen that by adding 0.15%wt of rare earth promoter (Ce), the benzene selectivity of rare earth promoted catalysts are nearly the same as the unpromoted. For the conversion, the addition of rare earth promoter did not improve the catalytic performance in clean condition. That maybe because of rare earth elements may have some undesirable effect on the adsorption of n-hexane on Platinum, resulting in the low conversion as shown in Figure 4.3 (a).

However, an observation as illustrated in Figure 4.4 that the rare earth promoted Pt/KL catalysts show significantly higher in both conversion and benzene selectivity than those unpromoted in the 2.5 ppm sulfur-poisoned condition. The idea to increase sulfur tolerance of Pt/KL catalysts prepared by vapor-phase impregnation method by adding Thulium as rare earth promoter was reported (Jacobs *et al.*, 1999). As the activity enhancement due to the rare earth promoter in sulfur-poisoned condition for n-

hexane aromatization, by the rare earth elements may act as anchoring sites for the Pt particles, thus preventing the Pt agglomeration or they may act as sulfur getters to protect Pt from sulfur poisoning.

4.1.1.4 Effect of Water

The study of effect of water have done by feeding 17%wt water vapor at time on stream (TOS) = 9 hr. As illustrated in Figure 4.5, from TOS = 10 hr, it was observed the catalyst deactivation as shown from the drop of aromatization activity and selectivity. The deactivation of catalysts in the presence of water vapor may due to the Pt agglomeration to PtO in hydrothermal conditions (Ohtsuka and Tabata, 1999). Moreover, it can be seen that the addition of rare earth promoter helped to increase the stability of the aromatization catalysts after exposing to water vapor.

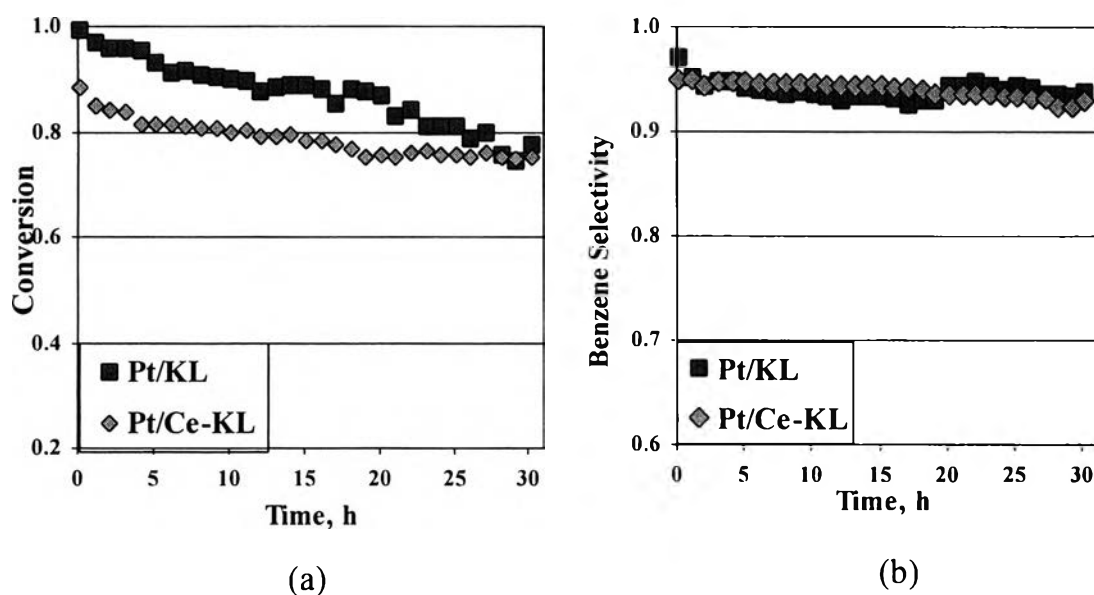


Figure 4.3 The variation of conversion and benzene selectivity with time on stream of VPI catalysts in clean condition, at 500°C, WHSV = 5 h⁻¹.

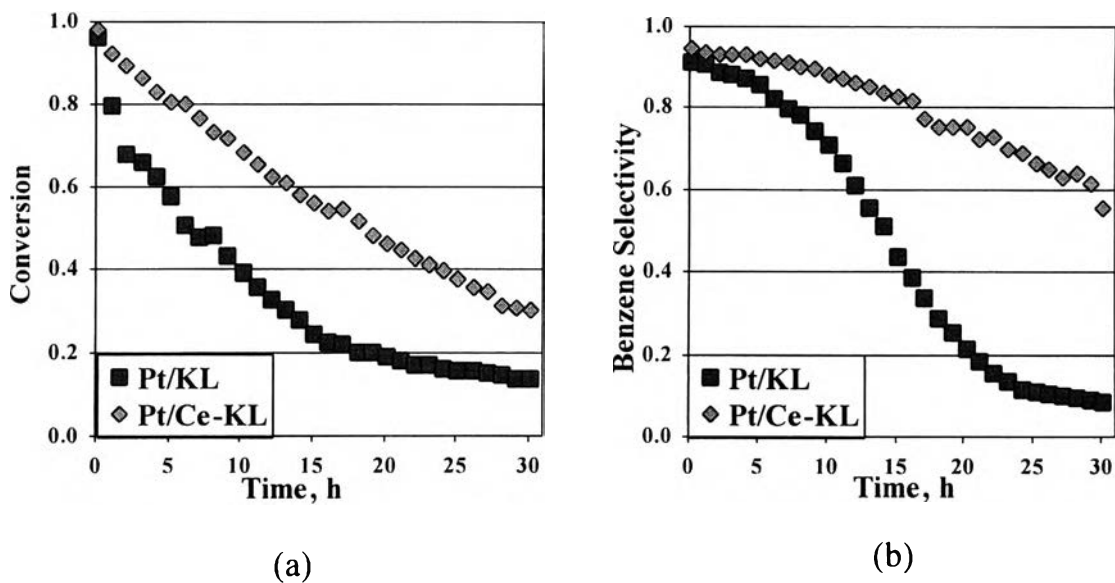


Figure 4.4 The variation of conversion and benzene selectivity with time on stream of VPI catalysts in 2.5 ppm sulfur-poisoned condition, at 500°C, WHSV = 5 h⁻¹.

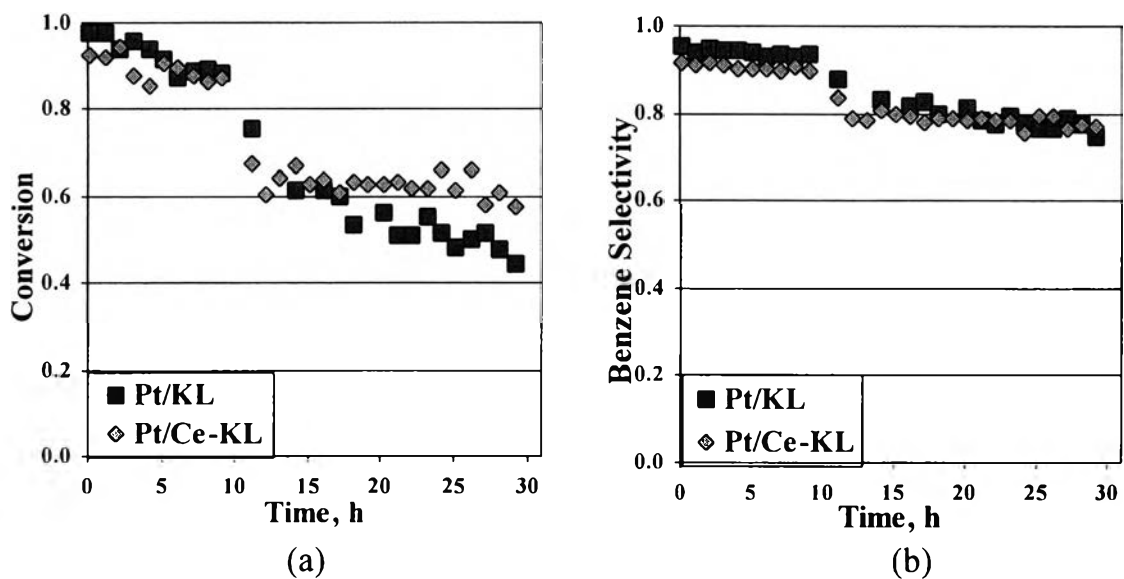


Figure 4.5 The variation of conversion and benzene selectivity with time on stream of VPI catalysts in water vapor-poisoned condition, at 500°C, WHSV = 5 h⁻¹.

4.2 The Aromatization of n-Octane

4.2.1 Catalytic Activity Measurement

The aromatization of n-octane was conducted in the flow reactor at 500°C, keeping a H₂/n-octane (molar) feed ratio of 6 and weight hourly space velocity (WHSV) of 5 h⁻¹ over the IWI, VPI, and Ce promoted catalyst. The activities of all catalysts were measured as function of conversion, total aromatic selectivity, and time. In this section, the results and discussion be divided into 4 parts: (I) Effect of preparation method, (II) Effect of sulfur in the feed, (III) Effect of rare earth promoter and (IV) Effect of water.

4.2.1.1 *Effect of Preparation Method*

For the study of n-octane aromatization on the effect of preparation method by using the two preparation methods, conventional incipient wetness impregnation (IWI) and vapor-phase impregnation (VPI) the results are as shown in Figure 4.6. It can be seen obviously that the VPI catalysts gave higher value of conversion, total aromatic selectivity than those IWI catalysts. This results also consistent with the n-hexane aromatization that the VPI catalysts reveal the higher fraction of small Pt particles inside the channel of L-zeolite. Therefore the characteristic morphology of Pt particles produced by the VPI method gave the better catalytic performance for n-octane aromatization.

4.2.1.2 *Effect of Sulfur in the Feed*

Figure 4.7 show the aromatization of n-octane by using Pt/KL catalysts, when comparing with the clean condition, the presence of 2.5 ppm sulfur in the feed caused the drop of conversion, total aromatic selectivity for both IWI and VPI catalysts. As mentioned before that the deactivation of Pt/KL catalysts resulting from the Pt agglomeration which was accelerated by sulfur.

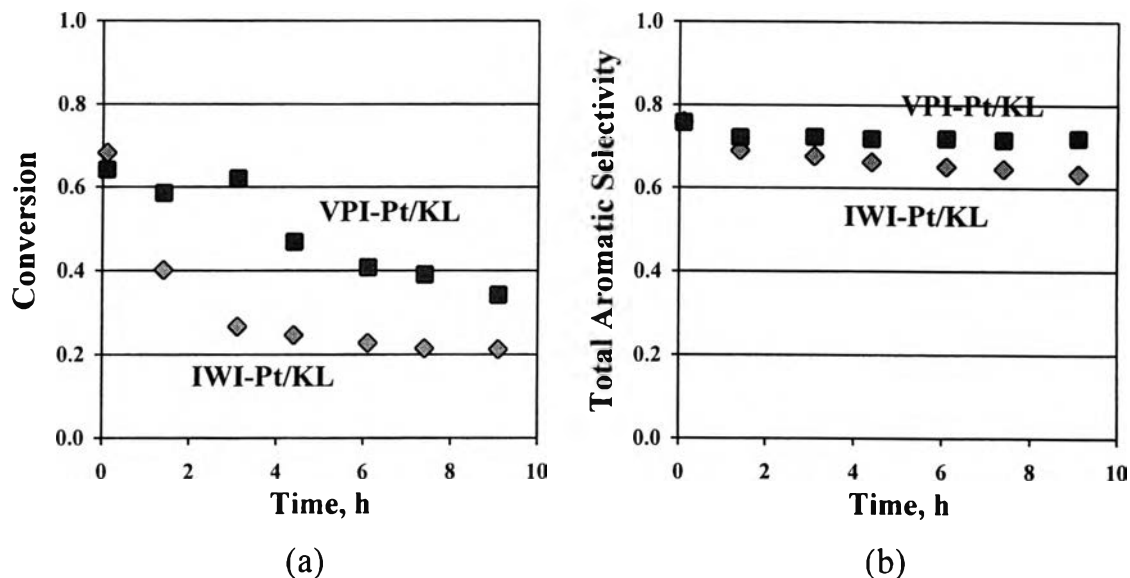


Figure 4.6 The variation of conversion and total aromatic selectivity with time on stream of Pt/KL catalysts prepared by IWI and VPI method, at 500°C. WHSV = 5 h⁻¹.

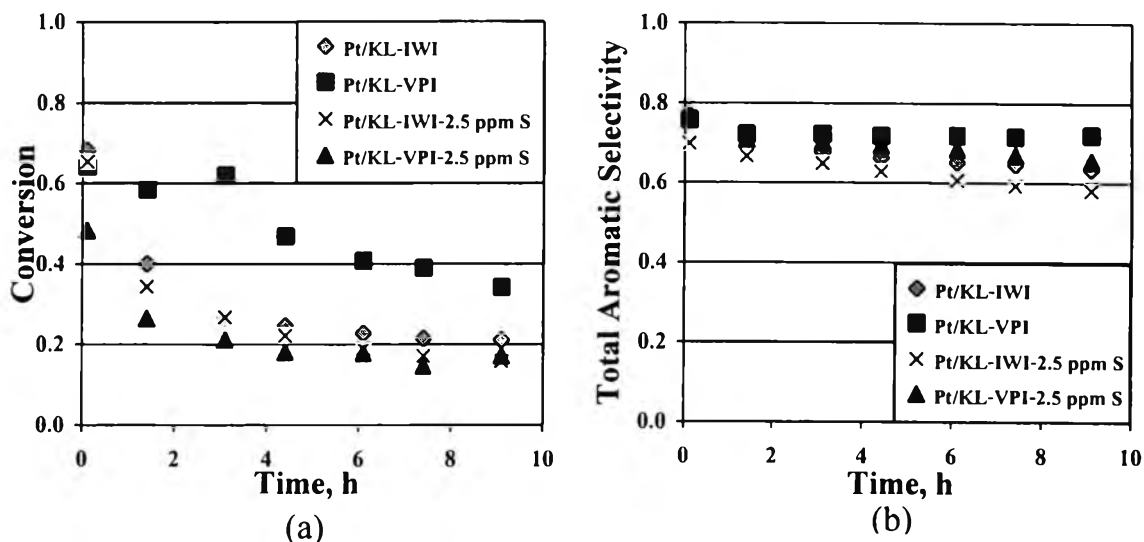


Figure 4.7 The variation of conversion and total aromatic selectivity with time on stream of Pt/KL catalysts in clean condition and in the presence of 2.5 ppm sulfur, at 500°C, WHSV = 5 h⁻¹.

Furthermore, these results also demonstrated that although in the presence of sulfur, the VPI catalysts usually gave the better performance than the IWI catalysts.

4.2.1.3 Effect of Rare Earth Promoter

As illustrated in Figure 4.8, in clean condition, the promoted Pt/Ce-KL catalysts give nearly the same catalytic activity and selectivity as the unpromoted Pt/KL catalysts for the same preparation method. It signified that Ce did not affect on the catalytic performance.

Figure 4.9 shows the effect of rare earth promoter in 2.5 ppm sulfur-poisoned condition. It can be observed that the addition of rare earth promoter show a little help to increase sulfur tolerance for this reaction, as the Ce-promoted catalyst shows a higher in conversion than the unpromoted, and the total aromatic selectivity of both catalyst are nearly the same. Anyhow, the improvement of the catalytic performance due to Ce-promoted in sulfur-poisoned condition maybe seen in the longer run as the C₆ aromatization results. Furthermore, the preparation method still had a strong effect even in sulfur-poisoned condition.

4.2.1.4 Effect of Water

The study of effect of water was done by feeding 16.8 %wt water vapor at time on stream (TOS) = 4.3 hr. Figures 4.10 and 4.11 show the conversion, total aromatic selectivity of the unpromoted and Ce promoted Pt/KL catalysts, respectively. It can be found that for the n-octane aromatization, the catalyst deactivation due to water vapor may occur slightly. Hence the decrease of the catalytic performance was not clearly observed.

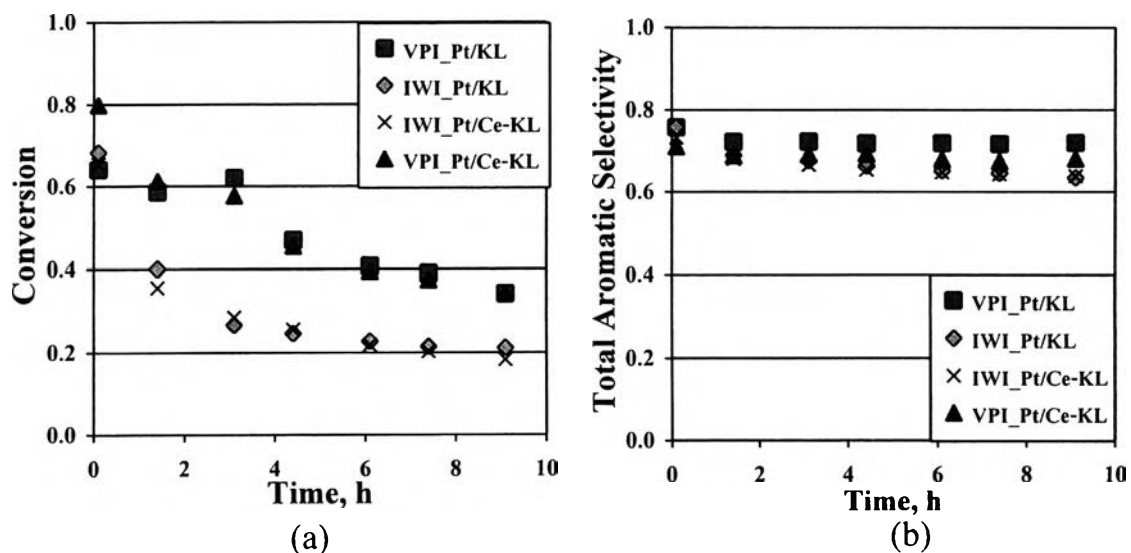


Figure 4.8 The variation of conversion and total aromatic selectivity with time on stream of Pt/KL catalysts in clean condition at 500°C, WHSV = 5 h⁻¹.

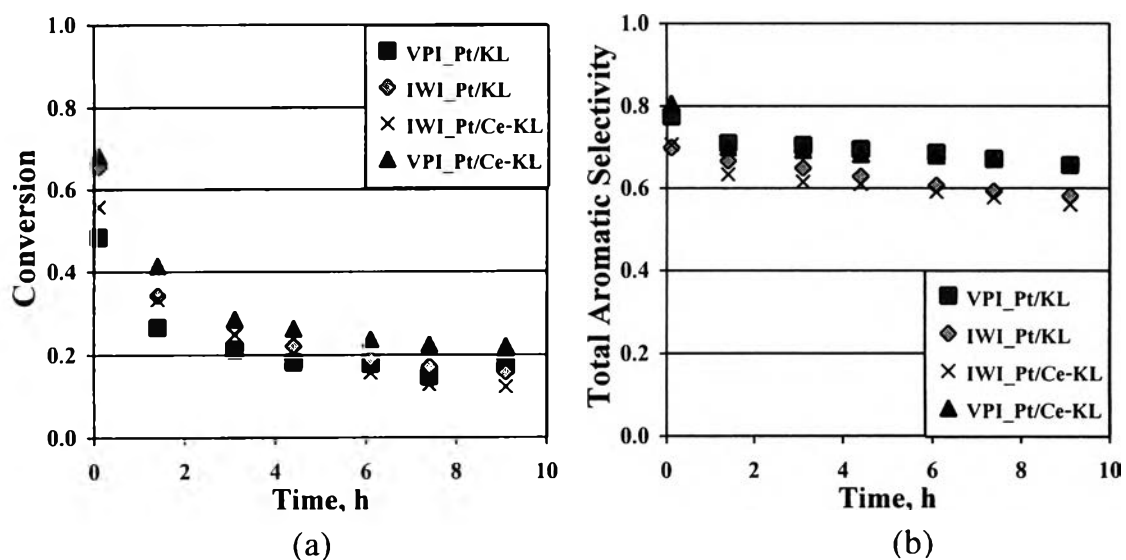


Figure 4.9 The variation of conversion and total aromatic selectivity with time on stream of Pt/KL catalysts in 2.5 ppm sulfur-poisoned condition by at 500°C, WHSV = 5 h⁻¹.

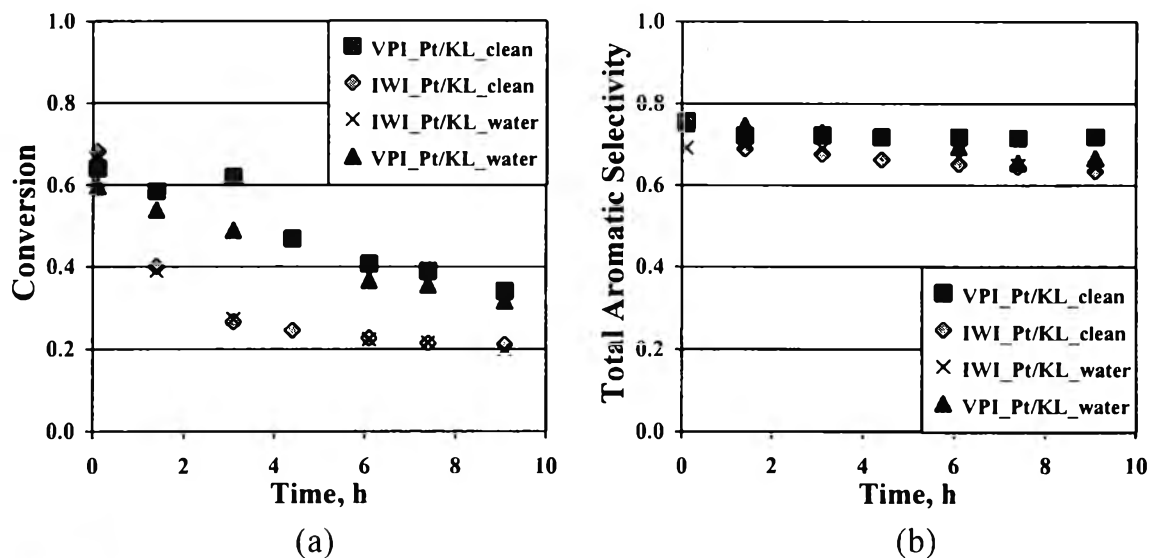


Figure 4.10 The variation of conversion and total aromatic selectivity with time on stream of unpromoted Pt/KL catalysts in clean condition and in water vapor-poisoned condition, at 500°C, WHSV = 5 h⁻¹.

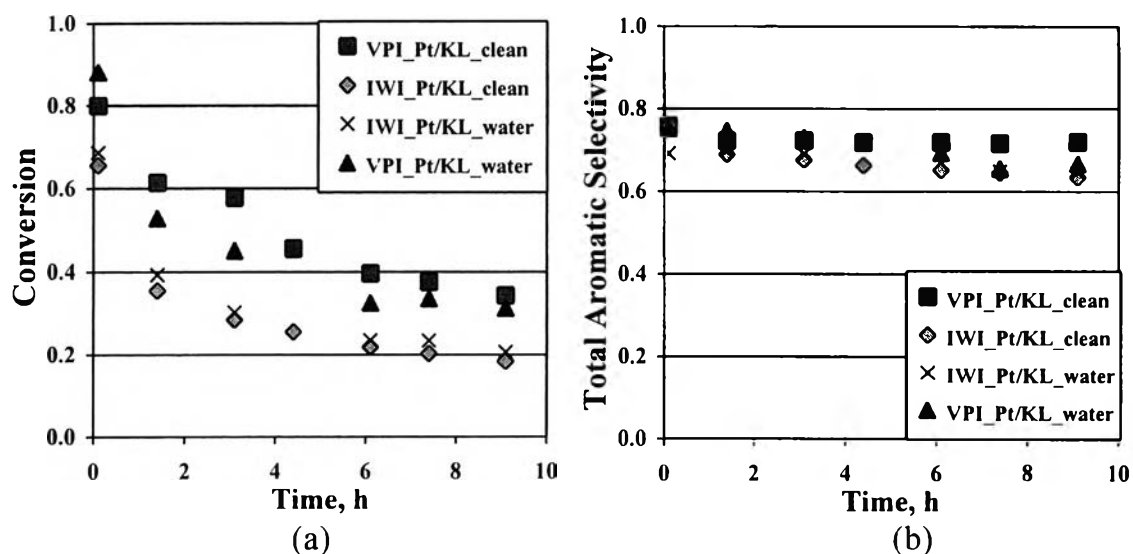


Figure 4.11 The variation of conversion and total aromatic selectivity with time on stream of promoted Pt/Ce-KL catalysts in clean condition and in water vapor-poisoned condition, at 500°C, WHSV = 5 h⁻¹.

4.2.2 Catalyst Characterization

The several characterization techniques are applied in this work to investigate the properties of all catalysts.

4.2.2.1 Hydrogen Chemisorption Measurement

The Pt/KL catalysts prepared by different methods (IWI and VPI) and the Ce-promoted catalysts were characterized to quantify %Pt dispersion by using hydrogen chemisorption techniques. The %Pt dispersion of all catalysts after the reduction in either 400°C or 500°C is reported in Table 4.1. For the same batch of fresh Pt/KL catalyst that prepared by same VPI preparation method, after reduced at lower temperature (400°C), it can be observed the higher %Pt dispersion than those reduced at 500°C. These results are consistent with the report by M'Kombe *et al.* (1997). They investigated that the reduction at high temperature (600°C) can caused the sintering of Pt while it did not have this effect on the catalyst which reduced at below 350°C. When comparing the %Pt dispersion of the Pt/KL catalysts prepared by different method (IWI and VPI) after reduced at the same 500°C, the VPI catalysts resulting higher %Pt dispersion than those of IWI catalysts. This result agrees with the work done by Jacobs *et al.* (2001) which shows that the Pt/KL catalyst prepared by VPI method is effective in dispersing Pt. It can be seen that, after the reduction at similar temperature (500°C), the addition of Ce as promoter showed lower %Pt dispersion value than the unpromoted Pt/KL catalysts, that maybe because of Ce exhibited the undesired effect to the catalyst that caused the loss in active area of Pt particles.

Table 4.1 The %Pt dispersion of catalysts by hydrogen chemisorption.

Catalyst	Preparation method	Temperature (°C)	Pt dispersion (%)
Pt/KL	VPI	400	97.14
		500	81.51
Pt/KL	IWI	500	78.39
PtCe/KL	VPI	500	63.45

4.2.2.2 Fourier Transform-Infrared Spectroscopy of Adsorbed CO

The fresh and spent catalysts were characterized by FT-IR of adsorbed CO to determine the morphology and location of Pt clusters on the catalysts. This technique is useful for making general conclusions about the location (i.e. inside the L-zeolite or external) and the distribution of the Pt clusters prior to disruption (Jacobs *et al.*, 2000). It has been proposed by Stakheev *et al.* (1995), that the different regions of wavenumber corresponding to the variations of morphology of Pt clusters. Regarding to these hypotheses for the low-wavenumber bands (2050-1930 cm^{-1}), are assigned to Pt-CO species arise from the disruption of small Pt clusters inside the L-zeolite channels. The bands between 2050 and 2075 cm^{-1} are associated with larger Pt clusters in the near-surface region of the L-zeolite. In contrast, the bands at and above 2075 cm^{-1} are in general assigned to larger Pt particles on the external surface of the L-zeolite. In this section, the spectra of FT-IR of adsorbed CO of the fresh and spent catalysts were examined, the results and discussion are divided into 4 parts: (I) Effect of preparation method, (II) Effect

of sulfur in the feed, (III) Effect of rare earth promoter and (IV) Effect of water.

(I) Effect of preparation method

Figure 4.12 demonstrated the comparison of FT-IR spectra of fresh Pt/KL catalysts prepared by IWI and VPI method. It was remarkably observed the band around at low wavenumber of the VPI catalysts, while the IWI catalysts represented the band at higher wavenumber. These results agreed very well with previous work that the VPI catalysts favor the formation of Pt carbonyls during CO adsorption which represent the small Pt clusters inside the L-zeolite rather than the IWI catalysts (Jacobs *et al.*, 2000). These FT-IR results are one of the explanations that the VPI catalysts gave better catalytic performance than those of IWI.

(II) Effect of sulfur in the feed

When compare the FT-IR spectra of fresh and sulfur-contaminated Pt/KL catalysts at 500°C as shown in Figure 4.13, it was obviously seen the loss of low wavenumber bands due to sulfur. As the previous catalytic activity results of the aromatization of n-C₆ and n-C₈, both conversion and aromatic selectivity significantly drop due to sulfur poisoning. It was a previous study (Jacobs *et al.*, 2000), which indicated that sulfur can cause Pt agglomeration or sulfur strongly competitively adsorbed on Pt metal surface. Both cases might reduce the quantity of CO adsorbed on Pt surface, therefore the FT-IR results showed the decrease of low-frequency bands and appeared the more Pt clusters at outer L-zeolite channels at high-frequency bands.

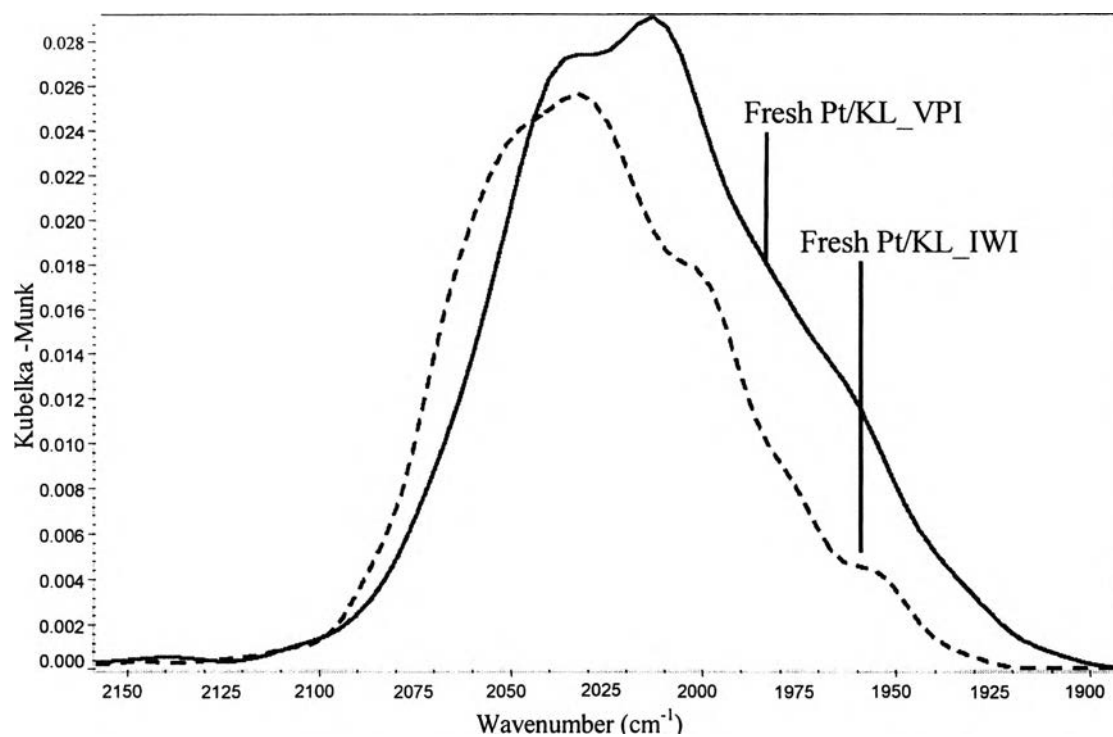


Figure 4.12 FT-IR spectra of Pt/KL catalysts prepared by IWI and VPI method reduced at 500°C. (Effect of preparation method)

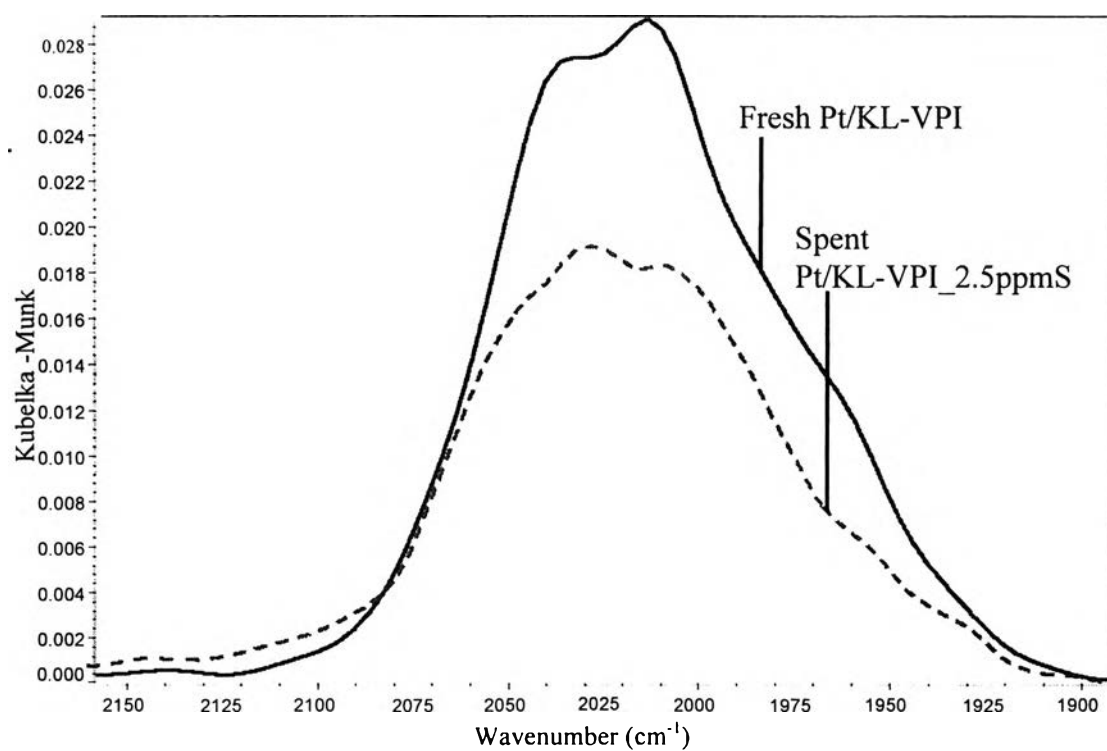


Figure 4.13 FT-IR spectra of Pt/KL_VPI catalysts freshly reduced and after spent in 2.5 ppm sulfur, reduced at 500°C. (Effect of sulfur in the feed)

(III) Effect of Rare Earth Promoter

For n-C₈ aromatization, the addition of Ce as promoter show a higher intensity at the low wavenumber bands as illustrated in Figure 4.14. These results indicated that in the 2.5 ppm sulfur-poisoned condition, the Pt/Ce-KL catalysts represented the small Pt clusters inside the channels of the L-zeolite rather than the unpromoted Pt/KL catalysts. As the work indicated that Ce might acts as sulfur getter, therefore the loss of Pt active area by sulfur are decreased.

(IV) Effect of Water

Figure 4.15 illustrated the FT-IR spectra of the spent Pt/KL and Pt/Ce-KL catalysts after exposing to water. The bands at high wavenumber, at or above 2075 cm⁻¹ were remarkably observed. It can be proposed that the water vapor can significantly cause larger Pt particles on the external surface of the L-zeolite. That maybe due to under water vapor-poisoned condition has much more Pt agglomeration. Moreover, the Ce-promoted Pt/KL catalysts show a little higher intensity at low wavenumber which represented the small Pt clusters inside the channels of L-zeolite rather than the unpromoted Pt/KL catalysts.

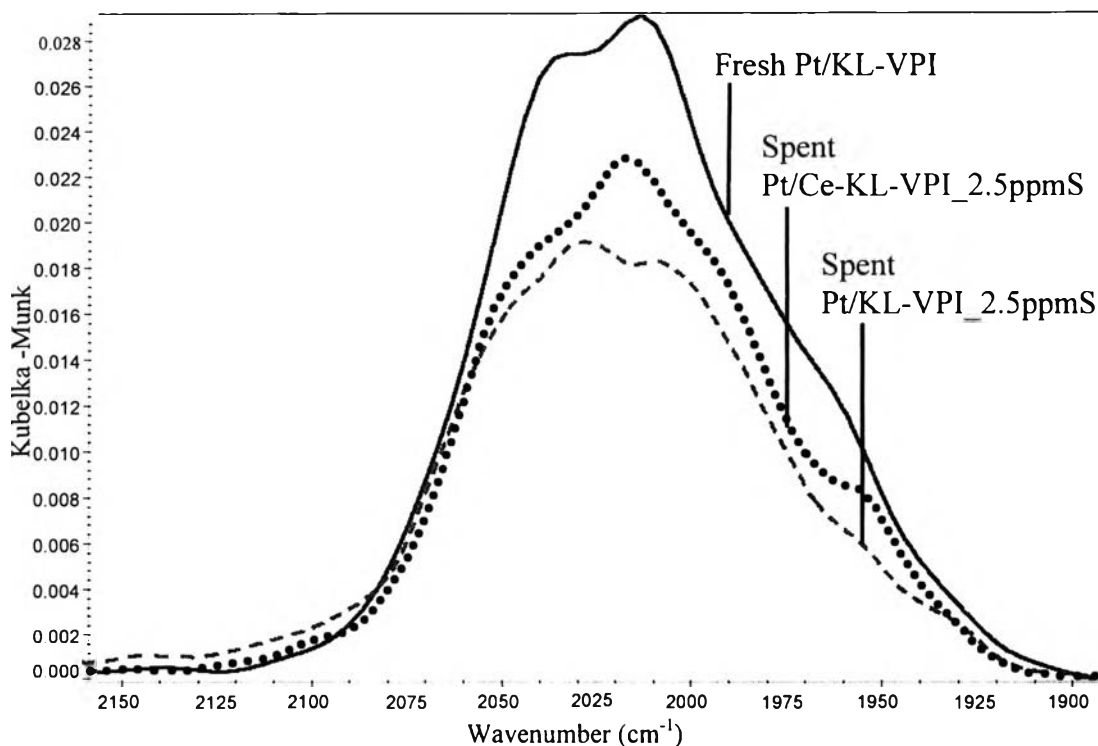


Figure 4.14 FT-IR spectra of Pt/KL-VPI catalysts freshly reduced, Pt/KL-VPI and Pt/Ce-KL-VPI after spent in 2.5 ppm sulfur, reduced at 500°C. (Effect of rare earth promoters_sulfur-poisoned condition)

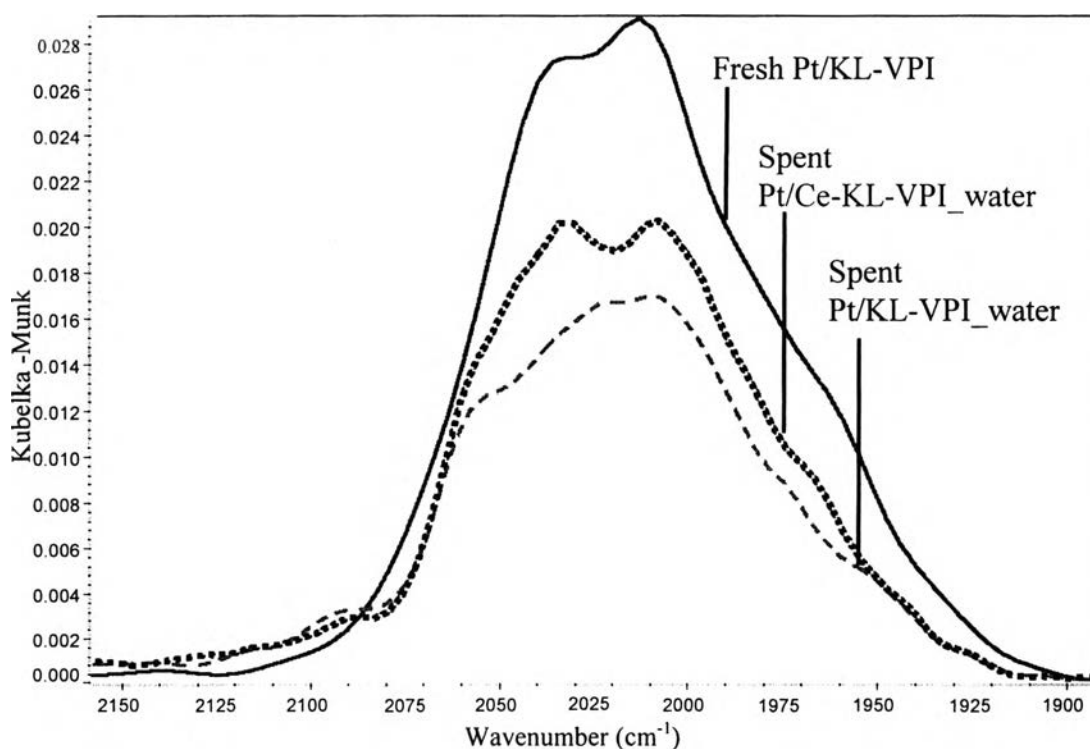


Figure 4.15 FT-IR spectra of Pt/KL-VPI catalysts freshly reduced, Pt/KL-VPI and Pt/Ce-KL-VPI after spent in water containing feed, reduced at 500°C. (Effect of water)

4.2.2.3 Temperature-Programmed Oxidation

The spent catalysts were conducted with TPO measurements in order to examine the amount and nature of the coke deposited on the different catalyst during clean, sulfur- and water-poisoned runs. In this section, the results and discussion be divided into 4 parts: (I) Effect of preparation method, (II) Effect of sulfur in the feed, (III) Effect of rare earth promoter and (IV) Effect of water.

(I) Effect of preparation method

Table 4.2 summarized the amount of carbon deposited in the n-C₈ aromatization reaction of each spent catalyst after 9 h on stream with clean, 2.5 ppm sulfur and water condition. When comparing the amount of coke deposition of Pt/KL catalysts prepared by different methods (IWI and VPI) after 9 h run in clean condition. It was observed that the %C of both IWI and VPI catalysts are nearly the same. Anyway, as illustrated in Figure 4.16 of the TPO profiles of both IWI and VPI catalysts, the IWI catalysts gave the profile that shifted to higher temperature that caused the difficult to Pt-catalyzed oxidation of carbon during TPO.

Table 4.2 Amount of carbon deposited in the n-C₈ aromatization reaction, as determined by TPO.

Catalyst	% C after 9-h run, clean condition	% C after 9-h run, 2.5 ppm S condition	% C after 9-h run, water condition
Pt/KL-IWI	2.15	-	-
Pt/KL-VPI	2.26	2.40	2.75
Pt/Ce-KL-VPI	2.52	2.42	-

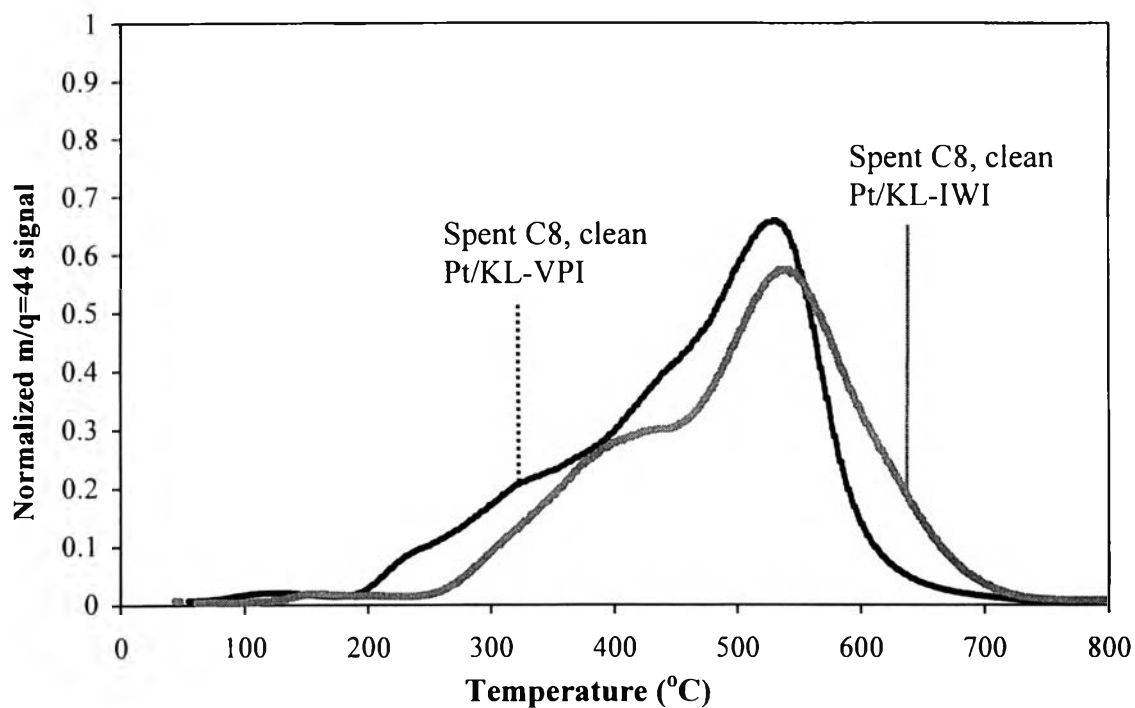


Figure 4.16 TPO profiles for the Pt/KL catalysts prepared by IWI and VPI method after clean run of n-C₈ aromatization. (Effect of preparation method)

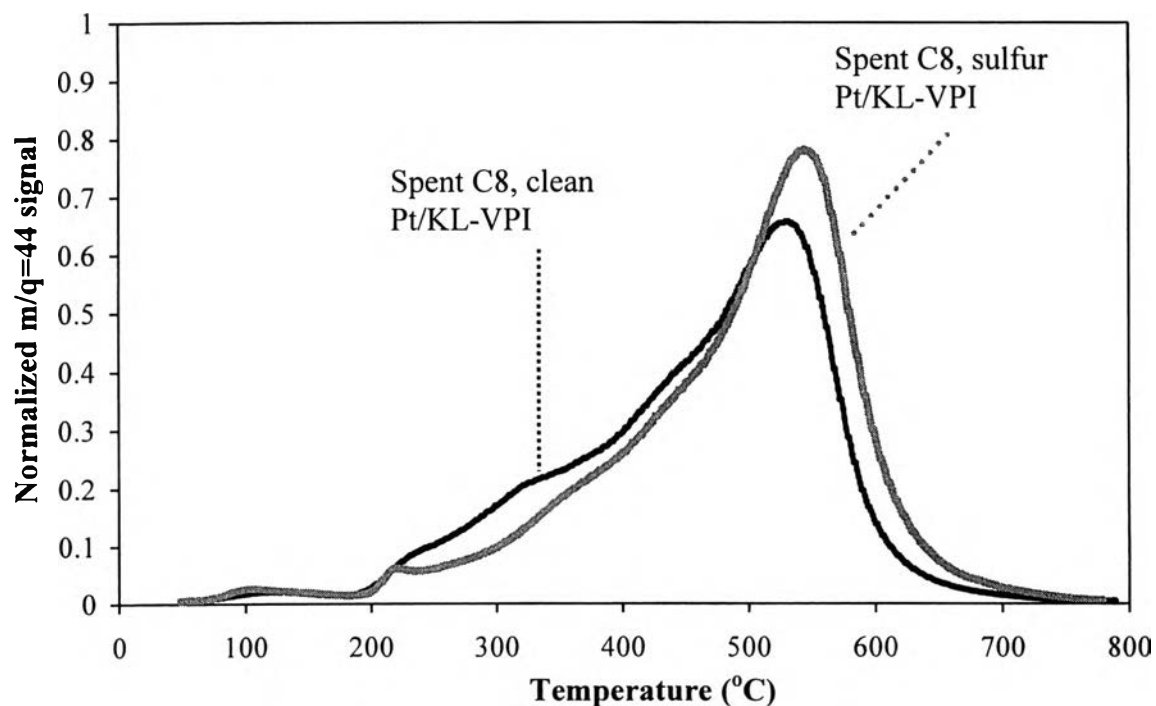


Figure 4.17 TPO profiles for the Pt/KL-VPI catalysts after clean run and after spent in 2.5 ppm sulfur of n-C₈ aromatization. (Effect of sulfur in the feed)

(II) Effect of sulfur in the feed

For the TPO measurements of n-C₈ aromatization reaction for Pt/KL catalysts after exposing to 2.5 ppm sulfur condition, it was investigated the amount of carbon deposited of Pt/KL catalysts as summarized in Table 4.2 that the spent of sulfur gave a little higher coke formation than the spent of clean. This result may be caused by the Pt agglomeration due to sulfur generated more coke than the Pt clusters that were well dispersed. Moreover, the sulfur-poisoned catalysts showed the TPO profile that shifted to higher temperature as illustrated in Figure 4.17. It was a study by Jacobs *et al.* (2000) for n-C₆ aromatization that the presence of sulfur on the poisoned platinum clusters inhibited Pt-catalyzed oxidation of carbon during the TPO, thus it showed the shifting to higher temperature. The same observation for the Ce-promoted Pt/KL catalysts had also been shown in Figure 4.18.

(III) Effect of rare earth promoter

As indicated in Table 4.2, the amount of carbon deposited for the spent of unpromoted Pt/KL and Ce-promoted Pt/KL catalysts are nearly similar. However, as illustrated in Figure 4.19 for the unpromoted Pt/KL catalysts, the oxidation shifted to higher temperature, while the overall area under the profile remained exactly the same. This is the one observation that could explain that the rare earth could help as a sulfur getter. As the previous study that sulfur inhibited Pt-catalyzed oxidation of carbon, therefore the decrease of sulfur due to rare earth, the spent of Pt/Ce-KL profile shows the lower-temperature peak than the unpromoted Pt/KL catalysts.

(IV) Effect of water

As per the previous discussion that water vapor may cause Pt agglomeration, it was observed from the TPO measurement that the presence of water caused more amount of carbon deposited as shown in Table 4.2 from the spent of Pt/KL-VPI catalyst after clean run and water vapor-poisoned run. This may be caused from the Pt agglomeration giving more

coke formation than the well dispersed Pt particles. In addition, the TPO profile of spent Pt/KL which poisoned by water vapor show the shifting at high temperature peak as illustrated in Figure 4.20. This observation maybe caused from the same explanation of water that inhibited Pt-catalyzed oxidation of carbon during TPO measurement.

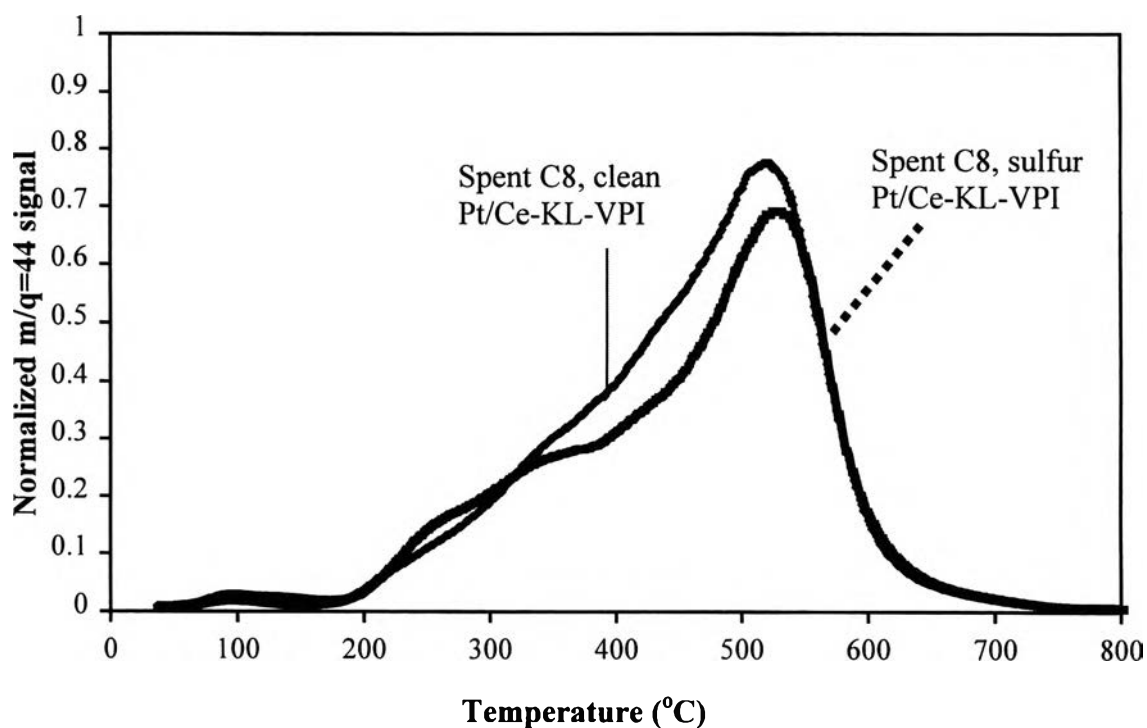


Figure 4.18 TPO profiles for the Pt/Ce-KL-VPI catalysts after clean run and after spent in 2.5 ppm sulfur of n-C₈ aromatization (Effect of sulfur in the feed)

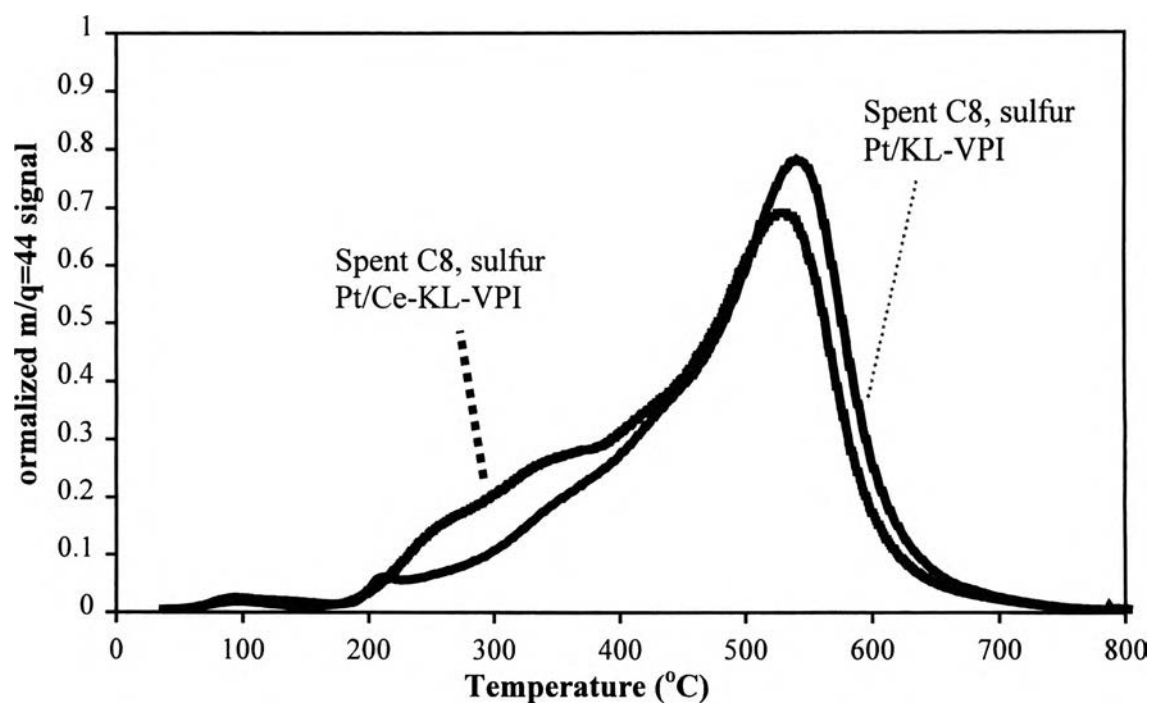


Figure 4.19 TPO profiles for the Pt/KL-VPI and Pt/Ce-KL-VPI catalysts after spent in 2.5 ppm sulfur of n-C₈ aromatization. (Effect of rare earth promoters_sulfur-poisoned condition)

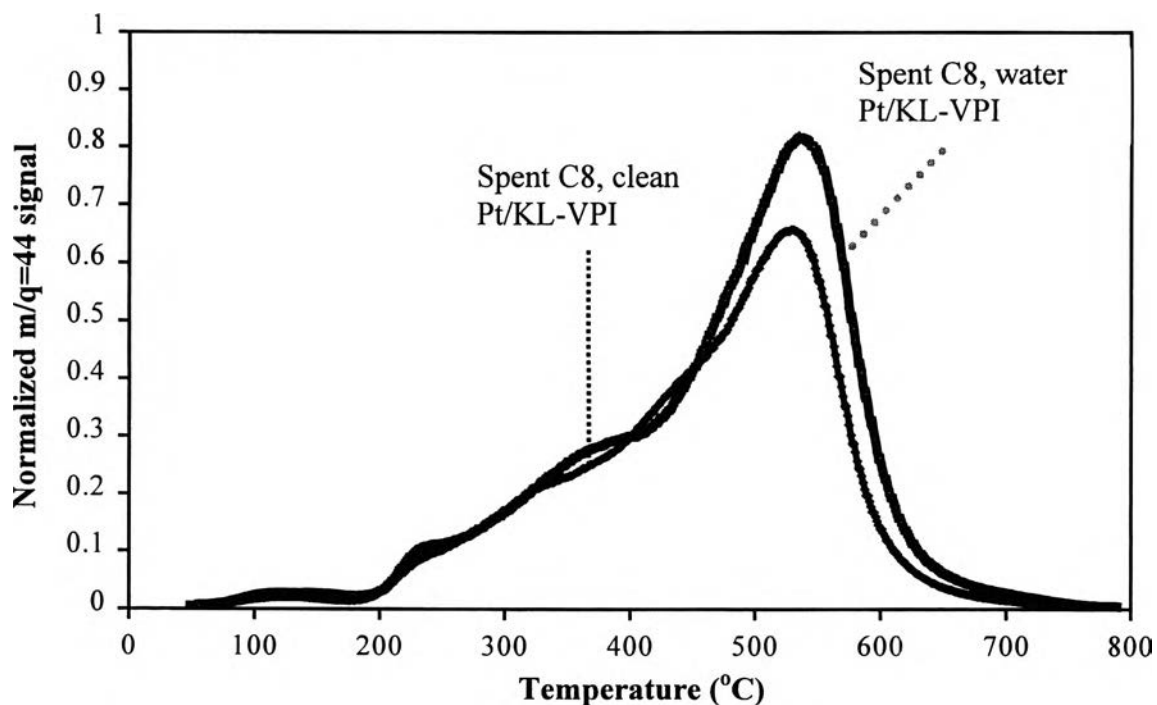


Figure 4.20 TPO profiles for the Pt/KL-VPI catalysts after clean run and after spent in water vapor of n-C₈ aromatization. (Effect of water vapor)

Besides the observation on the amount of carbon deposited in the n-C₈ aromatization, the TPO measurement of the spent Pt/KL catalyst of n-C₆ aromatization was also done in this work in order to compare the amount of coke generate by this two reactions.

Table 4.3 summarized the amount of carbon deposited in the n-C₆ and n-C₈ aromatization reaction of the spent Pt/KL catalysts after 9 h on stream with clean and 2.5 ppm sulfur condition. It can be investigated that the n-C₈ aromatization generate higher amount of carbon than those by n-C₆ aromatization reaction for both sulfur-free and sulfur-poisoned condition. That maybe because of the higher of C atom of C₈ which is not aromatized may cause the coke formation than the C₆ which is suitable for dehydrocyclization in the channels of L-zeolite. It could be the one reason that the C₆ aromatization on Pt/KL catalysts gave higher activity than the C₈ aromatization at the same condition.

Table 4.3 Amount of carbon deposited in the n-C₆ and n-C₈ aromatization reaction, as determined by TPO.

Catalyst	% C after 9-h run, clean condition	% C after 9-h run, 2.5 ppm S condition
VPI-C ₆	1.02	1.03
VPI-C ₈	2.26	2.40

It was investigated that for the spent of C₆ aromatization presented the low temperature peak when compare with the spent of C₈ aromatization as illustrated in Figure 4.21. These situations maybe caused from the reason that C₈ aromatization generate more coke and coke maybe blocking the pore of L-zeolite, thus TPO results of C₈ aromatization presented at higher temperature peak.

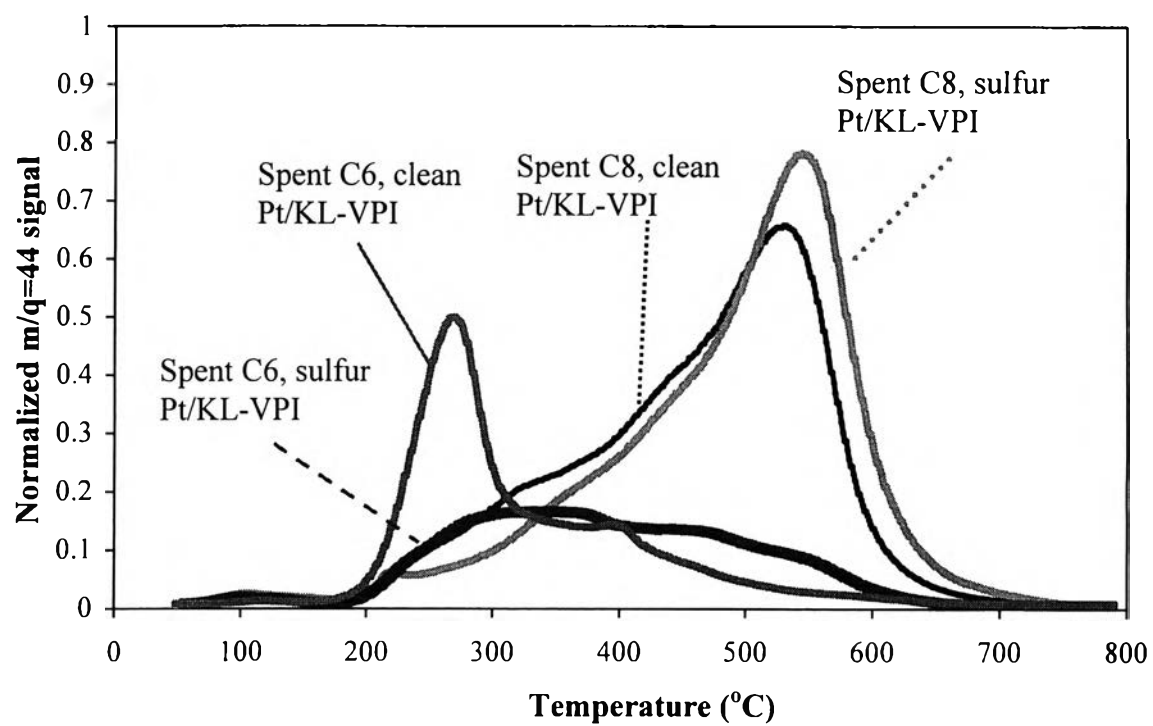


Figure 4.21 TPO profiles for the Pt/KL-VPI catalysts after clean run and after spent in 2.5 ppm sulfur for both the aromatization of n-C₆ and n-C₈.