

## CHAPTER IV

### RESULTS AND DISCUSSION

#### 4.1 Catalyst Characterization

##### 4.1.1 Hydrogen Chemisorption Measurement

All of the catalysts from IWI and CVD methods were characterized by Hydrogen Chemisorption Technique to quantify % Pt dispersion. The results in Table 4.1 showed the effect of reduction temperature on the dispersity of Pt metal loaded on the zeolite catalysts . Pt could disperse greatly at the low temperature (400°C) whereas this value would be decreased after being reduced at higher temperature (500°C). The result agrees well with those reported by M'Kombe *et al.* (1997) who found that reduction at 600°C resulted in sintering of the Pt while it did not have a marked effect on dispersion at below 350°C. The addition of Ce as promoter showed higher % Pt dispersion value than Pt/KL. It meant that added Ce helped increasing Pt dispersion on the zeolite L surface. This corresponded to the effect of Tm which was one of rare earth metals on Pt/KL examined by Jacobs *et al.* (2000). The presence of Tm resulted in a catalyst with higher Pt dispersion.

##### 4.1.2 Fourier Transform-Infrared Spectroscopy

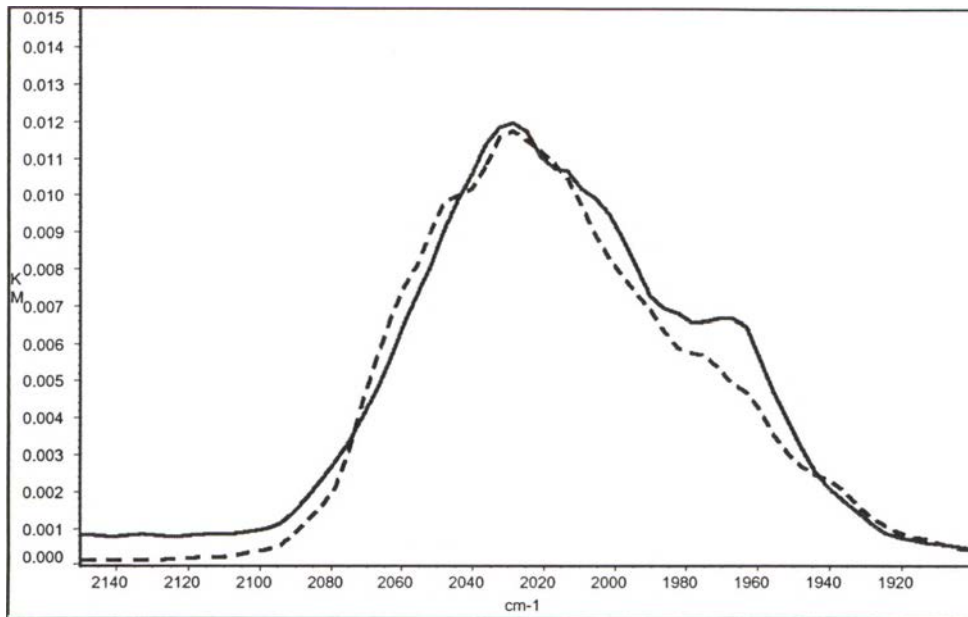
The fresh and spent catalysts were characterized by FT-IR of adsorbed CO to determine the morphology and location of Pt clusters on the catalysts. The wave number of the 2100-1950  $\text{cm}^{-1}$  region of the infrared spectra was emphasized on because this region is the range of CO adsorbed on Pt surface. At 400°C, a shoulder, at 1970  $\text{cm}^{-1}$ , appeared on a spectrum of Pt/KL prepared by CVD method while it was not observed on that of Pt/KL

**Table 4.1** Comparison % Pt dispersion of catalysts.

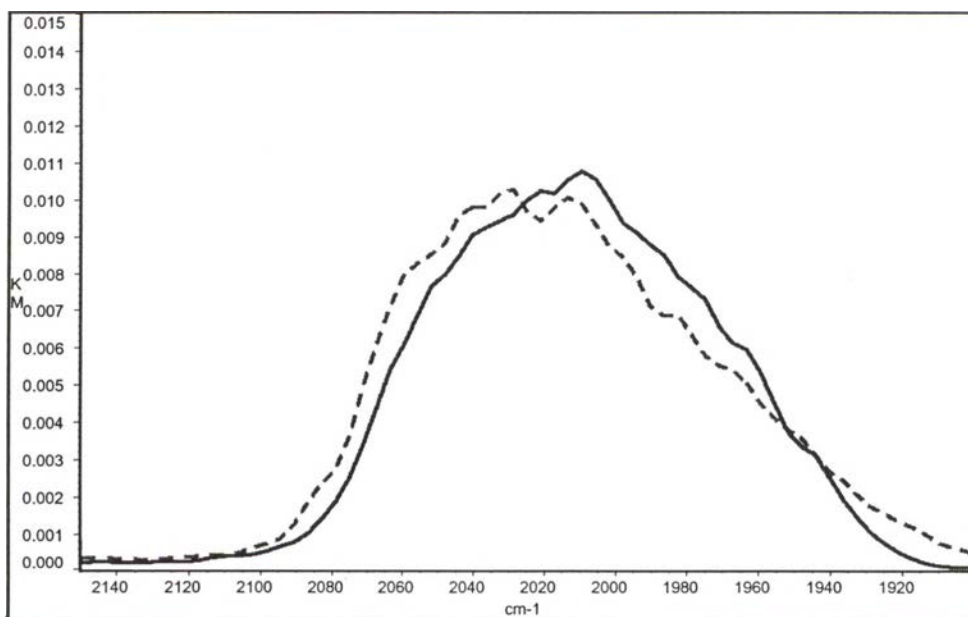
Catalyst	Preparation method	Temperature (°C)	Pt dispersion (%)
Pt/KL	IWI	400	
		500	70.19
Pt/KL	CVD	400	90.30
		500	70.99
PtCe/KL	CVD	400	
		500	75.59

prepared by IWI method as shown in Figure 4.1. This shoulder indicated small Pt clusters inside L-zeolite channels (Stakheev *et al.*, 1995 and Jacobs *et al.*, 1999). It meant that Pt dispersed greatly on Pt/KL catalyst prepared by CVD method than that prepared by IWI method. Moreover, at higher temperature (500°C) as shown in Figure 4.2, both spectra were similar but the shift to high wave number occurred on IWI catalyst whereas the spectrum of CVD catalyst was still at low wave number. At higher temperature, Pt clusters can be easily agglomerated on IWI catalyst than CVD catalyst or CVD catalyst had more resistance to Pt particle growth than IWI catalyst.

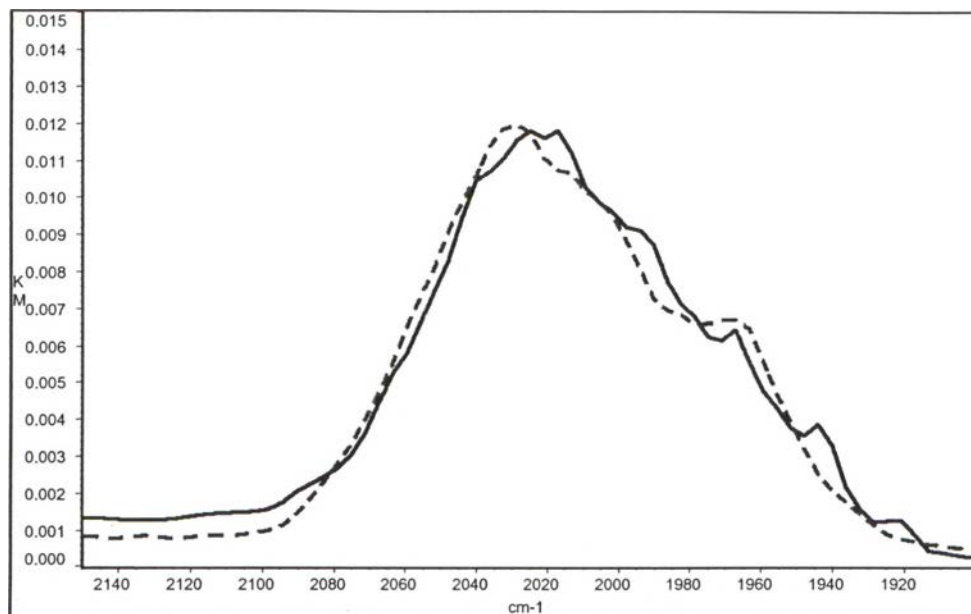
For the effect of added Ce, it was found that both spectra of Pt/KL and PtCe/KL, at 400°C, were similar. There were shoulders in low wave number region as shown in Figure 4.3. It was shown in Figure 4.4 that a spectrum of PtCe/KL was still in the low wave number region while a spectrum of Pt/KL shifted to high wave number at higher temperature condition. Both spectra rarely had shoulders. The above results supported that Ce might improve a resistance to Pt cluster growth.



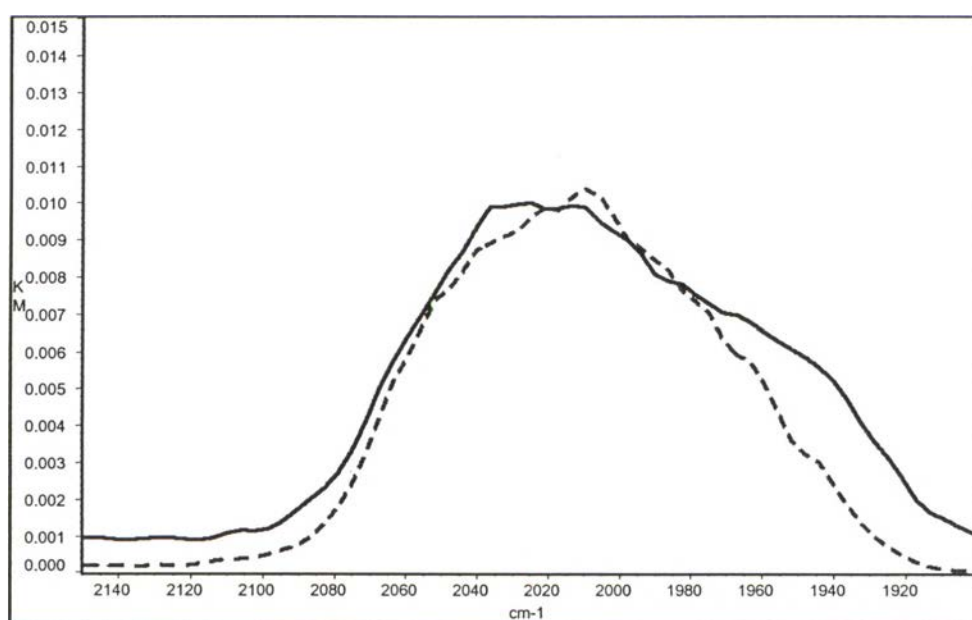
**Figure 4.1** FT-IR spectra of Pt/KL reduced at 400°C, (---) IWI method, (—) CVD method.



**Figure 4.2** FT-IR spectra of Pt/KL reduced at 500°C, (---) IWI method, (—) CVD method.



**Figure 4.3** Effect of added Ce on Pt/KL, reduced at 400°C, prepared by CVD method , (---) Pt/KL, (—) PtCe/KL.



**Figure 4.4** Effect of added Ce on Pt/KL, reduced at 500°C, prepared by CVD method , (---) Pt/KL, (—) PtCe/KL.

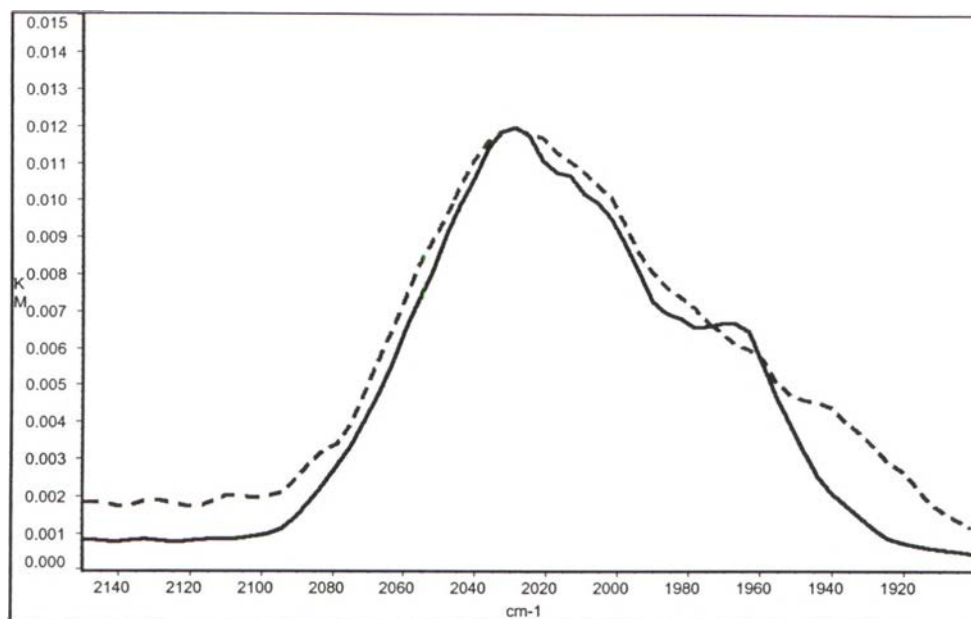
Figure 4.5 demonstrated the comparison of IR spectra of fresh and sulfur-contaminated Pt/KL at 400°C. There was a loss of the shoulder at low wave number region after Pt/KL was exposed to sulfur condition that meant Pt agglomeration occurred or sulfur strongly competitively adsorbed on Pt metal surface. Both explanations might reduce quantity of CO adsorbed on Pt surface. The clear evidence was observed in Figure 4.6. Most spectra of Pt/KL under sulfur condition was at the high wave number region that indicated the appearance of Pt clusters at outer L-zeolite channels. (Stakheev *et al.*, 1995 and Jacobs *et al.*, 1999). In the case of PtCe/KL, there was not much differences between the spectra obtained from sulfur-free and sulfur-containing conditions at both temperatures as shown in Figure 4.7 and 4.8. Ce may act as a sulfur getter (Jacobs *et al.*, 2000) so sulfur did not have much effect on Pt clusters in the catalyst.

In case of increasing sulfur concentration, the spectra were different, especially at high temperature as shown in Figure 4.9 and 4.10. The area under peak of less sulfur condition at low wave number region was greater than that of more sulfur conditions. Moreover, the spectrum of 2.5 ppm sulfur concentration at 500°C showed a much narrow peak at about 2037  $\text{cm}^{-1}$  that indicated the presence of Pt clusters near pore-mouth of L-zeolite (Stakheev *et al.*, 1995). There were more Pt clusters inside L-zeolite channels in 0.6 ppm-sulfur spent catalyst than in 2.5 ppm sulfur-spent catalyst. A loss of Pt dispersion was proportional to sulfur concentration. The similar results were also found on PtCe/KL as illustrated in Figure 4.11 and 4.12.

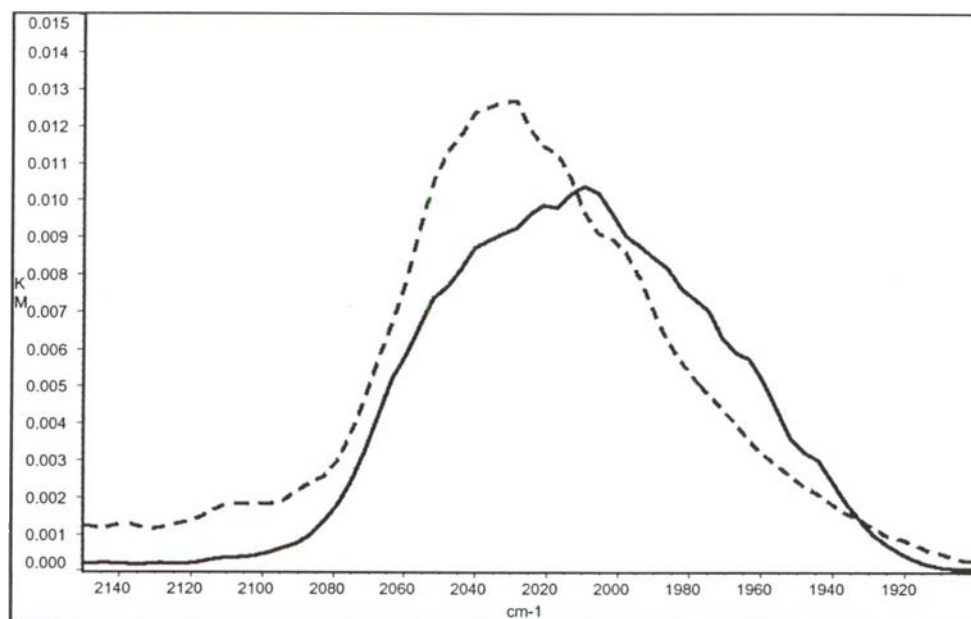
## 4.2 Catalyst Activity

### 4.2.1 Comparison of Catalyst Preparation

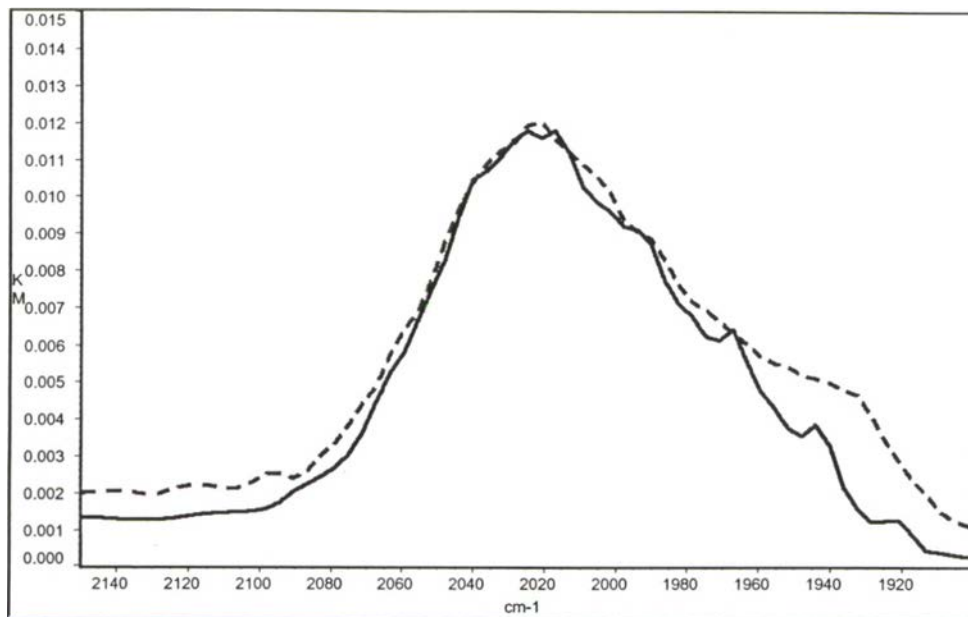
All catalysts were tested for the catalytic activity of n-hexane aromatization reaction. The activity of catalyst was measured as functions of



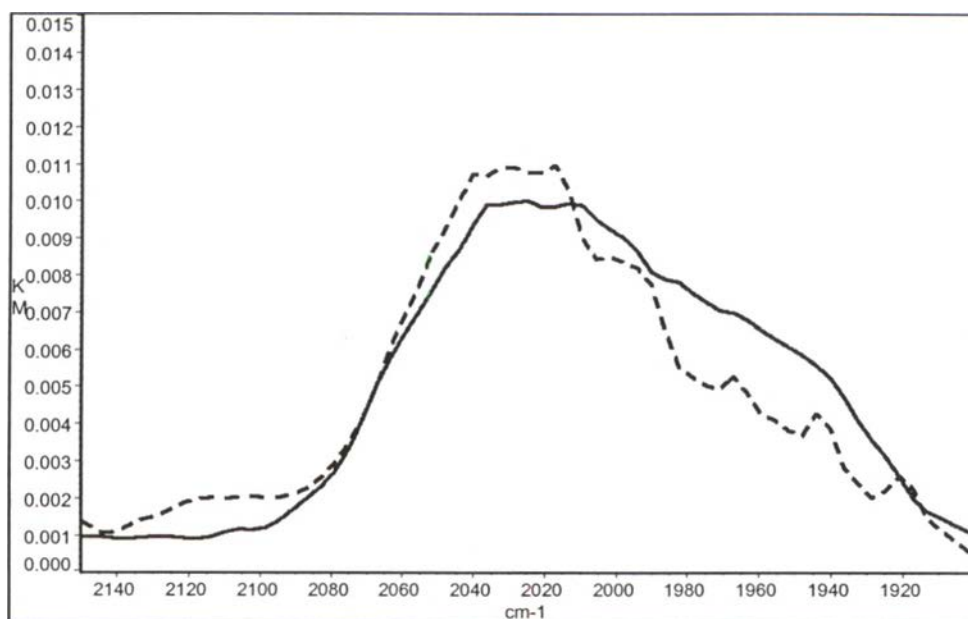
**Figure 4.5** Effect of 0.6 ppm sulfur on Pt/KL, reduced at 400°C, prepared by CVD method, (—) sulfur free, (---) 0.6 ppm sulfur.



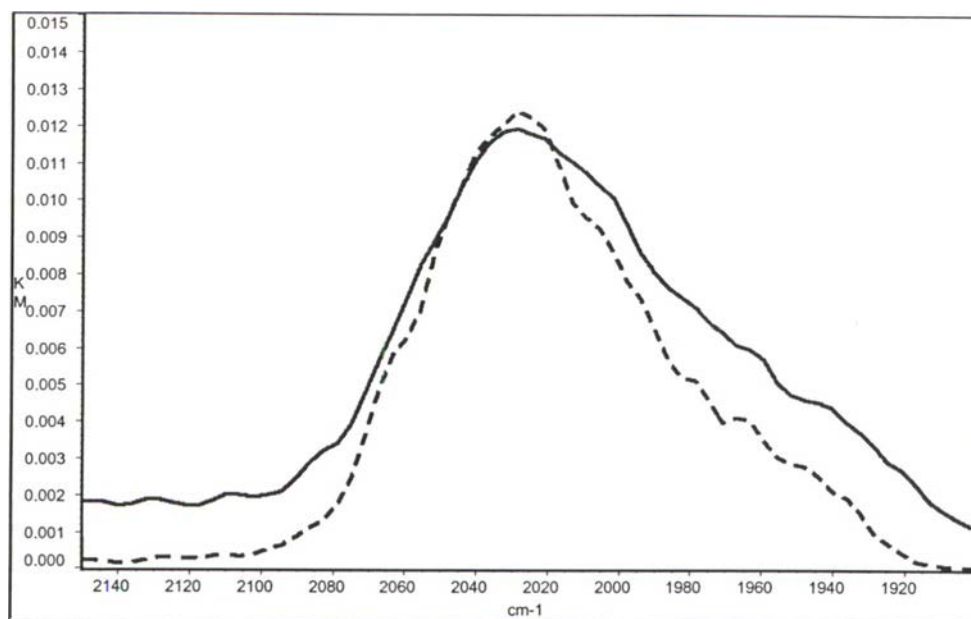
**Figure 4.6** Effect of 0.6 ppm sulfur on Pt/KL, reduced at 500°C, prepared by CVD method, (—) sulfur free, (---) 0.6 ppm sulfur.



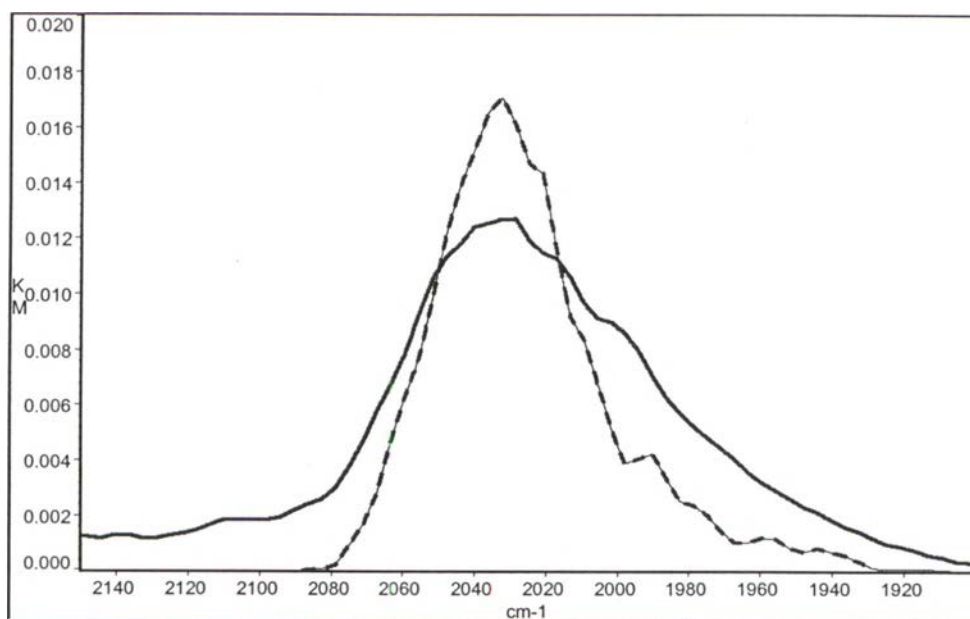
**Figure 4.7** Effect of 0.6 ppm sulfur on PtCe/KL, reduced at 400°C, prepared by CVD method , (—) sulfur free, (---) 0.6 ppm sulfur.



**Figure 4.8** Effect of 0.6 ppm sulfur on PtCe/KL, reduced at 500°C, prepared by CVD method , (—) sulfur free, (---) 0.6 ppm sulfur.

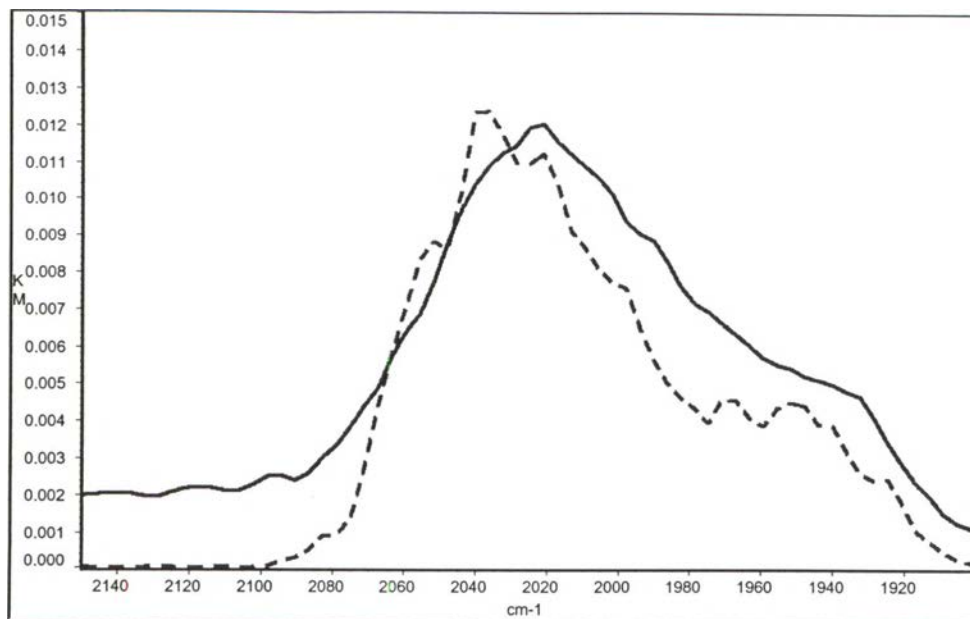


**Figure 4.9** Effect of sulfur concentration on Pt/KL, reduced at 400°C, prepared by CVD method, (—) 0.6 ppm sulfur, (---) 2.5 ppm sulfur.

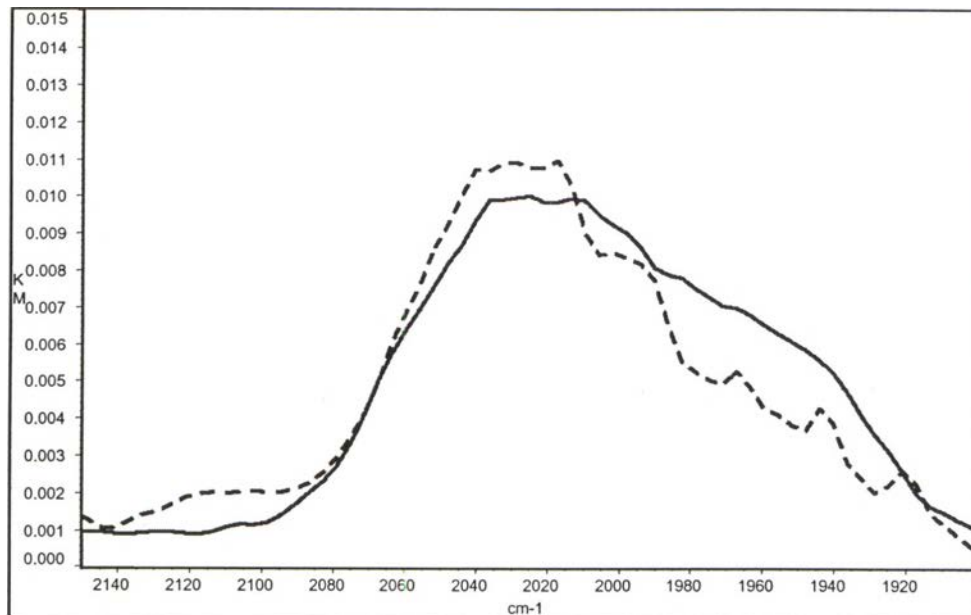


**Figure 4.10** Effect of sulfur concentration on Pt/KL, reduced at 500°C, prepared by CVD method, (—) 0.6 ppm sulfur, (---) 2.5 ppm sulfur.



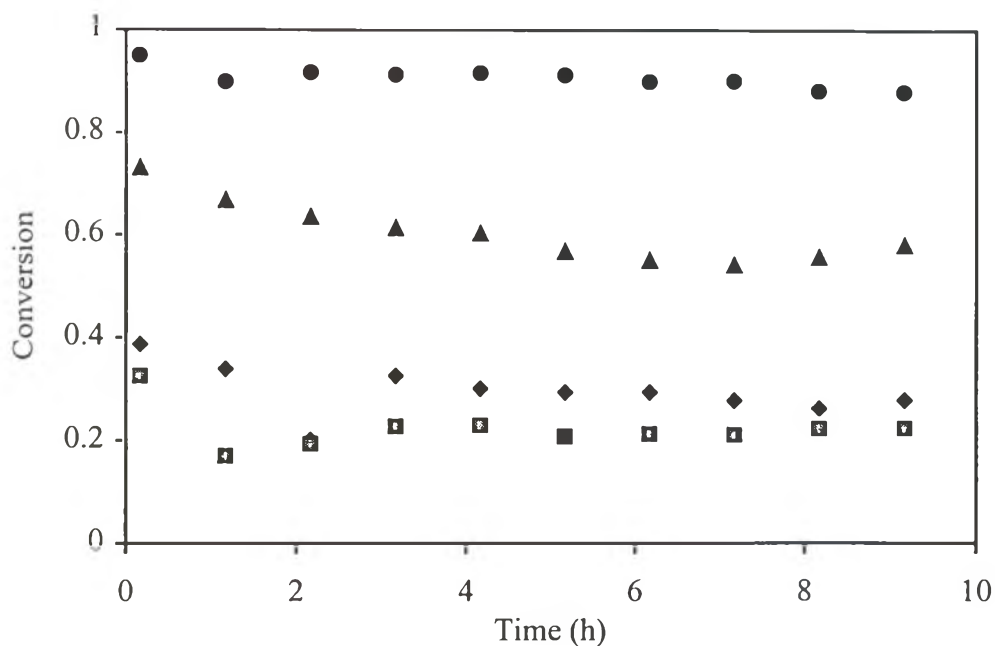


**Figure 4.11** Effect of sulfur concentration on PtCe/KL, reduced at 400°C, prepared by CVD method , (—) 0.6 ppm sulfur , (---) 2.5 ppm sulfur.

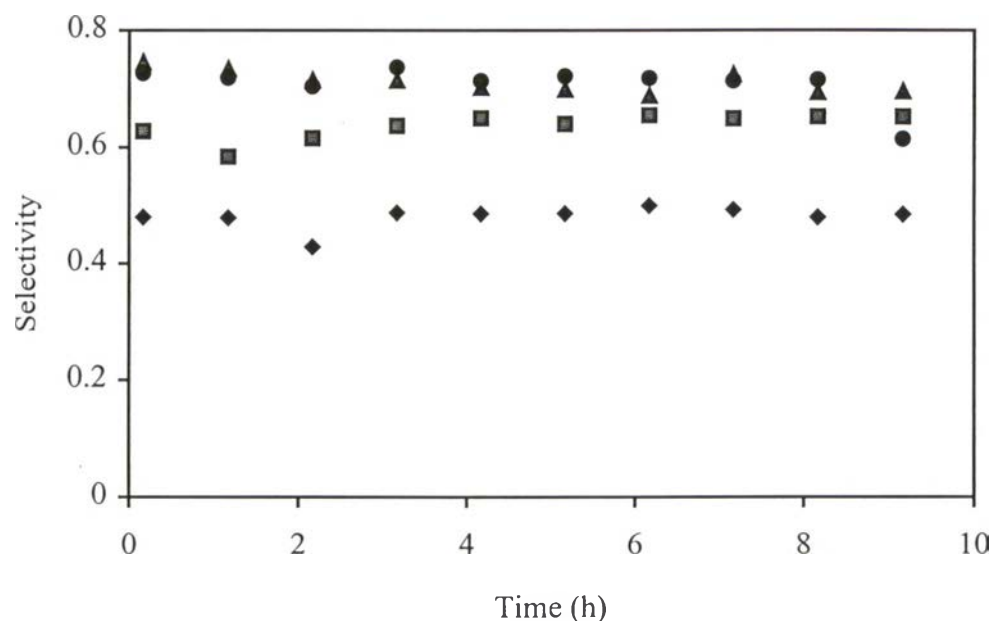


**Figure 4.12** Effect of sulfur concentration on PtCe/KL, reduced at 500°C, prepared by CVD method , (—) 0.6 ppm sulfur , (---) 2.5 ppm sulfur.

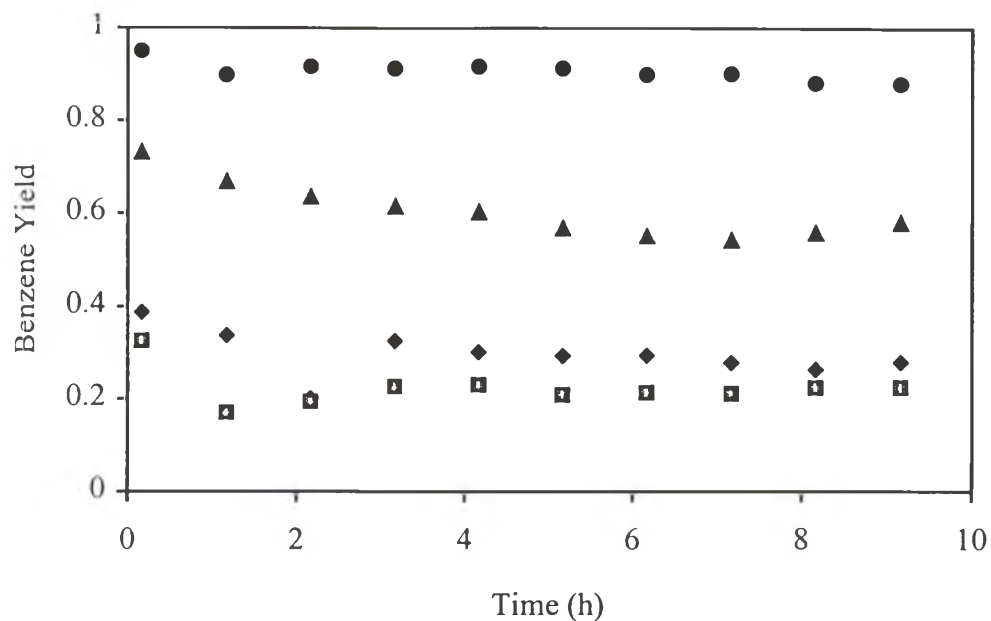
conversion, selectivity, benzene yield or hexenes yield and time. Weight hourly space velocity (WHSV) and hydrogen/n-hexane were kept constant at 5 and 6 h<sup>-1</sup>, respectively. Figure 4.13 showed the relationship between conversion and time. It was found that conversion decreased with time, especially on IWI catalyst at 500°C that a more drop of conversion was clearly observed. In contrast with Pt/KL prepared by IWI method at 500°C, the conversion of CVD catalyst at the same temperature was constant at the first 4 h but it started decreasing a little later. For both catalysts at 400°C, their conversions were similar and these values were less than those at 500°C. However, the conversion still decreased with time. Selectivity results shown in Figure 4.14 also showed that CVD catalysts at both temperatures exhibited higher value when compared to IWI catalysts. Therefore it meant that Pt/KL prepared by CVD method gave higher catalytic activity, conversion and selectivity than that prepared by IWI method. In order to confirm that CVD method was better than IWI method, the results must be presented in terms of the relationship between benzene yield or hexenes yield with time as illustrated in Figures 4.15 and 4.16. The reduction of benzene yield was a function of time and for IWI catalyst it dropped dramatically at 500°C while it was comparable on both catalysts at 400°C. The decrease in benzene yield is due to coke formation which causes catalyst deactivation (Jacobs *et al.*, 1998). Furthermore, Figure 4.16 showed that IWI catalysts can produce more amounts of hexenes, which are by-products, than IWI, especially at higher temperature. The production of hexenes indicated Pt cluster growth (Bellatreccia *et al.*, 1995). It meant that IWI catalyst was agglomerated easier than CVD catalyst. Therefore CVD catalysts were better than IWI catalyst for n-hexane aromatization. In order to confirm the good performance of Pt/KL prepared by CVD method, WHSV was varied at 400°C and 500°C using 0.1 g of catalyst. The results revealed that Pt/KL catalysts prepared by CVD method



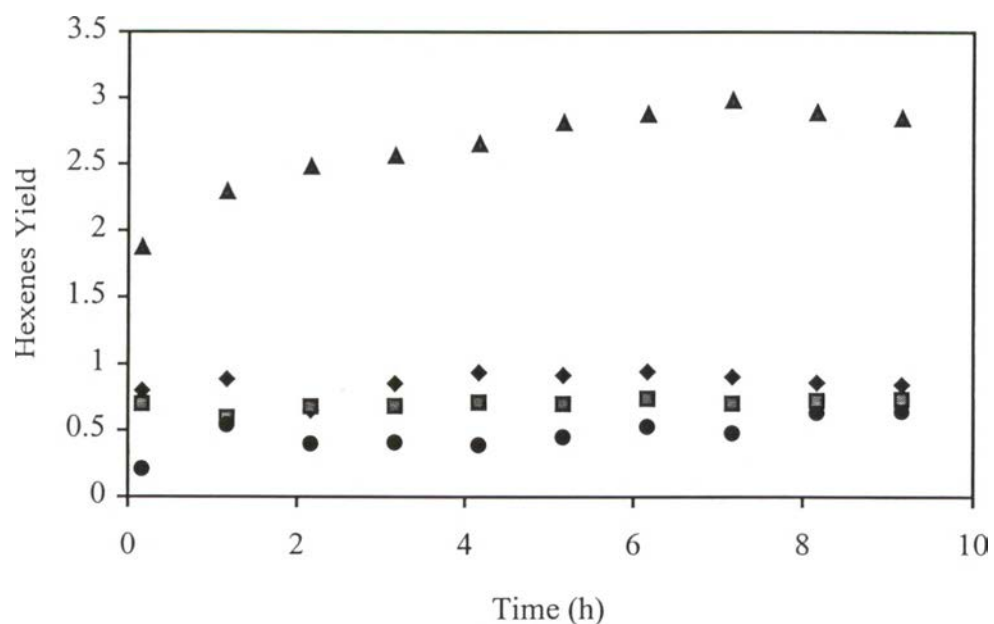
**Figure 4.13** Comparison of conversion of Pt/KL catalysts prepared by different methods at various temperature, (◆) = IWI 400°C, (▲) = IWI 500°C, (■) = CVD 400°C, (●) = CVD 500°C.



**Figure 4.14** The variation of the benzene selectivity with time in sulfur free condition for Pt/KL catalysts, (◆) = IWI 400°C, (▲) = IWI 500°C, (■) = CVD 400°C, (●) = CVD 500°C.



**Figure 4.15** Yield of benzene as a function of time for Pt/KL catalysts, (◆) = IWI 400°C, (▲) = IWI 500°C, (■) = CVD 400°C, (●) = CVD 500°C .



**Figure 4.16** The plot between hexenes yield and time for Pt/KL catalysts, (◆) = IWI 400°C, (▲) = IWI 500°C, (■) = CVD 400°C, (●) = CVD 500°C.

gave high selectivity at even low conversion. These phenomena occurred at both 400°C and 500°C as shown in Figures 4.17 and 4.18.

#### 4.2.2 Effect of Added Ce

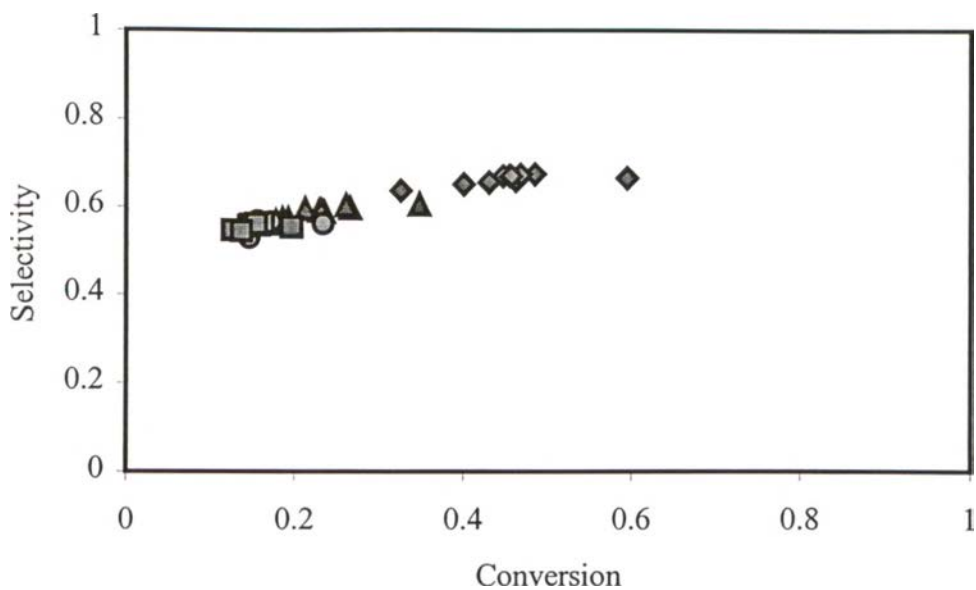
The amount of 0.15 % wt of Ce was added as a promoter on Pt/KL by CVD method. Figure 4.19 showed the effect of Ce on conversion of Pt/KL at 400°C and 500°C. It was observed that the conversion of Pt/KL and PtCe/KL were not significantly different, especially in a case of 400°C the conversion of both catalysts are close together as the same line. For selectivity as illustrated in Figure 4.20, the results were much more comparable for both temperatures. It signified that Ce did not affect extremely on the catalytic activity of Pt/KL prepared by CVD method. The results shown in Figure 4.21 certainly supported the later conclusion. It was observed that PtCe/KL presented the benzene yield like Pt/KL at both temperatures.

#### 4.2.3 Effect of Sulfur

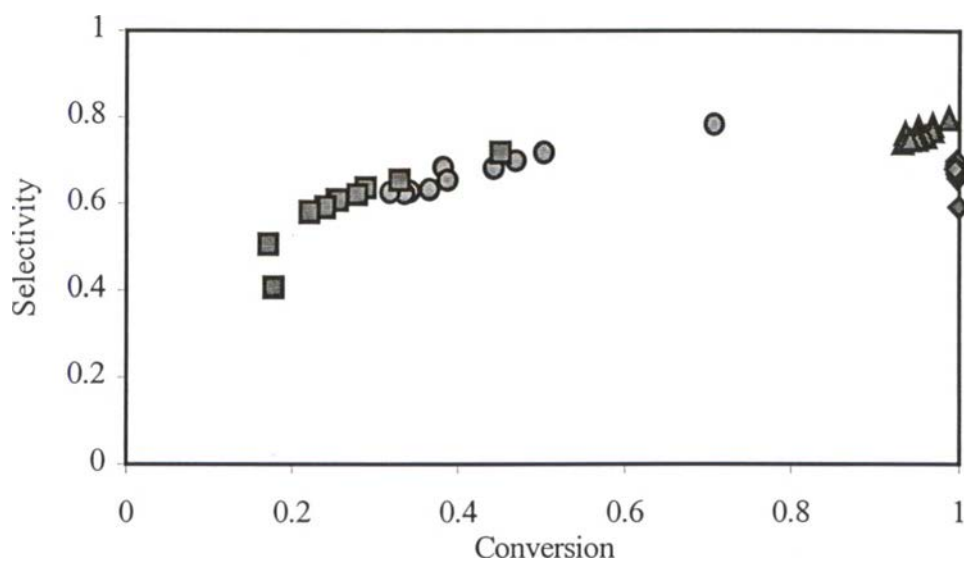
The amount of 0.6 ppm and 2.5 ppm of sulfur were introduced into the reactor to investigate the effect of sulfur on the catalytic activity of Pt/KL and PtCe/KL on n-hexane aromatization reaction. The conversion of Pt/KL exposed to sulfur containing feed was dramatically dropped at both temperatures (Figure 4.22). Moreover, sulfur affected the production of benzene which caused the faster reduction of benzene formation with time when compared to the sulfur-free condition as shown in Figure 23. The results were clearly observed in Figure 4.24 that Pt/KL under sulfur condition produced more amount of hexenes than that under normal condition. Besides, the amount of hexenes was increased with increasing reaction time. Sulfur-contaminated catalysts had a sharp trend in hexenes yield more than normal catalysts. Sulfur can make large Pt clusters so catalysts were deactivated fast.

Figure 4.25 showed the comparison of conversion of PtCe/KL under various conditions. It was found that the conversions were not different between sulfur free and sulfur containing feed at both 400°C and 500°C. It was observed that conversion tended to decrease with time at 500°C more than at 400°C. Benzene yields of PtCe/KL under sulfur-free and sulfur containing conditions were similar as shown in Figure 4.26. The plot of hexenes yield and time showed the increase in the amount of hexenes with increasing reaction time as shown in Figure 4.27. Addition of Ce exhibited the enhancement of sulfur resistance of Pt/KL catalyst because it helped stabilizing Pt clusters.

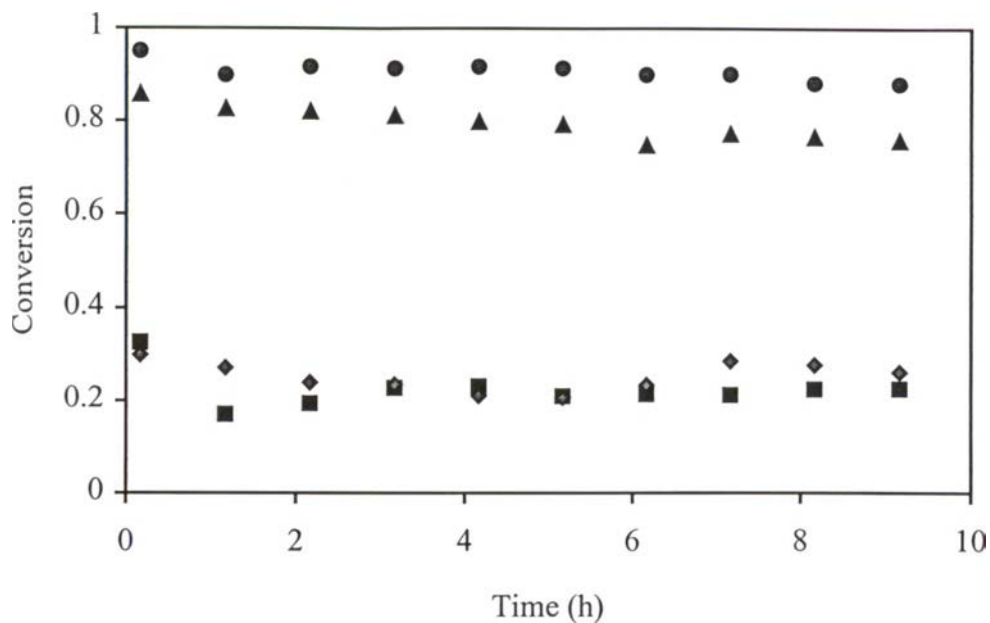
When sulfur concentration was increased, the results were shown in Figures 4.28-4.31. The conversion of 2.5 ppm sulfur was decreased greater than that of 0.6 ppm sulfur on Pt/KL (Figure 4.28). In addition, amount of hexenes yield increased with increasing sulfur concentration. The results shown in Figure 4.29 indicated that at 500°C hexenes yield of 2.5 ppm sulfur increased sharply when compared to others. In the case of PtCe/KL catalyst, the conversion decreased greatly at high sulfur concentrations as illustrated in Figure 4.30. For the amount of hexenes produced in the reaction, it was observed that hexenes yield of PtCe/KL at 500°C increased sharply, especially with increasing sulfur concentration. It meant that the deactivation rate of Pt/KL and PtCe/KL was proportional to sulfur concentration.



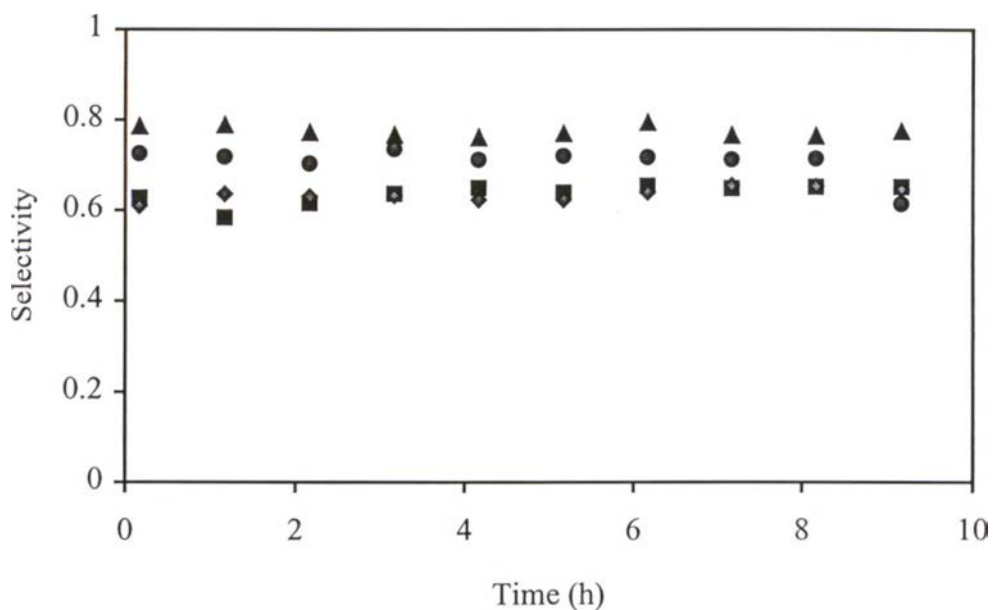
**Figure 4.17** Comparison between the selectivity and conversion patterns at various WHSV for Pt/KL prepared by CVD method at 400°C, (◆) = 5, (▲) = 10, (■) = 15, (●) = 20.



**Figure 4.18** Comparison between the selectivity and conversion at various WHSV for Pt/KL prepared by CVD method at 500°C, (◆) = 5, (▲) = 10, (■) = 15, (●) = 20.

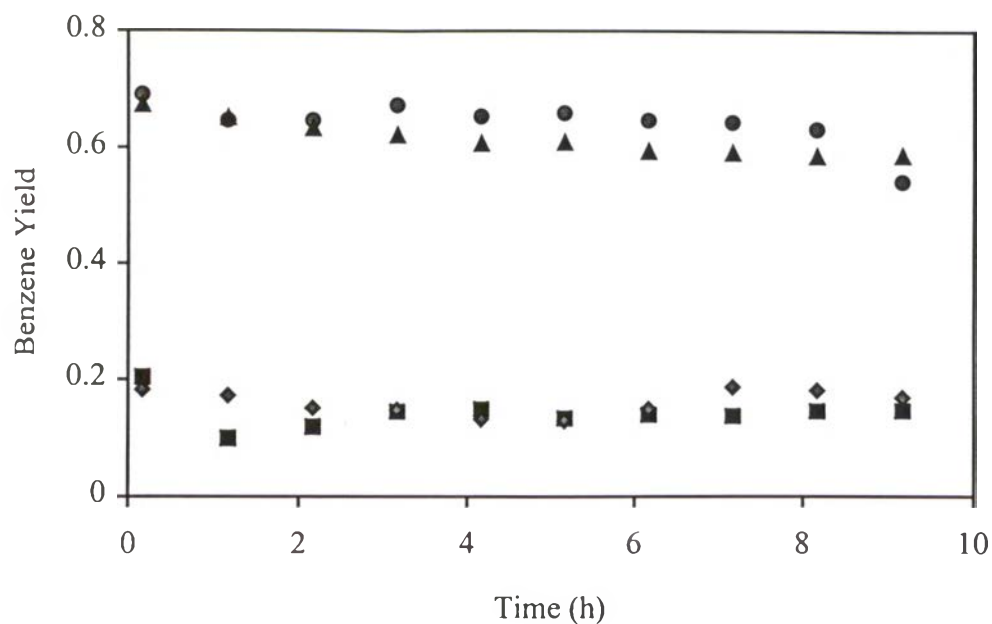


**Figure 4.19** Comparison of conversion of the catalysts at various temperatures, (■) = Pt/KL at 400°C, (●) = Pt/KL at 500°C, (◆) = PtCe/KL at 400°C, (▲) = PtCe/KL at 500°C.

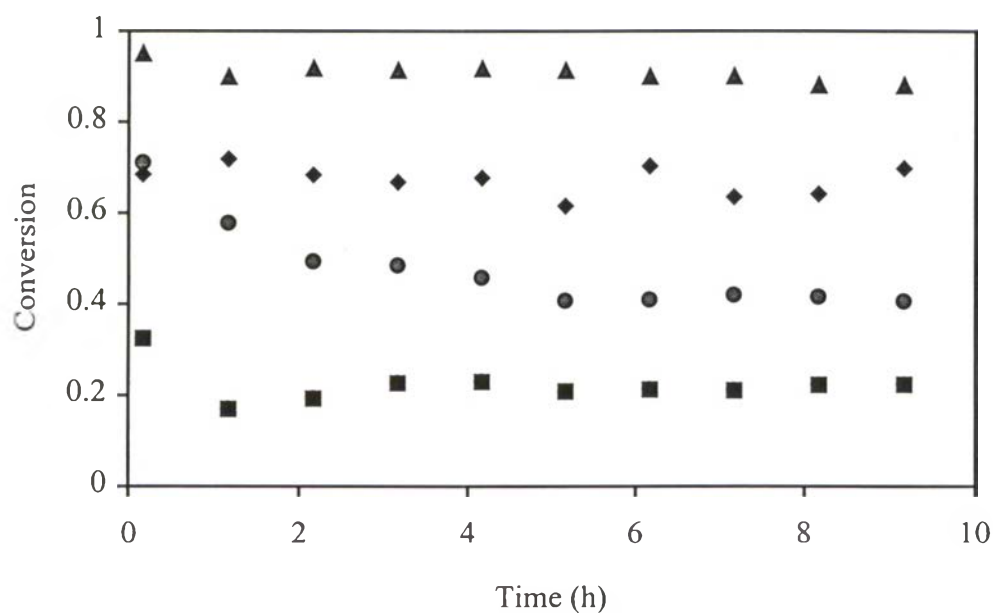


**Figure 4.20** The variation of the benzene selectivity with time under sulfur-free condition for the catalysts at various temperatures, (■) = Pt/KL at 400°C, (●) = Pt/KL at 500°C, (◆) = PtCe/KL at 400°C, (▲) = PtCe/KL at 500°C.

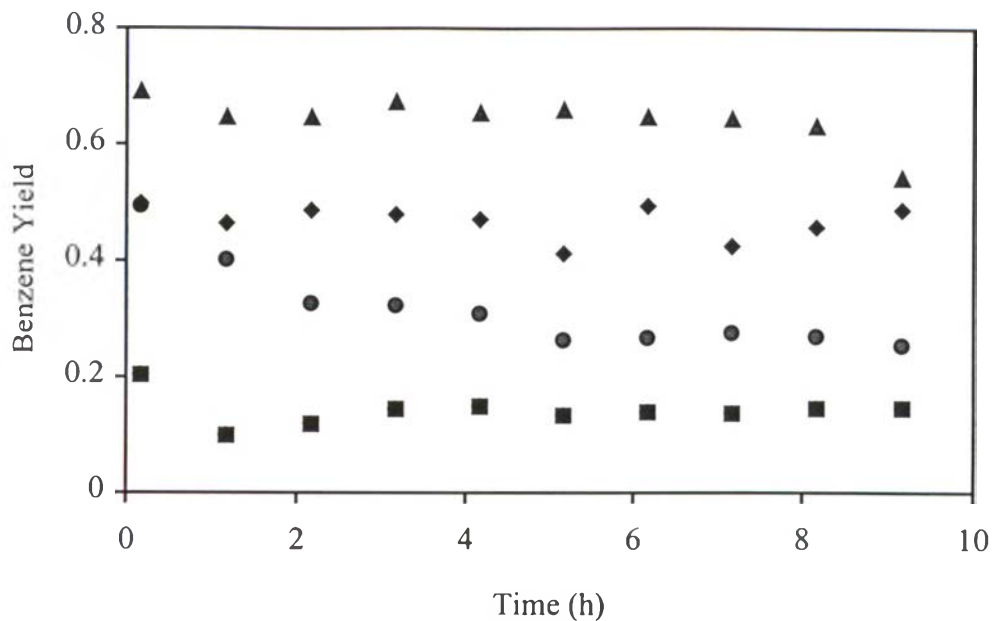




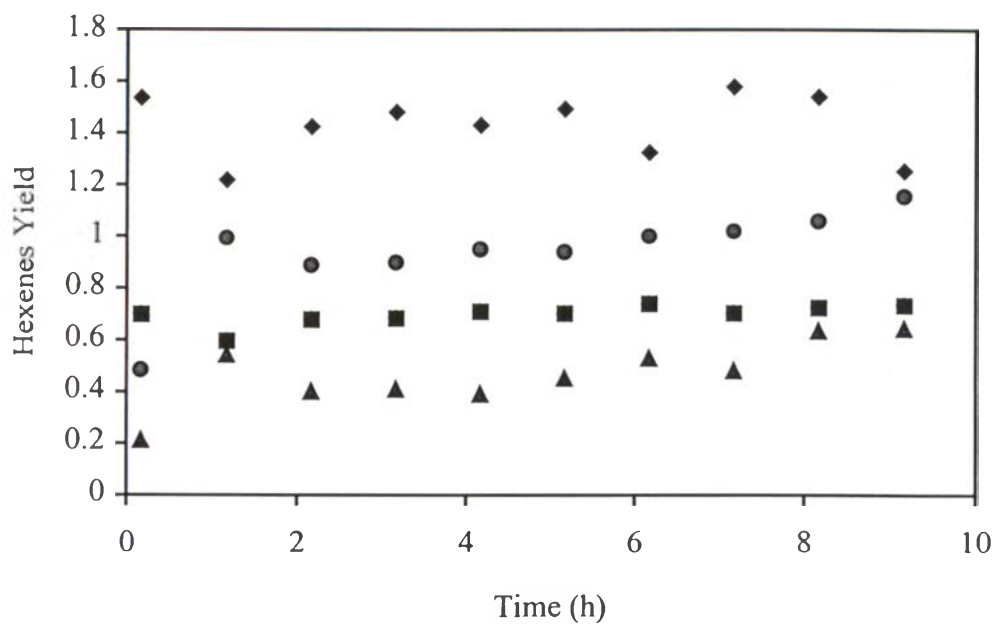
**Figure 4.21** Yield of benzene as a function of time for the catalysts, (■) = Pt/KL at 400°C, (●) = Pt/KL at 500°C, (◆) = PtCe/KL at 400°C, (▲) = PtCe/KL at 500°C.



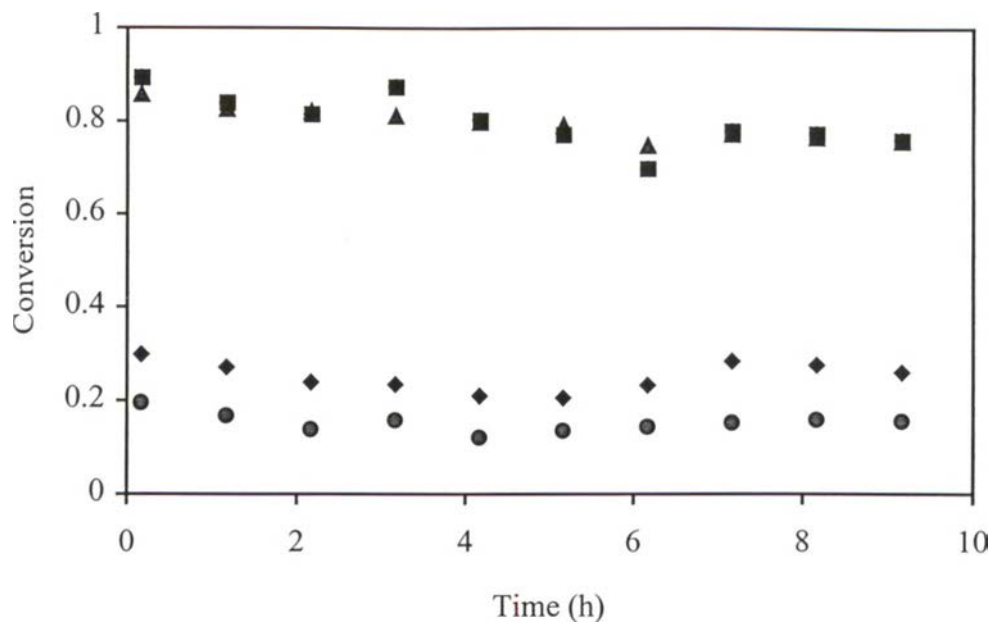
**Figure 4.22** Comparison of conversion of Pt/KL at various temperatures under sulfur-free feed, (■) = 400°C, (▲) = 500°C, and 0.6 ppm sulfur containing feed, (●) = 400°C, (◆) = 500°C.



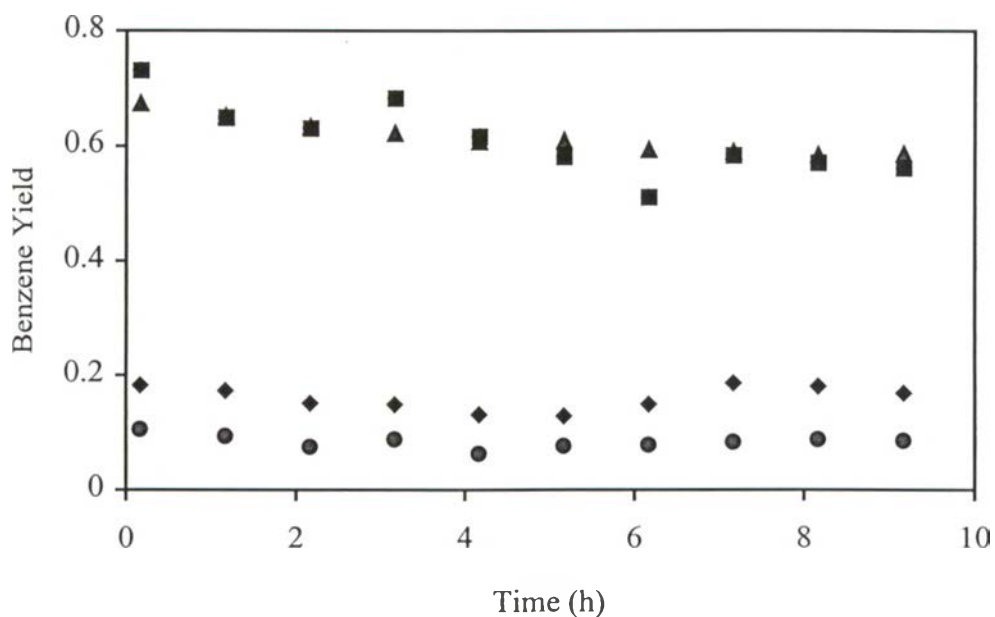
**Figure 4.23** Yield of benzene as a function of time for Pt/KL at various temperatures under sulfur-free feed, (■) = 400°C, (▲) = 500°C, and 0.6 ppm sulfur containing feed, (●) = 400°C, (◆) = 500°C.



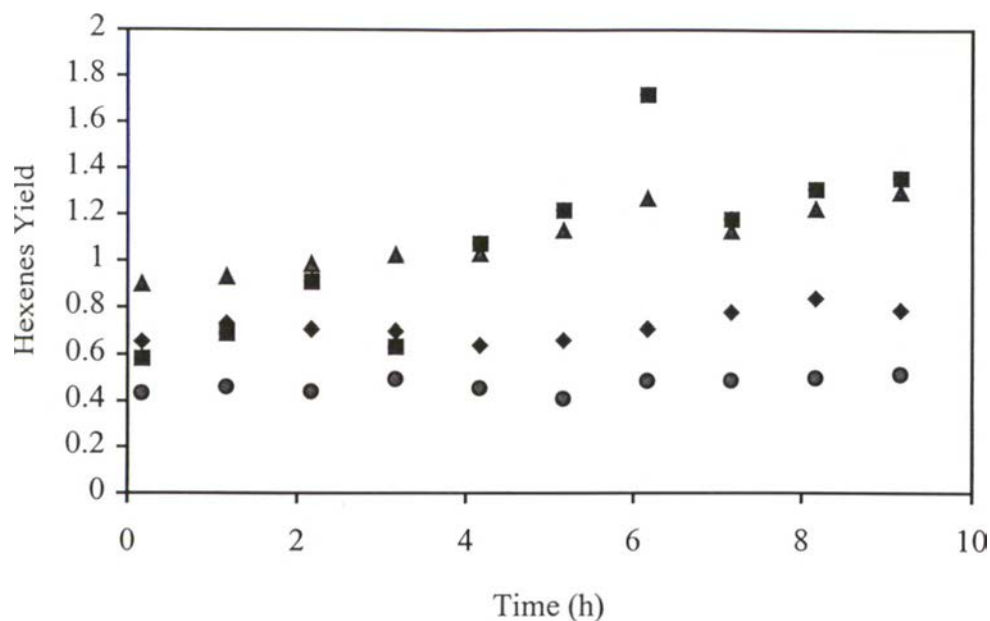
**Figure 2.24** The plot between hexenes yield and time for Pt/KL at various temperatures under sulfur-free feed, (■) = 400°C, (▲) = 500°C, and 0.6 ppm sulfur containing feed, (●) = 400°C, (◆) = 500°C.



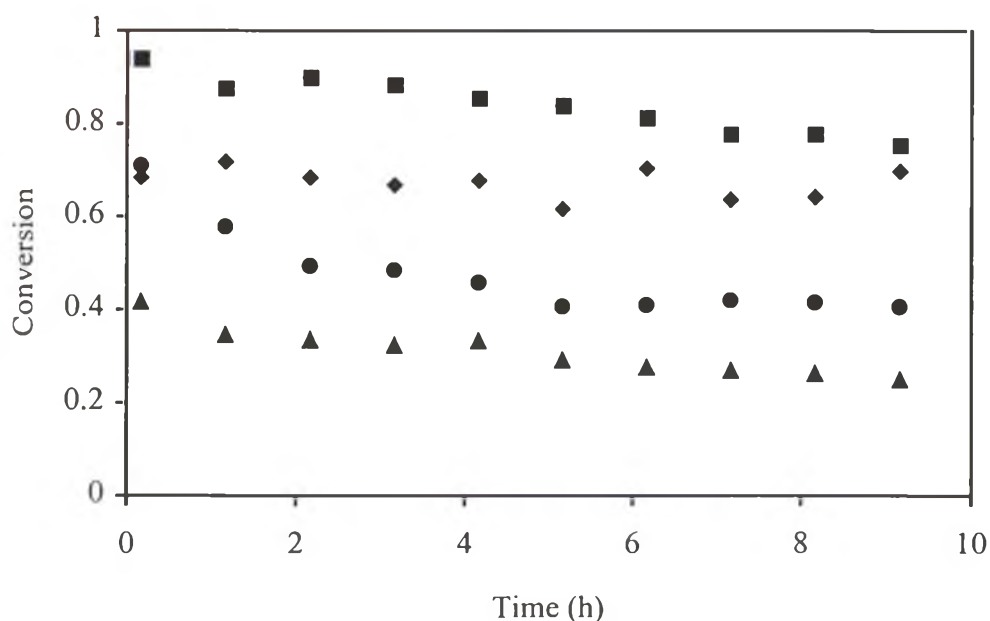
**Figure 4.25** Comparison of conversion of PtCe/KL at various temperatures under sulfur-free feed, (◆) = 400°C, (▲) = 500°C, and 0.6 ppm sulfur containing feed, (●) = 400°C, (■) = 500°C.



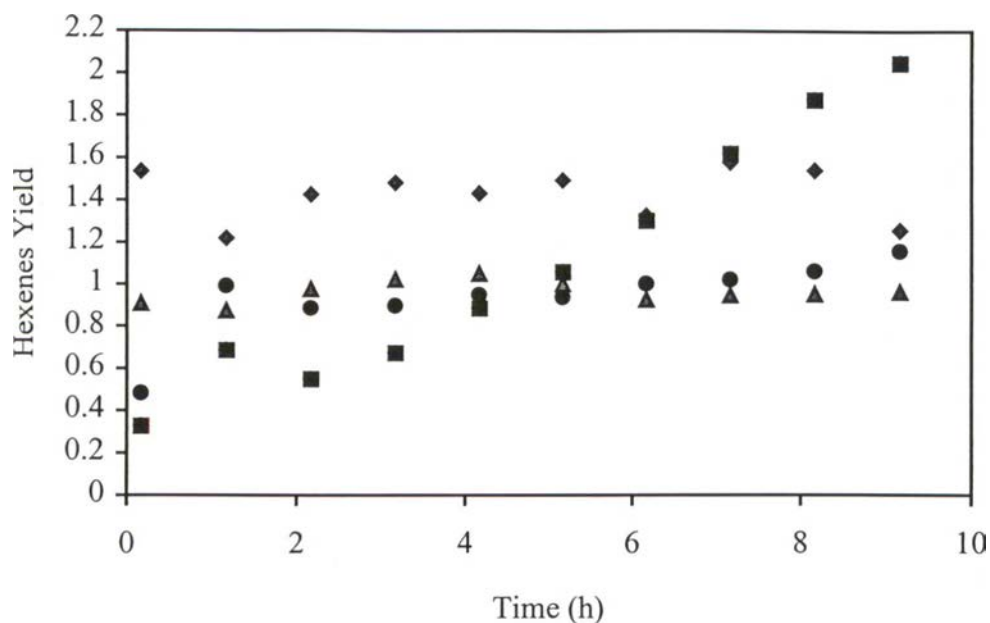
**Figure 4.26** Yield of benzene as a function of time for PtCe/KL at various temperatures under sulfur-free feed, (◆) = 400°C, (▲) = 500°C, and 0.6 ppm sulfur containing feed, (●) = 400°C, (■) = 500°C.



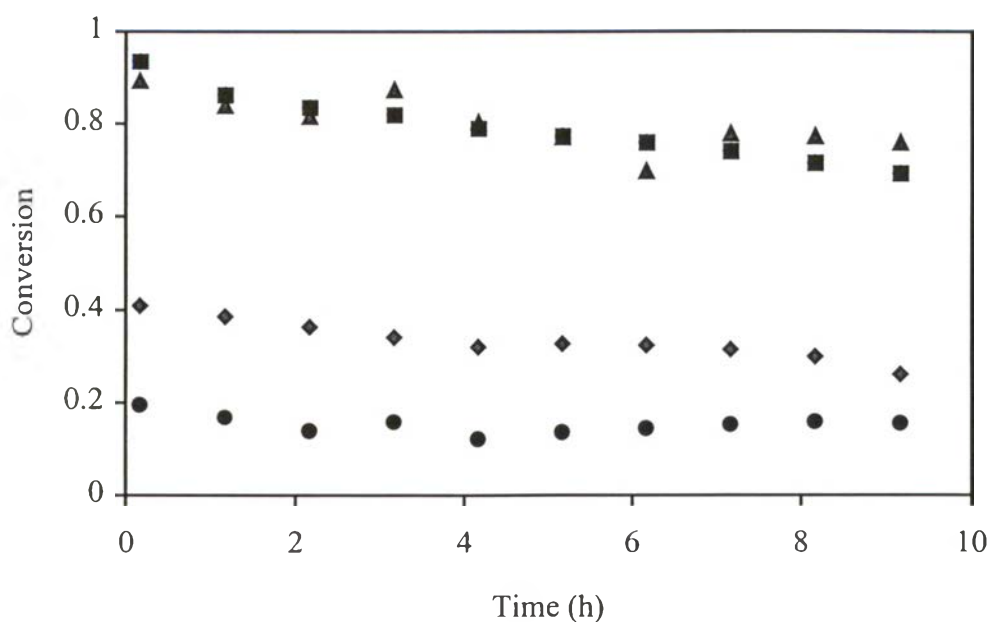
**Figure 4.27** The plot between hexenes yield and time for PtCe/KL at various temperatures, under sulfur-free feed, (◆) = 400°C, (▲) = 500°C, and 0.6 ppm sulfur containing feed, (●) = 400°C, (■) = 500°C.



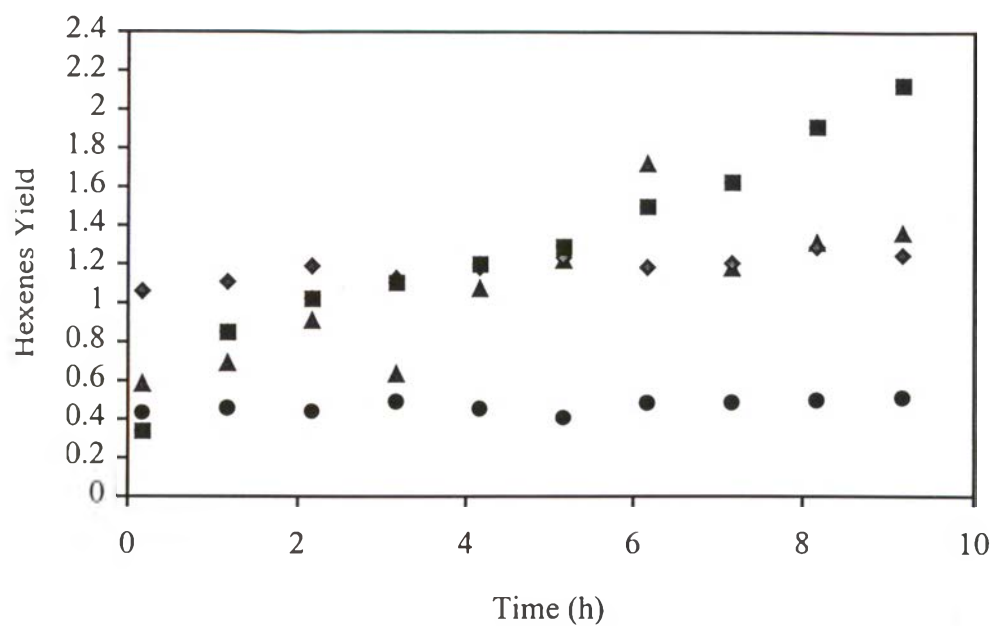
**Figure 4.28** Comparison of conversion of Pt/KL at various temperatures under 0.6 ppm of sulfur, (●) = 400°C, (◆) = 500°C, and 2.5 ppm of sulfur, (▲) = 400°C, (■) = 500°C.



**Figure 4.29** The plot between hexenes yield and time for Pt/KL at various temperatures, under 0.6 ppm of sulfur, (●) = 400°C, (◆) = 500°C, and 2.5 ppm of sulfur, (▲) = 400°C, (■) = 500°C.



**Figure 4.30** Comparison of conversion of PtCe/KL at various temperatures under 0.6 ppm of sulfur, (●) = 400°C, (▲) = 500°C, and 2.5 ppm of sulfur, (◆) = 400°C, (■) = 500°C.



**Figure 4.31** The plot between hexenes yield and time for PtCe/KL at various temperatures under 0.6 ppm of sulfur, (●) = 400°C, (▲) = 500°C, and 2.5 ppm of sulfur, (◆) = 400°C, (■) = 500°C.