CHAPTER IV
RESULTS AND DISCUSSION

4.1 Regeneration in Air of Pt/KL Catalysts

The optimal conditions for the regeneration in air of Pt/KL catalysts were investigated in terms of catalytic activity such as conversion, selectivity, product yield. The catalysts were characterized by means of DRIFTS and TPO providing the distribution of Pt particles inside the pores and amount of carbon deposits on the catalysts respectively.

The activities of catalysts were measured as a function of conversion versus time on stream, and the average value of conversion after regeneration, total aromatic and C_8 aromatic selectivity after 7 reaction-regeneration cycles (1.5 h of reaction time per each cycle). The results and discussion of the study of the effect of experimental parameters toward the regeneration are divided into 3 parts: (I) Effect of regeneration temperature (II) Effect of regeneration time (III) Effect of air flow rate.

4.1.1 Effect of Regeneration Temperature
In this part, catalytic activity measurement and catalyst characterization were discussed.

4.1.1.1 Catalytic activity measurement
Figure 4.1 shows the variation of n-octane conversion at $500^{\circ}C$ without regeneration in air. Figure 4.2 shows The variation of *n*-octane conversion with regeneration in air of various regeneration temperatures; operated at regeneration time = 0.5 h, air flow rate = 100 ml/min/g.
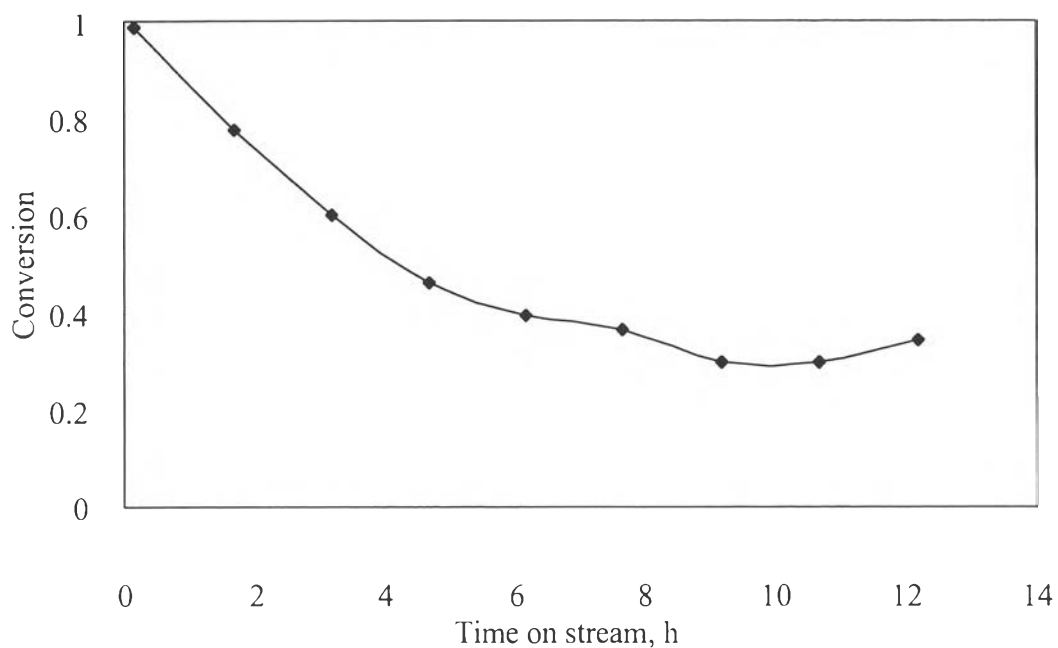
Figure 4.1 The variation of *n*-octane conversion at 500°C without regeneration in air
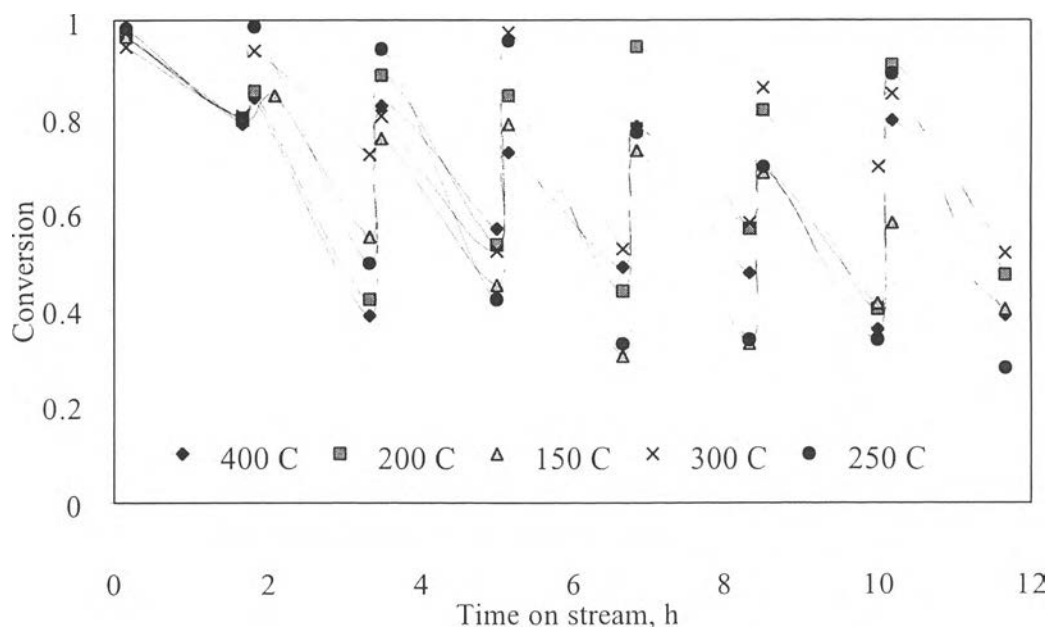

Figure 4.2 The variation of *n*-octane conversion with regeneration in air of various regeneration temperature; operated at regeneration time = 0.5 h, air flow rate = 100 ml/min/g.

It was clearly seen that the Pt/KL catalysts could be practically regenerated in air because the conversion of the spent Pt/KL can be regained closely to the original of the fresh Pt/KL after the *in situ* regeneration. However, the variation of *n*-octane conversion with regeneration in air is still difficult to determine for the optimal regeneration conditions. Therefore, all obtained results were calculated in terms of the average value as shown in Figure 4.3 to Figure 4.6.

Figure 4.3 to Figure 4.6 show the average value of conversion, total aromatics selectivity, C_8 aromatics yield and EB/OX ratio of various regeneration temperatures (150-400°C) after regeneration in air, respectively. The most suitable regeneration conditions must be able to recover performance and properties of catalysts as close as possible to the fresh one. For instance, high C_8 aromatics yield, conversion, aromatic selectivity. Moreover, EB/OX ratio and benzene/C_8 aromatics ratio was considered to indicate diffusional effects that limit the production of C_8 aromatics which are desired for of *n*-octane aromatization (Jongptiwut *et al.*,2003). The lower the EB/OX ratio and benzene/C_8 aromatics ratio, the lower the diffusional effects. Initially, as presented in Figure 4.3, regeneration temperature in a range of 200-300 ^{o}C performed the particular high conversion of *n*-octane aromatization. It was observed that, even though the regeneration at 250°C provided the lowest total aromatics selectivity as shown in Figure 4.4, C_8 aromatics yield obtained from this regeneration was greatly high compared with that obtained from the other regeneration conditions as presented in Figure 4.5. Interestingly, the EB/OX ratios at various regeneration temperatures were slightly different, as illustrated in Figures 4.6. The EB/OX ratio on the lower regeneration temperature seems to increase slightly. This slight difference could be due to an inhibition of the OX mobility inside the channels of the zeolite caused by the presence of the fraction of carbon residues in the regenerated catalysts. This restrictive movement results in a longer residence time of OX than EB inside the zeolite channels. It is important to note that high EB/OX ratios have only been observed on Pt/zeolite catalysts (Meriaudeau *et al.*, 1994), which reveals the role that shape-selectivity may have in this reaction. It is apparent that, EB was the main C_8 aromatic products obtained from the reaction and regeneration cycles. This is due to the diffusional effects that xylenes produced inside the zeolite diffuse out of the system with much higher

difficulty than EB and benzene respectively (Jongptiwut *et al*.,2003). Therefore. by looking at the activity results, the most suitable regeneration temperature was 250°C.
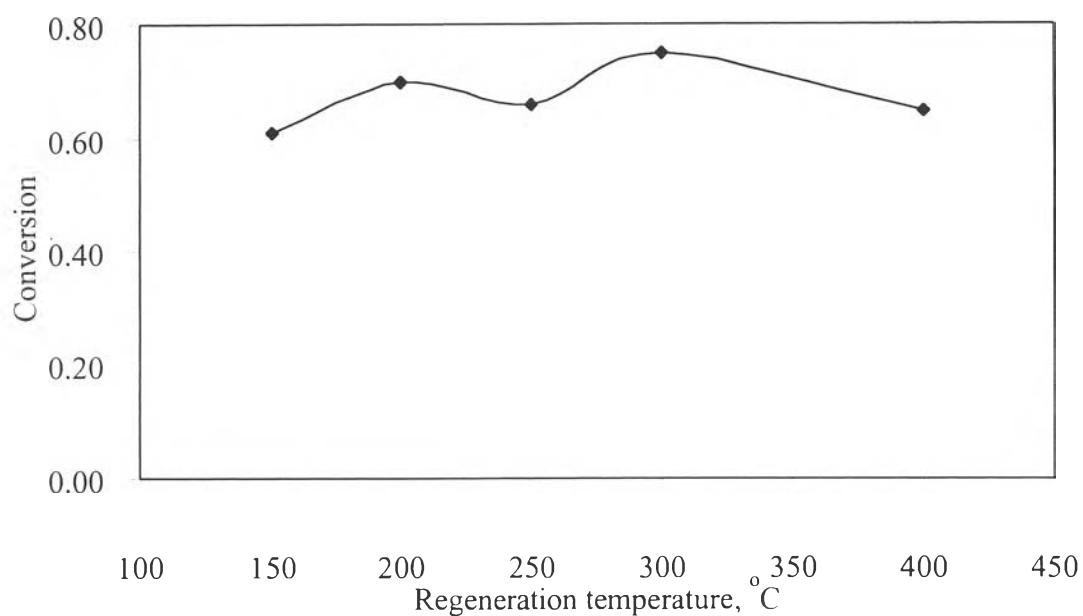
Figure 4.3 The average value of conversion of various regeneration temperature (150-400°C) after regeneration in air.
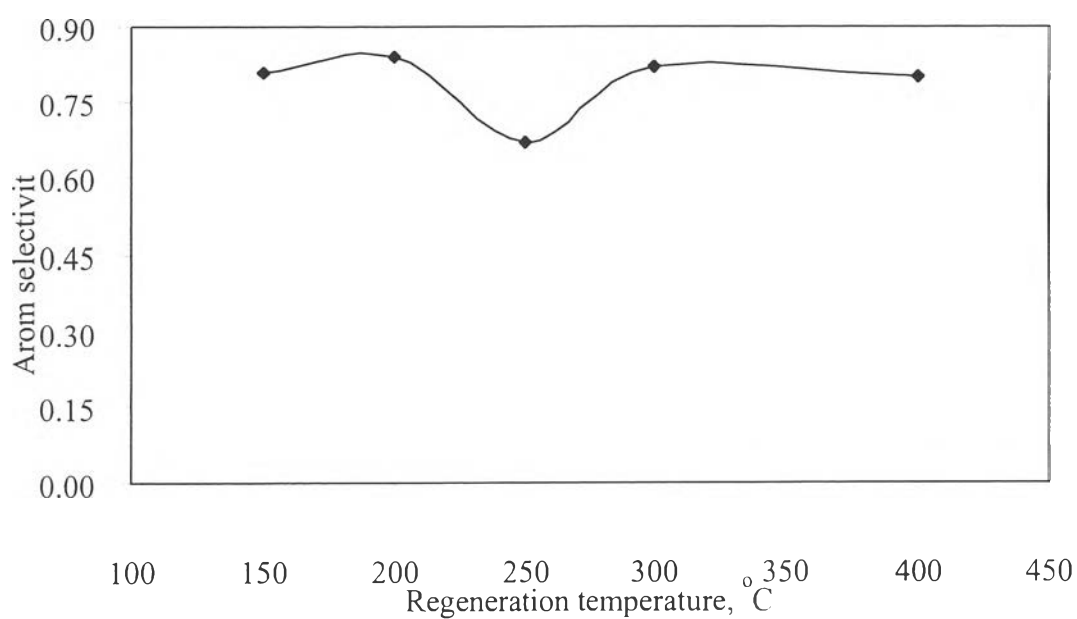
Figure 4.4 The average value of total aromatics selectivity of various regeneration temperature (150-400°C) after regeneration in air.
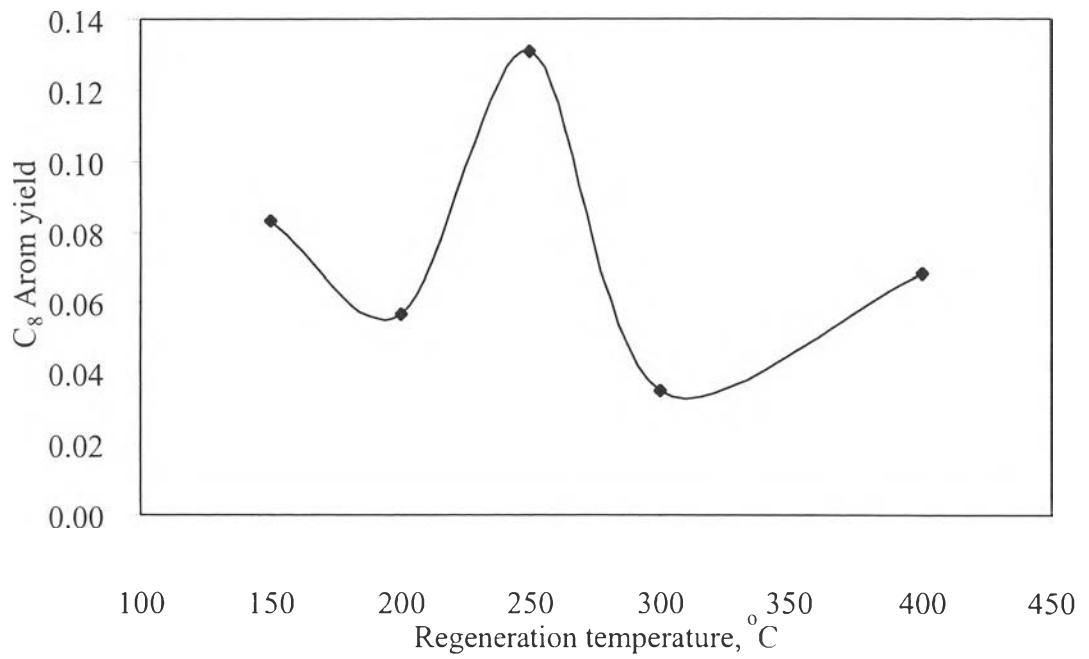
Figure 4.5 The average value of C_8 aromatics yield of various regeneration temperature (150-400°C) after regeneration in air.
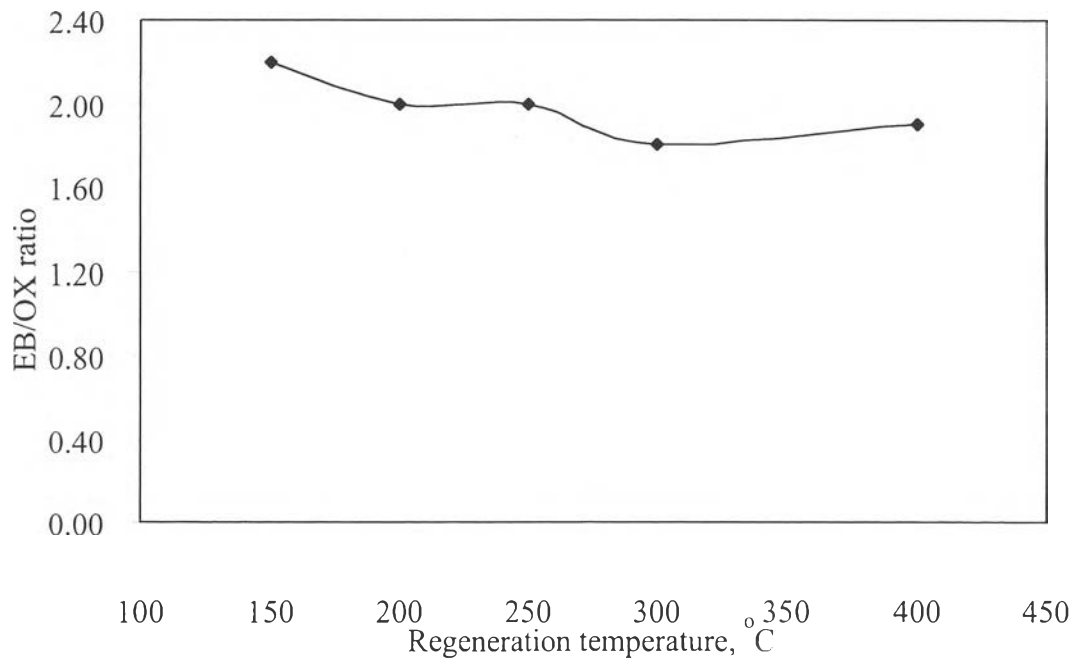

Figure 4.6 The average value of EB/OX ratio of various regeneration temperature (150-400°C) after regeneration in air.

4.1.1.2 Characterization of catalysts

Fresh, spent and regenerated catalysts were characterized by means of DRIFTS of adsorbed CO and TPO to qualify Pt particles distribution and to determine amount of carbon deposits on the catalysts respectively.

(I) DRIFTS of Adsorbed CO

The fresh and the spent Pt/KL catalysts were characterized by means of DRIFTS of adsorbed CO in order to compare the morphology of Pt particles inside the KL zeolite, regenerated under particular regeneration conditions.

DRIFTS of adsorbed CO has been widely used to characterize the distribution and location of Pt particles (Lane *et al.*, 1993). The results in this work are consistent with the previous work (Jacobs *et al.*, 1999) that Pt/KL catalyst displayed complex bands which typically extend from 2080 cm^{-1} to much lower wave number (e.g., as low as 1930 cm^{-1}). The interpretations of the results in this work are based on three important regions that have been believed to correspond with three variations of morphology of Pt clusters (Stakheev *et al.*, 1995);

(1) Bands below 2050 cm^{-1} are assigned to Pt-CO species arising from the disruption of small Pt clusters inside the L-zeolite channels.

(2) Bands between 2050 and 2075 cm^{-1} are associated with larger Pt clusters in the near-surface region of the L-zeolite.

(3) Bands at around 2080 cm^{-1} are in general assigned to larger Pt particles on the external surface of the L-zeolite.

The comparison between fresh and regenerated Pt/KL catalysts after reaction-regeneration cycles of various regeneration temperatures in the range of 150-400°C are shown in Figure 4.7 to Figure 4.11.
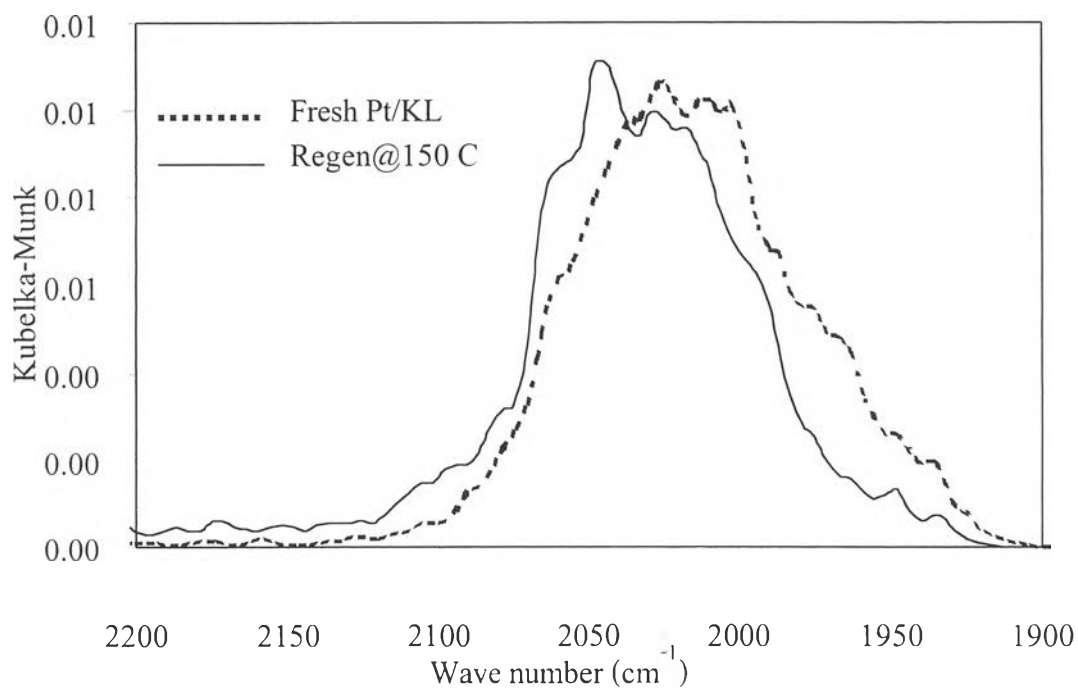
Figure 4.7 DRIFTS of adsorbed CO spectra of fresh and regenerated Pt/KL catalysts after reaction-regeneration cycles at 150°C of regeneration temperature.
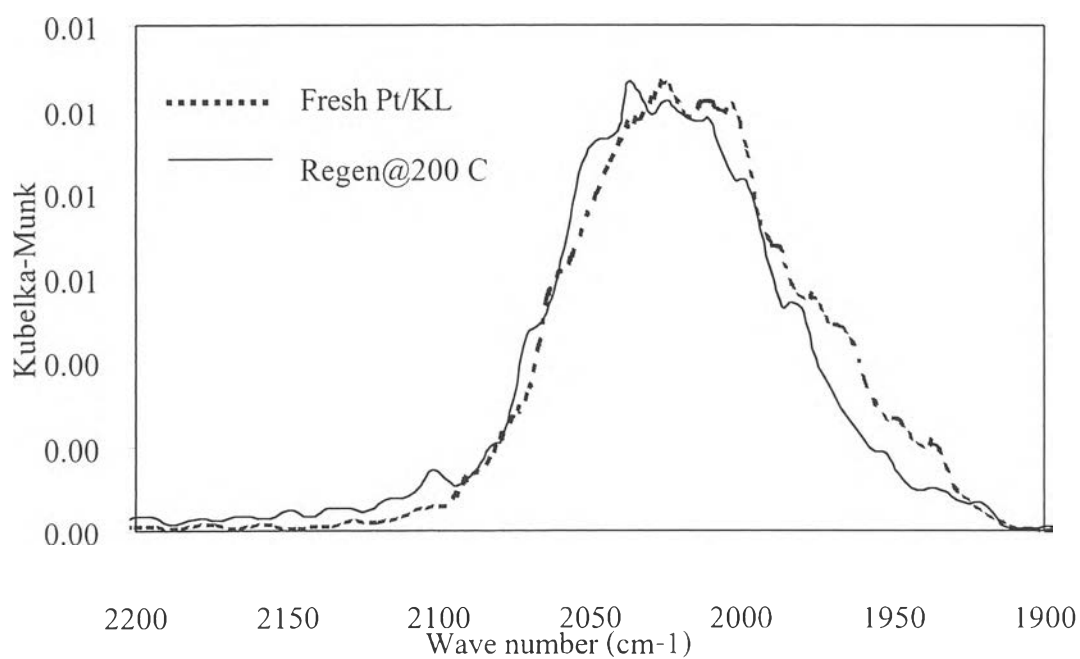

Figure 4.8 DRIFTS of adsorbed CO spectra of fresh and regenerated Pt/KL catalysts after reaction-regeneration cycles at 200°C of regeneration temperature.
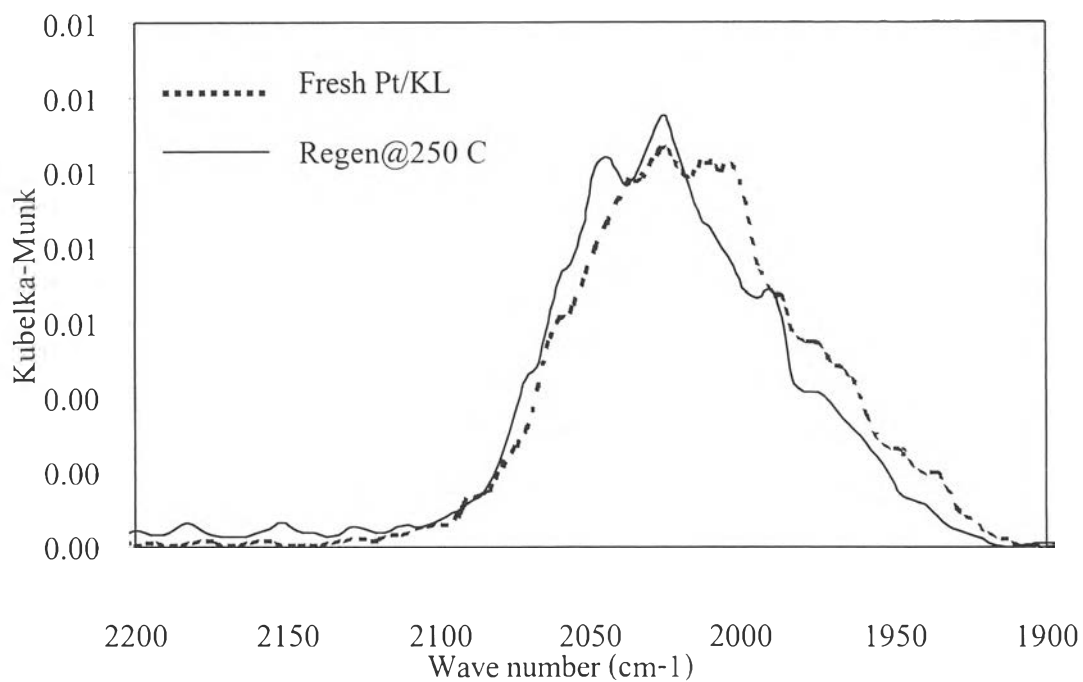
Figure 4.9 DRIFTS of adsorbed CO spectra of fresh and regenerated Pt/KL catalysts after reaction-regeneration cycles at 250°C of regeneration temperature.
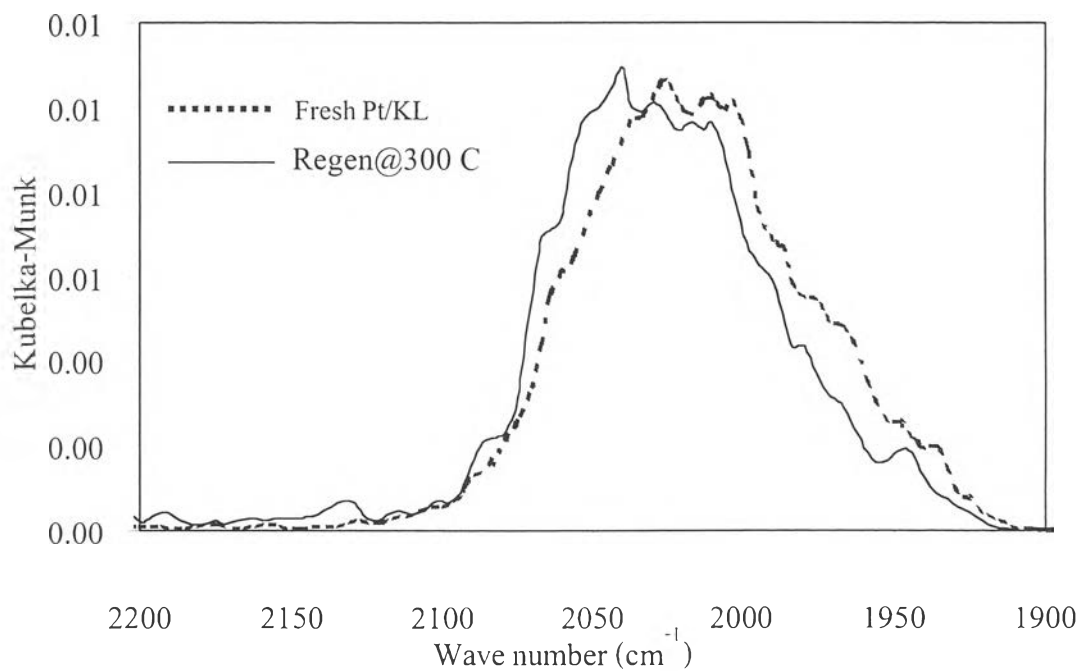

Figure 4.10 DRIFTS of adsorbed CO spectra of fresh and regenerated Pt/KL catalysts after reaction-regeneration cycles at 300°C of regeneration temperature.
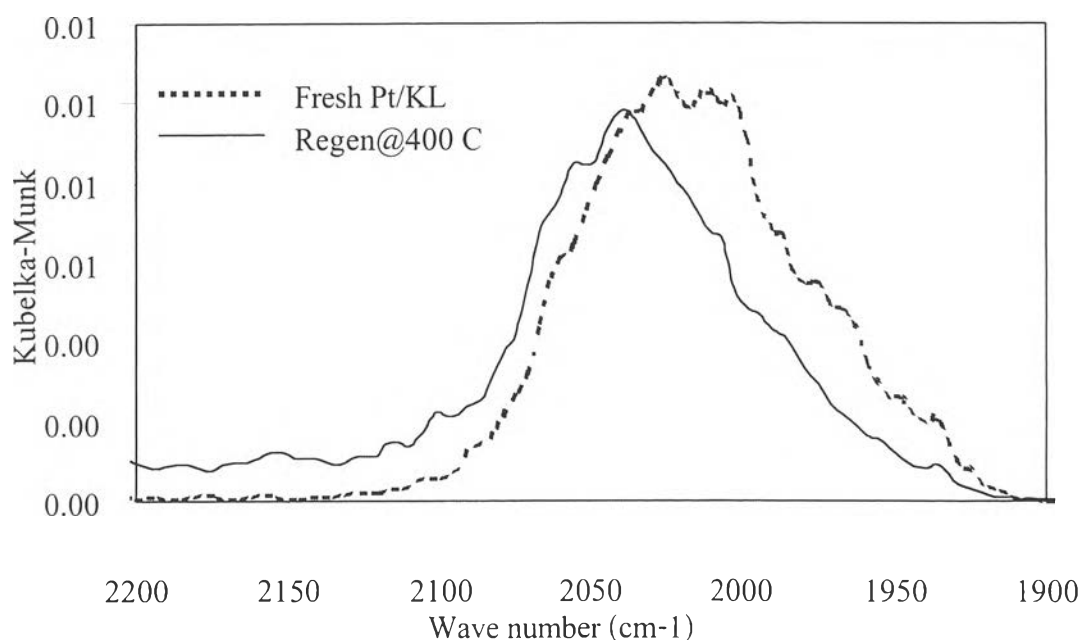
Figure 4.11 DRIFTS of adsorbed CO spectra of fresh and regenerated Pt/KL catalysts after reaction-regeneration cycles at 400°C of regeneration temperature.

Figures 4.7 to Figure 4.11 show DRIFTS of adsorbed CO spectra of fresh and regenerated Pt/KL after reaction-regeneration cycles at 150, 200, 250, 300 and 400 °C of regeneration temperature. It was observed that by increasing the regeneration temperature to 400°C, the bands around 2050-2075 cm^{-1}, corresponding to the larger Pt clusters in the near-surface region of the L-zeolite (Stakheev *et al.*, 1995) are more pronounced. Furthermore, the bands below 2050 cm^{-1}, which assigned to small Pt clusters inside the L-zeolite channels, are more pronounced for the catalysts regenerated within the range of 200 °C to 250 °C. This interpretation was in a good agreement with the results obtained from the catalytic activity measurement part that this range of temperature provided high activity of *n*-octane aromatization. Moreover, a shift of spectrum to high wave number can be remarkably observed in the catalysts regenerated at 150°C and at 400°C when compare to the spectrum of the fresh catalyst. This shift of spectrum could be due to the coke formation and agglomeration of Pt particles into larger particles when regenerated at 150°C and at 400°C, respectively.

(II) Temperature Programmed Oxidation (TPO)

The spent and regenerated catalysts were also characterized by TPO to determine the amount of carbon deposits on the catalysts in terms of percent weight of carbon per gram of catalysts.

Table 4.1 shows percent carbon contained in the spent and regenerated Pt/KL catalysts at different regeneration temperatures.

Table 4.1 TPO characterization of spent and regenerated Pt/KL catalysts at different regeneration temperatures

Temperature of regeneration(^{o}C)	Time of regeneration (h)	Air flow rate (ml/min/g)	%C (wt.%)
150			0.79
200			0.64
250	0.5	100	0.40
300			0.39
400			0.36
Spent Pt/KL (after 12 h on stream)			2.26

Initially, it was found that regeneration in air gave the profile that shifted to lower temperature leading to the less difficult to oxidize carbon during TPO when compare to that of the spent catalyst without the regeneration as shown in Figure B1. It was observed that the amount of coke burned corresponded to the temperature of regeneration that the higher regeneration temperature, the higher percent carbon removal. In other words, the lower regeneration temperature, the higher coke formation in the regenerated catalysts as shown in Table 4.1, that when regeneration temperature was increased from 150°C to 250°C, amount of coke formation was decreased sharply and then slightly decreased at regeneration temperature above 250°C. According to the DRIFTS of adsorbed CO results, it can be confirmed that a shift of spectrum to high wave number when regenerated at 150°C which represents the poor Pt dispersion in the catalysts was caused by high coke formation leading to pore blocking of L-zeolite. This explanation was

corresponded to the high EB/OX ratio obtained at low regeneration temperature (150°C). Furthermore, at high regeneration temperature (400°C), sintering of Pt particles into larger particles could be observed. Therefore, the optimal regeneration temperature should be high enough in order to burn coke, on the other hand, it should not be too high to avoid the sintering of Pt particles.

4.1.2 Effect of Regeneration Time

In this part, catalytic activity measurement and characterization of catalysts will be discussed.

4.1.2.1 Catalytic activity measurement

The reaction-regeneration cycles were performed under a constant regeneration temperature and air flow rate at various regeneration time in the range of 0.5-8 h. The comparison among the different regeneration time was investigated in terms of the average value of catalytic activity after the reaction-regeneration cycles as illustrated the previous effect.

Figure 4.12 to Figure 4.15 shows the average value of C_8 aromatics yield, aromatics selectivity, conversion and EB/OX ratio of various regeneration time (0.5-8 h) after regeneration in air respectively. The regeneration for 0.5 h resulted in the highest C_8 aromatics yield, as shown in Figure 4.12, which is one of the main criteria to evaluate the optimal conditions in this work. According to Figure 4.13 the variation of aromatics selectivity was not significantly influenced by the regeneration time. Unexpectedly, the regeneration for 2 h resulted in a little higher conversion and lower EB/OX ratio as shown in Figure 4.14 and Figure 4.15, respectively. This can be explained in terms of B/C_8 aromatics ratio as illustrated in Figure 4.16. The higher B/C_8 aromatics ratio, the higher hydrogenolysis products compared with aromatization products. It was observed that regeneration for 2 h gave remarkably the highest B/C_8 aromatics ratio resulting from the hydrogenolysis of EB and OX, which are the expected products from the direct closure of the six-member ring (Davis and Venuto, 1969), to benzene. This could lead to the low EB and OX selectivity as presented in Figure 4.17. that regeneration for 2 h had the lowest EB and OX selectivity.
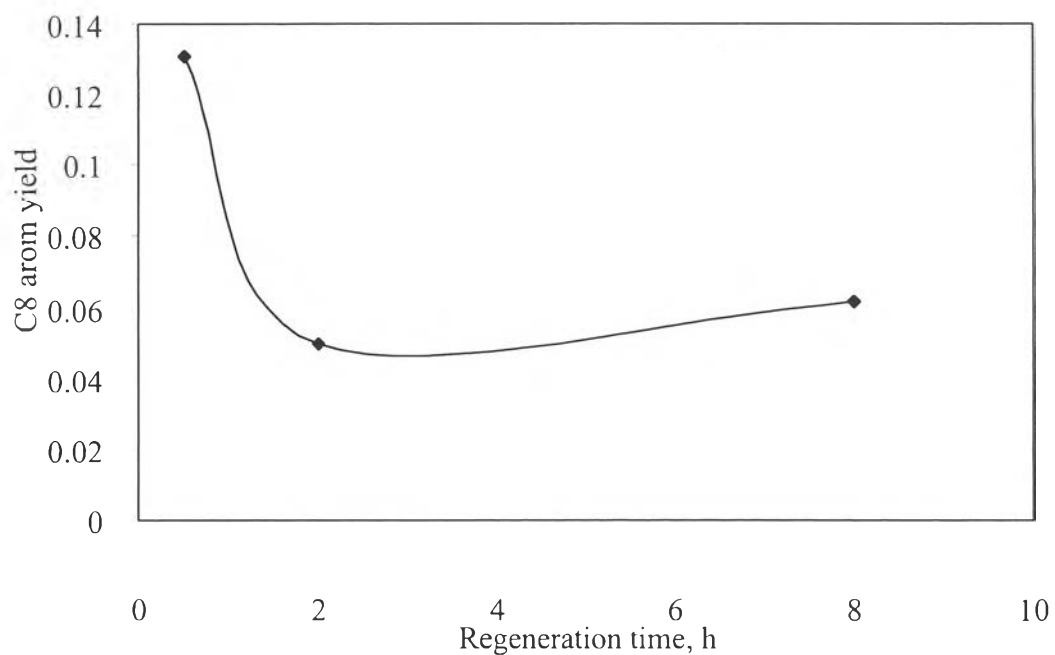
Figure 4.12 The average value of C_8 aromatics yield of various regeneration time (0.5-8 h) after regeneration in air
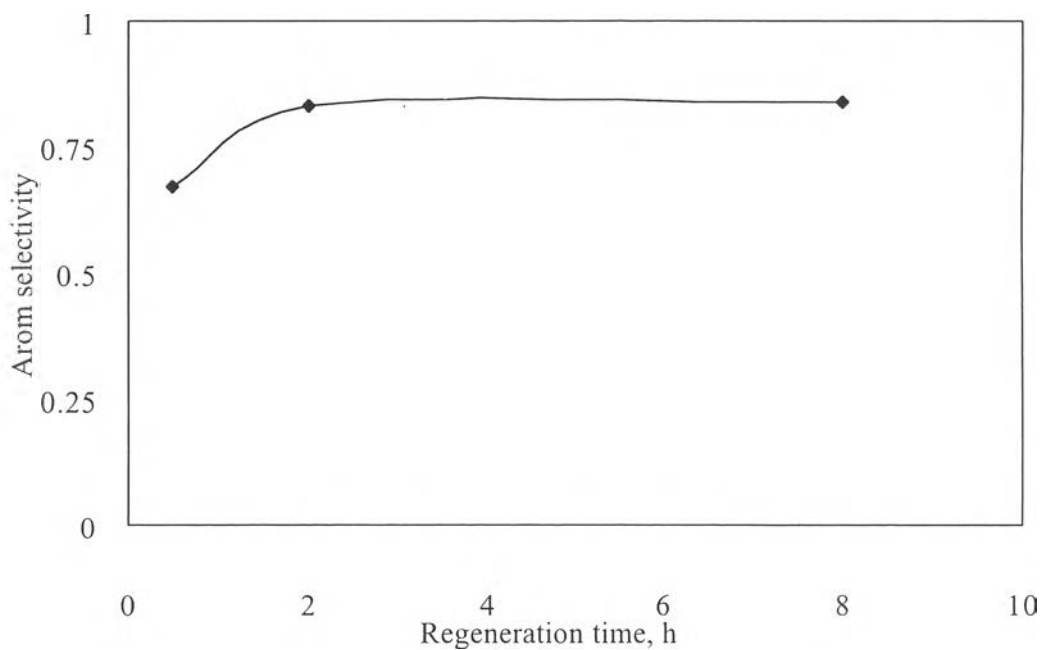

Figure 4.13 Average value of aromatics selectivity of various regeneration time (0.5-8 h) after regeneration in air
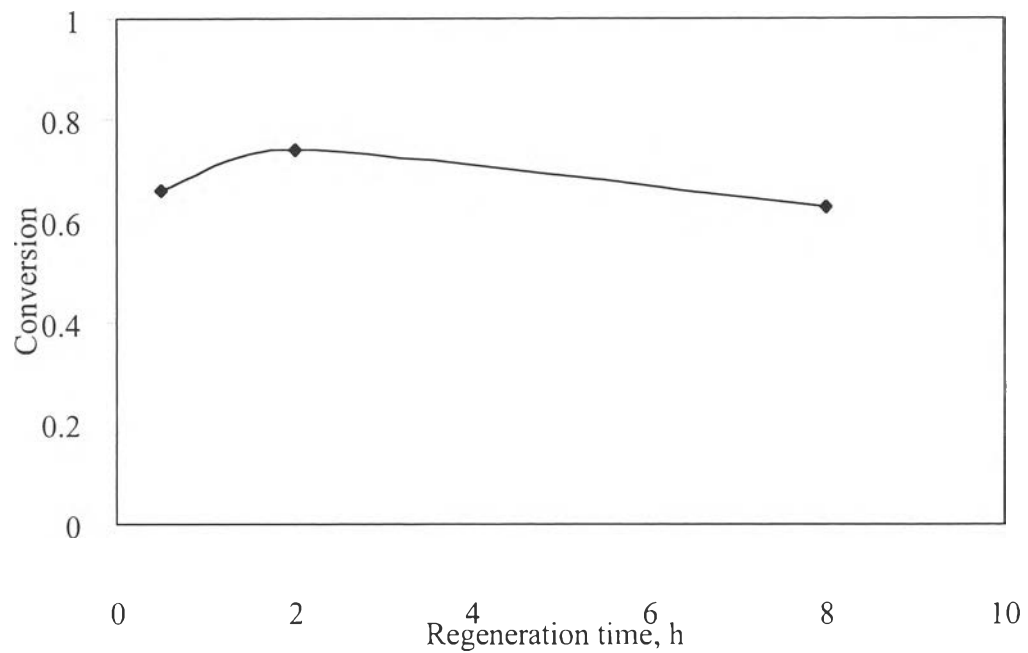
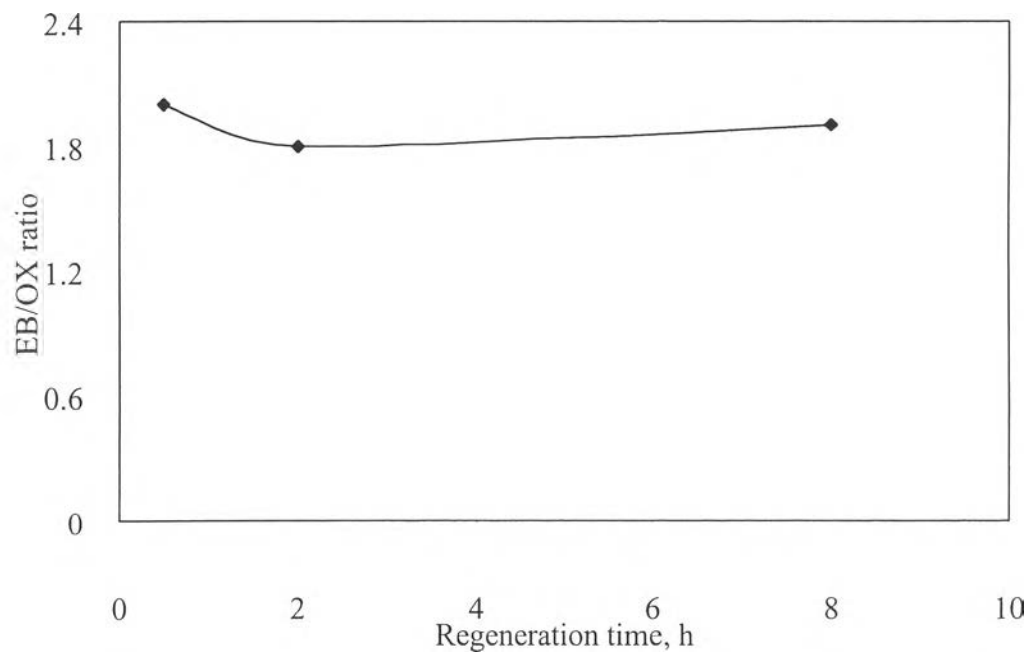**Figure 4.14** Average value of conversion of various regeneration time (0.5-8 h) after regeneration in air

Figure 4.15 Average value of EB/OX ratio of various regeneration time (0.5-8 h) after regeneration in air
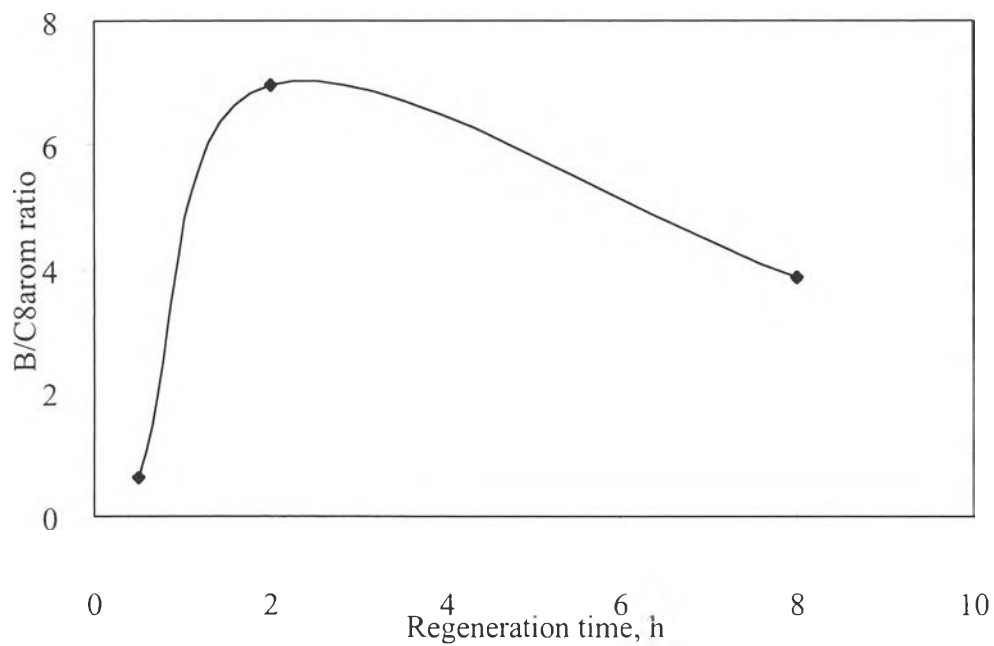
Figure 4.16 Average value of B/C$_8$ aromatics ratio of various regeneration time (0.5-8 h) after regeneration in air.
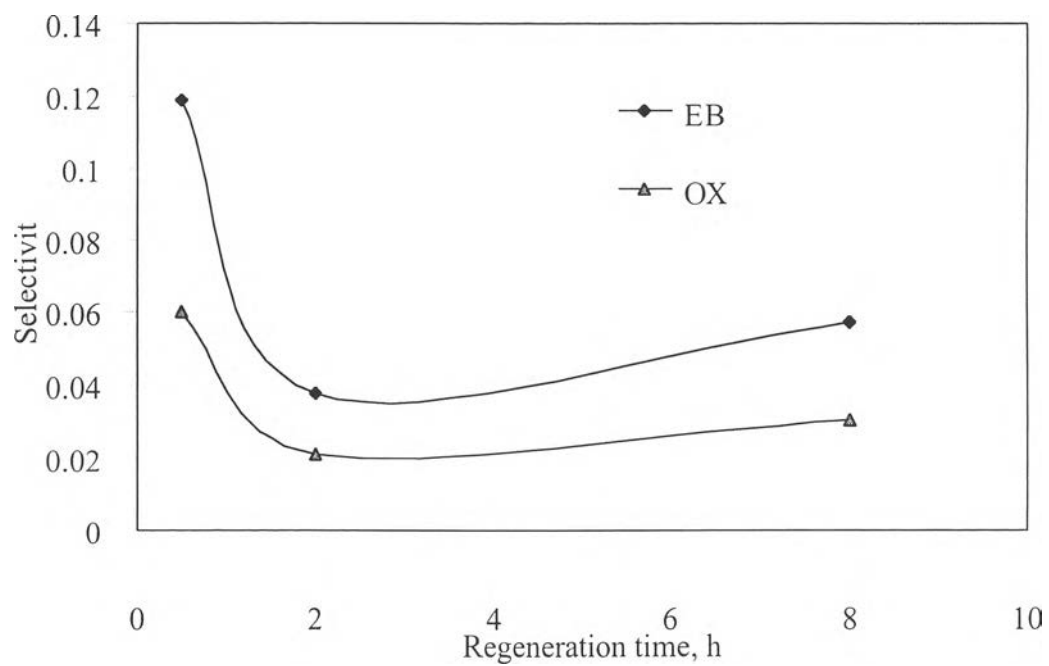

Figure 4.17 EB and OX selectivity of various regeneration time (0.5-8 h) after regeneration in air.

Consequently, the particular low EB/OX ratio and high conversion of 2h-regeneration were based on the hydrogenolysis of EB and OX (Jongpatiwut *et al.*, 2003). Therefore, regeneration for 2 h was not the most suitable regeneration time even it gave the highest conversion and the lowest EB/OX ratio among the others. In contrast, regeneration for 0.5 h provided significant high EB and OX selectivity even it had a little lower conversion and higher EB/OX. As a result of the particular high C_8 aromatics yield, the proposed optimal regeneration time was 0.5 h.

4.1.2.2 Characterization of catalysts

Fresh, spent and regenerated catalysts were characterized by means of DRIFTS of adsorbed CO and TPO to qualify Pt particles distribution and to determine amount of carbon deposits on the catalysts respectively.

(I) DRIFTS of Adsorbed CO

Figure 4.18 shows DRIFTS of adsorbed CO spectra of fresh and regenerated Pt/KL for regeneration time of 0.5, 2 and 8 h.
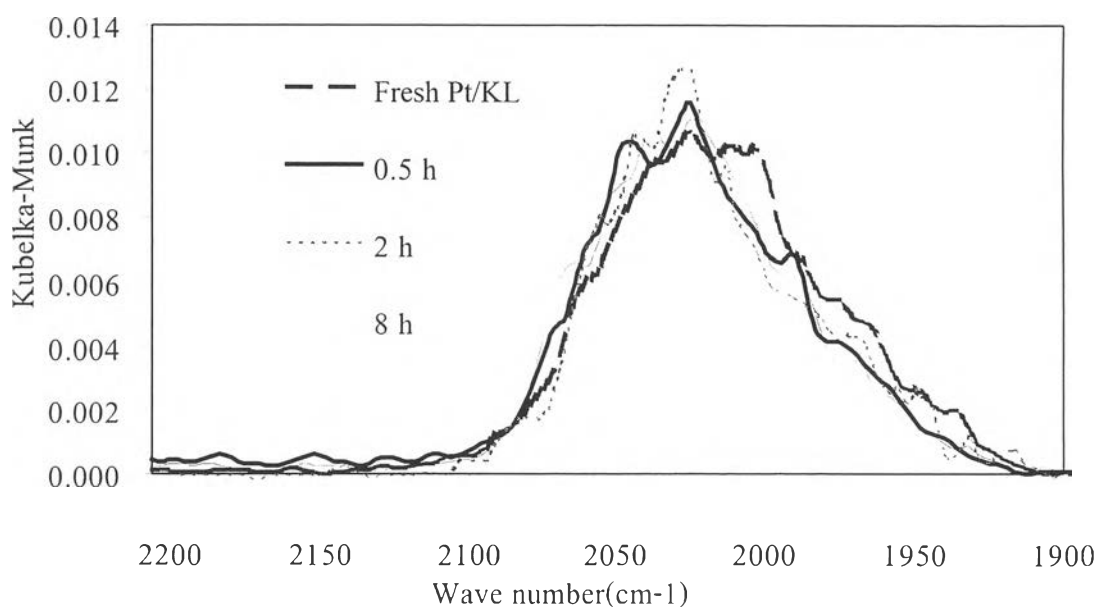

Figure 4.18 DRIFTS of adsorbed CO spectra of fresh and regenerated Pt/KL for regeneration time of 0.5, 2 and 8 h

It was found that the spectra of regenerated catalysts were quite similar to the spectrum of fresh catalyst. Consequently, regeneration time did not directly affect the location of Pt particles inside the KL zeolite.

(II) Temperature Programmed Oxidation (TPO)

Table 4.2 shows percent carbon contained in the spent and regenerated Pt/KL catalysts at three different regeneration time.

Table 4.2 TPO characterization of spent and regenerated Pt/KL catalysts at different regeneration time

Temperature of regeneration(^{o}C)	Time of regeneration (h)	Air flow rate (ml/min/g)	%C (wt.%)
	0.5		0.40
250	2	100	0.42
	8		0.38
Spent Pt/KL (after 12 h on stream)			2.26

The results shows that there was no significant change in carbon remained in the regenerated catalysts when regeneration time was increased. This was in good agreement with the results obtained from characterization by DRIFTS of adsorbed CO that regeneration time was not the most critical parameter that directly affects catalytic activity, location of Pt particles and coke formation in the catalyst.

4.1.3 Effect of Air Flow Rate

In this part, catalytic activity measurement and characterization of catalysts will be discussed.

4.1.3.1 Catalytic activity measurement

The reaction-regeneration cycles were performed under a constant regeneration temperature and regeneration time operated under 50, 100, 200 ml/min/g of catalysts in each reaction-regeneration cycle.

Figure 4.19 to Figure 4.22 shows the variation of C_8 aromatics yield, total aromatics selectivity, conversion, and EB/OX ratio after the reaction-regeneration cycles among the different air (as coke oxidant mixture) flow rate respectively.
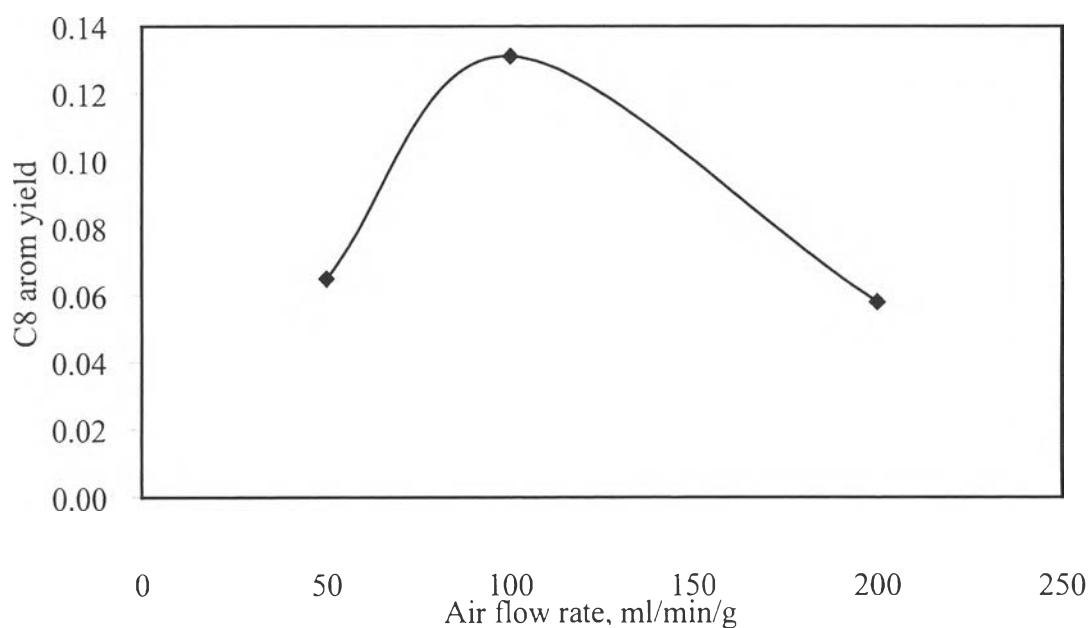

Figure 4.19 Average value of C_8 aromatics after regeneration in various air flow rate (50-200 ml/min/g)
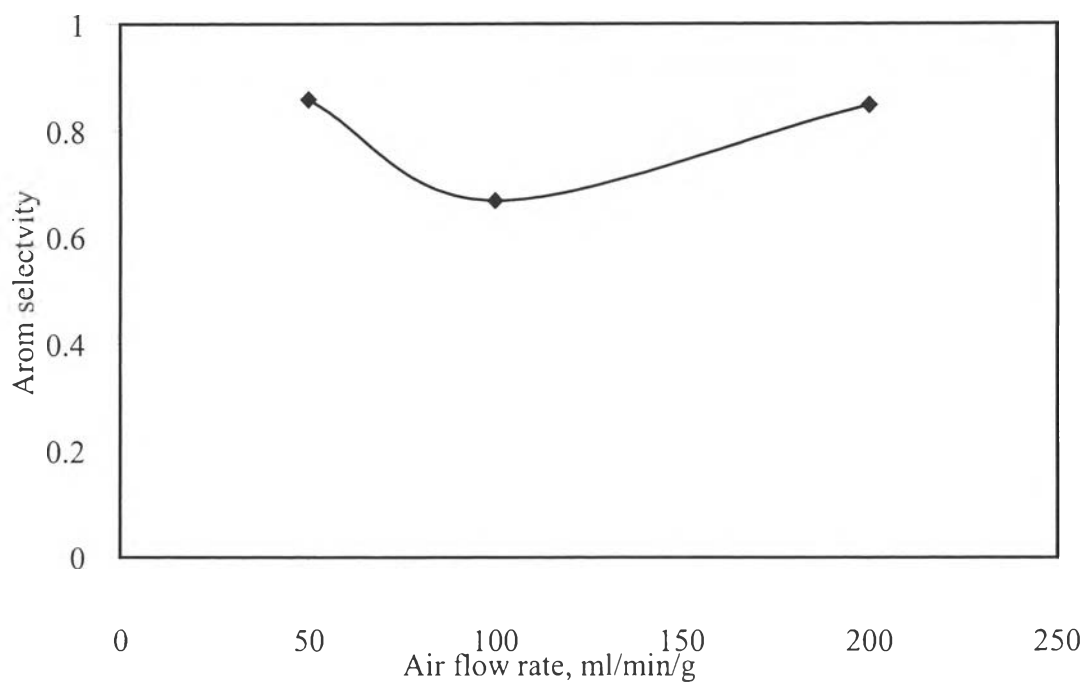
Figure 4.20 Average value of aromatics selectivity after regeneration in various air flow rate (50-200 ml/min/g)
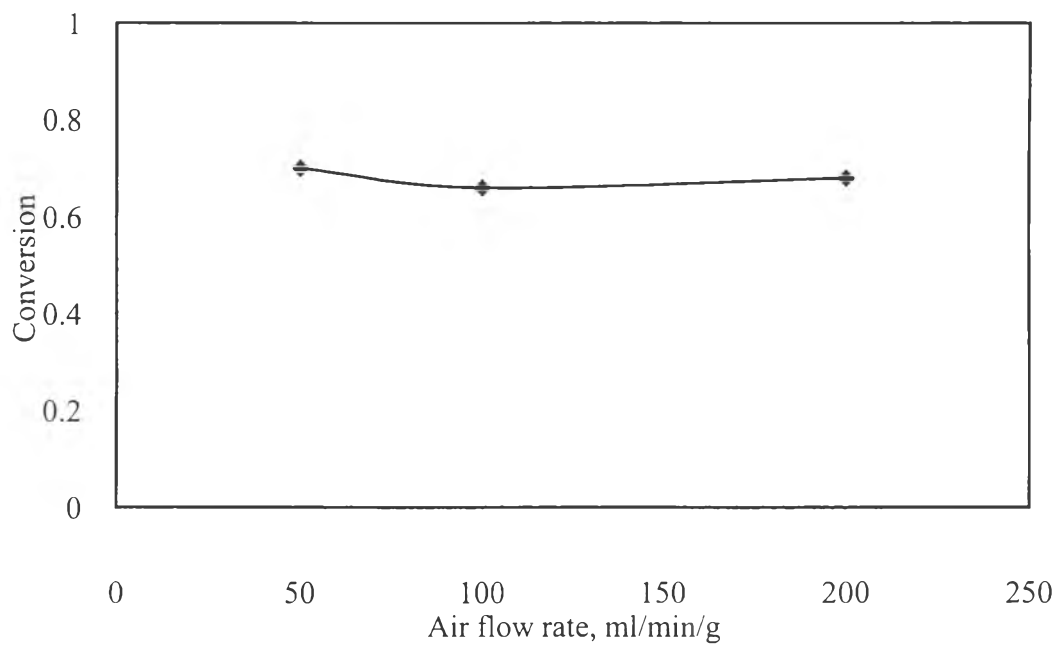

Figure 4.21 Average value of conversion after regeneration in various air flow rate (50-200 ml/min/g)
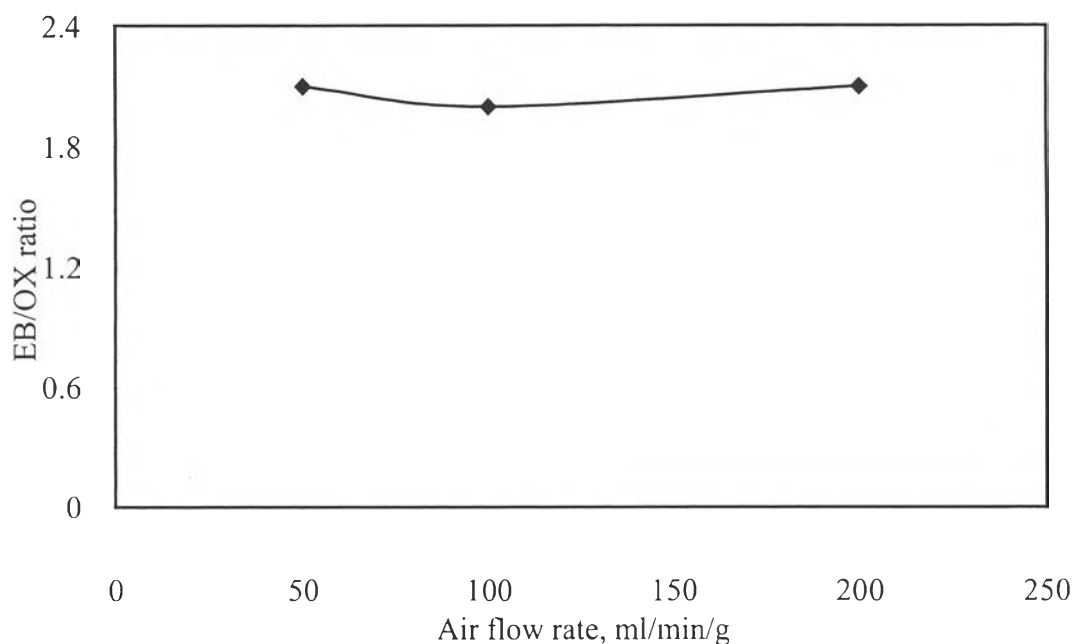
Figure 4.22 Average value of EB/OX ratio after regeneration in various air flow rate (50-200 ml/min/g)

According to Figure 4.19 and Figure 4.20 regeneration in air at 100 ml/min/g resulted in exactly the highest C_8 aromatics yield whereas aromatic selectivity among the other flow rate was lower. There was a small variation in conversion and also in EB/OX ratio as a function of air flow rate as shown in Figure 4.21 and Figure 4.22, respectively. Regeneration at 50 ml/min/g exhibited the highest conversion. This result was in the same reason with that of the previous effect, according to Figure 4.23, that regeneration at 50 ml/min/g had the highest B/C_8 aromatics ratio resulting from the high hydrogenolysis products compared with aromatization products leading to the low EB and OX selectivity as presented in Figure 4.24. Therefore, regeneration at 50 ml/min/g could not be selected as the optimal air flow rate as a result of the undesired products resulting from the hydrogenolysis reaction. This evident can be confirmed by catalyst characterization results in the next section.
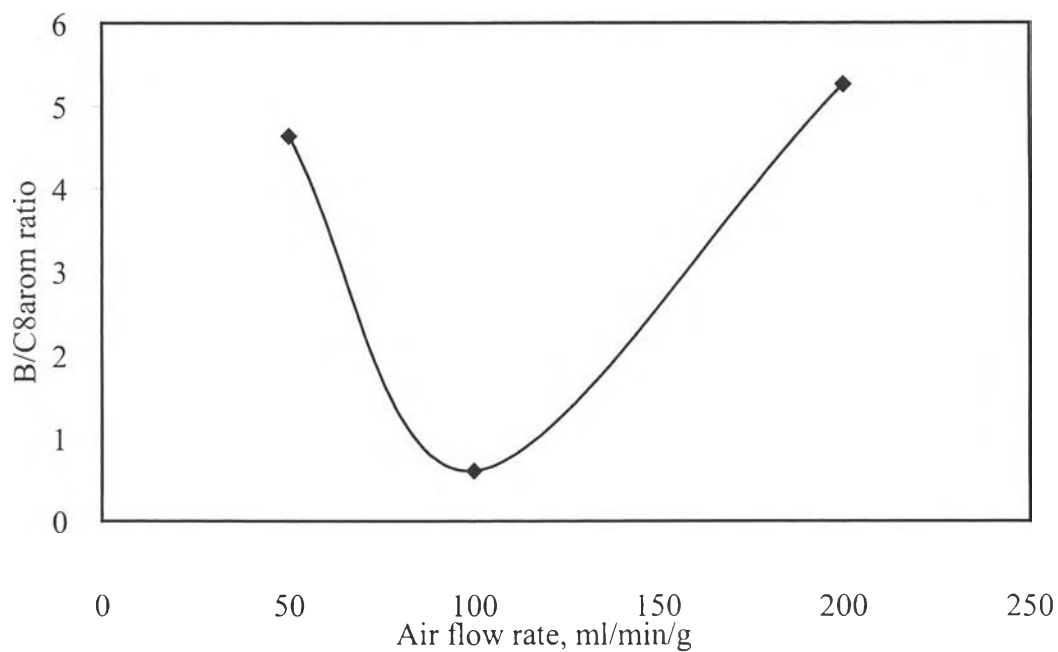
Figure 4.23 Average value of B/C_8 aromatics ratio after regeneration in various air flowrate (50-200 ml/min/g)
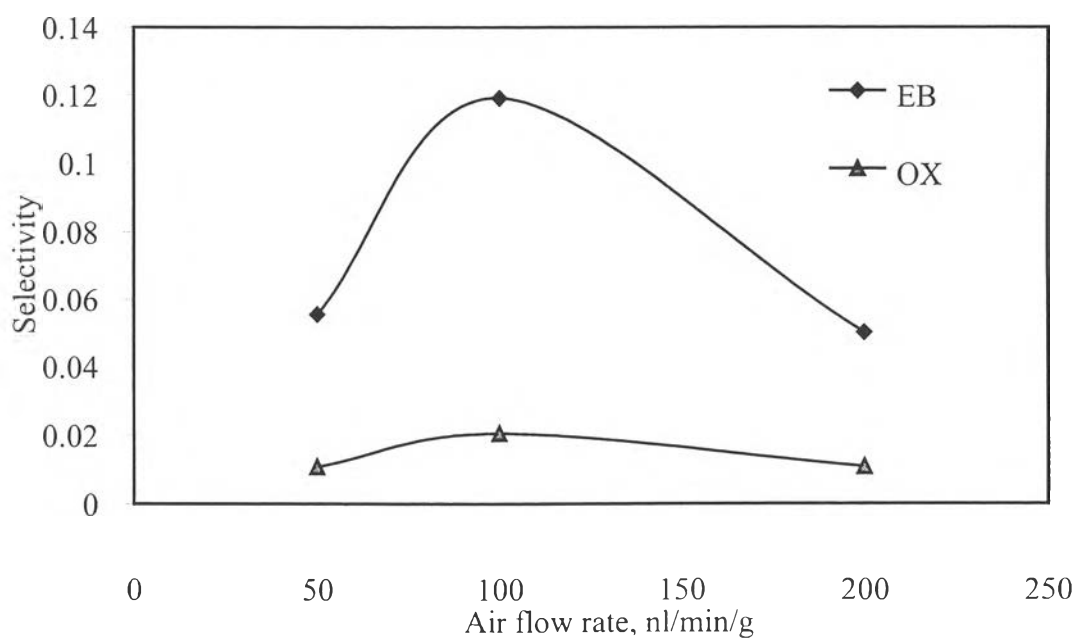

Figure 4.24 EB and OX selectivity of different air flow rate (50-200ml/min/g) after regeneration in air.

In addition, an interesting observation could be seen on the EB and OX which are the only two expected products from direct six membered ring closure (Davis and Venuto, 1969). The EB/OX ratio indicates the relative amount of EB and OX which do not undergo secondary hydrogenolysis. By regeneration in air, it seems that the EB/OX could not be remarkably decreased as low as that obtained from the different catalysts such as Pt/SiO_2. On the Pt/SiO_2 catalyst, this ratio was almost one (Huang *et al.*, 1992). This could be explained that the OX is more effectively converted into hydrogenolysis products than the EB (Jongpatiwut *et al.*, 2003) and caused by the carbon residues inside the zeolite.

4.1.3.2 Characterization of catalysts

Fresh, spent and regenerated catalysts were characterized by means of DRIFTS of adsorbed CO and TPO to qualify Pt particles distribution and to determine amount of carbon deposits on the catalysts respectively.

(I) DRIFTS of Adsorbed CO

Figure 4.25 shows DRIFTS of adsorbed CO spectra of fresh and regenerated Pt/KL in air flow rate of 50, 100 and 200 ml/min/g. It was investigated that a shift of spectrum to high wave number was significantly observed in the catalysts regenerated at 50 ml/min/g when compare to the spectrum of the fresh catalyst. It was confirmed that the unexpected performance as presented in the catalytic activity results was due to the change in location of Pt particles that leads to the poor Pt dispersion inside the KL channels resulting from only the regeneration at low air flow rate.
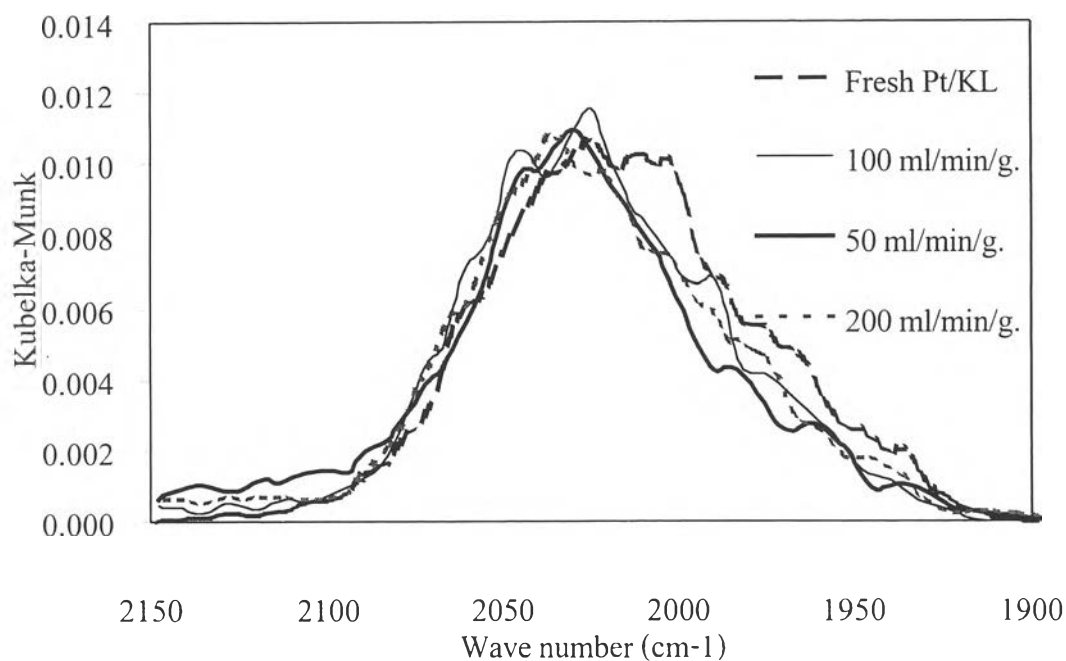
Figure 4.25 DRIFTS of adsorbed CO spectra of fresh and regenerated Pt/KL in air flow rate of 50, 100 and 200 ml/min/g

(II) Temperature Programmed Oxidation (TPO)

Table 4.3 shows percent carbon contained in the spent and regenerated Pt/KL catalysts .

Table 4.3 TPO characterization of spent and regenerated Pt/KL catalysts at different air flow rate

Temperature of regeneration(^{o}C)	Time of regeneration (h)	Air flow rate (ml/min/g.cat.)	%C (wt.%)
		50	0.62
250	0.5	100	0.40
		200	0.40
Spent Pt/KL (after 12 h on stream)			2.26

It was found that regeneration in air at 50 ml/min/g gave remarkably the high coke formation resulting in the high carbon percent in the regenerated catalyst as presented in Figure B3. These results were in good agreement with the results obtained from the DRIFTS of adsorbed CO part.

In conclusion, regeneration via coke oxidation in air at 250°C, 0.5 h, air flow rate = 100 ml/min/g of catalysts was selected to be the optimal regeneration conditions provided 81% of carbon removed from spent Pt/KL catalysts. The product distribution of n-octane aromatization over Pt/KL catalysts after reaction-regeneration cycles operated under the optimal regeneration conditions was summarized in Table 4.4. It was observed that the conversion and products selectivity of regenerated catalysts were relatively high compared with that of the spent catalysts without the regeneration treatment.

Table 4.4 Product distribution of n-octane aromatization over Spent Pt/KL catalysts. Reaction conditions: 500°C, $H_2/$ n-octane molar ratio 6:1, WHSV 5 h^{-1} Regeneration conditions: 250 °C, 0.5 h, air flow rate 100 ml.min^{-1}

	Without regeneration	With regeneration
Conversion, % (after 12 h on stream)	50	66
Products selectivity, %		
C_1-C_5	31	15
Benzene	31	9
Toluene	26	30
C_8 aromatics	**8**	**20**
Ethlybenzene	5	12
m- and p-Xylenes	1	2
o-Xylene	2	6

These results were in proportion to the previous work (Jongpatiwut *et al.*, 2003). Furthermore, the conversion and products selectivity of regenerated catalysts, especially conversion and xylenes selectivity, are more

pronounced after the regeneration. This can conclude that the regeneration via coke oxidation in air was clearly a good regeneration treatment for *n*-octane aromatization over Pt/KL catalysts.

In addition, although, after the suitable regeneration, C_8 aromatics were dominated, however, the majority of the aromatic products obtained were benzene and toluene which results from secondary reaction of EB and OX. It is apparent that the zeolite structure plays an important role on the product distribution.

As a conclusion, according to the three effects mentioned, temperature of regeneration is probably the most critical parameter in regeneration process because it influences directly the morphology of Pt particles and also the activity and selectivity of the catalysts. This was found to be in agreement with the regeneration of Pt-Sn/Al_2O_3 catalyst via burning in air in the previous work (Afonso *et al.*, 1997).

4.2 Pt Redispersion Study

After regeneration by coke oxidation in air, the three different regenerated Pt/KL catalysts were conducted to Pt redispersion via oxychlorination treatment. The comparison in terms of DRIFTS of adsorbed CO spectra of the fresh, regenerated catalysts with and without Pt redispersion of the three catalysts differed in regeneration temperature are shown in Figure 4.26 to Figure 4.27.

It was found that after regeneration in air, growth of Pt particles was still observed resulting in the shift of DRIFTS spectra at the low wave number below 2050 cm^{-1} to the high wave number which represents the poor Pt dispersion. By contrast, regeneration with oxychlorination treatment results in Pt redispersion and recovery of the location of Pt clusters as close as that of the fresh catalysts.
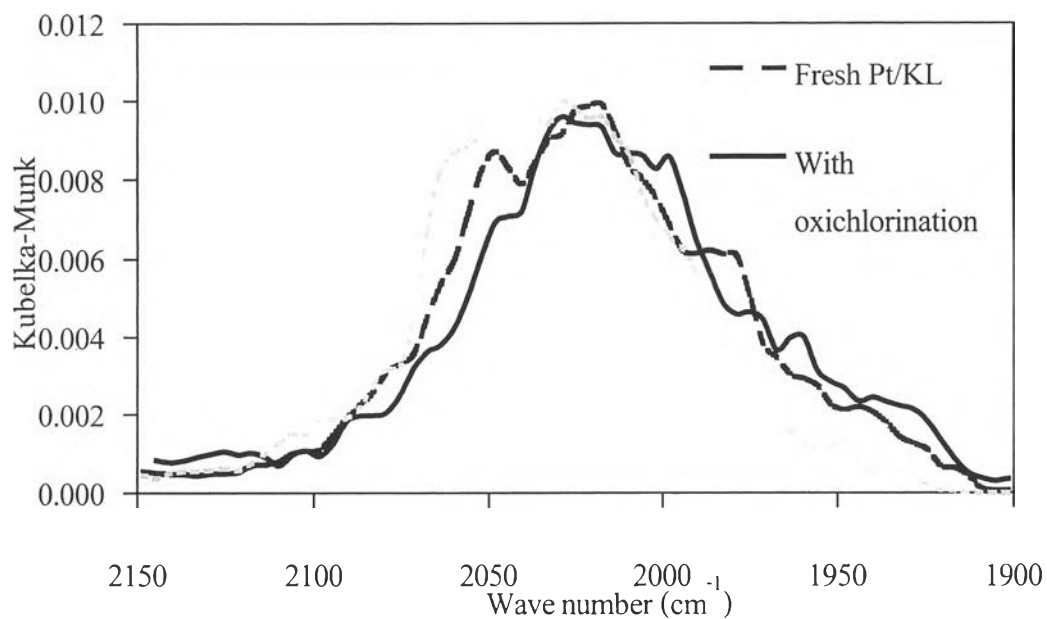
Figure 4.26 DRIFTS of adsorbed CO spectra after regeneration in air of fresh and regenerated Pt/KL with and without Pt redispersion at regeneration temperature of 150°C
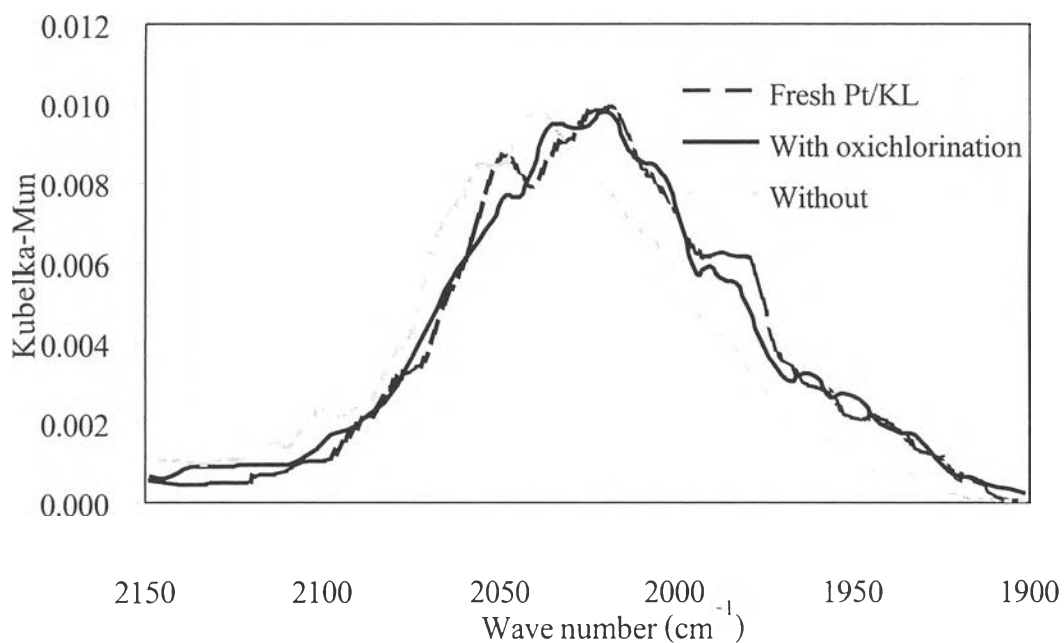

Figure 4.27 DRIFTS of adsorbed CO spectra after regeneration in air of fresh and regenerated Pt/KL with and without Pt redispersion at regeneration temperature of 400°C