

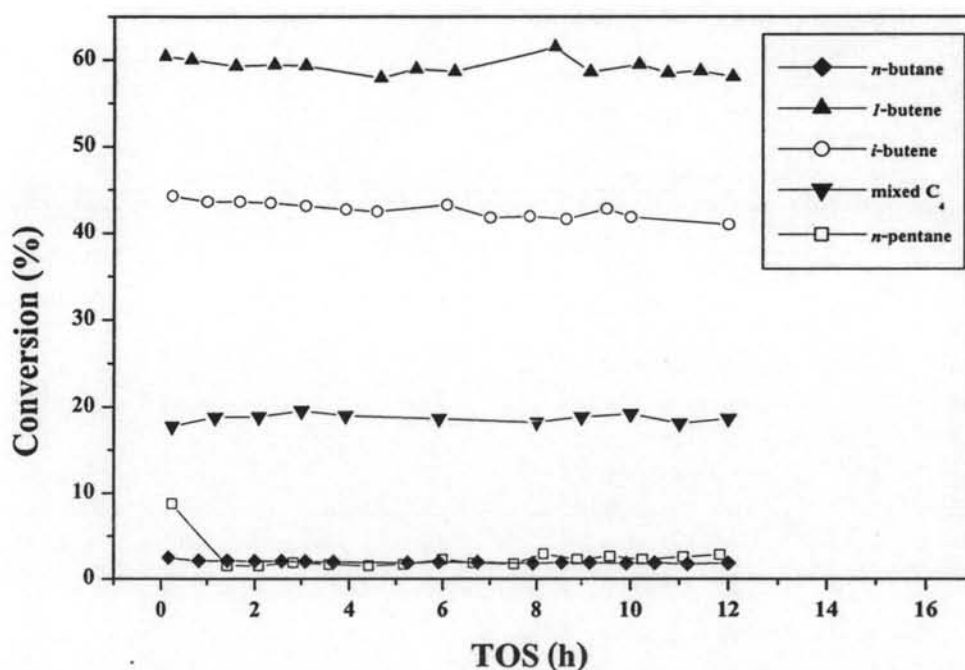
## CHAPTER IV

### RESULTS AND DISCUSSION

#### 4.1 Catalytic Cracking of Individual Feeds

##### 4.1.1 Activity Test

Previously, we investigated the effect of reaction conditions over ZSM-5 zeolite with various Si/Al ratio by using the mixed feed. We found that low Si/Al ratio gave the best propylene production but resulted in easier coke formation. Here, the influence of coke deactivation in the catalytic cracking of individual feeds was studied over ZSM-5 (Si/Al = 175) catalyst. Under the reaction conditions:  $T = 600^{\circ}\text{C}$ ,  $P = 1 \text{ atm}$ ,  $\text{GHSV} = 21,220 \text{ h}^{-1}$ , time-on-stream (TOS) = 12 h, 50% of reactant (diluted with He), the effects of reactant feeds on the performance of catalytic cracking are shown in Figures 4.1 and 4.2.



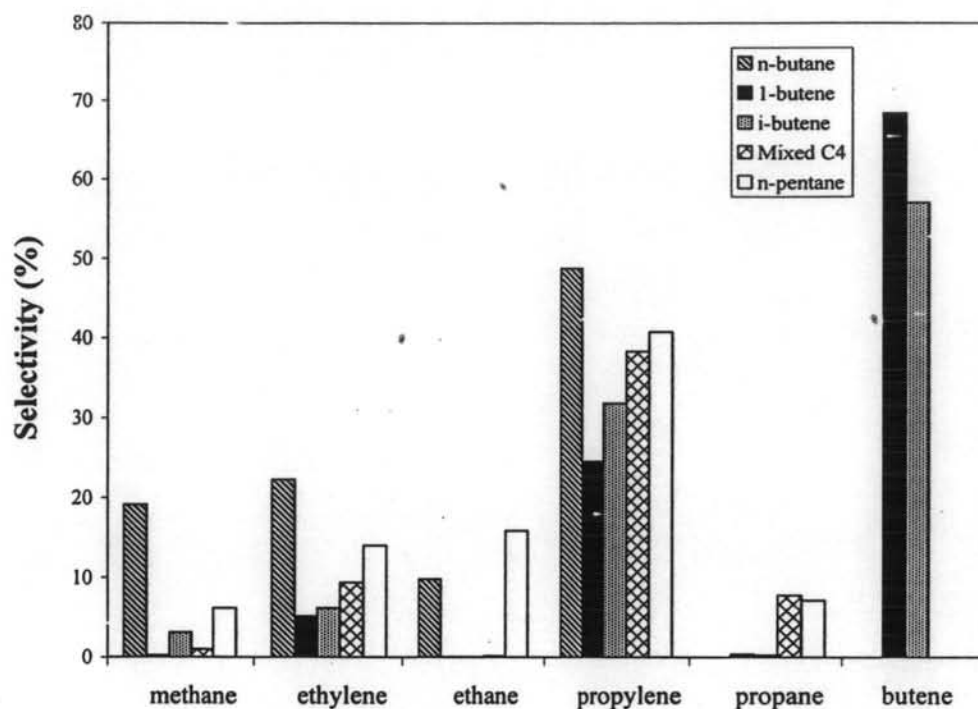
**Figure 4.1** Effect of 50% reactant feeds on the conversion for catalytic cracking reaction over ZSM-5 (Si/Al = 175) catalyst at the temperature of  $600^{\circ}\text{C}$  with the conditions of space velocity =  $21,220 \text{ h}^{-1}$ .

Compared with paraffins, the olefins are easily cracked, which can be found in Figure 4.1 that the conversion decreased in the order 1-butene > *i*-butene > mixed C<sub>4</sub> > *n*-butane ~ *n*-pentane. The conversion of 1-butene was higher than *i*-butene, although there both are olefin, due to the pores in ZSM-5 are only 5-6 Å wide, which is not large enough for these large molecule to enter. This is a so-called “shape-selectivity” effect (Anderson *et al.*, 2002). However, it was more interesting that mixed C<sub>4</sub> feed, which were containing 45% paraffins (*n*- and *i*-butane) and 55% olefins (butene), showed conversion between paraffin and olefin species. These results suggest that conversion depend on type of reactant but not competitive with each reactant when it was mixed.

The distributions of products obtained using ZSM-5 (Si/Al = 175) as catalyst are shown in Figure 4.2. It was found that methane, ethane, ethylene, propane, propylene, and butene (1- and 2-butene) were detected as the cracking products. No aromatic products (BTX; benzene, toluene, xylene) were observed. It might be due to high Si/Al ratio of ZSM-5 catalyst or high space velocity of feed. It is well-known that hydrogen is usually presented as a by-product for catalytic cracking reaction. However, hydrogen was not quantified in this experiment. The exact amount of all product yields is shown in Table 4.1.

**Table 4.1** Conversion of 50% reactant feeds and product yields for catalytic cracking reaction over ZSM-5 (Si/Al = 175) catalyst at 600°C after 12 h of reaction time using various reactant feeds with the conditions of space velocity = 21,220 h<sup>-1</sup>

	Feed				
	<i>n</i> -butane	<i>I</i> -butene	<i>i</i> -butene	Mixed C4	<i>n</i> -pentane
Conversion (%)	1.86	58.09	41.05	18.70	2.85
Yield (%)					
methane	0.36	0.15	1.27	0.19	0.18
ethylene	0.41	3.00	2.53	1.75	0.40
ethane	0.18	0.04	0.03	0.04	0.45
propylene	0.91	14.27	13.07	7.17	1.16
propane	0.00	0.24	0.13	1.46	0.20



**Figure 4.2** Effect of 50% reactant feed on the products distributions for catalytic cracking reaction over ZSM-5 (Si/Al = 175) catalyst after 12 h of reaction time at the temperature of 600°C with the conditions of space velocity = 21,220 h<sup>-1</sup>.

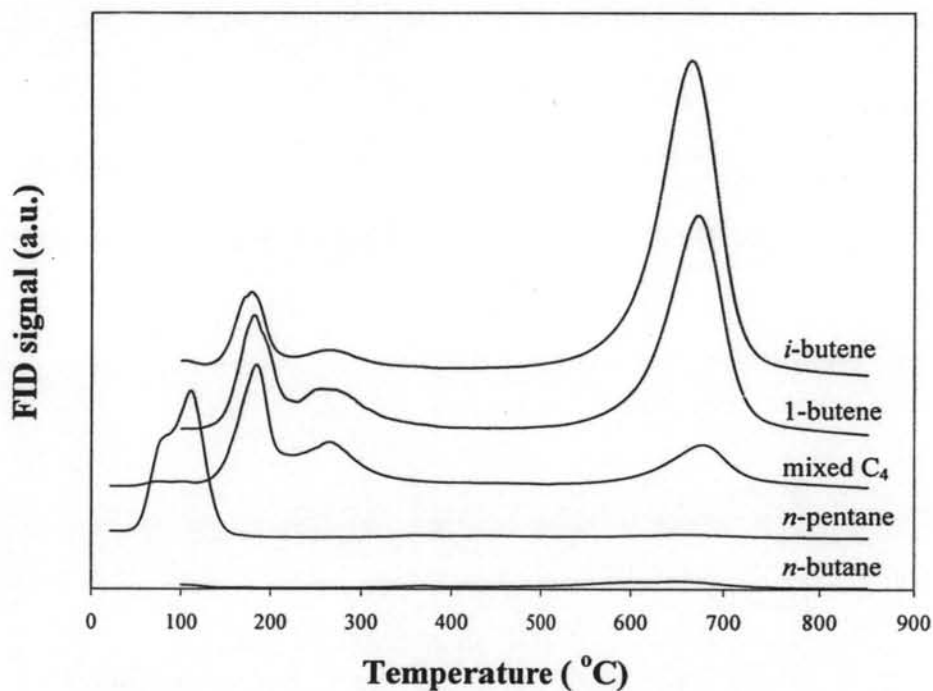
#### 4.1.2 Coke Analysis by TPO

The temperature programmed oxidation (TPO) is performed to analyze coke deposited on the spent catalyst after reaction time. As shown in Figure 4.3, the TPO profiles show peaks with the maximum temperatures at two temperature regions (100-300 and 650-700°C). At high temperature region, the TPO profiles show the maximum peak at the temperature about 680°C for all reactant feeds except *n*-pentane while those of all reactants show two peaks in the low temperature region at the temperature about 180 and 280°C except *n*-butane and *n*-pentane.

According to the literature reported by Li *et al.* (2000), they suggest that the oxidization of coke in low temperature region could form coke in type of condensation of polyaromatic molecules because the coke residues were more easily

oxidized at low temperature. On the other hand, the peaks in high temperature region might be due to the oxidation of pseudo-graphitic carbon in the pore of ZSM-5 zeolite.

Interestingly, the TPO profile of *n*-pentane shows the peak at the lower temperature (ca. 100°C) when compared with the other reactants. Hence, the results indicate that nature of reactant effected on the type of carbonaceous residues on the catalyst.



**Figure 4.3** TPO profiles of spent catalyst after exposure to reaction at 600°C for 12 h-time on stream and space velocity = 21,220 h<sup>-1</sup> with a heating rate of 10°C/min, an oxidizing gas containing 2% oxygen in He with a flow rate of 40 ml/min.

The amount of coke is presented in term of percent weight of carbon deposition on the catalyst as shown in Table 4.2. Coking occurs rapidly from alkenes and polyaromatics or reactant undergoing a rapid transformation into these coke-maker molecules (Guisnet and Magnoux, 1997). A large amount of coke was presented in C<sub>4</sub> olefin species due to the highly reactive olefins oligomerize to form larger intermediates, which then rapidly cyclize and dehydrogenate to aromatics (coke precursors).

**Table 4.2** Amounts of coke deposited on the catalysts, as determined by TPO, using 2%O<sub>2</sub> in He and heating rate of 10°C/min, after 12 h-time on stream at 600°C and space velocity = 21,220 h<sup>-1</sup>

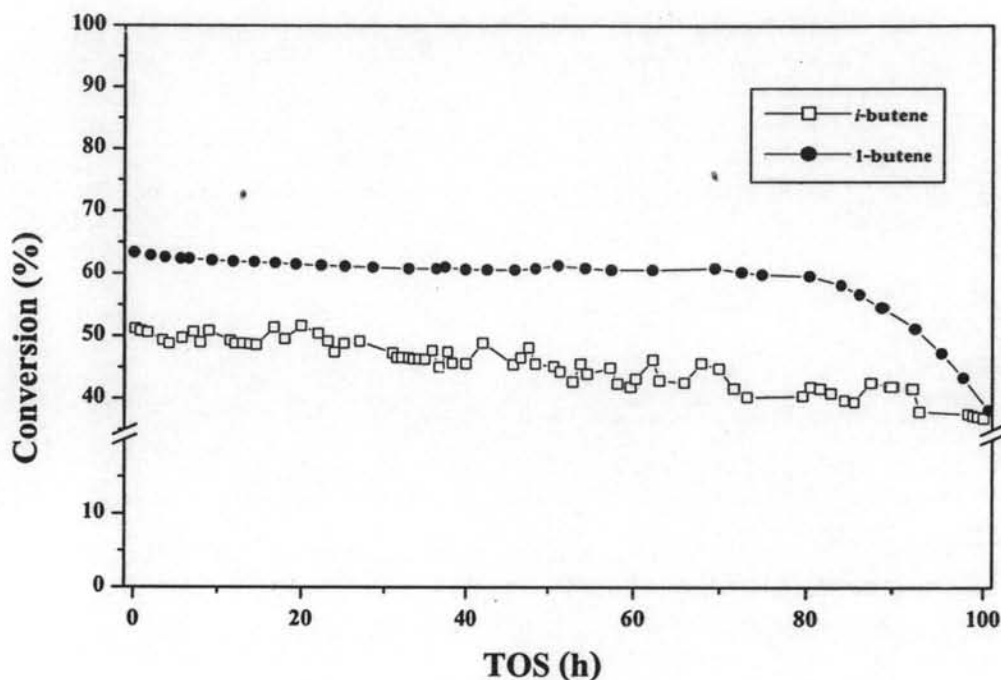
Feed	Amount of coke (wt%)
<i>n</i> -butane	0.08
<i>l</i> -butene	5.53
<i>i</i> -butene	5.81
mixed C <sub>4</sub>	3.48
<i>n</i> -pentane	1.30

#### 4.1.3 Stability Test

The stability of the catalyst can define as the ability of the catalyst to retain its activity under the operating conditions. The three most common causes of catalyst decay are fouling, poisoning or thermal degradation. Fouling involves the deposition of material on a catalyst surface to block active site (Trimm, 2001). Coke deposition is the most causes of a loss in activity of ZSM-5 zeolites, which will accumulate on surface or pore system of zeolite.

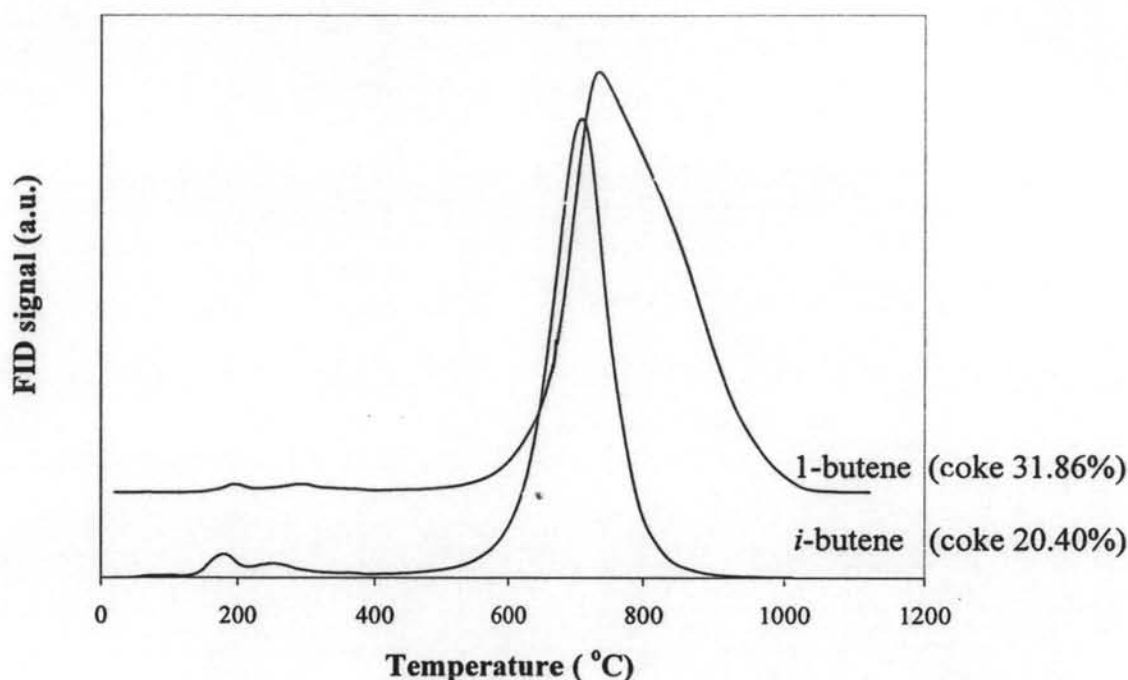
The stability test is performed to test the stability of two reactants (1-butene and *i*-butene) over ZSM-5 (Si/Al = 175) catalyst due to the results obtained from activity test shown that those two reactants are highly active for catalytic cracking. Under the same reaction conditions with activity test : T = 600°C,

$P = 1 \text{ atm}$ ,  $\text{GHSV} = 21,220 \text{ h}^{-1}$  and 50% of reactant (diluted with He). The results are monitored until the conversion reduces to 40%.



**Figure 4.4** Conversion of 1-butene and *i*-butene over ZSM-5 (Si/Al = 175) catalyst at the temperature of  $600^{\circ}\text{C}$  with the conditions of space velocity =  $21,220 \text{ h}^{-1}$ .

From Figure 4.4, when 1-butene is tested, the conversion starts with 63% at initial time on stream (TOS) and maintains to 60% at 80 h-TOS. Afterward, the conversion is significantly decrease to 40% at 100 h-TOS. In case of *i*-butene, the initial conversion is 52% (less than 1-butene) and slightly decrease to 40% at the end of the test. The differences in the stability of both reactants may be related to its structure. The structure of 1-butene is linear-hydrocarbon, not only products but also the reactants can get into the pore of ZSM-5 and can be effortless coke formation. Therefore, the stability of 1-butene is shorter than *i*-butene but conversion is higher.



**Figure 4.5** TPO profiles of spent catalyst after exposure to reaction at 600°C for 100 h-time on stream and space velocity = 21,220 h<sup>-1</sup> with a heating rate of 10°C/min, an oxidizing gas containing 2% oxygen in He with a flow rate of 40 ml/min.

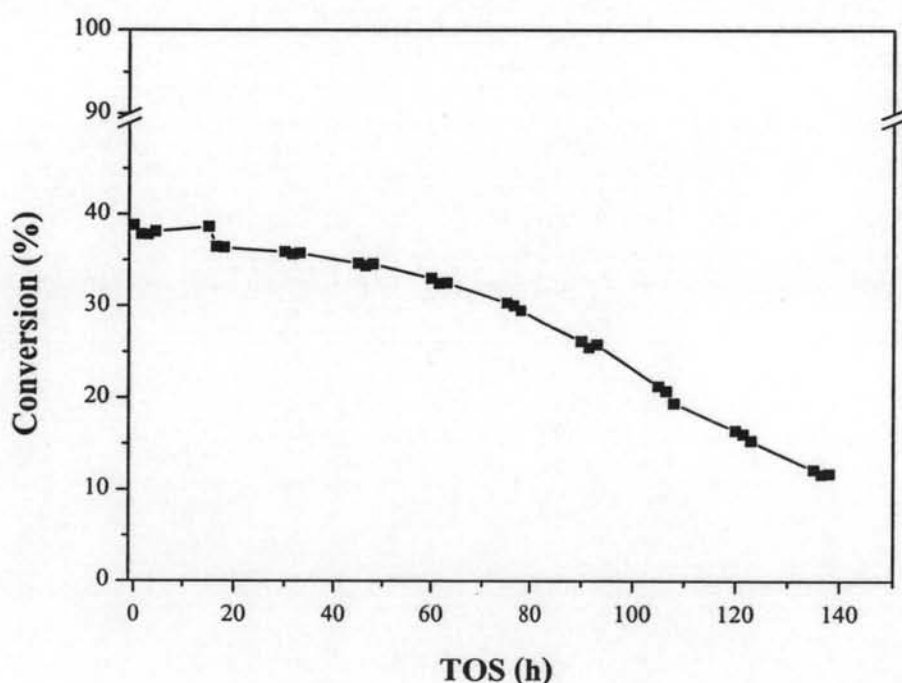
Due to the eminent active of 1-butene, the TPO results show the huge quantity of coke (31.86%) and asymmetry of profile (Figure 4.5). Two peaks of coke were observed, the first one at low temperature about 200°C and the rest at temperature about 750°C. The discussion from section 4.1.2 are similar describe for the profile. The little peak at lower temperature may come from the heavy hydrocarbon which physically adsorb on the outer surface of the zeolite and vaporized when temperature is increased. The bigger peaks at high temperature are come from the oxidation of pseudo-graphitic carbon in the pore of ZSM-5 zeolite coke oxidation.

Interestingly, an asymmetry peak of high temperature might be due to either a large amount of coke inside the zeolite pores in which are located most of the acid sites (Guisnet and Magnoux, 2001) or from another type of coke. In addition, the small peak at low temperature indicated that the reaction of *i*-butene trended to take place on outer surface of ZSM-5.



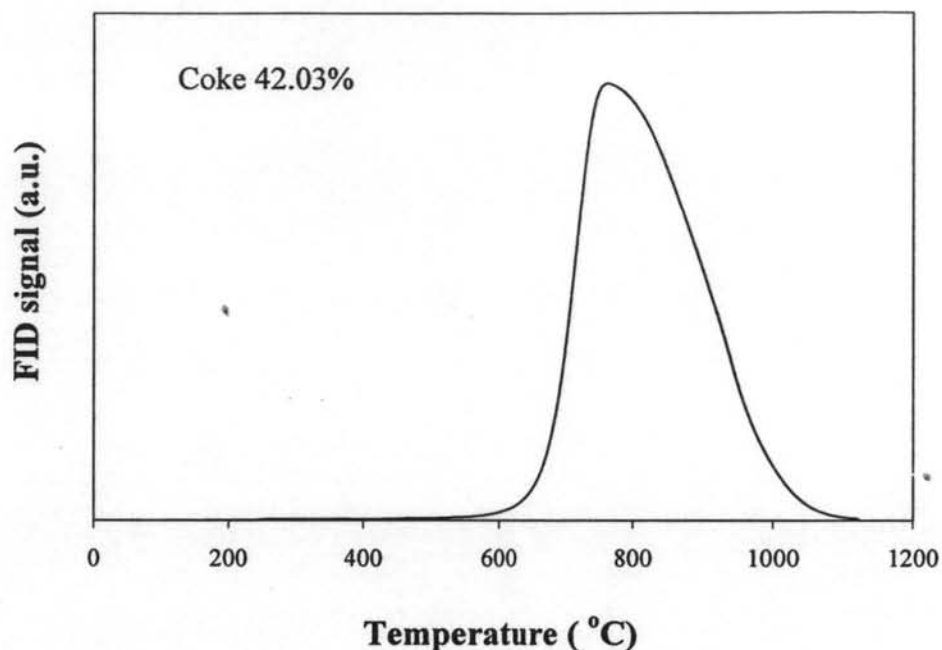
#### 4.1.4 Regeneration

In order to investigate the influence of temperature and oxygen concentration on the regeneration of catalytic cracking over ZSM-5 zeolite (Si/Al ratio = 175), the mixed C<sub>4</sub> was picked up as reactant because it is representative of mixture from the real industrial feedstocks. A severity reactant was used, which is 100% concentrated feed (non-diluted with He), for reaction. The purpose of using such high concentration is to promote high conversion and, hence, to ease the formation of coke. Under the same reaction conditions with activity test : T = 600°C, P = 1 atm, GHSV = 21,220 h<sup>-1</sup>. The 40% of conversion was found in the initial TOS, which presented in Figure 4.6, and it is slightly change to 30% of conversion with 80 h-TOS. At the end of reaction, conversion drop to 10% at 140 h-TOS. For the selectivity, it is similar to activity test (see Figure 4.2).



**Figure 4.6** Conversion of mixed C<sub>4</sub> over ZSM-5 (Si/Al = 175) catalyst at the temperature of 600°C with the conditions of space velocity = 21,220 h<sup>-1</sup>.





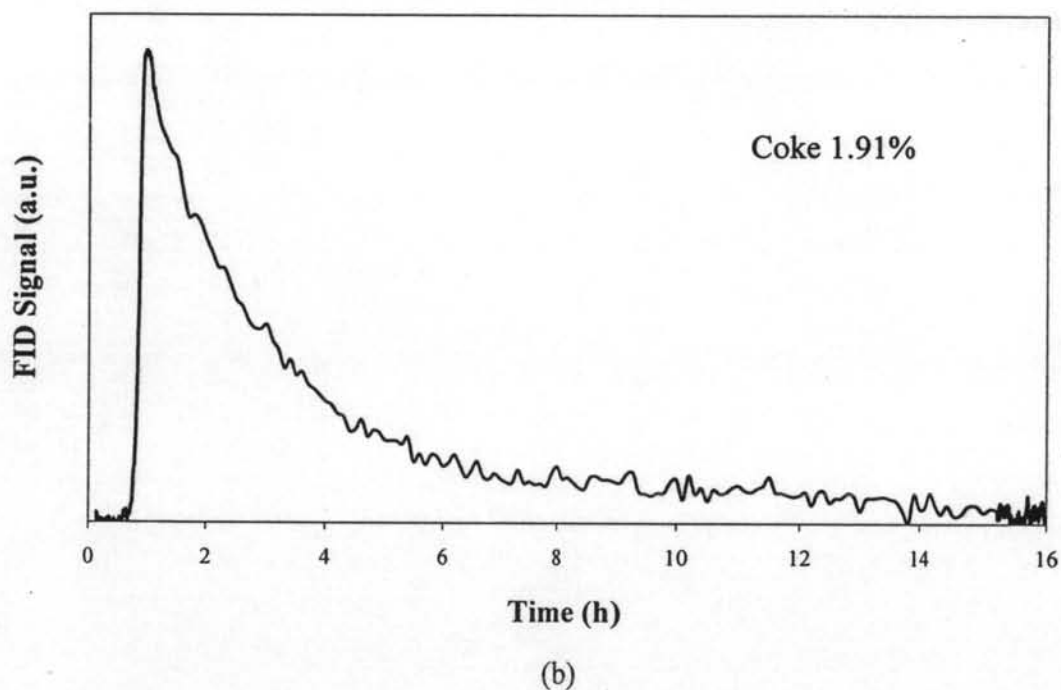
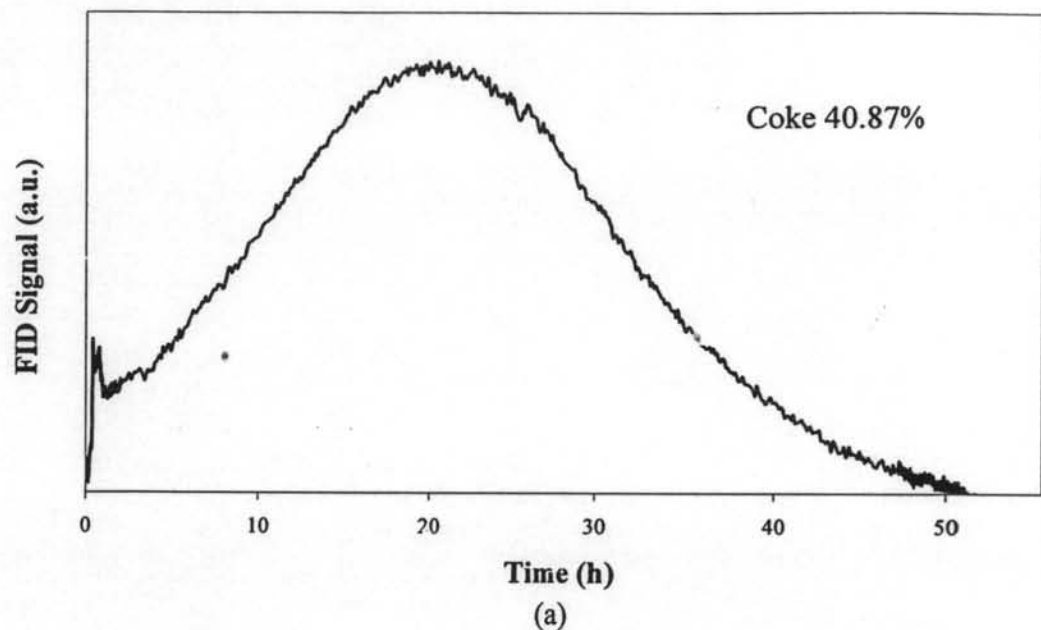
**Figure 4.7** TPO profiles of spent catalyst after exposure to reaction at 600°C for 140 h-time on stream and space velocity = 21,220 h<sup>-1</sup> with a heating rate of 10°C/min, an oxidizing gas containing 2% oxygen in He with a flow rate of 40 ml/min.

Figure 4.7 presents the TPO results of ZSM-5 with Si/Al ratio = 175 from mixed C<sub>4</sub> of 1-cycle test. The results show only one peak at temperature about 770°C. It is interesting to note that the another peak at lower temperature does not appear in long test but this peak can find in short run (see Figure 4.3). According to Guisnet and Magnoux, 2001, they found that the coke molecules formed inside the micropores of zeolites are less polyaromatic. Therefore, part of them can be recovered in organic solvents after dissolution of the zeolite matrix and identified by classical analysis methods such as GC, MS, and GC/MS. However, whereas at short time-on-stream all the coke molecules are generally soluble in organic solvents (soluble coke) and easily to oxidize at low temperature, this is no more the case at long time-on-stream hence at high coke contents. Therefore, it could be concluded that insoluble coke consists of very polyaromatic molecules resulting from the transformation of soluble coke molecules trapped inside the zeolite micropores.

On the other hand, the profile is an asymmetry peak and oxidized temperature is too high when compared with short time-on-stream. These results might be due to the heating rate of TPO analysis is too fast ( $10^{\circ}\text{C}/\text{min}$ ) or the amount of 2%  $\text{O}_2/\text{He}$  is not excess for total combustion. The large amount of coke (42.03%) was analyzed and the oxidized peak starts at temperature around  $500^{\circ}\text{C}$ . If the temperature was hold at  $500^{\circ}\text{C}$ , the coke could be completely oxidized at this temperature.

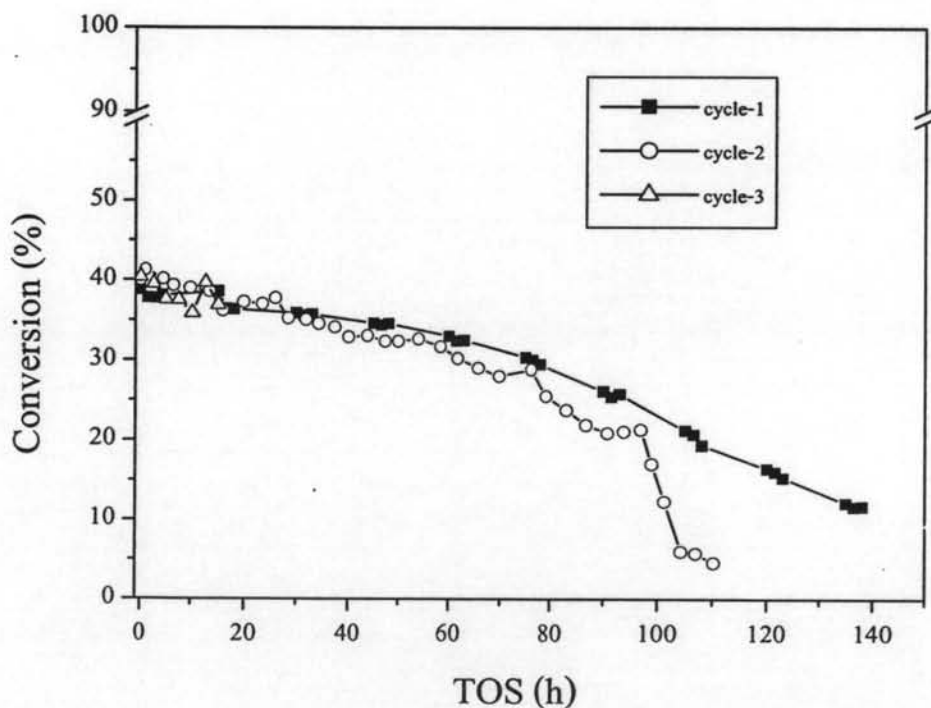
This hypothesis was confirmed by the same experiment with TPO technique but modify the part of temperature program. The temperature program was set to heat from room temperature to  $500^{\circ}\text{C}$  with  $10^{\circ}\text{C}/\text{min}$  heating rate and then hold at this temperature until the FID signal dropped to base line. Afterward the same sample was cooled down to room temp and heated to desired temperature,  $550^{\circ}\text{C}$  and  $600^{\circ}\text{C}$  consequently.

An oxidized temperature  $500^{\circ}\text{C}$ , the results show that at this temperature could remove the major fraction of coke (40.87%) by the duration of oxidize is 50 h, as show in Figure 4.8(a). Form Figure 4.8(b) (an oxidized temperature is  $550^{\circ}\text{C}$ ), a small amount of coke (1.91%) was found and spent 16 h-TOS for this temperature. For oxidized temperature  $600^{\circ}\text{C}$ , it was not found the amount of coke so this can identify that the temperature  $550^{\circ}\text{C}$  is completely remove coke. Therefore, the regeneration temperature was chosen at  $500^{\circ}\text{C}$  due to it can remove the major fraction of coke and for economics reason.



**Figure 4.8** TPO profiles of spent catalyst after exposure to reaction at 600°C for 140 h-time on stream and space velocity = 21,220 h<sup>-1</sup> with a heating rate of 10°C/min from room temperature to desired temperature and hold at this temperature, an oxidizing gas containing 2% oxygen in He with a flow rate of 40 ml/min: (a) 500°C and (b) 550°C.

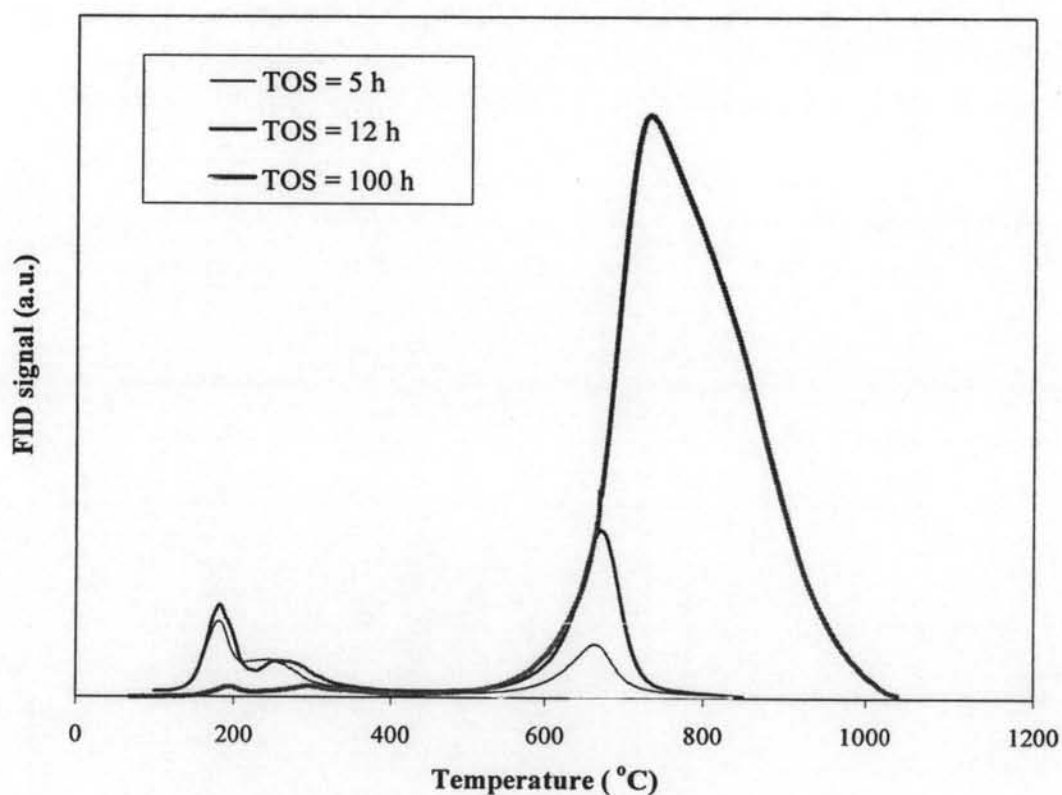
It should be noted that after the regeneration of 1<sup>st</sup>-cycle under 10% O<sub>2</sub> balanced with N<sub>2</sub> at 500°C for 11 h, the original activity was regained as shown in Figure 4.9. The conversion of 2<sup>nd</sup>-cycle is slightly change to 30% of conversion with 80 h-TOS (the results resemble with the 1<sup>st</sup>-cycle). However, the conversion is significantly decrease to 7% after 95 h-TOS. For the 3<sup>rd</sup>-cycle, it used only 9 h for regeneration, it can provide the initial conversion with the same as a fresh catalyst. This result suggested that the catalyst can recovery the initial activity by regeneration with 10% O<sub>2</sub> at 500°C in many cycle. However, the shorter stability might be due to the fact that the total amount of coke was not absolutely removed at the given regeneration temperature. The other reason is the structure of zeolite could be collapse due to a high thermal and long run reaction.



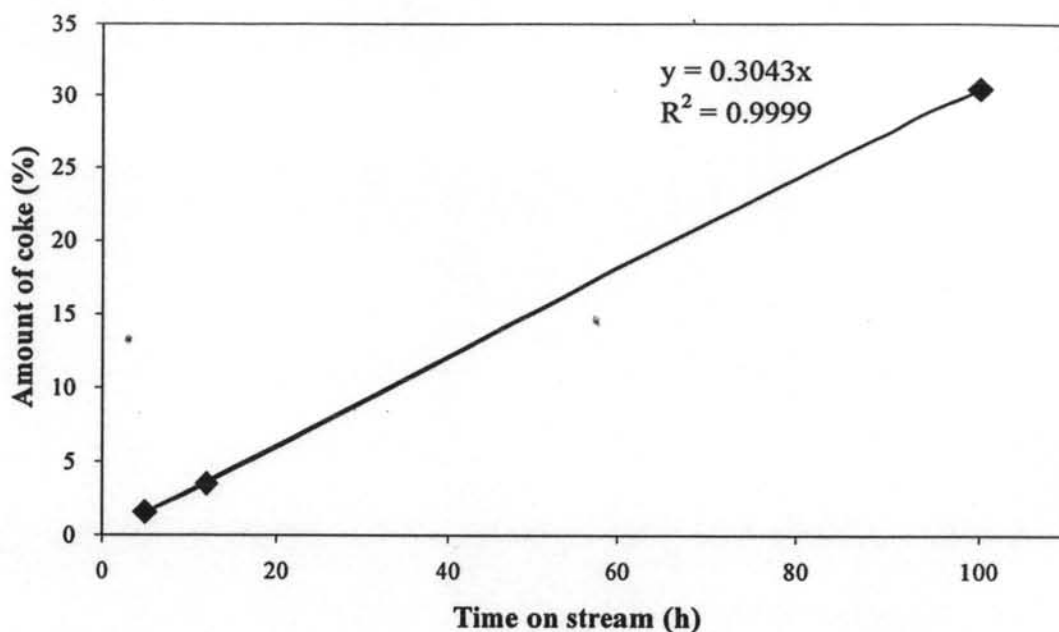
**Figure 4.9** Conversion of mixed C<sub>4</sub> over ZSM-5 (Si/Al = 175) catalyst at the temperature of 600°C with the conditions of space velocity = 21,220 h<sup>-1</sup>.

#### 4.1.5 Relationship of TOS and Amount of Coke

From the results of regeneration part, it shows that the shorter time-on-stream requires shorter duration of regeneration. Those results correspond to this experimental part. 1-Butene, highly reactive reactant, was carried out as feed in catalytic cracking reaction over ZSM-5 zeolite (Si/Al ratio = 175). As shown in Figure 4.10, TPO profiles show two peaks, only a high temperature peak is bigger when TOS is increasing. In contrast, a low temperature peak was reduced. This might be due to the coke at low temperature that consists of polyaromatic molecules transformed to pseudo-graphitic carbon and trapped inside the zeolite micropores. However, the relationship between TOS and amount of coke are linear (Figure 4.11).

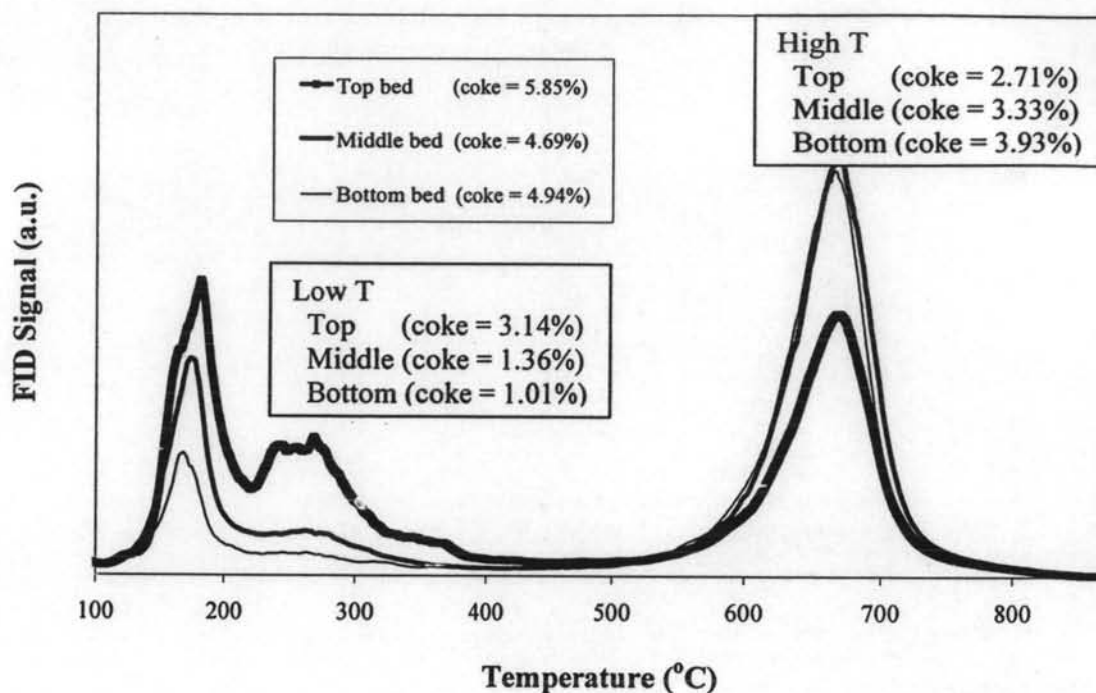


**Figure 4.10** TPO profiles of spent catalyst after exposure to reaction at 600°C and space velocity = 21,220 h<sup>-1</sup> with a heating rate of 10°C/min, an oxidizing gas containing 2% oxygen in He with a flow rate of 40 ml/min.



**Figure 4.11** The relationship of time-on-stream and amount of coke that observed from 1-butene cracking over ZSM-5 with Si/Al ratio = 175.

To investigate the phenomena that cause the low temperature peak disappeared when time-on-stream was increased, the three beds in one reactor with feed downward were set and tested for catalytic cracking using *i*-butene as reactant. As shown in Figure 4.12, the TPO profiles at low temperature region show the amount of coke was reduce with the top bed to bottom bed whereas the TPO profiles at high temperature region, the larger coke was found at the bottom bed. These results suggest that the coke in top bed might be come form the reactant in low temperature region and the products in high temperature region due to the pore size limitation. At the middle bed, the coke at low temperature was reduced and the coke at high temperature was enhanced when compared with the top bed. This might be due to in middle bed not only *i*-butene but also the products act as the reactants and cause coke formation in high temperature type. The bottom bed had the same trend with the middle bed.



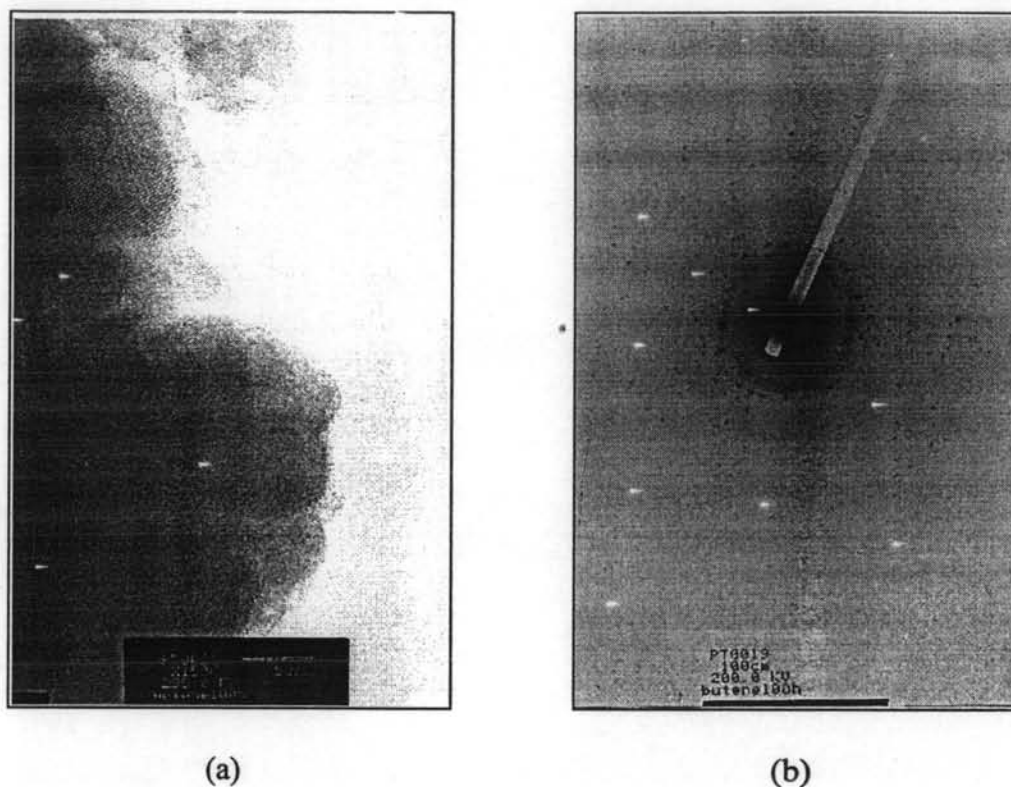
**Figure 4.12** TPO profiles of spent catalyst after exposure to reaction 12 h-TOS at 600°C and space velocity = 21,220 h<sup>-1</sup> with a heating rate of 10°C/min, an oxidizing gas containing 2% oxygen in He with a flow rate of 40 ml/min.

#### 4.1.6 TEM of Spent Catalysts

Although the two oxidation regions in TPO profiles might be due to the presence of two types of carbon deposition, the different location of carbon deposited on the catalyst surface cannot be ruled out (Noronha et al., 2001). In order to prove this hypothesis, TEM analysis was used.

In TEM, a high intensity primary electron beam (typically 100-200 keV) passes through the sample and the transmitted and diffracted electrons are collected. In this work, TEM photograph was taken of spent ZSM-5 catalyst with Si/Al ratio = 175, after exposure to reaction of 1-butene at 600°C and space velocity = 21,220 h<sup>-1</sup> for 100 h-TOS.





**Figure 4.13** TEM image of spent catalyst that tested with 1-butene reactant at the temperature of  $600^{\circ}\text{C}$  with the conditions of space velocity =  $21,220\text{ h}^{-1}$  and 100 h-TOS: (a) bright-field image and (b) diffraction pattern image.

The bright-field TEM image of spent catalyst is shown in Figure 4.13(a). Two phases, gray and dark area, were observed. It was seen to be that the dark area was surrounded by the gray area. Moreover, disorder fringes were observed in the gray area indicating an amorphous phase. On the other hand, a perfect lattice structure was observed in the dark area.

The atomic of elements composition at the gray and dark area identified in Figure 4.13(a) was quantified by EDX analysis. It was found that the detected amount of carbon was observed in the gray area while the amount of Si and carbon were observed in the dark area.

In order to clarify the lattice structure which appeared in the dark area, accurate values of lattice spacing were obtained by analyzing the diffraction pattern of the image (Figure 4.13(b)). The lattice spacing of  $d = 11.09 \text{ \AA}$ ,  $d = 7.68 \text{ \AA}$ ,  $d = 5.55 \text{ \AA}$ ,  $d = 3.84 \text{ \AA}$  and  $d = 3.03 \text{ \AA}$  calculated from the diffraction pattern are not match with Si or graphitic carbon. Therefore, it appears that the different peaks that we observe in TPO are not due to different forms of carbon, but rather to different locations on the catalyst surface.

This is in agreement with TPO result in which at high coke content the oxidation of coke is zero order (not depend on concentration). It means that the coke are only one type but the coke located outside the pores of zeolite has to be burned off, then the burning of coke located inside the pores is allowed.

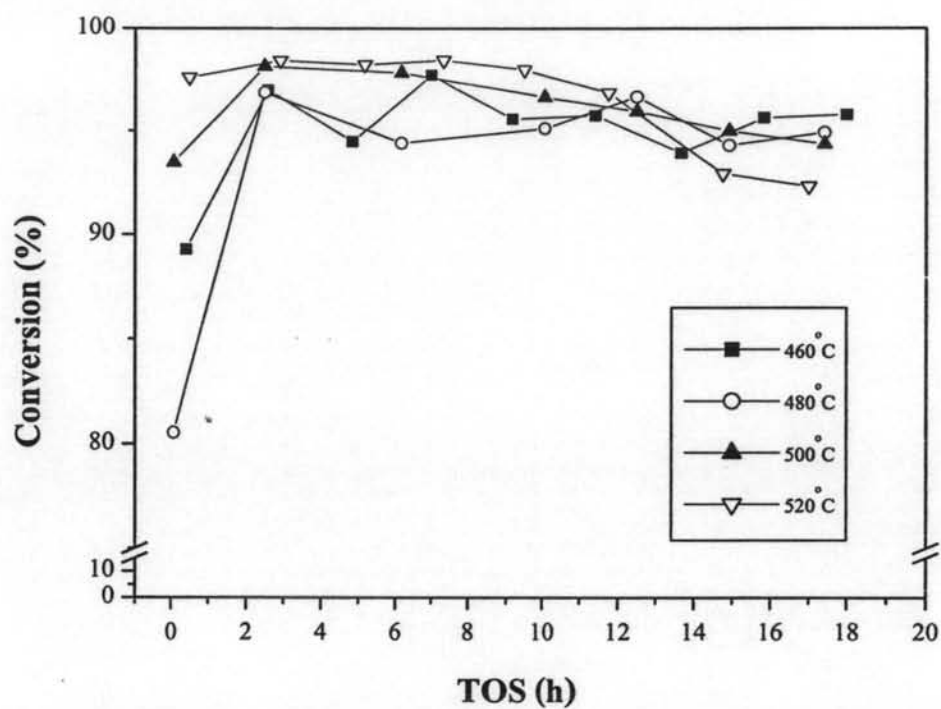
## 4.2 Aromatization of Mixed C<sub>4</sub> Feedstock

### 4.2.1 Effect of Temperature

The aromatization reaction of mixed C<sub>4</sub> feedstock was conducted using ZSM-5 with Si/Al ratio = 18. The effects of reaction temperature on the reactant conversion were studied at the various temperatures: 460, 480, 500 and 520°C as shown in Figure 4.14. The results show that the conversion of mixed C<sub>4</sub> feedstock increased with an increasing temperature. However, the conversion slightly increased when the temperature above 500°C.

As shown in Figure 4.14, the conversion seems to be stable during 18 h period of time on stream. On the other hand, the conversion was drastically dropped after 12 h of time-on stream at the reaction temperature of 520°C. This might be due to the fact that a coke formation is easier to occur at this temperature.

The conversion and product selectivities after 15 h period of time on stream are shown in Table 4.3. We found that the selectivity of interesting product, (*m, p*)-xylene, was not significantly different at the reaction temperature of 480, 500 and 520°C. However, catalyst is stable after prolonged operation of the catalyst at 480°C temperature for 18 h as shown in Figure 4.14. Therefore, we chose this reaction temperature as an appropriate reaction temperature for further investigation.



**Figure 4.14** Effect of reaction temperature on the mixed C<sub>4</sub> feedstock conversion for aromatization reaction over ZSM-5 (Si/Al = 18) catalyst at the conditions of space velocity = 1,490 h<sup>-1</sup>.

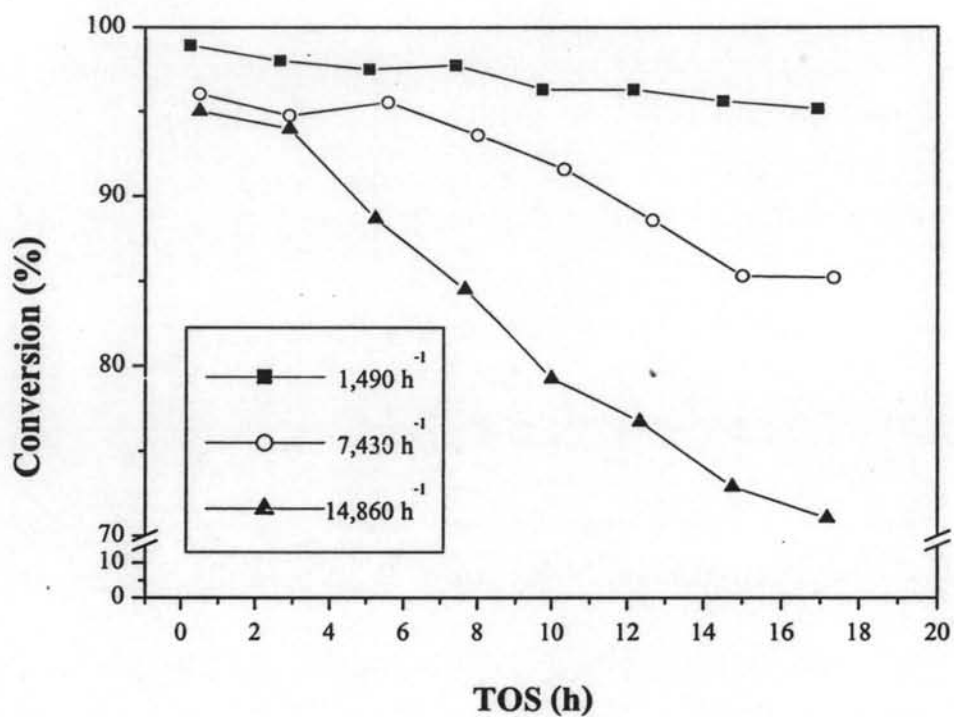
**Table 4.3** Conversion of mixed C<sub>4</sub> feedstock and product selectivities at 15 h-TOS for aromatization reaction over ZSM-5 (Si/Al = 18) catalyst using various reaction temperatures with the conditions of space velocity = 1,490 h<sup>-1</sup>

	Temperature (°C)			
	460	480	500	520
Conversion (%)	95.65	94.31	95.01	92.94
Selectivity (%)				
methane	0.02	0.07	0.18	0.14
ethylene	0.09	0.23	0.32	0.62
ethane	0.04	0.15	0.28	0.20
propylene	0.27	0.51	0.58	1.32
propane	1.14	3.33	3.50	2.26
benzene	1.65	3.06	2.19	2.07
toluene	21.83	16.05	15.85	19.91
EB & (m,p)-xylene	17.32	31.36	29.11	36.29
o-xylene	30.08	8.79	9.67	11.73
>C <sub>8</sub>	25.63	35.16	37.01	24.23
Other (C <sub>5</sub> 's and C <sub>6</sub> 's)	1.93	1.28	1.31	1.24
Total C <sub>8</sub> -aromatic	47.40	40.15	38.78	48.02
Total aromatic	70.88	59.27	56.81	70.00
Total liquid	96.51	94.42	93.82	94.23

#### 4.2.2 Effect of Space Velocity

The influence of space velocity on the conversion and selectivities for aromatization at the reaction temperature of 480°C are presented in Figure 4.15 and Table 4.4. It was found that the conversion and the selectivities of aromatic products were decreased with the rise of the space velocity whereas the selectivities of unsaturated compounds, like ethylene, and propylene were increased. This result indicated that cracking reaction dominates at high space velocity.

It should be noted that the selectivities of C<sub>8</sub><sup>+</sup> products was rather high at the space velocity of 1,490 h<sup>-1</sup>. Since C<sub>8</sub><sup>+</sup> products are not valuable product, we try to reduce them by increasing space velocity. As shown in Table 4.4, the selectivities of C<sub>8</sub><sup>+</sup> products were not affected by an increase of space velocity.

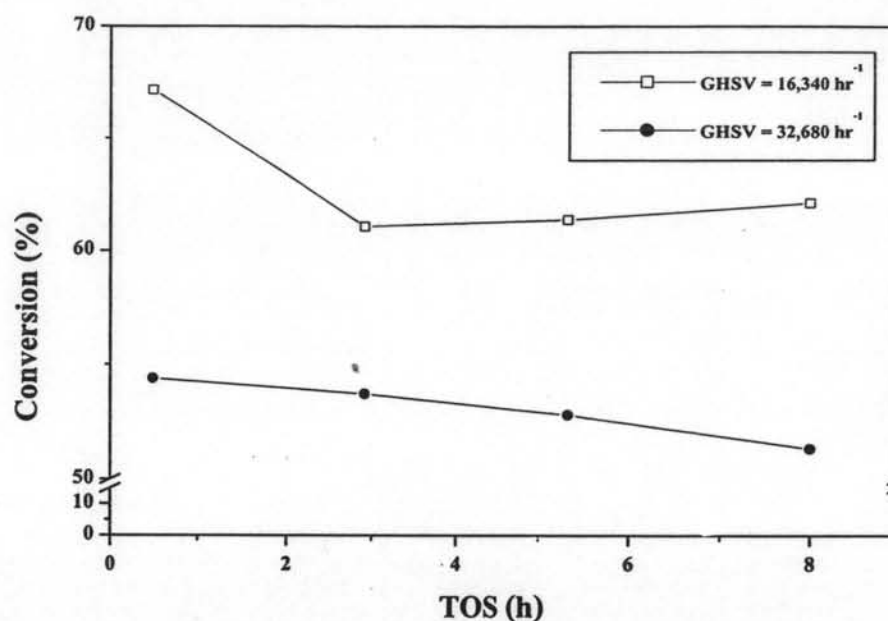


**Figure 4.15** Effect of space velocity on the mixed C<sub>4</sub> feedstock conversion for aromatization reaction over ZSM-5 (Si/Al = 18) catalyst at the reaction temperature of 480°C.

**Table 4.4** Conversion of mixed C<sub>4</sub> feedstock and product selectivities at 15 h-TOS for aromatization reaction over ZSM-5 (Si/Al = 18) catalyst using various space velocity with the reaction temperature of 480°C

	GHSV (h <sup>-1</sup> )		
	1,490	7,430	14,860
<b>Conversion (%)</b>	94.31	86.23	72.90
<b>Selectivity (%)</b>			
methane	0.07	0.01	0.00
ethylene	0.23	0.47	0.87
ethane	0.15	0.03	0.03
propylene	0.51	1.99	5.24
propane	3.33	1.14	1.48
benzene	3.06	0.59	0.32
toluene	16.05	8.91	5.18
EB & (m,p)-xylene	31.36	28.67	17.77
o-xylene	8.79	8.04	5.71
>C <sub>8</sub>	35.16	37.54	39.00
Other (C <sub>5</sub> 's and C <sub>6</sub> 's)	1.28	12.61	24.41
<b>Total C<sub>8</sub>-aromatic</b>	44.90	36.71	23.47
<b>Total aromatic</b>	66.71	46.21	28.97
<b>Total liquid</b>	95.98	83.75	67.97

In order to clarify the effect of space velocity on the selectivities of C<sub>8</sub><sup>+</sup> products from aromatization reaction, the conversion was reduced by using diluent (He), with reactant gas containing 10% feed in He. From Figure 4.16, it can be found that with increment of GHSV of reaction, the decrease in conversion of mixed C<sub>4</sub> feedstock was observed. In case of product selectivities (Table 4.5), the yield of BTX was lowered and yield of olefins was improved. Comparing the results obtained at low and high conversion, one sees that the yield of C<sub>8</sub><sup>+</sup> was abated but it still got the large quantity. Therefore, it was suggested that the high space velocity (short contact time) might not have enough time for the combination of light olefin in products and/or feedstock to form larger molecules (oligomerization reaction), led to could not undergo to secondary reaction (cyclization reaction).



**Figure 4.16** Effect of space velocity on the mixed C<sub>4</sub> feedstock conversion for aromatization reaction over ZSM-5 (Si/Al = 18) catalyst at the temperature of 480°C with a reactant feed gas containing 10% feed in He.

**Table 4.5** Conversion of reactant feed and product selectivities at 8 h-TOS for aromatization reaction over ZSM-5 (Si/Al = 18) catalyst using various space velocity and diluent with the reaction temperature of 480°C (a reactant feed gas containing 10% feed)

	GHSV (h <sup>-1</sup> )			
	10,400 <sup>a</sup>	10,400 <sup>b</sup>	16,340 <sup>b</sup>	32,680 <sup>b</sup>
<b>Conversion (%)</b>	71.29	84.44	62.12	51.33
<b>Selectivity (%)</b>				
methane	0.22	0.08	0.17	0.10
ethylene	4.11	1.77	5.66	5.51
ethane	0.31	0.09	0.13	0.07
propylene	9.33	4.36	15.17	20.40
propane	5.96	2.02	4.33	4.11
benzene	1.34	1.18	1.05	0.70
toluene	10.24	11.25	9.03	7.17
EB & (m,p)-xylene	22.05	25.72	17.30	15.90
o-xylene	7.30	8.03	5.47	4.62
>C <sub>8</sub>	32.92	40.78	19.98	25.59
Other (C <sub>5</sub> 's and C <sub>6</sub> 's)	6.22	4.73	21.72	15.82
<b>Total C<sub>8</sub>-aromatic</b>	29.35	33.74	22.77	20.53
<b>Total aromatic</b>	40.93	46.18	32.85	28.40
<b>Total liquid</b>	73.85	86.96	52.82	55.99

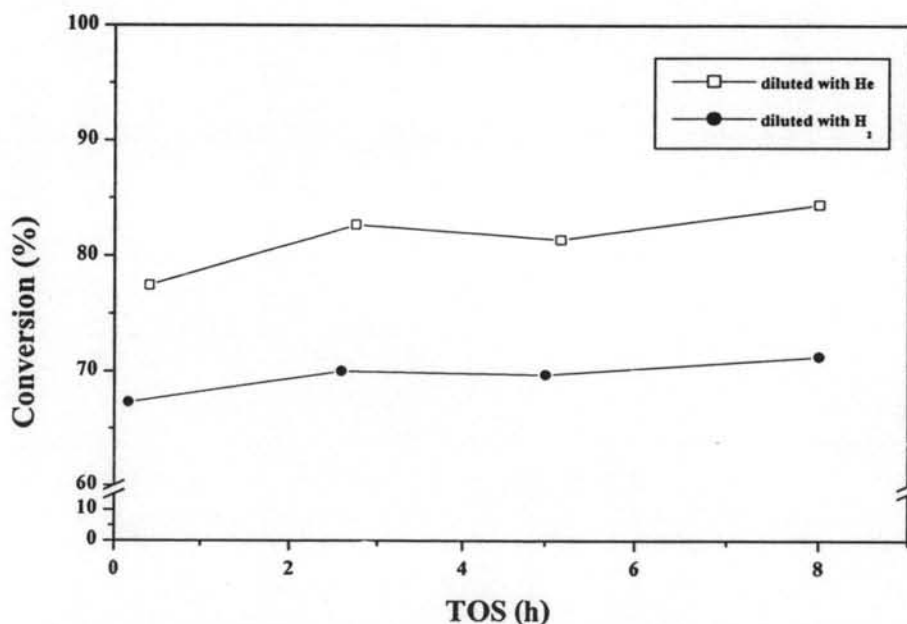
<sup>a</sup> diluted with H<sub>2</sub>

<sup>b</sup> diluted with He



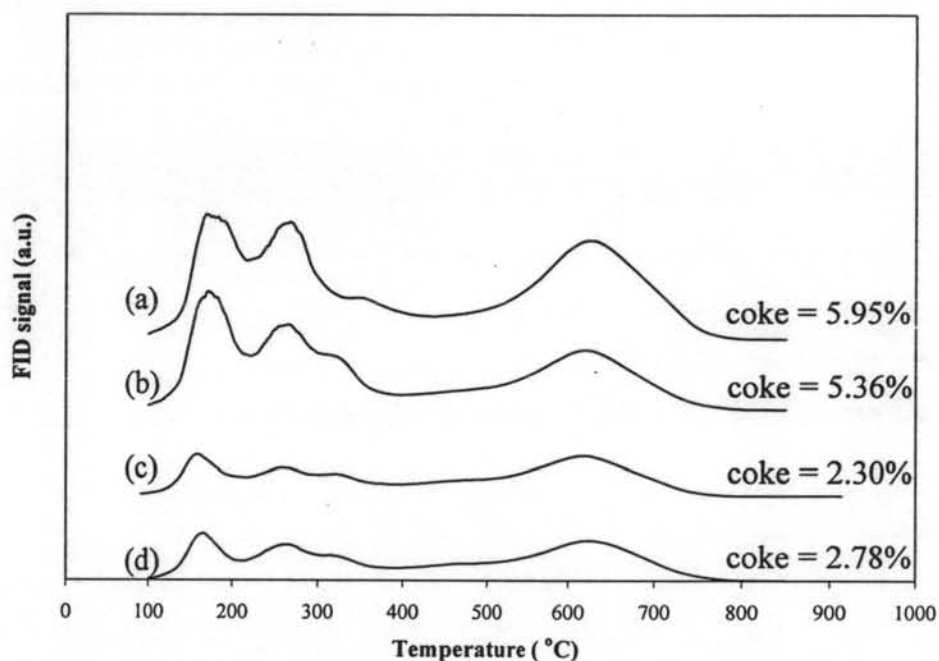
### 4.2.3 Effect of Diluent

The variation in the performance of mixed C<sub>4</sub> aromatization with the diluted reactants was studied. The reaction of He and H<sub>2</sub> diluted feeds are compared under the reaction conditions: T = 480°C, P = 1 atm, GHSV = 10,400 h<sup>-1</sup>, time-on-stream = 7.5 h, and the catalytic performances on the two diluents are shown in Figure 4.17. Since hydrogen had been found to be an effective to decrease the formation of coke and to improve the zeolite stability for typical reaction of acid catalyst such as toluene and cumene disproportionation (Guisnet and Magnoux, 1997). The mixed C<sub>4</sub> conversion with H<sub>2</sub> diluted feed was somewhat lower than that on the He diluted feed. This result might be due to H<sub>2</sub> can hydrogenate the reactants or products and push the backward reaction. The content of aromatics in liquid products was higher with He diluted feed than that with H<sub>2</sub> diluted feed (Table 4.5). For H<sub>2</sub> diluted feed, less aromatics and the large light olefins such as ethylene and propylene were observed, it should be note that cyclization reaction is hardly to take place under atmospheric of H<sub>2</sub>. Whereas the He diluted feed was reported in opposite of H<sub>2</sub> diluted feed.



**Figure 4.17** Effect of diluent on the mixed C<sub>4</sub> feedstock conversion for aromatization reaction over ZSM-5 (Si/Al = 18) catalyst at the temperature of 480°C with a reactant feed gas containing 10% feed and the same space velocity = 10,400 h<sup>-1</sup>.

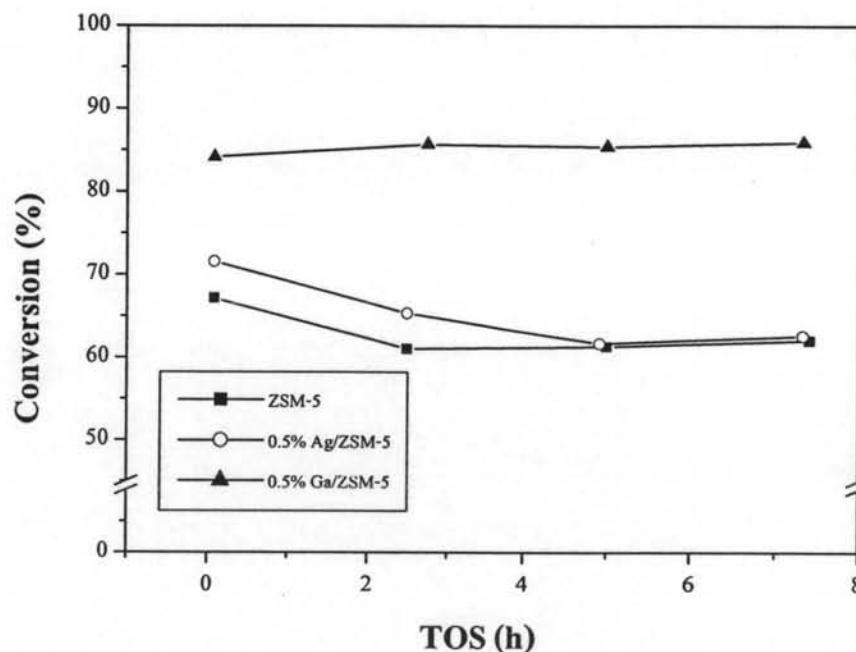
Furthermore, the TPO results (Figures. 4.18 (a)-(d)) show the large amount of coke in low space velocity. At the same time the TPO profiles are similar with the different space velocity or different diluent. Interestingly, it is not significant quantity of carbon deposited on ZSM-5 was observed in both He and H<sub>2</sub> diluted feed. Therefore, H<sub>2</sub> diluted feed is not effect on coke formation of this reaction.



**Figure 4.18** TPO profiles of spent catalyst after exposure to reaction at 480°C for 8 h-time on stream and space velocity = 21,220 h<sup>-1</sup> with a heating rate of 10°C/min, an oxidizing gas containing 2% oxygen in He with a flow rate of 40 ml/min. The varied diluent and GHSV are follow by: (a) H<sub>2</sub>:GHSV = 10,400 h<sup>-1</sup>, (b) He:GHSV = 10,400 h<sup>-1</sup>, (c) He:GHSV = 16,340 h<sup>-1</sup> and (d) He:GHSV = 32,680 h<sup>-1</sup>.

#### 4.2.4 Effect of Metal Loading

To investigate the effect of metal on ZSM-5 support, ZSM-5 zeolites (Si/Al ratio = 18) without and with (Ag and Ga) metal were prepared. The basic characteristic of a sample of the catalysts was obtained. The Ag/ZSM-5 was characterized by XRF. The result reported that Ag contain in support is 0.433% due to it was prepared by ion-exchange. On the other hand, Ga-supported catalyst was prepared by incipient wetness impregnation so it is not necessary to test for content. ZSM-5 with Ag-supported exhibited higher conversion of mixed C<sub>4</sub> than ZSM-5 without metal in 4 h-TOS (see Figure 4.19). After 4 h-time on stream, both conversion of ZSM-5 and Ag/ZSM-5 are equal. For product selectivity, the results show a non-significant increase in cracking products (ethylene and propylene) and aromatic products (Table 4.6). However, the higher amount of C<sub>8</sub><sup>+</sup> and the lower C<sub>5</sub>'s and C<sub>6</sub>'s were observed in Ag/ZSM-5 catalyst. This results suggested that Ag-supported catalyst much active for aromatization reaction than ZSM-5 zeolite but Ag/ZSM-5 preferred to produce too large molecules.

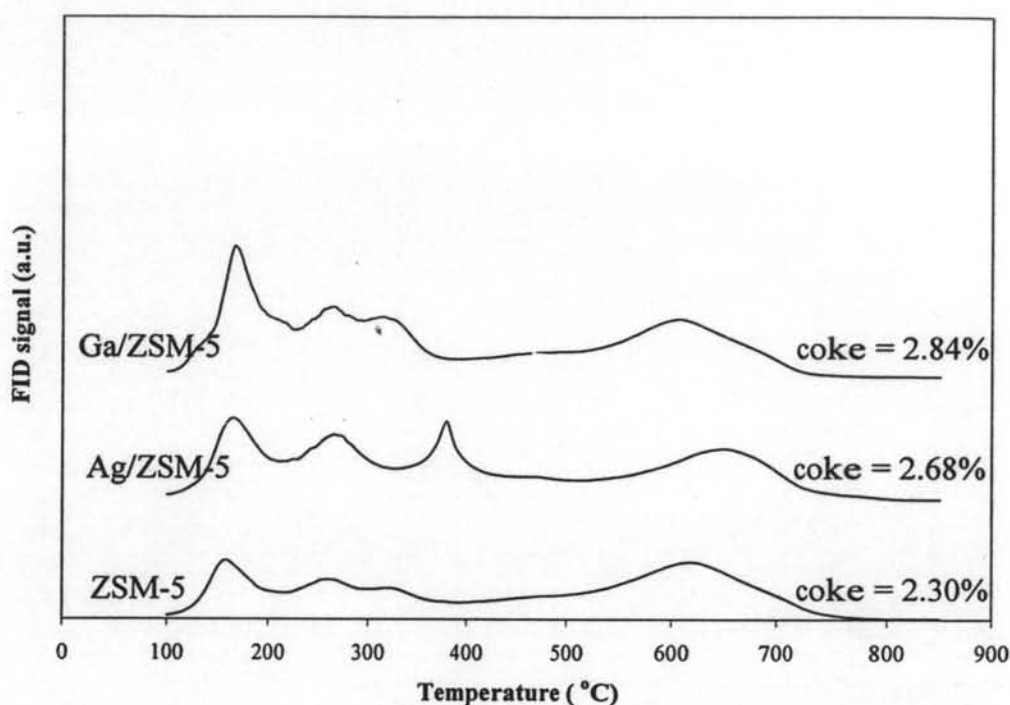


**Figure 4.19** Effect of metal loading on the mixed C<sub>4</sub> feedstock conversion for aromatization reaction over ZSM-5 (Si/Al = 18) catalyst at the temperature of 480°C with a reactant feed gas containing 10% feed and the same space velocity = 16,340 h<sup>-1</sup>.

Much better catalytic performance was experienced, when Ga was deposited on ZSM-5 support. Results are displayed in Figure 4.19. A different order of selectivities was obtained for Ga-supported catalyst. In this case highest selectivities were determined for ethylbenzene and (*m,p*)-xylene followed by toluene, *o*-xylene and benzene. The cracking products such as ethylene and propylene were reduced. It might be due to cracking products become to cyclize and dehydrogenate to be aromatic products or larger molecules. This results indicated that Ga-supported ZSM-5 is suitable for aromatization reaction, while Ag-supported ZSM-5 and ZSM-5 preferred side reaction of cracking.

**Table 4.6** Conversion of reactant feed and product selectivities at 7.5 h-TOS for aromatization reaction over ZSM-5 (Si/Al = 18) catalyst using various metal loading with the reaction temperature of 480°C (a reactant feed gas containing 10% feed in He)

	Metal		
	non	0.5% Ag	0.5% Ga
Conversion (%)	62.12	62.66	85.96
Selectivity (%)			
methane	0.17	0.36	0.38
ethylene	5.66	7.65	1.79
ethane	0.13	0.17	0.11
propylene	15.17	16.74	3.91
propane	4.33	6.03	1.49
benzene	1.05	1.69	2.77
toluene	9.03	10.78	18.34
EB & ( <i>m,p</i> )-xylene	17.30	16.79	24.23
<i>o</i> -xylene	5.47	5.23	7.74
>C <sub>8</sub>	19.98	24.35	37.04
Other (C <sub>5</sub> 's and C <sub>6</sub> 's)	21.72	10.22	2.21
<b>Total C<sub>8</sub>-aromatic</b>	22.77	22.02	31.96
<b>Total aromatic</b>	32.85	34.49	53.07
<b>Total liquid</b>	52.82	58.84	90.12



**Figure 4.20** TPO profiles of spent catalyst after exposure to reaction at 480°C for 7.5 h-time on stream and space velocity = 21,220 h<sup>-1</sup> with a heating rate of 10°C/min, an oxidizing gas containing 2% oxygen in He with a flow rate of 40 ml/min.

Figure 4.20 shows the TPO results of three different spent catalysts which are ZSM-5, Ag-supported ZSM-5 and Ga-supported ZSM-5. The quantity of coke is increasing in order of ZSM-5, Ag/ZSM-5 and Ga/ZSM-5, respectively. However the profiles are quite different, the TPO profiles show peaks with the maximum temperatures at two temperature regions (100-400 and 500-750°C). For ZSM-5 and Ga/ZSM-5, the profiles of these two catalysts are analogous but the amount of coke in low temperature region of Ga/ZSM-5 is higher. For Ag/ZSM-5 profile show three peak at low temperature and the maximum peak at high temperature region is shift to 650°C. This results suggested that metal could reduce the oxidizing temperature to easier coke removal.