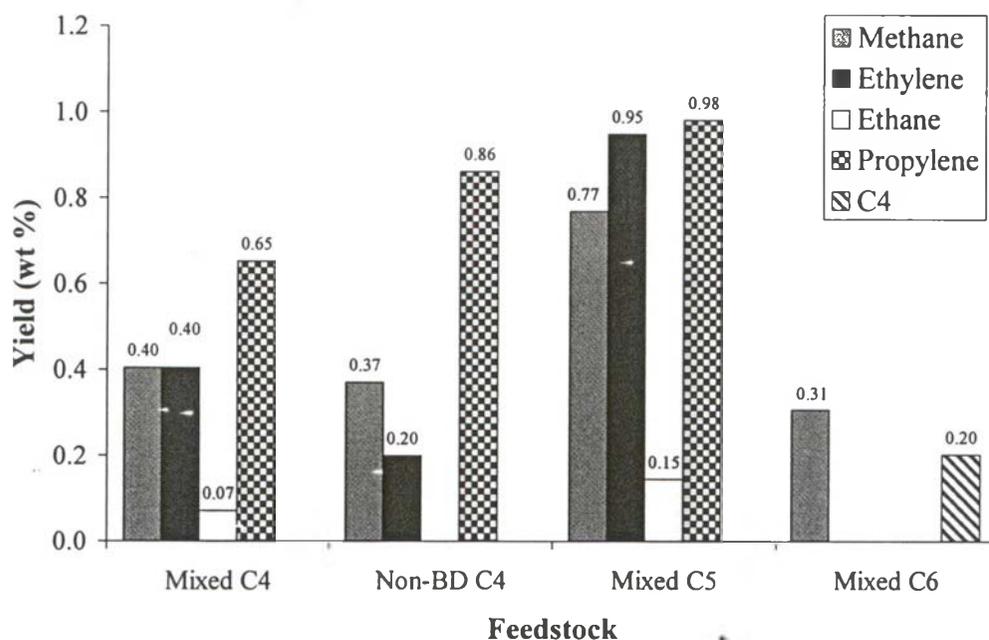


## CHAPTER IV

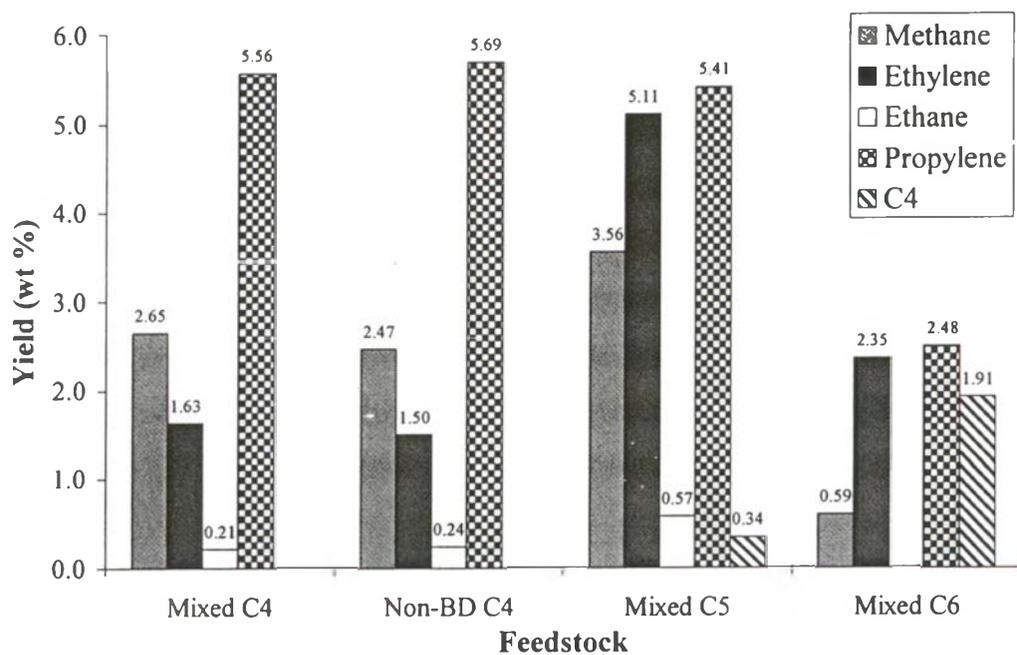
### RESULTS AND DISCUSSION

#### 4.1 Thermal Cracking of Selected Feed

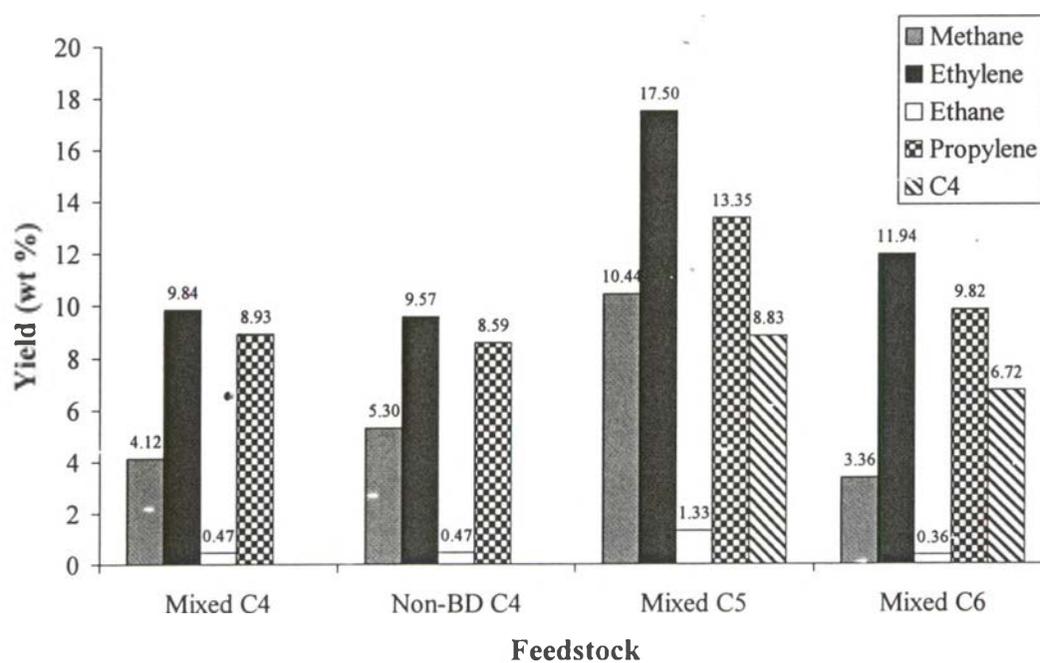
Thermal cracking (blank test) of the mixed C<sub>4</sub>, non-BD C<sub>4</sub>, mixed C<sub>5</sub> and mixed C<sub>6</sub> were performed to test the amount of products yield for each feed. The thermal cracking was observed after the temperature has reached 650°C and plays more important role at higher temperature. The product distributions from thermal cracking of the selected feeds at temperature 650°C, 700°C and 750°C are presented in Figure 4.1 to 4.3, respectively.



**Figure 4.1** Products distribution from thermal cracking of different feeds at 650°C after 5 minutes time on stream.



**Figure 4.2** Products distribution from thermal cracking of different feeds at 700°C after 5 minutes time on stream.



**Figure 4.3** Products distribution from thermal cracking of different feeds at 750°C after 5 minutes time on stream.

From Figure 4.1 to 4.3, it can be observed that, at higher temperature, the total conversion is higher for all feeds. Furthermore, the propylene selectivity is higher than the ethylene selectivity for the cracking temperatures of 650 and 700°C. However, the selectivity toward propylene is lower than ethylene for the thermal cracking at 750°C. This observation is typical in thermal cracking process, which gives higher yield of ethylene than propylene. Thermal cracking of mixed C<sub>5</sub> showed the highest conversion because paraffin is thermally cracked easier than olefin, and mixed C<sub>5</sub> contain more paraffin than other feeds. Therefore, the highest conversion is observed on thermal cracking of mixed C<sub>5</sub>.

#### **4.2 Catalytic Cracking of Mixed C<sub>4</sub>**

The catalytic cracking are tested with ZSM-5 ratio = 20, 40, 190 and 398. The products that are observed and are reported only ethylene and propylene. The mixed C<sub>4</sub> is mainly composed of C<sub>4</sub> olefins. Butadiene in feed is the key factor to study the stability of the catalyst, which will discuss in further section.

Table 4.1 is showing the components in the effluent streams after cracking at various temperatures. Propylene and ethylene are observed as main products, which are the desired products for this experiment, meanwhile methane, ethane, propane, and remain feed are by product.

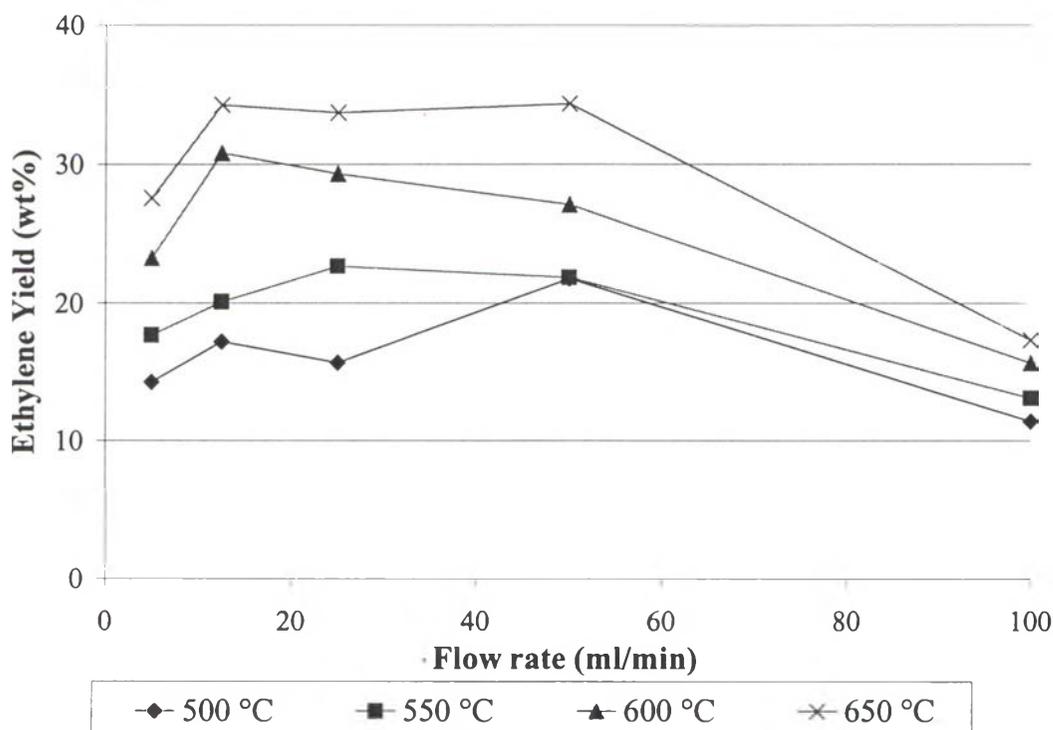
**Table 4.1** Product compositions from catalytic cracking of mixed C<sub>4</sub> by ZSM-5 zeolite, Si/Al = 40, feed flow rate 50 ml/min and 5 minutes time on stream

Species	Composition (Wt %)			
	500°C	550°C	600°C	650°C
methane	0.90	0.90	2.01	4.45
ethylene	21.77	21.83	27.09	34.31
ethane	1.11	1.14	2.20	3.00
propylene	33.08	32.71	33.25	31.73
propane	6.03	7.52	6.70	3.63
<i>trans</i> -2-butene	-	-	-	-
<i>i</i> -butene	7.83	6.08	3.90	2.87
1,3-butadiene	10.33	11.51	9.85	9.34
1-butene	16.09	15.09	12.13	8.12
<i>n</i> -butane	2.86	3.23	2.87	2.54
total	100.00	100.00	100.00	100.00

#### 4.2.1 Effect of Retention Time

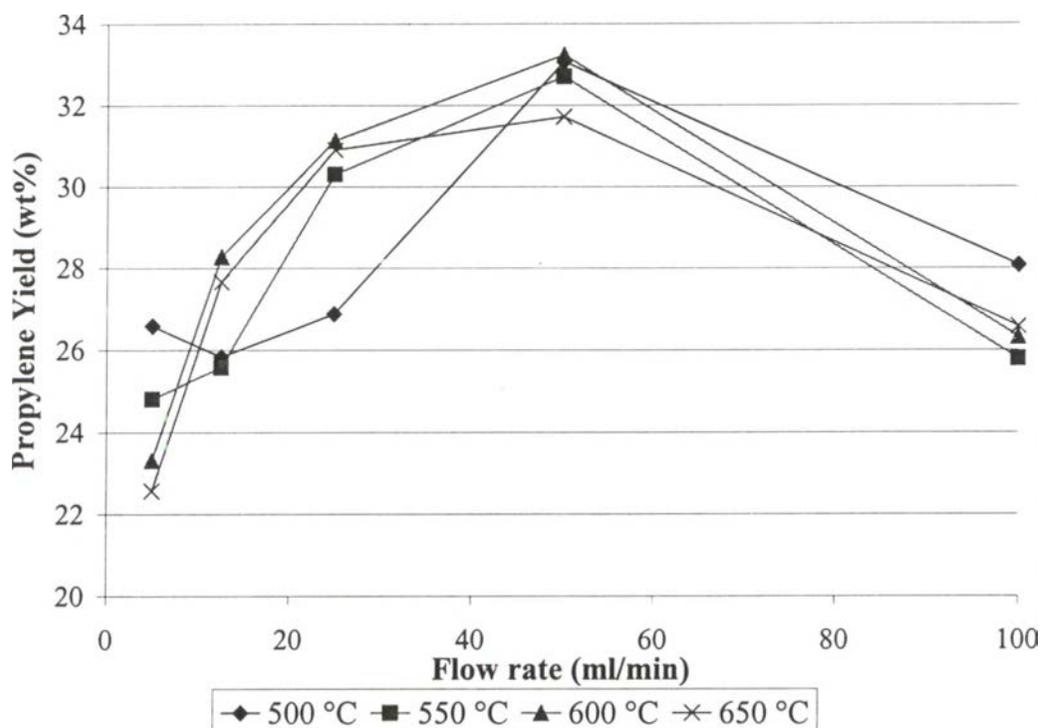
The effect of retention time is studied by changing the flow rate of feedstock. When the flow rate is varied the yield of products at each temperature will be changed, but only ethylene and propylene are concerned in this experiment.

From Figure 4.4 and 4.5, the yield of ethylene and propylene at the flow rate of 100 ml/min is the lowest when compared with the other lower flow rates. This is probably due to the high feed flow rate resulting in small retention time (about 0.17 seconds). During this time the feeds may not have enough time in the reactor to be cracked before it is flushed out.



**Figure 4.4** Ethylene yields from mixed C<sub>4</sub> cracking at different temperatures with ZSM-5 zeolite, Si/Al = 40 at flow rate about 5, 12.5, 25, 50 and 100 ml/min after 5 minutes time on stream.

Moreover, for the lowest feed flow rate (at 5 ml/min), the yield of ethylene is relative low and the yield of propylene is the lowest. This is possibly due to the combination of light olefins in products and/or feedstock to form larger hydrocarbon molecules (oligomerization reaction) when longer retention time are used. From figure 4.5, the propylene yield is maximum value at the feed flow rate 50 ml/min for all temperatures. Therefore the flow rate of 50 ml/min is chosen for further studies.

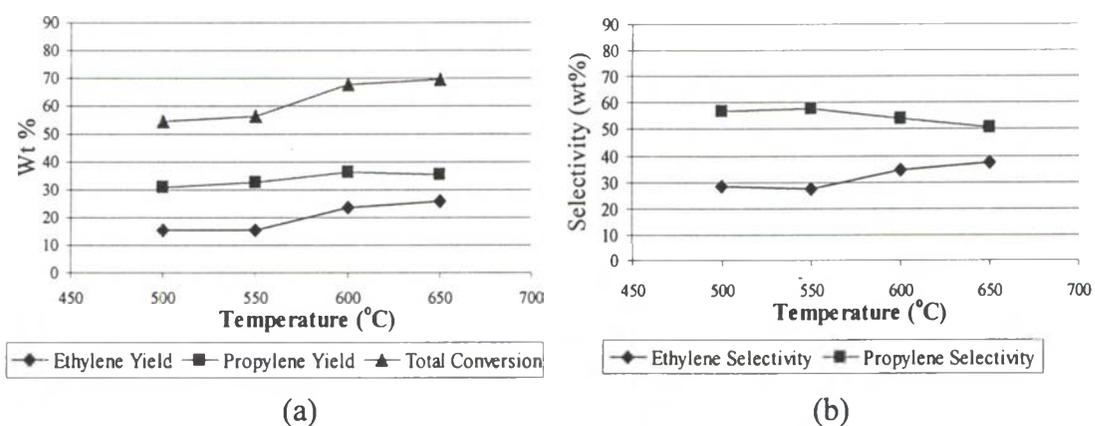


**Figure 4.5** Propylene yields from mixed C<sub>4</sub> cracking at different temperatures with ZSM-5 zeolite, Si/Al = 40 at flow rate about 5, 12.5, 25, 50 and 100 ml/min after 5 minutes time on stream.

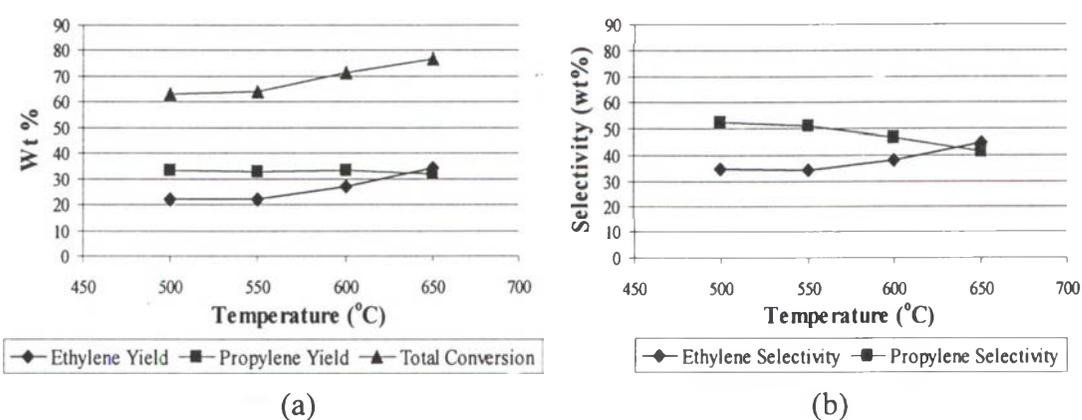
#### 4.2.2 Effect of Reaction Temperature

Temperature plays an important role in both thermodynamics and kinetics of a reaction. Cracking of a longer hydrocarbon molecule to several shorter molecules is an endothermic reaction. Therefore, increasing cracking temperature will result in higher conversion and faster cracking rate. Figure 4.6 to 4.8 shows the conversion, yields, and selectivity of mixed C<sub>4</sub> cracking at 500, 550, 600, and 650°C over ZSM-5 zeolites having Si/Al ratio of 20, 40 and 190. When the reaction temperature is increased, the total conversion and ethylene yield are significantly increased, while the yield of propylene is relatively constant. It is interesting to note that the yield of propylene is, in fact, dropped with the increasing temperature when the Si/Al of 190 is used. Therefore, when the reaction temperature is higher, the selectivity towards propylene is reduced while the ethylene selectivity is increased. For the example, as shown in Figure 4.6, when reaction temperature is raised from

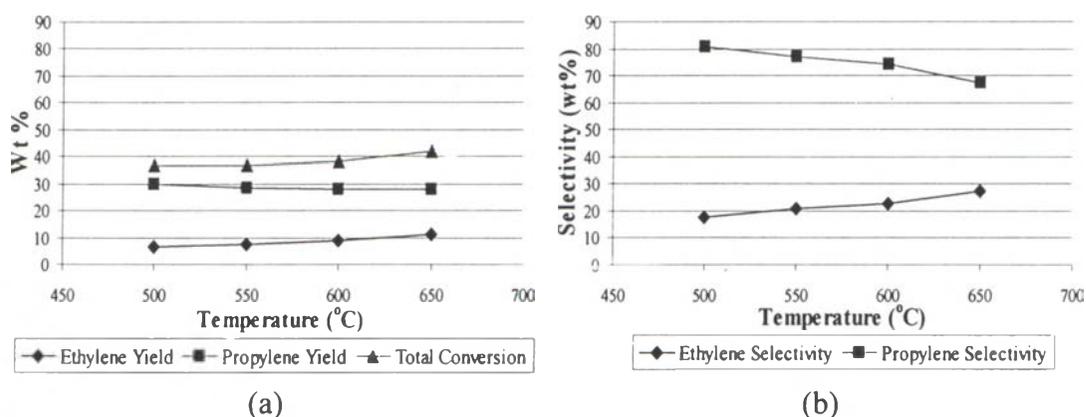
550°C to 650°C, propylene selectivity falls from 58.0 to 50.7 wt% while ethylene selectivity increases from 27.4 to 37.3 wt%. The reduction of propylene selectivity comes from the higher yield of ethylene probably resulting from the thermal crack effect. The maximum propylene yield is 36.4 wt% at 600°C. At 650°C yield of propylene is a little less than at 600°C. From these results, it can be summarized that propylene productions from mixed C<sub>4</sub> prefer to lower temperature.



**Figure 4.6** Mixed C<sub>4</sub> cracking over ZSM-5, Si/Al = 20 with total flow rate 50 ml/min at 500, 550, 600, and 650°C after 5 minutes time on stream: (a) production yields and conversion, and (b) product selectivity.



**Figure 4.7** Mixed C<sub>4</sub> cracking over ZSM-5, Si/Al = 40 with total flow rate 50 ml/min at 500, 550, 600, and 650°C after 5 minutes time on stream: (a) production yields and conversion, and (b) product selectivity.



**Figure 4.8** Mixed C<sub>4</sub> cracking over ZSM-5, Si/Al = 190 with total flow rate 50 ml/min at 500, 550, 600, and 650°C after 5 minutes time on stream: (a) production yields and conversion, and (b) product selectivity.

When the ZSM-5 with Si/Al = 40 are used (Figure 4.7), the similar trends are observed, however, the ethylene yield is higher while the propylene yield is lower. Especially at 650°C, the yield of ethylene is 34.3 wt%, which is the maximum ethylene yield from mixed C<sub>4</sub> cracking.

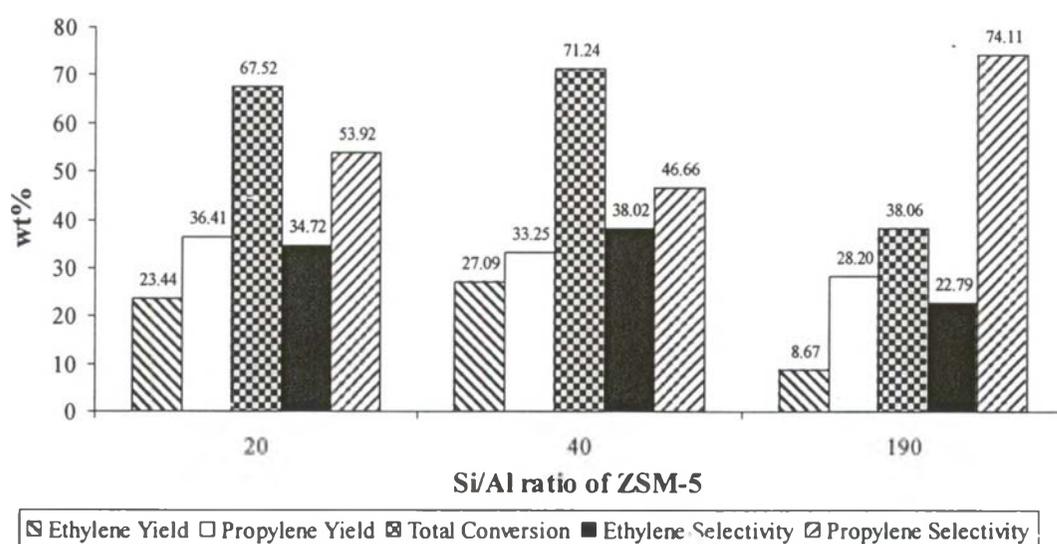
However, in Figure 4.8 which is the results from using ZSM-5 with Si/Al = 190, the maximum yield of propylene is 29.9% at 500°C and slightly decreases to 28.1wt% when temperature is increased to 650°C. The effect of Si/Al ratio will be reported and discussed in the following section.

#### 4.2.3 Effect of Silicon to Aluminum Ratio over Mixed C<sub>4</sub> Cracking

The Si to Al ratio (Si/Al) of zeolite is directly related to the strength and amount of acid site as well as the stability of zeolite. The Si/Al ratio strongly affects the cracking reaction. The ZSM-5 with Si/Al ratio of 20, 40, 190 and 398 were tested with the mixed C<sub>4</sub> for cracking reaction at 600°C. When ZSM-5 with Si/Al of 398 was used, there are ethylene yield 0.41 wt% and propylene yield 0.57 wt% at 650°C, which are very close to the yields obtained from blank test result at 650°C. This suggests that the cracking is probably due to the thermal effect. Therefore, it was reasonable to conclude that ZSM-5 with Si/Al = 398 has less acidity for crack the mixed C<sub>4</sub>.

From Figure 4.9, even though Si/Al ratio 40 has the higher conversion than Si/Al ratio 20, but it has lower propylene yield. The cracking results from ZSM-5 with Si/Al = 20 and 40 show quite comparable results then it hard to summarize the relation between acidity and Si/Al by comparing these two ratios.

For the Si/Al of 190, the ethylene yield is lower than 10% while there is a little drop in propylene when compare with the Si/Al of 20 and 40. The propylene yiled is 28.2% and the propylene selectivity is relatively high (74.1%). The acidity of zeolite typically decreases with increasing of Si/Al (Buchanan, 1998). Therefore, from these results, it suggests that ethylene production from mixed C<sub>4</sub> require more acidity of the zeolite than the propylene production.

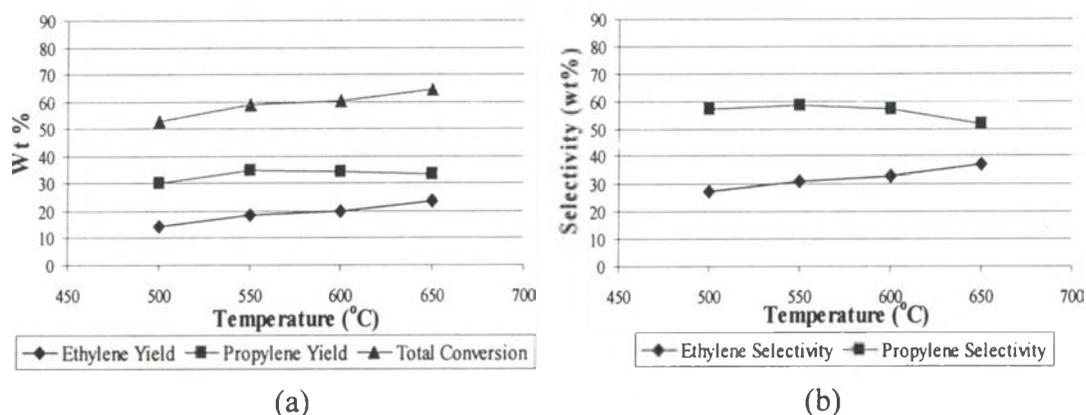


**Figure 4.9** Products yields, conversion and selectivity from mixed C<sub>4</sub> cracking at 600°C with total flow rate 50 ml/min over ZSM-5 ratio 20, 40 and 190 after 5 minutes time on stream.

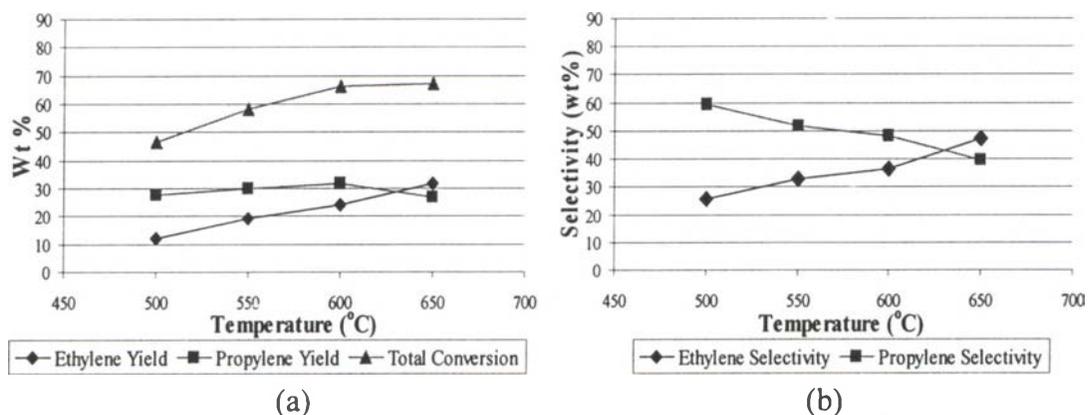
### 4.3 Catalytic Cracking of Non-Butadiene C<sub>4</sub>

All cracking reactions of Non-butadiene C<sub>4</sub> are performed at the same temperature as in mixed C<sub>4</sub> cracking and used flow rate at 50 ml/min. The results

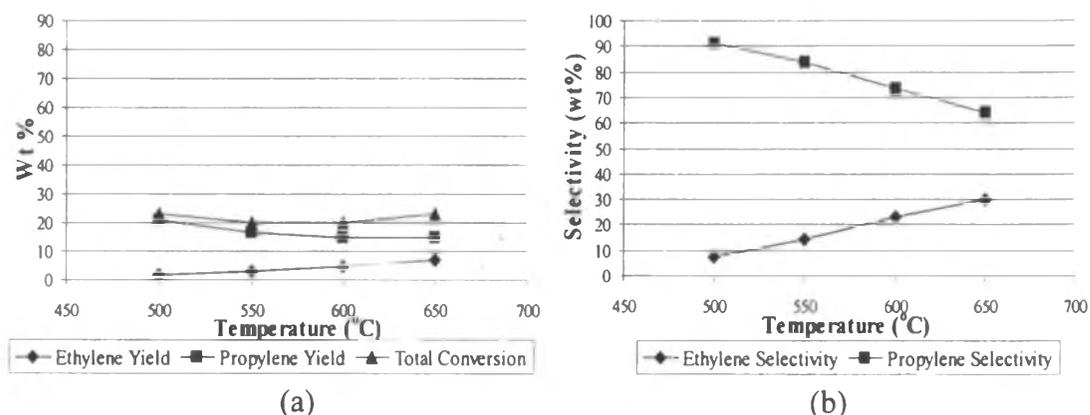
have the similar trend as observed in mixed C<sub>4</sub> cracking, as shown in Figure 4.10-4.12.



**Figure 4.10** Non-BD C<sub>4</sub> cracking over ZSM-5, Si/Al = 20 with total flow rate 50 ml/min at 500, 550, 600, and 650°C after 5 minutes time on stream: (a) production yields and conversion, and (b) product selectivity.



**Figure 4.11** Non-BD C<sub>4</sub> cracking over ZSM-5, Si/Al = 40 with total flow rate 50 ml/min at 500, 550, 600, and 650°C after 5 minutes time on stream: (a) production yields and conversion, and (b) product selectivity.



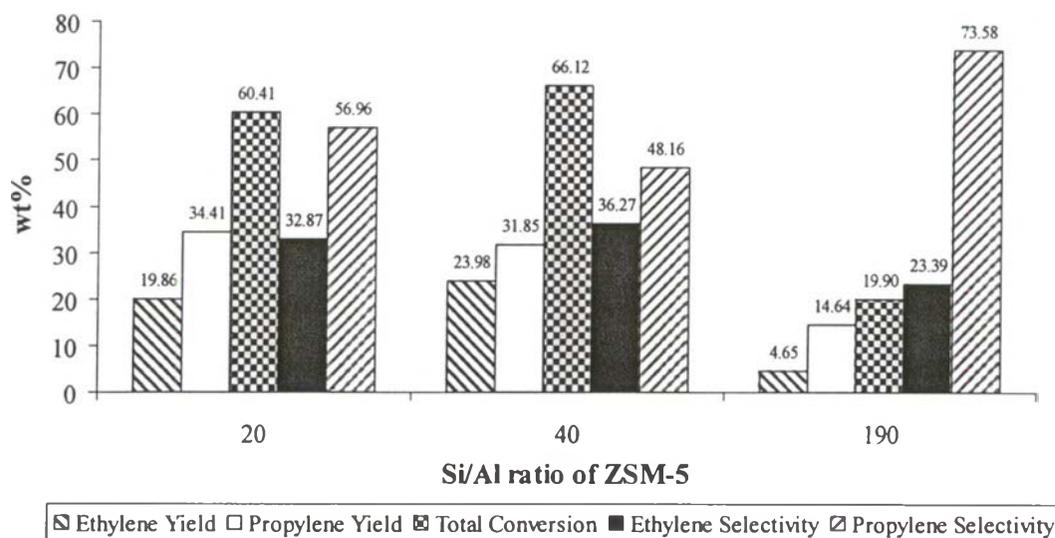
**Figure 4.12** Non-BD C<sub>4</sub> cracking over ZSM-5, Si/Al = 190 with total flow rate 50 ml/min at 500, 550, 600, and 650°C after 5 minutes time on stream: (a) production yields and conversion, and (b) product selectivity.

From Figure 4.10 and 4.11 the cracking results of non-BD C<sub>4</sub> over ZSM-5 ratio 20 and 40 show the same trend as observed in mixed C<sub>4</sub> cracking but non-BD C<sub>4</sub> cracking gave the higher product selectivity and the lower conversion and production yield compare with the previous one. ZSM-5 ratio 190 shows dramatically decreased in yield of propylene from 21.0 to 14.9 wt% as shown in Figure 4.12. Comparing the propylene yields from these two feed stocks over ZSM-5 ratio 20 and 40 (the result from ZSM-5 ratio 190 will discuss in the effect of Si/Al section), cracking of non-BD C<sub>4</sub> gave the higher propylene yields and lower in ethylene yields than mixed C<sub>4</sub> (the higher in propylene yields mean higher in propylene selectivity). These results may come from effect of the different species in feedstocks, non-BD C<sub>4</sub> contained *i*-butene as a main species which higher than in mixed C<sub>4</sub>. The cracking mechanism of *i*-butene has more selective for propylene production than ethylene, then the increasing of *i*-butene cause increasing of propylene yields (Narbeshuber *et al.*, 1997).

#### 4.3.1 Effect of Silicon to Aluminium Ratio over Non-BD C<sub>4</sub> Cracking

The cracking of non-BD C<sub>4</sub> were tested over four ratios (20, 40, 190 and 398) of zeolite at the same temperature and flow rate which performed in cracking of mixed C<sub>4</sub>. When ZSM-5 ratio 398 was tested, the products did not

appear if the reaction temperature below 650°C. Moreover, negligible amount of products (0.26 wt% for ethylene and 0.75 wt% for propylene) were observed at 650°C. These results are close to blank test results at 650°C, then these products may come from thermal cracking effect.



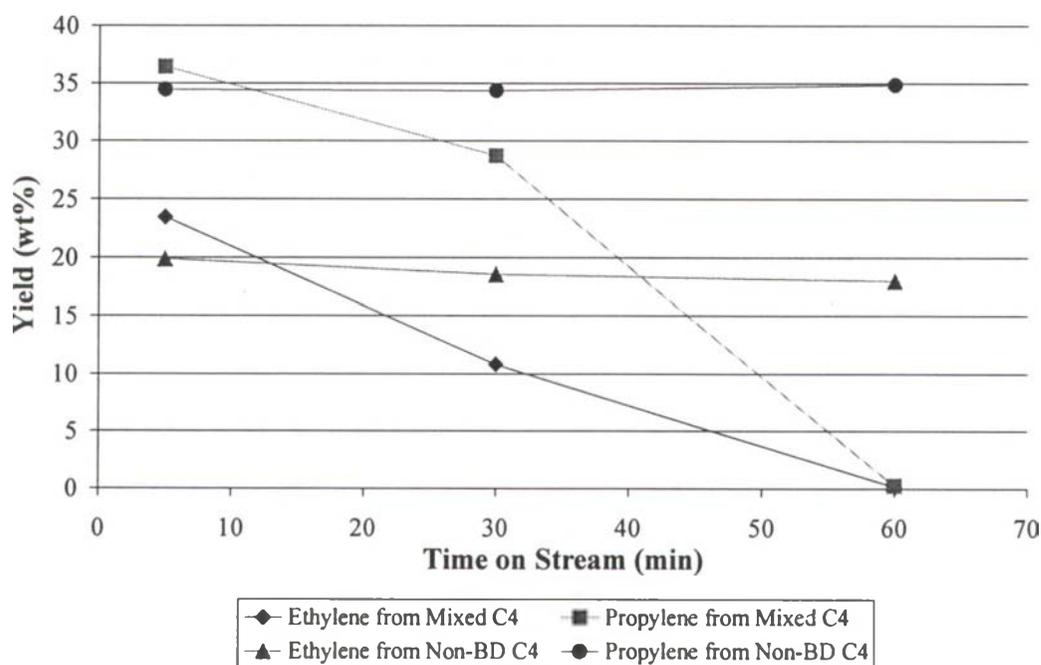
**Figure 4.13** Products yields, conversion and selectivity from non-BD C<sub>4</sub> cracking at 600°C with total flow rate 50 ml/min over ZSM-5 ratio 20, 40 and 190 after 5 minutes time on stream.

From Figure 4.13, the Si/Al ratio 40 has the higher conversion than Si/Al ratio 20, but it has lower propylene yield. The similar trend are found in cracking of mixed C<sub>4</sub>. For the Si/Al ratio 190, yield of ethylene and propylene obtained from this catalyst are very low compared with the other catalysts. When compared the product yields from non-BD C<sub>4</sub> and mixed C<sub>4</sub> feedstock over ZSM-5 ratio 190, cracking of non-BD C<sub>4</sub> shows less in conversion, ethylene and propylene yield but comparable in selectivity of both ethylene and propylene. These results show the same relationship between Si/Al ratio of zeolite and the acidity that explain in mixed C<sub>4</sub> cracking. Moreover, from the different between products yield over ZSM-5 ratio 190 which are obtained from these two feeds, it can be summarize that

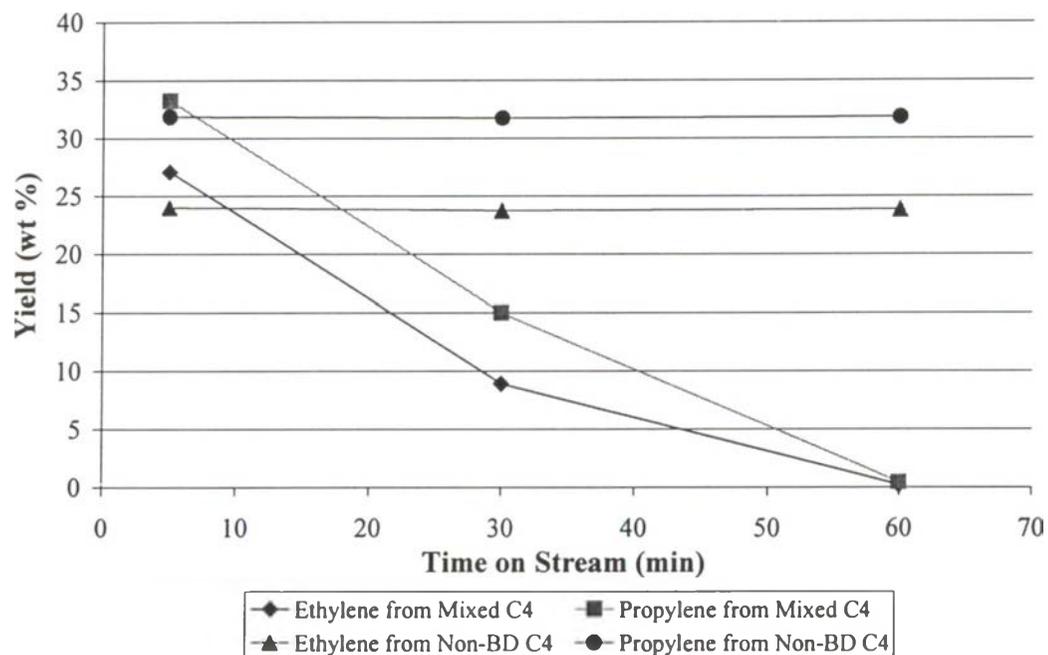
ethylene and propylene productions from non-BD C<sub>4</sub> required more acidity of the zeolite than the mixed C<sub>4</sub>, this phenomena play more important role at higher ratio.

#### 4.3.2 Effect of Butadiene

Butadiene in feed stocks shows negligible effect to the products yield, but has strong effect to the catalysts lifetime, particularly with Si/Al = 20 and 40 which result on the shorter lifetime. As explain in chapter III the sample gases after reaction were detected after 5, 30 and 60 minutes, which presented in Figure 4.14 to 4.16, that compare the products yield of mixed C<sub>4</sub> and non-BD C<sub>4</sub>.



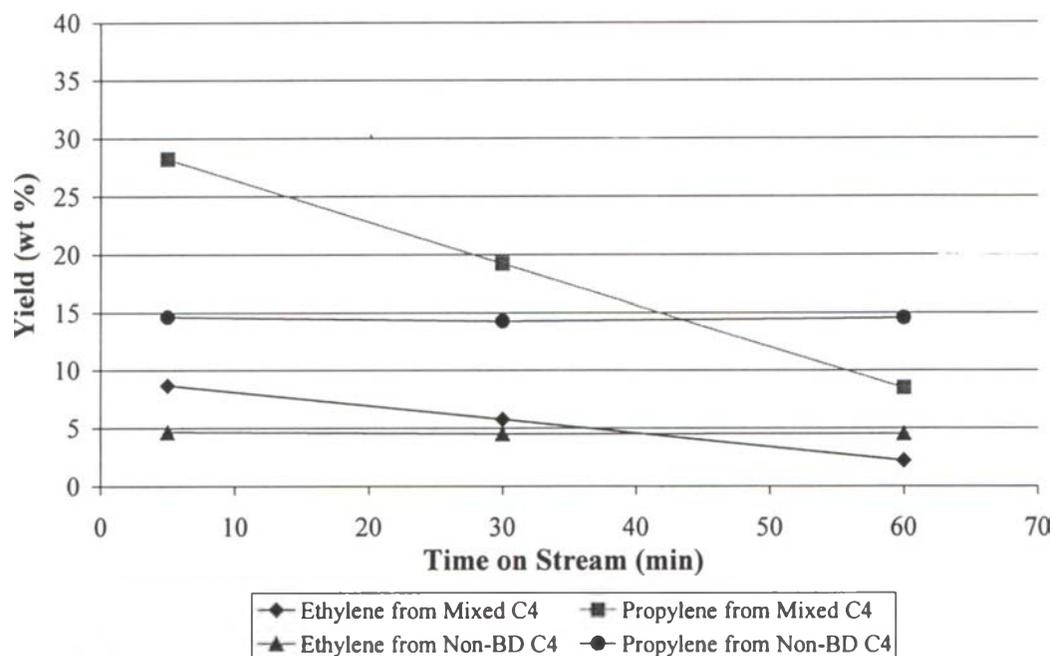
**Figure 4.14** Ethylene and propylene production from mixed C<sub>4</sub> and non-BD C<sub>4</sub> cracking at 600°C with total flow rate 50 ml/min over ZSM-5, Si/Al = 20 after 5, 30 and 60 minutes time on stream.



**Figure 4.15** Ethylene and propylene production from mixed C<sub>4</sub> and non-BD C<sub>4</sub> cracking at 600°C with total flow rate 50 ml/min over ZSM-5, Si/Al = 40 after 5, 30 and 60 minutes time on stream.

After five minutes time on stream, the mixed C<sub>4</sub> gave the higher product yields than non-BD C<sub>4</sub> for all tested catalysts. After 30 and 60 minutes time on stream, the product yields are dramatically dropped to almost zero for ZSM-5 ratio 20 and 40, and below 10 wt% for ZSM-5 ratio 190. The decreasing of products yield in mixed C<sub>4</sub> cracking came from catalysts deactivation, due to butadiene contained in feed. Butadiene is very active specie which rapidly initiates carbonaceous deposits (coke) during it passes through the pore of zeolite. Coke is generally formed by the carbon containing little or no hydrogen such as butadiene then the more butadiene in feed causes more coke (Satterfield, 1993).

From non-BD C<sub>4</sub> cracking result, after 60 minutes time on stream, products yield are not dropped much, then non-BD C<sub>4</sub> is selected as a feed stock for catalyst stability test.



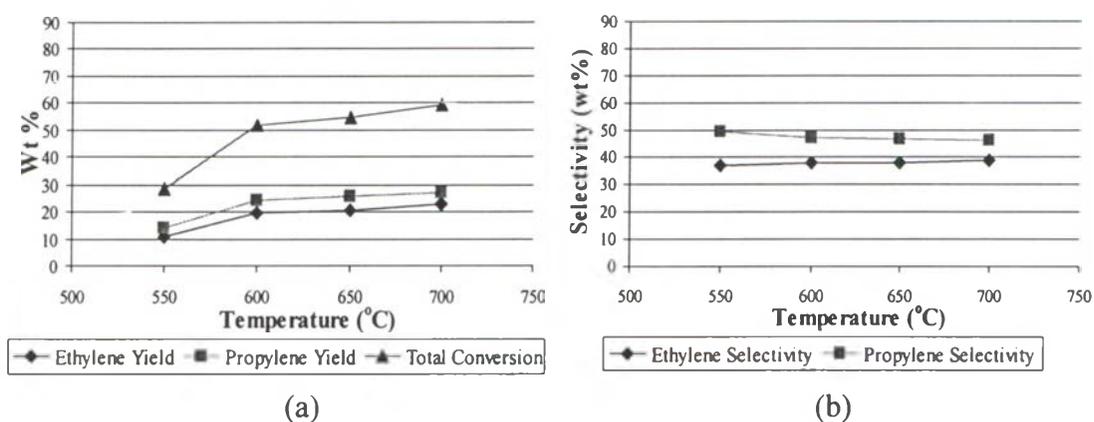
**Figure 4.16** Ethylene and propylene production from mixed C<sub>4</sub> and non-BD C<sub>4</sub> cracking at 600°C with total flow rate 50 ml/min over ZSM-5, Si/Al = 190 after 5, 30 and 60 minutes time on stream.

#### 4.4 Catalytic Cracking of Mixed C<sub>5</sub>

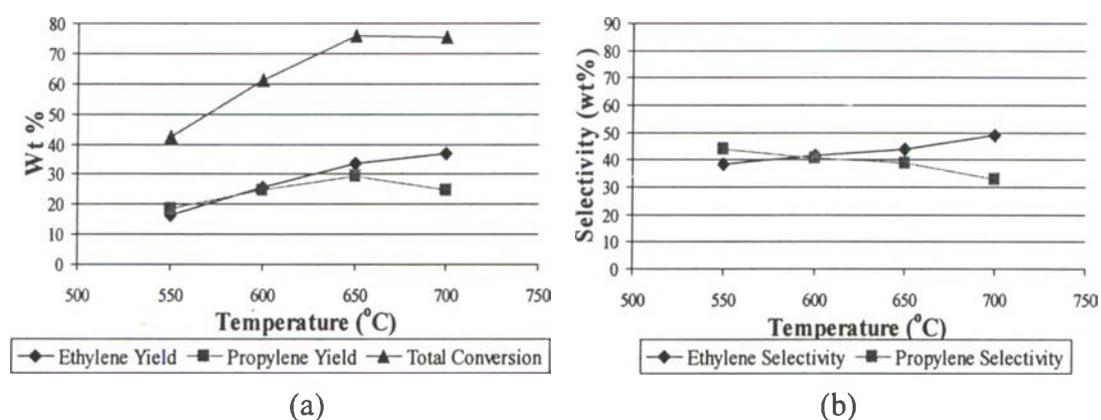
Cracking of mixed C<sub>5</sub> is performed by feeding the mixed C<sub>5</sub> vapor phase at concentration of 20% by volume in helium and the cracking is tested at temperature 550, 600, 650 and 700°C. The results are shown in Figure 4.17 to 4.19.

As shown in Figure 4.17, conversion, ethylene and propylene yields are greatly increased when the reaction temperature increases from 550 to 600°C and then slightly increase when temperature is raised to 700°C. At 700°C the maximum conversion, ethylene and propylene yields are 59.2, 22.9 and 27.3 wt%, respectively. When the ZSM-5 with Si/Al = 40 are used (Figure 4.18), the maximum conversion and propylene yield at 650°C are 75.8 and 29.3 wt%, respectively, while maximum ethylene is 37.0 wt% at 700°C. Figure 4.18 and 4.19 obviously show the increasing of conversion and product yield with the reaction temperature. From the ZSM-5 with Si/Al = 190 catalysts, the maximum conversion of mixed C<sub>5</sub> at 700°C is 49.9

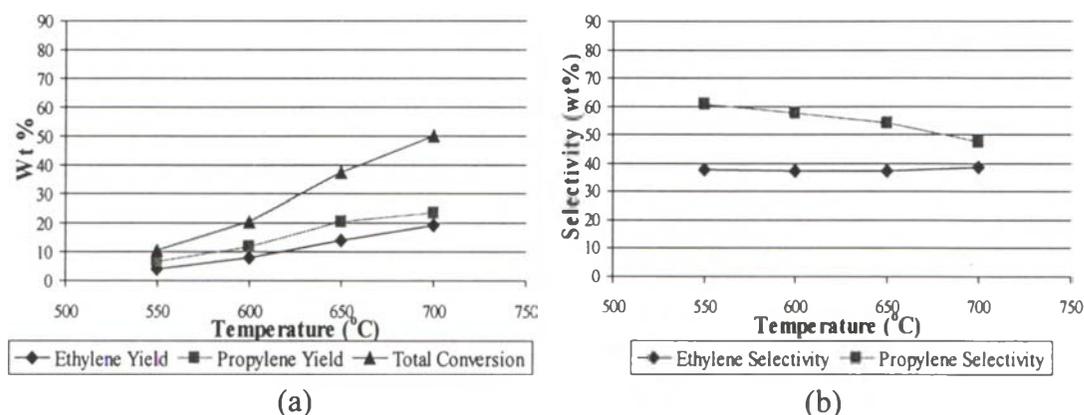
wt% and propylene yield is 23.6 wt%. This may be due to the mixed C<sub>5</sub> contains C<sub>5</sub> paraffin as major component, which is easier thermally cracked than olefins.



**Figure 4.17** Mixed C<sub>5</sub> cracking over ZSM-5, Si/Al = 20 with total flow rate 50 ml/min at 550, 600, 650 and 700°C after 5 minutes time on stream: (a) production yields and conversion, and (b) product selectivity.



**Figure 4.18** Mixed C<sub>5</sub> cracking over ZSM-5, Si/Al = 40 with total flow rate 50 ml/min at 550, 600, 650 and 700°C after 5 minutes time on stream: (a) production yields and conversion, and (b) product selectivity.



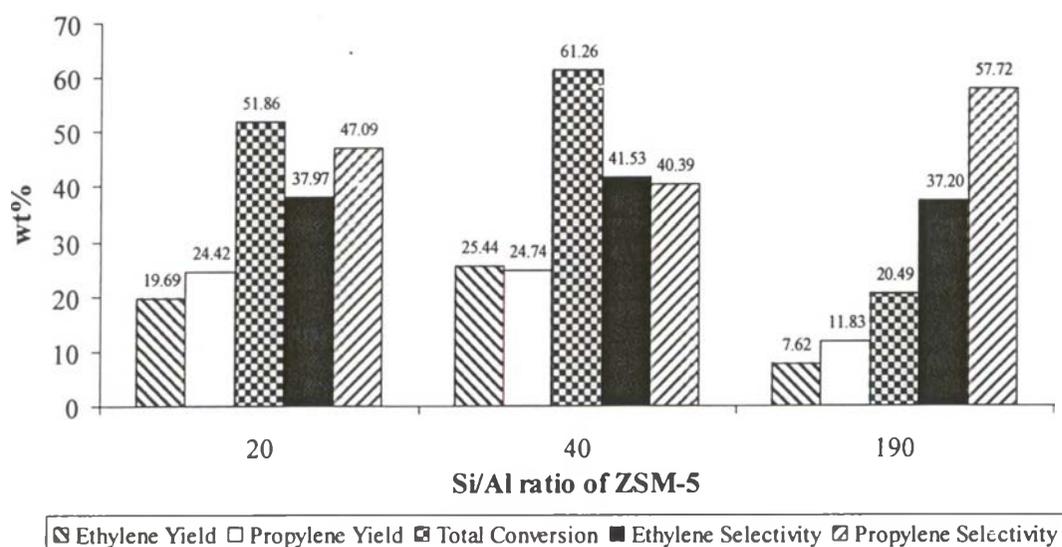
**Figure 4.19** Mixed C<sub>5</sub> cracking over ZSM-5, Si/Al = 190 with total flow rate 50 ml/min at 550, 600, 650 and 700°C after 5 minutes time on stream: (a) production yields and conversion, and (b) product selectivity.

It is also interesting to note that, when the reaction temperature is increased, the propylene selectivity is decreased while the ethylene selectivity is relatively constant (for Si/Al of 20 and 190) or increases significantly (for Si/Al of 40). This suggests that the propylene production from cracking of mixed C<sub>5</sub> prefers to lower temperature.

#### 4.4.1 Effect of Silicon to Aluminium Ratio over Mixed C<sub>5</sub> Cracking

Figure 4.20 presents the product yields, conversion and selectivity obtained from mixed C<sub>5</sub> catalytic cracking over ZSM-5 with Si/Al = 20, 40 and 190. For ZSM-5 with Si/Al = 398, the cracking reaction does not take place as observed in the cracking of C<sub>4</sub>.

From Figure 4.20, ZSM-5 with Si/Al = 40 shows the highest results in term of conversion, ethylene and propylene yield. Then, it can be summarized that ZSM-5 with Si/Al = 40 is the best catalyst for C<sub>5</sub> catalytic cracking compare with the other one. When focused on the products selectivity, the maximum propylene selectivity is 57.7 wt% when ZSM-5 with Si/Al = 190 is used. The selectivity of ethylene and propylene which obtain from mixed C<sub>5</sub> cracking are closer than the observation in mixed C<sub>4</sub>, because of propylene producing from mixed C<sub>4</sub> produce methane as by product but ethylene producing found incase of C<sub>5</sub> cracking.

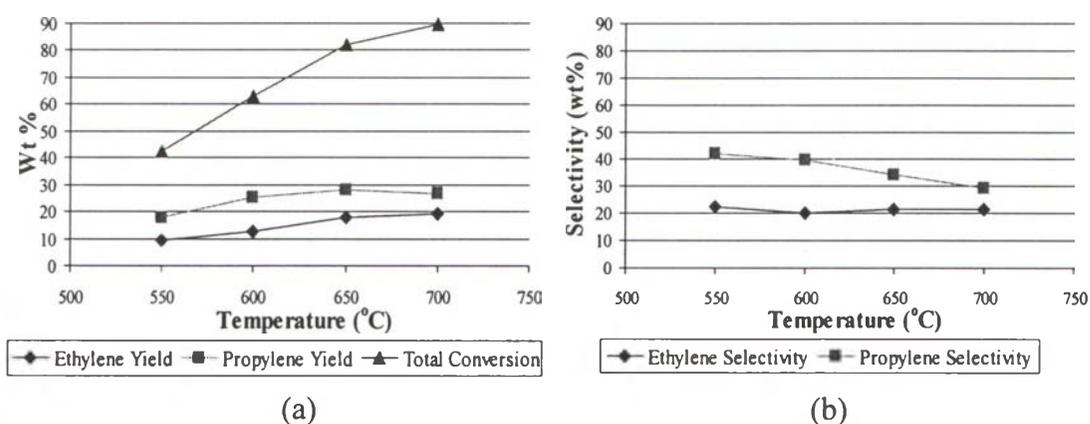


**Figure 4.20** Products yields, conversion and selectivity from mixed  $C_5$  cracking at  $600^\circ\text{C}$  with total flow rate  $50\text{ ml/min}$  over ZSM-5 ratio 20, 40 and 190 after 5 minutes time on stream.

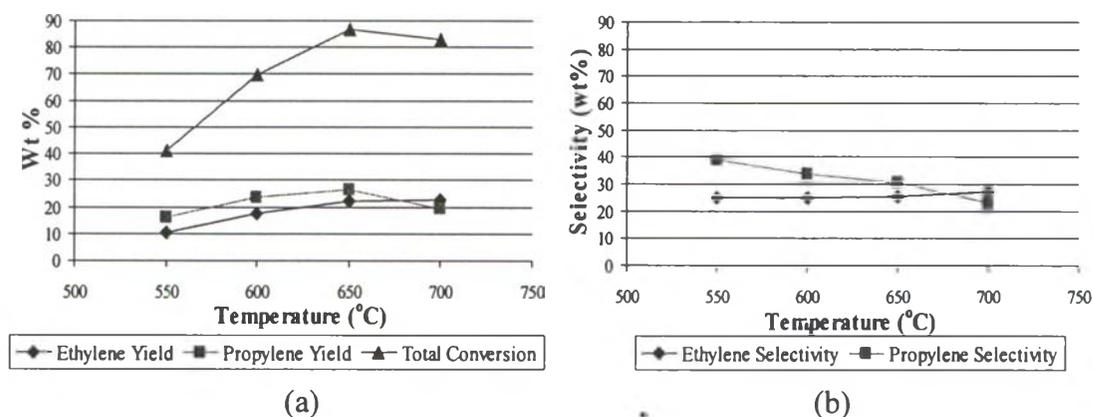
#### 4.5 Catalytic Cracking of Mixed $C_6$

Cracking of mixed  $C_6$  are performed in gas phase at concentration and cracking temperature as in the case of mixed  $C_5$ . In Figure 4.21 and 4.22, the maximum total conversions are 89.7 and 86.8 wt% when the ZSM-5 with  $\text{Si/Al} = 20$  and 40 are used. When reaction temperature is increased the conversion greatly increasing while the yields of desired products slightly increase. The different in conversion and desired products yield of mixed  $C_6$  cracking may come from the fact that there are more cracking positions in the longer hydrocarbon molecules, resulting in more species of cracked hydrocarbon. Therefore, cracking of mixed  $C_6$  can produce various kinds of paraffins and olefins that are in range of  $C_1$ - $C_5$  and/or  $C_6$  aromatic and cyclic. For product selectivity when the reaction temperature is higher, the selectivity towards propylene is reduced while the ethylene selectivity is relatively constant. For example, as shown in Figure 4.21, when reaction temperature is raised from  $550$  to  $700^\circ\text{C}$ , propylene selectivity significantly drops

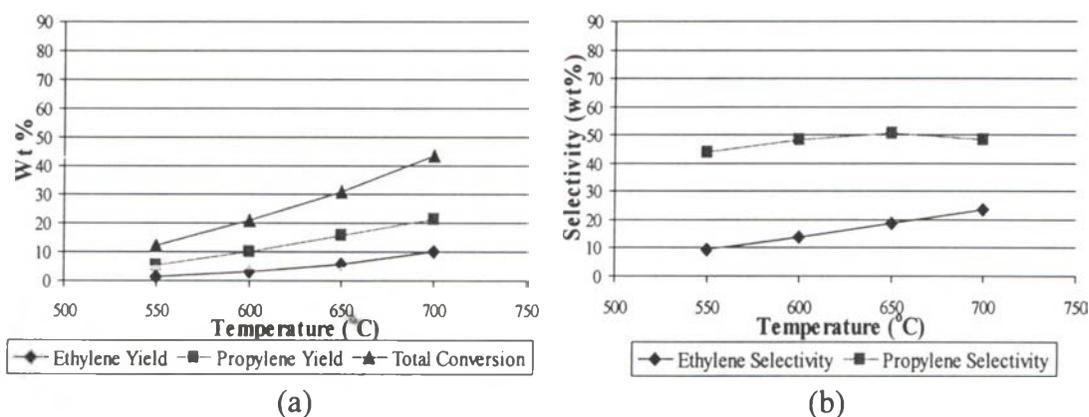
from 42.2 to 29.4 wt% while ethylene selectivity decreases from 22.4 to 21.4 wt%. It can be concluded that cracking of mixed  $C_6$  over ZSM-5 with Si/Al = 20 and 40 for propylene producing prefer to low temperature (below 650°C).



**Figure 4.21** Mixed  $C_6$  cracking over ZSM-5, Si/Al = 20 with total flow rate 50 ml/min at 550, 600, 650 and 700°C after 5 minutes time on stream: (a) production yields and conversion, and (b) product selectivity.



**Figure 4.22** Mixed  $C_6$  cracking over ZSM-5, Si/Al = 40 with total flow rate 50 ml/min at 550, 600, 650 and 700°C after 5 minutes time on stream: (a) production yields and conversion, and (b) product selectivity.



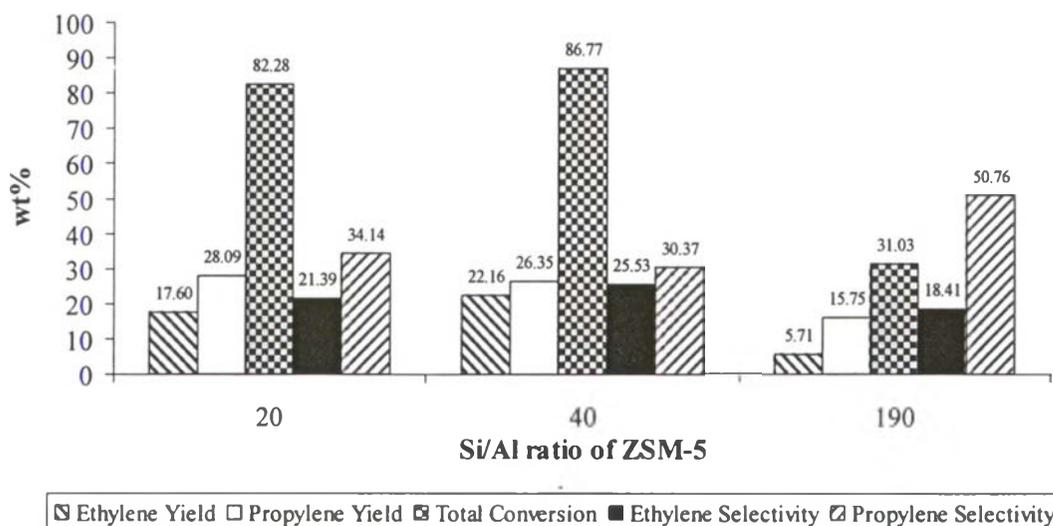
**Figure 4.23** Mixed C<sub>6</sub> cracking over ZSM-5, Si/Al = 190 with total flow rate 50 ml/min at 550, 600, 650 and 700°C after 5 minutes time on stream: (a) production yields and conversion, and (b) product selectivity.

However, in Figure 4.23, which is the results from using ZSM-5 with Si/Al = 190, the results show different trends from the previous catalysts. When temperature is increased, the conversion, products yield and product selectivity also increased as well. From these results, it can be concluded that the cracking of mixed C<sub>6</sub> over this catalyst produces undesired products less than the ZSM-5 with Si/Al = 20 and 40.

#### 4.5.1 Effect of Silicon to Aluminium Ratio over Mixed C<sub>6</sub> Cracking

Figure 4.24 presents the product yields, conversion and selectivity obtained from mixed C<sub>6</sub> catalytic cracking over ZSM-5 with Si/Al = 20, 40 and 190. The ZSM-5 with Si/Al = 398 also shows no product from catalytic cracking as in previous observation. From Figure 4.24, the ZSM-5 with Si/Al = 40 shows the highest in conversion and ethylene yield (86.8 and 22.2 wt%) while ZSM-5 with Si/Al = 20 shows the highest propylene yield (28.1 wt%). The results from these two catalysts present a lot of by-product yield which are 36.6 and 38.3 wt% for ZSM-5 with Si/Al 20 and 40 respectively. In case of ZSM-5 with Si/Al = 190, this catalysts show the highest propylene selectivity (50.8 wt%) with mixed C<sub>6</sub>. The yields of undesired products from this catalyst is 9.6 wt% which very low compare with the other two catalysts that mean these by-products required more acidity than propylene

producing and the acidity of ZSM-5 with Si/Al = 190 has lower acidity for produce another products.



**Figure 4.24** Products yields, conversion and selectivity from mixed C<sub>6</sub> cracking at 650°C with total flow rate 50 ml/min over ZSM-5 ratio 20, 40 and 190 after 5 minutes time on stream.

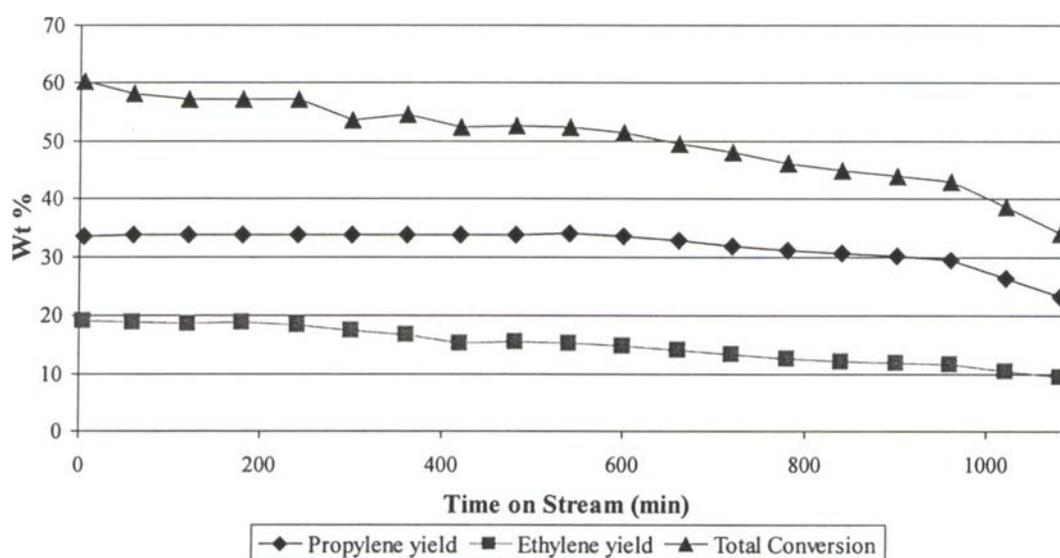
#### 4.6 Stability Test of Catalysts

The stability of the catalyst is the ability of the catalyst to retain its activity under the operating conditions. The loss in activity of the catalyst can be caused by coke formation, which will accumulate on surface or in pore of catalysts.

In this thesis, the stability of three zeolites (ZSM-5 with Si/Al = 20, 40, and 190) are tested by catalytic cracking of non-BD C<sub>4</sub>, mixed C<sub>5</sub> and mixed C<sub>6</sub> under the conditions which give the best yield of propylene. The results are presented at the time which yield of propylene reduces by 30% from the maximum yield.

#### 4.6.1 Non-Butadiene C<sub>4</sub> Stability Test

Non-BD C<sub>4</sub> is used for the stability at 600°C over three Si/Al ratio of zeolite, the results are shown in Figure 4.25 to 4.27. From Figure 4.25, when ZSM-5 with Si/Al = 20 is tested, the total conversion is 60.5 wt% at 5 minutes time on stream (TOS), and gradually decreases to 34.0 wt% at 1080 minutes (18 hours) TOS. Propylene yield is constant at about 34.0 wt% until 600 minutes (10 hours) TOS, after that the propylene yield dropped to 23.0 wt% at 1080 minute TOS, which is dropping decreasing 30% from the maximum yield. In case of ethylene, the interval constant yield is shorter than observed in propylene. Ethylene yield is 19.0 wt% until 240 minutes (4 hours) TOS and slightly decrease to 9.4 wt% at the end of the test. The dropping of conversion and products yield come from coke formation, which deactivated the catalyst.

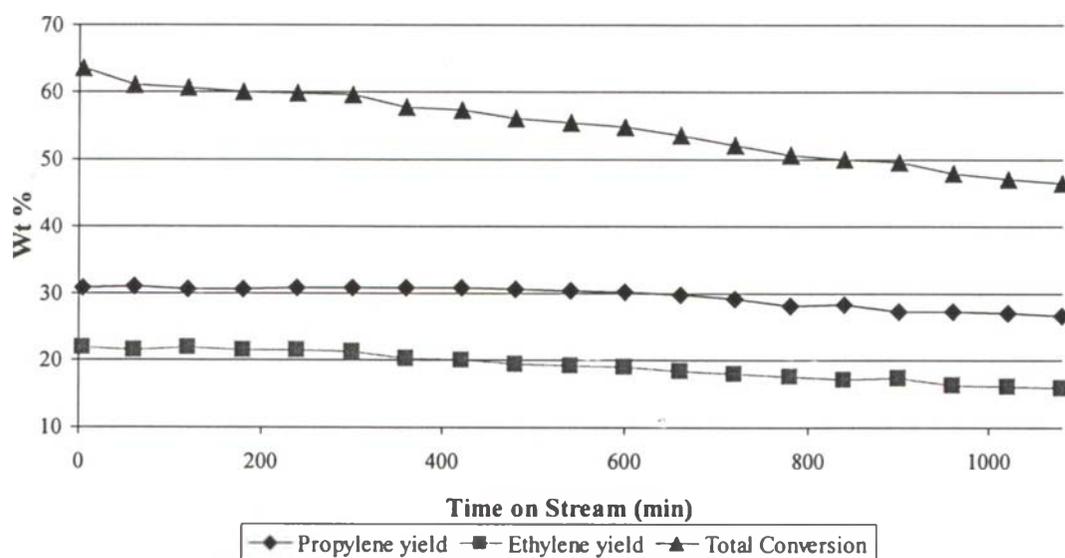


**Figure 4.25** Products yields and conversion from non-BD C<sub>4</sub> stability test at 600°C with 50% vol feed concentration at total flow rate 50 ml/min over ZSM-5, Si/Al = 20.

Therefore, when the dropping is investigated that mean some of acid sites were deposited by coke. These results can be explained as following reason. During the catalytic cracking process, paraffins and/or olefins are cracked by

carbenium ion mechanism, leading to lower olefins. Olefins can undergo a rapid oligomerization reaction. On acid site, olefins easily form allylcarbonium ions by hydride ion abstraction at the carbon in the  $\alpha$ -position to form a diene. The diene can again undergo hydride abstraction to form triene, which would increase the degree of unsaturation. Cyclization of triene results in the formation of aromatics. Hydrogen transfer reaction proceeds at the polycyclic aromatic referred as coke (Oudar and Wise, 1985).

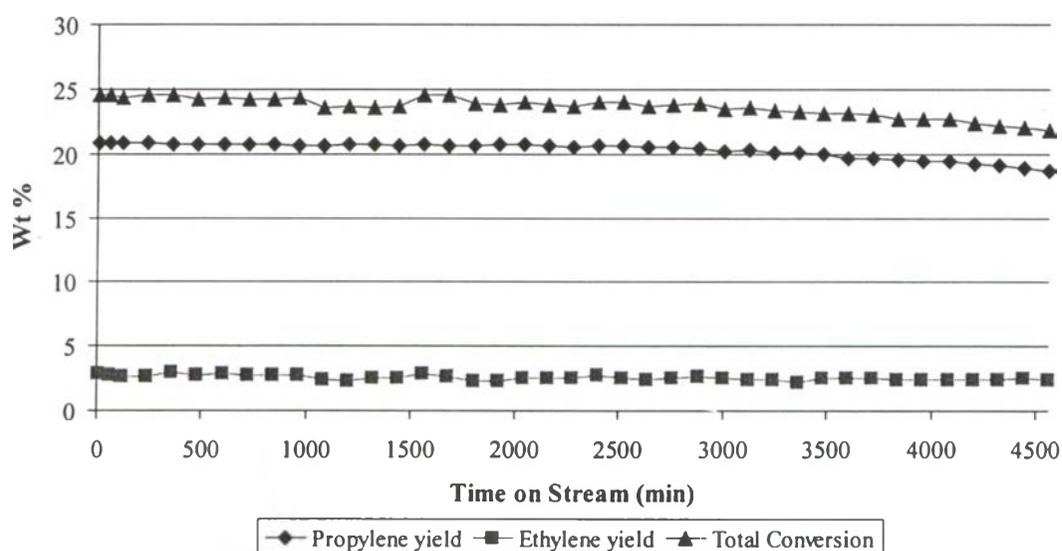
As mentioned in the previous section, ethylene and propylene are produced from different reactions. Ethylene producing requires more acidity of the zeolite than the propylene, and coke formation prefer to initiate at the stronger acid site (Mhindou-Koumba *et al.*, 2001), these causes the ethylene yield decreasing faster than propylene.



**Figure 4.26** Products yields and conversion from non-BD C<sub>4</sub> stability test at 600°C with 50% vol feed concentration at total flow rate 50 ml/min over ZSM-5, Si/Al = 40.

When the ZSM-5 with Si/Al = 40 is tested (Figure 4.26), the experiment is end up at the same time as result on the first catalysts that help for clearly comparison because of these two ratio gave quite the same results in activity

test and may be they show different results in stability test. From Figure 4.26, the total conversion starts with 63.6 wt% at 5 minutes TOS and slightly decreases to 46.4 wt% at 1080 minutes (18 hours) TOS. Propylene yield is constant at about 30.9 wt% until 600 minutes (10 hours) TOS, after that it dropped to 26.7 wt% at 1080 minute. For ethylene, the constant yield period is shorter than observed in propylene. Ethylene yield is 21.8 wt% until 240 minutes (4 hours) TOS and slightly decrease to 15.7 wt% at the end of the test. Compared these results with the previous catalysts, the ZSM-5 with Si/Al = 40 show the same results in constant yield period but the better results in decreasing rate because of at 1080 minute this catalyst show the higher conversion and product yields.



**Figure 4.27** Products yields and conversion from non-BD C<sub>4</sub> stability test at 600°C with 50% vol feed concentration at total flow rate 50 ml/min over ZSM-5, Si/Al = 190.

The ZSM-5 with Si/Al = 190 shows the best result in stability test. As shown in Figure 4.27, after 4560 minutes (76 hours) TOS the total conversion, propylene yield and ethylene yield slightly decreased from 24.5, 20.8 and 2.8 wt% to 21.8, 18.7 and 2.4 wt% respectively. At this time the decreasing of propylene yield, is 10.3% from the beginning. The ZSM-5 with Si/Al =190 shows the least products

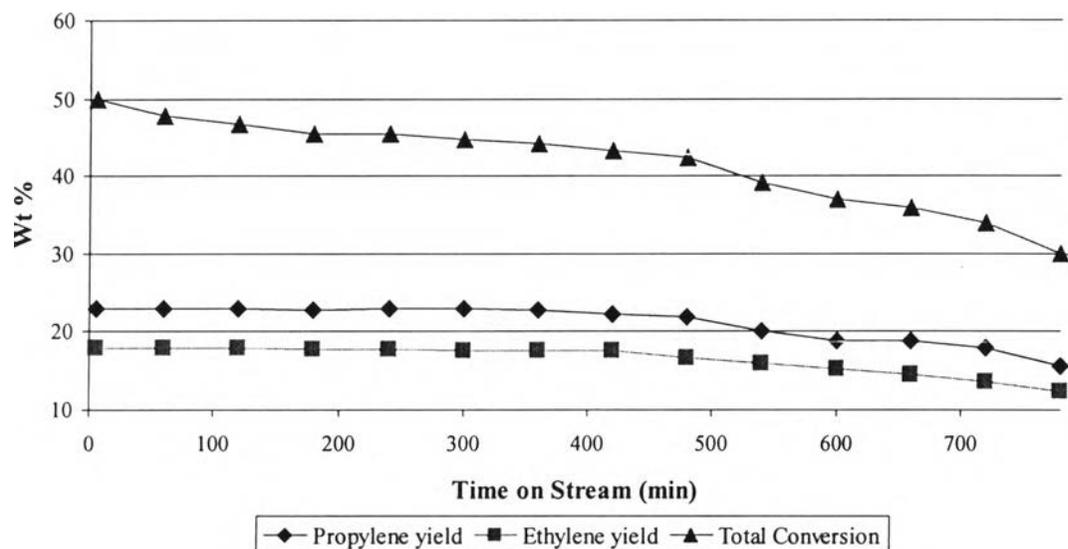
yields in activity test but shows the highest stability in this test. From these results it suggests that the more acidity in the catalysts results in easier coke formation (Mhindou-Koumba *et al.*, 2001).

#### 4.6.2 Mixed C<sub>5</sub> Stability Test

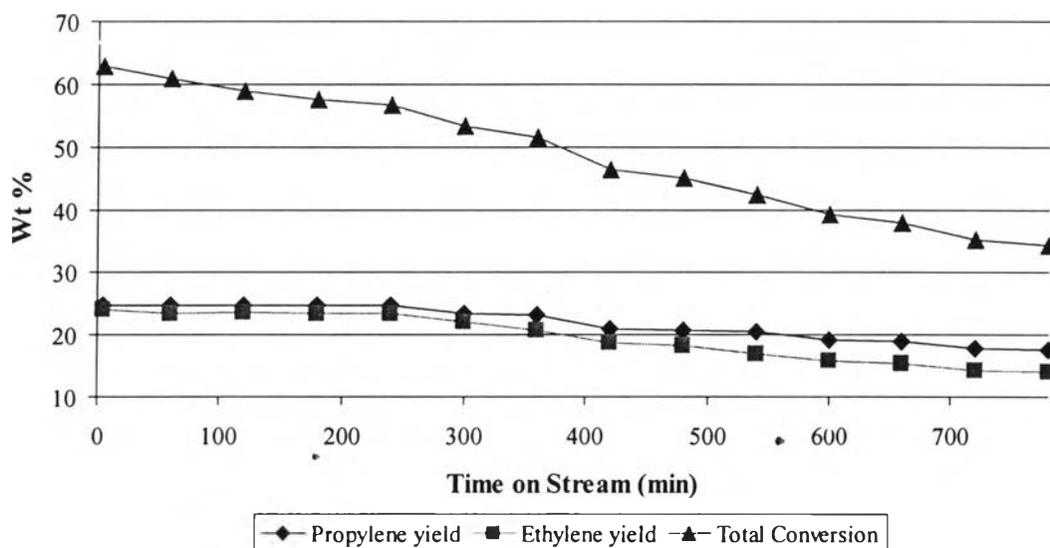
The stability tests of mixed C<sub>5</sub> are performed at 600°C over three Si/Al ratio of zeolite, the results are shown in Figure 4.28 to 4.30. The results from ZSM-5 with Si/Al = 20 testing is shown in Figure 4.28, yield of propylene drops by 30% at 780 minutes (13 hours) TOS. The total conversion starts at 49.9 wt% and decreases to 29.9 at 1080 minutes. Propylene shows constant yield at 23.0 wt% until 360 minutes (6 hours) TOS after that propylene yield drops to 15.67 wt% after 780 minutes. Ethylene yield is relatively constant yield period as over the testing in propylene. Yield of ethylene is 17.9 wt% at the beginning and starts to drop after 360 minutes to 12.4 wt% at the end. The same constant interval of propylene and ethylene yields, which are at the same time, may explain by propylene and ethylene production come from the same reaction, cracking of C<sub>5</sub> almost obtains C<sub>2</sub> and C<sub>3</sub> olefins (Narbeshuber *et al.*, 1997)

The constant interval of propylene and ethylene yields are observed at the same time when the ZSM-5 with Si/Al = 40 are tested (Figure 4.29). The total conversion is at 62.9 wt%, at the beginning and significantly decreases to 34.4 wt% at the end. Propylene shows the constant yield at about 24.8 wt% until 240 minutes (4 hours) TOS, after that the propylene yield drops to 17.5 wt% at 780 minute. Ethylene yield stats at 23.9 wt% for 240 minutes (4 hours) and decreases to 14.0 wt% at the end of test. Comparing these results with the previous catalysts, the ZSM-5 with Si/Al = 40 shows the shorter time interval before the catalyst start to deactivate, and has less coke formation rate because of at the ending time this catalyst show the higher conversion and product yields.

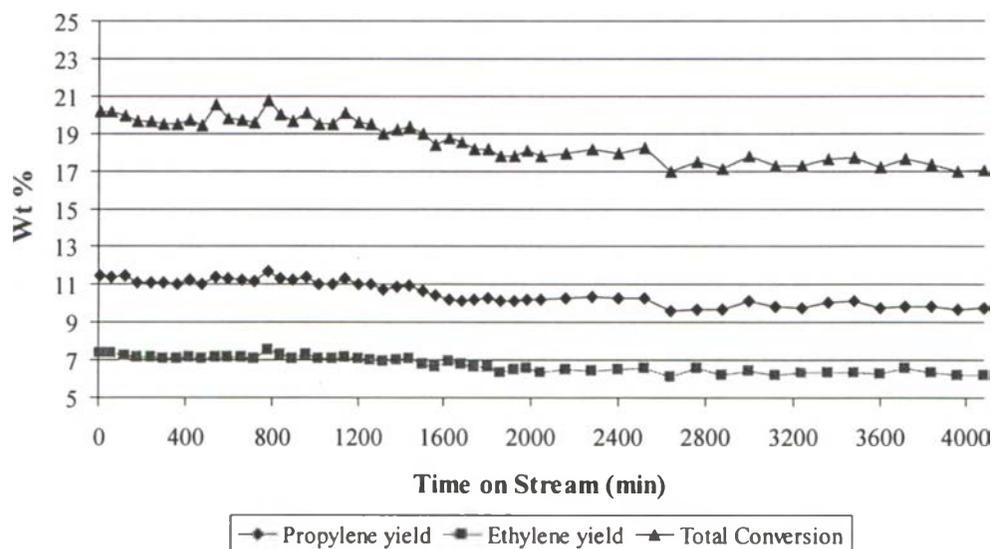
The ZSM-5 with Si/Al = 190 shows the best result in stability test as observed in the non-BD C<sub>4</sub>. As shown in Figure 4.30, after 4080 minutes (68 hours) TOS the total conversion, propylene yield and ethylene yield little decreases from 20.2, 11.4 and 7.4 wt% to 17.1, 9.7 and 6.2 wt% respectively.



**Figure 4.28** Products yields and conversion from mixed C<sub>5</sub> stability test at 600°C with 50% vol feed concentration at total flow rate 50 ml/min over ZSM-5, Si/Al = 20.



**Figure 4.29** Products yields and conversion from mixed C<sub>5</sub> stability test at 600°C with 50% vol feed concentration at total flow rate 50 ml/min over ZSM-5, Si/Al = 40.



**Figure 4.30** Products yields and conversion from mixed  $C_5$  stability test at  $600^\circ\text{C}$  with 50% vol feed concentration at total flow rate 50 ml/min over ZSM-5, Si/Al = 190.

The stability tests of mixed  $C_5$  over these three zeolites show the shorter TOS (less stability) than that observed in non-BD  $C_4$ . These results may be explained by the rate of coke formation, which depends strongly on the structure of the coke precursors: Aromatics generate more coke than do on naphthenes, olefins and paraffins (Brillis and Manos, 2003).

Mixed  $C_5$  contains more coke precursors such as *cyclo*-pentene, *cyclo*-pentadiene and pentadiene than non-BD  $C_4$  therefore mixed  $C_5$  shows the less stability.

#### 4.6.3 Mixed $C_6$ Stability Test

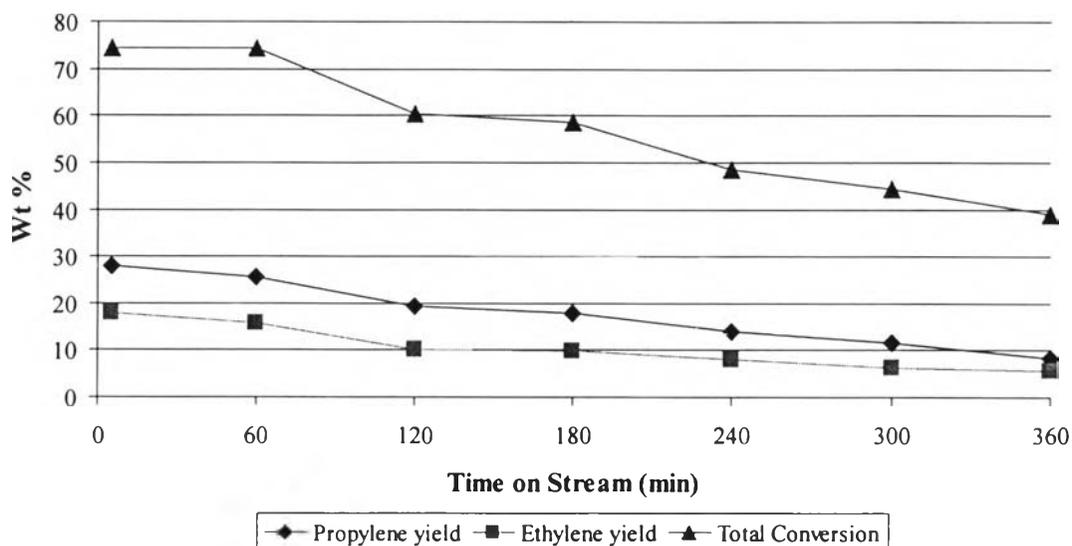
The stability test of mixed  $C_6$  is performed at  $650^\circ\text{C}$  which higher temperature than previous test because of cracking of mixed  $C_6$  at this temperature shows the highest conversion and products yield, and no effect from thermal cracking. The results are shown in Figure 4.31 to 4.33.

Figure 4.31 presents results from the test over ZSM-5 with Si/Al = 20, yield of propylene dramatically decreases with the increasing of TOS. The dropping

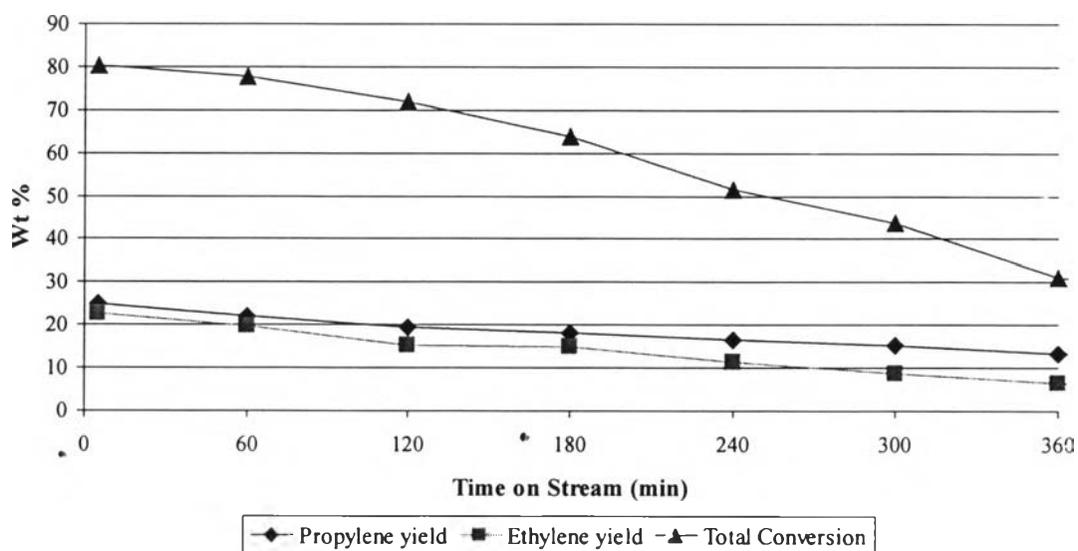
starts immediately at the beginning of the test. Propylene yield is 28.1 wt% at the beginning and drops down to 8.2 wt% at 360 minutes (6 hours) TOS. The total conversion and ethylene yield starts at 74.5 and 18.0 wt% after that it decreases to 39.1 and 5.5 wt% at the end of test. The results from ZSM-5 with Si/Al = 40 (Figure 4.32) show the same trend as observed in previous catalyst. The rapid decreasing in products yield is found with increasing of TOS. The total conversion, propylene and ethylene yield rapidly decreased from 80.3, 25.1 and 22.5 wt% to 31.1, 13.4 and 6.3 wt% respectively.

The ZSM-5 with Si/Al = 190 also shows the best result in mixed C<sub>6</sub> stability test. As shown in Figure 4.33, the total conversion starts at 34.8 wt% and drops with time to 22.4 wt% while propylene yield is constant at 15.9 wt% for 180 minutes (3 hours) TOS and decreases to 9.5 wt% after 2400 minutes (40 hours). Ethylene yield is constant at 5.5 wt% for 180 minutes and slightly decreases to 3.9 wt% at the end of test.

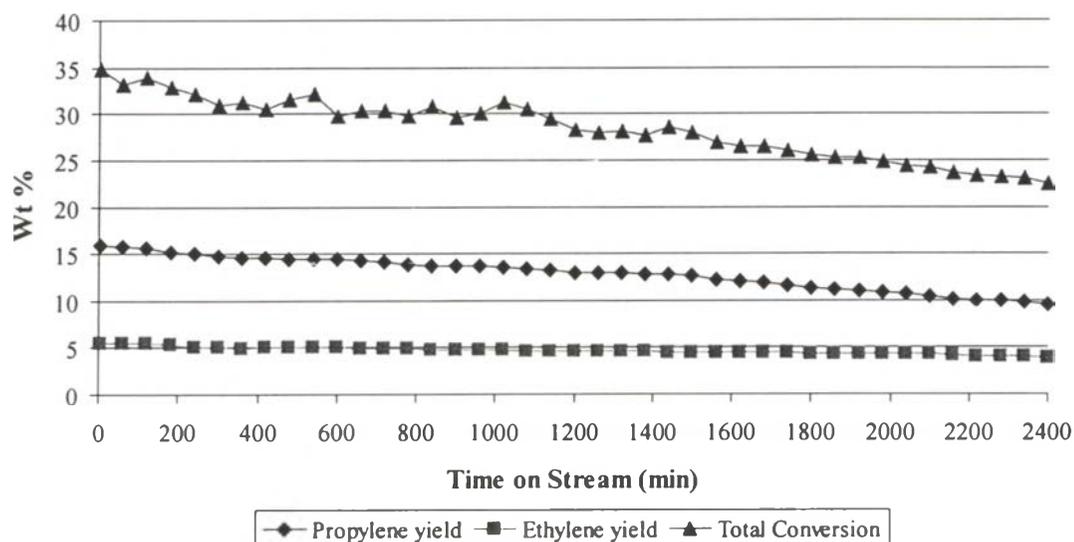
The stability test of mixed C<sub>6</sub> shows the shortest TOS when compares with others feedstock. As mentioned these results can be explained by the coke precursor theory. Mixed C<sub>6</sub> contains a lot of coke precursors that make it has the least stability.



**Figure 4.31** Production yields and conversion from mixed C<sub>6</sub> stability test at 650°C with 50% vol. feed concentration at total flow rate 50 ml/min over ZSM-5, Si/Al = 20.



**Figure 4.32** Production yields and conversion from mixed C<sub>6</sub> stability test at 650°C with 50% vol. feed concentration at total flow rate 50 ml/min over ZSM-5, Si/Al = 40.



**Figure 4.33** Production yields and conversion from mixed C<sub>6</sub> stability test at 650°C with 50% vol. feed concentration at total flow rate 50 ml/min over ZSM-5, Si/Al = 190.

All results from the stability test are related with the conclusion about coke formation which are the coke content increased with the increasing of (i) reaction temperature, (ii) coke precursor, (iii) time on stream (TOS), (iv) retention time and (v) reactant composition (Brillis and Manos, 2003).

## 4.7 Catalysts Characterization

### 4.7.1 X-ray Diffraction

All catalyst are characterized by X-ray Diffraction (XRD) to confirm the structure of all tested catalysts. Figure 4.34 presents the peak pattern of ZSM-5 with Si/Al = 20, 40, 190 and 398. Figure 4.35 is the XRD pattern of ZSM-5 obtained from other work (Round *et al.*, 2001). It is clearly seen that all zeolites that are used in these studies show all main peaks as shown in the reference. Therefore, all tested zeolites have ZSM-5 structure.

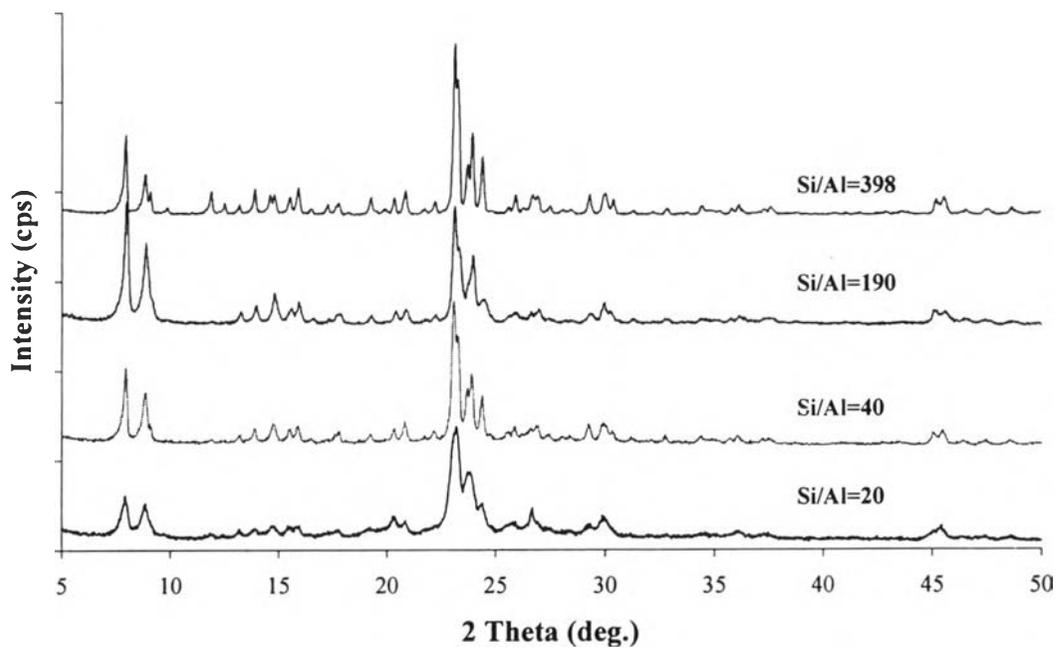


Figure 4.34 XRD peak pattern obtained from ZSM-5 with Si/Al = 20, 40, 190 and 398.

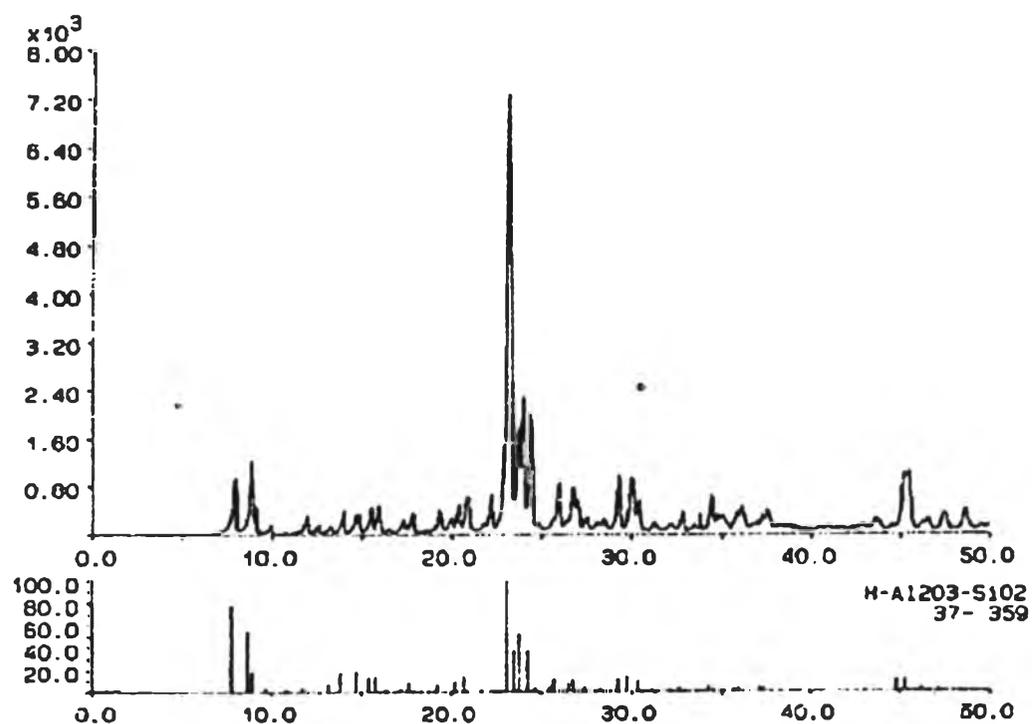
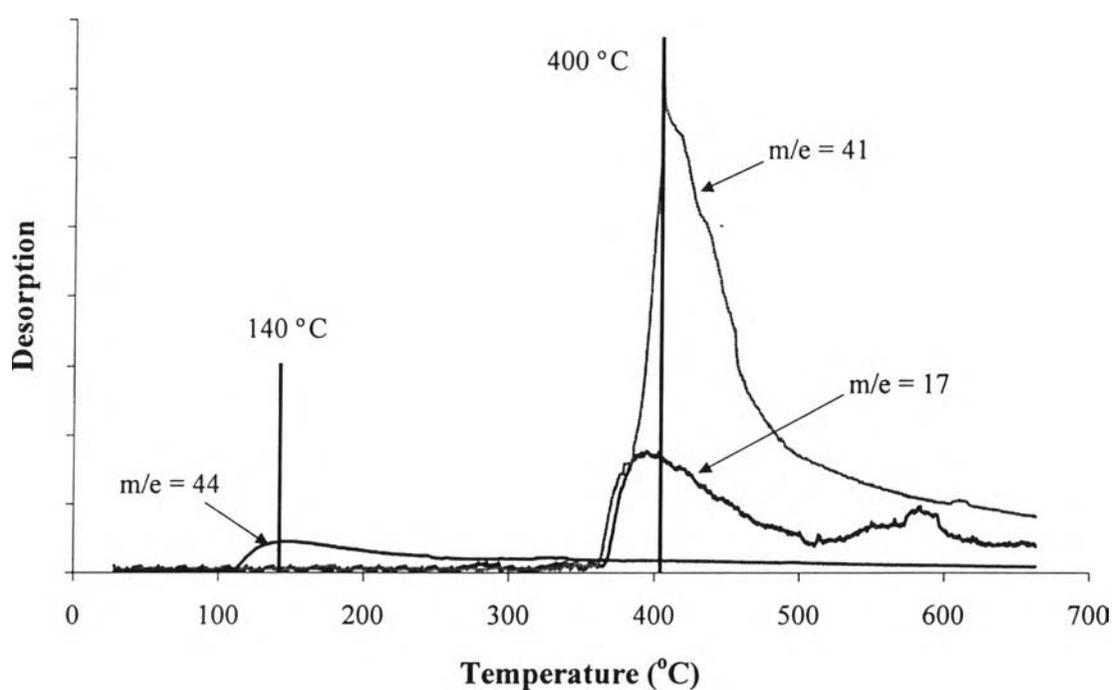


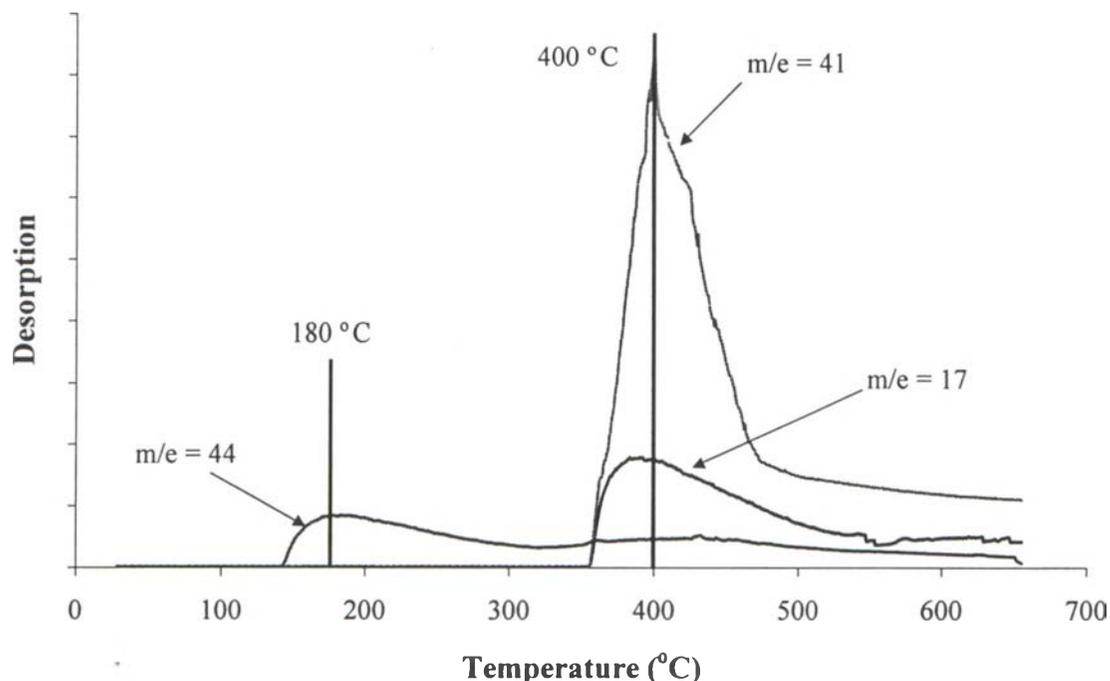
Figure 4.35 XRD peak pattern obtained from H-ZSM-5 (Round *et al.*, 2001).

#### 4.7.2 Temperature Programmed Desorption

The temperature programmed desorption (TPD) is performed to analyze the acidity of the zeolite. TPD of isopropylamine can determine both weak and strong acid sites of the ZSM-5. The TPD of isopropylamine over ZSM-5 with Si/Al = 20, 40 and 190 are shown in Figure 4.36 to 4.38. A mass spectrometer was used to determine the desorbed gases, with signals for isopropylamine ( $m/e = 44$ ), propylene ( $m/e = 41$ ), and ammonia ( $m/e = 17$ ).



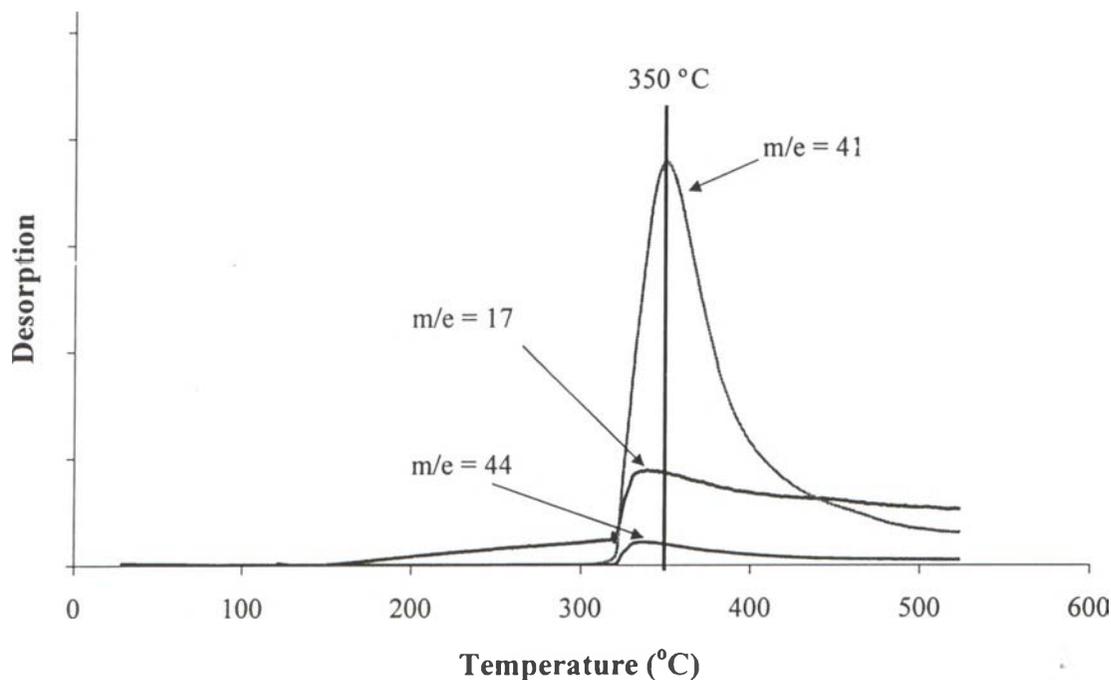
**Figure 4.36** TPD of isopropylamine from ZSM-5 catalyst with Si/Al = 20.



**Figure 4.37** TPD of isopropylamine from ZSM-5 catalyst with Si/Al = 40.

From Figure 4.36 and 4.37, TPD results show both weak and strong acid sites of the ZSM-5. The isopropylamine desorbed out from the sample at lower temperature is come from weak acid sites. The maximum desorption temperature of weak site is at 140 and 180°C for ZSM-5 with Si/Al = 20 and 40 respectively. Generally, the higher desorption temperature indicated the higher acidity of the zeolite (Gorte, 1996), then it can be summarized that ZSM-5 with Si/Al = 40 has higher acidity in weak acid site than the Si/Al = 20. For strong acid site, isopropylamine will be break to propylene and ammonia before desorbed out from the sample. The higher temperatures that propylene and ammonia desorbed out of the sample refer to higher acidity. Both Si/Al = 20 and 40 of ZSM-5 show peak at 400°C that means these two zeolites have the same acidity in strong acid site.

The higher acidity of ZSM-5 with Si/Al = 40 correspond with the catalytic cracking results which is little higher in total conversion than ZSM-5 with Si/Al = 20.



**Figure 4.38** TPD of isopropylamine from ZSM-5 catalyst with Si/Al = 190.

The TPD results of ZSM-5 with Si/Al = 190 (Figure 4.38) show only one desorption temperature at 350°C. It can be concluded that this zeolite has no weak acid site or these weak acid sites are too weak for isopropylamine adsorption. The ZSM-5 with Si/Al = 190 has lower desorption temperature, therefore it has lower acidity than the two previous zeolites. These results correspond with the catalytic cracking results that has the lower total conversion and products yield than the two previous zeolites.

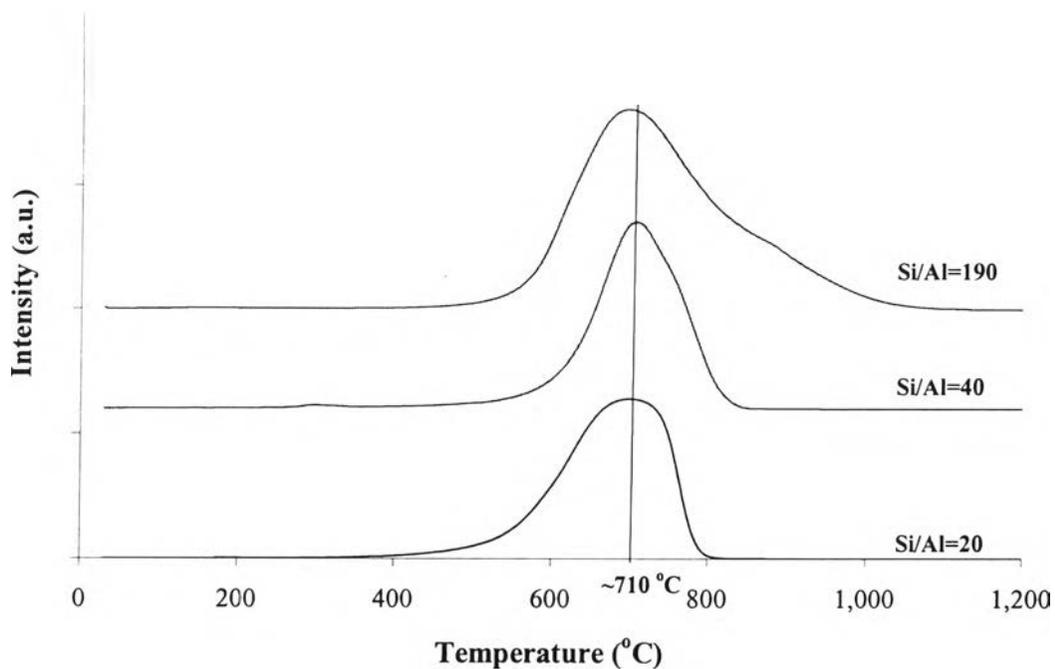
#### 4.7.3 Temperature Programmed Oxidation of Spent ZSM-5

The temperature programmed oxidation (TPO) is performed to analyze coke deposited on the catalysts after the stability test. Figure 4.39 presents the TPO results of ZSM-5 with Si/Al = 20, 40, and 190 from non-BD C<sub>4</sub> stability test. The results show one peak in each ratio at temperature about 710°C. It is interesting to note that the oxidation temperature from these results is relatively high. The high oxidation temperature may come from many reasons; one of them is the

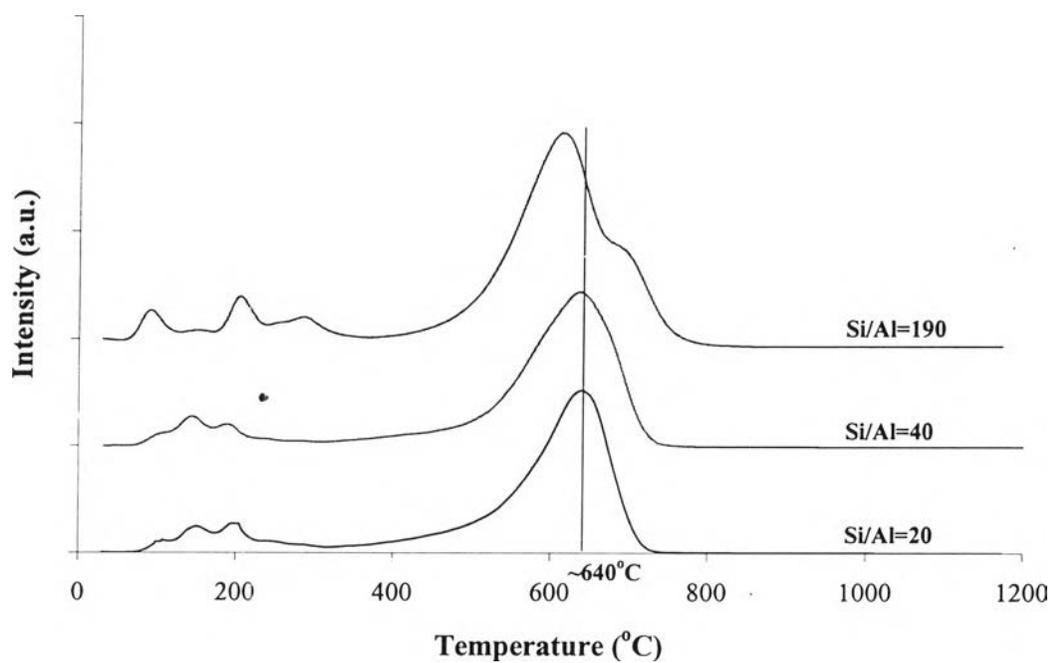
effect of pore structure and coking. ZSM-5 is a medium pore zeolite, which has a pore size about 0.56 nm. The smaller pores are easier to be blocked by the deposited coke, therefore oxygen diffusion and recirculation are harder. These phenomena make ZSM-5 has low oxidation rate and high oxidation temperature (Satterfield, 1993).

From TPO results of catalyst in mixed C<sub>5</sub> stability test (Figure 4.40). The results show two peaks in all catalysts, the first one at low temperature, about 200°C, and other one at temperature about 640°C. The smaller peak at lower temperature may come from the adsorbed larger hydrocarbon that vaporized out when temperature is increased. The big peaks at high temperature are come from coke oxidation. The lower oxidation temperature of mixed C<sub>5</sub> may come from the effect of coke structure. When the hydrogen-carbon ratio (H/C) decreased the coke becomes more resistant to removal by oxidation. The hydrogen-carbon ratio depends on reaction temperature, reaction time and coke precursor (Satterfield, 1993). Coke precursor from mixed C<sub>5</sub> come from paraffin then the hydrogen-carbon ratio in mixed C<sub>5</sub> coke is higher than other feeds that make oxidation temperature of mixed C<sub>5</sub> is the lowest.

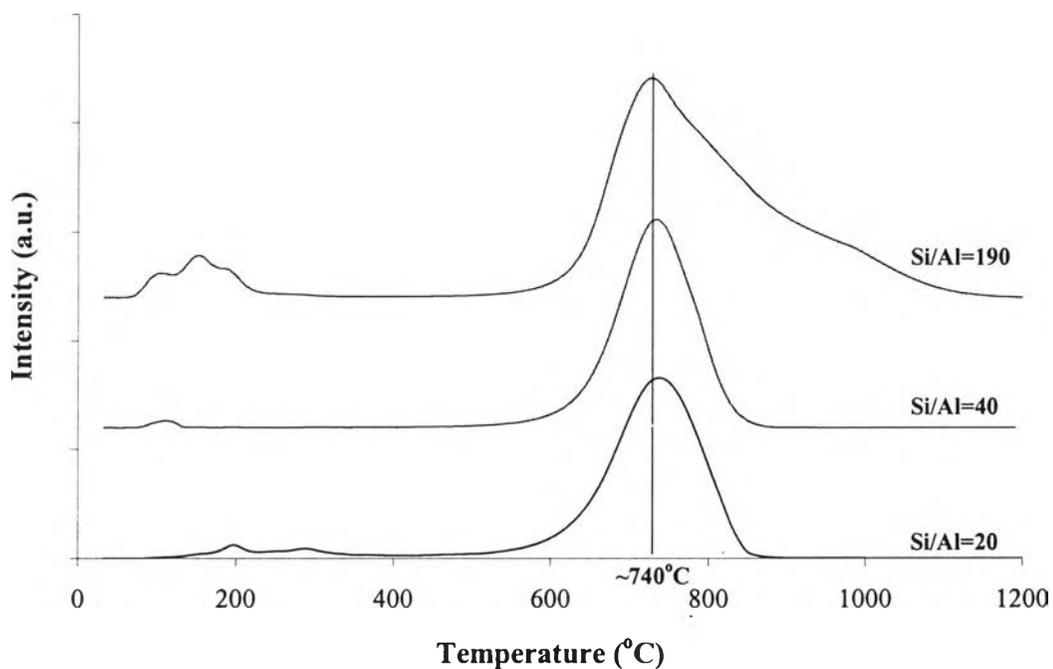
Figure 4.41 presents the TPO results from mixed C<sub>6</sub> stability test. The results show the same trend as found on mixed C<sub>5</sub> but the higher oxidation temperatures are observed. The higher oxidation temperature come from the same reason of mixed C<sub>5</sub> but mixed C<sub>6</sub> contained aromatic and olefin that make the coke less hydrogen-carbon ratio than mixed C<sub>5</sub>. These bring to the results on harder oxidation and higher temperature required.



**Figure 4.39** TPO results from ZSM-5 ratio about 20, 40 and 190 after used for non-BD C<sub>4</sub> stability test.



**Figure 4.40** TPO results from ZSM-5 ratio about 20, 40 and 190 after used for mixed C<sub>5</sub> stability test.



**Figure 4.41** TPO results from ZSM-5 ratio about 20, 40 and 190 after used for mixed C<sub>6</sub> stability test.

The amount of coke present in term of percent weight of carbon on the catalysts as shown in Table 4.2. These results cannot directly compare for any feed because they test on different time on stream. Carbon contained in ZSM-5 with Si/Al = 190 is very high because of these zeolite are used in stability test longer than the others are.

**Table 4.2** Percent carbon contained in the ZSM-5 with Si/Al = 20, 40, and 190 after used in stability test over non-BD C<sub>4</sub>, mixed C<sub>5</sub> and mixed C<sub>6</sub>

Feed Stock	Carbon Contained (wt%)		
	Si/Al = 20	Si/Al = 40	Si/Al = 190
Non-BD C <sub>4</sub>	15.57	19.30	40.56
Mixed C <sub>5</sub>	9.07	7.96	21.56
Mixed C <sub>6</sub>	8.88	9.27	23.01