

CHAPTER V

RESULTS AND DISCUSSION

5.1 X-Ray Diffraction Patterns

The x-ray diffraction patterns for the crystals are shown in Figure 5.1. The patterns of H-ZSM-5, prepared in this laboratory by quick method, were almost the same as that of Mobil Oil Corporation [108]. This indicates that the H-ZSM-5 also has the pentasil pore-opening structure typical for the general ZSM-5 catalyst. When compared the metal (Pt, Re and Re-Pt) ion-exchanged H-ZSM-5 catalysts with the parent H-ZSM-5, the patterns of the metal ion-exchanged H-ZSM-5 are similar to that of H-ZSM-5. This indicates that the metal ion-exchanged H-ZSM-5 catalysts have the same crystalline structure, the pentasil pore-opening structure, as the parent H-ZSM-5. Consequently, the metals ion-exchange do not change the structure of H-ZSM-5 catalyst.

5.2 Specific Surface Area

BET surface areas of crystals are shown in Figure 5.2. The surface area of all metal ion-exchanged H-ZSM-5 crystals were almost as large as that of the parent H-ZSM-5 catalyst. This is consistent with the above-mentioned result that the XRD patterns of all metal

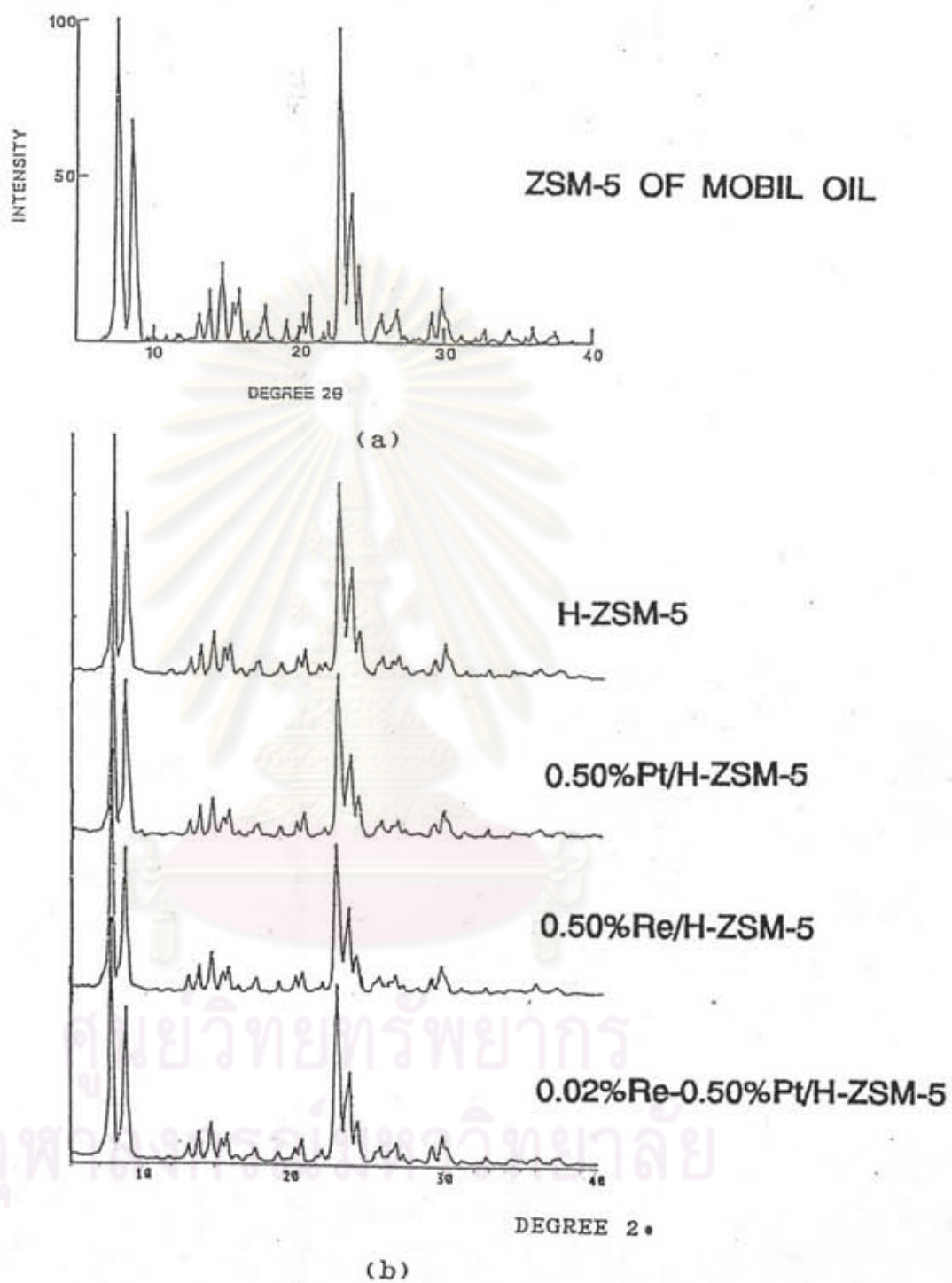


Figure 5.1 X-ray diffraction patterns for (a) H-ZSM-5 of Mobil Oil Corporation [108]. (b) metal loaded and non-loaded H-ZSM-5.

ion-exchanged H-ZSM-5 catalysts were almost the same as that of ZSM-5 catalyst. The metal loading does not effect on the total surface area of catalyst. From Table 5.1 shows the difference in BET surface area of H-ZSM-5, 0.50%Pt/H-ZSM-5, and 0.02%Re-0.50%Pt/H-ZSM-5 on methanol conversion reaction for 12 h on stream. It can be seen that 0.02%Re-0.50%Pt/H-ZSM-5 has higher surface area than 0.50%Pt/H-ZSM-5 but less than the total surface area of parent H-ZSM-5. Therefore, the 0.50%Pt/H-ZSM-5 has less reactive surface area than 0.02%Re-0.50%Pt/H-ZSM-5 and the parent H-ZSM-5 catalysts.

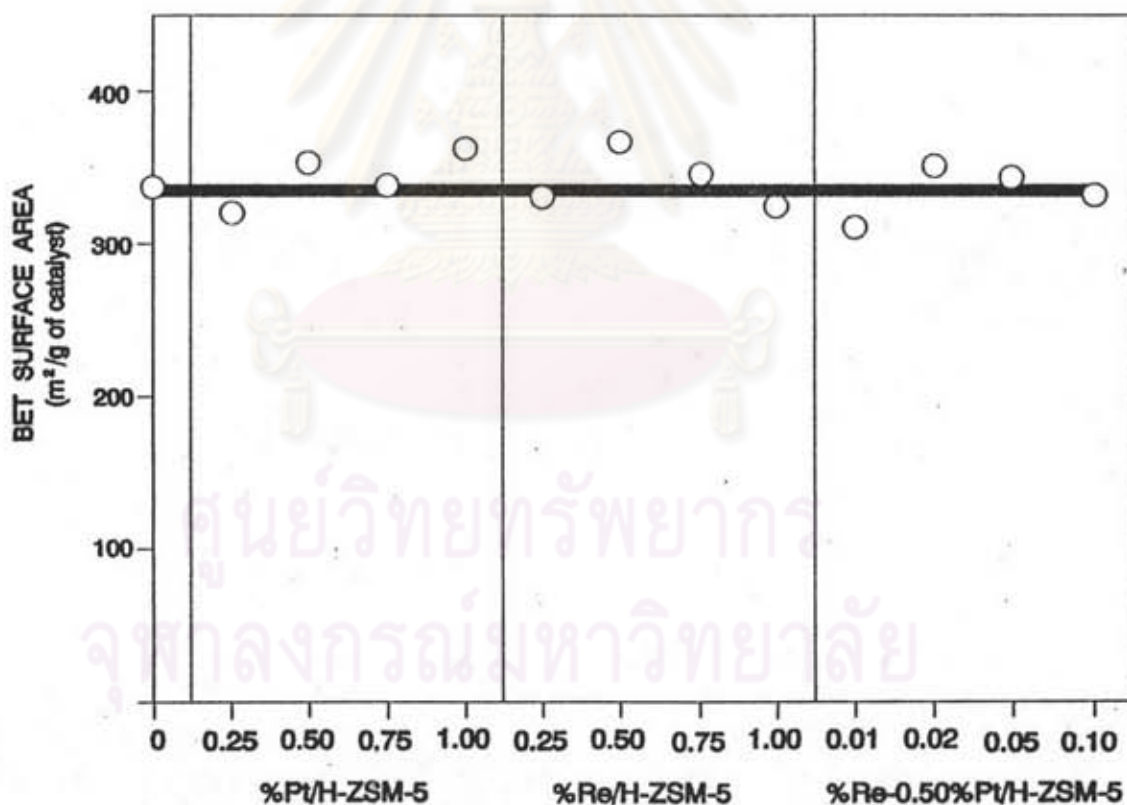


Figure 5.2 BET surface areas of the catalysts.

Table 5.1 The specific surface area of deactivation catalysts

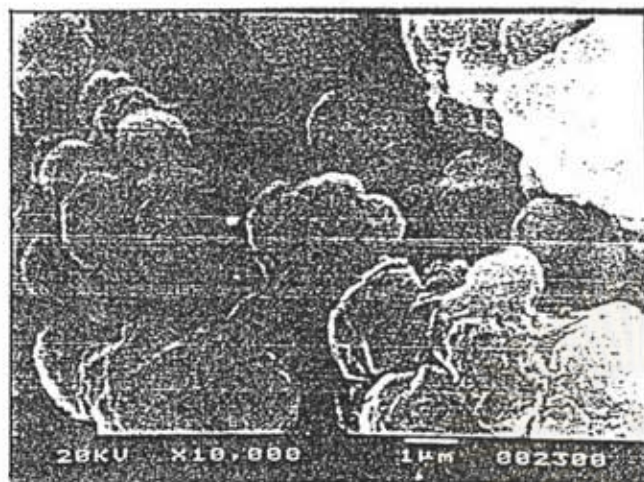
| Catalyst | Specific Surface Area (m ² /g of catalyst) |
|-------------------------|--|
| H-ZSM-5 | 263.84 |
| 0.50%Pt/H-ZSM-5 | 184.64 |
| 0.02%Re-0.50%Pt/H-ZSM-5 | 190.27 |

5.3 Morphology

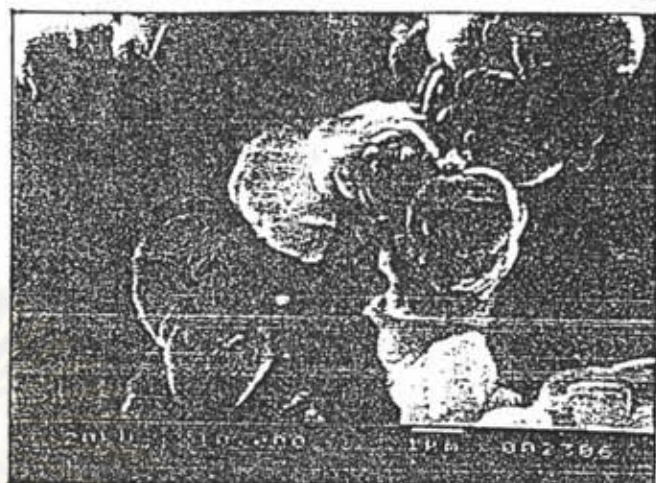
Photographs of the scanning electron microscope in Figure 5.3 show morphology of the metal loaded and non-loaded catalysts. The crystal shape and size of metal loaded catalysts (Pt, Re and Re-Pt) were identical with the parent H-ZSM-5 catalyst and conformed to their characteristics of catalysts on 5.1 and 5.2.

5.4 Acidity

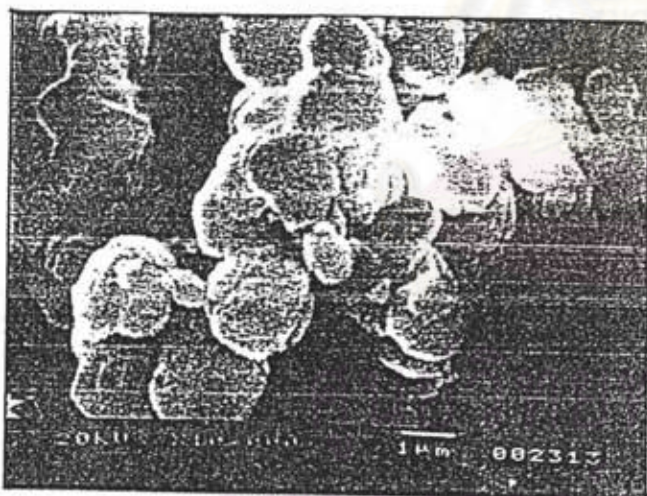
The TPD profile of desorbed NH₃ from metal loaded and non-loaded catalysts are shown in Figure 5.4. The profile is composed of two peaks, i.e., a high temperature peak of strong acid sites and a low temperature peak of weak acid sites [7,33,109,110]. The separation of high temperature and low temperature peaks was made at 300°C. For strong acid sites, the amount of the acidic site of metal



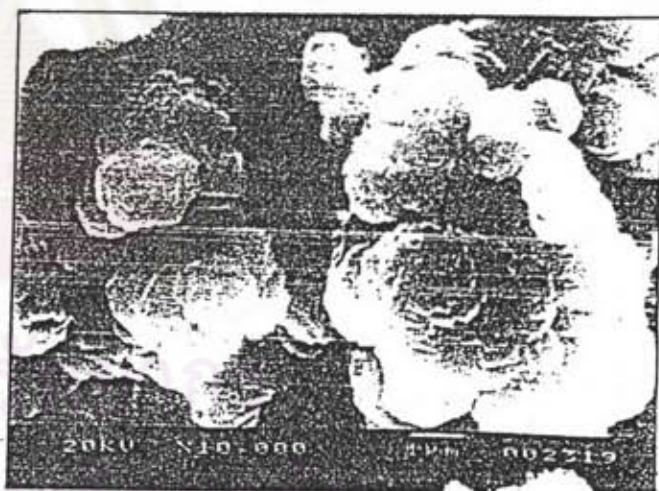
(a)



(b)



(c)



(d)

Figure 5.3 SEM photographs of metal loaded and non-loaded H-ZSM-5 catalysts. (a) H-ZSM-5. (b) 0.50%Pt/H-ZSM-5. (c) 0.50% Re/H-ZSM-5. and (d) 0.02%Re-0.50%Pt/H-ZSM-5.

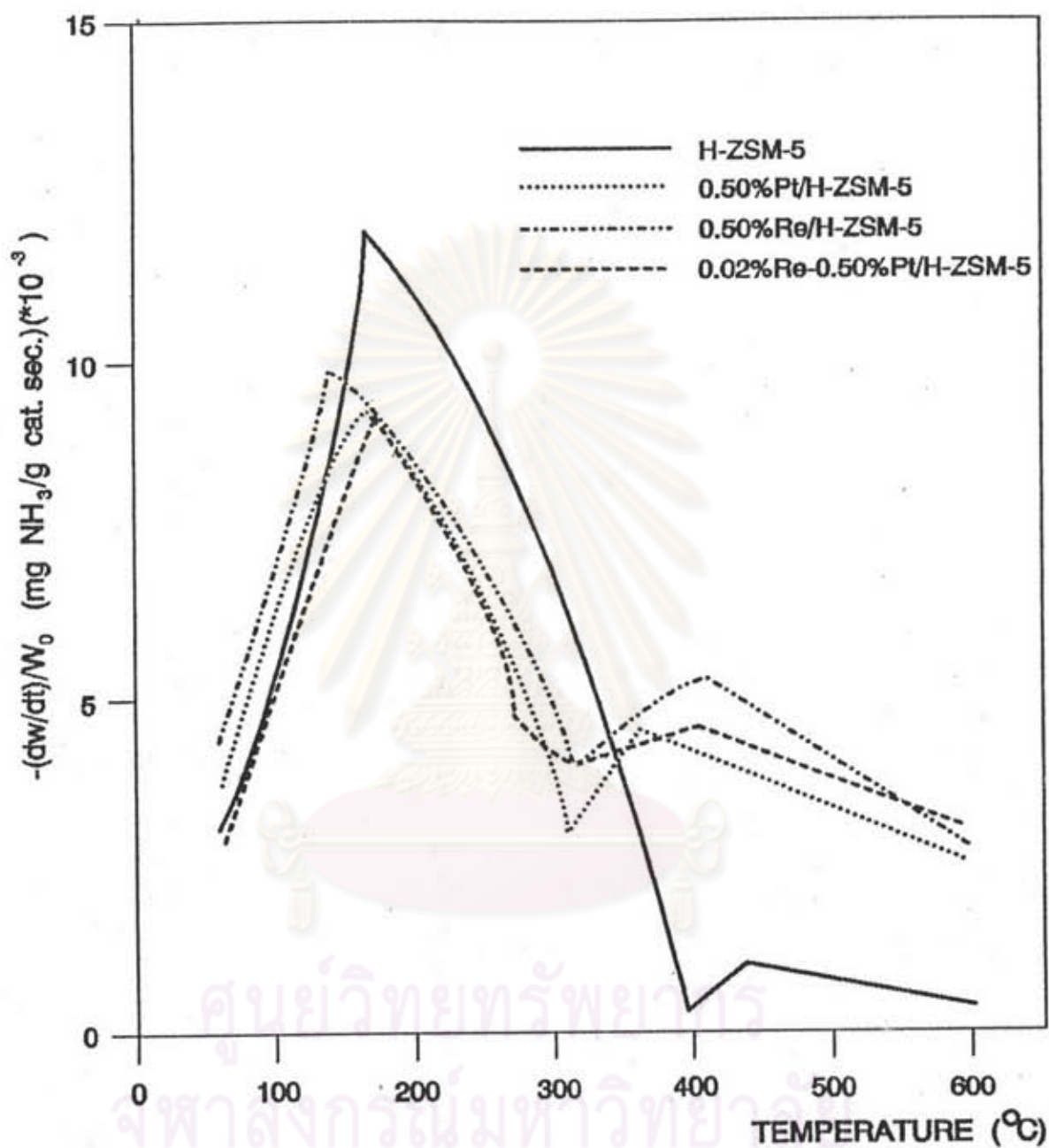


Figure 5.4 TPD profile of desorbed NH₃ from metal loaded and non-loaded H-ZSM-5 catalysts.

loading on H-ZSM-5 were higher than the parent H-ZSM-5 catalyst, but weak acid sites were lower than the parent H-ZSM-5 catalyst. This indicates that the strong acid sites from the parent H-ZSM-5 catalyst were increased by the metal loading on H-ZSM-5.

5.5 Mole Ratio Si/Al of H-ZSM-5 Catalyst

By using AA, the mole ratio Si/Al of H-ZSM-5 catalyst, prepared in this study, was about 98.

5.6 Effect of Reaction Temperature on H-ZSM-5 Catalyst

The effect of reaction temperature on the product distribution was considered. The methanol conversion on H-ZSM-5 (Si/Al=50) was carried out at GHSV $2,000 \text{ h}^{-1}$, feed gas mixture of 20% MeOH and 80% N_2 and 1 h on stream. In the whole temperature range (300, 350, 400, and 450°C) tested, the methanol conversion was completed. The hydrocarbon distribution obtained at each temperature is shown in Figure 5.5. The selectivity to aromatics increased when the reaction temperature increased, but it decreased abruptly after the temperature over 400°C . Figure 5.6 shows the percentage of aromatics relative with time on stream at the reaction temperature 400 and 450°C . For the first 30 min on stream, the amount of aromatics at 450°C were higher than the amount of aromatics at 400°C . However, when the reaction was operated over 30 min until steady state, the amount of aromatics at 400°C were higher than those at 450°C . This result can be explained that, at high temperature, some

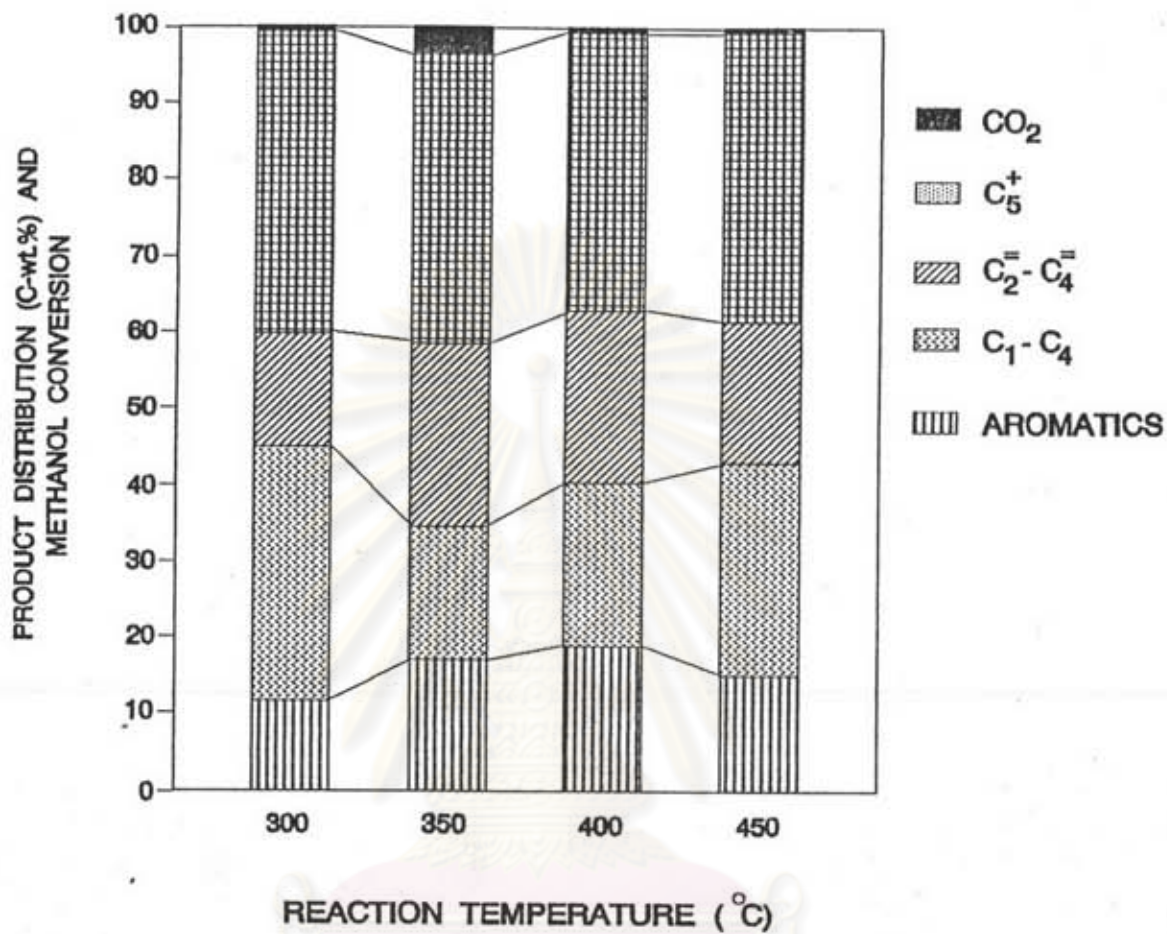


Figure 5.5 Effect of reaction temperature on product distribution on H-ZSM-5 catalyst.

Condition: 20% MeOH and 80% N₂; GHSV 2,000 h⁻¹;
time on stream 1 h.

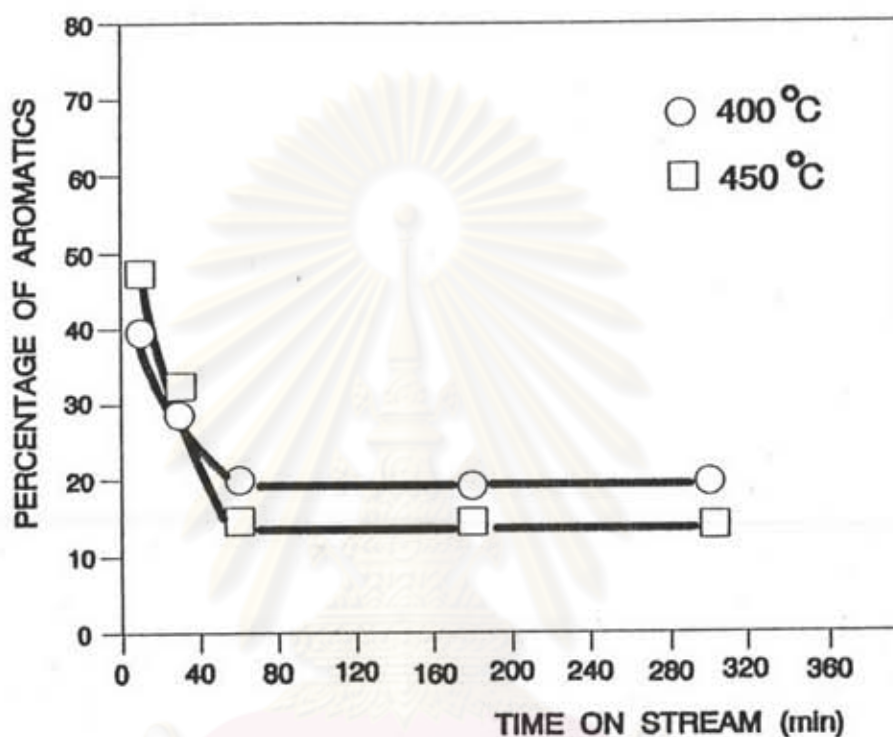


Figure 5.6 The percentage of aromatics relative with time on stream at two reaction temperatures
Condition ; 20% MeOH and 80% N₂, GHSV 2,000 h⁻¹.

strong acid sites of the catalyst are covered by carbonaceous compounds during the early 1 hour on stream.

5.7 Effect of Pt Ion-exchanged H-ZSM-5 Zeolite Catalyst

The hydrocarbon distribution of methanol conversion on Pt ion-exchanged H-ZSM-5 zeolite catalyst of various percentage of Pt-- 0.25, 0.50, 0.75, and 1.00 wt.% (the calculation see appendix A-3)-- are shown in Table 5.2 and Figure 5.7. Methanol was completely converted to hydrocarbons for all percentage of Pt loading on H-ZSM-5 zeolite catalysts. The reaction was carried out at the reaction temperature of 400°C, 20% MeOH and 80% N₂, GHSV 2,000 h⁻¹ and 1 hour on stream. As shown in Figure 5.7, the Pt/H-ZSM-5 catalysts were much more active than the parent H-ZSM-5. The selectivity to aromatics and C₁-C₄ paraffins on Pt/H-ZSM-5 catalysts were considerably higher than selectivity of the parent H-ZSM-5. When increase the percentage of Pt, the selectivity to aromatics and C₁-C₄ paraffins were also increased. On the other hand, the selectivity to C₅⁺ and C₂⁼-C₄⁼ decreased with the increase in percentage of Pt. Thus, the presence of Pt in H-ZSM-5 crystal greatly increases the selectivity to aromatics in the reaction of higher paraffins (C₅⁺). However, the small amount of the initial intermediate products (ethylene, propylene, and butene) in the output stream were observed. These results suggest that higher paraffins in the product are converted to olefins on Pt by dehydrogenation reaction. The olefins, which occurred on Pt, are transferred and converted to aromatics and lower hydrocarbons on the strong acid site of H-ZSM-5. This reaction

Table 5.2 Product distribution of Pt loading on H-ZSM-5.

Condition; reaction temperature 400°C; 20% MeOH and 80% N₂, GHSV 2,000 h⁻¹, time on stream 1 h.

| Product Distribution (C-wt.%) | % Pt/H-ZSM-5 Catalyst | | | | |
|----------------------------------|-----------------------|-------|-------|-------|-------|
| | 0.00 | 0.25 | 0.50 | 0.75 | 1.00 |
| C ₁ | 0.96 | 0.78 | 0.93 | 1.46 | 2.31 |
| C ₂ -C ₄ | 24.92 | 31.09 | 34.69 | 44.56 | 51.16 |
| C ₂ ⁼ | 8.86 | 5.30 | 3.55 | 1.03 | 0.27 |
| C ₃ ⁼ | 13.04 | 7.79 | 6.14 | 3.81 | 2.52 |
| C ₄ ⁼ | 10.92 | 7.89 | 6.03 | 3.19 | 0.93 |
| C ₅ ⁺ | 21.42 | 16.94 | 14.24 | 10.25 | 7.88 |
| Aromatics | 19.68 | 29.78 | 33.82 | 34.48 | 32.04 |
| CO ₂ | 0.19 | 0.43 | 0.60 | 1.22 | 2.89 |
| CO | 0 | 0 | 0 | 0 | 0 |
| Benzene | 1.03 | 1.27 | 1.58 | 1.66 | 1.57 |
| Toluene | 4.26 | 6.07 | 7.21 | 7.11 | 6.32 |
| Xylene | 10.11 | 15.59 | 17.55 | 18.40 | 17.10 |
| Other aromatics | 4.28 | 6.85 | 7.48 | 7.31 | 7.05 |
| Dimethyl ether | 0 | 0 | 0 | 0 | 0 |
| MeOH conversion (%) | 100 | 100 | 100 | 100 | 100 |

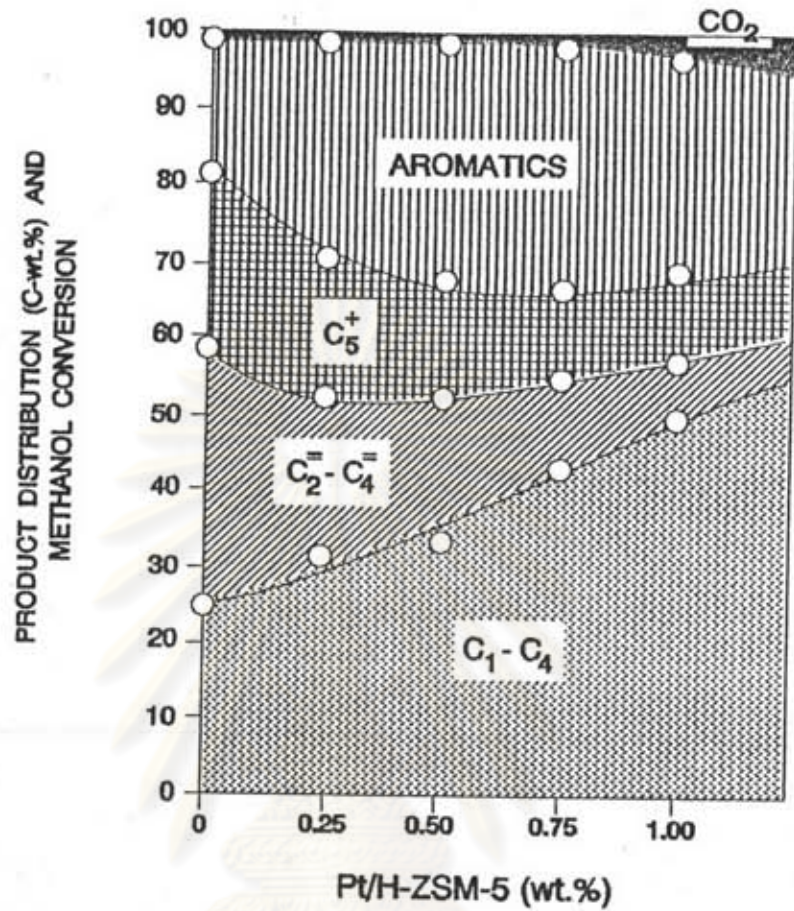


Figure 5.7 Effect of Pt on product distribution when vary percentage of Pt loading on H-ZSM-5 catalyst.

Condition; reaction temperature 400°C; 20% MeOH and 80%

N₂, GHSV 2,000 h⁻¹, time on stream 1 h.

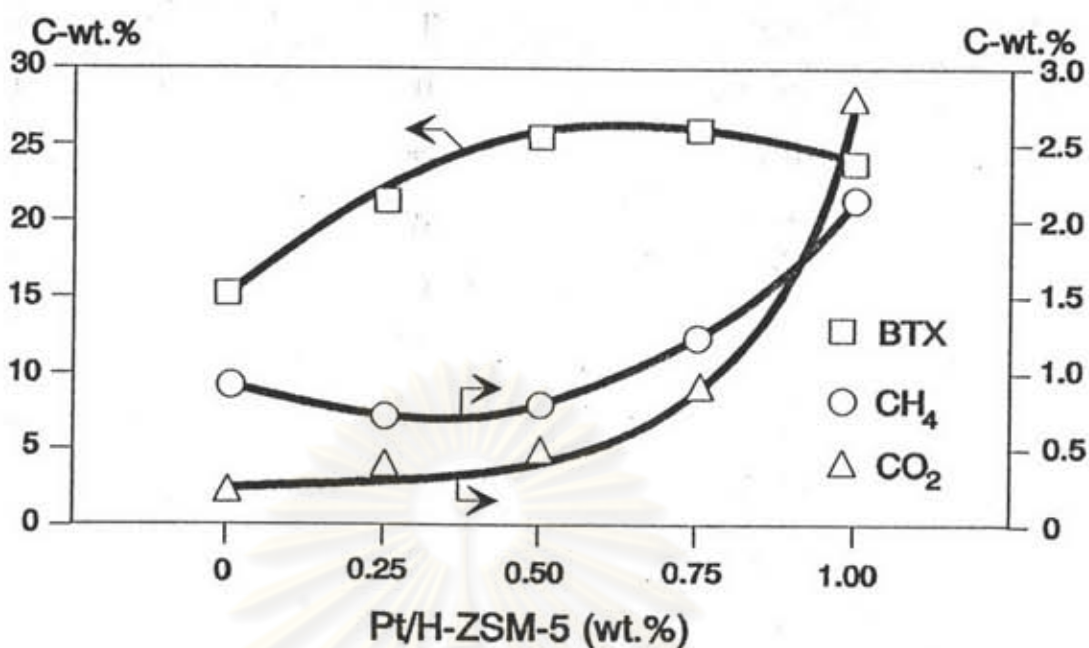


Figure 5.8 Relative between percentage of BTX, CH₄ and CO₂ on Pt loading on H-ZSM-5

sequence may lead to the higher selectivity to aromatics on Pt/H-ZSM-5.

Figure 5.8 shows the percentage of BTX (Benzene, Toluene, Xylene) as the main products of aromatics, CO₂, and CH₄ of product distribution versus the percentage of Pt loading. At 0.50 and 0.75 wt% Pt/H-ZSM-5 gave the highest percentage of BTX. But, at 0.75 wt% Pt/H-ZSM-5 gave percentage of CO₂ and CH₄ much higher than 0.50 wt% Pt/H-ZSM-5. Therefore, 0.50 wt% Pt/H-ZSM-5 is the optimum value which giving high BTX but low CO₂ and CH₄.

5.8 Effect of Re Ion-exchanged H-ZSM-5 Zeolite Catalyst

As shown in Table 5.3 and Figure 5.9, the effect of Re on

Table 5.3 Product distribution of Re loading on H-ZSM-5.

Condition; reaction temperature 400°C; 20% MeOH and 80%
N₂, GHSV 2,000 h⁻¹, time on stream 1 h.

| Product Distribution (C-wt.%) | % Re/H-ZSM-5 Catalyst | | | | |
|----------------------------------|-----------------------|-------|-------|-------|-------|
| | 0.00 | 0.25 | 0.50 | 0.75 | 1.00 |
| C ₁ | 0.96 | 0.75 | 0.81 | 0.69 | 0.87 |
| C ₂ -C ₄ | 24.92 | 29.96 | 28.12 | 31.68 | 32.51 |
| C ₂ ⁼ | 8.86 | 5.95 | 6.40 | 5.37 | 5.18 |
| C ₃ ⁼ | 13.04 | 8.36 | 9.66 | 7.71 | 6.93 |
| C ₄ ⁼ | 10.92 | 8.35 | 10.94 | 8.34 | 6.82 |
| C ₅ ⁺ | 21.42 | 18.00 | 20.24 | 17.84 | 16.96 |
| Aromatics | 19.68 | 28.24 | 23.61 | 27.96 | 30.34 |
| CO ₂ | 0.19 | 0.39 | 0.22 | 0.41 | 0.39 |
| CO | 0 | 0 | 0 | 0 | 0 |
| Benzene | 1.03 | 1.07 | 1.01 | 1.06 | 1.08 |
| Toluene | 4.26 | 5.17 | 4.75 | 5.17 | 5.32 |
| Xylene | 10.11 | 14.65 | 12.10 | 14.37 | 14.87 |
| Other aromatics | 4.28 | 7.35 | 5.75 | 7.36 | 9.07 |
| Dimethyl ether | 0 | 0 | 0 | 0 | 0 |
| MeOH conversion (%) | 100 | 100 | 100 | 100 | 100 |

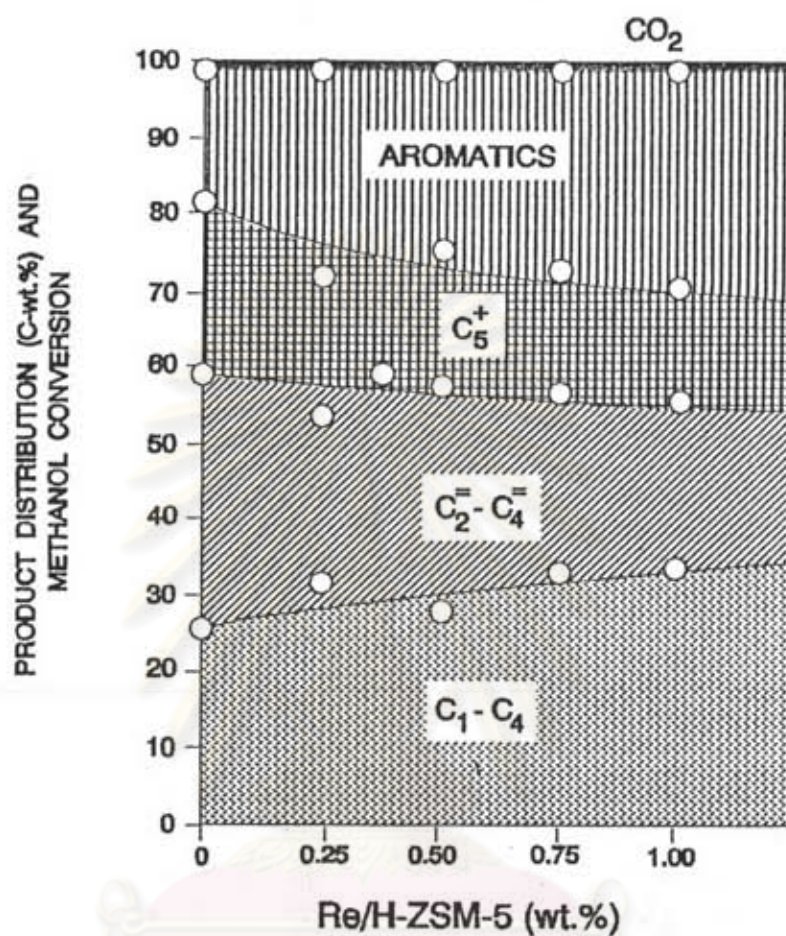


Figure 5.9 Effect of Re on product distribution when vary percentage of Re loading on H-ZSM-5 catalyst.

Condition; reaction temperature 400°C; 20% MeOH and 80% N₂, GHSV 2,000 h⁻¹, time on stream 1 h.

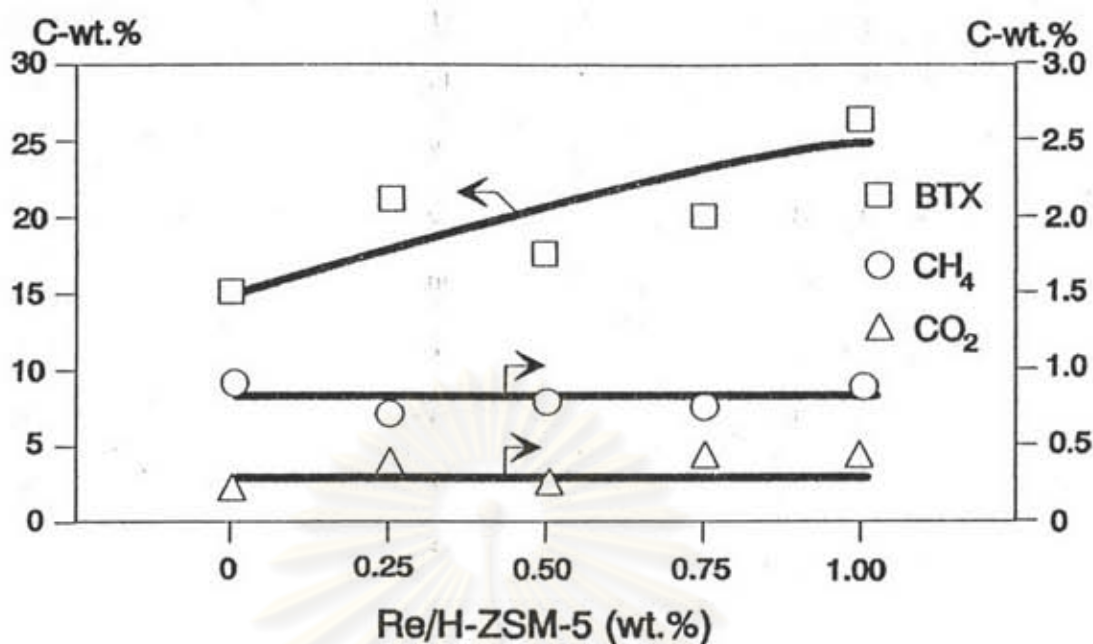


Figure 5.10 Relative between percentage of BTX, CH₄ and CO₂ on Re loading on H-ZSM-5 catalyst.

the product distribution was observed at the same condition as 5.2. The percentage of Re used was 0.25, 0.50, 0.75, and 1.00 wt.%, respectively (the calculation see Appendix A-3). The methanol was completely converted to hydrocarbons on all percentage of Re loading on H-ZSM-5 zeolite catalyst. The selectivity to aromatics of all percentage of Re ion-exchange H-ZSM-5 was not different but still higher than the selectivity of the parent H-ZSM-5. The C₂-C₄ olefins and C₅⁺ hydrocarbon decreased slightly with the increase in percentage of Re. On the other hand, C₂-C₄ paraffins increased slightly with the increase in percentage of Re. The selectivity to CO₂ and CH₄ was not significantly different (see Figure 5.10). Therefore, the action of Re is more moderated than the action of Pt on the same H-ZSM-5 catalyst.

5.9 Effect of Pt and Re Ion-exchanged H-ZSM-5 Zeolite Catalyst

In this study, the use of Pt loading on H-ZSM-5 zeolite catalyst was constant at 0.50 wt% with varying in percentage of Re (0.01, 0.02, 0.05, and 0.10 wt.%). The reaction condition was operated at the same condition as 5.2. Table 5.4 and Figure 5.11 show the product distribution at 1 h on stream. The results of the product selectivities were not different when percentage of Re was increased. The selectivity to aromatics of all of the Re-Pt/H-ZSM-5 catalysts was higher than the parent H-ZSM-5 catalyst but lower than 0.50%Pt/H-ZSM-5 catalyst. However, the amount of CH₄ and CO₂, of all catalysts (See Figure 5.12), were not different. This suggested that the amount of Re loading do not effect on the product distribution but it will affect on the function of Pt loading on H-ZSM-5 crystal.

5.10 Deactivation of Catalysts on Methanol Conversion Reaction

The deactivation of catalysts was observed. The reaction condition was carried out at the reaction temperature 550°C, GHSV 4,000 h⁻¹, 20% MeOH and 80% N₂ and ca. 100 mg of catalyst. Figure 5.13 shows the methanol conversion versus time on stream of three catalysts (H-ZSM-5, 0.50%Pt/H-ZSM-5, and 0.02%Re-0.50%Pt/H-ZSM-5). It was found that 0.50%Pt/H-ZSM-5 catalyst deactivated after 3 h on stream while 0.02%Re-0.50%Pt/H-ZSM-5 and the parent H-ZSM-5 catalyst deactivated after 4 h and 5 h on stream, respectively. It can be seen that the Pt loading on H-ZSM-5 catalyst deactivated faster than

Table 5.4 Product distribution of Re loading on 0.50%Pt/H-ZSM-5.

Condition; reaction temperature 400°C; 20% MeOH and 80%

N₂, GHSV 2,000 h⁻¹, time on stream 1 h.

| Product Distribution (C-wt.%) | H-ZSM-5 | %Re-0.50%Pt/H-ZSM-5 Catalyst | | | | |
|----------------------------------|---------|------------------------------|-------|-------|-------|-------|
| | | 0.00 | 0.25 | 0.50 | 0.75 | 1.00 |
| C ₁ | 0.96 | 0.93 | 0.89 | 0.81 | 0.95 | 0.94 |
| C ₂ -C ₄ | 24.92 | 34.69 | 32.60 | 29.16 | 32.96 | 32.50 |
| C ₂ ⁼ | 8.86 | 3.55 | 6.83 | 6.35 | 6.71 | 6.78 |
| C ₃ ⁼ | 13.04 | 6.14 | 10.86 | 10.17 | 10.79 | 10.81 |
| C ₄ ⁼ | 10.92 | 6.03 | 7.07 | 10.11 | 6.65 | 6.74 |
| C ₅ ⁺ | 21.42 | 14.24 | 17.41 | 16.92 | 15.90 | 16.29 |
| Aromatics | 19.68 | 33.82 | 23.79 | 25.99 | 25.44 | 25.26 |
| CO ₂ | 0.19 | 0.60 | 0.55 | 0.49 | 0.60 | 0.68 |
| CO | 0 | 0 | 0 | 0 | 0 | 0 |
| Benzene | 1.03 | 1.58 | 1.28 | 1.34 | 1.31 | 1.35 |
| Toluene | 4.26 | 7.21 | 5.63 | 5.91 | 5.70 | 5.85 |
| Xylene | 10.11 | 17.55 | 12.27 | 13.14 | 12.88 | 13.25 |
| Other aro. | 4.28 | 7.48 | 4.62 | 5.60 | 5.55 | 4.81 |
| DME | 0 | 0 | 0 | 0 | 0 | 0 |
| MeOH conv. | 100 | 100 | 100 | 100 | 100 | 100 |

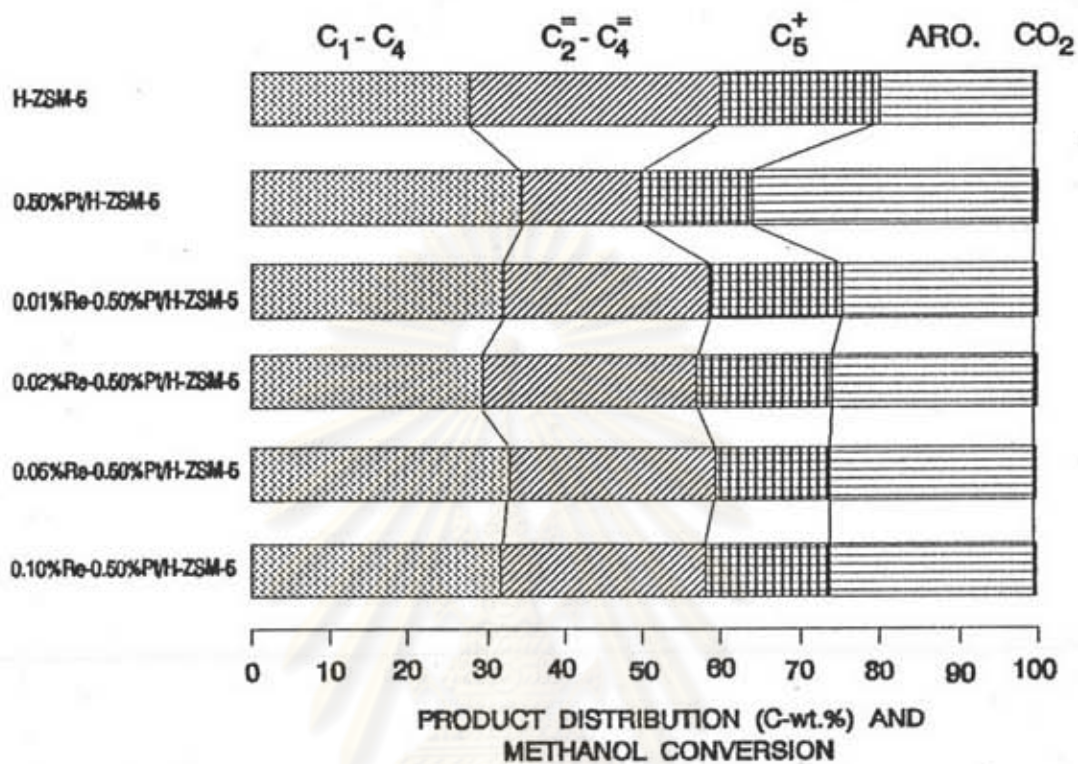


Figure 5.11 Effect of Re-Pt on product distribution when vary percentage of Re loading on 0.50%Pt/H-ZSM-5 catalysts. Condition; reaction temperature 400°C; 20% MeOH and 80% N₂, GHSV 2,000 h⁻¹, time on stream 1 h.

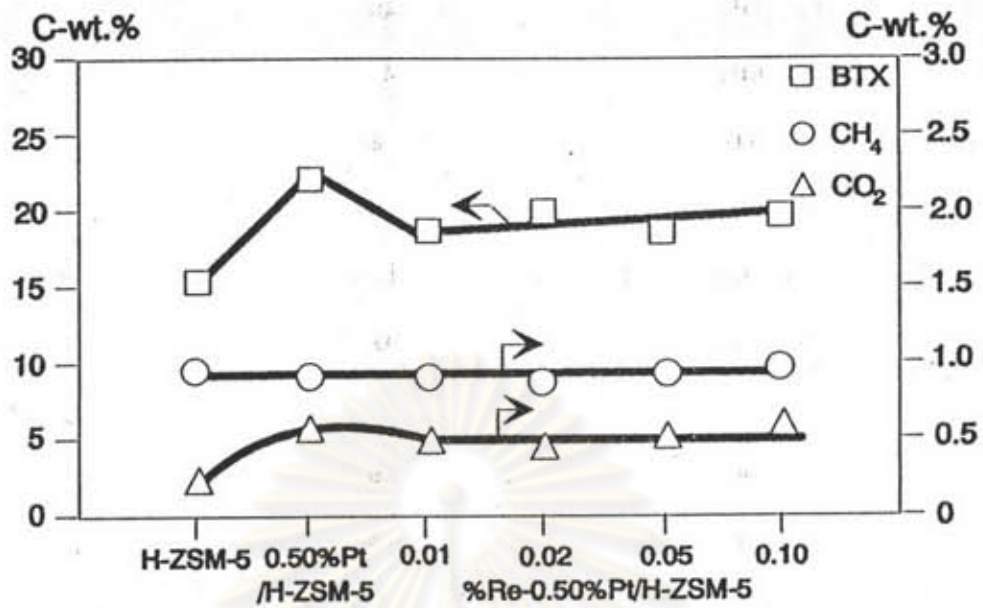


Figure 5.12 Relative between percentage of BTX, CH₄ and CO₂ on Pt and Re-Pt loading on H-ZSM-5 catalysts.

the other two catalysts.

It is clear that the role of Pt as the function of catalyst is the strong dehydrogenation and hydrogenation reaction. Because the Pt has no hydrogen content, It will first act the dehydrogenation reaction and hydrogen spillover from this reaction make the hydrogenation reaction. Many researchers studied about the Pt loading in other catalysts such as Pt/Ga-silicate on propane conversion reaction [110], Pt/H-ZSM-5 on n-hexane and n-octane conversion reaction [111]. They concluded that Pt will convert paraffin hydrocarbon to olefin by using dehydrogenation reaction [110] and this reaction conformed to the result in 5.6.

There was the experiment for determine the Pt particle loading on H-Ga-silicate found that the size of Pt particle is

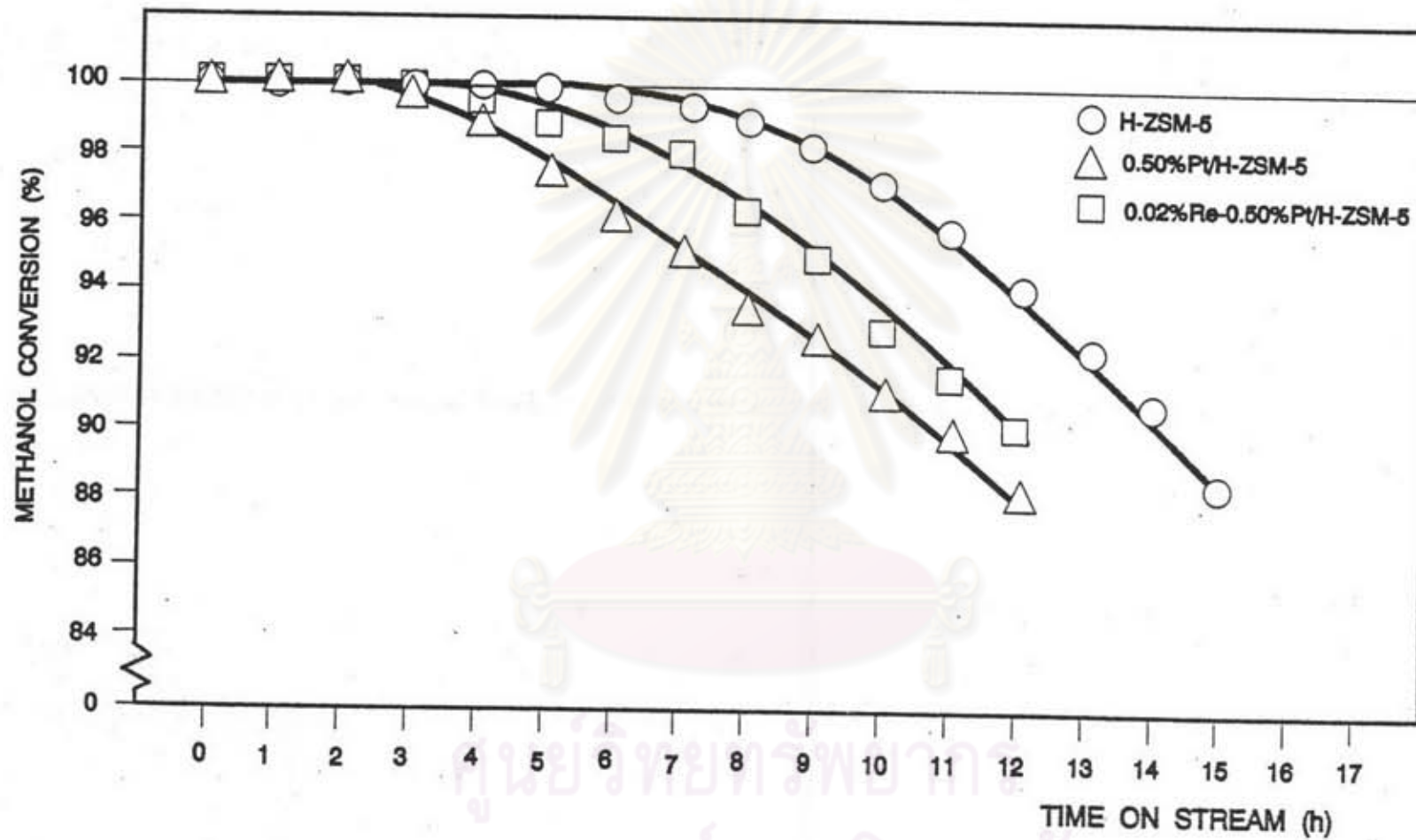


Figure 5.13 The deactivation of catalysts on methanol conversion.

Condition: reaction temperature 550°C; 20% MeOH and

80% N₂; GHSV 4,000 h⁻¹.

larger than pore size of H-Ga-silicate (average diameter of Pt particle ca. 30.4 Å and H-Ga-silicate average pore size diameter ca. 5.5 Å) [112]. This H-Gasilicate was also prepared by quick method so that it was the same structure as H-ZSM-5. However, Pt will also have the location on the outer surface of H-ZSM-5 crystal after ion exchanged.

In Europe, zeolite catalysts were prepared by slow crystallization method (slow method) and added some metal into zeolites called "Metallosilicate" which made catalysts act as bifunctional catalysts. When comparing the metallosilicates prepared by rapid crystallization method (quick method) and slow method, the results showed clearly that the metallosilicate prepared by quick method gave better reaction than the other one. Prof. Tomoyuki Inui (Department head of Hydrocarbon Chemistry, Kyoto University, Japan) suggested that the preparation of quick method will be given the metal cooperated into the structure of the crystal of zeolite, so the reaction could be occurred inside the crystal. That is the reason why metallosilicate prepared by quick method gave the result better than the other one. And also Prof. Piyasan Prasertthdam suggested that all particle sizes of metals have larger than pore size of zeolite, so metals cannot penetrate into the structure of zeolite in both methods. So it may locate at the outer surface of zeolite crystal. However, the metallosilicate prepared by quick method giving the smaller crystal than the other one which is encouraged to be better in term of reaction. When compared active sites per gram of catalysts, the catalysts prepared by quick method have higher active sites than slow method. When the metal was added into the

crystal, It still located on the outer surface of crystal and the amount of metal site per gram of catalyst prepared by quick method was also higher than that from the slow method. That is the reason why the metallosilicate catalyst prepared by quick method has given better reaction.

The effect of Re upon Pt [114] confirmed by the experiment in 5.6, 5.7, and 5.8 show that Pt is the domain catalyst whilst Re have little effect on product distribution (see 5.7). The Re is performed on the dehydrogenation and hydrogenation reaction but not as strong as Pt. Both Pt and Re were reduced to the metallic state, the reduction of the rhenium compound being strongly catalyzed by Pt [113].

There are many researchers studied on the deactivation of Pt loaded and non-loaded catalysts on propane, n-hexane and n-octane [110,111]. They found that Pt give a good reaction because it can increase activity of catalyst and prevent coke formation. Prof. Tomoyuki Inui described the reaction by modelling the reaction scheme on the light paraffins conversion on Pt/H-Ga-silicate or Pt/H-Zn-silicate [114]. The reaction scheme proposed by Prof. Tomoyuki Inui explained the roles of Pt as follow:

- (a) Dehydrogenation of paraffins to make olefins.
- (b) Porthole for hydrogen spillover prevents the coke formation.

The reaction scheme proposed by Prof. Tomoyuki Inui is shown in Figure 5.14.

In this research, the deactivation of catalysts was studied by using 3 catalysts, i.e., the parent H-ZSM-5, Pt/H-ZSM-5 and

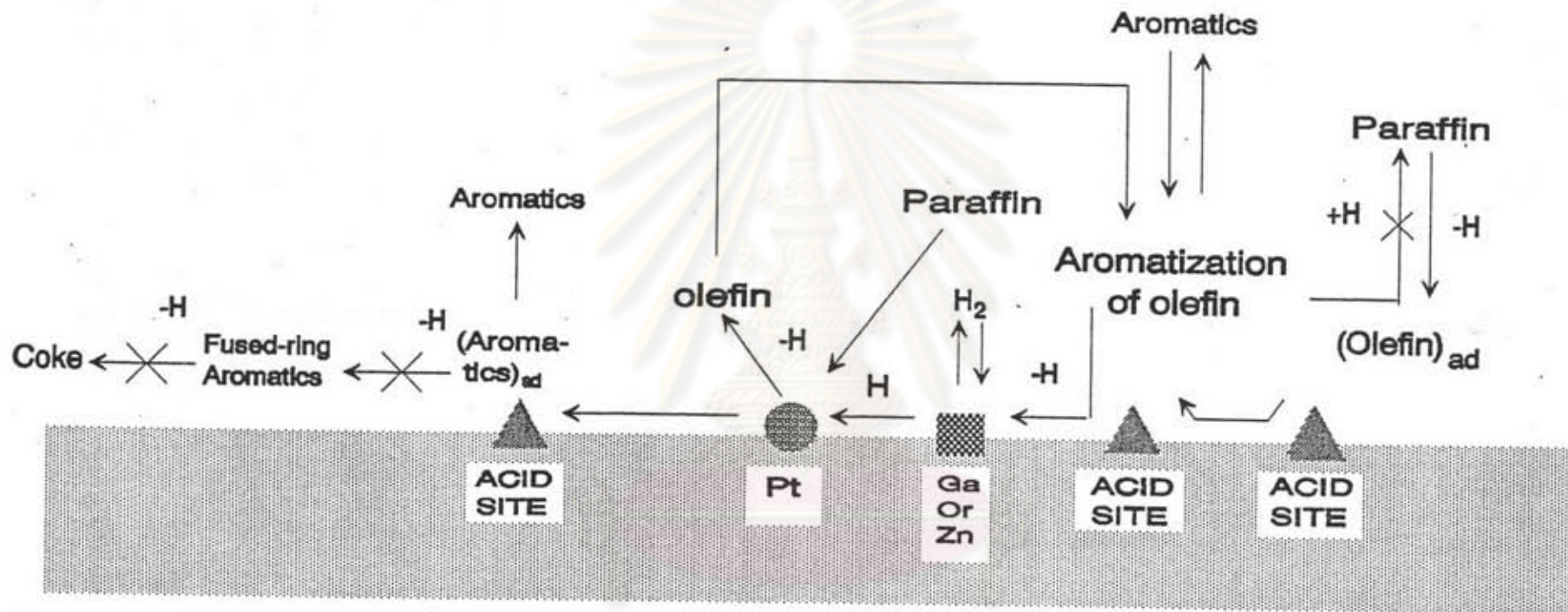
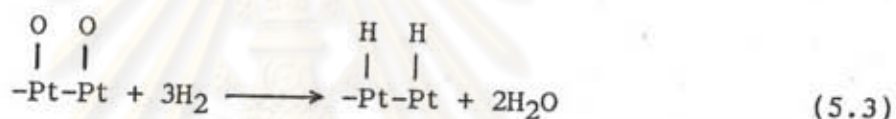
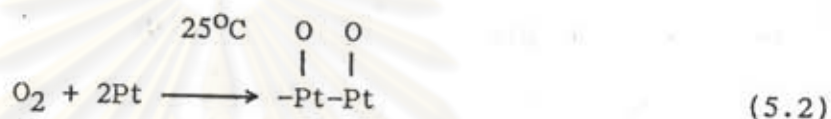
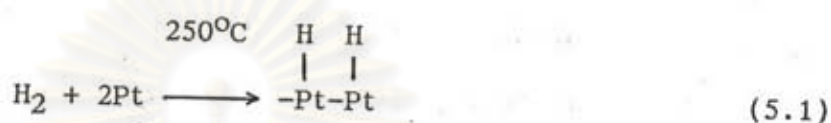


Figure 5.14 The work mechanism of Pt/H-Ga-silicate or Pt/H-Zn-silicate on propane conversion proposed by Prof. Tomoyuki Inui [114].

Re-Pt/H-ZSM-5 on methanol conversion reaction(see 5.9). Surprisingly, the Pt/H-ZSM-5 deactivated faster than the parent H-ZSM-5, the function of Pt can be explained in another important property, that it was a good adsorbent on oxygen and hydrogen. Oxygen will be adsorbed by Pt 3 times better than hydrogen [115] as the equation :



The result of this experiment showed that the reactant methanol was reacted and left oxygen ion on the surface of acid sites of catalyst and Pt. At the same time, Pt played role only on changing n-paraffins to olefins by dehydrogenation reaction. And hydrogen ion from this reaction was caught by oxygen ion on Pt surface, so it could not transfer (or spillover) to acid sites preventing the coke formation (normally, in propane conversion by model proposed by Prof. Tomoyuki Inui as shown in Figure 5.14, which hydrogen ion from dehydrogenation reaction will go to prevent coke formation on acid site). Olefins from the Pt can generate large amount of coke at nearby acid site which located at the outer surface of catalyst. It would make the pore mouth blockage. This pore mouth blockage made Pt/H-ZSM-5 to deactivate rapidly and faster than the parent H-ZSM-5 catalyst. The model of this deactivation can explain in Figure 5.15.

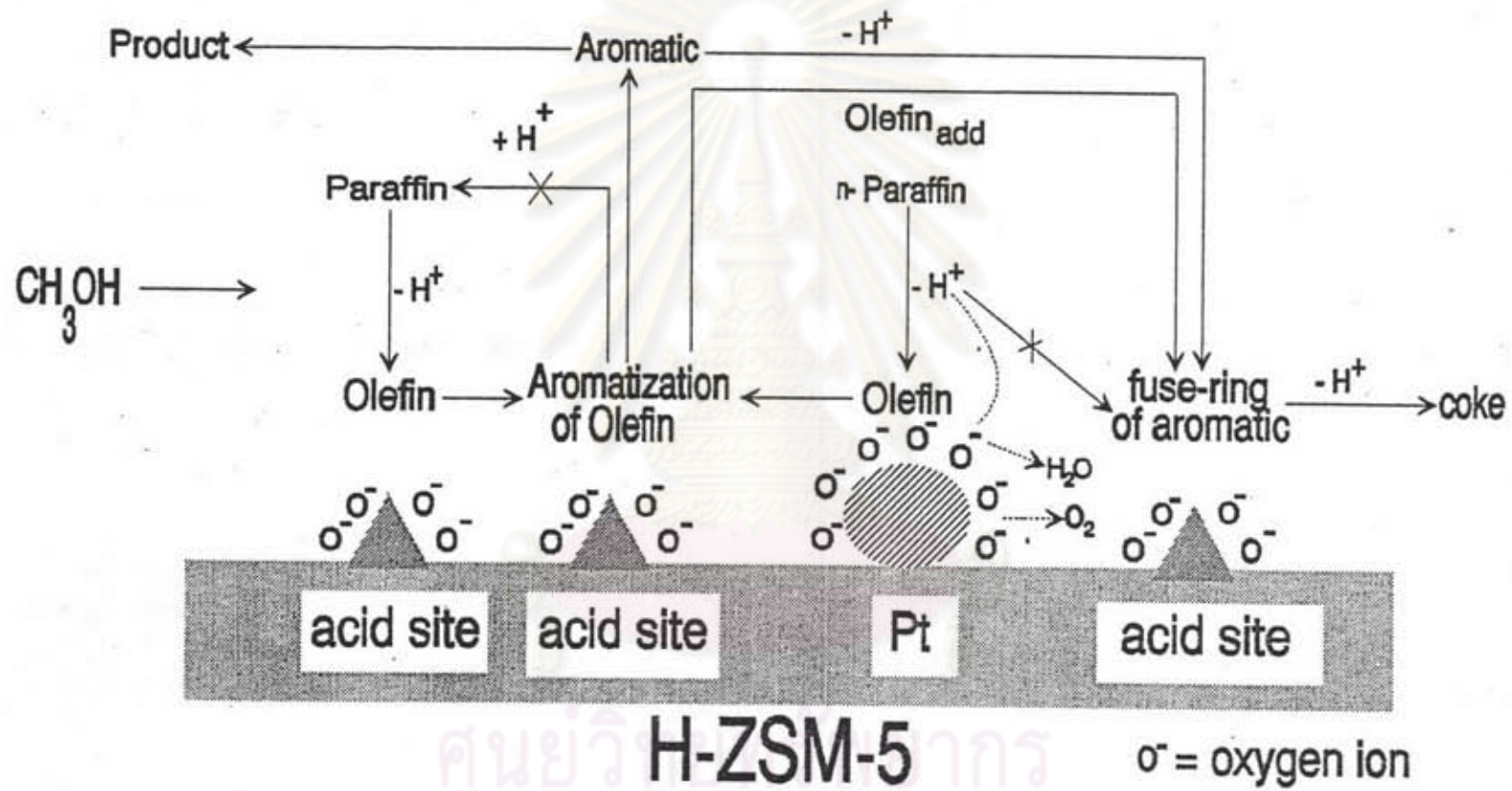


Figure 5.15 The work mechanism of Pt/H-ZSM-5 on MeOH conversion.

For Re added catalyst, it had effected on Pt by sharing oxygen ion and make the decreasing in density of oxygen ion on the surface of Pt [113]. When the density of oxygen ion on the surface of Pt decreased, it made some hydrogen ion spillover to the acid site and finally prevent coke formation. This result supported that the deactivation of Re-Pt/H-ZSM-5 are much slower than the deactivation of Pt/H-ZSM-5 but still faster than that of the parent H-ZSM-5. The model of the reaction on Re-Pt/H-ZSM-5 is shown in Figure 5.16.

To confirmed both models by checking BET surface area after operation the reaction 12 h on stream, the residue surface area of Re-Pt/H-ZSM-5 was higher than the residue surface area of Pt/H-ZSM-5 but still less than the residue surface area of parent H-ZSM-5 (see Table 5.1). The acidity of metal loaded H-ZSM-5 have the strong acid site higher than the parent H-ZSM-5. This is the good evident to support that the aromatics and coke occur on the strong acid site. Therefore, the metal loaded H-ZSM-5 catalyst gave much more aromatics and coke than the parent H-ZSM-5 catalyst.

ศูนย์วิทยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย

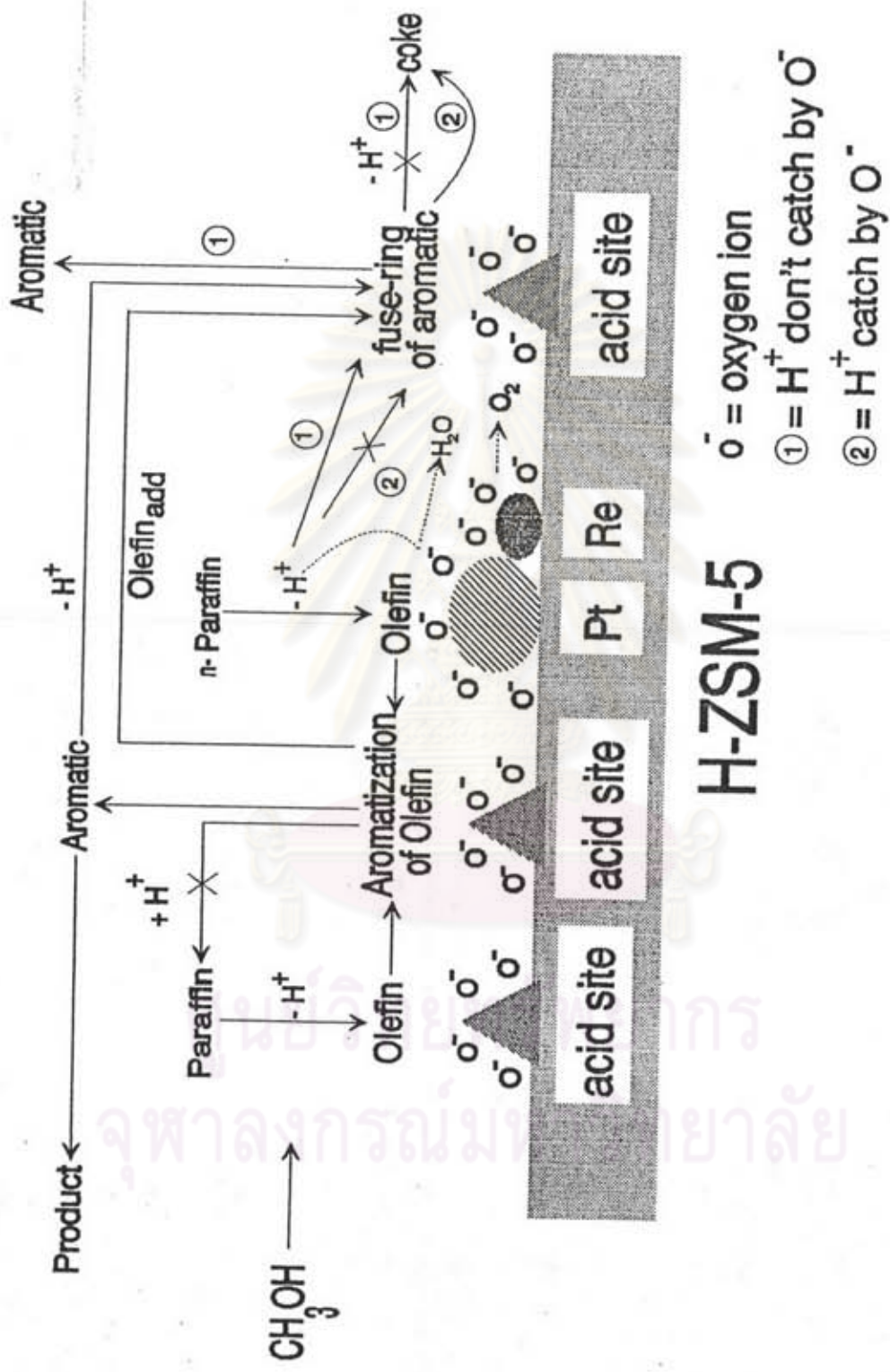


Figure 5.16 The work mechanism of Re-Pt/H-ZSM-5 on MeOH conversion.