# CHAPTER IV
RESULTS AND DISCUSSION

4.1 Catalyst Characterization

Characterization methods are used to study the properties and characteristics of the prepared catalysts. The different treatment temperatures, treatment gases and silica to alumina ratios of ZSM-5 are affected to the activity and selectivity of the catalyst, so characterization methods are important for analytical catalysts. The characterization techniques utilized in this work are presented in detail.

4.1.1 Temperature program reduction (TPR)

4.1.1.1 TPR of indium(III)oxide

In Figure 4.1, temperature program reduction measurement is carried out to estimate the reduction behavior of the indium(III)oxide. The reduction peak shows that at the reduction temperature higher to 950 °C, In^{3+} change into metallic indium (In^{0}) form. Due to the crystallite form of indium(III)oxide, the reduction of indium(III)oxide into metallic indium (In^{0}) requires high temperature (Solt et al., 2008).
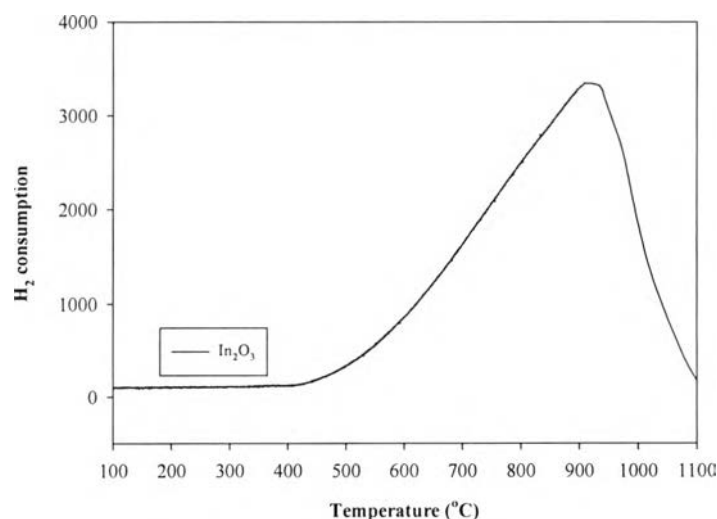
Figure 4.1 H_2-TPR profiles of indium(II)oxide.

4.1.1.2 TPR of physical mixing $In_2O_3/HZSM-5$

TPR technique is used to examine the reduction profiles of the catalysts. Figure 4.2 shows the TPR profiles of physical mixing $In_2O_3/HZSM-5$ with SiO_2/Al_2O_3 ratio of HZSM-5 23, 30, 50, 80 and 280 and In/Al ratio 0.5. The temperature reduction peak of indium exhibit a broad peak situated in the range of 600 to 800 °C that is referred to the bulk reduction from In_2O_3 to In^{2+}, In^{1+} and In^0.
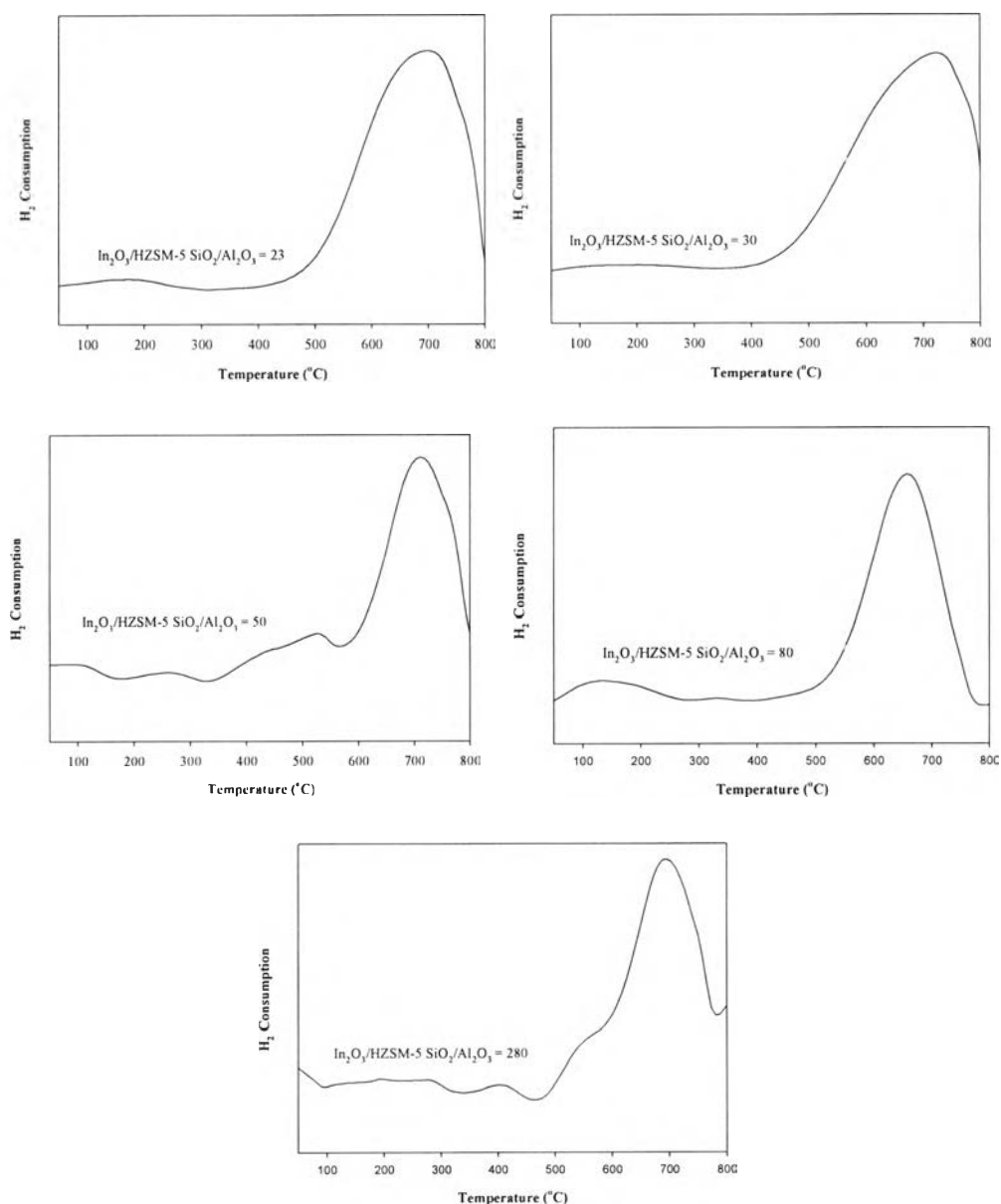
Figure 4.2 H_2-TPR profiles of physical mixing $In_2O_3/HZSM-5$ with SiO_2/Al_2O_3 of HZSM-5 23, 30, 50, 80 and 280 and In/Al ratio 0.5.

4.1.2 X-ray diffraction spectroscopy (XRD)

To investigate the changes on the crystalline structure of HZSM-5, physical mixing In_2O_3/HZSM-5 and In/HZSM-5 which produced by hydrogen treatment, oxygen treatment and hydrogen followed by oxygen treatment, XRD measurements were carried out. The main diffraction peaks of crystalline In_2O_3 show at 2 Theta = 30.64°, 35.48°, 51.16° and 60.80° as shown in Figure 4.3 with circle signal. For In/HZSM-5 under oxygen treatment the peaks of crystalline In_2O_3 are detected the same peaks as physical mixing In_2O_3/HZSM-5. But for In/HZSM-5 under hydrogen treatment and In/HZSM-5 under hydrogen followed by oxygen treatment the peaks of In_2O_3 phase are not observed. According to under these treatments condition, indium is well dispersed in support HZSM-5. Therefore, it can be concluded that indium is presumably located in In/HZSM-5 as a charging balancing species.
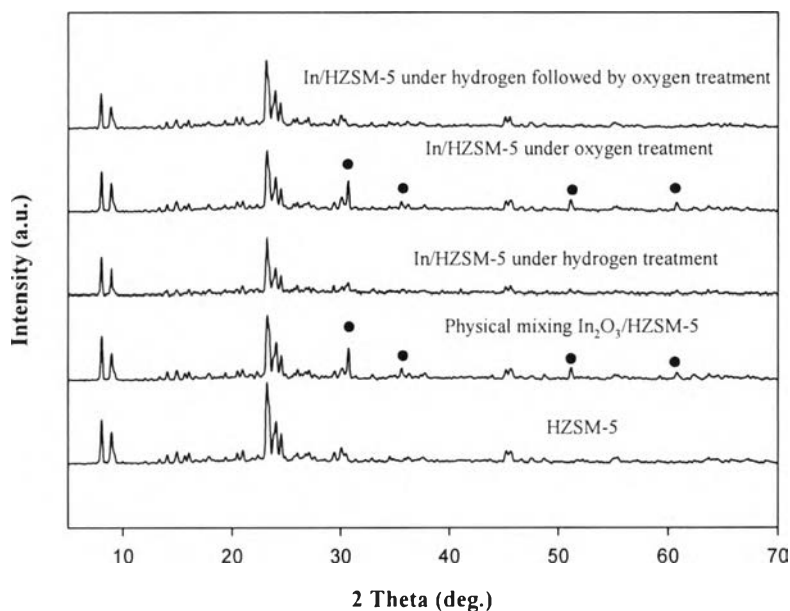
Figure 4.3 X-ray diffraction patterns of HZSM-5, physical mixing In_2O_3/HZSM-5, In/HZSM-5 under hydrogen treatment, In/HZSM-5 under oxygen treatment, and In/HZSM-5 under hydrogen followed by oxygen treatment.

4.1.3 X-ray fluorescence spectroscopy (XRF)

X-ray fluorescence spectroscopy is a non-destructive analytical technique which used to identify and determine the actual metal loading of indium to aluminum ratios 0.1, 0.3, 0.5 and 1.0 and composition of H-ZSM-5 with different SiO_2/Al_2O_3 ratios of HZSM-5 23, 30, 50, 80 and 280. The results in Table 4.1 showed the measured indium loading on the support H-ZSM-5. The results measured from X-ray fluorescence technique are similar with the actual loading.

**Table 4.1** XRF of H-ZSM-5 with different SiO_2/Al_2O_3 ratios and In/Al ratios

SiO_2/Al_2O_3	In/Al 0.1	In/Al 0.3	In/Al 0.5	In/Al 1.0
23	0.09	0.28	0.51	0.91
30	0.09	0.24	0.54	0.90
50	0.09	0.26	0.57	0.92
80	0.09	0.29	0.58	0.95
280	0.11	0.24	0.59	0.96

4.1.4 UV-visible spectroscopy

4.1.4.1 UV-visible spectrum of indium(III)oxide physically mixed with ZSM-5 and treated In_2O_3/HZSM-5

UV-visible spectrum of indium(III)oxide physically mixed with HZSM-5 and In_2O_3/ZSM-5 treated in different atmosphere are showed in Figure 4.4. Indium(III)oxide physically mixed with HZSM-5 shows the intensive peak around 350 nm as same as In_2O_3/ZSM-5 treated in oxygen atmosphere. But indium(III)oxide shows a higher intensity than In_2O_3/ZSM-5 treated in oxygen atmosphere. Referring to the XRD result, In/HZSM-5 treated in oxygen treatment shows the peaks of crystalline In_2O_3 the same peaks as physical mixing In_2O_3/HZSM-5. So both the results of XRD and UV-visible spectroscopy use to confirm that In_2O_3/ZSM-5 treated in oxygen atmosphere does not change to active species which may indicate to the remaining of indium(III)oxide species. The UV-

visible spectrum of In_2O_3/ZSM-5 treated in hydrogen and hydrogen followed by oxygen atmosphere differ from In_2O_3/ZSM-5 treated in oxygen atmosphere. These results can support the concept that hydrogen and hydrogen followed by oxygen treatment provided the different species which may be attributed to the indium cation.
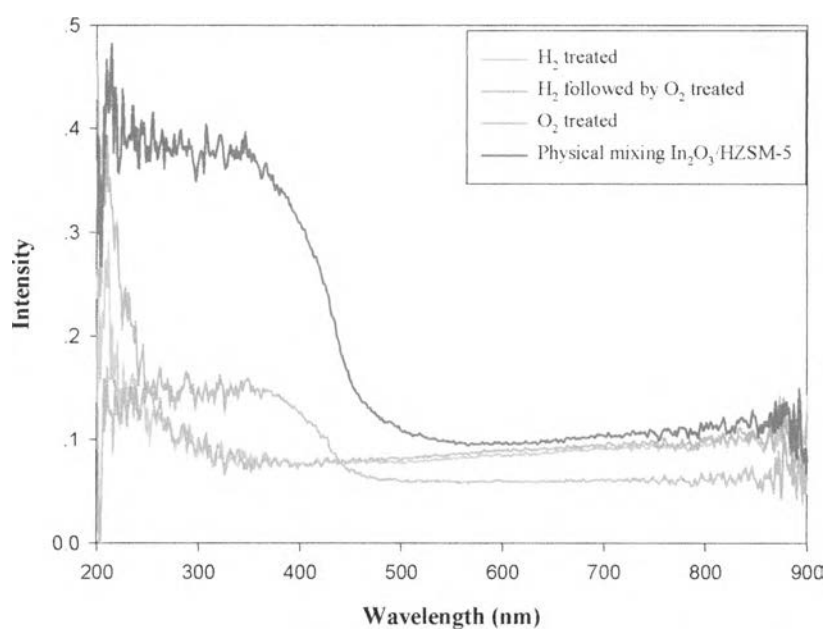
Figure 4.4 UV-Visible spectrum of In_2O_3 physically mixed with ZSM-5 and In_2O_3/ZSM-5 treated in different atmosphere in the range of 200 to 900 nm.

4.1.5 Surface Area Analysis

Table 4.2 shows the BET surface area of HZSM-5 catalyst with silica/alumina ratio of 23, 30, 50, 80 and 280. The surface area of HZSM-5, SiO_2/Al_2O_3 280 shows the highest area.

Table 4.2 BET surface area of HZSM-5 catalysts

Sample	BET surface area (m^2/g)
HZSM-5 SiO_2/Al_2O_3 23	353.2
HZSM-5 SiO_2/Al_2O_3 30	358.1
HZSM-5 SiO_2/Al_2O_3 50	361.4
HZSM-5 SiO_2/Al_2O_3 80	380.0
HZSM-5 SiO_2/Al_2O_3 280	427.9

After mixed with In_2O_3, the catalysts surface area decrease (Table 4.3) and continue to decrease after further treatment (Table 4.4). In the group of treated catalyst (O_2, H_2 and H_2 followed by O_2), the surface area of catalyst from each treatment gas shows insignificant different to the others.

Table 4.3 BET surface area of physical mixing catalysts

Sample	BET surface area (m^2/g)
In_2O_3/HZSM-5, SiO_2/Al_2O_3 23	326.8
In_2O_3/HZSM-5, SiO_2/Al_2O_3 30	330.5
In_2O_3/HZSM-5, SiO_2/Al_2O_3 50	337.1
In_2O_3/HZSM-5, SiO_2/Al_2O_3 80	366.0
In_2O_3/HZSM-5, SiO_2/Al_2O_3 280	400.8

Table 4.4 BET surface area of In/HZSM-5 catalysts with different atmospheres

| Sample	BET surface area (m²/g)
In/HZSM-5, SiO_2/Al_2O_3 50 (oxygen treatment)	322.8
In/HZSM-5, SiO_2/Al_2O_3 50 (hydrogen treatment)	317.9
In/HZSM-5, SiO_2/Al_2O_3 50 (hydrogen followed by oxygen treatment)	301.2

4.2 Catalytic activity measurement

The physical mixing In/HZSM-5 was prepared by solid-state ion exchange of HZSM-5 with solid Indium(III)oxide. The prepared catalyst is then packed in the quartz tube reactor for the catalytic activity measurement. To investigate the performance of the prepared catalyst, the effect of treatment gas, treatment temperature, reaction temperature, carrier gas, indium to aluminum ratios, space velocity, methane to benzene feed molar ratio and silica to alumina ratios are studied in detail.

4.2.1 Effect of treatment gas and treatment temperature

The effect of treatment gas and treatment temperature are studied in hydrogen atmosphere in the range of 600 to 800 °C, oxygen atmosphere at 350 °C and hydrogen atmosphere in the range of 600 to 800 °C followed by oxygen atmosphere at 350°C. The other parameters are fixed, the reaction temperature is at 350 °C, the carrier gas is nitrogen, the Indium/Aluminum ratio using value of 0.5, the space velocity (WHSV) at 2.8 h^{-1}, the Methane/Benzene feed ratio equal to 70 and SiO_2/Al_2O_3 of HZSM-5 equal to 50.

The treatment gases (hydrogen, oxygen, and hydrogen followed by oxygen) play a crucial role in the activation of In/H-ZSM-5 as shown in Figure 4.5 and Figure 4.6. Oxygen treatment (oxidation) and hydrogen treatment (reduction)

provide the lowest conversion near zero at the initial time on stream and then drop to zero after time on stream of 40 minute. The treatment gas that provides the highest benzene conversion is hydrogen treatment (reduction) followed by oxygen treatment (oxidation). It provides benzene conversion of 2.0% but rapidly dropped after 40 minute. However, the benzene conversion of this condition also higher than that the catalyst treated by hydrogen and oxygen.
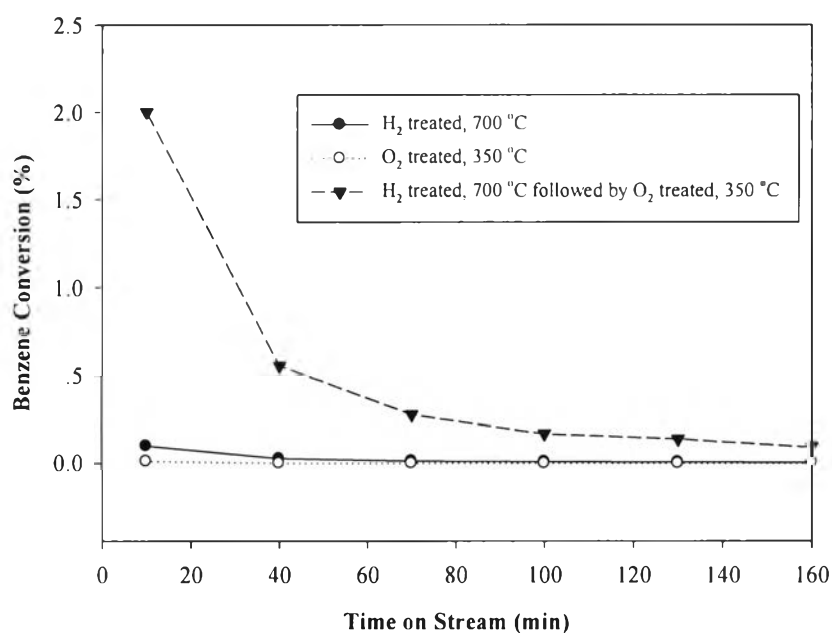
Figure 4.5 Benzene conversion as a function of time on stream at different treatment atmosphere and treatment temperature.
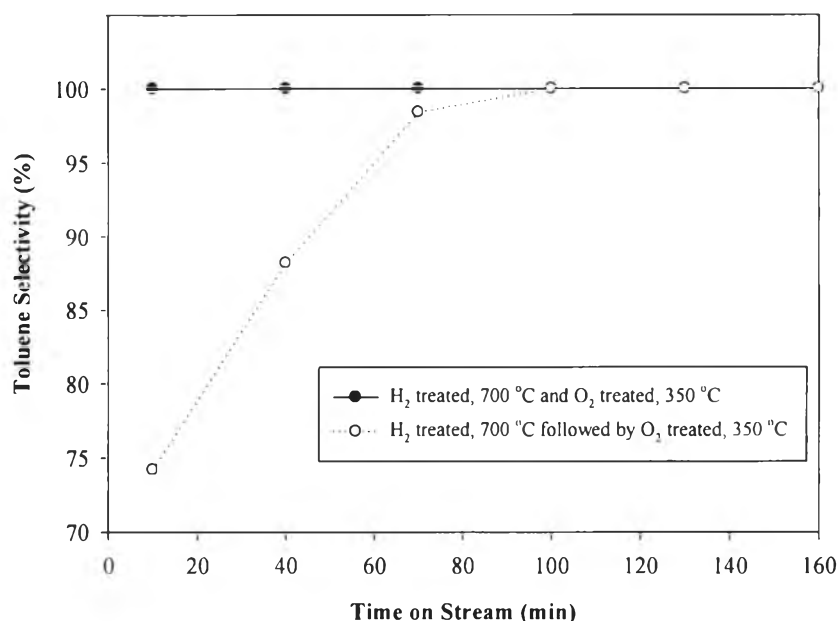
Figure 4.6 Toluene selectivity as a function of time on stream at different treatment atmosphere and treatment temperature.
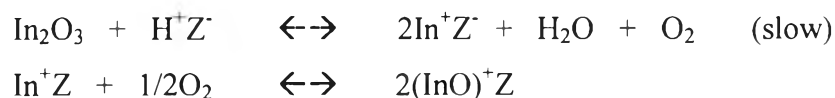
The differences of treatment gas are important for the catalytic activity test. In hydrogen treatment atmosphere, the physical mixing In/H-ZSM-5 can be transformed into In^+ cation (Mihalyi *et al.*, 1998). This mechanism which shown below is called reductive solid-state ion.

$$In_2O_3 + 2H_2 + 2H^+Z^- \quad \longleftrightarrow \quad 2In^+Z^- + 3H_2O$$

The In^+ cation is expected to be an electron donor (or proton accepter) that possibly generates the alkyl intermediate.

However, the activity of oxidative treatment expected to be higher than hydrogen treatment because the mechanism of oxidative solid-state ion generates the active form of oxyindium cation, InO^+ which can act as electron accepter (or hydride accepter) and generates carbenium species.

This type of ion exchange is described by two steps of mechanism as shown below (Schutze *et al.*, 2001).

$$In_2O_3 \; + \; H^+Z^- \quad \longleftrightarrow \quad 2In^+Z^- \; + \; H_2O \; + \; O_2 \quad \text{(slow)}$$

$$In^+Z \; + \; 1/2O_2 \quad \longleftrightarrow \quad 2(InO)^+Z$$

Although the mechanism of oxidative solid-state ion generates the active form of InO^+ cation the activity of oxidative treatment provides the lowest benzene conversion due to the slow step on the first mechanism.

According to the result, the hydrogen treatment (reduction) followed by oxygen treatment (oxidation) gives the highest benzene conversion. In order to get InO^+ cation, the first step of treatment should be hydrogen treatment to obtain In^+ cation and then oxygen treatment step is applied to change In^+ cation form to be InO^+ cation. The mechanism reductive-oxidative solid-state ion is shown below.

$$In_2O_3 \; + \; 2H_2 \; + \; 2H^+Z^- \longleftrightarrow 2In^+Z^- \; + \; 3H_2O$$

$$In^+Z \; + \; 1/2O_2 \quad \longleftrightarrow \quad 2(InO)^+Z$$
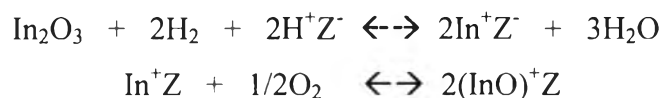
The initial time on stream shows the high conversion which is presumably catalyzed by InO^+ species. Nevertheless, the conversion was found dropped after a short time reaction. This describes by the active InO^+ converted back to In^+ species which may be resulted from two reasons, (1) the reduction of InO^+ by hydrogen formed as a by-product and/or (2) the removing of oxygen atom in InO^+ cation by the formation of water by-product instead of hydrogen.

The hydrogen treatment (reduction) followed by oxygen treatment (oxidation) is further studied in the treatment temperature in the range of 600 to 800 °C in each treatment gas. Figure 4.7 and Figure 4.8 show that the increasing or decreasing of treatment temperature provided insignificant difference in benzene conversion and also toluene selectivity; it majorly depends on treatment atmosphere.
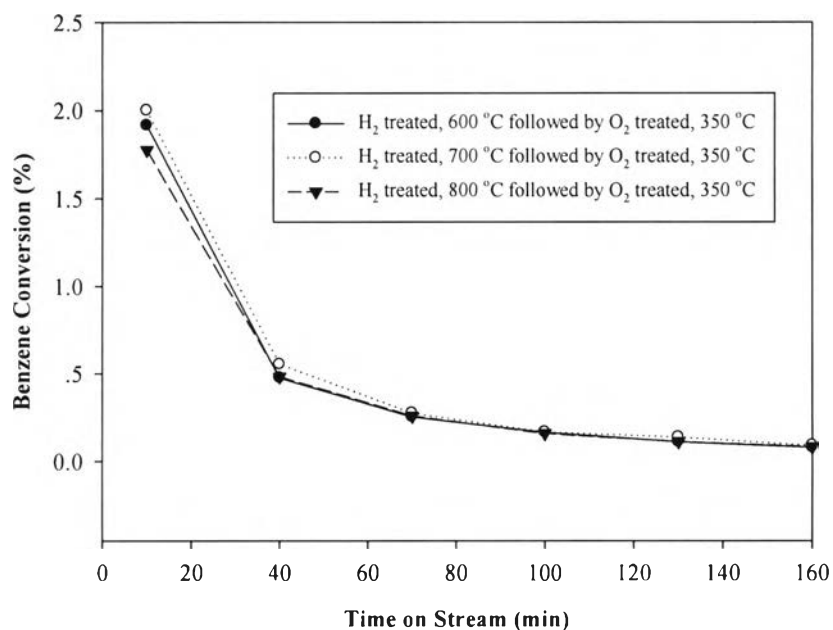
Figure 4.7 Benzene conversion as a function of time on stream at different treatment atmosphere and treatment temperature.
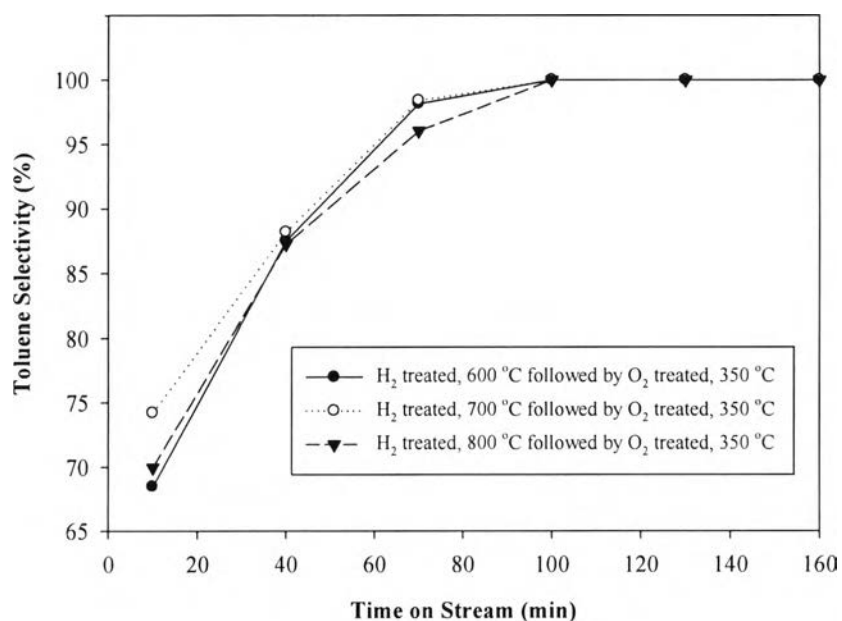

Figure 4.8 Toluene selectivity as a function of time on stream at different treatment atmosphere and treatment temperature.

4.2.2 Effect of reaction temperature

The effect of reaction temperature is studied in the range of 300 to 500 °C. The other parameters are fixed, the treatment atmosphere is in hydrogen at 700 °C followed by oxygen at 350 °C, the carrier gas is nitrogen, the Indium/Aluminum ratio using value of 0.5, the space velocity (WHSV) at 2.8 h^{-1}, the Methane/Benzene feed ratio equal to 70 and SiO_2/Al_2O_3 of HZSM-5 equal to 50.

From the results as shown in Figure 4.10 and Figure 4.11, each reaction temperature; 300, 350, 400, 450 and 500 °C provides the highest benzene conversion only at the initial time on stream and after that it drops to below 0.5 %. Benzene conversion shows the same trend as thermodynamic calculation in the Figure 4.9, it increase with the reaction temperature. Because methylation reaction is endothermic reaction, higher temperature has the necessary activation energy resulting in higher potential to force the reaction.
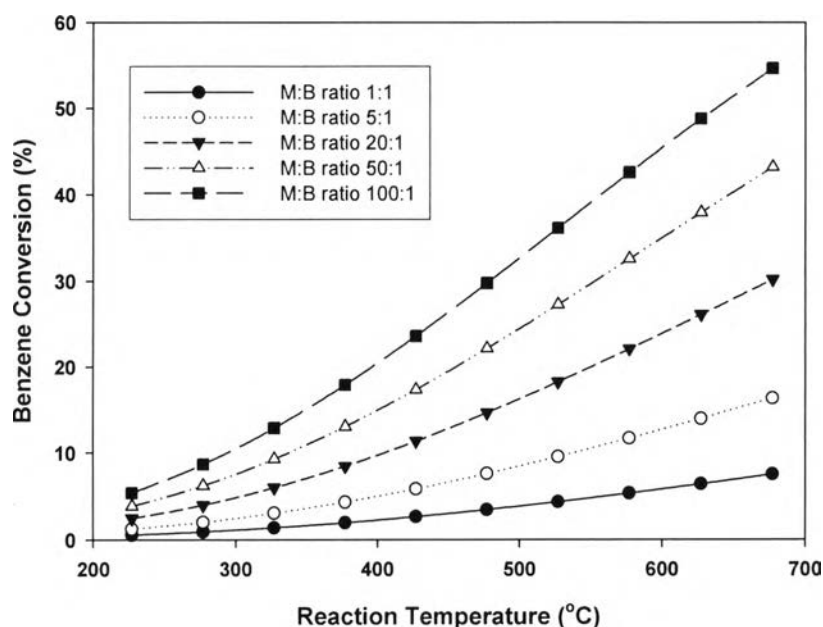

**Figure 4.9** Thermodynamic calculation for benzene methylation reaction.

The reaction temperature at 500 °C shows the highest benzene conversion, however the toluene selectivity is observed very low. In contrast with reaction temperature at 300 and 350 °C, they provide lower benzene conversion with

higher toluene selectivity. Moreover after 10 minute time on stream, the benzene conversion of all the reaction temperature is easily dropped. The decreasing in benzene conversion comes from the coke formation which possibly more generates by the increasing of reaction temperature.

According to the highest yield and high toluene selectivity, the reaction temperature would be fixed at 350 °C for the following experiment. These result is similar to Srisayan (2012), who studied the methylation of benzene with methane using indium(III)chloride loading on HZSM-5.
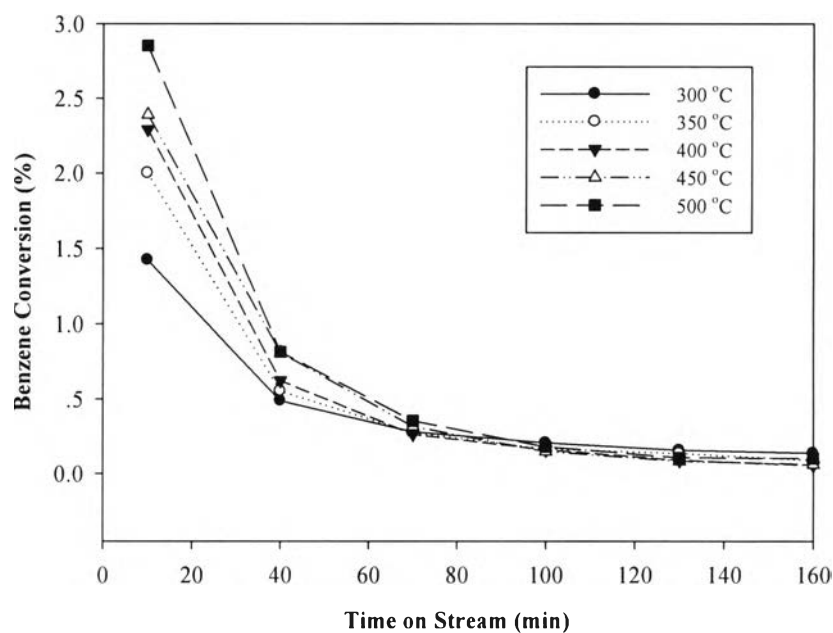
Figure 4.10 Benzene conversion as a function of time on stream at different reaction temperature.
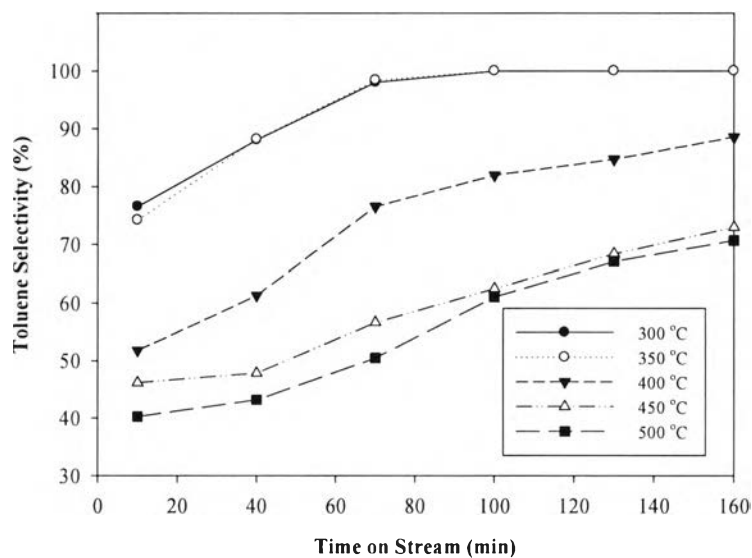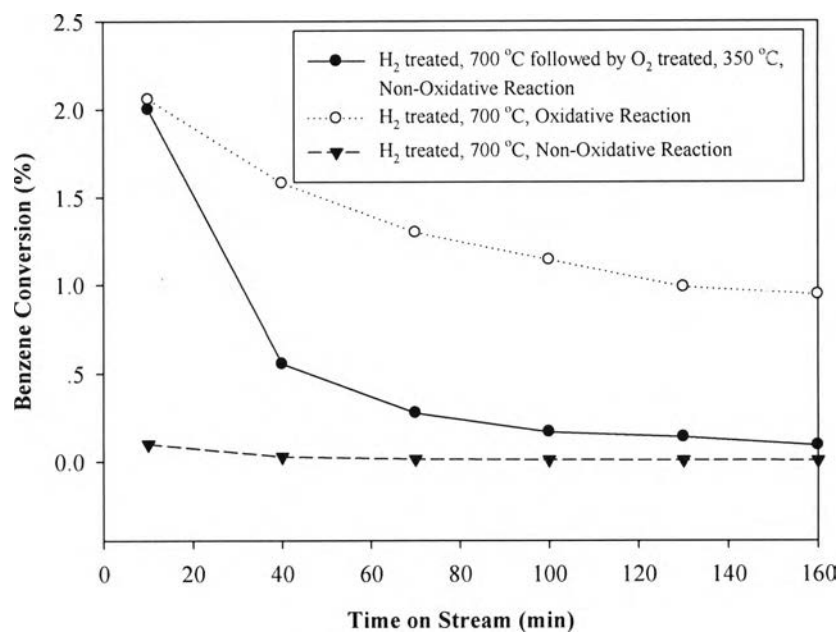
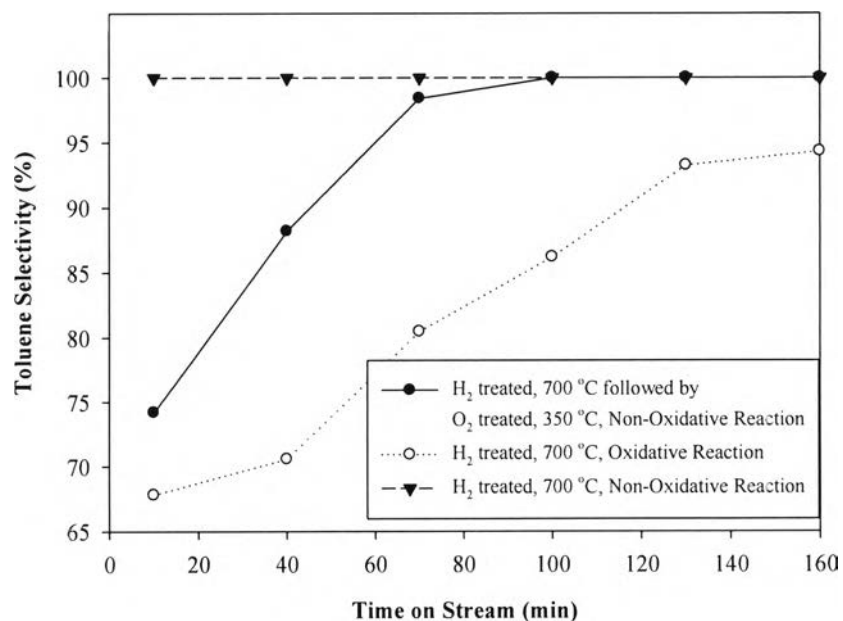**Figure 4.11** Toluene selectivity as a function of time on stream at different reaction temperature.

4.2.3 Effect of oxidative reaction (carrier gas)

The effect of carrier gas is compared between nitrogen (under hydrogen treatment gas and hydrogen followed by oxygen treatment gas) and oxygen (under hydrogen treatment gas). The other parameters are fixed, the reaction temperature is at 350 °C, the Indium/Aluminum ratio using value of 0.5, the space velocity (WHSV) at 2.8 h^{-1}, the Methane/Benzene feed ratio equal to 70 and SiO_2/Al_2O_3 of HZSM-5 equal to 50.

At the initial time on stream, benzene conversion of oxygen carrier gas (oxidative reaction) under hydrogen treatment gas is close to nitrogen carrier gas (non-oxidative reaction) under hydrogen followed by oxygen treatment gas as shown in Figure 4.12 and Figure 4.13. After the running time of 10 minute, benzene conversion of oxygen carrier gas under hydrogen treatment gas is higher than nitrogen carrier gas under hydrogen followed by oxygen treatment gas. For the result of nitrogen carrier gas under hydrogen treatment gas, it shows the lowest benzene conversion. This result can be explained by the difference of indium species generated in difference carrier gas which possibly is In^+ cation and InO^+ cation.

Figure 4.12 Benzene conversion as a function of time on stream at different oxidative condition.

Figure 4.13 Toluene selectivity as a function of time on stream at different oxidative condition.
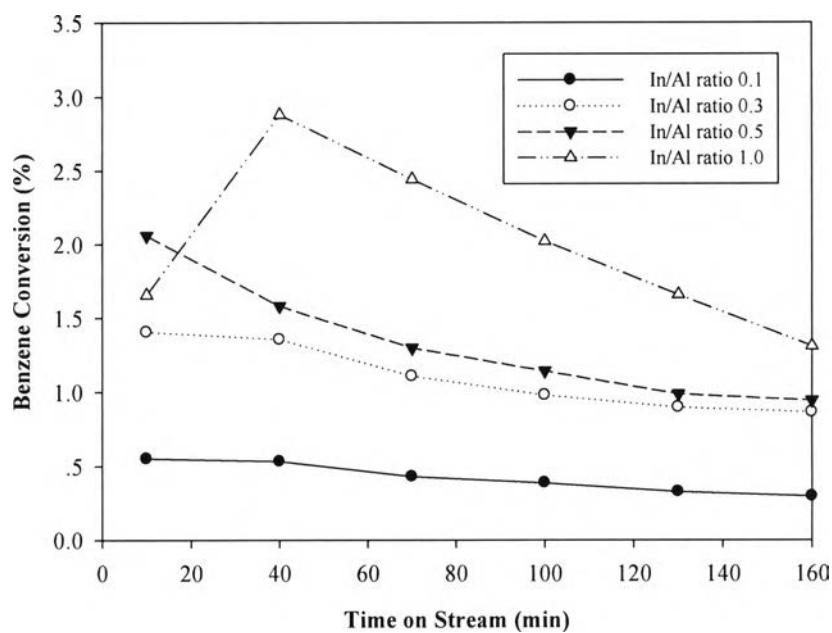
4.2.4 Effect of Indium to Aluminum Ratio

The effect of Indium/Aluminum ratio is studied in the range of 0.1 to 1.0. The other parameters are fixed, the reaction temperature is at 350 °C, the treatment is performed in hydrogen at 700 °C, the carrier gas is oxygen, the space velocity (WHSV) at 2.8 h^{-1}, the Methane/Benzene feed ratio equal to 70 and SiO_2/Al_2O_3 of HZSM-5 equal to 50.

The increasing of indium to aluminum ratio is the increasing of indium cation existing at the negative site of ZSM-5 framework as a charge balancing species compared with proton (Brønsted acid) exists. The results of temperature program desorption (TPD) in Table 4.5 demonstrated that amount of Brønsted acid depended on the indium loading amount. The higher In/Al ratio shows the lower of Brønsted acid on the catalyst surface.

Table 4.5 Temperature program desorption (TPD) results of catalysts with various indium loading ratios

Sample	In/Al ratios	Weak Brønsted acid (μmol/g)	Strong Brønsted acid (μmol/g)	Total Brønsted acid (μmol/g)	Brønsted acid remaining (%)
HZSM-5 (SiO_2/Al_2O_3 50)	-	6.0	82.4	88.4	100.0
In/HZSM-5 (SiO_2/Al_2O_3 50)	0.1	6.5	89.9	96.4	109.0
	0.3	8.1	74.6	82.7	93.6
	0.5	3.4	39.9	43.3	48.9
	1.0	1.8	13.8	15.6	17.6

Figure 4.14 Benzene conversion as a function of time on stream at different indium to aluminum ratios.
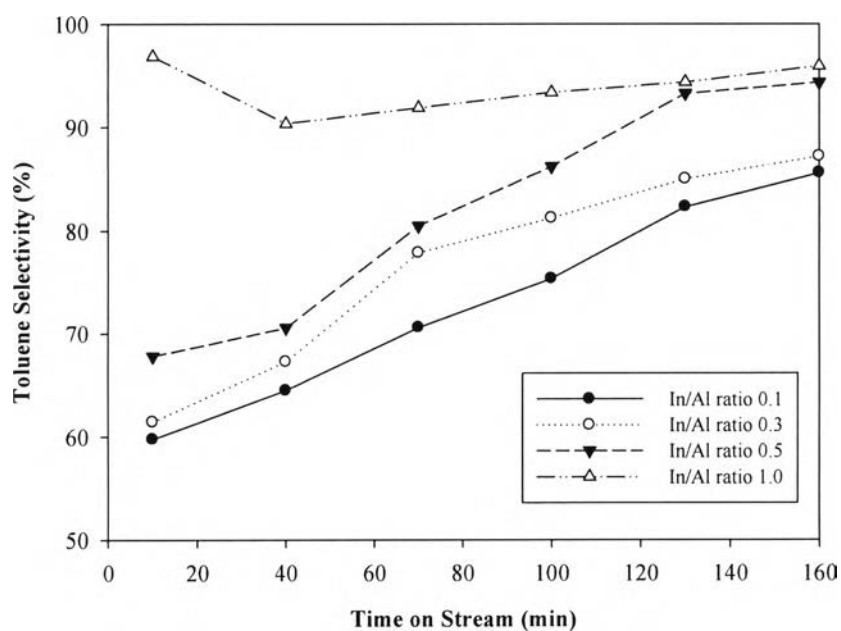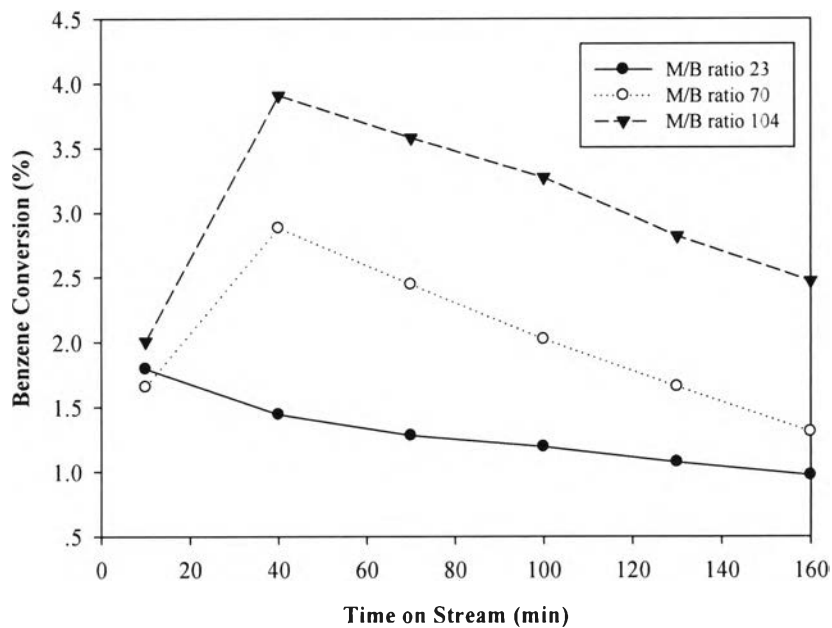

Figure 4.15 Toluene selectivity as a function of time on stream at different indium to aluminum ratios.

From Figure 4.14 and 4.15, increasing indium to aluminum ratios in catalyst provided higher benzene conversion with also higher toluene selectivity. The benzene conversion increased from 0.6 % of In/Al ratio 0.1 to 2.8 % of In/Al ratio 1.0 at time on stream on 10 minute, while the toluene selectivity increased from 60 % to 92 %.
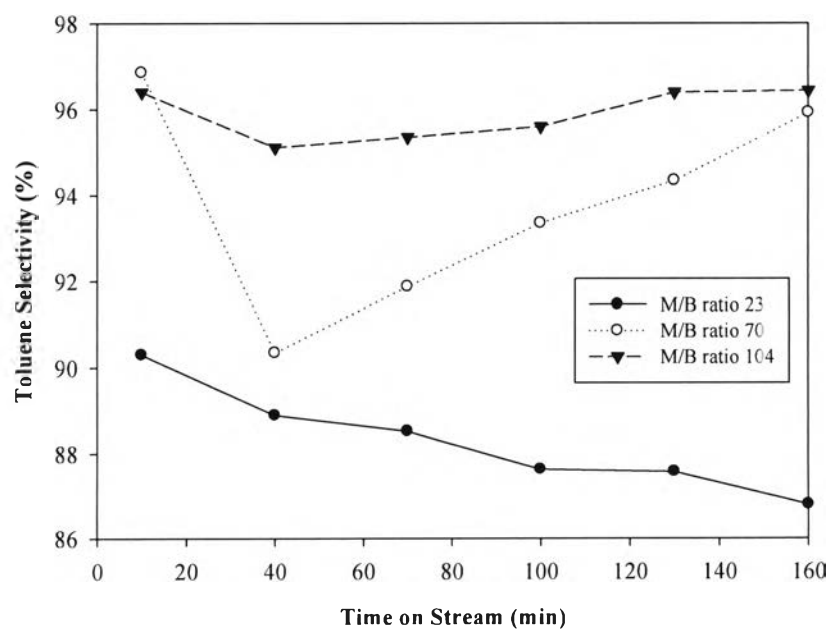
4.2.5 Effect of Methane to Benzene Feed Molar Ratio

The effect of methane to benzene feed molar ratio is studied in the range of 23 to 104. The other parameters are fixed, the reaction temperature is at 350 °C, the treatment is performed in hydrogen at 700 °C, the carrier gas is oxygen, the indium/aluminum ratio using value of 1.0, the space velocity (WHSV) at 2.8 h^{-1} and SiO_2/Al_2O_3 of HZSM-5 equal to 50.

The results of Figure 4.16 and Figure 4.17 show the same trend as the thermodynamic calculation in Figure 4.9. The benzene conversion when using methane to benzene feed ratio equal to 104 afforded 3.9 %. The conversion results show the similar trend to Srisayan (2012). He found that high methane to benzene feed molar ratio (105) provided higher benzene conversion (10.4%) than lower methane to benzene feed molar ratio. For selectivity, when increase methane to benzene feed ratios it found that toluene selectivity also increase. Increasing methane to benzene feed ratios could provide the higher potential to force the reaction as expected from *Le Chatelier's* principle. The lower of aromatic species in the system may be lead to increase the percentage of toluene selectivity and the side reaction to poly-rings aromatics products is also decrease.

Figure 4.16 Benzene conversion as a function of time on stream at different methane to benzene feed ratio.
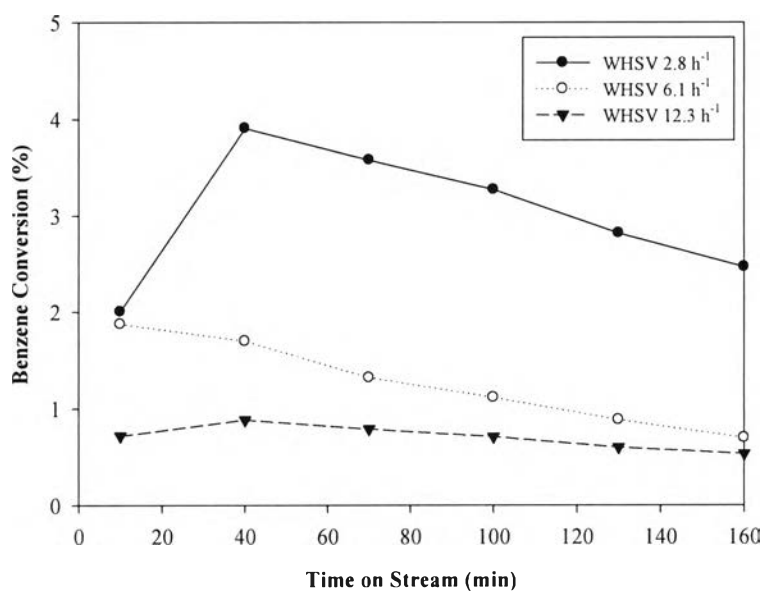

Figure 4.17 Toluene selectivity as a function of time on stream at different methane to benzene feed ratio.
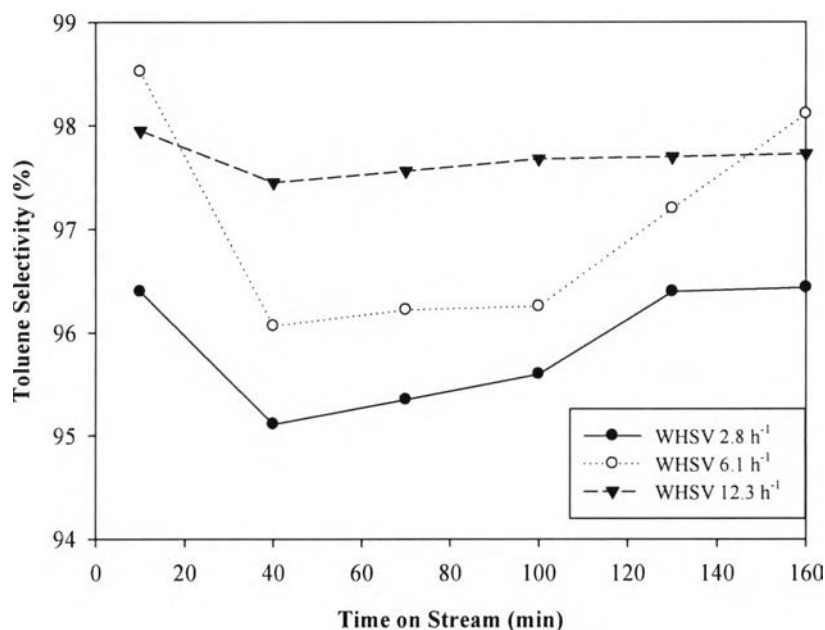
4.2.6 Effect of Space Velocity (WHSV)

The effect of space velocity (WHSV) is studied in the range of 2.8 to 12.3 h^{-1}. The other parameters are fixed, the reaction temperature is at 350 °C, the treatment is performed in hydrogen at 700 °C, the carrier gas is oxygen, the Indium/Aluminum ratio using value of 1.0, the methane to benzene feed molar ratio equal to 104 and SiO$_2$/Al$_2$O$_3$ of HZSM-5 equal to 50.

From Figure 4.18 and Figure 4.19, decreasing WHSV is referred as increasing contact time, so it shows that the benzene conversion increased with decreasing WHSV. Toluene selectivity at low WHSV (2.8 h^{-1}), the by-products are observed in higher amount than high WHSV which is possibly by the undesired products or any other side reactions when the chemicals stay in the catalyst bed for a long time.

Figure 4.18 Benzene conversion as a function of time on stream at different space velocity (WHSV).

Figure 4.19 Toluene selectivity as a function of time on stream at different space velocity (WHSV).

4.2.7 Effect of Silica to Alumina Ratio

The effect of silica to alumina ratio is examined with HZSM-5 ratio 23, 30, 50, 80 and 280. The other parameters is fixed, the reaction temperature is at 350 °C, the treatment is performed in hydrogen at 700 °C, the carrier gas is oxygen, the Indium/Aluminum ratio using value of 1.0, methane to benzene feed ratio equal to 104 and the space velocity (WHSV) at 2.8 h^{-1}.

TPD experiments were conducted with an aim of determining the acid property of HZSM-5 and In/HZSM-5 catalysts. The area of TPD profile reflects the amount of propylene adsorbed on the catalyst. As shown in Figure 4.20, area of TPD profile for HZSM-5 catalysts increased with increasing SiO_2/Al_2O_3 ratio.
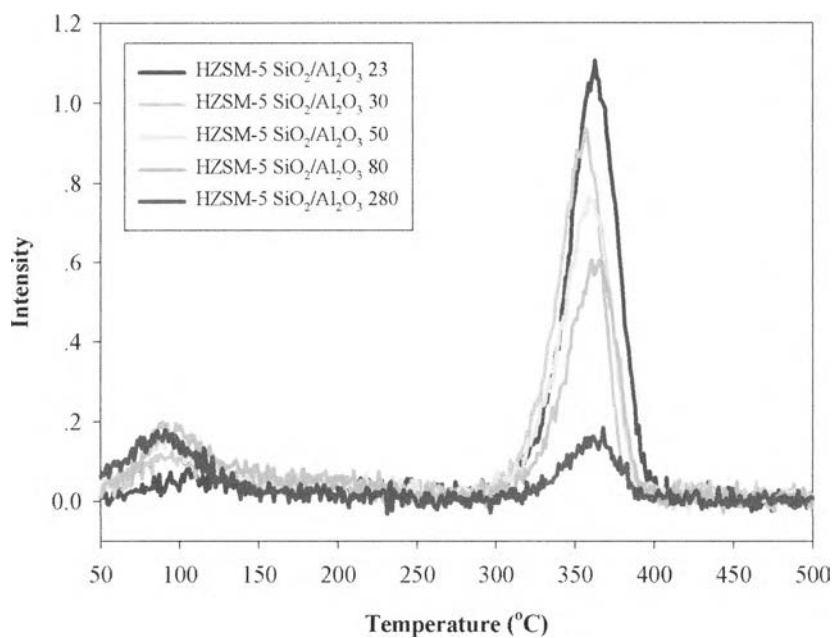
**Figure 4.20** Temperature program desorption (TPD) profiles of catalyst with various SiO_2/Al_2O_3 ratios.

The area of desorbed propylene in TPD profile was integrated to calculate the amount of brønsted acid by using the calibration factor of propylene. The total brønsted acid was calculated by combining weak and strong brønsted acid as display in Table 4.1. HZSM-5 with high SiO_2/Al_2O_3 provided lower total brønsted acid than low SiO_2/Al_2O_3 ratio.

**Table 4.6** Temperature program desorption (TPD) results of catalysts with various SiO_2/Al_2O_3 ratios

Sample	Weak Brønsted acid (μmol/g)	Strong Brønsted acid (μmol/g)	Total Brønsted acid (μmol/g)
HZSM-5 (SiO_2/Al_2O_3 23)	3.6	106.8	110.4
HZSM-5 (SiO_2/Al_2O_3 30)	7.2	95.5	102.7
HZSM-5 (SiO_2/Al_2O_3 50)	6.0	82.4	88.4
HZSM-5 (SiO_2/Al_2O_3 80)	8.0	61.3	69.3
HZSM-5 (SiO_2/Al_2O_3 280)	1.0	19.9	20.9

From Figure 4.21, benzene conversion of In/HZSM-5 with SiO_2/Al_2O_3 ratio 50 displayed the highest conversion 3.9% while SiO_2/Al_2O_3 ratio 80, 30, 23 and 280 showed the conversion 1.4, 1.1, 1.0 and 0.1%, respectively, at time on stream 40. The product selectivity of SiO_2/Al_2O_3 ratio 80 and 280 was 100%. SiO_2/Al_2O_3 ratio 50 provided the selectivity around 95% whereas SiO_2/Al_2O_3 ratio 30 and 23 provided about 86 to 88% as exhibited in Figure 4.22.

SiO_2/Al_2O_3 ratio 50 is possible higher Lewis sites than the ratio of 80 and 280 so it provided the higher conversion. As Brønsted acid sites could be found in SiO_2/Al_2O_3 ratio 23 and 30 more than ratio 50 that lead to unfavourable reaction such as cracking or isomerisation. It is also clear that the SiO_2/Al_2O_3 ratio plays some important roles in determining the conversions and product selectivities of the zeolite catalysts.
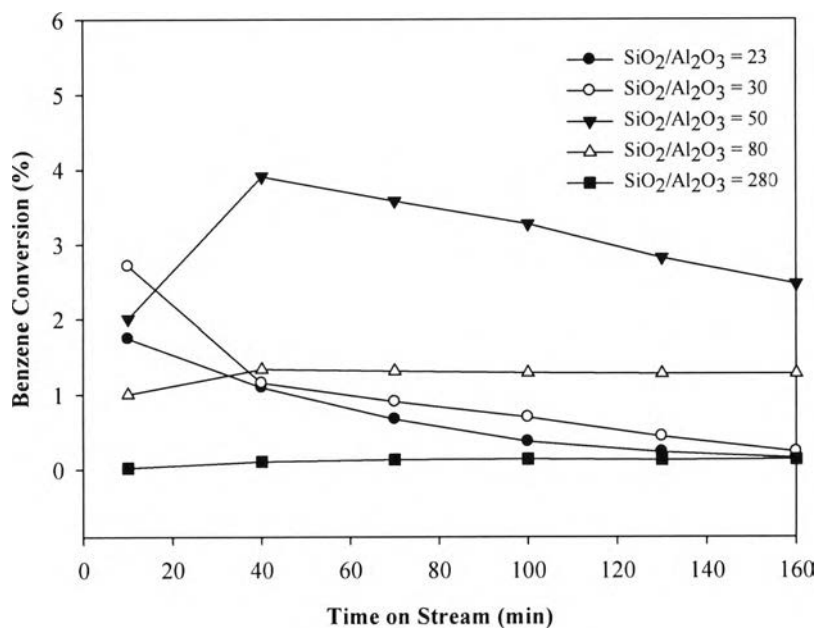
Figure 4.21 Benzene conversion as a function of time on stream at different silica to alumina ratios.
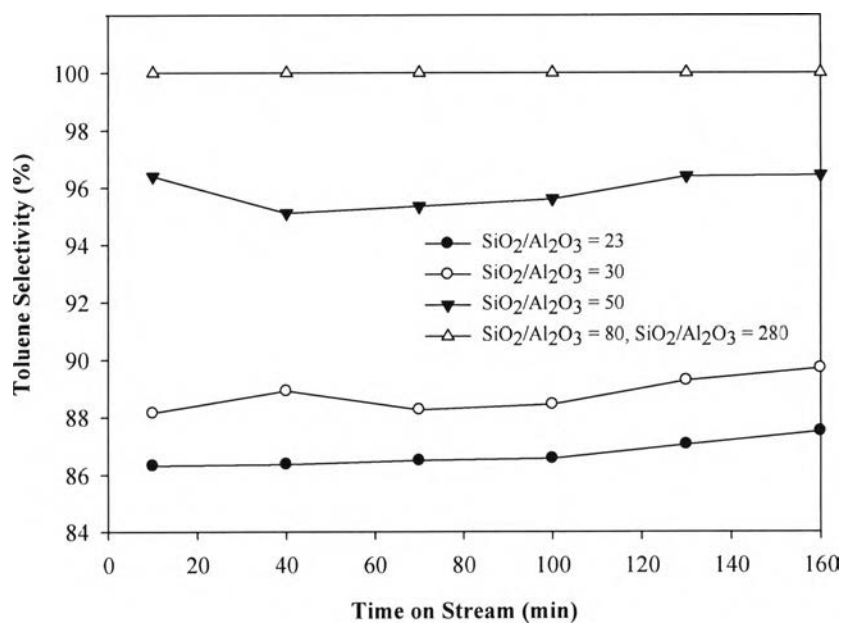
Figure 4.22 Toluene selectivity as a function of time on stream at different silica to alumina ratios.