



## CHAPTER IV

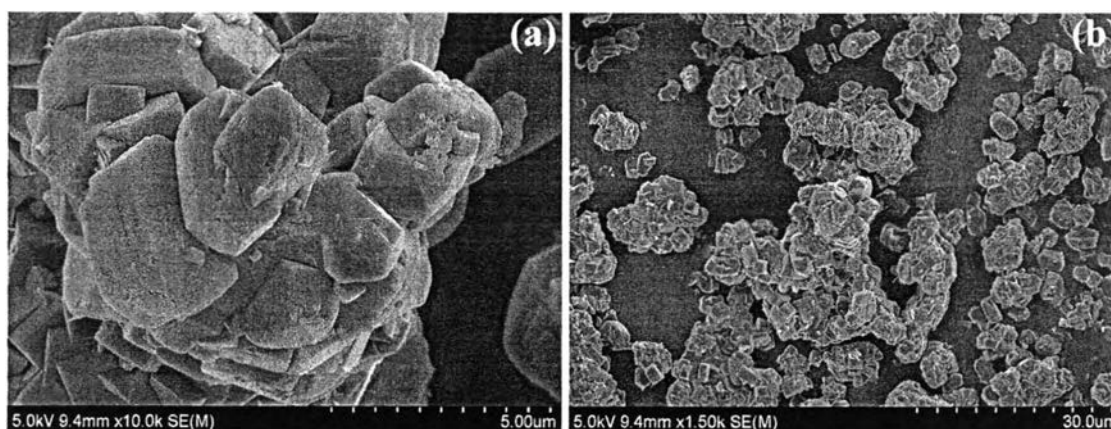
### RESULTS AND DISCUSSION

#### 4.1 Catalyst Characterization

##### 4.1.1 Scanning Electron Microscopy and Energy Dispersive X-ray Spectroscopy (SEM-EDX)

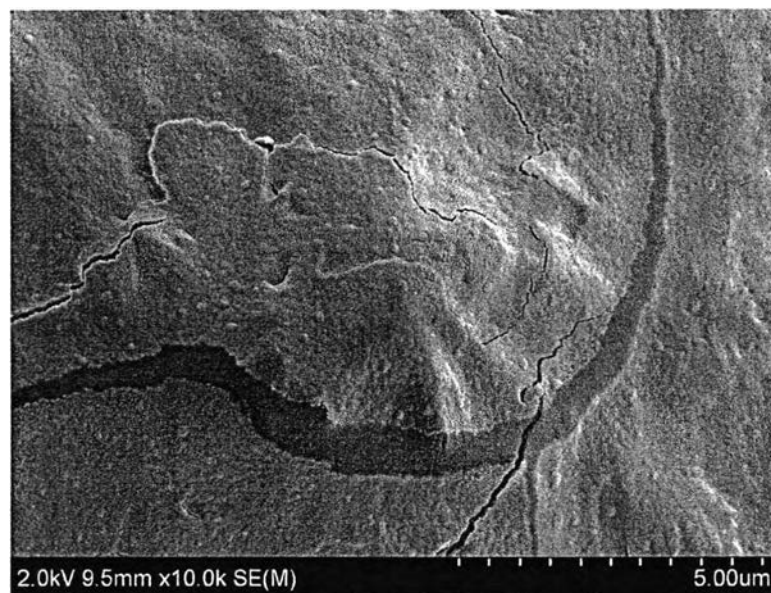
##### 4.1.1.1 *HZSM-5 and Indium Compound*

As observed from Figure 4.1, HZSM-5 particles consist of a small hexagonal-shape crystal. These crystals are agglomerated and formed a larger crystals in the size around 3-30  $\mu\text{m}$  as shown in Figure 4.1 (a) and (b).



**Figure 4.1** SEM image of HZSM-5 in the magnification 10000x (a) and 1500x (b).

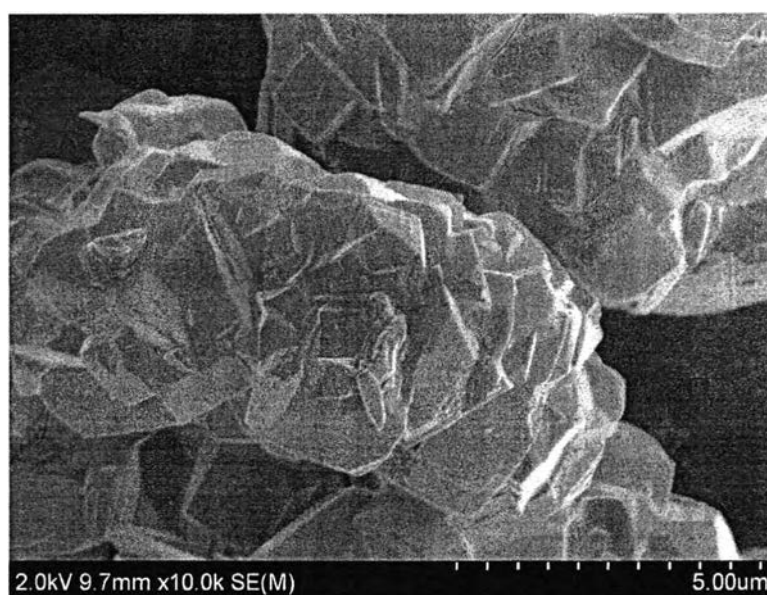
The image of indium(III)chloride is shown in Figure 4.2, it can be observed that indium(III)chloride does not show any crystal structure. The shape of this chemical is not perfectly clear from the image; it looks like the substance coating on the surface of the adhesive tape supported. This possibly comes from the characteristic of the chemical that can absorb moisture easily; this can make it dissolve and spread on the surface.



**Figure 4.2** SEM image of indium(III)chloride in the magnification 10000x.

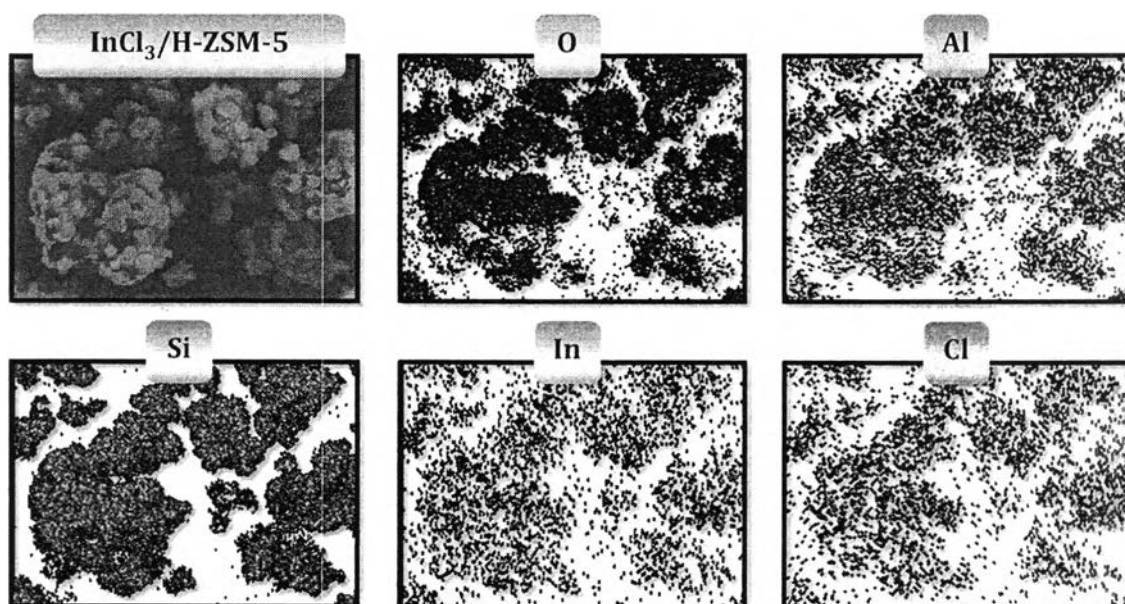
#### 4.1.1.2 Physical Mixing In/HZSM-5 Catalyst

The SEM image of HZSM-5 physical mixed with indium(III)chloride is shown in Figure 4.3. The surface and edge of indium(III)chloride mixed with HZSM-5 without any treatment looks smoother than the pristine HZSM-5. As shown in the Figure 4.2, indium(III)chloride is easily coat on any surface, when mixed with HZSM-5 it may coat on the HZSM-5 surface making the surface looks smoother.



**Figure 4.3** SEM image of HZSM-5 physical mixed with indium(III)chloride in magnification 10000x.

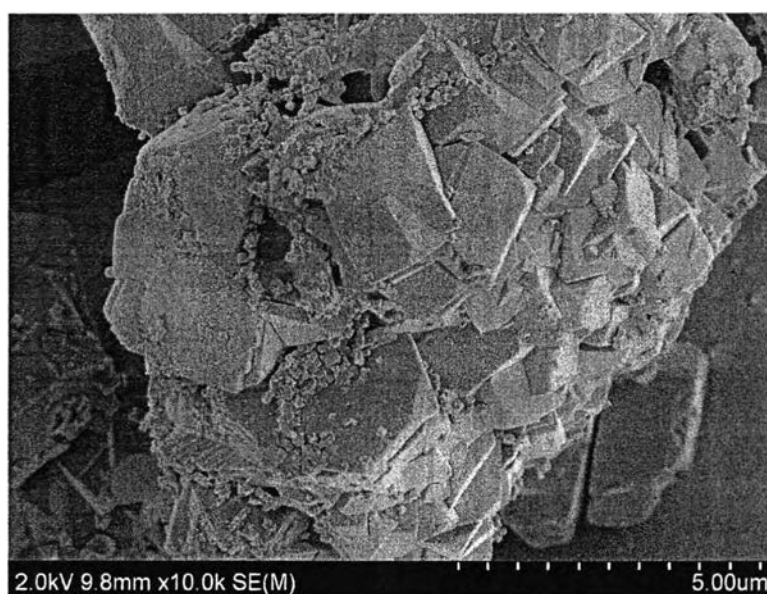
Figure 4.4 shows the elemental distribution of oxygen, aluminium, silicon, indium and chloride in the catalyst. After physical mixed indium(III)chloride with HZSM-5 without any treatment, the indium and chloride are present in the position with oxygen, aluminium and silicon which are the main composition of HZSM-5. This supports that indium(III)chloride are already well distributed on HZSM-5 surface.



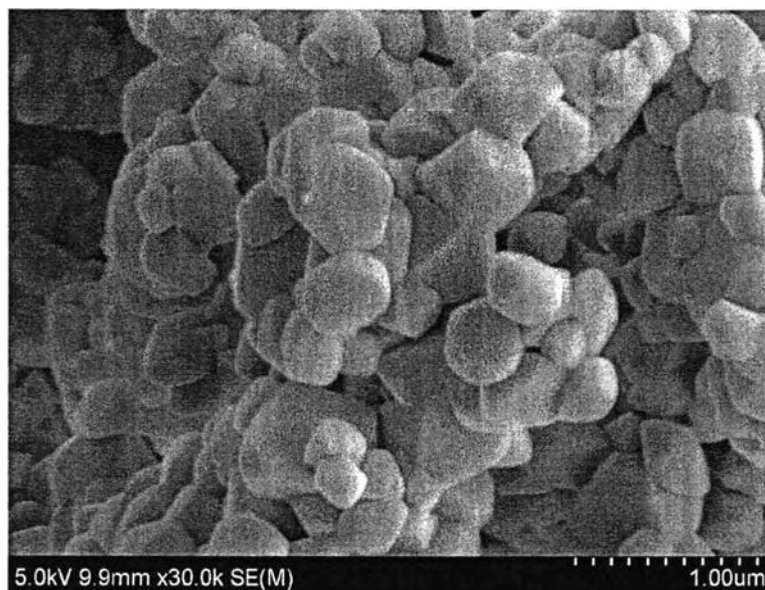
**Figure 4.4** EDX image of HZSM-5 physical mixed with indium(III)chloride in magnification 6000x.

#### 4.1.1.3 Oxygen Treated In/HZSM-5 Catalyst

From Figure 4.5, the surface of HZSM-5 physical mixed with indium(III)chloride followed by treatment in air looks sharper than that of Figure 4.3 but there are many small particles attached on HZSM-5 surface. This can be explained that indium(III)chloride coating on the surface is transformed into other forms of indium, possibly indium(III)oxide crystal or  $\text{In}_2\text{O}_3$  (Miro *et al.*, 1999). Compared indium(III)oxide crystal which is shown in Figure 4.6 with the small particles in Figure 4.5, it found that the crystal size and shape are similar.

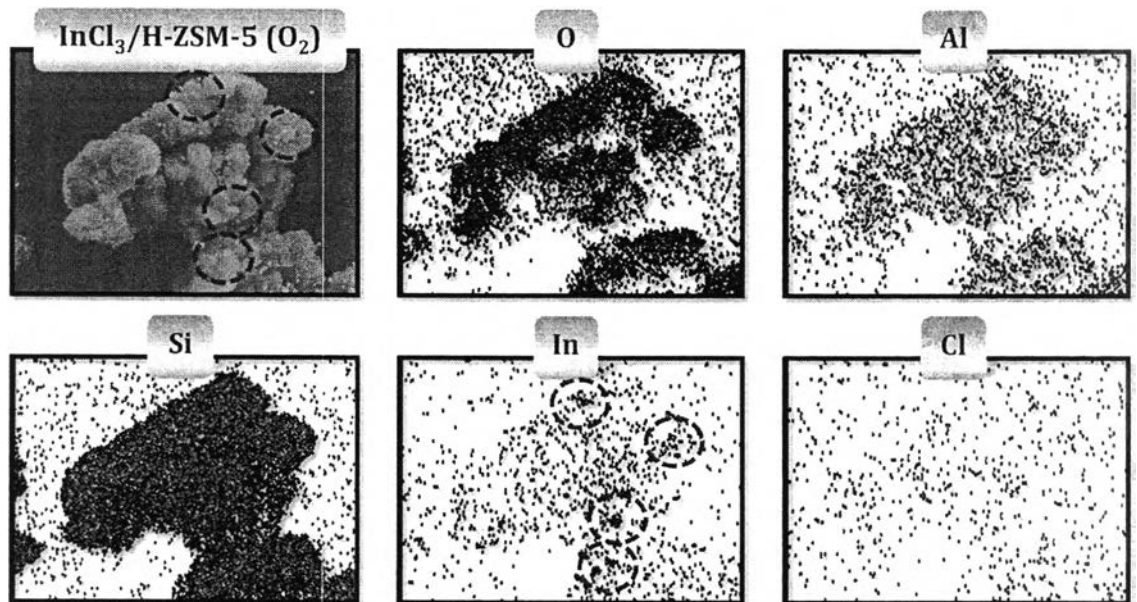


**Figure 4.5** SEM image of HZSM-5 physical mixed with indium(III)chloride followed by treatment in oxygen atmosphere in magnification 10000x.



**Figure 4.6** SEM image of indium(III)oxide ( $\text{In}_2\text{O}_3$ ) in magnification 30000x.

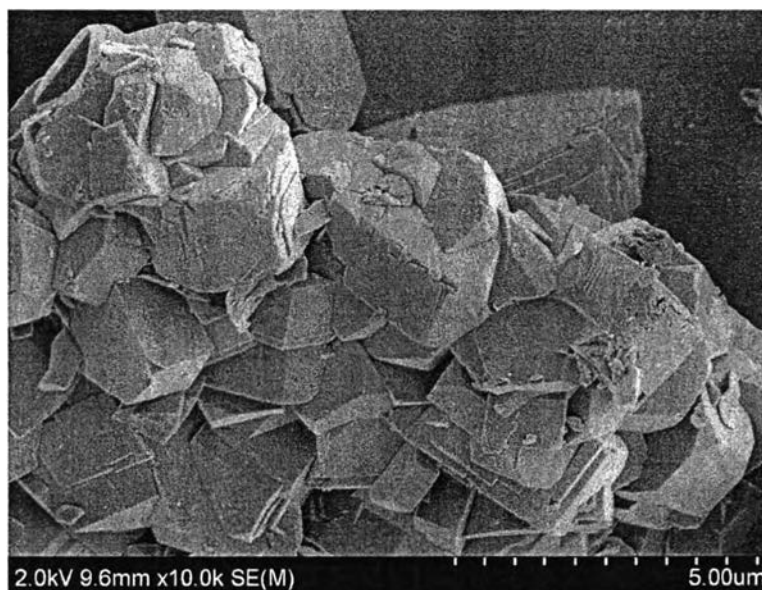
From Figure 4.7, after physical mixing of indium(III)chloride with HZSM-5 and treating in air, indium and chloride are still in the same site as the main composition of HZSM-5 but some clusters of indium is observed on the surface. This supports the possibility that indium(III)chloride can transform to indium(III)oxide ( $\text{In}_2\text{O}_3$ ) and then agglomerated.



**Figure 4.7** EDX image of HZSM-5 physical mixed with indium(III)chloride followed by treatment in oxygen atmosphere in magnification 6000x.

#### 4.1.1.4 Hydrogen Treated In/HZSM-5 Catalyst

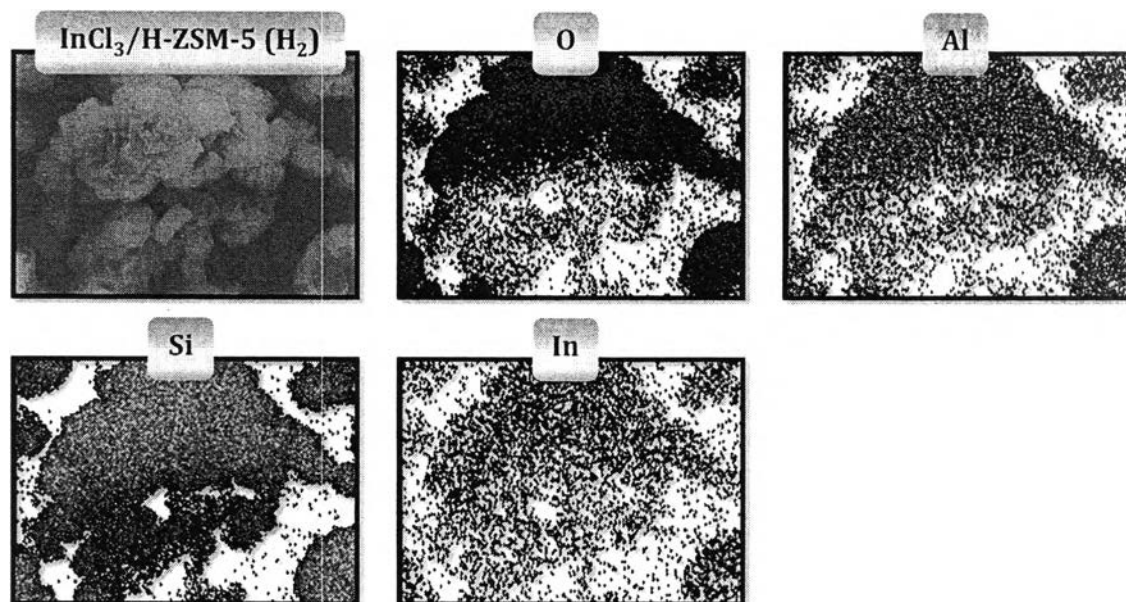
From Figure 4.8, the surface of HZSM-5 physical mixed with indium(III)chloride followed by treatment in 10% hydrogen in nitrogen atmosphere looks similar to the pristine HZSM-5. This suggested that indium species might be incorporate to the structure of HZSM-5 and possibly cannot be observed with the SEM at this magnification.



**Figure 4.8** SEM image of HZSM-5 physical mixed with indium(III)chloride followed by treatment in hydrogen atmosphere in magnification 10000x.

From Figure 4.9, after physical mixed indium(III)chloride with HZSM-5 followed by treatment under hydrogen atmosphere, the indium element is still at the same site as the main component of HZSM-5. This can indicate that indium is well distributed and is in the very small form. According to the literature review, one of the presumed forms is the indium cation. It has been suggested that, from solid-state ion exchange technique, indium on ZSM-5 after reduction should be  $\text{In}^+$  cation (Mihalyi and Beyer, 2001).

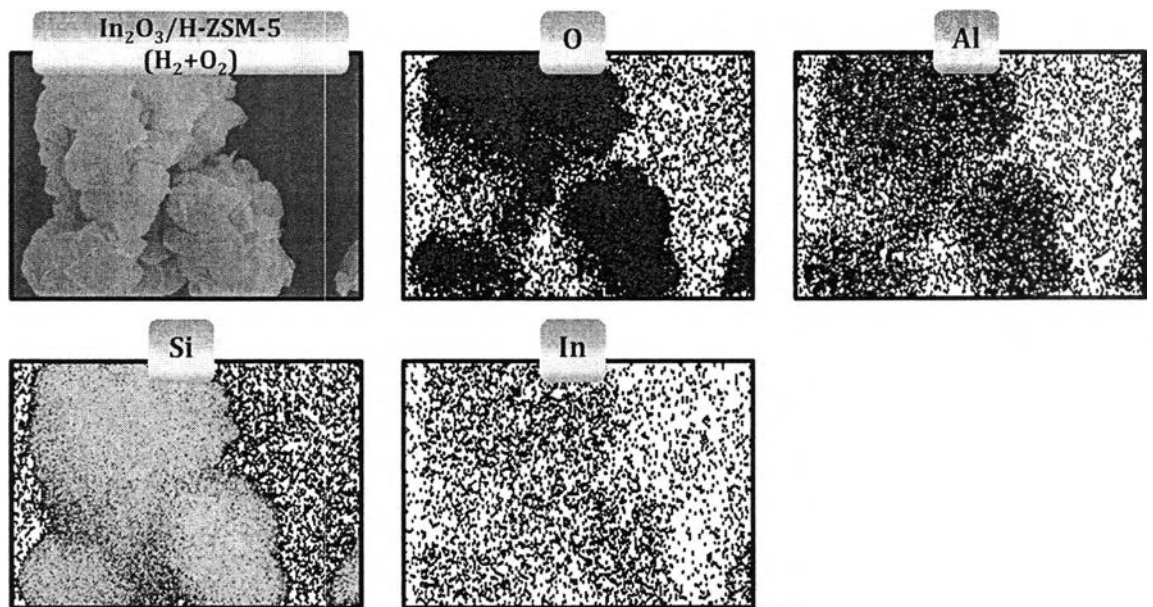




**Figure 4.9** EDX image of HZSM-5 physical mixed with indium(III)chloride followed by treatment in hydrogen atmosphere in magnification 6000x.

#### 4.1.1.5 Hydrogen Followed by Oxygen Treated In/HZSM-5 Catalyst

From Figure 4.10, after physical mixed indium(III)oxide with HZSM-5 followed by treatment under hydrogen and then oxygen atmosphere, the indium element is at the same site as the main component of HZSM-5 without any indium agglomeration. From the hydrogen treatment results, indium that firstly reduced to  $\text{In}^+$  cation provides highly indium distribution. After the following of oxygen treatment, the indium is still well distributed. This suggested that indium is not oxidized back to the  $\text{In}_2\text{O}_3$ , but it should be in some form of well distributed cation, and  $\text{InO}^+$  has been proposed as the cation in oxidized form (Schutze *et al.*, 2001).

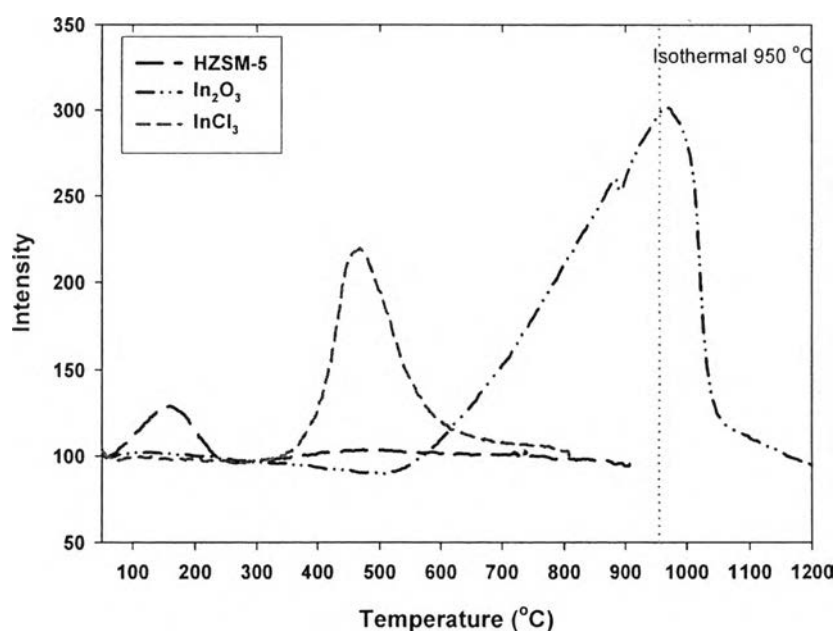


**Figure 4.10** EDX image of HZSM-5 physical mixed with indium(III)oxide treated in hydrogen followed by oxygen atmosphere in magnification 6000x.

#### 4.1.2 Temperature Program Reduction (TPR)

##### 4.1.2.1 TPR of HZSM-5, Indium(III)chloride and Indium(III)oxide

Figure 4.11 shows the TPR spectrum of HZSM-5, indium(III)oxide and indium(III)chloride. HZSM-5 shows a small reduction peak at around 180 °C. This peak may be a reduction of extra-framework aluminum ( $\text{AlO}^+$ ). For indium(III)chloride, the reduction peak that change  $\text{In}^{3+}$  into metallic indium ( $\text{In}^0$ ) is around 450 °C . In the case of indium(III)oxide, that reduction temperature is higher to about 950 °C. This because indium(III)oxide is in crystallite form with high bond strength, so the reduction of indium(III)oxide into metallic indium ( $\text{In}^0$ ) requires higher temperature (Solt *et al.*, 2008).



**Figure 4.11** Reduction temperature of HZSM-5, indium(III)oxide and indium(III)chloride.

#### 4.1.2.2 TPR of Indium(III)chloride and Indium(III)oxide Physically Mixed with HZSM-5

From Figure 4.12, each catalyst prepared from different indium precursors showed different profile of reduction temperature. However, it can be observed that every TPR profile has the same peak at 180 °C that is possibly due to extra-framework aluminum ( $\text{AlO}^+$ ) in HZSM-5.

For indium(III)oxide physically mixed with HZSM-5, the main reduction temperature is the highest around 650 °C, but compared to the indium(III)oxide raw materials which show the major peak at 950° C. The huge different in reduction temperature is due to the presence of HZSM-5. The negative-charge on the ZSM-5 framework can stabilize the indium in the form of  $\text{In}^+$  cation (Mihalyi and Beyer, 2001).

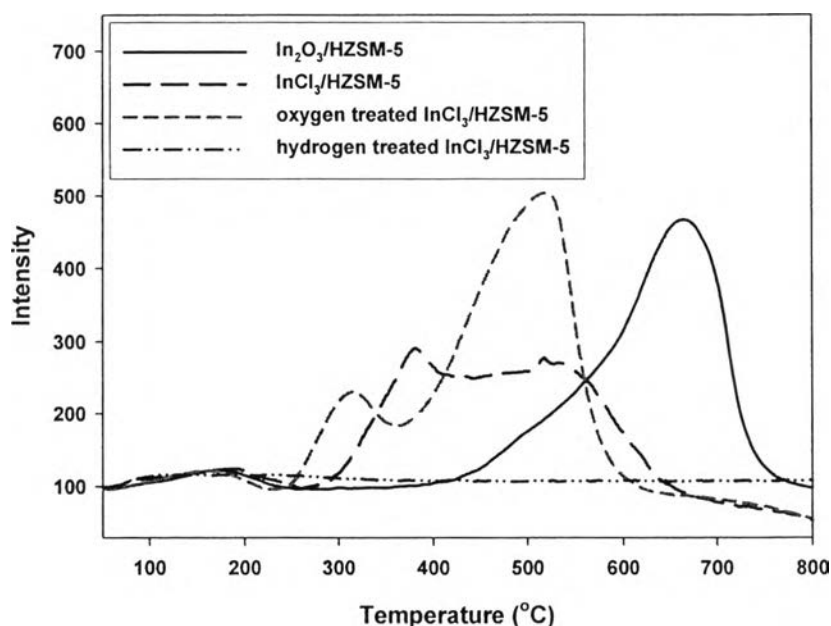
For indium(III)chloride physical mixed with HZSM-5, it shows a broad peak range from 300 to 600 °C. This may be comes from the overlap of more than one peak which cannot be identified yet. From the theory, in solid-state ion exchange process, indium element may be firstly formed some kind of intermediate species (Solt *et al.*, 2008) and then further transform to the indium cation species ( $\text{In}^+$ ).

For indium(III)chloride physical mixed with HZSM-5 followed by the oxygen treatment also shows wide peak ranging from 300 to 600 °C, possibly overlap of several peaks. It can be noticed that there is a major peak at around 500 °C and a minor at around 300 °C. For the peak at 500 °C, it may be attributed to two possibilities of reduced species, the first possibility is the reduction of chlorided indium species or  $\text{InCl}_x\text{O}_y$  that can be formed during the treatment (Sowade *et al.*, 2003), another possibility is the reduction of indium(III)oxide that formed during oxidation process. The reduction temperature of this indium(III)oxide (formed from the oxidized of indium(III)chloride) is lower than that of the “solid line” which is the reduction of the mixture between HZSM-5 and commercial indium(III)oxide. This attribute to the indium(III)oxide that may formed during oxidation process is not well crystalline compared to that of the “solid line” which is the commercial indium(III)oxide. The first peak at around 300 °C may be ascribed to indium that is in other oxidized form. This oxidized form having low reduction

temperature may be the indium that easier to reduce such as oxyindium cation,  $\text{InO}^+$  (Mihalyi and Beyer, 2001).

Indium(III)chloride physical mixed with HZSM-5 followed by the hydrogen treatment does not show any peak in TPR test. This due to the complete reduction of Indium(III)chloride during the hydrogen treatment prior to TPR experiment.

From the above results, indium(III)chloride is easier to be reduced than indium(III)oxide. Therefore, indium(III)chloride is selected as a indium precursor for catalysts preparation for subsequent study on methylation reaction.

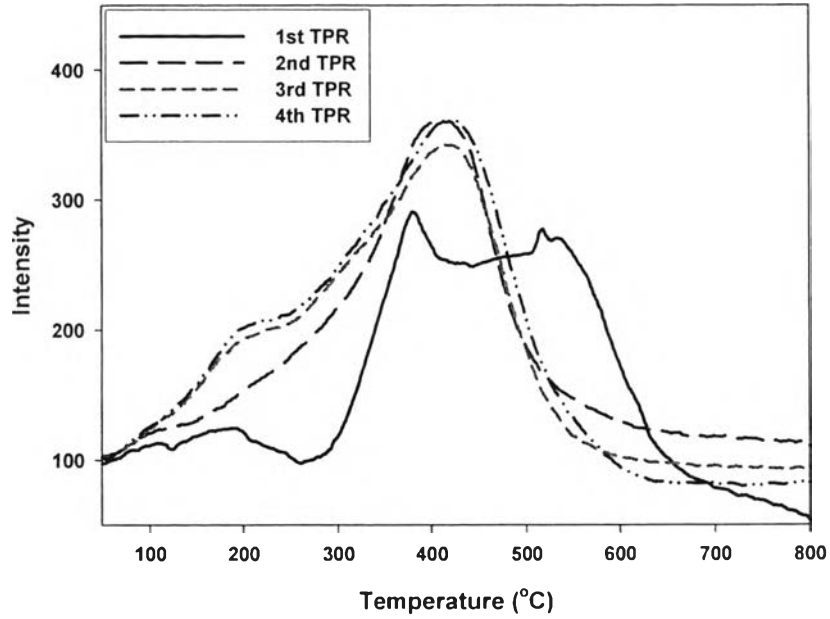


**Figure 4.12** Reduction temperature (heat from 50 to 800 °C in 5%  $\text{H}_2/\text{N}_2$ ) of indium(III)oxide, indium(III)chloride, oxygen treated indium(III)chloride and hydrogen treated indium(III)chloride physical mixed with HZSM-5.

#### 4.1.2.3 Reductive/Oxidative Cyclic Process of Indium(III)chloride Physically Mixed with HZSM-5

Figure 4.13 is showing the TPR of Indium(III)chloride mixed with HZSM-5 and subsequent TPR of the same sample after expose to the flowing air from high temperature. The results suggested that Indium(III)chloride was first reduced possibly to metallic indium, and then turn to be the indium oxide after expose to the air flow.

As observed from TPR, there are main peak at 400 °C with a small shoulder at around 200 °C. The peak at 400 °C possibly ascribe to the reduction of indium(III)oxide that has small crystal particle, while the shoulder at 200 °C may be ascribe to the reduction of indium that easier to reduce such as oxyindium cation,  $\text{InO}^+$ . This assumption is supported by the reduction temperature of extra-framework aluminum ( $\text{AlO}^+$ ), which is the similar species reduced at around 180 °C close to that reduction temperature. Moreover, the similar peak of the 2<sup>nd</sup> to the 4<sup>th</sup> after reductive/oxidative cyclic treatment are supported that the indium species in HZSM-5 can reversible convert between the reduced form ( $\text{In}^+$ ) and oxidized form ( $\text{InO}^+$ ) of cation (Schutze *et al.*, 2001).

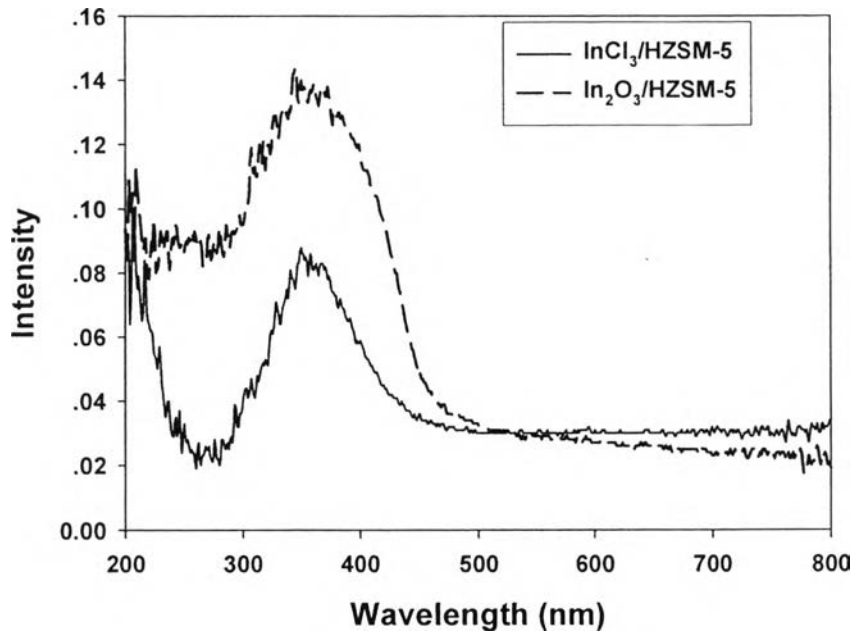


**Figure 4.13** Reduction behavior of indium(III)chloride physical mixed with HZSM-5 using a cyclic reduction (heat from 50 to 800 °C in 5% H<sub>2</sub>/N<sub>2</sub>) and oxidation (cool from 800 to 50°C in 5% O<sub>2</sub>/He) of the same sample for 4 cycles.

### 4.1.3 UV-Visible Spectroscopy

#### 4.1.3.1 UV-Visible Spectrum of Indium(III)chloride and Indium(III)oxide Physically Mixed with ZSM-5

Figure 4.14 shows the UV-Visible spectrum of indium(III)chloride and indium(III)oxide physically mixed with HZSM-5. Both two indium compounds show the similar of intensive peak around 350 nm. However, there are some different at the UV range below 300 nm that indium(III)oxide shows a higher intensity than indium(III)chloride.

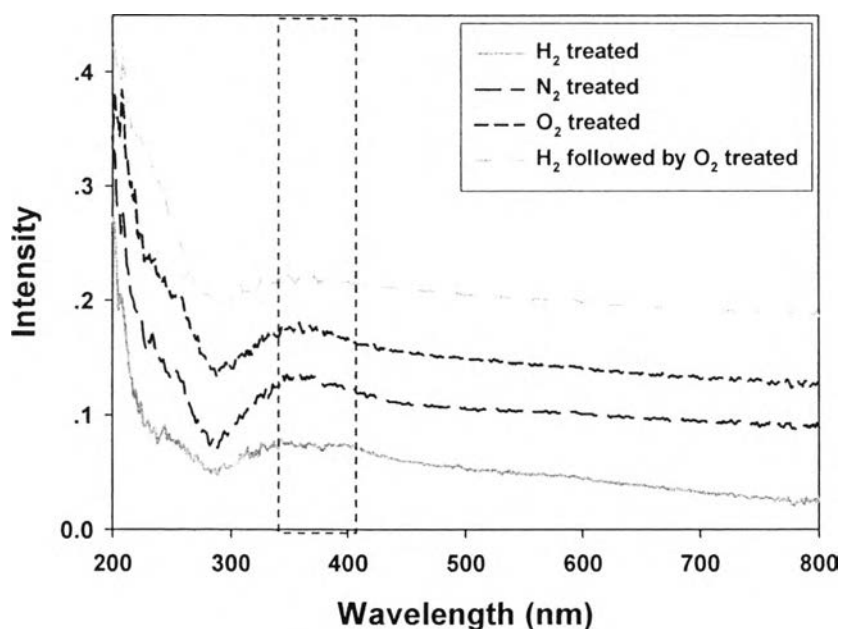


**Figure 4.14** UV-Visible spectrum of indium(III)chloride and indium(III)oxide physical mixed with HZSM-5 in the range of 200 to 800 nm.



#### 4.1.3.2 UV-Visible Spectrum of $\text{InCl}_3/\text{HZSM-5}$ with Different Treatment Atmosphere

Figure 4.15 shows the UV-Visible spectrum of  $\text{InCl}_3/\text{HZSM-5}$  treated in different atmosphere. Each of this shows a slightly different spectrum in the range around 350 nm. The height of the peak at around 350 nm which is assigned to indium(III)chloride or indium(III)oxide are smaller than those from the Figure 4.14, especially from hydrogen and hydrogen followed by oxygen treatment. This can support the idea that hydrogen treatment provided the different species which may be attributed to the indium cation, while the peak of nitrogen and oxygen treatment seem a little stronger which may indicate to the remaining of indium(III)oxide species.



**Figure 4.15** UV-Visible spectrum of  $\text{InCl}_3/\text{HZSM-5}$  treated in different atmosphere in the range of 200 to 800 nm.

#### 4.1.4 Surface Area Analysis

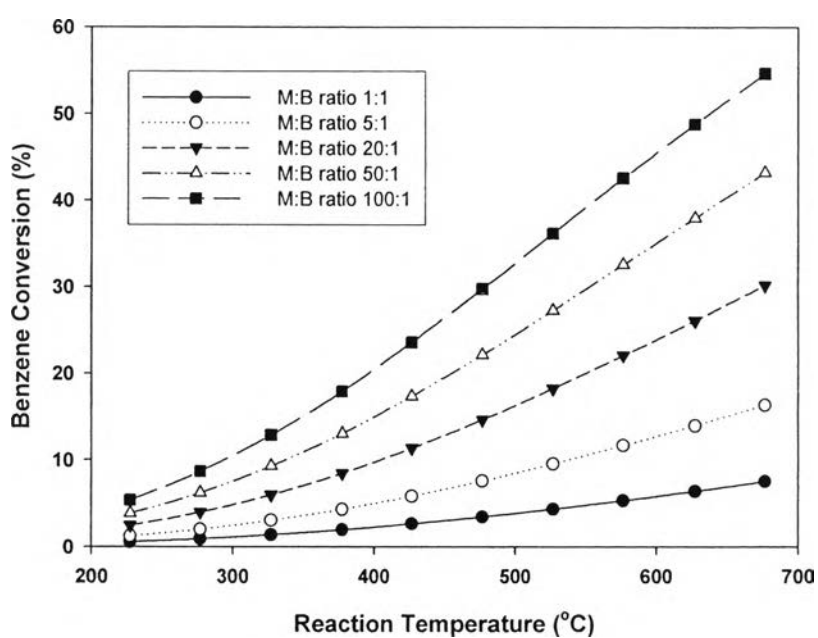
Table 4.1 shows the BET surface area of each catalyst. The surface area of HZSM-5 is the highest. After mixed with  $\text{InCl}_3$ , the catalysts surface area decrease and continue to decrease after further treatment. In the group of treated catalyst ( $\text{H}_2$ ,  $\text{N}_2$ ,  $\text{O}_2$  and  $\text{H}_2$  followed by  $\text{O}_2$ ), the surface area of catalyst from each treatment gas shows insignificant different to the others.

**Table 4.1** BET surface area of catalysts

Sample	BET surface area ( $\text{m}^2/\text{g}$ )
HZSM-5	365.0
$\text{InCl}_3/\text{HZSM-5}$ (physical mixed)	330.3
$\text{InCl}_3/\text{HZSM-5}$ (Nitrogen treatment)	308.9
$\text{InCl}_3/\text{HZSM-5}$ (Oxygen treatment)	284.5
$\text{InCl}_3/\text{HZSM-5}$ (Hydrogen treatment)	301.5
$\text{InCl}_3/\text{HZSM-5}$ (Hydrogen+Oxygen treatment)	304.7

## 4.2 Catalytic Activity Testing

From thermodynamics, the relations between reaction temperature and benzene conversion at different methane to benzene feed ratios are shown below. As expected, reaction temperature has significant effect to the benzene conversion, therefore the experiment is designed to find the optimal temperature.



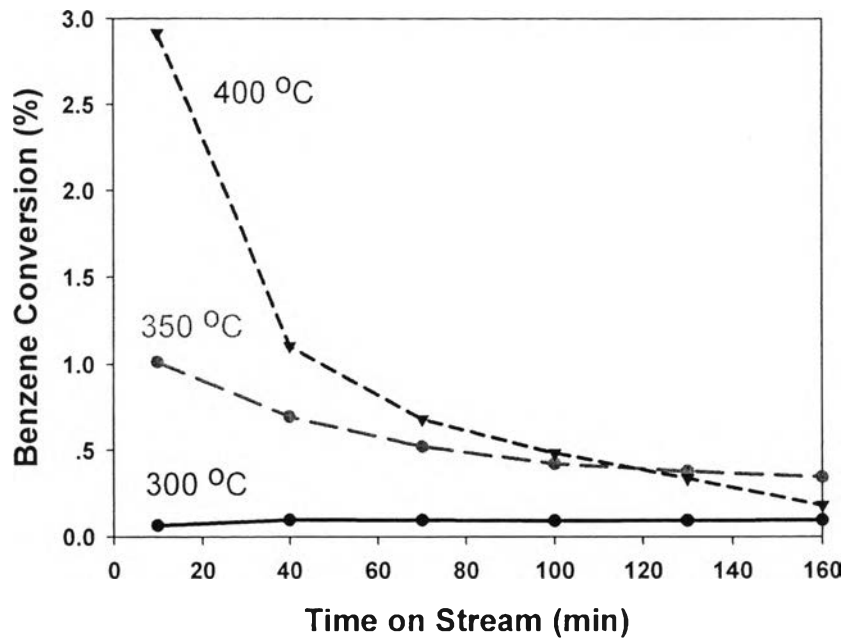
**Figure 4.16** Thermodynamic calculation for benzene methylation reaction.

#### 4.2.1 Effect of Reaction Temperature

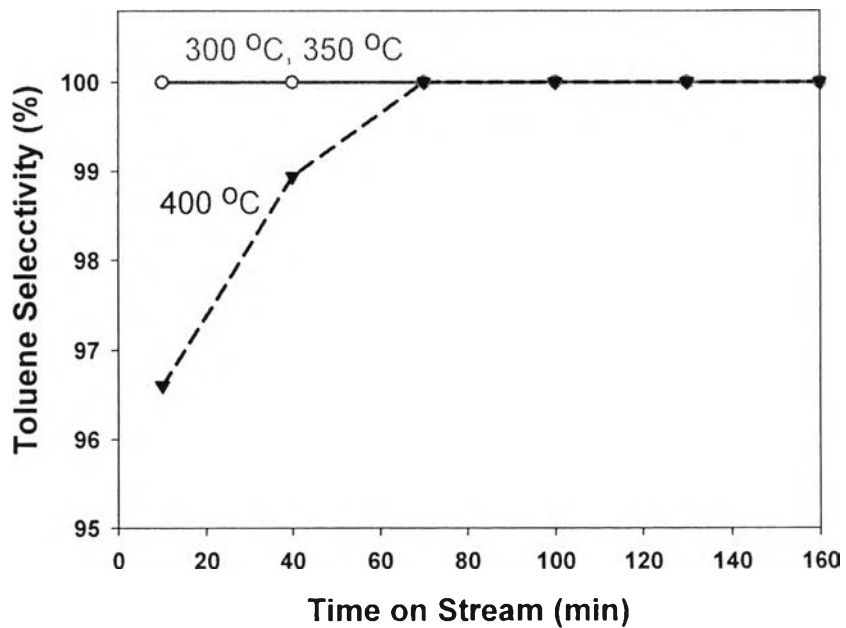
The effect of reaction temperature is examined in the range of 300 to 400 °C. The other parameters are fixed, the treatment atmosphere is in nitrogen at 350 °C, the carrier gas is nitrogen, the Indium/Aluminum ratio using value of 0.5, the space velocity (WHSV) at 6.6 h<sup>-1</sup> and the Methane/Benzene feed ratio equal to 45.

From Figure 4.17 and Figure 4.18, at the initial (10 minute), benzene conversion shows the same trend as thermodynamic calculation, it increases with the reaction temperature. Because methylation reaction is endothermic reaction, higher temperature causes higher potential to force the reaction. At 300 °C reaction temperature, the conversion is relatively constant and the catalytic activity is low. In the term of toluene selectivity, it observed that nearly hundred percent of converted benzene transformed to toluene. At 350 °C, the conversion is higher than at 300 °C but slightly decreases with time on stream, however, the toluene selectivity is still high. If the reaction temperature increases to 400 °C, the initial conversion is higher than that of at 300 and 350 °C, but the initial selectivity is decrease. Moreover, the conversion is easily dropped as showed by the rapid decrease in the benzene conversion. Especially after time on stream 120 minute the conversion is lower than the reaction temperature at 350 °C. This decreasing of benzene conversion is ascribed to the coke formation which possibly more generates by the increasing of reaction temperature.

According to the sufficient benzene conversion, good stability and high toluene selectivity, the reaction temperature would be fixed at 350 °C for the following experiment.



**Figure 4.17** Benzene conversion as a function of time on stream at different reaction temperature.



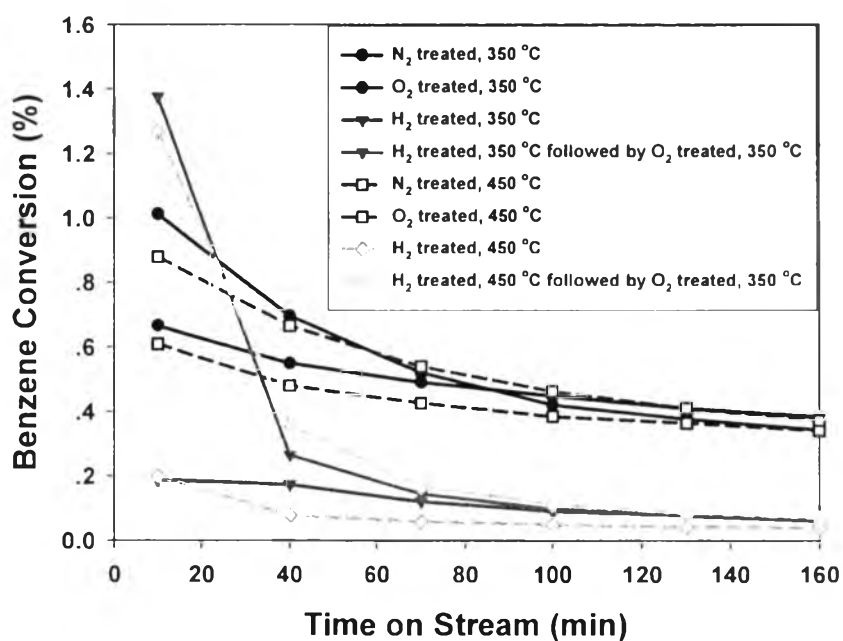
**Figure 4.18** Toluene selectivity as a function of time on stream at different reaction temperature.

#### 4.2.2 Effect of Treatment Gas and Treatment Temperature

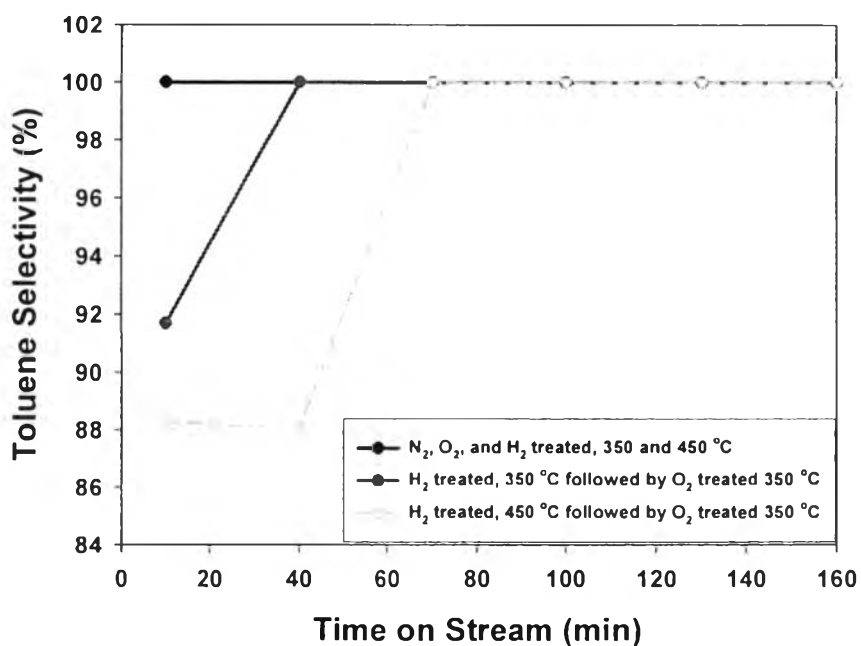
The effect of treatment temperature is examined in the range of 300 to 400 °C using various treatment gases (nitrogen, oxygen, hydrogen and hydrogen followed by oxygen). The other parameters are fixed, the reaction temperature is at 350 °C, the carrier gas is nitrogen, the Indium/Aluminum ratio using value of 0.5, the space velocity (WHSV) at  $6.6 \text{ h}^{-1}$  and the Methane/Benzene feed ratio equal to 45.

From Figure 4.19 and Figure 4.20, the treatment atmosphere also affected to the benzene conversion. Hydrogen treatment (reduction) provided the lowest conversion near zero. Oxygen treatment (oxidation) provided higher conversion, which is slightly different from nitrogen treatment (inert) in which the initial conversion is around 0.6-1.0% and dropped to around 0.4% after time on stream of 160 minute. The interesting one is the hydrogen treatment (reduction) followed by oxygen treatment (oxidation), it can achieve initial benzene conversion of 1.4% but rapidly dropped to nearly the same as that of the catalyst treated by hydrogen after 40 minute.

The treatment temperature is investigated between 350 °C and 450 °C in each treatment gas. It shows that the increasing of treatment temperature provided insignificant difference in both benzene conversion and toluene selectivity; it majorly depends only on the treatment atmosphere.



**Figure 4.19** Benzene conversion as a function of time on stream at different treatment atmosphere and treatment temperature.

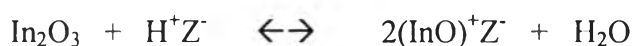


**Figure 4.20** Toluene selectivity as a function of time on stream at different treatment atmosphere and treatment temperature.

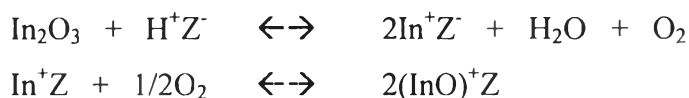
From the theory, after treatment in reducing atmosphere, indium compound mixed with HZSM-5 should be transformed into the  $\text{In}^+$  cation due to reductive solid-state ion exchange (Mihalyi and Beyer, 2001). The  $\text{In}^+$  cation is expected to be an electron donor (or proton acceptor) that possibly generates the alkyl intermediate.

In contrast, treatment in oxidizing atmosphere and inert atmosphere are expected to produce the different intermediate which possibly results in the oxyindium cation,  $\text{InO}^+$ . According to the results, the oxidized form ( $\text{InO}^+$ ) has higher activity for methylation reaction than  $\text{In}^+$  cation, possibly because  $\text{InO}^+$  can act as electron acceptor (or hydride acceptor) and generates carbenium species.

However, the transformation to  $\text{InO}^+$  cation by direct oxygen treatment or inert treatment may not effective because this treatment may firstly generate unexpected indium species. During the treatment, it possibly formed the chlorided indium species,  $\text{InCl}_x\text{O}_y$ , (Sowade *et al.*, 2003) or else formed crystallize  $\text{In}_2\text{O}_3$ , which both are considered as undesired inactive species for benzene methylation reaction. However, the  $\text{InO}^+$  cation can later slowly generate from  $\text{In}_2\text{O}_3$  by auto-reductive solid-state ion exchange (AR-SSIE) during both treatment and reaction period as shown below.



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

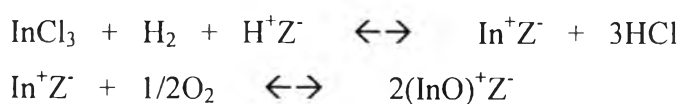


As the results at time on stream of 160 minute, oxygen and nitrogen treatment provided the similar conversion around 0.4% which higher than both hydrogen treatment and hydrogen followed by oxygen treatment which is less than 0.1% conversion. That phenomenon is explained by the limiting step of the first step that  $\text{In}_2\text{O}_3$  is converted to  $\text{In}^+$  cation, the slowly conversion made the  $\text{In}_2\text{O}_3$  still

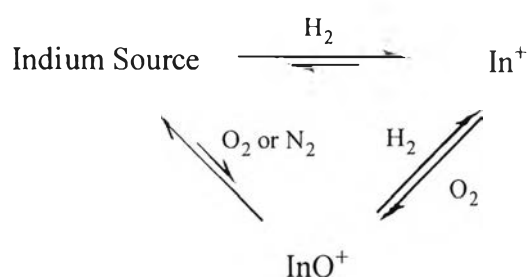


remain in the catalysts and continuously convert to  $\text{In}^+$  and  $\text{InO}^+$  cation after time on stream of 160 minute. So, the initial conversion of oxygen or nitrogen treatment is not much high but can stand for a long time.

Difference from the direct transformation that based on AR-SSIE, the indirect path firstly converts indium into reduced form and then oxidizes  $\text{In}^+$  cation into  $\text{InO}^+$  cation. This method has been therefore suggested by reducing the catalyst by hydrogen, and then followed by oxidation process as shown below.



This way, the treated catalyst shows high initial conversion which is presumably catalyzed by  $\text{InO}^+$  species. However, the conversion dropped after a short time reaction. This describes by the active  $\text{InO}^+$  converted back to  $\text{In}^+$  species which may be resulted from two reasons, (1) the reduction of  $\text{InO}^+$  by hydrogen formed as a by-product and/or (2) the removing of oxygen atom in  $\text{InO}^+$  cation by the formation of water by-product instead of hydrogen.



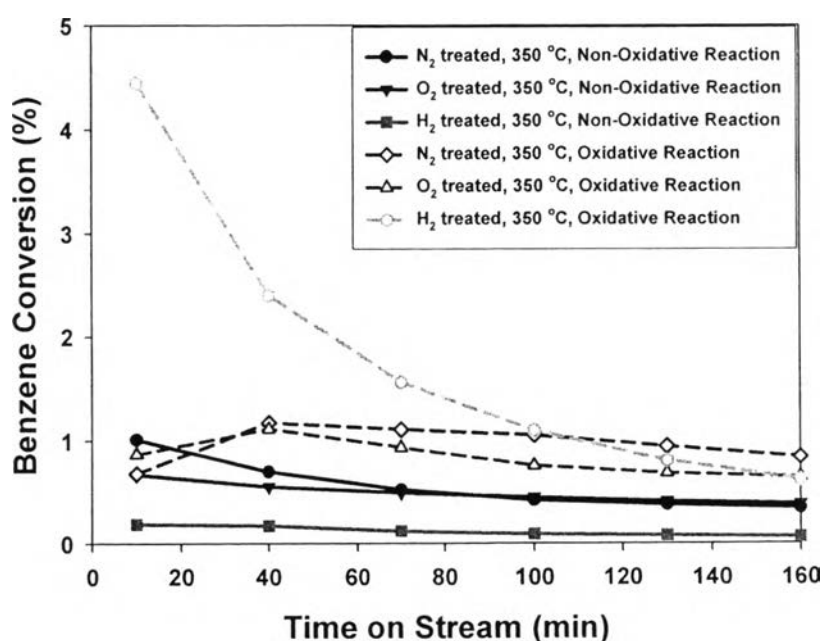
**Figure 4.21** Concept of direct and indirect indium converting.

From the inefficiency exchange to active species in the direct and also the drawback of indirect treatment which provides high conversion only at initial time on stream, therefore, the catalyst is treated with hydrogen prior to reaction and the oxygen was also fed as carrier gas had been performed.

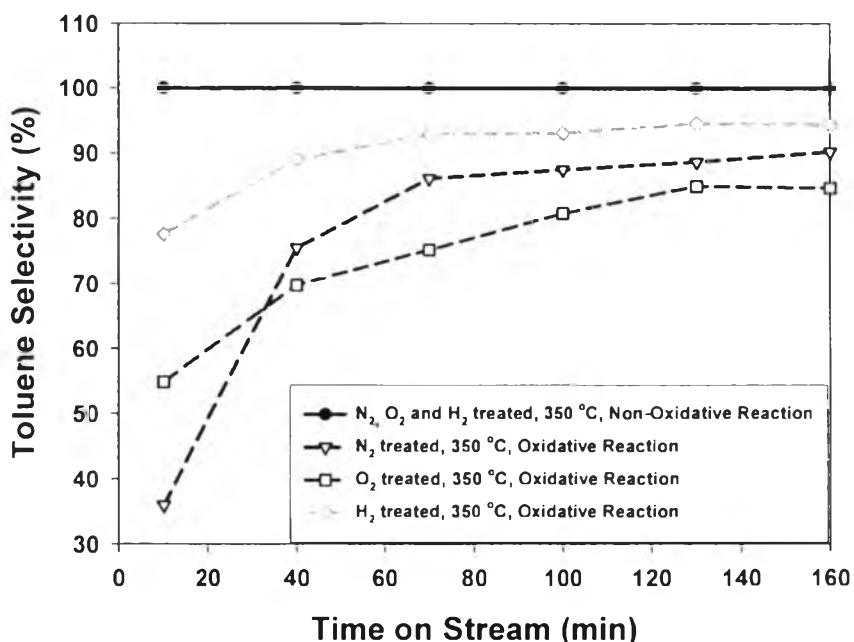
#### 4.2.3 Effect of Oxidative Reaction (Carrier Gas)

The effect of carrier gas is compared between nitrogen and oxygen under various treatment gases (nitrogen, oxygen and hydrogen). The other parameters is fixed, the reaction temperature is at 350 °C, the treatment is performed at 350 °C, the Indium/Aluminum ratio using value of 0.5, the space velocity (WHSV) at 6.6 h<sup>-1</sup> and the Methane/Benzene feed ratio equal to 45.

From Figure 4.22 and Figure 4.23, oxygen carrier (oxidative reaction) showed different benzene conversion compared to nitrogen carrier (non-oxidative reaction) in each treatment gas. From the results, the nitrogen treatment and oxygen treatment followed by oxidative reaction is similar, while they show a little higher conversion compared to the non-oxidative reaction of the same treatment atmosphere. The hydrogen treatment shows a large different result between oxidative and non-oxidative reaction. The benzene conversion is increasing from nearly zero of non-oxidative reaction to 4.4% of initial conversion in oxidative reaction. This can describe by the difference of indium species generated in difference carrier gas which possibly is In<sup>+</sup> cation and InO<sup>+</sup> cation.



**Figure 4.22** Benzene conversion as a function of time on stream at different treatment atmosphere in oxidative and non-oxidative reaction.



**Figure 4.23** Toluene selectivity as a function of time on stream at different treatment atmosphere in oxidative and non-oxidative reaction.

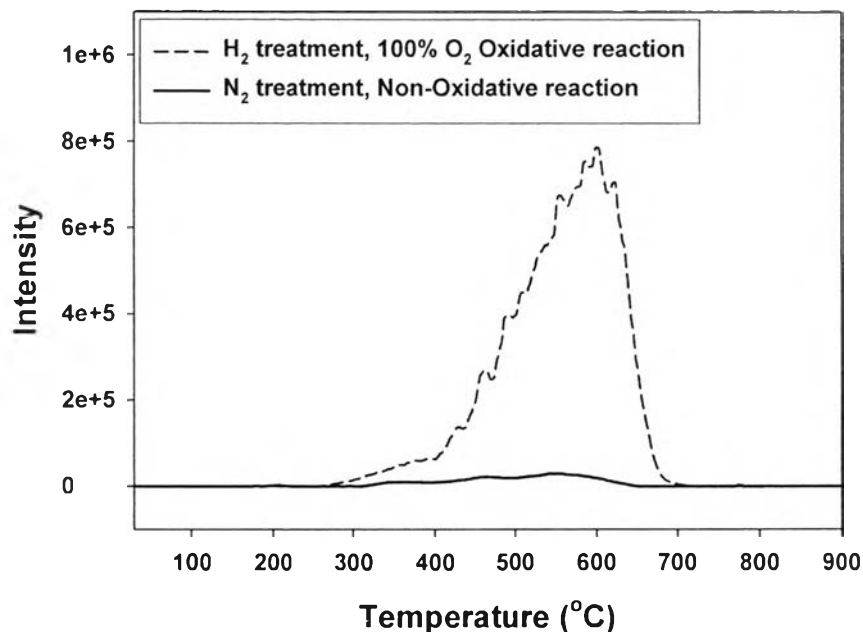
From the previous discussion, nitrogen treatment and oxygen treatment are expected to provide  $\text{In}_2\text{O}_3$  which is slowly converted to  $\text{InO}^+$  cation by AR-SSIE during the treatment and reaction period. As shown that AR-SSIE has two steps which both are related to the amount of oxygen, the increasing of oxygen may accelerate especially the second step that produce  $\text{InO}^+$  cation. However, as discussed that the limiting step should be the first one, the oxidative reaction does not make a greatly increase of benzene conversion.

That situation is difference for hydrogen treatment, the reduced indium, which should be in the form of  $\text{In}^+$  cation, is inactive when oxygen is not presence (non-oxidative reaction). In the case of oxidative reaction, the  $\text{In}^+$  cation are transformed to active  $\text{InO}^+$  cation which provided high benzene conversion. Moreover, oxygen in the system can continuously regenerate the  $\text{InO}^+$  cation that converted back to  $\text{In}^+$  cation by the two reasons that mentioned before, this can maintain high amount of active species along the reaction period.

However, the results showed the decreasing of benzene conversion by the time. This may not ascribe to the lower of active species but it may result from the formation of coke that deposit on the catalysts surface.

In the term of toluene selectivity, the nearly hundred percents toluene when using nitrogen carrier, dropped to around 78% at the initial when using oxygen carrier. Moreover, the oxygen and nitrogen treatment followed by oxygen carrier show more dropped to 55% and 36%, respectively. This possibly happened from the over reaction of benzene since the observed by-product are majorly naphthalene and other poly-rings aromatics. Another reason that make the decreasing of toluene selectivity in oxygen and nitrogen treatment possibly ascribe to the presence of chlorided indium species ( $\text{InCl}_x\text{O}_y$ ) that is considered as unselectively activated species for methane activation (Sowade *et al.*, 2003).

The TPO result which supported the assumption of coke deposition is shown in Figure 4.24. The TPO profile of nitrogen treated followed by non-oxidative reaction shows the small oxidized peak while the hydrogen treated followed by oxidative reaction shows a strong peak in the range around 400-700 °C. That peak is attributed to the carbon deposition on the spent catalyst, this can imply that oxygen in the carrier gas significantly affect to the coke formation.



**Figure 4.24** Temperature Program Oxidation (TPO) profiles of the spent catalysts compared between the oxidative and non-oxidative reaction.

#### 4.2.4 Effect of Oxygen Content

The effect of oxygen content is examined among 2%, 21% and 100% of oxygen balanced in nitrogen. The other parameters is fixed, the reaction temperature is at 350 °C, the treatment is performed in hydrogen at 350 °C, the Indium/Aluminum ratio using value of 0.5, the space velocity (WHSV) at 6.6 h<sup>-1</sup> and the Methane/Benzene feed ratio equal to 45.

From Figure 4.25 and Figure 4.26, oxygen content in oxidative reaction caused the different of benzene conversion. A hundred percent oxygen provided the highest initial benzene conversion followed by 21% and 2%, respectively. This may be ascribe to the production and regeneration rate of active InO<sup>+</sup> species increased with increasing oxygen content, but this active species also caused high coke production as shown in the rapid decreasing of conversion along the time.

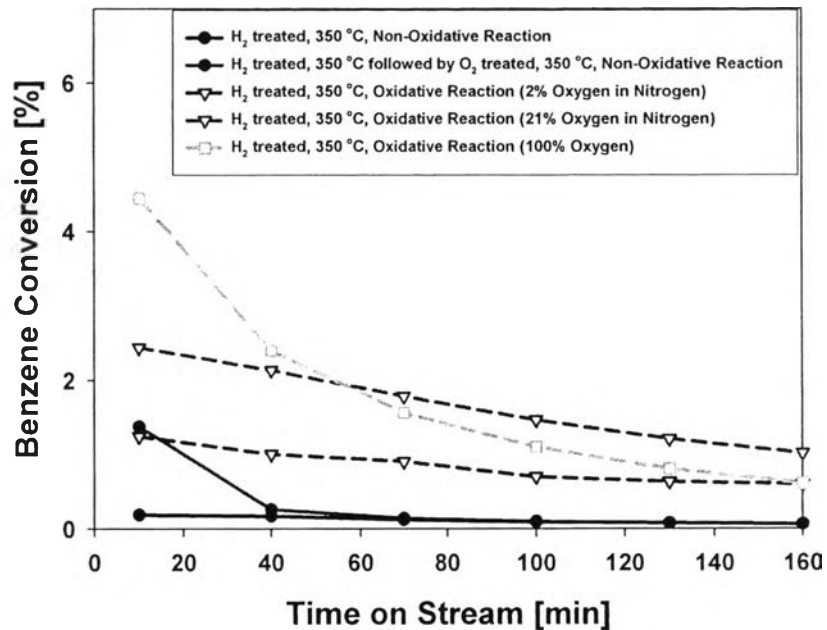


Figure 4.25 Benzene conversion as a function of time on stream at different oxygen content.

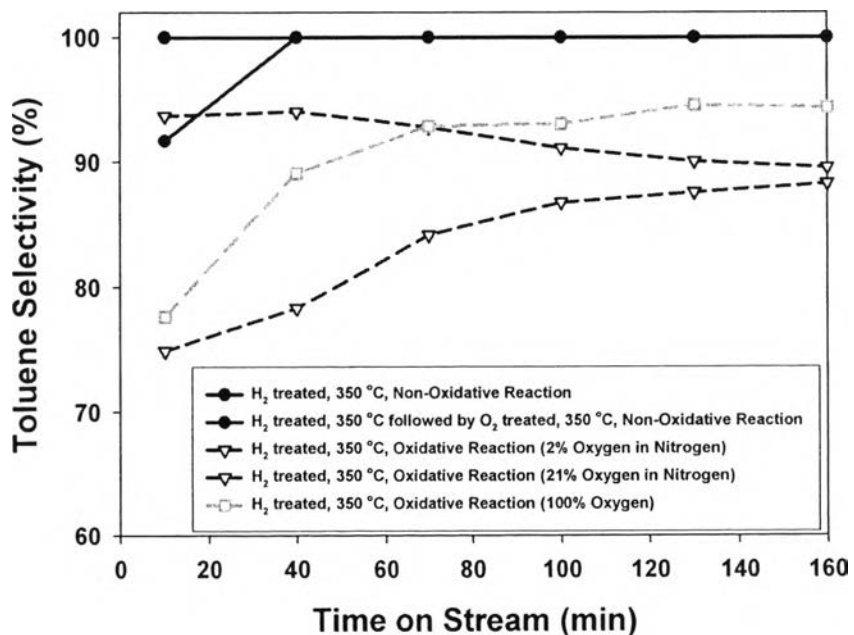
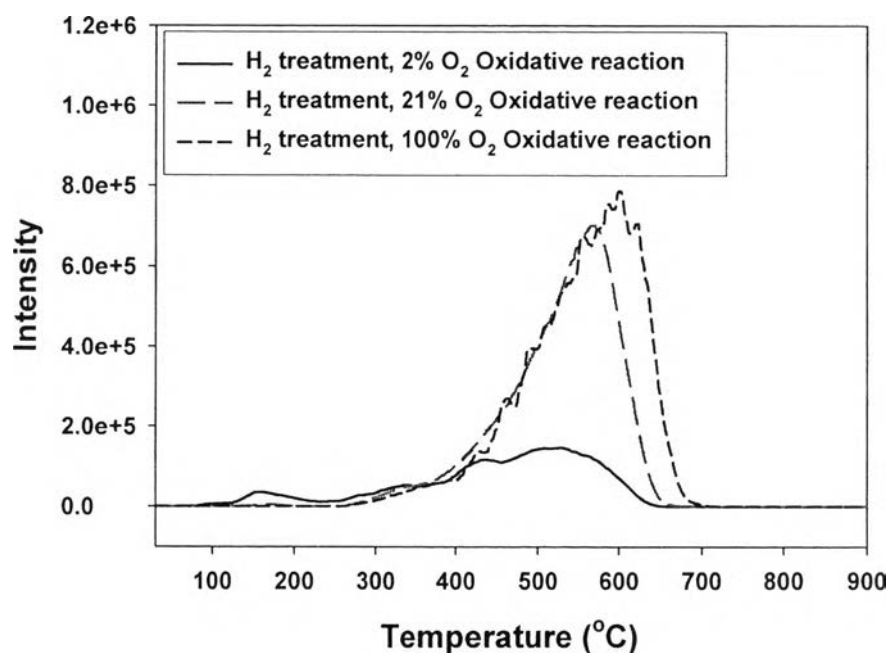


Figure 4.26 Toluene selectivity as a function of time on stream at different oxygen content.

Figure 4.27 shows the TPO profile of spent catalysts with different oxygen content in carrier gas. It support that the coke formation is depended on the oxygen content, higher oxygen amount contributed more coke. The reason of this might be ascribe to the presence of oxygen provided the continuous generation of active species, the excess of highly active species might caused an over activation to further undesired coke product.



**Figure 4.27** Temperature Program Oxidation (TPO) profiles of the spent catalysts compared between different oxygen content in oxidative reaction.

The amount of carbon deposition in each spent catalyst from TPO results is shown in Table 4.2.

**Table 4.2** Amount of carbon deposition of spent catalyst

Sample	%wt. of carbon deposition
N <sub>2</sub> treated, Non-Oxidative reaction	0.48
H <sub>2</sub> treated, 2% Oxygen in Oxidative reaction	2.94
H <sub>2</sub> treated, 21% Oxygen in Oxidative reaction	9.95
H <sub>2</sub> treated, 100% Oxygen in Oxidative reaction	12.89

The falling of benzene conversion along the time by the coke formation is supported by the decreasing of surface area which is shown in Table 4.3. The surface area of spent catalysts in both N<sub>2</sub> and H<sub>2</sub> treatment followed by N<sub>2</sub> carrier show insignificant decrease compared with the fresh catalysts which are shown in Table 4.1. In contrast, the catalysts with O<sub>2</sub> carrier show the greatly decrease of surface area which presumably occurred by the coke, the decreasing of surface area contributed to the decreasing of conversion along the time.

**Table 4.3** Surface area of spent catalysts

Sample	BET surface area (m <sup>2</sup> /g)
In/HZSM-5 (N <sub>2</sub> treatment, N <sub>2</sub> carrier)	289.9
In/HZSM-5 (H <sub>2</sub> treatment, N <sub>2</sub> carrier)	279.9
In/HZSM-5 (N <sub>2</sub> treatment, O <sub>2</sub> carrier)	155.2
In/HZSM-5 (H <sub>2</sub> treatment, O <sub>2</sub> carrier)	111.4



However, because of the highest initial benzene conversion of the reaction when using 100% oxygen as a carrier gas, the further experiment would be performed by using hydrogen treatment at 350 °C followed by the oxidative reaction with 100% oxygen carrier.

#### 4.2.5 Effect of Indium to Aluminum Ratios

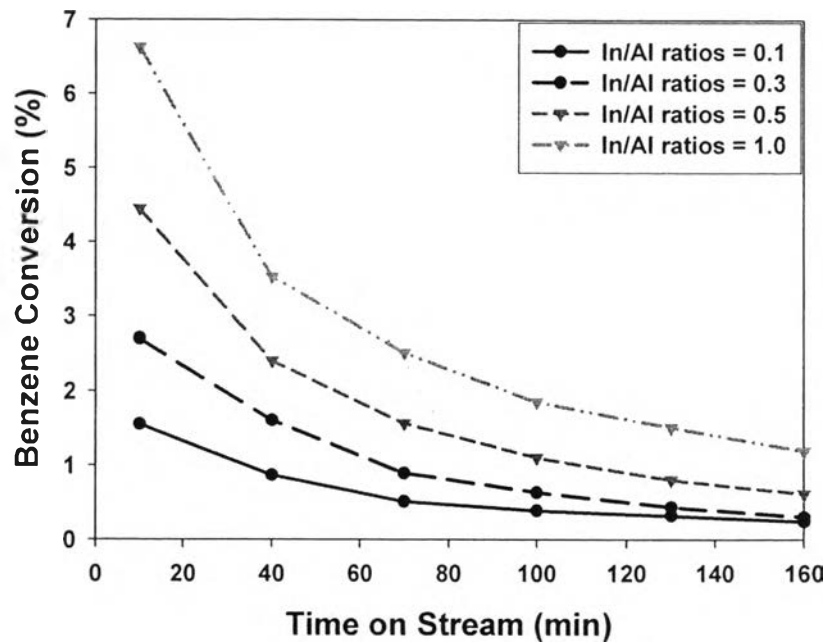
The effect of Indium/Aluminum ratio is examined in the range of 0.1 to 1.0. The other parameters is fixed, the reaction temperature is at 350 °C, the treatment is performed in hydrogen at 350 °C, the carrier gas is 100% of oxygen, the space velocity (WHSV) at  $6.6 \text{ h}^{-1}$  and the Methane/Benzene feed ratio equal to 45.

The increasing of indium to aluminum ratio is the same meaning as increasing indium cation existing at the negative site of ZSM-5 framework as a charge balancing species compared with proton (Bronsted acid) exists. The results of temperature program desorption (TPD) in Table 4.4 demonstrated that amount of Bronsted acid depended on the indium loading amount. The higher In/Al ratio shows the lower of Bronsted acid on the catalyst surface.

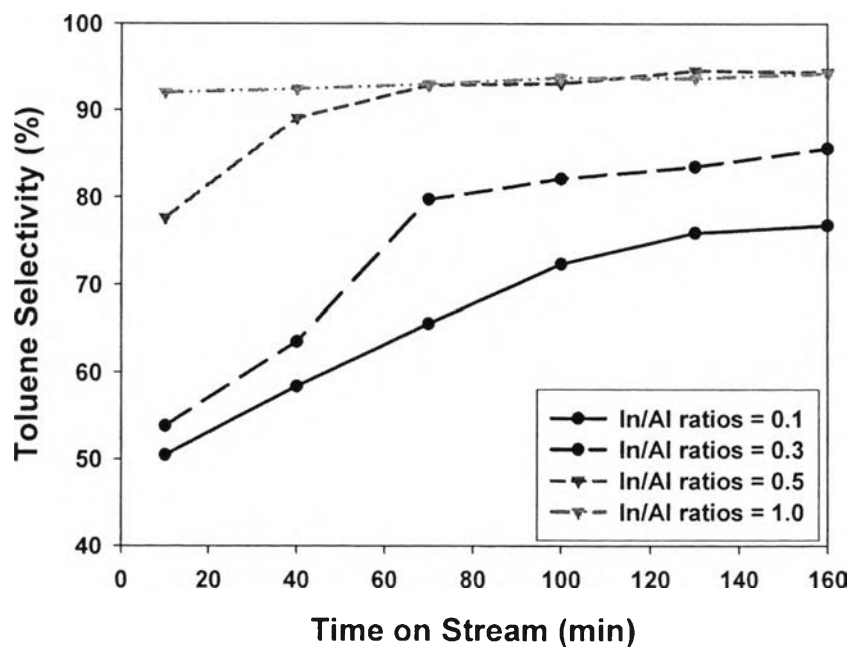
**Table 4.4** Temperature program desorption (TPD) results of catalysts with various indium loading ratios

Sample	In/Al ratios	Weak Bronsted acid ( $\mu\text{mol/g}$ )	Strong Bronsted acid ( $\mu\text{mol/g}$ )	Total Bronsted acid ( $\mu\text{mol/g}$ )	Bronsted acid remaining (%)
HZSM-5	-	18.1	180.6	198.7	100.0
In/HZSM-5	0.1	18.7	188.7	207.4	104.4
	0.3	28.3	149.8	178.1	89.6
	0.5	12.0	66.9	78.8	39.7
	1.0	5.1	19.1	24.2	12.2

From Figure 4.28 and Figure 4.29, increasing indium to aluminum ratios in catalyst provided higher benzene conversion with also higher toluene selectivity. The initial benzene conversion increased from 1.5 % of In/Al ratio 0.1 to 6.6 % of In/Al ratio 1.0, while the initial toluene selectivity increased from 50 % to 92 %.



**Figure 4.28** Benzene conversion as a function of time on stream at different indium to aluminum ratio.



**Figure 4.29** Toluene selectivity as a function of time on stream at different indium to aluminum ratio.

According to the results that benzene conversion increase with indium amount (or decrease with proton), it implies that proton site (or Bronsted acid) possibly does not have any crucial role to convert benzene in the presence of methane to the desired product. The activity of the catalyst mainly depends on the site of indium cation which should be  $\text{InO}^+$  species.

Moreover, the increasing of In/Al ratio also provided higher toluene selectivity. At low In/Al ratio or high proton site, effect of proton species (Bronsted acid) may contribute to the side reaction such as disproportionation and isomerization which the intermediates are the poly-rings aromatics species, this group of species may remain in product stream and affect to the product selectivity.

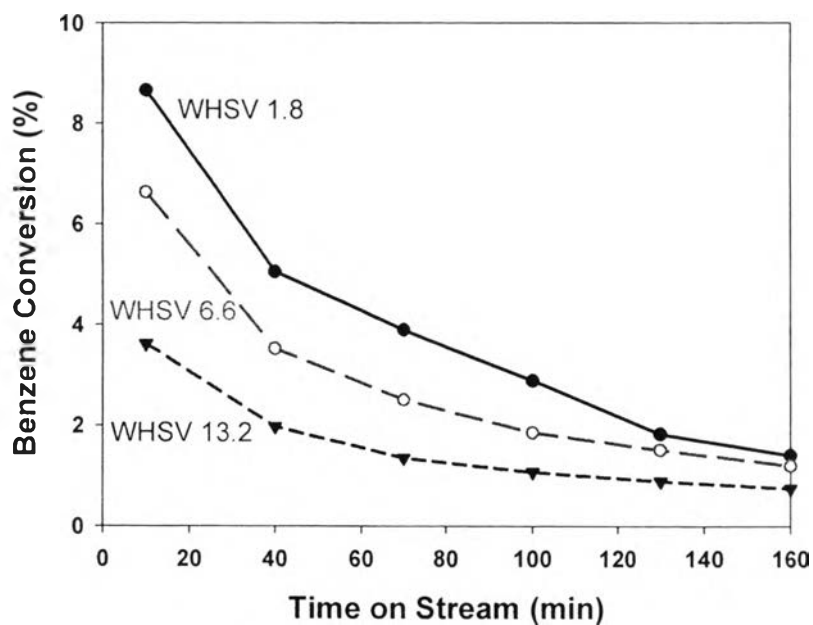
The In/Al ratios equal to 1.0 provided high benzene conversion of 6.6 % and also high toluene selectivity of 92 % because methylation is the main reaction activated by that ratio of catalyst, so the next experiment would be performed by using In/Al ratio equal to 1.0.

#### 4.2.6 Effect of Space Velocity (WHSV)

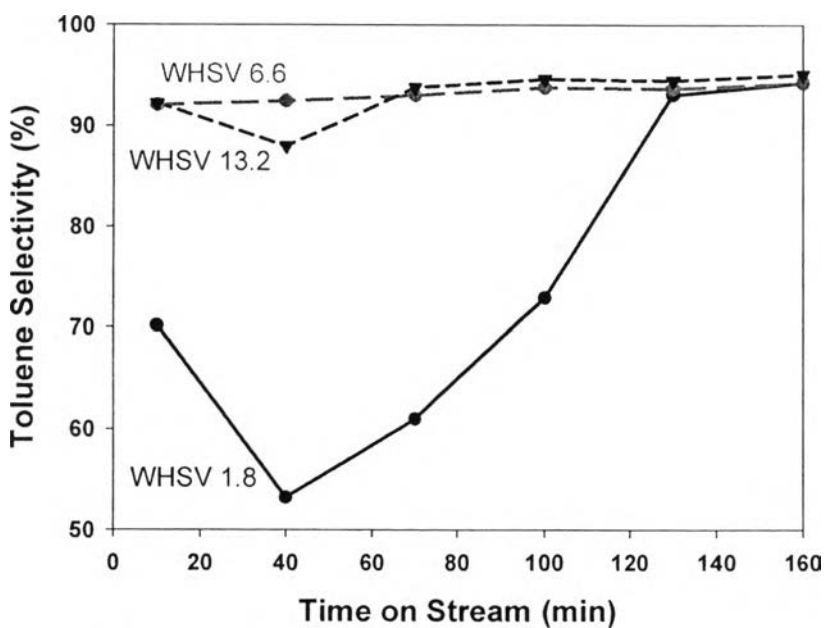
The effect of space velocity (WHSV) is examined in the range of 1.8 to 13.2  $\text{h}^{-1}$ . The other parameters is fixed, the reaction temperature is at 350 °C, the treatment is performed in hydrogen at 350 °C, the carrier gas is 100% of oxygen, the Indium/Aluminum ratio using value of 1.0 and the Methane/Benzene feed ratio equal to 45.

From Figure 4.30 and Figure 4.31, decreasing WHSV is the same meaning as increasing contact time, so it shows that the benzene conversion increased with decreasing WHSV. WHSV also affects to toluene selectivity, at low WHSV (1.8  $\text{h}^{-1}$ ) the by-products majorly naphthalene and other poly-ring aromatics are observed in high amount. This possibly occurs by the undesired over reaction or any other side reactions when the chemicals stay in the catalyst bed for a long time.

Comparing WHSV at 6.6 and 13.2  $\text{h}^{-1}$ , the benzene conversions are 6.6 % and 3.6 %, respectively, but the toluene selectivity is insignificant difference. From this reason, the next experiment would still use WHSV equal to 6.6  $\text{h}^{-1}$  in order to keeps high toluene selectivity with a sufficient benzene conversion.



**Figure 4.30** Benzene conversion as a function of time on stream at different space velocity (WHSV).

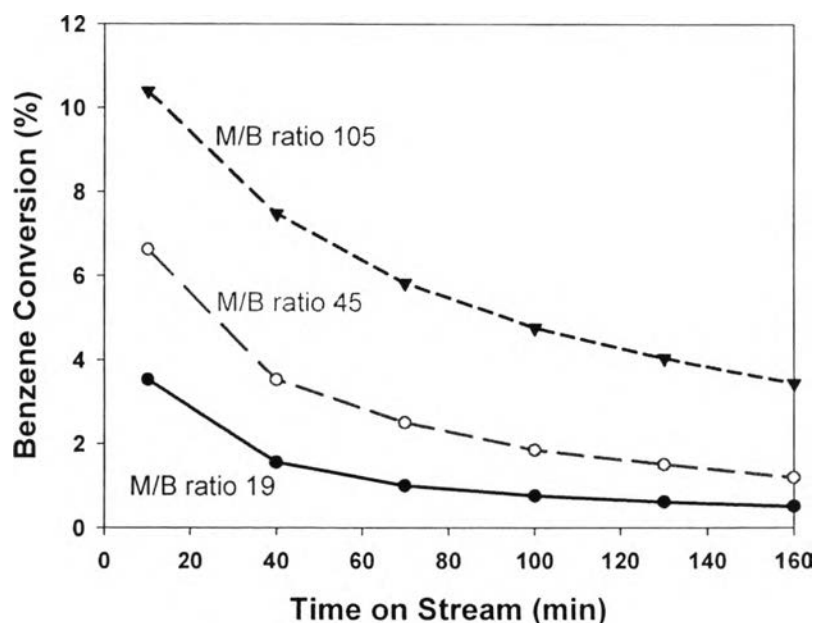


**Figure 4.31** Toluene selectivity versus time on stream at different space velocity (WHSV).

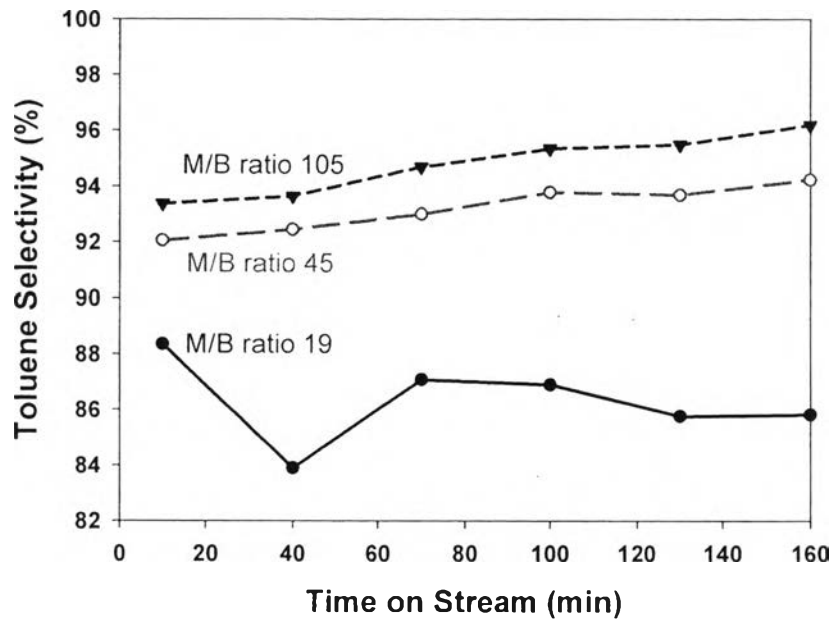
#### 4.2.7 Effect of Methane to Benzene Feed Ratio

The effect of Methane/Benzene feed ratio is examined in the range of 19 to 105. The other parameters is fixed, the reaction temperature is at 350 °C, the treatment is performed in hydrogen at 350 °C, the carrier gas is 100% of oxygen, the Indium/Aluminum ratio using value of 1.0 and the space velocity (WHSV) at 6.6 h<sup>-1</sup>.

From Figure 4.32 and Figure 4.33, the results show the same trend as the thermodynamic calculation in Figure 4.16. Increasing methane to benzene feed ratios provides the higher potential to force the reaction as expected from *Le Chatelier's* principle. The benzene conversion afforded 10.4 % when using methane to benzene feed ratio equal to 105. In the term of selectivity, it found that toluene selectivity also increase when increase methane to benzene feed ratios. The increasing of toluene selectivity may be ascribe to the lower of aromatic species in the system, the opportunity to find each others and occur the side reaction to poly-rings aromatics products is also decrease.



**Figure 4.32** Benzene conversion as a function of time on stream at different methane to benzene feed ratio.



**Figure 4.33** Toluene selectivity as a function of time on stream at different methane to benzene feed ratio.

#### 4.2.8 Reaction Results Evaluation

The methylation of benzene with methane is not commercial process yet, so the results evaluation is reasonable to use the value from thermodynamic calculation and the other research experiments (Baba, 2005, Baba *et al.*, 2005 and Lukyanov *et al.* 2009) to compare. Each experiment has been performed by using different reaction condition, the method to evaluate these experiments should use the percent of conversion afford compared to the limitation value in thermodynamic. The comparison table of various experiments is shown in Table 4.5.

**Table 4.5** Benzene conversion afford compared to the limitation value from thermodynamic calculation of various experiment

Experiment	Catalysts	Reaction conditions		Reaction results	Thermodynamic calculation	
		M/B ratios	Temperature (°C)	Benzene conversion (%)	Limitation conversion (%)	Conversion afford compared to limitation (%)
Baba, 2005	Ag/HZSM-5	25	400	6.1	10.82	56.4
Baba <i>et al.</i> , 2005	In/HZSM-5	25	400	6.4	10.82	59.1
Lukyanov <i>et al.</i> , 2009	Pt/HZSM-5	9	370	4.5	5.49	82.0
Present study	In/HZSM-5	19	350	3.5 (initial)	6.89	50.8
	In/HZSM-5	45	350	6.6 (initial)	10.40	63.5
	In/HZSM-5	105	350	10.4 (initial)	15.44	67.4

Compared all experiment, the Pt/HZSM-5 can provide the conversion nearest to the limitation value which is 82.0 %. In the case of In/HZSM-5, the value is in the range of 50.8 to 67.4 % depended on methane to benzene feed ratios and reaction temperature. The best conversion compared to the thermodynamic limitation of the present study achieved when using In/HZSM-5 with methane to benzene feed ratio equal to 105, which afford 67.4 % of maximum available value.