CHAPTER II
LITERATURE REVIEW

2.1 Methane Activation

Methane is the major component in natural gas which can be used as fuel or as a feedstock for petrochemicals industry. The world consumption of natural gas is about 80 trillion cubic foot per year (Lunsford, 2000), around 92% of all natural gas end-use is applied to be the energy source and 8% remaining is for the chemicals feedstock. (Hackworth *et al.*, 1995)

Comparing with other basic raw materials, methane is the cheapest and the most abundant, but the limitation of methane utilization is the thermodynamic stability in almost all reaction except for the combustion and partial oxidation. According to this reason, methane processing is typically divided into two groups; one-step reaction process or direct conversion, and multi-step reaction process or indirect conversion (Gesser and Hunter, 1998).

Direct conversion process requires only one reaction step to achieve the valuable product. The examples of this type are direct oxidation of methane to methanol or formaldehyde, oxidative coupling of methane to olefin, aromatization of methane, and another interesting one is the alkylation of other species (olefins or aromatics) with methane (Lunsford, 2000).

In multi-step reaction process, as the name implied, methane is first converted to more active species, usually carbon monoxide and hydrogen which called syngas. To convert methane into synthesis gas, the process can be either steam reforming, carbon dioxide reforming or partial oxidation. Then, several techniques can be used for further converting syngas to valuable products such as gasoline by Fischer-Tropsch process or methanol by the methanol synthesis process. The major disadvantage of indirect conversion is the requirement of more than one step, which definitely required higher capital and operating cost.

The methane intermediates can be in various activated forms. Typically three groups of intermediates are free radicals ($CH_3\cdot$), carbenium ion (CH_3^+), and alkyl species (CH_3^-).

Many reactions are explained by the pathway of methyl free radicals for example, the combustion of methane, the oxidative coupling methane to olefins and the oxidation of methane to methanol or formaldehyde. Although free radicals pathway is applied in many processes, disadvantage of this pathway is the limitation of product selectivity (Olah, 1987).

The other pathways, which provide better product selectivity, are via carbenium ion and alkyl species. There are evidences that both carbenium and alkyl intermediate can be occurred on bifunctional catalyst (Luzgin *et al.*, 2010). The theoretical simulation of methane activation over silver-exchange ZSM-5 catalyst suggested that metal on zeolite support prefers to generate alkyl species as intermediate due to their lower activation energy (Ding *et al.*, 2008). This alkyl group weakly bonded with silver while proton is on the zeolite support as shown in equation (1)

$$ZO^-Ag^+ \quad + \quad CH_4 \quad \longleftrightarrow \quad H^+OZO^-Ag^+CH_3^- \tag{1}$$

where ZO^- represents the fraction of zeolite possessing one negative charge.

Ga-modified BEA zeolites were studied for methane activation (Luzgin *et al.*, 2010). It was found that alkyl and carbenium intermediate were reversible depending on temperature and methane partial pressure. Alkyl species can be decomposed to form methane and generate carbenium ion in the form of Ga-methoxy species at 573 K after evacuate the system as shown in equation (2).

$$Ga\text{-}CH_3 \quad \longleftrightarrow \quad CH_4 \quad \longleftrightarrow \quad Ga\text{-}O\text{-}CH_3 \tag{2}$$
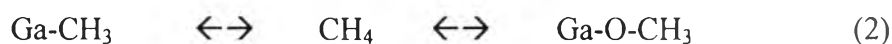
Alkyl species   Methoxy (Carbenium) species

2.2 Alkylation of Aromatic

The alkylation of aromatic is an important reaction in petrochemicals. Common alkylating agents are alkyl halide, alcohol and ether, alkene, alkyne, and dienes. The largest used is alkene due to easier transformation into more reactive species such as carbenium ion.

The alkylation reaction can occur through three different routes; electrophilic substitution, nucleophilic substitution, and free radical substitution mechanism.

Electrophilic substitution is the most common alkylation reaction of benzene. Typically, the benzene ring acts as nucleophiles for serving electrons to electrophiles. The reaction is presumed via a two-step mechanism. The first step is the attack of an electrophile (E^+) to form a carbocation intermediate (σ-complex) with the aromatic ring and, as a result, simultaneously destroy the aromaticity of the benzene ring. Then the formation of the final product by leaving proton with regaining the aromaticity of ring is occurred. The rate limiting step for an electrophilic aromatic substitution is the addition of the electrophile to the aromatic ring (Mcketta, 1993). The general mechanism of all electrophilic substitution reaction is illustrated by equation (3).

$$\tag{3}$$
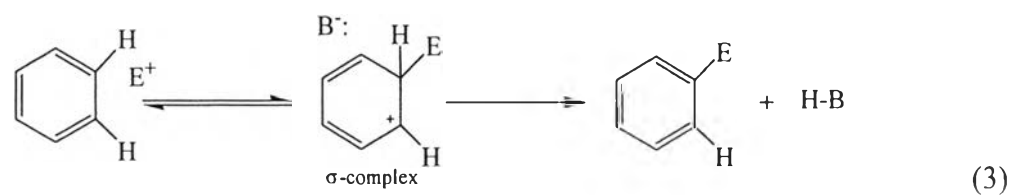
In the case of nucleophilic substitutions, nucleophiles can attack the aromatic ring to substitute into the ring in order to form alkylated product even though aromatic compound usually undergoes substitution by electrophiles. The mechanism involving the attack of an electron rich nucleophile on the aromatic ring which containing strong electron withdrawing group substituted follow by leaving the leaving group, such as a halide (X) on the aromatic ring, as a result, restore the aromaticity of aromatic ring. The reaction is represented by equation (4).

$$EWG = \text{electron withdrawing group}$$

σ -complex

(4)
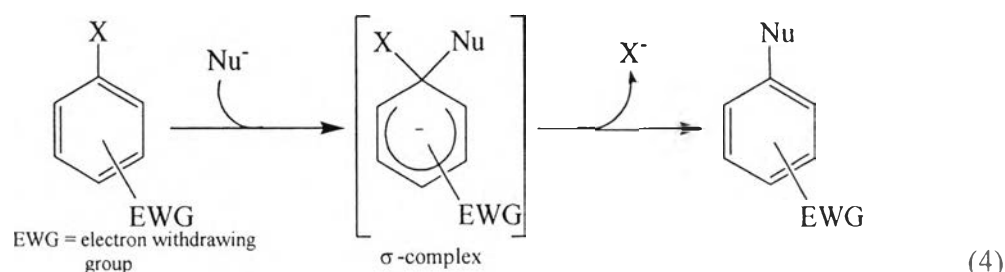
The nucleophilic substitution reaction on aromatic ring usually requires a strong withdrawing group and/or good leaving group at the aromatic ring. Therefore, the reaction of nucleophilic substitution hardly occurs on benzene and alkyl benzene, the possible reaction is supposed to be electrophilic substitution.

Carbenium ion, the intermediate in electrophilic substitution reaction, can generate not only from alkene but also from alkane. However, from the limitation of thermodynamic, more severe condition is usually required. And similar to higher (carbon atom) alkene, the higher alkane also has high reactivity than the lower alkane because of the formation of more stable intermediate carbenium ion. In the case of using methane as alkylating agent, very severe condition and high activity catalyst are required to promote reaction. From the theory, superacid is proposed to use as a catalyst in this reaction (Ertl, 2008).

2.3 Methylation of Benzene with Methane

As mentioned, the alkylation of aromatic can be performed by using alkyl halide or alcohol as an alkylating agent. For the indirect conversion, methane can be firstly transformed to more active species such as methyl halide and methanol by halogenations and hydrolysis, respectively, and then this methane derivative further reacts with benzene. The alkylation with these alkylating agents is commonly used in industrial applications, but if the raw material is methane, the process that required two reaction steps is the major disadvantage.

Direct methylation of aromatic with methane has been studied since He *el al.* (1994) demonstrated that metal substituted on aluminophosphate catalyst can be

used in methylation of naphthalene with methane at 400 °C in a batch reactor. Later, Kennedy *et al.* (1994) argued that methane reactant cannot be incorporated into the methylated aromatic product over H-beta zeolite in a high pressure flow reactor, while He *et al.* (1995) afterward confirmed that reaction by using copper-exchange zeolite (ZSM-5 and beta) and concluded that direct methylation of benzene with methane is possible under high pressure at 400 °C in a batch reactor.

Subsequently, the new route for methylation of benzene with methane has been investigated by Adebajo *et al.* (2000). They revealed that oxygen is essential to contribute the reaction, and found that methanol which is formed only in the present of oxygen by partial oxidation of methane is acted as a key intermediate species in benzene methylation. Luzgin *et al.* (2010) later used NMR technique to support this and observed that the formation of active carbenium ion was increased in the presence of oxygen. This suggested that the residual air can contribute direct methylation via the formation of methanol. Then, the direct methylation of benzene with methane was classified into two different routes; the methylation of benzene with methane in the presence of oxygen (Oxidative Benzene Methylation) and methylation of benzene with methane in the absence of oxygen (Non-Oxidative Benzene Methylation).

The oxidative methylation was further studied by Adebajo *et al.* (2001). The methylation of toluene with methane by various metals on ZSM-5 was investigated, and the results showed that toluene can be converted via two different pathways; methylation by methane and disproportionation. It was proposed that catalysts with more acid sites will mainly lead to disproportionation pathway (Adebajo *et al.*, 2001). Furthermore, Adebajo *et al.* (2005) studied on the effect of framework, Si/Al ratio and pore size structure. The presence of aluminum in the framework of the catalyst is important for the generation of the Bronsted acid sites that necessary for the reaction to occur, the pore structure is also effect to the product selectivity, 12-membered ring pore size (H-beta and H-Y) favor the secondary reaction to form more bulky product, while 10-menbered ring ZSM-5 shows higher selectivity to toluene.

The non-oxidative methylation of benzene with methane was studied in order to prevent the formation of undesired product such as CO_2, CO and H_2O. Prior

to mention on the methylation of benzene with methane, the non-oxidative activation of methane in the presence of other nucleophiles is mentioned.

Choudhary *et al*. (1997) reported that non-oxidative activation of methane can be occurred by hydrogen transfer reaction between methane and alkene over H-galloaluminosilicate ZSM-5 zeolite. The proposed mechanism is the activation of methane occurred over the non-framework Ga-oxide species which carbonium ion is an intermediate. However, Naccache *et al*. (2002) repeated the experiment with ^{13}C-labelled methane and showed that there was insignificant incorporation of ^{13}C into the products under that condition, contrasted with those of Choudhary *et al*. (1997).

The Choudhary's experiment was supported by the research of Baba and Sawada (2002). HZSM-5 loaded with silver cation was used as a catalyst and the results indicated that ^{13}C-labelled propylene was yielded from the reaction of methane in the present of ethylene which methane conversion can afford 13.2 mol%. In addition, the reaction of benzene with ^{13}CH$_4$ was done in gas circulation system, Ag/HZSM-5 produced toluene in a 5.8 mol% yield in 2 minute and the conversion of benzene was 6.1 mol%, while in a flow reactor system, the conversion of methane and benzene were 2.2 and 1.6 mol% , respectively. The proposed mechanism represented in Figure 2.1.
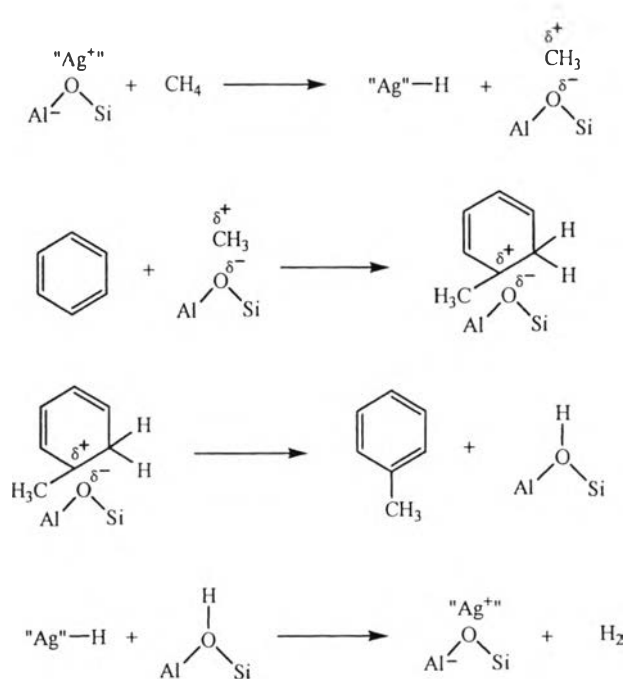

Figure 2.1 The mechanism of methylation of benzene with methane on Ag/HZSM-5 (Baba and Sawada, 2002).

Conversion of methane was examined over various metals loaded HZSM-5 in the present of ethylene. The results showed that methane provide high reactivity on HZSM-5 loaded with silver, molybdenum, and indium with the conversion of 13.2, 9.5 and 8.1 mol%, respectively, while non-metal loaded HZSM-5 cannot activate methane (Baba and Abe, 2003). Moreover, the conversion of methane in the present of ethylene was performed over silver-exchange zeolite with various structures (A, Y, and ZSM-5) and also different silver salt ($Ag_3PW_{12}O_4$), the results showed that propylene was produced over all of Ag-exchange zeolite which Ag loaded on ZSM-5 provides highest selectivity, while silver cation in silver salt cannot catalyze the reaction (Baba *et al.*, 2007).

Silver-exchange ZSM-5 seem to be the highest activity catalyst, however, the decreasing of activity with running time, due to the reduction of silver cation to silver metal, was the important problem. Indium was the next interested metal cation because of high resistant to reduce. In the optimum condition, the maximum conversion of methane in the present of ethylene can be reach 11.8 mol%. In addition, the reaction of benzene with methane by using $^{13}CH_4$ observed 6.4 % benzene conversion with 96 % toluene selectivity, Another experiment in a flow reactor showed the conversion of methane and benzene were 8.5 and 8.3 mol%, respectively, whose selectivity to toluene and xylene were 89 and 11 mol%, respectively (Baba, 2005 and Baba *et al.*, 2005).

Lukyanov *et al.* (2009) investigated the alkylation of benzene with methane to form toluene over Pt/H-MFI bifunctional catalyst. The reaction was carried out in continuous flow reactor at 370 °C, 1 atm with feed comprised of methane (90 mol%) and benzene (10 mol%) under non-oxidizing conditions, the results showed that the highest catalyst activity was observed at time on stream of 4 hr, toluene selectivity was around 96 mol% and conversion of benzene and methane were 4.5% and 0.53%, respectively.

2.4 Indium-Containing Zeolite

Since many researchers found that bifunctional catalyst can be applied in several processes, the various techniques to incorporate metal into support were studied. Like other supports, zeolite can be substituted by metal ions via metal substitution process which occur during both hydrothermal synthesis (primary synthesis) and the post synthesis treatment (secondary synthesis). As a result, metal ion may stay in the framework and/or in the extra-framework as metal oxide or counter ion.

Indium, which is one of the IIIA metal groups, is classified to trivalent metal ions as aluminum. Therefore, incorporation of indium into framework by replacement of existing T-atom site called "isomorphous substitution" is possible. The procedure of indium incorporation under hydrothermal condition was reported, however, the substitution degree is low when compared with other elements (Al, Ga, Fe and B), (Kosslick *et al.*, 1993). An example reaction catalyzed by indium isomorphous substituted catalyst is the benzoylation of naphthalene. However, the benzoylation results by indium-containing beta zeolite are similar to the results from aluminum-containing beta zeolite (Chatterjee *et al.*, 1998). In the case of post-synthesis treatment, Han *et al.* (2000) reported that the secondary synthesis step on ZSM-5 using aqueous InF_3 was unsuccessful, probably due to the hypothesis that In^{3+} ion is too large to substitute into the T-atom site of ZSM-5.

Alternatively, indium containing zeolite can be prepared by the incorporation of In ion into the extra-framework. Miro *et al.* (1999) identified the forms of In ion in the HZSM-5, which are In_2O_3 (indium sesquioxide crystals), In_xO_y (highly dispersed non-crystalline indium oxide), In^+Z^- (univalent indium cation), and $(InO)^+Z^-$ (oxyindium cation). The formation of these indium compounds on zeolites depended on their preparation methods. Almost all cases, both In_2O_3 crystals and highly dispersed non-crystalline indium oxide were found as the undesired inactive species.

2.4.1 Solid-State Ion Exchange of Indium-Containing Zeolite

Generally, there are three techniques to prepare indium cation (In^+ or InO^+) on zeolite supported. These techniques are the impregnation method, the standard (liquid) ion exchange method, and the solid-state ion exchange method (SSIE) which can be divided into two subgroups; reductive solid-state ion exchange (RSSIE), (Mihalyi and Beyer, 2001) and oxidative solid-state ion exchange (OSSIE), (Zamaro *et al.*, 2010).

Miro *et al.* (1999) also reported that indium containing zeolite prepared by impregnation method provided the In_2O_3 species that requires further treatment to generate the active InO^+ species, while the conventional ion exchange required only standard calcinations.

The solid-state ion exchange technique is the effective way to incorporate metals including indium into zeolite as a cation. The exchange process is possibly induced by moisture, high-temperature, and reaction (Price, 2006).

Indium(III)oxide (In_2O_3) is one of the most used for indium precursor in solid-state ion exchange of indium. Generally, the reduction of In_2O_3 in the absence of zeolite is leaded to create the metallic form of indium (In^0), (Solt *et al.*, 2008), as shown in equation (5).

$$In_2O_3 + 3H_2 \longleftrightarrow 2In^0 + 3H_2O \tag{5}$$

However, in the present of zeolites containing acidic hydroxyl group, the reduction process is different. Mihalyi and Beyer (2001) studied the various methods to incorporate indium in the form of cation into zeolites. The mechanism of reductive solid-state ion exchange is shown in equation (6)

$$In_2O_3 + 2H_2 + 2H^+Z^- \longleftrightarrow 2In^+Z^- + 3H_2O \tag{6}$$

where Z^- represents the fraction of zeolite framework contained one negative charge.

Moreover, without introduced hydrogen, the solid-state ion exchange can also occur as shown in equation (7).

$$In_2O_3 + 2H^+Z^- \leftrightarrow 2(InO)^+Z^- + H_2O \tag{7}$$

This phenomenon possibly comes from the auto-reductive solid-state ion exchange (AR-SSIE) which can occur at high vacuum condition. The first step mechanism of AR-SSIE is given in equation (8).

$$In_2O_3 + 2H^+Z^- \leftrightarrow 2In^+Z^- + H_2O + O_2 \tag{8}$$
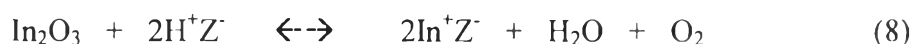
Furthermore, the reductive/oxidative process of indium loaded zeolites was studied by Schutze *et al.* (2001). The cyclic procedure by using oxidation/reduction treatment was performed. The results found that InO^+ species can also form by that cyclic treatment, after the reduction (equation (6)) the oxidation is occurred as shown in equation (9).

$$In^+Z^- + 1/2O_2 \leftrightarrow (InO)^+Z^- \tag{9}$$
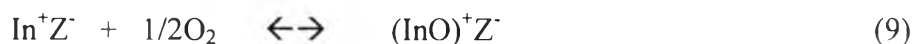
This reaction possibly is the second step of AR-SSIE.

For the oxidative solid-state ion exchange (Solt *et al.*, 2008), metallic indium (In^0) were used as indium precursor. The proposed of this process is given by equation (10).

$$In^0 + (H_3O)^+Z^- \leftrightarrow In^+Z^- + H_2O + 1/2H_2 \tag{10}$$
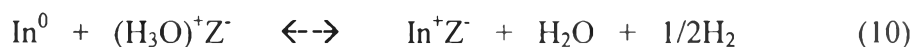
In the studied of indium solid-state ion exchange, there are many of proposed intermediates that might occur prior to the final exchanged species. That intermediate species included In_2O, InO^+ and InOH and it is interesting to know which intermediate is catalytically active for the specified reaction.

2.4.2 Catalytic Activities of Indium-Containing Zeolite

The application of indium-containing zeolite is the selective catalytic reduction (SCR) of NO by using methane as a reducing agent. Ogura *et al.* (1998) compared the preparation method between conventional and solid state ion exchange on various zeolite structures. The results showed that indium containing ZSM-5, mordernite, and beta zeolite prepared by solid-state ion exchange provided the conversion as high as those prepared by conventional ion exchange. This indicated that InO^+ is formed in both cases. Mihalyi *et al.* (2009) demonstrated that In_2O_3 or acidic site alone was inactive in NO conversion. Moreover, the procedure to produce the active species indium cation on ZSM-5 into both In^+ and InO^+ formation also reported. In the case of In^+, reductive solid-state ion exchange or auto-reductive solid state ion exchange should be used, while in the case of InO^+, thermal treatment in inert atmosphere or oxidation of In^+ was applied. Zamaro *et al.* (2010) studied on indium loaded zeolite prepared by oxidative solid-state ion exchange, the results showed that In-ZSM-5 provided high thermal stability of framework but low dispersion when indium loading higher than 4 wt%.

In addition, indium containing zeolite is also used in the toluene disproportionation, xylene isomerization and alkane activation.

In the case of toluene disproportionation, InO^+ cation was introduced into zeolite by RSSIE followed by oxidation in air. The reaction was examined at 450 °C, the toluene conversion was about 4-5 mol% and *p*-xylene selectivity was 30-40 mol% in various In/Al ratios on ZSM-5 (Mavrodinova and Popova, 2005). For the isomerization reaction of *m*-xylene, indium-containing beta zeolite which In/Al ratio of 0.5 and 1 were used, the conversion of *m*-xylene was about 60 mol% on fresh catalyst, while the reduced catalyst was decreased in catalytic activity (Mihalyi *et al*, 1998).

For alkane activation reaction, dehydrogenation and aromatization reaction were performed by utilizing propane (Halasz *et al.*, 1996), pentane, and hexane (Halasz *et al.*, 2003). ZSM-5, which has the individual property in high selectivity to aromatic product, loaded with indium was used as a catalyst with comparing the preparation method between conventional and solid-state ion exchange. The results showed that metal loading amount affected on the product

conversion and selectivity. ZSM-5 containing low indium loading, which contributes high Bronsted acid sites, prefers the cracking reaction, whereas the aromatization activity depends on the Lewis acid sites.

The only one research group which studied on methylation reaction over indium loaded ZSM-5 was Baba *et al.* (2005), which reported the effect of several parameters on the methylation reaction of methane in the present of ethylene. In the effect of calcinations temperature, the optimum point that achieved highest methane conversion was 630 °C, while the appropriate temperature for hydrogen treatment was at 450 °C. Indium content was also important, increasing indium loading provided more conversion but too large amount may cause the products undergo cracking. The optimum reaction temperature and contact time were examined, at temperature 400 °C and contact time (W/F) 3.6 g.h/mol, the conversion of methane achieved a highest value of 11.8 mol%. However, in the case of methylation of benzene with methane, it does not have any detailed research on the effect of each parameter.