CHAPTER II
LITERATURE REVIEW

2.1 Methane

Methane is a chemical compound which is a colorless and odorless. The chemical formula of methane is CH_4. It is the main component of natural gas, landfill gas and a by-product from oil refining and chemical processing. It is the most abundant organic compound which can be a source of clean fossil energy or a raw material.

Methane is a very stable, symmetrical molecule. Methane has a melting point of -182.5°C and a boiling point of -161.5°C. The C–H bonds are strong (425 kJ/mol) and it contains no functional group, magnetic moment or polar distribution to facilitate chemical attacks. Activation of methane by splitting of the C–H bond will require high temperatures or the use of oxidations agents. Catalysis will have to play an important role in most processes for methane conversion.

2.1.1 <u>Methane Activation</u>

Methane is abundant and inexpensive among the other basic raw materials. Thus, it is an attractive fuel which can be brought to the point of use economically. However, the thermodynamic stability is the limitation of methane utilization in almost all reaction except for the combustion and partial oxidation. According to this reason, many concepts have been developed for improving the industrial processes that convert methane into olefins, higher hydrocarbons and gasoline via indirect and direct conversion processes.

2.1.1.1 Indirect conversion process

Indirect conversion process of methane rely upon the production of synthesis gas, either by reforming reaction or by partial oxidation, followed by Fischer-Tropsch chemistry or methanol synthesis process, where methane can be converted to the desired products, such as ethylene, methanol, formaldehyde, and aromatics (Aboul-Gheit *et al.*, 2008). The major disadvantage of indirect conversion is the requirement of more than one step, which definitely need more than one reactor units, that leading to higher capital and operating cost.

2.1.1.2 Direct conversion process

The direct conversion process of methane to desirable commodity chemicals is a challenging approach to the utilization of methane resources. This process is required only one reaction step to develop the valuable product. The recent developments are relevant to the presence or absence of oxygen. The examples of direct conversion processes are oxidative coupling of methane to higher hydrocarbons such as ethane (Yoon and Tung, 1997), partial oxidation of methane to oxygenates such as formaldehyde (Herman *et al.*, 1997), methane cracking, methane aromatization, methane halogenations and oxyhalogenation (Alvarez-Galvan *et al.*, 2011), and another interesting one is the alkylation of aromatic such as benzene with methane (Weckhuysen *et al.*, 1998).

2.2 Intermediate of activated methane

The intermediate of activated methane can be divided in the typical three groups depending upon the process condition and catalyst. They consist of free radicals ($CH_3\cdot$), alkyl species (CH_3^-), and carbenium ion (CH_3^+).

2.2.1 Free radical

Free radicals are atoms, molecules, or ions with an odd number of electrons. The odd refers to an unpaired electron which causes free radicals to be highly chemically reactive. Free radicals may have positive, negative, or zero charge. A free radical readily reacts with another atom by seeking to pair (forming a bond) with another electron.

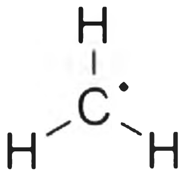


Figure 2.1 Methyl free radical.

Methyl free radicals as shown in Figure 2.1 play an important role in combustion process, oxidative coupling reaction of methane to olefins, partial oxidation of methane to methanol or formaldehyde and many other chemical processes. Nevertheless, this pathway has a drawback of the product selectivity limitation (Olah, 1987).

2.2.2 Alkyl species

Alkyl species or alkyl carbanion is an anion in which negative charge resides on the carbon atom. The carbon atom in carbanion although contains four pairs of electrons, its one pair is free which is an unshared pair. A carbanion is one of several reactive intermediates in organic chemistry. The example structure of methyl carbanion is shown in Figure 2.2.

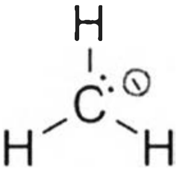


Figure 2.2 Methyl carbanion.

From the methane activation over silver-exchange ZSM-5 zeolites study, the results imply that the carbenium pathway is difficult to occur because of higher activation barrier than alkyl. Consequently, it was proposed that metal on zeolite support prefers to generate alkyl species as intermediate due to the lower activation energy (Ding *et al.*, 2008).

2.2.3 Carbenium ion

The one of two types of carbocation is a carbenium ion which is trivalent and classical type R_3C^+. The other is a carbonium ion which is pentavalent or hexavalent.

Carbenium ions as shown in Figure 2.3 have an incomplete octet of electrons so they are generally highly reactive. However, certain carbenium ions are relatively stable due to the positive charge being delocalised between the carbon atoms. Seeking to fill the octet of valence electrons as well as regain a neutral charge, Positive charge tries to attract negative charge on the target molecule.

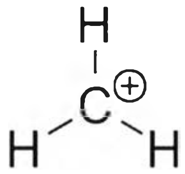


Figure 2.3 Methyl carbenium ion.

Carbeniumion is the intermediate for the reaction that can occur in bifunctional catalyst route (Wang *et al.*, 1993). This route provides more product selectivity than free radical route.

Ga-modifified BEA zeolites with ^{13}C NMR technique (Luzgin *et al.*, 2010) was used to investigate the pathway of methane activation. The results have shown that methane dissociated on Ga/H-BEA in the form of alkyl species while the carbenium ion were found in smaller amount. Temperature and amount of methane in gas phase are the important factors for the reversing of the alkyl and carbenium intermediate to each other. And the results have also shown that alkyl species can decompose into methane and shift to generate carbenium ion in the form of Ga-methoxy species at 573 K after evacuate the system as shown in equation 1.

$$\underset{\text{Alkyl species}}{Ga\text{-}CH_3} \leftrightarrow CH_4 \leftrightarrow \underset{\text{Methoxy (Carbenium) species}}{Ga\text{-}O\text{-}CH_3} \quad (1)$$

2.3 Alkylation of aromatic

The alkylation reaction of aromatic hydrocarbons can be performed using various alkylating agents: alkyl halides, alcohols, alkyl sulphates, and olefins. This reaction involves substitution reaction in which one atom or group (of atoms) replaces another atom or group in the structure of a molecule or ion. They involve the formation of a new bond and the breaking of an old bond. Substitution reactions can occur through three different routes; free radical substitution mechanism, electrophilic substitution, and nucleophilic substitution.

2.3.1 Free radical substitution mechanism

A free radical substitution reaction is a substitution reaction involving free radicals as a reactive intermediate. Free radicals are atoms or groups of atoms which have a single unpaired electron. The reaction always involves at least two steps, and possibly a third.

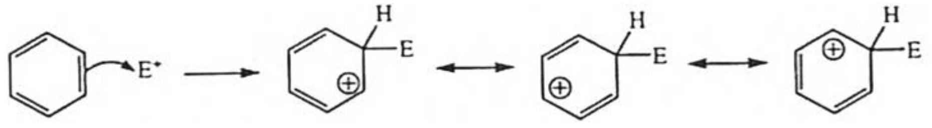
2.3.2 Electrophilic substitution mechanism

Electrophilic aromatic substitution is a substitution reaction in which an atom that is attached to an aromatic system (usually hydrogen) is replaced by an electrophile.

Electrophilic substitution is the most common alkylation reaction of benzene ring. Because the benzene ring is quite electron-rich, it almost always behaves as the nucleophile in a reaction which means that the substitution on benzene occurs by the addition of an electrophile (electrophilic aromatic substitution).

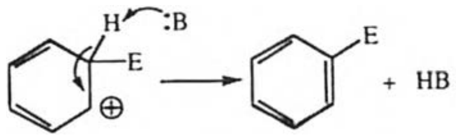
Electrophilic aromatic substitution reactions all follow the same general two-step mechanism.

Step 1: The π-electrons of the aromatic benzene ring are attacked by an electrophile which leads to the formation of a resonance stabilized carbocation. This carbocation is called the arenium ion and has three resonance contributors. Electrophilic attack is a very slow process which is the rate determining step. This step requires a high energy of activation because aromaticity is lost. The basic step one mechanism for all electrophilic aromatic substitutions is given by equation 2.



(2)

Step 2: A base attack the carbocation intermediate and loses a proton. These electrons are used to reform a π bond and restore aromaticity. In contrast to the first step, this step is fast and exergonic because aromaticity is regained. It is important to note that the carbocation loses a proton where the electrophile attacked the benzene ring. This step is given by equation 3.



(3)

2.3.3 Nucleophilic substitution mechanism

Nucleophilic substitution is the reaction of an electron pair donor (nucleophile) with the positive or partially positive charge of an atom or a group of atoms called the leaving group; the positive or partially positive atom is referred to as an electrophile or electron pair acceptor.

The most general form for the reaction may be given as equation 4.

$$\text{Nuc:} + \text{R-LG} \rightarrow \text{R-Nuc} + \text{LG:} \quad (4)$$

The electron pair (:) from the nucleophile (Nuc) attacks the substrate (R-LG) forming a new bond, while the leaving group (LG) departs with an electron pair. The principal product in this case is R-Nuc. The nucleophile may be electrically neutral or negatively charged, whereas the substrate is typically neutral or positively charged.

The strong withdrawing group and/or good leaving group are usually required in the nucleophilic substitution reaction on aromatic ring. Therefore, the reaction of nucleophilic substitution hardly occurs on benzene and alkyl benzene, so the possible reaction could be electrophilic substitution.

Carbenium ion, the intermediate of the electrophilic substitution reaction, can be generated from either alkene or alkane. More severe condition is also required because of the thermodynamic limitation. However, alkene has high reactivity than alkane because of more stable intermediate carbenium ion formation. In the case of using methane as alkylating agent, very severe condition and high activity catalyst are required to promote reaction. Superacid is used to be a catalyst in this reaction (Olah, 1987).

2.4 Methylation of aromatic with methane

The methylation of aromatic with methane was studied by the ability of methane to methylate aromatic compounds. For the indirect conversion, methane can be firstly transformed to more active species such as methyl halide and methanol by halogenations and hydrolysis, respectively. Then this methane derivative further reacts with aromatics. The alkylation with these alkylating agents is commonly used in industrial applications. However, the major disadvantage of using methane as a raw material is the two reaction steps will be required in the process. Many researchers demonstrated the methylation of aromatic with methane, the examples of research have been shown as follow:

2.4.1 Methylation of naphthalene with methane

Methylation of naphthalene by methane over substituted aluminophosphate molecular sieves was studied in by He *et al.* (1992). They found that metal substituted on aluminophosphate catalyst can be used at 400 °C in a batch reactor. Next two years, He *et al.* (1994) has subsequently confirmed, using $^{13}CH_4$, that the methyl groups in the substituted naphthalene products were derived from methane.

2.4.2 Methylation of toluene with methane

Methylation of toluene with methane is divided into two main groups of products by the different types of zeolite.

Ethylbenzene and styrene are the example products from this reaction which have been synthesized by applying basic zeolite. Zhou *et al.* (2000) studied in the basic zeolite catalysts promoted with alkali metal bromides and alkali metal oxides and found that these basic zeolites were effective catalyst for the oxidative methylation of toluene with methane.

Another main product is *p*-xylene which has been observed via methylation of toluene with methane by acid zeolite. As reported by Adebajo *et al.* (2001), they investigated the methylation of toluene with methane by various metals on ZSM-5 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.

2.4.3 Methylation of benzene with methane

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 studied by Adebajo *et al.* (2000). They demonstrated that the presence of oxygen is required for the production of the methylated products in the methylation of benzene with methane at 400 °C over ZSM-5 catalysts in a high pressure batch reactor. In 2004, Adebajo *et al.* revealed that a two-step mechanism involving the intermediate formation of methanol by partial oxidation of methane followed by the methylation of benzene with methanol in the second step. This research reported the results of the characterization of the zeolite catalysts used for the oxidative benzene methylation reaction in order to provide some information about their composition, structure, properties and their behavior before and after the reaction. The two steps of the reaction are represented by equations 5 and 6 (Adebajo and Frost, 2005):

$$CH_4 + \frac{1}{2}O_2 \rightarrow CH_3OH \qquad (5)$$

$$CH_3OH + C_6H_6 \rightarrow C_6H_5CH_3 + H_2O \qquad (6)$$

The overall reaction is thus given by equation (7):

$$C_6H_6 + CH_4 + \frac{1}{2}O_2 \rightarrow C_6H_5CH_3 + H_2O \qquad (7)$$

In support of this mechanism, the performance of the catalysts for both the benzene methylations with methanol (low pressure flow reaction) and with methane in the presence of oxygen (high pressure batch reaction) has subsequently been found to show excellent correlation activity. Luzgin *et al.* (2010) used NMR technique to observe the formation of active carbenium ion that was increased in the presence of oxygen. So the residual air can contribute direct methylation via the formation of methanol.

Compared with oxidative reaction, Non-oxidative reaction is considerate in the attractive choice because the formation of undesired product such as CO_2, CO and H_2O can be avoided. The non-oxidative reaction between benzene and methane was reported over H-Y zeolite in a high pressure flow reactor (Kennedy *et al.*, 1994), copper-exchange HZSM-5 and H-beta zeolite under high pressure at 400 °C in a batch reactor (He *et al.*, 1995). Choudhary *et al.* (1997) reported that methane and ethane could be converted into higher hydrocarbons over Ga-ZSM-5, when hydrogen was transferred under non-oxidative reaction conditions. Later, Baba and Sawada (2002) reported the conversion of methane under non-oxidative condition into higher hydrocarbons in the presence of ethylene over Ag/ZSM-5. The yield of ^{13}C-labelled propylene was provided from this reaction and methane conversion can afford 13.2 mol%. They also reported the reaction of benzene with $^{13}CH_4$ over Ag/ZSM-5 was done in gas circulation system which had toluene as a product 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 2.4.

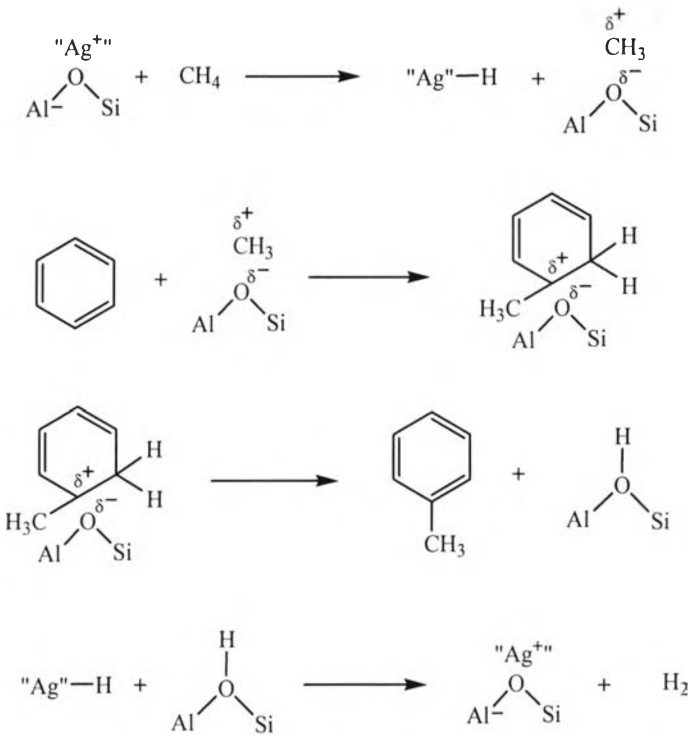


Figure 2.4 The mechanism of methylation of benzene with methane on Ag/HZSM-5.

The alkylation of benzene with methane into toluene over Pt/H-MFI bifunctional catalyst was investigated by Lukyanov *et al.* (2009). 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.

2.5 Zeolite

Zeolites are crystalline and porous materials with an open structure. In generally, they made of silicon, aluminum and oxygen that form a framework with cavities and channels inside where cations, water or small molecules may reside. Owing to their unique properties in ion exchange and adsorption capacity and catalytic activity, zeolites have been widely used as adsorbents, molecular sieving agents and catalysts for a variety of different chemical reactions. Many of zeolites occur naturally as minerals, and are involved in many parts of industrial applications. However, most of them have been made synthetically for specific commercial usage.

2.5.1 Zeolite structures

Zeolites are crystalline aluminosilicates with open 3D framework structures built of SiO_4 and AlO_4 tetrahedra. In almost all natural zeolites, aluminum or silicon occupies all the tetrahedra. In some synthetic molecular sieves, boron, gallium, germanium, iron, titanium, phosphorus, or other heteroatoms may substitute for aluminum or silicon. These tetrahedra are linked to each other by sharing all the oxygen atoms (their corners) to form regular intra-crystalline cavities and channels of molecular dimensions and make a rich variety of beautiful structures. The structure of tertahedra was shown in the Figure 2.5.

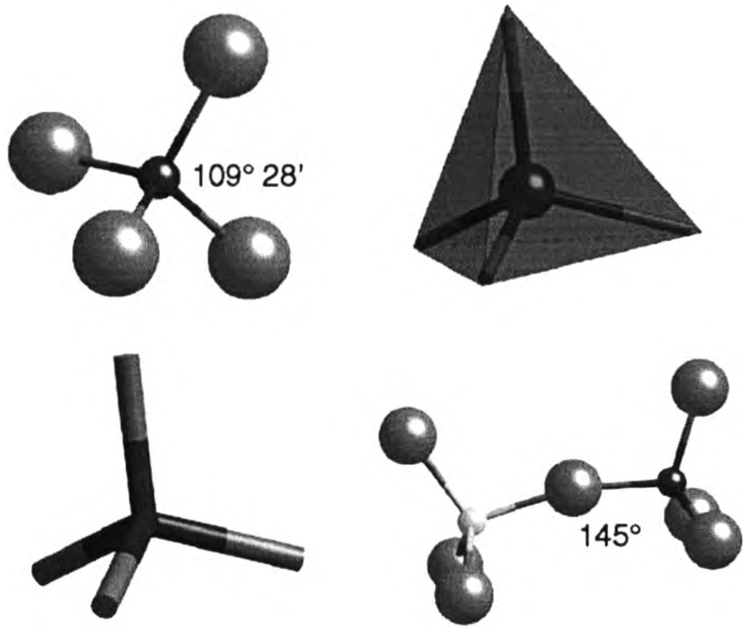


Figure 2.5 The tetrahedron structure (Raul, 2003).

The framework structure may contain linked cages, cavities or channels, which are big enough to allow small molecules to enter. These channels allow the easy drift of the resident ions and molecules into and out of the structure.

The aluminosilicate framework is negatively charged and attracts the positive cations that reside in cages to compensate negative charge of the framework.

Pore diameters depend on the number of tetrahedra in the ring around the pores. According to their pore dimensions, zeolites are grouped as follows:

- Small-pore zeolites (8-membered rings (MRs) up to 0.43 nm) – for example, Erionite;
- Medium-pore zeolites (10-MR up to 0.55 nm) – for example, ZSM-5, ZSM-11, ferrierite, MCM-22 (possessing 12-MR and large intracrystalline cavities pockets on the crystal surface);
- large-pore zeolites (12-MRs up to 0.75 nm) – zeolites Y, Beta, mordenite, ZSM-12; and
- extra-large-pore zeolites (14 or more MRs – for example, CIT-5, UTD-1, ECR-34, ITQ-33 and ITQ-37.

2.5.2 Acid sites

Zeolites have exchangeable cations, allowing the introduction of cations with various catalytic properties. When cationic sites are exchanged with H^+, they can have a high number of strong acid sites.

The Brønsted acid sites are associated with framework aluminum or other trivalent ions (e.g. B, Ga, Fe). The concentration of these framework trivalent ions sites is directly proportional to the number of the Brønsted acid. However, as a completely isolated Al tetrahedron will create the strongest type of Brønsted acid site, the strength of the acid site is usually inversely proportional to the concentration of framework aluminum, up to about a silica/alumina ratio of 10. Changing the framework silica/alumina ratio, either by direct synthesis or by post chemical synthesis, will change the acid strength.

The acid strength depends on the type of the heteroatom: gallium or iron zeolites are much less acidic than aluminum zeolites. Boron-substituted zeolites have very weak acidity.

Lewis sites in zeolites are usually associated with extraframework Al. The simultaneous presence of Brønsted and Lewis sites could enhance the acid activity of zeolites. However, extraframework Al affects different reactions differently and therefore could affect selectivities (Ernst, 2009).

2.5.3 Zeolite SiO_2/Al_2O_3

Multiple factors determine zeolite acidity, including the SiO_2/Al_2O_3 molar ratio. Zeolite acidity increase in strength as the molar ratio of SiO_2/Al_2O_3 decrease due to the increase in AlO^-_4 sites, which strengthens the electro-static field in the zeolite and increase the number of acid sites. However, the wide array of cage and channel arrangements and electrochemical properties that result from various crystalline structures and different SiO_2/Al_2O_3 ratios also affect zeolite acid strength. In certain conditions a high density of AlO^-_4 in the zeolite framework could actually lower the acid strength of the adsorbent. The reverse in acid strength can be explained by the dipolar repulsion of the AlO^-_4 groups outweighing the increase in polarizability. For the reasons stated, an increase in zeolite acidity as the molar ratio of SiO_2/Al_2O_3 increase is normally observed. Manipulating both the exchanged cations and the SiO_2/Al_2O_3 ratio offers a great flexibility in tailoring adsorbents for a specific application.

In addition to the zeolite SiO_2/Al_2O_3 molar ratio, the ionic radii and the valence of the cations exchanged into the zeolite also affect the total acidity of the zeolite. Exchanged cations with lower ionic radii and higher valence have been demonstrated experimentally to give higher zeolite acidity (Kulprathipanja, 2010).

Adebajo and Frost (2005) investigated the effect of SiO_2/Al_2O_3 molar ratio of the benzene methylation by using zeolite catalyst. The results showed that increasing of SiO_2/Al_2O_3 ratio of zeolite provided the low percentage of conversion while the percentage of selectivity had a trend to increase.

2.6 ZSM-5 Zeolite

Based on increasing framework Si/Al composition, the evolution of aluminosilicate zeolites is divided into four categories. These categories are low silica zeolites, intermediate silica zeolites, high silica zeolites and silica molecular sieves. ZSM-5 or Zeolite Socony Mobil-5, (structure type MFI – mordenite framework inverted) is the high silica zeolite with Si/Al of 10-100. Its chemical formula is $Na_nAl_nSi_{96-n}O_{192}\cdot 16H_2O$ ($0<n<27$). Patented by Mobil Oil Company in 1975, it is widely used in the petroleum industry.

ZSM-5 framework can be built from several five-rings, and contains cavities interconnected by straight ten-ring channel systems and zigzag ten-ring channel systems. Since ZSM-5 has a high silicon to aluminum ratio, whenever an Al^{3+}cation replaces a Si^{4+}cation, an additional positive charge is required to keep the material charge-neutral. With proton (H^+) as the cation, the material becomes very acidic. Thus the acidity is proportional to the aluminum content. If ZSM-5 contains a small concentration of aluminum in the framework, the number of cations is small. The well-known zeolite ion exchange reactions are essential to the development of acid hydrocarbon catalysis properties.

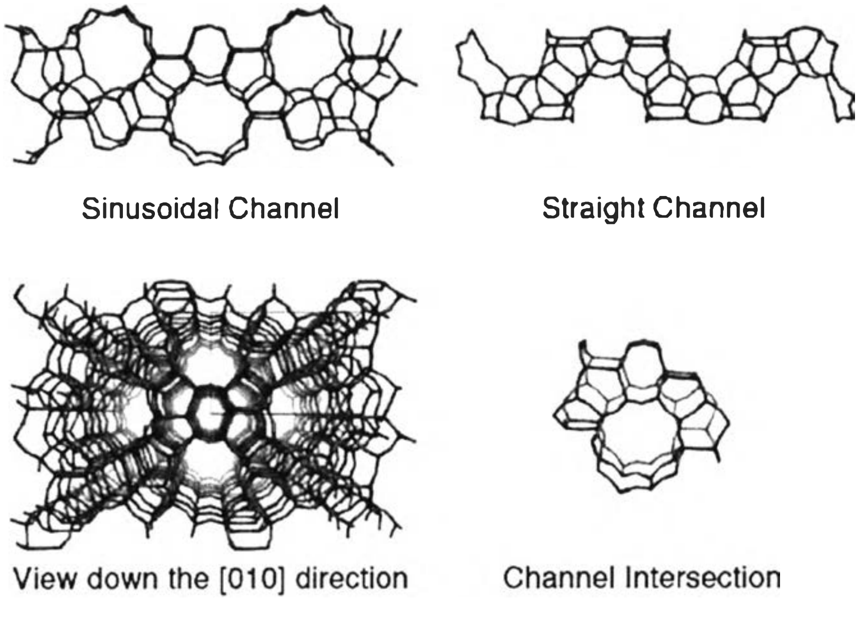


Figure 2.6 Framework structure of zeolite ZSM-5 (MFI) illustrating the straight and sinusoidal pores and the pore intersections. A view of the complete structure down the straight pores is depicted in the lower left lower corner (Raul, 2003).

ZSM-5 zeolite is typically used for shape selectivity reaction. The well-known examples of product selectivity on ZSM-5 are the methylation of toluene and disproportionation of toluene. All three isomers *ortho*, *meta* and *para* xylene are formed in both reactions. The desired product *p*-xylene can be obtained with selectivities of over 90 %. This is explained by the smaller molecule of *p*-xylene has a rate of diffusion that is faster by factor of 10^4 than those of the other two isomers.

Adebajo and Frost (2005) studied the effect of framework, Si/Al ratio and pore size structure in the benzene methylation with methane over MCM-41 and zeolite catalysts. The important thing for the generation of the Brønsted acid sites is the presence of aluminum in the framework of the catalyst. The pore structure is also effect to the product selectivity such as 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.

In 2003, Baba and Abe investigated the conversion of methane in the presence of ethylene over metal cations-loaded H-ZSM-5. They reported that the catalytic activity and selectivity for hydrocarbons depended on the kind of metal cations loaded on H-ZSM-5. The activation of methane on H-ZSM-5 loaded with silver, molybdenum, and indium has 13.2, 9.5 and 8.1 mol% conversions, respectively. On the other hand, non-metal loaded HZSM-5 cannot activate methane. Baba (2005) reported the catalytic activities of almost all catalysts decreased with the running time. The activity decay of Ag/ZSM-5 was rapid while the conversion of methane slightly decreased when In/H-ZSM-5 was used as a catalyst. Because indium cations are more resistant against reduction compared with silver cations. Aboul-Gheit *et al.* (2008) investigated that Mo/H-ZSM-5 is the most promising catalyst over which near equilibrium conversion of CH_4 can be achieved with a higher selectivity to aromatics at 700 °C. However, the methane conversion decreases drastically with time-on-stream owing to the heavy carbonaceous deposits on the catalyst, which is a vital drawback for the reaction. Furthermore, Baba *et al.* (2005) showed the reaction of benzene with methane over In/ZSM-5 by using $^{13}CH_4$ and 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. They also presumed that xylenes are formed by methylation of toluene with methane.

2.7 Indium containing zeolite

From lots of researches, bifunctional catalyst plays an important role in catalysis of many reactions. Bifunctional catalyst comprises a hydrogenation/ dehydrogenation component, often a noble metal, and a Brønsted acid component. Generally the substitution process of zeolite can be substituted by metal ions which take place 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 is chemical element of the IIIA metal groups. It is classified to trivalent, which is three valence electrons, metal ions. The replacement of existing T-atom sites with indium ions known as isomorphous substitution. Chatterjee *et al.* (1998) reported the benzoylation reaction of naphthalene by indium-containing beta zeolite which is involved the reaction of indium isomorphous substituted catalyst. In the case of post-synthesis treatment, Han *et al.* (2000) demonstrated that In^{3+} ion from InF_3 unsuccessfully inserted into the ZSM-5 framework due to the hypothesis that In^{3+} ion is too large to substitute into the T-atom site of ZSM-5.

The more popular way to prepare indium containing zeolite is the incorporation into the extra-framework. Miro *et al.* (1999) identified the main species of indium in In/HZSM-5, which is classified into four groups; 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 containing 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.

2.7.1 The method of preparation of indium-containing zeolite

The three ways of preparing active species generally in the form of indium cation (In^+ or InO^+) on zeolite supported consist of 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 *et al.*, 1998) and oxidative solid-state ion exchange (OSSIE), (Zamaro *et al.*, 2010).

2.7.1.1 Impregnation method

Miro *et al.* (1999) demonstrated the preparation of indium containing zeolite by impregnation method. It provided majorly the In_2O_3 species that requires the further treatment before using in order to generate the active InO^+ species, while the conventional ion exchange required only standard calcinations.

2.7.1.2 Solid-state ion exchange technique

The solid-state ion exchange method is the most promising procedure for introducing metal ions into zeolites. Indium(III)oxide (In_2O_3) is one of the most used for indium source 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 8.

$$In_2O_3 + 3H_2 \leftrightarrow 2In^0 + 3H_2O \qquad (8)$$

However, in the present of zeolites that contain acidic hydroxyl group, the reduction process is difference.

a.) Reductive solid-state ion exchange technique

Reductive solid-state ion exchange (RSSIE) has proved to be a promising method for the post-synthesis modification of zeolites. However, until now its application seems to be limited to only a few elements. Mihalyi *et al.* (1998) studied the reductive solid-state ion exchange of indium into an NH_4-beta zeolite. The mechanism of reductive solid-state ion exchange is shown in equation 9.

$$In_2O_3 + 2H_2 + 2H^+Z^- \leftrightarrow 2In^+Z^- + 3H_2O \qquad (9)$$

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

In addition, without introduced hydrogen, the solid-state ion exchange can also occur as shown in equation 10.

$$In_2O_3 + 2H^+Z^- \leftrightarrow 2(InO)^+Z^- + H_2O \qquad (10)$$

Mihalyi and beyer (2001) investigated that this phenomenon possibly comes from the auto-reductive solid-state ion exchange (AR-SSIE) which can be occurred at high vacuum condition. The first step mechanism of AR-SSIE is given in equation 11.

$$In_2O_3 + 2H^+Z^- \leftrightarrow 2In^+Z^- + H_2O + O_2 \qquad (11)$$

The reductive/oxidative process of indium loaded zeolites was also 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 9) the oxidation is occurred as shown in equation 12.

$$In^+Z^- + 1/2O_2 \leftrightarrow (InO)^+Z^- \qquad (12)$$

This reaction is also possibly the second step of AR-SSIE.

b.) Oxidative solid-state ion exchange technique

For the oxidative solid-state ion exchange, metallic indium (In^0) was used as indium source. The proposed of this process is given by equation 13 (Solt *et al.*, 2008).

$$In^0 + (H_3O)^+Z^- \leftrightarrow In^+Z^- + H_2O + 1/2H_2 \qquad (13)$$

In the case of indium solid-state ion exchange method, many of proposed intermediates such as In_2O, InO^+ and InOH might occur prior to the final exchanged species. So it is very interesting to study which intermediate is catalytically active for the specified reaction.

2.7.2 Catalytic activities of indium-containing zeolite

The high catalytic activity is the ultimate goal of all researches. Many researches tried to find the suitable condition in order to get highest catalytic activity. The reactions, which shown below, are used to investigate the catalytic activity with indium-containing ZSM-5.

2.7.2.1 Selective catalytic reduction (SCR) of NO

The widely researches on indium-containing zeolite was the application on selective catalytic reduction (SCR) of NO by using methane as a reducing agent. Ogura *et al.* (1998) studied in the preparation method by comparing between conventional and solid state ion exchange on various zeolite structures. Indium containing ZSM-5, mordernite, and beta zeolite which were prepared by solid-state ion exchange provided the conversion as high as those prepared by conventional ion exchange. This result indicated that InO^+ is formed in both cases of preparation. Mihalyi *et al.* (2009) exhibited that In_2O_3 or acidic site alone was inactive in NO conversion. Furthermore, In^+ and InO^+ formation were also reported. For In^+ formation, reductive solid-state ion exchange or auto-reductive solid state ion exchange should be used, while thermal treatment in inert atmosphere or oxidation of In^+ was applied in InO^+ formation. Zamaro *et al.* (2010) demonstrated the oxidative solid-state ion exchange for preparing indium loaded on zeolite, In-ZSM-5 provided high thermal stability of framework but low dispersion after loading indium higher than 4 wt%.

2.7.2.2 Toluene disproportionation

Mavrodinova and Popova, (2005) studied the reductive solid-state ion exchange (RSSIE) followed by oxidation in air for introducing InO^+ cation into zeolite. They also examined the various In/Al ratios on ZSM-5 with reaction at 450 °C, the toluene conversion was observed about 4-5 mol% and *p*-xylene selectivity was 30-40 mol%.

2.7.2.3 Isomerization reaction

Mihalyi *et al.* (1998) investigated the isomerization reaction of *m*-xylene over indium-containing beta zeolite. They used In/Al ratio of 0.5 and 1 and obtained about 60 mol% conversion of *m*-xylene on fresh catalyst, while the reduced catalyst was decreased in catalytic activity.

2.7.2.4 Alkane activation, dehydrogenation and aromatization reaction

Alkane activation reaction, dehydrogenation and aromatization reaction were performed by utilizing propane (Halasz *et al.*, 1996), pentane, and hexane (Halasz *et al.*, 2003). The preparation method between conventional and solid-state ion exchange were examined. Indium loaded on ZSM-5 was used as a catalyst. The results showed that metal loading amount affected on the product conversion and selectivity. ZSM-5 containing low indium loading, which contributes high Brønsted acid sites, prefers the cracking reaction, whereas the aromatization activity depends on the Lewis acid sites.

2.7.2.5 Methylation reaction

The methylation reaction over indium loaded ZSM-5 was studied by the only one research group Baba *et al.*, 2005, who studied the effect of several parameters on the methylation reaction of methane in the present of ethylene. The effect of calcinations temperature exhibited that the optimum point 630 °C provided highest methane conversion, while the appropriate temperature for hydrogen treatment was at 450 °C. For the effect of indium content, increasing indium loading provided more conversion. Nevertheless, the large amount indium loading may cause the products undergo cracking. 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, it does not have any detailed research on the effect of each parameter for methylation of benzene with methane.