

## CHAPTER II

### THEORETICAL BACKGROUND AND LITERATURE REVIEW

#### 2.1 Background

Natural gas exists in gaseous form or as a mixture with oil in natural underground reservoirs all around the world. Methane is the primary component of natural gas and it is a greenhouse gas. Methane is the simplest and most stable hydrocarbon molecule, and its conversion into more useful compounds has been studied in both homogeneous and heterogeneous catalysts. Several methods are used to convert methane to higher hydrocarbons such as ethylene and aromatics. The first one is indirect route conversion which requires the intermediate syngas step. Another one is direct route conversion in both oxidative condition and non-oxidative condition. The conversion of methane into more valuable chemical under absence oxygen condition is the new challenge because it was proposed to skip syngas step in indirect route and avoid  $\text{CO}_x$  formation in oxidative coupling reaction. Many researches try to enhance the ethylene and aromatics selectivity by using the several catalyst such as Mo/HZSM-5 (Chen *et al.*, 1995; Wong *et al.*, 1996; Solymosi *et al.*, 1997; Tang *et al.*, 2001) and bimetallic support on zeolite (Aboul-Ggeit *et al.*, 2011; Vosmerikov *et al.*, 2009) but it provides the low selectivity for ethylene. In order to improve the ethylene selectivity and yield, bimetallic Ni-Mo incorporated on HZSM-5 zeolite prepared by polyol mediate process was studied for methane dehydrogenation and coupling under non-oxidative condition.

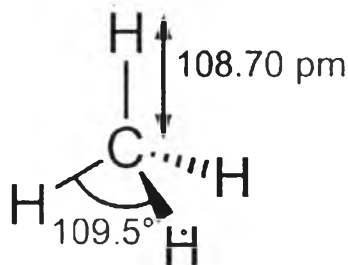
## 2.2 Methane

Methane is the major component of natural gas a mixture containing about 75 % CH<sub>4</sub>, 15 % ethane (C<sub>2</sub>H<sub>6</sub>), and 5 % other hydrocarbons, such as propane (C<sub>3</sub>H<sub>8</sub>) and butane (C<sub>4</sub>H<sub>10</sub>) (Shakhashiri, 2012). The physical properties of methane are a colorless, odorless gas. At room temperature, methane is a gas less dense than air. It melts at -183 °C and boils at -164 °C. It is not very soluble in water. Methane is combustible, and mixtures of about 5 to 15 % in air are explosive. Methane is not toxic when inhaled, but it can produce suffocation by reducing the concentration of oxygen inhaled. However, because it is a gas and not a liquid or solid, methane is difficult to transport from the areas that produce it to the areas that consume it. Converting methane to form that is more easily transported, such as LNG (liquefied natural gas) and methanol.

Generally, over 60 % of total CH<sub>4</sub> emissions come from human activities. Methane is emitted from industry, agriculture, and waste management activities. In industry, natural gas and petroleum systems are the largest source of CH<sub>4</sub> emissions from industry. Some CH<sub>4</sub> is emitted to the atmosphere during the production, processing, storage, transmission, and distribution of natural gas. In agriculture, domestic livestock such as cattle, buffalo, sheep, goats, and camels produce large amounts of CH<sub>4</sub> as part of their normal digestive process. Methane is generated in landfills as waste decomposes and in the treatment of wastewater.

The chemical formula for methane is CH<sub>4</sub>. The carbon atom central to the methane molecule has 4 valence electrons and thus needs 4 more electrons from four hydrogen atoms to complete its octet. The hydrogen atoms have a 109.5 degree bond angle giving the molecule a tetrahedral geometry as shown in Figure 2.1. Thermodynamically, methane is unstable only above 530 °C. According to these properties, methane is difficult to convert to other hydrocarbon. In order to convert methane to higher hydrocarbons, coupling and formation is required to splitting C-H bond of methane which is high-dissociation energy makes this highly endothermic.

Therefore, high temperatures are employed to convert methane to higher value-added hydrocarbon (Choudhary *et al.*, 2003).



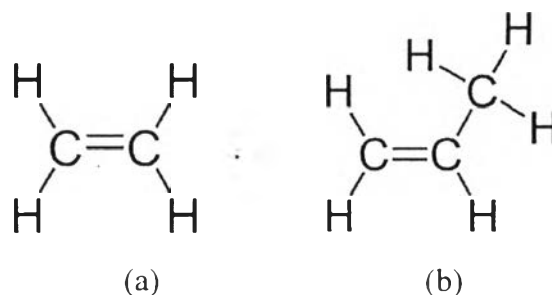
**Figure 2.1** The structure of methane.

(<https://www.boundless.com/chemistry/textbooks/boundless-chemistry-textbook>)

### 2.3 Olefins

Olefins or alkene are in a class of hydrocarbons with a single double bond as shown in Figure 2.2 and a chemical formula of  $C_nH_{2n}$ . The two most important olefins are ethylene and propylene. In petrochemical industry, ethylene is an important basic material for petrochemical industries due to it can be converted to petrochemical products especially plastics and chemicals. Some examples of the major chemicals and polymers that are produced from ethylene include low, linear low and high density polyethylenes (LDPE, LLDPE and HDPE respectively), ethylene dichloride (EDC), vinyl chloride (VCM), polyvinyl chloride (PVC) and its copolymers, alpha-olefins (AO), ethylene oxide (EO) used primarily to make mono ethylene glycol (MEG) for use in polyester and antifreeze production, vinyl acetate (VAM), ethyl alcohol (ethanol), ethylene propylene diene monomer (EPDM), a comonomer for polypropylene, ethylbenzene (EB), styrene (SM), polystyrene (PS) and its copolymers.

Generally, olefins are undesirable for finishing products because olefins can be further integrated to higher value-added hydrocarbon like polyethylene, polypropylene in polymer industries. Due to the importance of olefins for feedstock, several technologies have been developed to synthesis olefin. Most light olefins are produced by steam cracking. Alternatively, Olefins can be produced from methane (about 90 % of natural gas) (Ren *et al.*, 2008).



**Figure 2.2** The structure of light olefins.

(a) Ethylene (<http://www.chemeddl.org/resources/models360>)

(b) Propylene (<http://www.process-worldwide.com>)

## 2.4 Methane Conversion Routes to Higher Hydrocarbons and Chemicals

Many concepts have been developed for improving the industrial processes that convert methane into olefins, higher hydrocarbons, some chemicals such as methanol and formaldehyde via indirect and direct conversion processes. The indirect route involves the production of hydrocarbons via intermediates formed from the reaction of methane with steam, oxygen etc., whereas the direct route involves coupling of the methane in the presence of oxygen (oxidative coupling of methane) or non-oxidative coupling. Figure 2.3 shows a number of possible routes for methane conversion process.

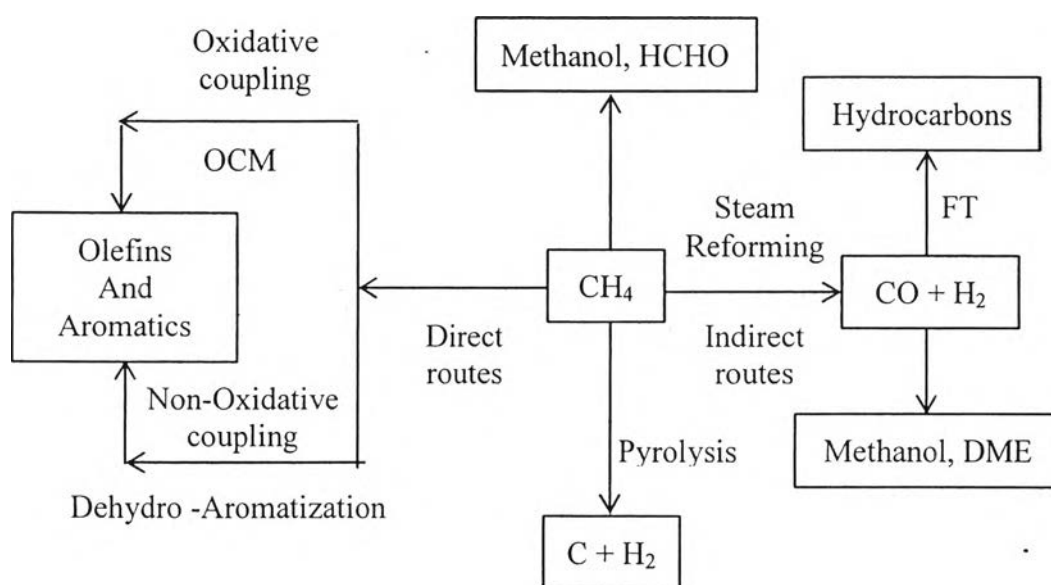
### 2.4.1 Indirect Conversion

In indirect routes (Gharibi *et al.*, 2012), methane is first converted to a methane derivative, most commonly to synthesis gas or syngas (a mixture of hydrogen and carbon monoxide and some carbon dioxide of variable compositions). The syngas is subsequently converted to the desired product by a related catalytic conversion. At present, most of commercialized natural gas conversions are based on indirect routes.

Steam reforming of methane, currently the major route to methane conversion, can be represented as the following Equation 1.



This highly endothermic process results in the formation of synthesis gas that can be further processed into methanol and ammonia. The methanol to gasoline (MTG) process can then be utilized for the production of gasoline. Alternatively, synthesis gas can be directly processed into hydrocarbons via the Fischer–Tropsch process.

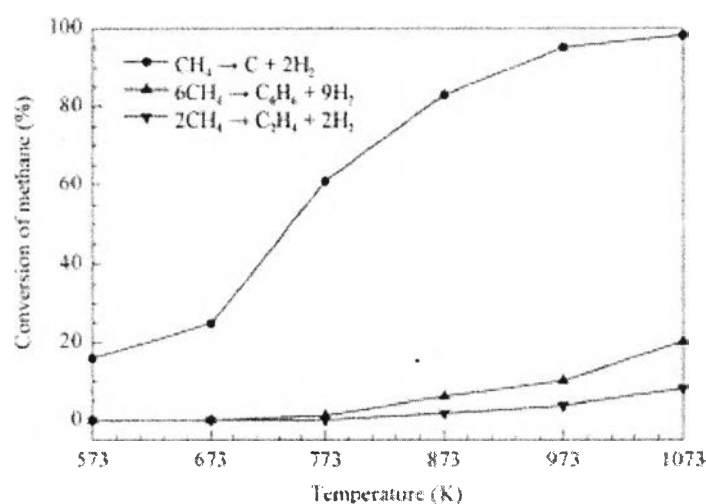


**Figure 2.3** Different routes of methane conversion (Majhi *et al.*, 2013; Gharibi *et al.*, 2012; Galvan *et al.*, 2011; Ren *et al.*, 2008; Lunsford, 2000).

#### 2.4.2 Direct Conversion

Direct paths involve C-H bond activation and the conversion of the resulting  $\text{CH}_x$  or  $\text{CH}_y\text{O}$  species to desired products within a single vessel (Gharibi *et al.*, 2012). Pyrolysis, oxidative coupling (to acetylene, ethylene, benzene), selective oxidation (to methanol or formaldehyde), partial oxidation (to synthesis gas;  $\text{H}_2/\text{CO}$ ) and reforming with either steam or carbon dioxide are direct natural gas conversion routes

The direct conversion has advantage over indirect processes (Majhi *et al.*, 2013), as it eliminates the intermediate step of producing syngas and requires high temperature, usually above 600 °C, with the corresponding high energy consumption. Although, direct conversion should have a distinct economic advantage over indirect conversion but to date no direct processes have reached a commercial stage because product yields are generally small (Galvan *et al.*, 2011). Recently, the conversion of methane to higher hydrocarbons, especially aromatics under non-oxidative conditions, is receiving increasing attention. Thermodynamically, it is more favorable to convert methane into aromatics than olefins, as shown in Figure 2.4.



**Figure 2.4** Thermodynamics of direct conversion of methane under non-oxidative conditions (Majhi *et al.*, 2013).

#### 2.4.2.1 Direct Oxidative Conversions

##### *Partial Oxidation of Methane to Methanol and Formaldehyde*

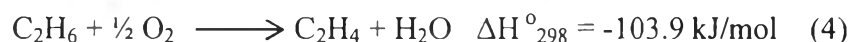
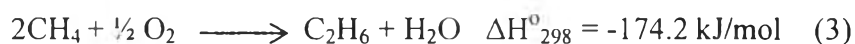
The direct conversion of methane into methanol (CH<sub>3</sub>OH) and formaldehyde (HCHO), also called C1 oxygenates involves partial oxidation under specific reaction conditions as shown in Equation 2 (Galvan *et al.*, 2011). This reaction operates at 350–500 °C under fuel-rich mixtures with the oxidant to minimize the extent of combustion reactions. Under these conditions, the gas-phase

oxidation reactions of methane operate at high temperatures, which are detrimental to the control of selectivity to C1 oxygenates.



#### *Oxidative Coupling of Methane to Higher Hydrocarbons*

The oxidative coupling of methane (OCM) involves the reaction of  $\text{CH}_4$  and  $\text{O}_2$  over a catalyst at high temperatures to form  $\text{C}_2\text{H}_6$  as a primary product and  $\text{C}_2\text{H}_4$  as a secondary product. Unfortunately, both the  $\text{CH}_4$  and the  $\text{C}_2\text{H}_4$  may be converted to  $\text{CO}_2$ , and the single-pass combined yield of  $\text{C}_2\text{H}_4$  and  $\text{C}_2\text{H}_6$  ( $\text{C}_2$  products) is limited to about 25 % (Lunsford, 2000). In the OCM process at around 800 °C, the following selective reaction (Equations 3-5) and non-selective reactions (Equation 6) (Galvan *et al.*, 2011).



The processes in OMC route can be summarized as follow. First, methane is separated from natural gas and is purified. Oxygen is separated from air cryogenically. A common oxidative coupling reactor design has a fluidized bed, though many other designs are also being considered. In the reactor, methane ( $\text{CH}_4$ ) and oxygen react over a catalyst to form water and a methyl radical ( $\text{CH}_3$ ). This reaction is called partial oxidation of methane. Methyl radicals that are formed at the surface of the catalyst enter the gas phase where they couple to form ethane. At atmospheric pressure, this coupling occurs mainly in the void space between catalyst particles, but by two techniques, the methyl radicals have been detected in the gas phase after they exit the catalyst bed. In addition to coupling, the gas phase radicals may enter into chain reactions that result in the formation of CO and subsequently  $\text{CO}_2$ . Isotopic labeling experiments have demonstrated that at small conversion levels most of the  $\text{CO}_2$  is derived from  $\text{CH}_4$ , but at commercially significant conversion

levels, C<sub>2</sub>H<sub>4</sub> would be the dominant source of CO<sub>2</sub>. Additional experiments have shown that this occurs mainly via a heterogeneous reaction. One of the challenges in catalyst development is to modify a material so that the secondary reaction of C<sub>2</sub>H<sub>4</sub> will be inhibited while the activation of CH<sub>4</sub> will still occur. There is no inherent reason that these two reactions should take place on the same types of sites.

In spite of the work existing on OCM, this technology has not yet been commercialized (Galvan *et al.*, 2011) because there are important hurdles to be overcome in this process. The first reason, since C<sub>2</sub> hydrocarbons are much more reactive than methane. High selectivity in the process can be obtained only at low methane conversion. The reaction is conducted at high temperatures a catalyst with high thermal and hydrothermal stability is required. Another reason using a low O<sub>2</sub>/CH<sub>4</sub> molar ratio in the feed, the selectivity to C<sub>2</sub> hydrocarbons is high, but CH<sub>4</sub> conversion is rather low and due to the low concentration of ethylene in the exit stream the cost of its separation is high, thereby rendering its separation uneconomical.

#### 2.4.2.2 Non-Oxidative Conversion of Methane

In the absence of an oxidant, the activation of the C–H bonds of the highly stable CH<sub>4</sub> molecule requires high temperatures. Under such conditions, radical reactions in the gas phase prevail. However, as the strength of the C–H bond in the resulting C-containing products is weaker than methane, the products will be more reactive than methane. This means that the challenge in methane conversion is related to selectivity rather than to reactivity. In order to circumvent these hurdles, several different approaches based on catalysis and reaction engineering have been proposed and tested.

Some of these approaches are briefly described below.

##### *Methane Cracking*

The thermal cracking of methane in an O-free environment produces hydrogen and elemental carbon. This reaction is a moderately endothermic process. The energy required per mole of H<sub>2</sub> produced is much lower than that required by steam reforming. In addition to H<sub>2</sub>, the process also yields carbon.





Thermodynamic calculations indicate that the thermal decomposition of methane at high temperatures may also give ethylene, acetylene and benzene as the main products, provided that the reaction can be stopped before carbon is formed. Excessive carbon formation can be avoided using short reaction times and low partial pressures of methane. When using metal catalysts, H<sub>2</sub> production according to this simple approach involves two steps: catalytic methane decomposition follows Equation 7 and the regeneration of deactivated catalyst in the presence of an oxidant such as air, O<sub>2</sub>, CO<sub>2</sub>, or H<sub>2</sub>O.

#### *Methane Dehydrogenation and Aromatization*

The catalytic conversion of methane to higher hydrocarbons, especially to aromatics such as benzene, toluene, and naphthalene, in the absence of oxygen was extensively studied. The catalyst is bifunctional, typically metal-supported zeolite. Consequently, a large number of works have been devoted to the study of modification of the catalyst, of the interaction between the transition metal component and the zeolite support. Over Mo/H-ZSM5 catalysts, aromatization involves sequential formation of ethylene on MoC<sub>x</sub> clusters followed by conversion of the C<sub>2</sub> intermediates to aromatics on acid sites aided by hydrogen desorption from MoC<sub>x</sub> sites.

Wang *et al.* (1993) reported the dehydro-aromatization of methane (DAM) for the production of benzene and hydrogen over zeolite HZSM-5 supported molybdenum catalyst (Mo/HZSM-5) in a fixed-bed reactor. Among the several catalysts tested, Mo/HZSM-5 was found the most promising. This may be due to its zeolite framework active sites located in pores or channels on the zeolite, and its nature particularly the shape and size of pores. The nature of the products formed during the reaction is controlled by the properties of the zeolite. With its two-dimensional porous structure and a pore diameter close to the dynamic diameter of a benzene molecule, HZSM-5, as support for the aromatization of methane inhibition, effectively ensures the formation of other products.

Zhou *et al.* (2012) studied the structure of the molybdenum active center in Mo/HZSM-5 zeolite catalyst and the reaction mechanisms of the methane dehydrogenation and coupling to ethylene (MDHC). The catalytic cycle consists of four elementary steps:

(1) *Dissociation of the Methane C–H Bond*

This step is the molybdenum and carbon of  $\text{Mo}=\text{CH}_2$  represent a Lewis acid–base pair able to polarize and break the methane  $\text{C}^{\delta-}-\text{H}^{\delta+}$  bond.

(2) *Dehydrogenation and C–C Coupling*

In the second step of this route, the dehydrogenation occurs in carbon atom by rupture of two C–H bonds from the adjacent methyl groups on the Mo atom.

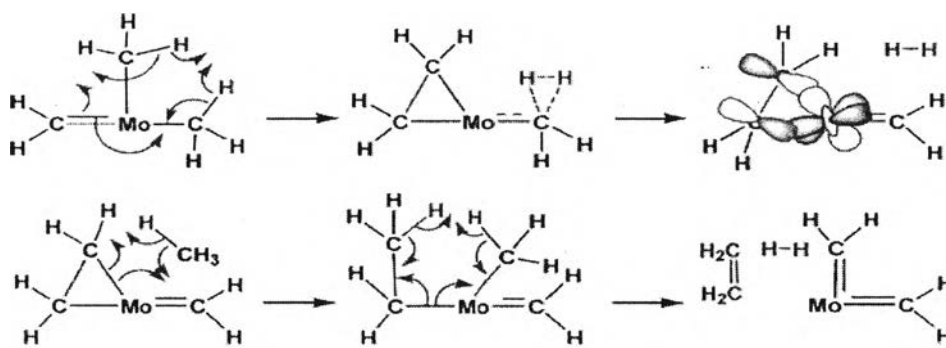
(3) *Activation of the Second Methane Molecule*

In this step, a methane molecule approaches then the  $\text{H}_3\text{C}-\text{H}$  bond breakdown and  $\text{H}^{\delta+}$  was split and transferred to C1 of adsorbed ethylene to form the  $\text{Mo}-\text{C}_2\text{H}_5$

(4) *Elimination of Ethylene and Molecular Hydrogen.*

In this step, dehydrogenation occurs between the  $\beta$ -hydrogen of the  $\text{Mo}-\text{C}_2\text{H}_5$  group and the hydrogen of the  $\text{Mo}-\text{CH}_3$  group. Then the ethylene is generated and adsorbed on Mo.

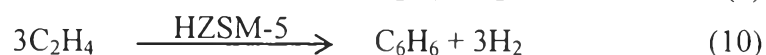
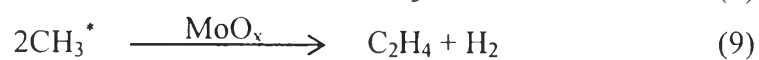
Regarding the mechanism of methane activation and dehydrogenation it is demonstrated in Figure 2.5.



**Figure 2.5** Mechanism of C–C coupling and elimination of molecular hydrogen and ethylene on zeolite-supported Mo carbides (Zhou *et al.*, 2012).

$\text{Mo}/\text{HZSM-5}$  is a bifunctional catalyst. The metal is responsible for the hydro/dehydrogenation of the reactions and the acid sites provided by zeolites is responsible for the aromatization. Shu *et al.* (1999) studied bifunctional behavior of  $\text{Mo}/\text{HZSM-5}$  catalysts in methane aromatization. They

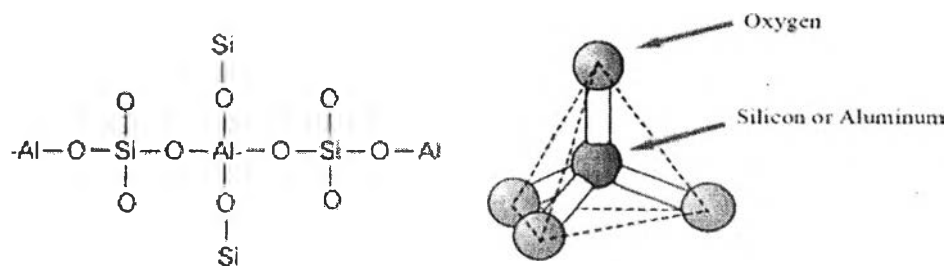
found that in the aromatization process, methane is probably converted into ethylene by dehydrodimerization over molybdenum sites in the first step. Whether ethane is an intermediate to produce ethylene during methane aromatization is still not clear. Once ethylene is formed inside the ZSM-5 channels, this intermediate is ready to undergo aromatization with the help of the acidic sites of zeolite, according to Equations 8-10.



## 2.5 Zeolites

The following section has been included in this chapter so as to give a general background on zeolites. H-ZSM-5 is one of the main components of the methane dehydroaromatization reaction. Therefore, it is appropriate to give some detailed information about zeolites in general.

Zeolites are microporous crystalline aluminosilicate solids with well-defined structures. In general they consist of silicon, aluminium and oxygen in their framework and cations, water and/or other molecules within their pores. Zeolites are complex, they comprise of an infinitely extending three dimensional four connected framework of  $\text{AlO}_4$  and  $\text{SiO}_4$  tetrahedra linked by the sharing of oxygen atoms as shown in the Figure 2.6. Each  $\text{AlO}_4$  has a net negative charge and is balanced by a cation. The primary structural units,  $\text{AlO}_4$  and  $\text{SiO}_4$  join together to form a wide variety of cages and rings known as secondary-building units.



**Figure 2.6** The structure of zeolite.

(<http://ariixinternetteam.com/zeolite-a-remarkable-natural-detoxifier/>)

The wide application of zeolite for methane conversion is due to its high crystallinity, availability of weak and strong acid sites, thermal stability, and large surface areas to ensure the shape selective reaction in catalysis science. The framework of zeolites contains channels and pores with molecular dimensions. The pore sizes range from 0.3-0.8 nm and subsequently zeolites are classified according to their pore dimensions. The pore dimensions of a few well-known zeolites are shown in Table 2.1.

**Table 2.1** Selected zeolites and their pore dimensions (Xu *et al.*, 1992)

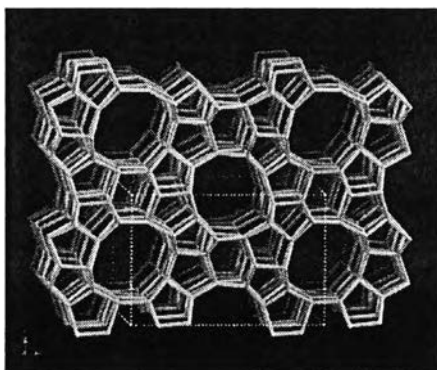
Zeolite	Pore Dimension (nm)
Erionite	0.36 × 0.52
Zeolite A	0.41
ZSM-5	0.51 × 0.55, 0.54 × 0.56
Faujasite	0.74

These pore dimensions enable zeolites to be used for specific applications. The principal applications are ion exchange, desiccants, gas filtration, cracking for gasoline products and shape selective catalysis. Although zeolites are classified according to their pore dimensions they can be further classified depending upon their Si/Al ratio. With increasing Si/Al ratio the stability of the crystal framework increases. Moreover, a zeolite is more stable in the presence of a concentrated acid

when the Si/Al ratio is high compared to those with low Si/Al ratio and vice versa for basic solutions

Structurally, zeolites with pore diameters of 5–6 Å (Majhi *et al.*, 2013) are suitable for the methane conversion reaction. Zeolites are usually synthesized under hydrothermal conditions in alkaline medium at temperatures between 353–473 K. ZSM-5 zeolite is made from the unit pentasil, and it is a main catalyst support for methane conversion which actively participates in the catalytic process.

Several zeolites are used for methane dehydroaromatization in the absence of oxygen especially HZSM-5 zeolite. The structure of HZSM-5 is referred to as pentasil based, this is because the tetrahedra combine to form a ring consisting of five oxygen atoms. These five ring-building units lead to the lattice structure arranged in a ten-ring-way. The three-dimensional structure of HZSM-5 is shown in Figure 2.7. The pore structure of HZSM-5 is a set of linear pores having diameters of 0.51 × 0.56 nm, which are perpendicular arranged to zigzag pores with a diameter of 0.54 × 0.56 nm.

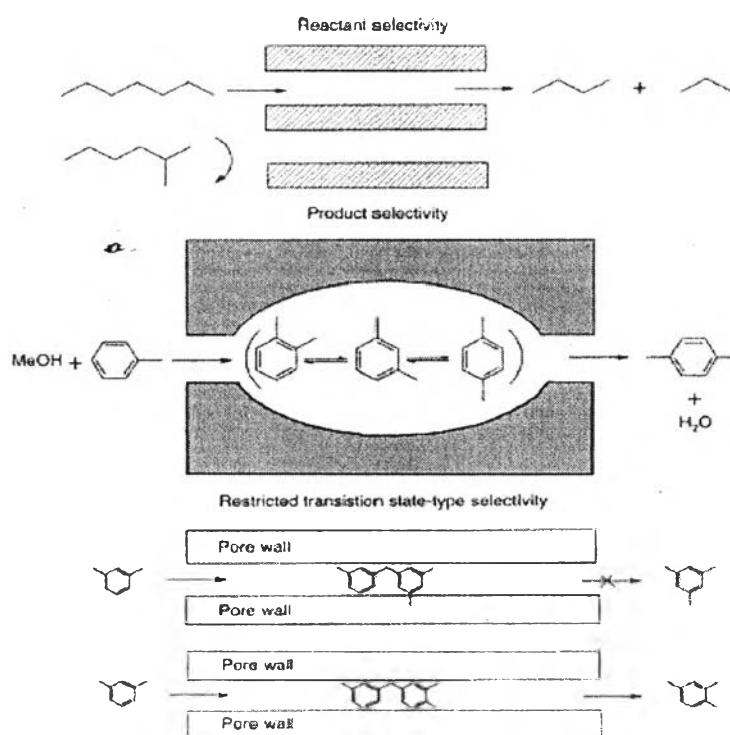


**Figure 2.7** 3D structure of ZSM-5 (<http://www.iza-structure.org/databases>).

Zeolites can exhibit three different types of shape selective catalysis, reactant-selective, product-selective and transition-state-selective catalysis. Reactant selective catalysis is when only molecules with dimension less than a critical size can enter the pore of zeolites and reach the catalytic sites. Product-selective catalysis is when only products less than a certain dimension can leave the active sites and diffuse out through the channels. Transition-state-selective catalysis is when certain

reactions are prevented because the transition-state requires more space than is available in the cavities. The three types of shape selective catalysis that a zeolite can exhibit are shown schematically in Figure 2.8.

Zhang *et al.* (1998) studied the catalytic performance of Mo-based catalysts supported on various zeolites. It was found that H-type silica-alumina zeolite, such as ZSM-5, ZSM-8, ZSM-11, and  $\beta$  zeolite has two dimensional pore structures that a pore diameter near to the dynamic diameter of benzene molecule. Catalysts supported on MCM-41, SAPO-34, MOR exhibit low activity for aromatization because it has pore diameter smaller than the dynamic diameter of benzene. The catalyst that supported on X and Y zeolite gives only a little amount of ethylene and those supported on SAPO-5, SAPO-11 zeolite no hydrocarbons were detected. SAPO-5, SAPO-11, X, Y zeolites have a large pore size and three dimensional structure. Moreover, X and Y zeolites also have a cage structure, it cause coke is readily deposited and blocked a channel.



**Figure 2.8** Schematic representations of the three types of shape selectivity. (Stocker *et al.*, 2005).

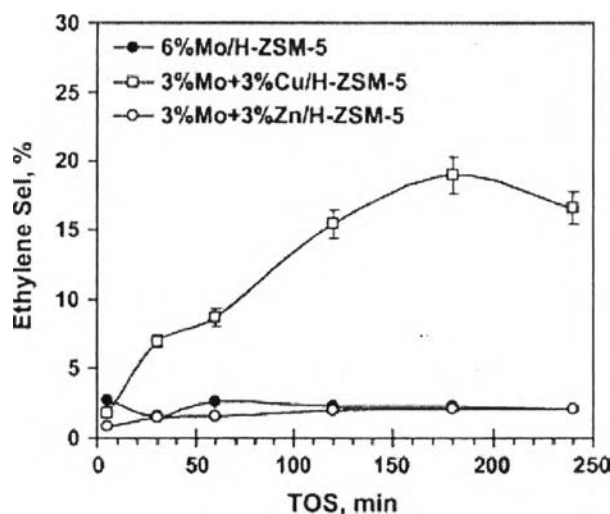
## 2.6 Bimetallic Catalysts

Tang *et al.* (2001) studied the effects of cobalt additive on methane conversion and selectivity to aromatics for non-oxidative conversion of methane to aromatics. The Mo-Co/HZSM-5 was prepared by co-impregnated with a mixed solution of ammonium heptamolybdate and cobalt nitrate. It was found that the addition of 1 % Co to 3 % Mo over HZSM-5 raised methane conversion and selectivity to ethylene increase when compared with 3%Mo/HZSM-5. This may be ascribed to the acceleration of CH<sub>4</sub> dehydrogenation, promoted by cobalt.

Vosmerilov *et al.* (2009) studied the modifying effect of nickel on the catalytic properties of molybdenum-containing zeolite ZSM-5 in the methane dehydro-aromatization reaction. Catalysts were prepared by mechanically mixing zeolite ZSM-5. The concentration of Mo in the zeolite was 4.0 wt%, and the concentration of Ni in the 4%Mo/ZSM-5 catalytic system was varied from 0.1 to 2.0 wt%. The catalyst containing 0.5 % Ni was found less active and stable than the sample of 0.1%Ni-4%Mo/ZSM-5, although it was more stable than the parent Mo/ZSM-5 catalyst. After the addition of 1.0 and 2.0 % Ni nanopowder, the activity and stability of the 4%Mo/ZSM-5 catalyst dramatically decreased. It is likely that this behavior of the samples containing a relatively large amount of nickel oxide was due to the fact that a considerable portion of this oxide was reduced to nickel metal under the action of a reducing atmosphere. It is well known that nickel metal particles catalyze the growth of carbon filaments. A bifunctional mechanism of methane dehydroaromatization due to the participation of both Mo containing active centers and the Bronsted acid sites of ZSM-5, it was of interest to study the effect of Ni nanopowder additives on the acid properties of both the unmodified and Mo containing zeolites. Increasing in the concentration of nickel introduced into the parent zeolite from 0.1 to 0.5 % did not result in a considerable change in the strength of acid sites.

Aboul-Gheit *et al.* (2011) investigated the influence of substituting half the Mo content in a standard 6%Mo/H-ZSM-5 catalyst with either Cu or Zn in H-ZSM-5 support, on the direct conversion of methane. The monometallic catalyst containing 6 wt% Mo supported on H-ZSM-5 was prepared via incipient wetness impregnation

of H-ZSM-5 zeolite with an aqueous solution of ammonium heptamolybdate. The bimetallic 3%Mo-3%Cu/H-ZSM-5 or 3%Mo-3%Zn/H-ZSM-5 catalysts were prepared via co-impregnating the H-ZSM-5 zeolite. The 6%Mo/H-ZSM-5 catalyst is globally considered the most active for benzene yield and selectivity in direct natural gas conversion, however, the present work may admit considering the 3%Mo-3%Zn/H-ZSM-5 catalyst to be yet more active. Moreover, it is advantageous for its lower carbon deposition. A 3%Mo-3%Cu/H-ZSM-5 catalyst is relatively highly selective for ethylene by virtue of its high dehydrogenation activity and lower oligomerization activity. Due to the higher carbon deposition on the Mo-Cu catalyst has caused a greater inhibition of the continuation of ethylene to perform its consecutive oligomerization to produce higher molecular weight hydrocarbons (i.e., aromatics), thus leading to ethylene accumulation as shown in Figure 2.9.

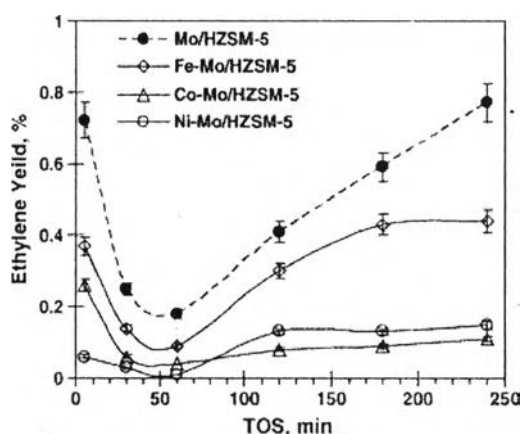


**Figure 2.9** Ethylene selectivity using Mo, Mo-Cu, Mo-Zn/HZSM-5 catalyst (Aboul-Gheit *et al.*, 2011).

Aboul-Gheit *et al.* (2012) investigated the activities of Mo/HZSM-5 catalyst as well known high performance aromatization catalyst after substituting half its Mo with Fe, Co or Ni. The catalysts were prepared by the mechanical mixing. The results showed that the bimetallic 3%Mo-3%Fe, 3%Mo-3%Co and 3%Mo-3%Ni containing catalysts significantly decreased ethylene yield as compared to the monometallic



6%Mo/HZSM-5 catalyst. The substitution of group VIII metals enhances the rate of coke and hydrogen formation in the direction of going from Fe → Co → Ni. This behavior can be attributed to the electronic properties of these metals. The benzene yield is found to be inversely proportional to electronegativity. For Fe, Co and Ni the electronegativity is 1.83, 1.88 and 1.91, respectively. The susceptibility of interaction with the H<sup>+</sup> proton of HZSM-5 by the metal species increases by increasing the electronegativity from Fe to Co to Ni, where the metal oxide/carbide prefers to deposit on the strong acid sites of the HZSM-5 zeolite surface and channels, causing a coverage of a part of the acid sites and consequently decreases the zeolite acid site number and strength, and hence the benzene yield and selectivity decrease. The conversion of natural gas to ethylene, the monometallic catalyst exhibits higher activity for this reaction than the bimetallic catalysts at all time on stream under study as shown in Figure 2.10. The Fe based catalyst showed somewhat higher ethylene production than the Co- or Ni-containing catalysts. Ethylene yield is accumulated according to the rate of ethylene cyclization reaction.



**Figure 2.10** Ethylene formation using Mo, Mo-Fe, Mo-Co and Mo-Ni/HZSM-5 Catalyst (Aboul-Gheit *et al.*, 2012)

## 2.7 Effect of Si/Al Ratio on Methane Conversion

The presence of aluminum atoms in the structure of a zeolite is compensated by various cation. The ion exchange of cation by NH<sub>4</sub><sup>+</sup> ions followed by heat

treatment at about 773–873 K gives rise to so-called Brönsted acid sites. The ratio of  $\text{SiO}_2/\text{Al}_2\text{O}_3$  in zeolite has a strong influence on its acidic properties: the lower the ratio, the greater the amount of Brönsted acid sites. It has been reported that  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio strongly affects the dehydroaromatization of methane over Mo/HZSM-5. The number of the Brönsted acid sites is proportional to the aluminum content of the HZSM-5, low Si/Al ratio should more Brönsted acid sites and thus shows better methane conversion and benzene selectivity.

## 2.8 Effect of Metal Loading on Methane Conversion

The effect of metal loading used in the synthesis of catalysts for dehydroaromatization was evaluated by several authors. Early work has shown that whatever the nature of the transition metal used, the best performance is achieved for catalysts prepared with 2 % to 3 % metal loading, while larger quantities of metal are not useful.

Since the methane dehydroaromatization reaction was first reported there have been many transition metal ions that have been tested for methane activity, including, Mo, W, Fe, V, Cr, Re, Cu and Zn. Burns et al. (2006) found that most effective metal ion precursor for the zeolite is molybdenum and the trend in activity in methane conversion is as follows:  $\text{Mo} > \text{W} > \text{Fe} > \text{V} > \text{Cr}$ . Mo/H-ZSM-5 has been the most well studied catalyst. It has been reported that the most favorable loading of  $\text{MoO}_3$  on ZSM-5 for MDA is in the range of 2-6 wt.%  $\text{MoO}_3$  loadings greater than 6 % lead to blockage of channels and dealumination of the zeolite and therefore a loss in catalytic activity.

Li *et al.* (2006) found that the conversion and selectivity to benzene also increased with the increase of weight percentage of molybdenum in Mo/HZSM-5.

Vosmerikov *et al.* (2009) studied the modifying effect of nickel on the catalytic properties of molybdenum containing zeolite ZSM-5. They found that 0.1 wt% Ni was found high active and stable. After the addition of 1.0 and 2.0 % Ni, the activity and stability of the 4.0%Mo/ZSM-5 catalyst dramatically decreased. Ni content was increased from 0.1 to 2 wt%, the rate of deactivation of the catalytic system increased because of blocking pores in the zeolite structure.

## 2.9 Effect of Operating Parameters on the Non-oxidative Conversion of Methane

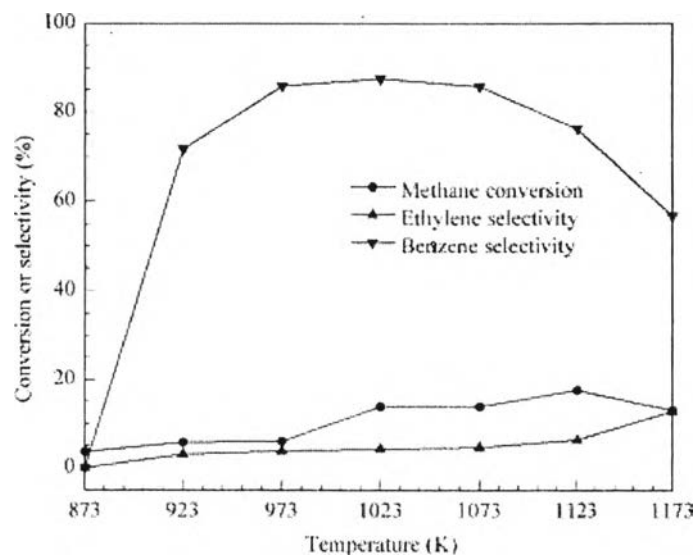
### 2.9.1 Effect of Temperature

As the dehydroaromatization of methane is an endothermic reaction limited by equilibrium, temperatures higher than 700 °C are required to achieve significant conversions of CH<sub>4</sub> to aromatic in fixed-bed reactors. The conversion rate for the dehydroaromatization reaction of methane as a function of temperature calculated from thermodynamics, endorsed the need for high temperatures. These conditions may cause catalyst deactivation by coke deposition, promote sintering, and reduce the active phase. Moreover, very high temperatures reflect a high energy value, which makes the process economically unviable.

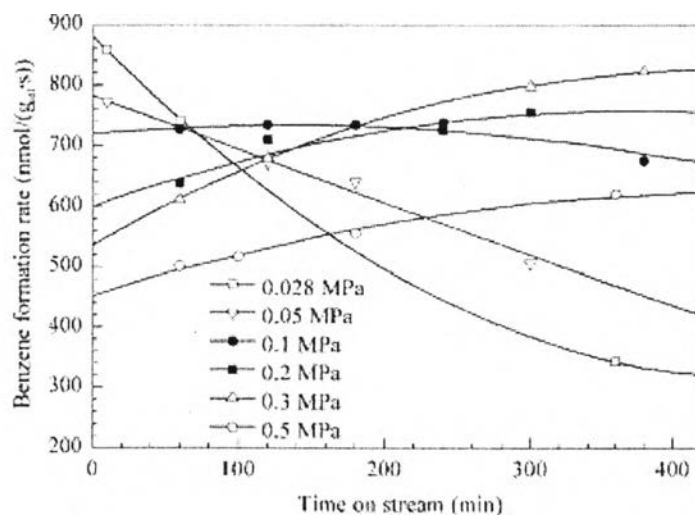
Chen *et al.* (1995) suggested that an optimum conversion can be found between 700–800 °C. The authors observed that temperature above that would bring a decrease in conversion and selectivity, probably due to the loss of active phase, as shown in Figure 2.11

### 2.9.2 Effect of Pressure

From the Figure 2.12, the greater stability of the reactions carried out at moderate pressures (between 0.1 and 0.3 MPa) could be explained by the fact that greater variation in molar number is to the side reactions leading to coke formation. Thus, these reactions would be favored by a moderate increase in pressure.



**Figure 2.11** Effect of reaction temperature on conversion and selectivity (Majhi *et al.*, 2013).



**Figure 2.12** Effect of pressure on benzene formation rate (Majhi *et al.*, 2013).

### 2.9.3 Effect of Space Velocity

Reducing the space velocity (SV) not only increases the conversion of methane to aromatics, but also increases the duration of the induction time for temperatures of 600–725 °C and space velocity of 270–5000 mL/(g·h). Chen *et al.* reported that the increase in space velocity increases the selectivity to ethylene and decreases that to benzene.

## 2.10 Preparation of Catalysts

Generally all research groups have prepared the Mo/H-ZSM-5 catalyst by the impregnation method using  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$  as the precursory in both monometallic and bimetallic (Chen *et al.*, 1995; Shu *et al.*, 1999; Burns *et al.*, 2006). It is believed that when the catalyst is calcined, the Mo containing ions, which are present on the external surface of the zeolite from the previous stage of impregnation decompose into  $\text{MoO}_3$  crystallites. Some of these crystallites migrate into the channels of the zeolite and interact with the Brönsted acid sites. The appropriate temperature for the catalyst calcination is reported as 773 K to allow the migration of Mo ions and interaction with Brönsted acid sites.

Recently, a Mo/H-ZSM-5 catalyst for MDA was prepared by microwave heating (Qi *et al.*, 2004). It was reported that catalysts prepared by microwave heating exhibited a greater selectivity towards benzene than catalysts prepared by conventional heating methods. They attributed the better catalytic performance for catalysts prepared by microwave heating to more Mo species being located on the outer surface of the catalyst.

Aboul-Gheit *et al.* (2012) studied oxygen free conversion of natural gas to useful hydrocarbons and hydrogen over monometallic Mo and bimetallic Mo–Fe, Mo–Co or Mo–Ni/HZSM-5 catalysts prepared by mechanical mixing. This research investigated approach the activities of Mo/HZSM-5 catalyst as well known high performance aromatization catalyst after substituting half its Mo with Fe, Co or Ni for hydrocarbons and hydrogen production. The catalytic performance was carried out under the nonoxidative in a fixed bed flow reactor at 700 °C and gas hourly space velocity (GHSV) of 1,500 ml/g/h. The results showed that bimetallic 3%Mo-3%Fe, 3%Mo-3%Co or 3%Mo-3%Ni containing catalysts significantly decreased hydrocarbon (ethylene and aromatics) yield and selectivity as compared to the monometallic 6%Mo/HZSM-5 catalyst. The substitution of group VIII metals enhances the rate of coke and hydrogen formation in the direction of going from Fe→Co→Ni.

Sarkar *et al.* (2012) used Ni-nanoparticle supported on mesoporous ZSM-5 for dry reforming of methane. The catalysts were prepared by using Ni nanoparticle

supported on ZSM-5 zeolite in ethylene glycol medium. The methodology for catalyst preparation was explained following. For 5%Ni-ZSM-5 catalyst 0.49 g  $\text{Ni}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  was dissolved in 50 ml of ethylene glycol with 0.4 g (1 M) NaOH on it. The solution was stirred for 30 min and reduced at 160 °C for 3 h in reflux condition. The aliquot of colloidal nanoparticle was mixed with 2 g of prepared mesoporous ZSM-5 and stirred for 24 h. The supported Ni catalyst was dried at 160°C overnight. The obtained solid was grounded thoroughly to fine powder and subsequently calcined at different temperatures for 3 h under static air. Ni loading was varied from 3 to 10 wt% with respect to support material mesoporous ZSM-5.

These catalysts were tested for dry reforming of methane and the results showed that Ni nanoparticle supported on mesoporous ZSM-5 highly active for reforming of methane with  $\text{CO}_2$ . The 5 % Ni loaded Ni-ZSM-5 catalyst showed 96.2 % methane conversion at 800 °C. The activity of the catalyst remained constant up to 5 h and then decreased with the time on stream. It was also found that, the deactivation of the catalyst was due to the coke deposition and also the formation of  $\text{NiCO}_3$  over the catalyst