CHAPTER II
THEORETICAL BACKGROUND AND LITERATURE REVIEW

2.1 Background

Methane is the main composition of natural gas which has been produced with the large amount from many reserves over the world. For efficiency utilization of natural gas, methane is the key component to improve both product value and variety of using. Methane converted into ethylene which is important feed stock and vast application for petrochemical industries is very interesting. To convert methane to higher hydrocarbons such as ethylene, several ways for methane conversion has been developed. Typically, methane can be converted through three routes, (I) the in direct route which methane is first converted in existence of water (stream reforming), CO_2 (carbon dioxide reforming), or oxygen (partial oxidation) to produce syngas (CO and H_2) then the syngas can be utilized; (II) direct coupling in presence of oxygen (oxidative coupling of methane , OCM) or hydrogen (two-step polymerization); and (III) direct conversion in the presence of oxygen to oxygenates (CH_3OH, HCOH), in the presence of Cl_2, HCl to methane chlorides in and the presence of ammonia to HCN (Guczi et al., 1996). To study the ethylene production, many researches on OCM were published but this route has a problem with CO_x species generated form the presence of oxygen in the system. Alternatively, methane converted into ethylene under non-oxydative condition was proposed to skip the syngas step and avoid CO_x specie formation. In order to improve an ethylene yield and selectivity, Ni nanoparticle incorporated on HZSM-5 or HZSM-5 (HF) prepared by poyol mediat process was studied for methane dehydration and coupling under non-oxidative condition.

2.2 Methane

Methane is an aliphatic compound which is also known as paraffin or saturated aliphatic hydrocarbons (William C. Lyons et al., 2011) showed as in Figure 2.1 Methane structurally composed of four single bonds of carbon and hydrogen (C-

H) which are covalent bonds with high bond energies (435 kJmol^{-1}). The structure of methane represents as tetrahedral structure with bond angle 109° (Joesten *et al.*, 2007) as shown in Figure 2.2 According to methane structure, it has the special properties with zero dipole moment, no multiple bonds or functional groups and no asymmetry. These properties are responsible for very high stable or low methane reactivity of methane molecule. Thermodynamically, methane is unstable only above 530 °C (Ngobeni, 2007).
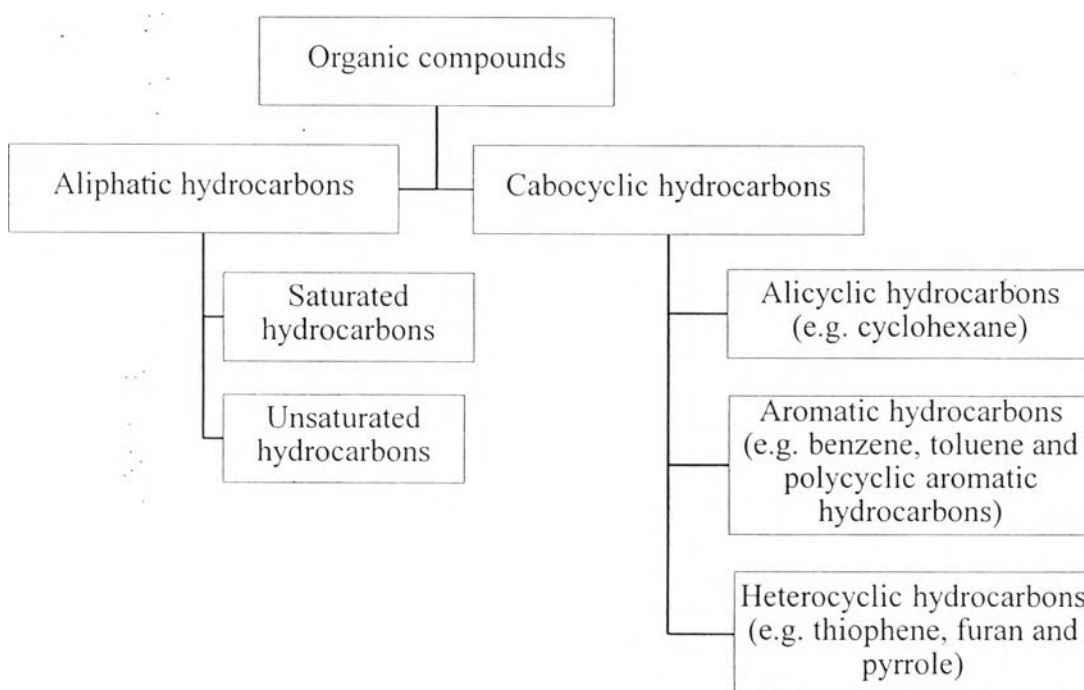

Figure 2.1 Classification of organic compounds (Thompson *et al.*, 2009).

Generally, methane is found associated with coal and petroleum in gaseous form which is recovered and processed as natural gas. Typically, methane exists as a principal component of natural gas reserves about 75-90% (Sivasankar *et al.*, 2008, Stoker, 2009). The very large reserves of methane and high heating value, methane plays an important role in energy source for home and industrial heating and also for the generation of electricity. Alternatively, methane utilization by transformation into higher hydrocarbons draws more considerable attention and methane conversion by

direct and indirect routes was investigated as shown in Figure 2.3 (Sivasankar, 2008), (Stoker, 2009)
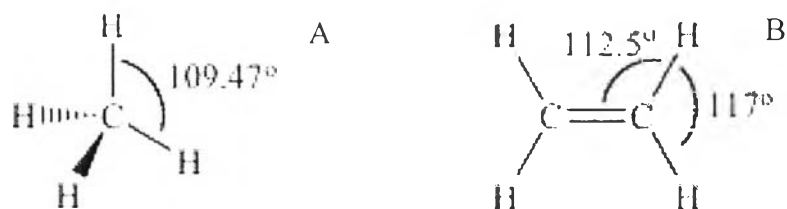

Figure 2.2 The structure of a) methane and b) ethylene.
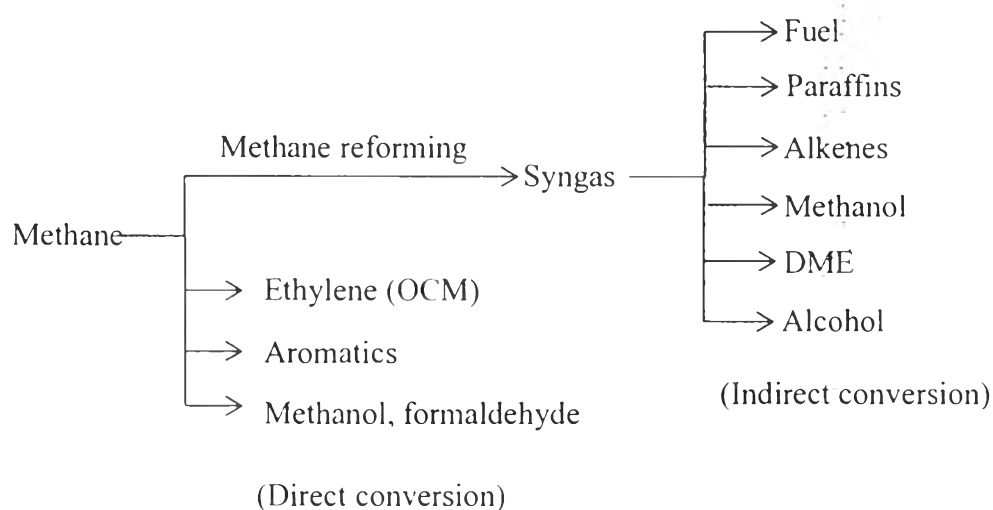(http://www.chem.ucla.edu/harding/IGOC/B/bond_angle.html)

Figure 2.3 Schematic of comparison of indirect and direct routes for methane conversion (Ma *et al.*, 2013).

2.3 Ethylene

Ethylene (C_2H_4) is the simplest of the organic compound known as alkene. The structure of ethylene is planar molecule which consists of one double bond as shown in Figure 2.2 therefore it is classified as unsaturated hydrocarbons. The general properties of ethylene are a colorless, non-corrosive, flammable gas with a faint, sweet odor at ambient temperature and pressure.

In petrochemical industry, ethylene is an important building block for petrochemical industries due to it can be converted to vast 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), e thylene propylene diene monomer (EPDM), a co-monomer for polypropylene, ethylbenzene (EB), styrene (SM), polystyrene (PS) and its copolymers.
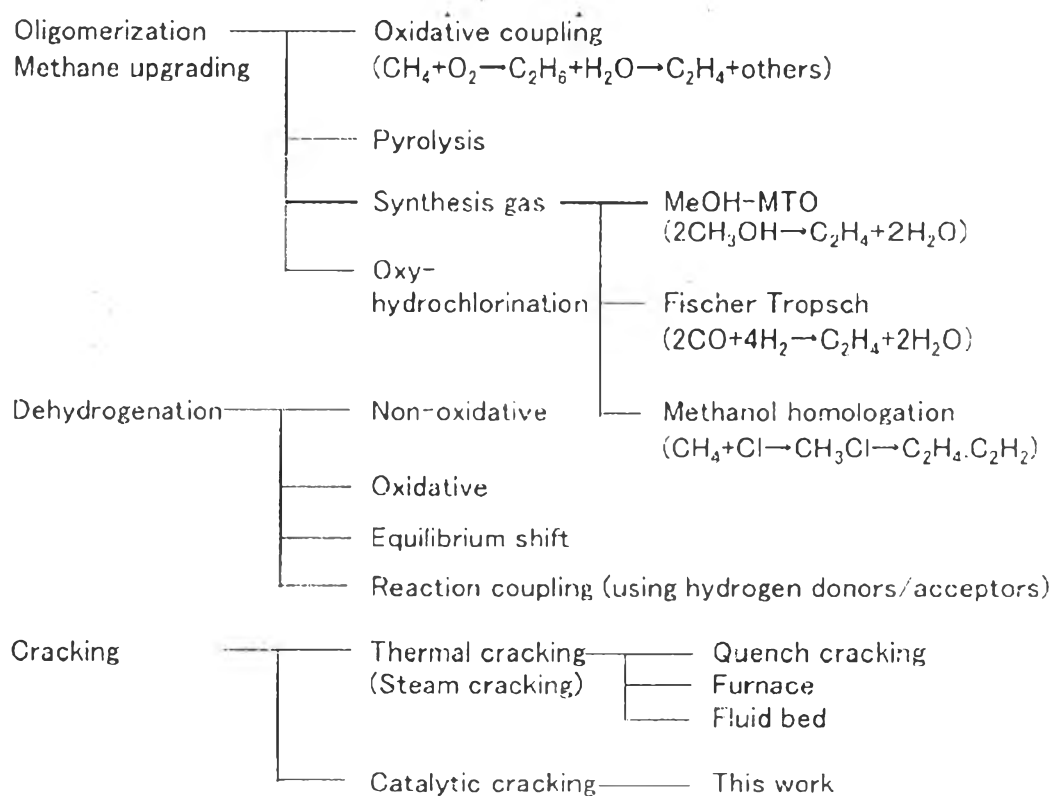

Figure 2.4 Schematic of olefin production processes (Yoshimura *et al.*, 2001).

Commercially, ethylene is mainly produced by steam cracking of various hydrocarbon feed-stocks such as light paraffins, naphthas or gas oils. In addition, uses of alternative feedstock such as methane, LPG, gas oil and ethanol have also been pursued. With this reaction, the yield of ethylene and propylene varies between 24–55% and 1.5–18%, respectively depending greatly on the feedstock type and operating condition. Besides steam cracking, ethylene also produced by various reaction which is concluded in Figure 2.4 To produce ethylene in this research, dehydrogenation under non-oxidative condition using methane as feedstock was proposed.

2.4 Non-oxidative Methane Conversion

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 hydrocarbons (Choudhary *et al.*, 2003). Non-oxidative methane dehydrogenation and coupling is the reaction that directly converts methane to higher hydrocarbons under oxygen free condition. This reaction has been investigated to avoid the formation of CO_x (CO and CO_2) species which are generated from the presence of oxygen in oxidative coupling of methane (OCM) process. Even thought, the OCM process is thermodynamically feasible (exothermic process) than non-oxidative condition but this process has low selectivity towards C_{2+}. Alternatively, direct methane conversion under non-oxidative conditions has been more attended. Thermodynamically, the transformation of CH_4 under non-oxidative conditions is more favorable to aromatics than to olefins, as shown in Figure 2.5 (Xu, 2003).

To synthesize ethylene, non-oxidative methane conversion involves in two main steps that are methane activation (dehydrogenation) and carbon-carbon bond formation (coupling) between CH_x fragments and some higher hydrocarbon fragments. Under this condition, methane directly converted to ethylene is endothermic reaction with large positive change of free energy as shown in Table 2.1. This reaction provides high selectivity of C_{2+} but low yield because of

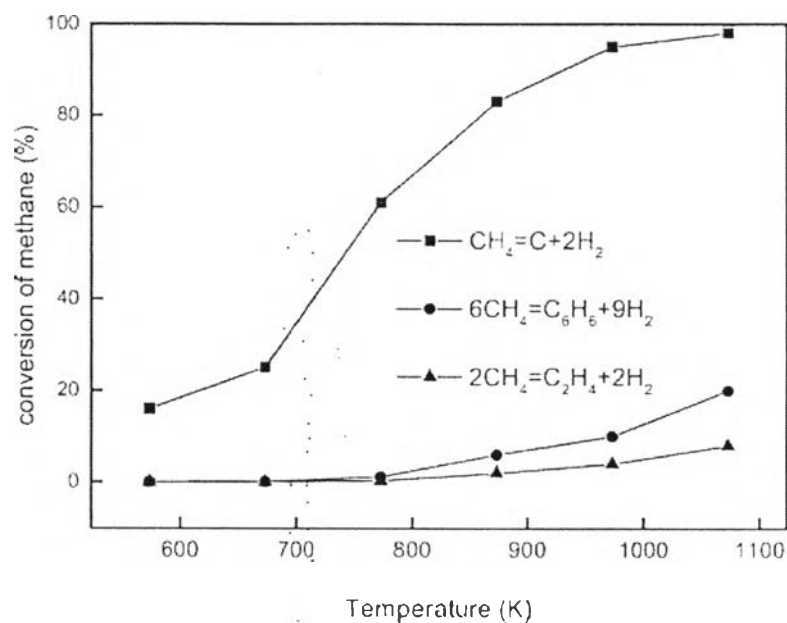unfavorable thermodynamic resulted from low conversion of CH_4 (Guczi *et al.*, 1996).

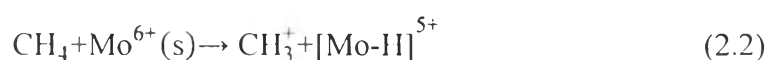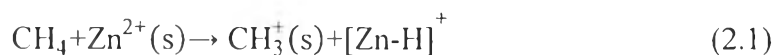**Figure 2.5** Thermodynamics of direct conversion of CH_4 under non-oxidative conditions (Xu, 2003).

Table 2.1 Thermodynamic data, change of free energy, ΔG°, for methane transformation (Guczi *et al.*, 1996)

Reaction	ΔG° (kcal mol^{-1})			
	400 K	600 K	800 K	1000 K
$2CH_4 \rightarrow C_2H_4 + 2H_2$	18.9	15.9	12.8	9.5
$2CH_4 \rightarrow C_2H_6 + H_2$	8.6	8.4	8.5	8.5
$2CH_4 + O_2 \rightarrow C_2H_4 + 2H_2O$	-34.6	-35.1	-35.8	-36.4
$2CH_4 + O_2 \rightarrow C_2H_6 + H_2O$	-18.4	-17.1	-15.8	-14.5
$CH_4 + O_2 \rightarrow CH_2OH$	-25.4	-23.0	-20.5	-18.0
$CH_4 + O_2 \rightarrow HCHO + H_2O$	-69.0	-70.0	-70.8	-71.2

Table 2.1 (cont.)Thermodynamic data, change of free energy, ΔG°, for methane transformation

Reaction	ΔG° (kcal mol^{-1})			
	400 K	600 K	800 K	1000 K
$CH_4+CO \rightarrow CH_3CHO$	16.0	21.9	27.7	33.6
$CH_4+CO_2 \rightarrow CH_3COOH$	19.2	24.9	30.4	35.5
$CH_4+H_2O \rightarrow CO_2+3H_2$	28.6	17.3	5.5	-6.5
$CH_4+C_2H_4 \rightarrow C_2H_8$	-6.4	0.1	6.5	12.8
(ΔG° at 300 K = -6.2)				

According to the large positive of ΔG° for ethylene production, many catalysts and reaction conditions have been investigated to overcome the thermodynamic limitation. Wang et al., (1993) studied dehydrogenation and aromatization of methane under non-oxidizing conditions on modified ZSM-5 zeolite catalysts under non-oxidizing conditions. The result of catalytic performance of HZSM-5 compared to MHZSM-5 (M=Mo, Zn) catalysts suggested that the activation of methane over HZSM-5 and MHZSM-5 zeolite catalysts is via the carbenium ion mechanism as shown in Reactions 2.1, 2.2 and 2.3 for ZnHZSM-5, MoHZSM-5 and HZSM-5 respectively.

$$CH_4+Zn^{2+}(s) \rightarrow CH_3^+(s)+[Zn\text{-}H]^+ \qquad (2.1)$$

$$CH_4+Mo^{6+}(s) \rightarrow CH_3^++[Mo\text{-}H]^{5+} \qquad (2.2)$$

$$CH_4+H^+(s) \rightarrow CH_3^+(s)+H_2 \qquad (2.3)$$

For catalytic performance, the Mo modified ZSM-5 catalysts exhibited excellent catalytic activity and selectivity to benzene for the conversion of methane at 973 K under non-oxidizing conditions. The Mo or Zn loaded in the ZSM-5 played a significant role in methane activation. The aromatization reaction of methane with a conversion of 7-8% and the selectivity to benzene of 100% is quite stable over

Mo/HZSM-5 catalyst under the given conditions. H_2 and ethene may be the primary products in the conversion of methane to benzene. In additional, The yield of benzene increased with increasing partial pressure of methane (Wang et al., 1993).

Chen *et al.*, (1995) studied dehydro-oligomerization of methane to ethylene and aromatics using Mo/HZSM-5. The results showed that methane conversion using 2%Mo/HZSM-5 catalyst decreased at the beginning of reaction. Then the conversion reached a constant level for 2 hours and was less than 1% for 4 hours on stream due to the catalyst deactivation. For selectivity to benzene and ethylene, they demonstrated that increasing time on stream improved the selectivity to ethylene while the selectivity to benzene was decreased. This evidence could be suggested that ethylene is a primary product while benzene is a final product for this reaction. Possibly in the initial period of the reaction, the Bronsted acid sites were not blocked by deposited carbon therefore ethylene as primary product could easily aromatize into benzene on the acid sites. For catalyst deactivated period, the acidic sites of the catalysts were blocked and covered by the deposited carbon resulting in that ethylene could not transform into benzene which could cause high selectivity to ethylene product. In additional, an hourly gas space velocity also affected the selectivity to ethylene. Increasing the hourly gas space velocity or decreasing the contact time of methane increased the ethylene selectivity with low conversion of methane. Furthermore, this research also suggested the possible mechanism of methane conversion over Mo/HZSM-5 which demonstrated as Reactions 2.4, 2.5, and 2.6.

$$CH_4 \xrightarrow[H^\cdot]{MoO_x} CH_3 \cdot + H \cdot \tag{2.4}$$

$$2CH_4 \xrightarrow{MoO_x} C_2H_4 + H_2 \tag{2.5}$$

$$CH_4 \xrightarrow{H^+} C_6H_6 + 3H_2 \tag{2.6}$$

In the first step, the activation of methane to form $CH_3 \cdot$ free radicals occurred via a concerted action between MoO_x and Brønsted acidic sites. Then the $CH_3 \cdot$ free radicals could dimersize to form ethane and then ethylene. Finally, ethylene aromatized to benzene with the aid of protons of HZSM-5 zeolite

Zhou *et al.*, (2012) investigated the entire catalytic cycle for methane dehydrogenation and coupling to ethylene (MDHC) over a Mo/HZSM-5 catalyst by DFT calculations. Three different active center models of $Mo_2(CH_2)_5^{2+}$, $Mo_2(CH_2)_4^{2+}$, and $Mo(CH_2)_2CH^{3+}$ exchanged on HZSM-5 zeolite were optimized, and the reaction mechanisms of MDHC on these models were studied and compared. They proposed that the catalytic cycle of MDHC consisted of four elementary steps; (1) dissociation of the methane C–H bond, (2) dehydrogenation and C–C coupling; (3) activation of the second methane molecule, and (4) elimination of ethylene and molecular hydrogen.
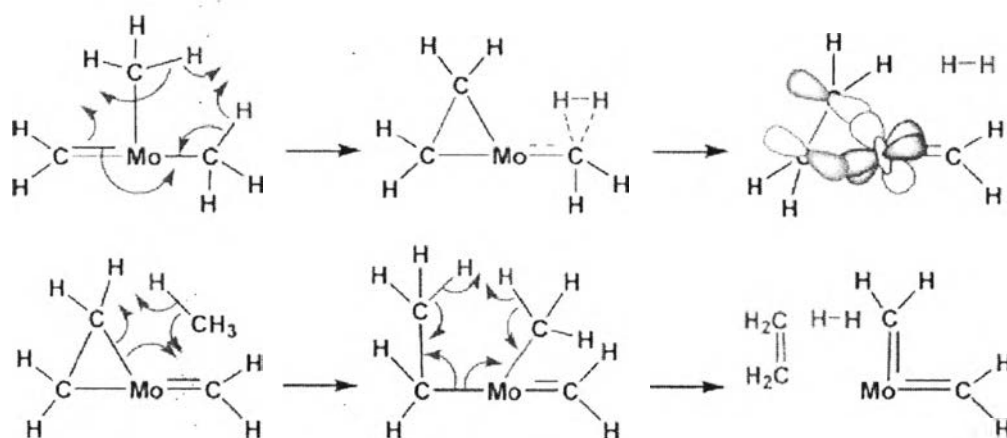

Figure 2.6 Schematic mechanism of C–C coupling and elimination of molecular hydrogen and ethylene on zeolite-supported Mo carbides (Zhou *et al.*, 2012).

The mechanism of C–C coupling and elimination of molecular hydrogen and ethylene on zeolite-supported Mo carbides was shown in Figure 2.6 For the first step, the methane activation occurred via heterogeneous dissociation of the C–H bond, with $H^{\delta+}$ and $H_3C^{\delta-}$ bonded to C and Mo of the $Mo=CH_2$ group, respectively. Then, dehydrogenation preceded by rupture of two C–H bonds in the neighboring methyl groups on the Mo atom. The residual methylidene groups bonded on the adjacent d orbitals of Mo can combine to form quasi-ethylene adsorbed on the Mo atom. After the second methane molecule was activated via the similar process, the

hydrogen molecule and ethylene were removed, and the original active center was regenerated. The three models of $Mo_2(CH_2)_5^{2+}$, $Mo_2(CH_2)_4^{2+}$, and $Mo(CH_2)_2CH^{3+}$ present similar catalytic mechanisms for MDHC. The π-orbitals of the $Mo=CH_2$ group were responsible for methane C–H bond activation, and the neighboring d orbitals of the Mo atom encourage C–C coupling. Dehydrogenation and C–C coupling occurred in a synergetic process, which can reduce the activation energy of the dehydrogenation reaction. It was suggested that dehydrogenation was the rate determining step for methane dehydrogenation and C–C coupling to ethylene.

2.5 Catalysts for Non-oxidative Methane Conversion

According to the achievement of direct methane conversion under non-oxidative condition, several types of catalysts were investigated to improve the selectivity and yield of higher hydrocarbon products. To synthesize ethylene via non-oxidative methane condition, catalysts and reaction conditions were investigated from following literatures.

Yagita *et al.*, (1996) studied catalytic dehydrogenative coupling of methane on active carbon effect of metal supported on active carbon. This research investigated the effect of operating parameter and the effect of metals supported on active carbon. Methane dehydrogenation and coupling was performed on fixed bed catalyst with CH_4 diluted with H_2. The results of the dehydrogenative coupling of methane in the presence of active carbon (AC) and metal oxides as catalysts showed that AC gave the highest C_2 hydrocarbon yields and the activities of tested catalysts were in this following order: AC> Al_2O_3> SiO_2> ZnO> MgO. The products of this reaction were ethane (C_2H_6), ethene (C_2H_4) and ethyne (C_2H_2). Furthermore, the effect of the CH_4/H_2 feed molar ratio on the product yields was also investigated. This result suggested that increase in CH_4 proportion in the reactant mixture promoted C_2 hydrocarbon yield. Whereas the small proportion of CH decreased the yields of C_2 hydrocarbons almost zero. As suggested on the effect of total reaction pressure, H_2 strongly inhibited the dehydrogenative coupling. They concluded that the product yield increased with an increase the contact time and active carbon. In addition, the product yield also increased with increasing reaction temperature. In

particular, the yields of C_xH_4 and C_2H_2 rose sharply at temperature above 1000°C. This behavior was in good agreement with the fact that dehydrogenative coupling of CH_4 is endothermic.

Vosmerikov *et al.,* (2006) studied the production of Mo-ZSM-5 catalysts by impregnation and mechanical mixing for methane dehydroaromatization. For the mechanical mixing method, Mo-ZSM-5 was prepared by Mo oxide (MOO_3) and nanosized powder (NP) of molybdenum produced by electroexplosion of the molybdenum wire in argon. The reaction was carried out at atmospheric pressure under pure methane flow conditions in a quartz reactor (12 mm i.d.) at750 °C and GHSV of 1000 h^{-1}. The volume of catalyst loaded in the reactor was 1 cm^3 and the particles size was 0.5-1.0 mm. From catalytic testing, the results demonstrated that methane conversion over an unmodified zeolite under this reaction conditions was very low and does not exceed 2% while methane conversion increased with the increase in Mo concentration in a zeolite and reached maximal values over the catalysts containing 4.0% Mo. Moreover, Mo nanoparticle supported on ZSM-5 exhibited highest activity and high methane conversion was reached at a low Mo content (0.5%) with 12%. When Mo concentration in zeolite catalysts exceeded 4%, the methane conversion decreased especially over the samples prepared by mechanical mixing. For the effect of Mo loading on acidic sites, they reported that and strong acid sites decreased with increasing in Mo especially at Mo nanoparticle introduction. It resulted from Mo blocking by different Mo forms generated during calcination at the preparation of catalysts. They concluded that it had a relationship between the concentration of acidic sites of different types of zeolite and Mo content. In this connection, to produce a catalyst exhibiting a high activity in the process of methane dehydroaromatization, it was necessary to optimize the relationship between the acidic sites number of a zeolite and the number of active sites connected with different Mo forms. The highest methane conversion per one run and maximal yield of aromatic hydrocarbons were reached for the sample containing 4.0 mass% of Mo nanopowder.

Vosmerikov *et al.,* (2009) studied the nonoxidative conversion of methane into aromatic hydrocarbons on high-silica zeolites ZSM-5 containing nanosized powders of molybdenum (4.0 wt %) and nickel (0.1–2.0 wt %). Catalysts were

prepared by mechanically mixing zeolite ZSM-5 with the molar ratio SiO_2/Al_2O_3 = 40. They conclude that the Mo-containing zeolite ZSM-5 with the addition of 0.1% Ni nanopowder was superior to other samples in not only catalytic activity but also stability. It exhibited advantages in the course of regeneration because a smaller amount of coke characterized by a lower degree of polycondensation was formed on this zeolite. and the less severe conditions of oxidative thermal treatment are required for the removal of this coke.

Moya *et al.,* (2011) intended to syntheses nano structured Ni/SiO_2 catalyst and the conditions of highly dispersed nickel particles for the non- oxidative methane activation. The catalysts were prepared by impregnation using nickel acetated solution incorporated o silica support and then reduced with $NaBH_4$ (NiB/SiO_2). This catalyst exhibited only small NiO particles of order of 15 nm which is the metallic particle sizes of the $Ni-Ox/SiO_2$ smaller than NiB/SiO_2 for five times. Part of these prepared catalysts was then oxidized under mild conditions ($Ni-Ox/SiO_2$) and reduced at 773K with pure hydrogen at 60 $mLmin^{-1}$ and at 5 $Kmin^{-1}$ before reaction. Two different prepared catalysts were test under non-oxidative condition in two stages. The first stage was methane chemisorption at atmospheric pressure in the temperature range 373–873K and the second stage was temperature programmed surface hydrogenation (TPSH) at 553, 673 and 773 K. Form the experiment results, both catalysts showed that the evolution of ethane and ethane occurs in less extension in the gas phase. For The NiB catalyst, the C_3 in the gas phase was observed which confirms the coupling methane capacity at the surface, although the high potential hydrogenolysis on metallic Ni. On the other hand. the $Ni-Ox/SiO_2$ catalyst did not evidence coupling products in the hydrogenation step. The absence of ethene in the first step suggests that the NiB surface was not as active to form carbon species being dehydrogenated when compared to the $Ni-Ox/SiO_2$ catalyst. These results can be correlated to the surface properties, suggesting that the nano particles of the $Ni-Ox/SiO_2$ catalyst with low coordination, such as kinks and edges favor higher reactivity which does not provide coupling of carbon species partially hydrogenated. On the other hand. the NiB catalyst exhibited larger particles than the $Ni-Ox/SiO_2$ catalyst and favors coupling of carbon species. Indeed. these results agreed with that have postulated that the carbon–carbon formation was a structure sensitive reaction

very similar to the reverse process, the hydrogenolysis. Therefore, larger particles may be favorable to the formation of C–C binding. The selectivity to C_{2+} increased on this catalyst.

Aboul-Gheit *et al.*, (2012) aimed to examine the impact of adding Fe, Co or Ni to Mo/HZSM-5 on catalytic performance during the direct conversion of natural gas under non-oxidative condition to aromatics (benzene and naphthalene), ethylene and hydrogen. The catalysts include 3%Mo-3%Fe, 3%Mo-3%Co and 3%Mo-3%Ni were prepared by deep mechanical mixing of the respective metal oxides with HZSM-5 zeolite. The catalyst evaluation was carried out under at atmospheric pressure with 0.5 g of catalyst at 700 °C under nitrogen flow of 60 cm^3 min^{-1}. It is evident that the methane conversion increases with increasing TOS to reach a maximum at 60 min, beyond which the formation of hydrocarbons slightly declined as a function of time. The maximum yield of total hydrocarbons amounts to 6.11, 4.08, 3.62 and 3.34% using 6%Mo, 3%Mo–3%Fe, 3%Mo–3%Co and 3%Mo–3%Ni/HZSM-5 catalysts, respectively. Beyond 60 min the hydrocarbon production declined slowly to reach 5.6, 3.3, 2.6 and 2.5% at 240 min. The drop of the catalytic activities of all catalysts, beyond 60 min can be principally attributed to the heavy carbonaceous deposits on the catalyst. Generally, the monometallic catalyst exhibited higher activity for this reaction than the bimetallic catalysts at all time. It was also evident that the bimetallic Fe–Mo, Co–Mo and Ni–Mo catalysts exhibited higher carbon deposition compared to the monometallic 6%Mo/HZSM-5 catalyst. Furthermore, the Ni based catalyst was the most active for coke formation among the metals of group VIII investigated and the order of coke formation on the bimetallic was Mo–Ni>Mo–Co>Mo–Fe. Corresponding to widely reported that the metal based catalysts proposed for thermal catalytic decomposition of methane or natural gas to carbon nanostructured materials and hydrogen, mainly constituted by elements of the iron group (Fe, Co, and Ni) either unsupported or supported on oxides (TiO_2, SiO_2, Al_2O_3, etc.),were more active. For the conversion of natural gas to ethylene as a function of time on stream. the yield of ethylene shows a drop beyond TOS of 5 to 60 min and then increases again with a further increase of TOS. These data clearly proved that C_2H_4 was the intermediate of the reaction on supported molybdenum catalysts and it could form via a carbene-type intermediate or via carbidic surface

species. The mechanism of CH_4 converted into higher hydrocarbons; Mo^{6+} ions originally incorporated in the zeolite were reduced by CH_4 to Mo_2C accompanied by deposits of coke. The authors suggested that Mo_2C provides active sites for ethylene formation from methane, while the acidic sites catalyze the subsequent conversion to benzene.

Mial *et al.,* (2014) studied the Ag species in Ag/ZSM-5 and their catalytic roles in the title reaction. The Ag/ZSM-5 catalysts were prepared by the conventional wetness impregnation method using ZSM-5 with $SiO_2/Al_2O_3=50$). To investigate the Ag species, 5 wt % Ag were evaluated for methane activation under nonoxidative conditions. The result revealed that C2-hydrocarbons were produced only above 873K. Additionally, the acidity of H-ZSM-5 could also catalyze methane coupling at high temperature. Moreover the C2-hydrocarbons (including ethane and ethylene) yield was significantly improved when a certain amount of Ag was loaded compared with pure H-ZSM-5. Obviously, the supported silver also effects on the temperature for methane activation and C2-hydrocarbons yield by decreases the methane activation temperature as low as 673 K. These results confirmed the positive effect of Ag on methane coupling to C2-hydrocarbons under the nonoxidative condition. The yield of C2-hydrocarbons increased with Ag loading until a maximum reached at the loading of 10 wt %.

2.6 Zeolite

Zeolite is the crystalline aluminosilicate with three-dimensional topologies framework which compose of the primary building unit (PBU) in zeolite framework is SiO_4 and AlO_4 tetrahedral, and ion-exchange capability. The PBU and structure of zeolite show in Figure 2.7. Regularly, zeolite is a micro-pore system with diameters less than 2 nm as shown in Figure 2.8. Zeolite based catalysts have successfully used in variety of commercial process in petroleum and petrochemical industries. Furthermore, zeolite base catalysts in HZSM-5 type have been studied for direct conversion of methane via dehydrogenation and coupling of methane.

$$M_{x/n}\left[\left((AlO_2)_x(SiO_2)_y\right)\right] \cdot mH_2O$$
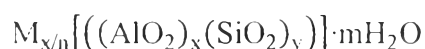
Where n is the valence of cation M, x and y are the number of tetrahedral silicon-and aluminumoxide units respectively and m is the number of water molecules per unit cell.
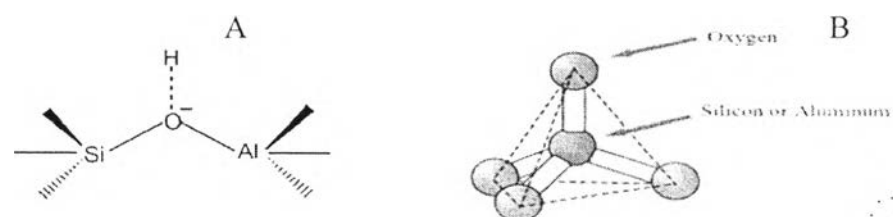

Figure 2.7 a) Chemical structure of zeolite b) Primary building unit of zeolite structure (Georgiev *et al.*, 2009).
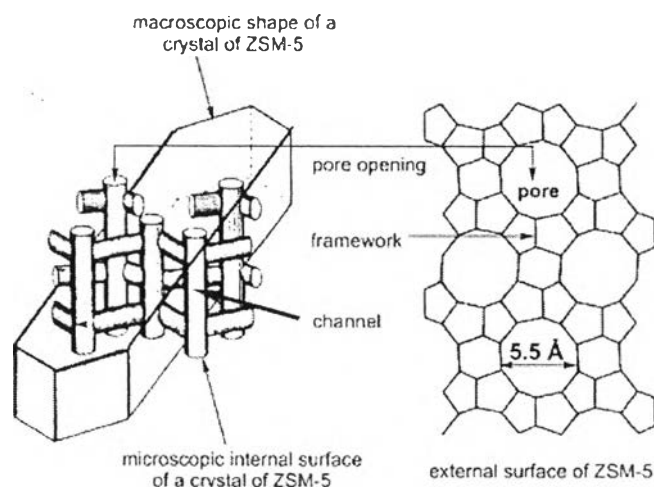

Figure 2.8 Schematic of ZSM-5 zeolite consisting of an intersecting two-dimensional pore structure. There are two types of pores, both formed by 10-membered oxygen rings. One is straight with an elliptical cross section, while the second type of circular cross-section pores intersects the straight pores at right angles in a zig-zag pattern. The effective pore diameter is 0.59 nm, (Lei *et al.*, 2003).

Rahimi *et al.*, (2011) reviewed the important current ideas about acid-catalyzed hydrocarbon cracking that has resulted in high yield of ethylene and propylene. Zeolitic materials are being extensively used in three major catalytic

reactions in the area of petroleum refining, petrochemicals and pollution control. Zeolites, e.g. ZSM-5, are active catalysts and/or supports for a variety of reactions such as cracking, alkylation, aromatization, isomerization of hydrocarbons, etc., owing to their activity, shape selectivity, ion-exchanging properties and special pore structure, such as the tri-dimensional micro-pore topology and large specific surface area in ZSM-5 Zeolites have not yet been employed for on-purpose olefin production through catalytic cracking of hydrocarbons because of the existing well-established industrial steam cracking process; nevertheless, they play an important role in the olefin industry, especially in the processes that are under development or improvement, in order to meet the requirements for more efficient technologies.

HZSM-5 zeolites with different Si/Al ratios, acidity of the zeolites is largely dependent on their Si/Al molar ratios and the employed modifying promoters. In general, the extremely high hydrothermal stability is closely related to the high Si/Al ratio of ZSM-5 zeolite. The low Al content in ZSM-Metals induces the dehydrogenating properties of the material whereas acid sites are responsible for the oligomerization of the dehydrogenation products (bifunctional mechanism).

Recently, HZSM-5 treated by hydrofluorination for non-oxidative conversion of natural gas to aromatic, ethylene and hydrogen was investigated. Aboul-Gheit et al., (2014) studied bifunctional Mo loaded on HZSM-5 compared to hydro-fluorinated HZSM-5 catalysts. Hydrofluorinated HZSM-5 was treated by aqueous solution of hydrofluoric acid (HF) containing quantity to obtain 2.0wt% HF in the catalyst. The catalyst was placed to dry at 110 °C for 24 h and calcined in air at 500 °C for 3 h. Then 6.0 wt% Mo supported on HZSM-5 and HZSM-5(HF) was prepared by incipient wetness impregnation. The catalytic reaction was performed at atmospheric pressure in the absence of oxygen at 700 °C and the natural gas feed GHSV 1500 ml/g/h. The results showed that Mo/HZSM-5(HF) exhibited higher performance for ethylene production and selectivity than untreated Mo/HZSM-5. The treated catalyst increased ethylene yield from 0.08 to 4.05% (42.0% selectivity) with increasing the time-on-stream from 5 to 180 min.

2.7 Nanoparticle Preparation

Two approaches, namely, 'Top-down' and 'Bottom-up', are employed for the synthesis of nanomaterials as shown in Figure 2.9. Top down approach involves division of bulk solid into smaller portions. It includes physical methods like attrition or milling, repeated quenching etc. Bottom-up approach involves condensation of atoms or molecular entities to build up a nanomaterial. It includes chemical methods like reduction of metal salts. The latter approach is far more popular for the synthesis of nanoparticles since it gives better homogeneous size distribution than the former approach.
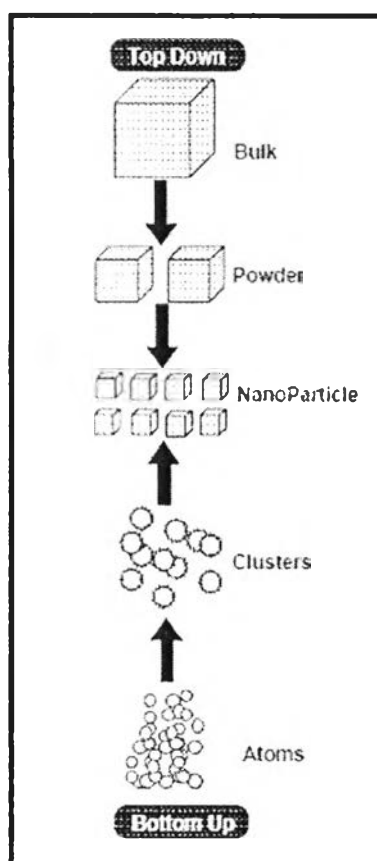

Figure 2.9 Top-down and Bottom-up approaches for nanomaterial synthesis .

2.7.1 Polyol Mediated Synthesis

Nickel nanoparticles supported on HZSM-5 were synthesized by conventional polyol mediated synthesis. Polyol process for nanoparticle synthesis uses polyalcohol--ethylene glycol or trimethylene glycol--as a solvent and metal reduction. In this research, ethylene glycol was selected because it has high dielectric constants. Ethylene glycol as a solvent can dissolve inorganic compounds with a wide range of operation temperature from 25°C to boiling points of preparing inorganic compounds. Moreover, ethylene glycol also acts as a protective agent to prevent the agglomeration when the zero valent metal is nucleated from the bivalent metal ion at high boiling point of ethylene glycol. Under ethylene glycol environment, metal particles are surrounded by lone pair of electrons of oxygen of butane-2, 3-dione as shown in Equation 2.8, 2.9. According to the presence of a lone pair of electrons, it retains the metal particles well dispersed without surfactants in the system (Khurana et $al.$, 2013).

$$HOCH_2CH_2OH \rightarrow CH_3CHO + H_2O \quad (2.8)$$

$$2M^+ + 2CH_3CHO \rightarrow CH_3COCOCH_3 + 2M + 2H^+ \quad (2.9)$$
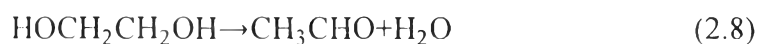
Sarkar et al. (2012) used Ni-nanoparticle supported on mesoporous ZSM-5 for dry reforming of methane. The catalysts were prepared by using Ni nanoparticle supported on ZSM-5 zeolite in ethylene glycol medium. The methodology for catalyst preparation was explained following. For 5%Ni-ZSM-5 catalyst 0.49 g $Ni(NO_3)_3 \cdot 6H_2O$ 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 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 $NiCO_3$ over the catalyst (Sarkar *et al.*, 2012).