

## CHAPTER II

### THEORETICAL BACKGROUND AND LITERATURE REVIEW

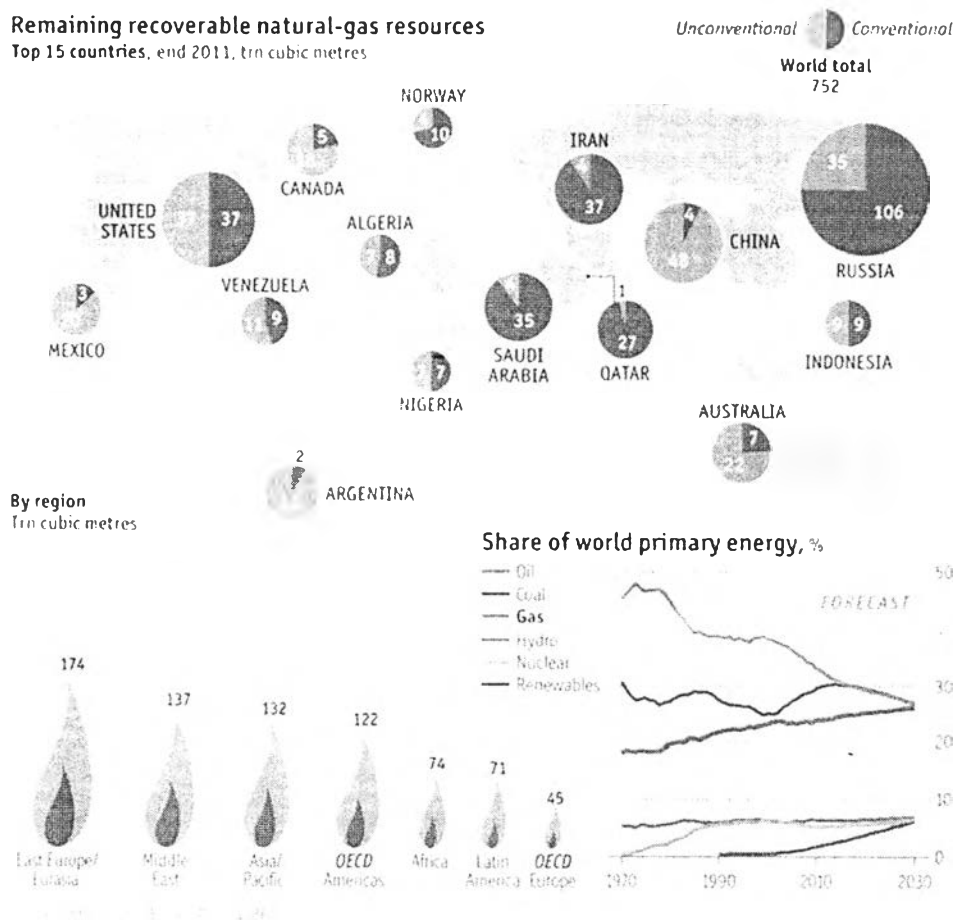
#### 2.1 Methane

Methane ( $\text{CH}_4$ ) is the simplest alkane and the main component of natural gas, generally composed of about 75%  $\text{CH}_4$ , 15% ethane ( $\text{C}_2\text{H}_6$ ), and 5% other hydrocarbons, such as propane ( $\text{C}_3\text{H}_8$ ) and butane ( $\text{C}_4\text{H}_{10}$ ). The cheap price and relative abundance of methane make it attractive both as a fuel and as a chemical feedstock. Moreover, the tightening of crude oil supplies and the more strict environmental legislation are also key driving forces in utilizing methane.

##### 2.1.1 Source of Methane

###### *2.1.1.1 Natural Reserve*

Methane is a major component in natural gas. Global natural gas reserves have been steadily increasing for at least 30 years. Only half a decade ago it looked like the world might have only 50 or 60 years-worth of gas. Currently, shale and other unconventional (e.g., coal bed methane, natural gas from aquifers, and gas hydrates) as well as new conventional gas discoveries have increased estimates of the world natural gas reserve period up to 200 years or more (Economist, 2012). A summary of remaining recoverable natural gas resources by top ten countries, by region, and share of world primary energy is portrayed in Figure 2.1.



**Figure 2.1** Global natural gas reserves and share of work primary energy.

### 2.1.1.2 Origins of Methane

Naturally occurring methane is mainly produced by the process of methanogenesis. This multistep process is used by microorganisms as an energy source. The net reaction is:



The final step in the process is catalyzed by the enzyme methyl-coenzyme M reductase. Methanogenesis is a form of anaerobic respiration used by organisms that occupy landfill, ruminants (e.g., cattle), and the guts of termites. Methane could also be produced by a non-biological process called serpentinization involving water, carbon dioxide, and the mineral olivine, which is known to be common on Mars.

Methane can be produced by hydrogenating carbon dioxide through the Sabatier process. Methane can also be synthesized by the destructive distillation of acetic acid in the presence of soda lime or similar agent. Acetic acid is decarboxylated in this process. Methane can also be prepared by reaction of aluminium carbide with water or strong acids (Wikipedia, 2014b).

### 2.1.2 Utilization

Methane is the major component in natural gas which can be used as fuel and feedstock for the chemical industry. In the International Energy Outlook 2013 (IEO2013) Reference case, natural gas is the world's fastest-growing fossil fuel, with consumption increasing from 113.0 trillion cubic feet in 2010 to 185.0 trillion cubic feet in 2040. Growth in consumption occurs in every region around the world. In the Reference case, total world consumption of natural gas for industrial uses increases by an average of 1.5 percent per year through 2040, and consumption in the electric power sector grows by 2.0 percent per year. The industrial and electric power sectors together account for 77 percent of the total projected increase in natural gas consumption, and together they account for 74 percent of total natural gas consumption in 2040, up slightly from 73 percent in 2010 (U.S. Energy Information Administration, 2013).

#### *2.1.2.1 Fuel*

It has been known that the combustion of methane, in the form of natural gas, is used directly to heat homes and commercial buildings. It is moreover used in power generation plants and other industries. During the past decade, natural gas accounted for about one-fifth of total global energy consumption, and about one-third in the United States. As it will be an important fuel for the future, methane in the form of compressed natural gas (CNG) is recently attractive as an alternative vehicle fuel with a cheaper price and more environmentally friendly nature compared with conventional fossil fuels (i.e., gasoline and diesel); nonetheless, design of a suitable methane storage tank is still a major obstacle. Accordingly, research on adsorption methods of methane storage for use as an automotive fuel has been conducted (Düren et al., 2004; Wikipedia, 2014b). The combustion of methane is highly exothermic, and the reaction shown below:

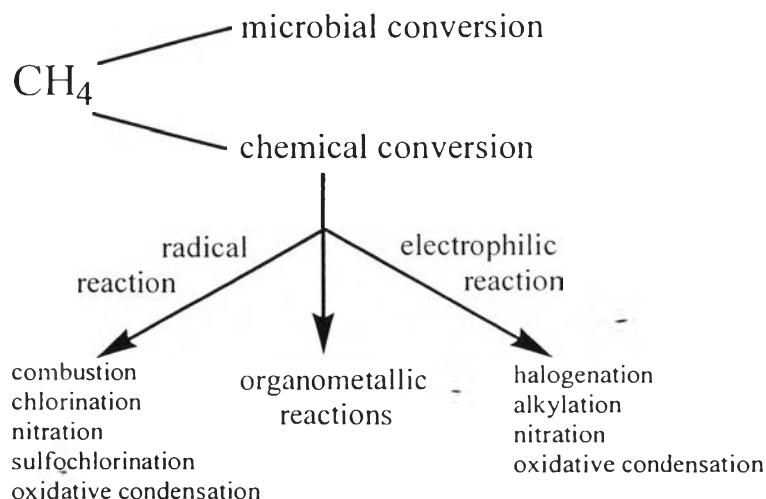


### 2.1.2.2 Chemical Feedstock

Compared with other basic chemical feedstocks, methane is cheap and highly abundant, but converting methane is rather difficult due to its high thermodynamic stability; thus, high temperature is required. Methane processing is typically divided into two approaches; (1) one-step reaction process or direct conversion, and (2) multi-step reaction process or indirect conversion (Gesser et al., 1998). The direct conversion process requires only one reaction step to achieve valuable product, for instance, direct oxidation of methane to methanol or formaldehyde (Olah, 1987), oxidative coupling of methane to olefin (Miao et al., 2004), aromatization of methane, another interesting one being the alkylation of olefins or aromatics with methane into methylated products (e.g., xylenes) (Baba et al., 2002; Lukyanov et al., 2009; Lunsford, 2000). Although this approach seems to be interesting, it is less practical. In a multi-step reaction process, methane is first converted to a gas mixture of carbon monoxide and hydrogen, synthesis gas. Conversion of methane into synthesis gas can be achieved by several processes, such as steam reforming and/or carbon dioxide reforming (Choudhary et al., 1996), catalytic partial oxidation (Smet, 2000), and, newly solar thermal reforming (Agrafiotis et al., 2014). The further conversion of synthesis gas into other valuable products can be performed by many processes depending on a final desirable product, such as the Fischer-Tropsch process for synthetic fuel (e.g., gasoline, jet fuel, diesel), high quality wax, and the methanol synthesis process for producing methanol, etc. However, the major disadvantages of the indirect conversion approach are that two processes or two reactors are required and that syngas generation is a costly operation.

The possibilities of methane conversion are depicted in Figure 2.2. Many reaction routes are shown, including the pathway of methyl free radicals, organometallic reactions or electrophilic reactions. Although the free radicals pathway is applied in many processes, the major drawback of this pathway is the limitation of product selectivity. Biological conversion of methane to higher

hydrocarbons or to methyl alcohol may also be a possible route and significant for the future (Olah, 1987).



**Figure 2.2** Several alternatives for methane conversion. (Olah, 1987)

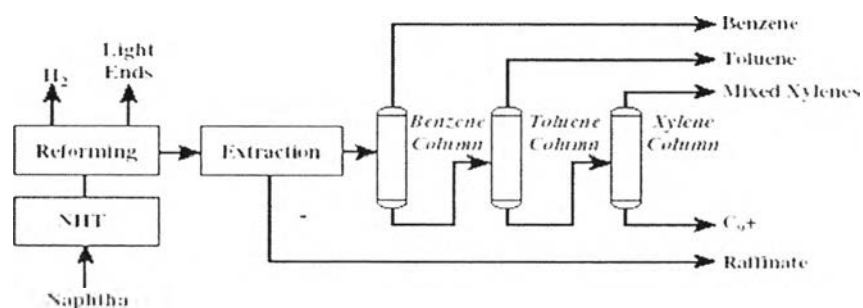
## 2.2 Aromatics and Alkylation Reaction

### 2.2.1 Production of Aromatics: the UOP Aromatics Complex Process

An aromatics complex is a combination of process units that can be used to convert petroleum naphtha and pyrolysis gasoline (pygas) into basic petrochemical intermediates: benzene, toluene, and xylenes (BTX). Benzene is a versatile petrochemical building block used in the production of more than 250 different products. The xylenes product, also known as mixed xylenes, contains four different C<sub>8</sub> aromatic isomers including *p*-xylene, *o*-xylene, and *m*-xylene. The most important C<sub>8</sub> aromatic isomer is *p*-xylene, which is primarily used for the production of polyester. A small amount of toluene is recovered for use in solvent applications and derivatives, but most of the toluene is used to produce xylenes via toluene disproportionation and transalkylation with C<sub>9</sub> aromatics.

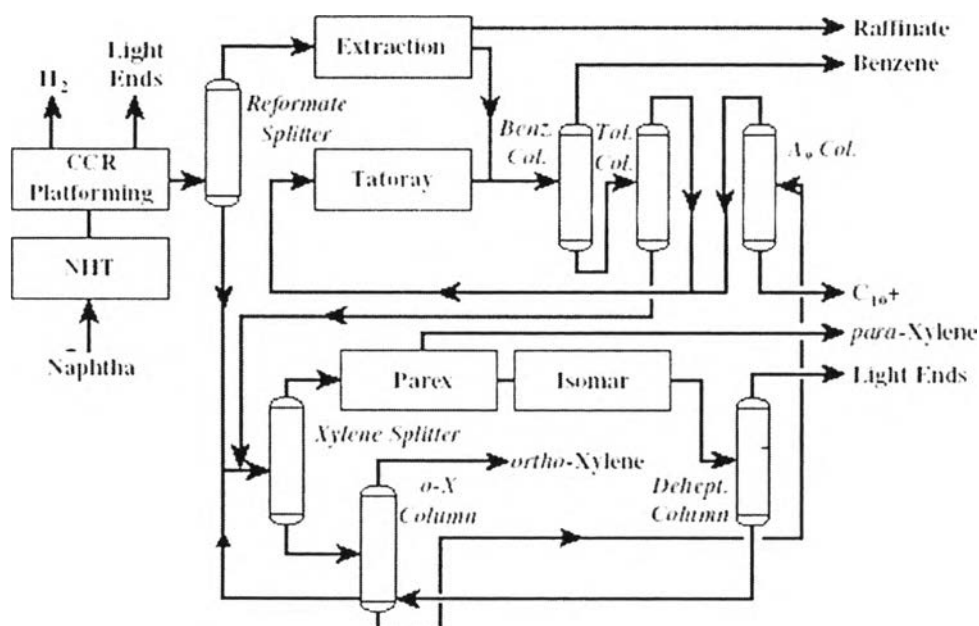
Aromatics complexes can have many different configurations. The simplest complex produces only benzene, toluene, and mixed xylenes. This complex, shown in Figure 2.3, is composed of the following major process units; naphtha

hydrotreating for the removal of sulfur and nitrogen contaminants, catalytic reforming for the production of aromatics from naphtha, and aromatics extraction for recovering BTX products.



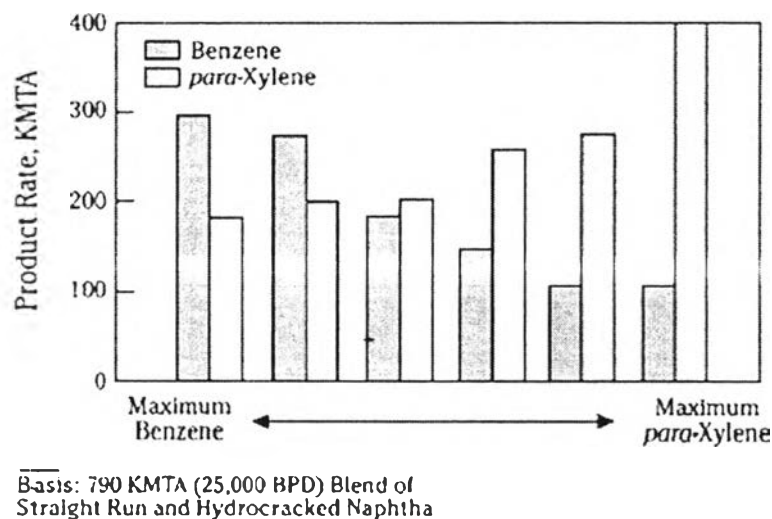
**Figure 2.3** Simple aromatics complex.

To maximize the yield of benzene and *p*-xylene, new aromatics complexes are developed. The configuration of a modern UOP aromatics complex is shown in Figure 2.4. This complex has been configured for maximum yield of *p*-xylene. The complex consists of the following UOP process technologies; CCR platforming for the production of aromatics from naphtha at high severity, Sulfolane Carom on extractive distillation for the recovery of benzene and toluene, Parex for the recovery of *p*-xylene by continuous adsorptive separation, Isomar for the isomerization of xylenes and the conversion of ethylbenzene, and Tatoray for the conversion of toluene and heavy aromatics to xylenes and benzene. The principal products from the aromatics complex illustrated in Figure 2.4 are benzene, *p*-xylene, and *o*-xylene. If desired, a fraction of the toluene and C<sub>9</sub> aromatics may be taken as products, or some of reformates may be used as a high-octane gasoline blending component. The naphtha is a raw material and first hydrotreated to remove sulfur and nitrogen compounds, and then sent to a CCR Platforming unit, where paraffins and naphthenes are converted to aromatics. This unit is the only one in the complex that actually creates aromatic rings. The rest are responsible for separation and conversion of undesired aromatics into high-value products.



**Figure 2.4** Integrated UOP aromatics complex.

The Tatoray process is used to produce additional xylenes and benzene by toluene disproportionation and transalkylation with C9 aromatics. Incorporation of a Tatoray unit increases more than two-fold the yield of *p*-xylene from this improved complex compared to a conventional one. Thus, the Tatoray process is used when *p*-xylene is the principal product or *p*-xylene demand is high. If the demand of benzene is high, it can be achieved by adjusting the boiling range of the naphtha feed to include more benzene and toluene precursors. In addition, the xylene/benzene ratio can also be manipulated by prefractionating the naphtha to remove benzene or C9 aromatic precursors. Because of the flexibility of this aromatics complex, the product slate can be varied to match downstream processing requirements. The xylene/benzene product ratio from an aromatics complex can be varied from about 0.6 to 3.8 as shown in Figure 2.5.



**Figure 2.5** Product slate flexibility of UOP aromatics process.

Although this aromatics complex can minimize benzene with maximizing xylenes by adjusting the operating conditions, it is more useful if benzene can be converted into xylenes. The alkylation of benzene with methyl species to produce more xylenes is an interesting processing strategy, especially in a situation where the demand of xylenes is significantly higher than that of benzene. To produce additional xylenes from benzene by the alkylation route seems to be the most possible, and many efforts have been devoted to such a challenge over the last decade.

### 2.2.2 Alkylation of Aromatics

Aromatic hydrocarbons contain replaceable hydrogen wherein those hydrogen atoms on the ring or side chain can be replaced by the alkyl group unless steric effects prevent access of alkyl groups. For example, little or no ortho substitution of alkylbenzenes takes place when the entering group is tertiary or when the aromatic hydrocarbon contains a tertiary alkyl group. Alkylable aromatic hydrocarbons include benzene and its homologs, polycyclic compounds (e.g., naphthalene, anthracene, phenanthrene, indene), and polycyclic ring assemblies (e.g., biphenyl, diphenylmethane, bibenzyl, tetraphenyls). The relative amounts of three

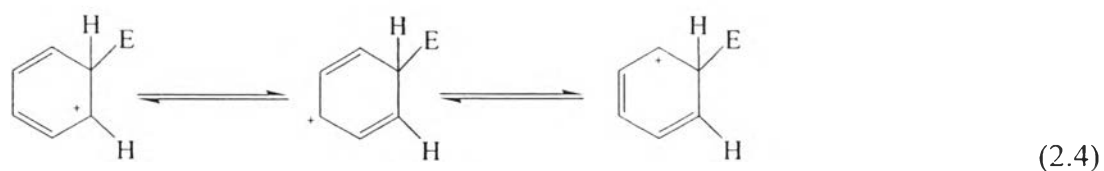
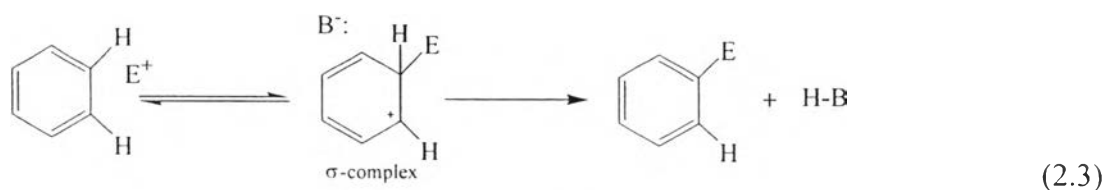


isomeric dialkylbenzenes (ortho-, meta-, and para-dialkylbenzene) that are produced depends on the aromatic hydrocarbon, the alkylating agent, the catalyst, and the reaction conditions. When considering mechanistic aspect, it is essential to differentiate kinetically controlled direct alkylation and thermodynamically affected isomerization reactions (Olah et al., 2003).

The mechanism of alkylation reactions can occur through three different routes which are electrophilic substitution, nucleophilic substitution, and free radical substitution. The catalyst and reaction conditions play important roles in these mechanisms.

### 2.2.2.1 Electrophilic Substitutions

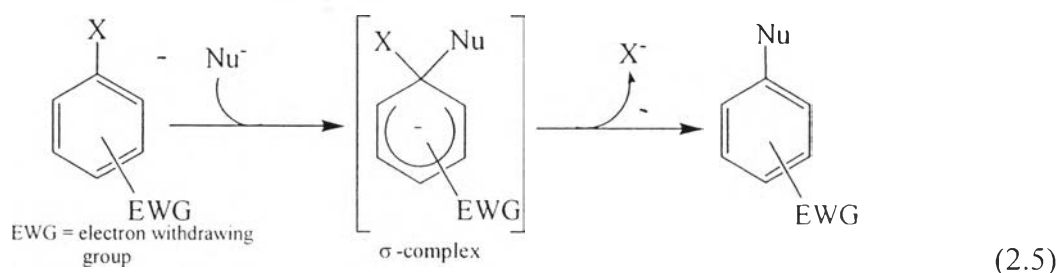
The most common alkylation reaction of benzene is electrophilic substitution. Typically, the benzene ring acts as a nucleophile for serving electrons to electrophiles. The reaction was presumed to occur via a two-step mechanism. The first step is the attack of an electrophile ( $E^+$ ) to form a carbocation intermediate ( $\sigma$ -complex) with the aromatic ring and, as a result, simultaneously destroys the aromaticity of the benzene ring. Then, the final product is formed by proton removal with retrieving the aromaticity of the ring. The rate limiting step for an electrophilic aromatic substitution is the addition of the electrophile to the aromatic ring (Mcketta, 1993). The general mechanism of all electrophilic substitution reactions is given by Eq. 2.3.



The  $\sigma$ -complex intermediate is a very important intermediate for this reaction and is stabilized by delocalization of the positive charge as shown in Eq. 2.4.

### 2.2.2.2 Nucleophilic Substitutions

Nucleophiles can attack the aromatic ring to substitute into the ring in order to form alkylated product even though the aromatic ring usually undergoes substitution by electrophiles. The mechanism involves the attack of an electron rich nucleophile on the aromatic ring containing strong electron withdrawing groups, then followed by removal of the leaving group, such as a halide (X) on the aromatic ring. As a result, the aromaticity of aromatic ring is restored. The reaction is represented by Eq. 2.5.



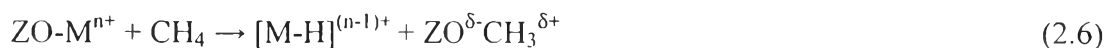
The nucleophilic substitution reaction on the aromatic ring usually requires a strong withdrawing group and/or a good leaving group on the aromatic ring; therefore, the reaction of nucleophilic substitution cannot occur on benzene and alkyl benzene; the possible reaction is instead based on electrophilic substitution. Carbenium ion, the intermediate in electrophilic substitution, and can be generated not only from alkene but also from alkane. However, from the limitations of thermodynamics, more severe conditions are usually required. And, similar to higher alkenes, higher alkanes also have higher reactivity than lower alkanes because of the formation of more stable intermediate carbenium ions. In the case of using methane as an alkylating agent, very severe conditions and catalysts with high activity are required to promote the reaction.

## 2.2.3 Methane as an Alkylating Agent

### 2.2.3.1 Conversion of Methane into Carbenium and/or Alkyl Intermediate over Solid Catalyst Surface

It is well known that methane is very stable and has very low reactivity with other substances. Converting methane into more reactive intermediates is a necessary step

in methane conversion. The activated methane in the form of a carbenium ion ( $\text{CH}_3^+$ ) would be suitable for methylation of benzene through electrophilic substitution. It has been found by Baba and co-workers (year) that metals loaded on H-ZSM-5 zeolites as a charge balancing species is able to activate methane into highly polarized  $\text{CH}_3^{\delta+}$  active species. As in the ethylene/methane atmosphere, where methane is activated, methylation of ethylene with highly polarized  $\text{CH}_3^{\delta+}$  takes place and propylene is mainly obtained. The activities of various metal loaded HZSM-5 catalysts in activating methane and catalyzing the reaction of ethylene to propylene are summarized in Figure 2.6 (Baba et al., 2003). Ag shows the best activity for methane conversion among all metals. Activation of methane on metal cation sites in metal-loaded HZSM-5 can be described by Eq. 2.6, in which methane dissociates on metal cations and metal hydride ( $[\text{M-H}]^{(n-1)+}$ ) and methyl cationic species ( $\text{CH}_3^{\delta+}$ ) are obtained.



Catalytic activities for methane conversion in the presence of ethylene over H-ZSM-5 loaded with various metal cations

	Metal											
	Ag	Mo	In	Fe	V	Ga	Pd	Pb	La	Zn	Cu	H <sup>a</sup>
Conversion (%)												
CH <sub>4</sub>	13.2	9.5	8.1	7.9	7.6	7.0	5.5	5.4	2.5	1.8	1.7	0
C <sub>2</sub> H <sub>4</sub>	86.3	80.2	97.6	88.8	94.0	97.2	95.5	78.1	93.2	88.8	97.0	93.9
Selectivity for hydrocarbons (%) <sup>b</sup>												
C <sub>2</sub> H <sub>6</sub>	1.8	0.0	1.7	1.0	2.3	3.7	3.7	0.0	1.7	1.2	1.7	2.0
C <sub>3</sub> H <sub>6</sub>	20.6	20.3	5.5	20.6	11.2	5.9	9.2	24.3	11.5	16.7	6.0	10.3
C <sub>3</sub> H <sub>8</sub>	11.7	13.7	25.0	18.2	24.8	28.6	22.4	13.0	23.0	7.9	24.6	26.5
C <sub>4</sub> H <sub>8</sub>	9.9	14.7	3.6	15.7	8.0	4.0	6.3	17.8	8.5	10.8	4.3	9.0
C <sub>4</sub> H <sub>10</sub>	13.7	16.0	24.9	14.8	22.1	23.5	18.5	11.3	18.9	11.9	36.5	18.2
C <sub>5</sub> -C <sub>7</sub>	12.7	14.2	13.4	13.9	11.5	7.4	8.7	14.2	10.6	12.4	8.1	11.9
Aromatics	30.3	21.1	25.9	15.8	20.1	26.9	31.2	19.4	25.8	39.1	18.8	22.1

Pressure (CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub>) = 33.8 kPa, running time = 1 h, W/F = 3.6 g h mol<sup>-1</sup>, reaction temperature = 673 K

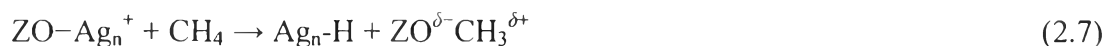
<sup>a</sup> H-ZSM-5.

<sup>b</sup> Selectivity in mol carbon in hydrocarbon products per 100 mol carbon of (CH<sub>4</sub> + C<sub>2</sub>H<sub>4</sub>) converted

**Figure 2.6** Summary of catalytic activity of various metals loaded on HZSM-5 for methane activation and methylation of ethylene. (Baba, et al., 2003)

Chemisorption of methane was characterized by <sup>1</sup>HMAS NMR with Ag-Y zeolite and studied by Baba and co-workers. They found that at 150°C, methane

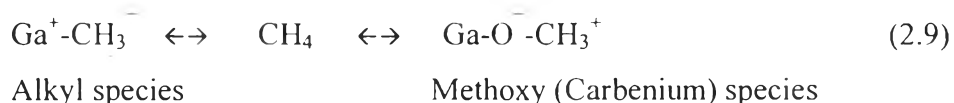
dissociatively adsorbs on Ag-Y and generates silver-hydride species ( $\text{Ag}_n\text{-H}$ ) and highly polarized methyl species ( $\text{CH}_3^{\delta+}$ ) on the surface according to Eq. 2.7 (Baba et al., 2002).



In addition to Ag cations in Y zeolite, Ag-exchanged HZSM-5 as a charge balancing species also shows the same activation (Baba et al., 2003; Baba et al., 2002). However, there is some evidence that both carbenium and alkyl intermediates can be formed on bifunctional catalysts, like Ga-modified zeolites (Luzgin et al., 2010). The simulation research in methane activation over silver-exchanged ZSM-5 catalyst proposed that metal on zeolite support prefers to generate alkyl species as intermediates due to the lower activation energy (Ding et al., 2008). This alkyl group weakly bonded with silver while proton bonds with the zeolite support as shown in Eq. 2.8. Note that  $\text{ZO}^-$  represents the fraction of zeolite possessing one negative charge.

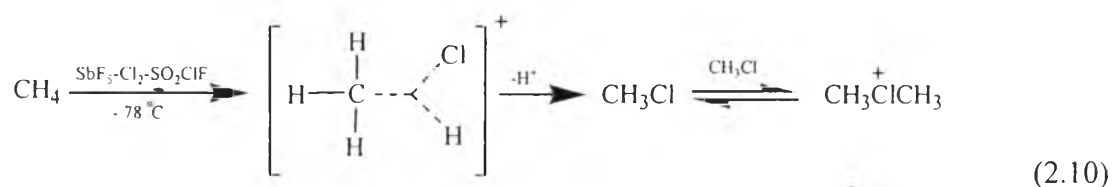


Another experiment regarding the pathway of methane activation was investigated on Ga-modified BEA zeolites with  $^{13}\text{C}$  NMR technique (Luzgin et al., 2010). The results were similar, with methane preferring to dissociate on Ga/H-BEA in the form of alkyl species while carbenium ions were found in smaller amounts. This experiment also demonstrated that alkyl and carbenium intermediates can be interchanged depending on temperature and amount of methane in the gas phase, and the results showed that alkyl species will decompose into methane and shift to generate carbenium ions in the form of Ga-methoxy species at 573 K after evacuating the system as shown below in Eq. 2.9.



### 2.2.3.2 Conversion of Methane into other Alkylating Substances

Olah reported that the chlorination of methane in low-nucleophilicity, superacidic solutions at low temperature gave methyl chloride in high selectivity (Olah, 1987).



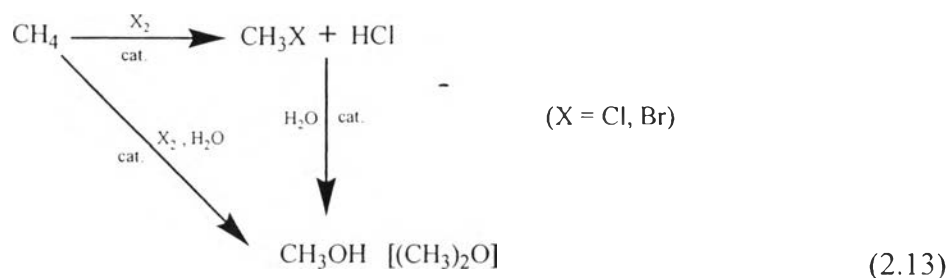
Moreover, the electrophilic halogenations (chlorination and bromination) of methane can be effected with catalytic heterogeneous gas-phase reactions by using various solid acid or supported platinum group metal catalysts that give methyl halides with high selectivity under relatively mild conditions. Recently, Liu and co-workers reported the production of methyl bromide ( $\text{CH}_3\text{Br}$ ) by means of the oxidative bromination of methane using  $\text{Rh}/\text{SiO}_2$  as a catalyst prepared by a sol-gel method (Liu et al., 2010). The reaction is shown in Eq. 2.11 below:



The catalyst containing 0.4 wt% Rh with calcination at  $900^\circ\text{C}$  for 10 h showed good performance in activity, selectivity, and stability. The reaction condition at  $660^\circ\text{C}$  with flowrates of gaseous and liquid feed: 20.0 ml/min of  $\text{CH}_4$ , 5.0 ml/min of  $\text{O}_2$ , 5.0 ml/min of  $\text{N}_2$ , and 6.5 ml/h of 48 wt%  $\text{HBr}/\text{H}_2\text{O}$  can promote the conversion of methane to around 40 mol% with selectivity to methyl bromide above 80 mol% after running 2 h. Interestingly, lifetime testing showed that both the methane conversion and  $\text{CH}_3\text{Br}$  selectivity kept increasing trends even at a time on stream of 650 h. Olah found that the oxygenation of methane using hydrogen peroxide or ozone in superacidic media gives methanol with very high (>95%) selectivity (Olah, 1987).



Moreover, the halogenation of methane followed by hydrolysis consequently is a suitable way to obtain methyl alcohol and dimethyl ether. This reaction can be achieved with better results over supported metal oxide-hydroxide catalysts, such as  $V_2O_5/Al(OH)_3/\gamma-Al_2O_3$  and  $MnO_2/Al(OH)_3/\gamma-Al_2O_3$  (Olah, 1987).



#### 2.2.4 Methylation of Benzene with Methane and its Derivatives

Methylation of benzene by using methane as an alkylating species can be performed by two different ways, which are direct methylation of benzene with methane and indirect methylation of benzene with methane derivatives (e.g., methyl halide or methyl alcohol). The first route is attractive in that only a one-step reaction process is required; however, a highly active catalyst and severe reaction conditions are strongly required because methane is a very stable chemical and the reaction between benzene and methane is highly endothermic. On the other hand, the latter might be easier, with milder reaction conditions due to the better activity of methane derivatives; nevertheless, a multi-step reaction process is necessary in that case.

##### 2.2.4.1 *Direct Methylation of Benzene with Methane*

Direct methylation of aromatic with methane was first studied by He and co-workers (He et al., 1994). They demonstrated that metals substituted on aluminophosphate catalyst can be used in methylation of naphthalene with methane at 400 °C in a batch reactor. Later, Kennedy and co-workers argued that methane reactant cannot be incorporated into the methylated aromatic product over H-beta zeolite in a high pressure flow reactor (Kennedy et al., 1994). In 1995, He and co-workers first studied the methylation of benzene with methane using methane  $^{13}C$  isotope and using a copper-exchanged zeolite (ZSM-5 and beta) as the catalyst. They

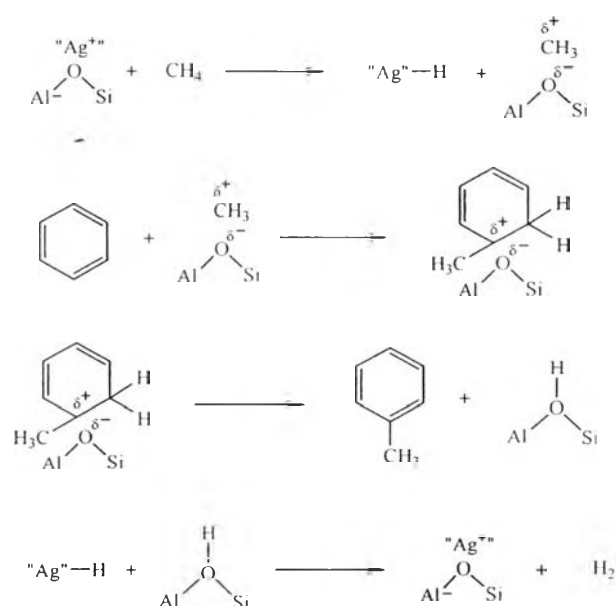
achieved the methylation reaction by methane and confirmed that the reaction is possible under high pressures at 400 °C in a batch reactor (He et al., 1995).

After that, a new route for methylation of benzene with methane was investigated. Adebajo and co-worker revealed that oxygen is essential to the reaction, and found that methanol which is formed only in the presence of oxygen by partial oxidation of methane acts as a key intermediate species in benzene methylation (Adebajo et al., 2000). Luzgin and co-workers later proved this assumption using the NMR technique and found that the formation of active carbenium ions ( $\text{CH}_3^+$ ) increased in the presence of oxygen. The discovery the batch reactor in He's experiment, which may contain residual air, can contribute to direct methylation via the formation of methanol (Luzgin et al., 2010). Then, the direct methylation of benzene with methane was classified into two different routes: the methylation of benzene with methane in the presence of oxygen (oxidative benzene methylation) and methylation of benzene with methane in the absence of oxygen (non-oxidative benzene methylation).

The oxidative methylation was primarily studied by Adebajo and co-workers. The methylation of toluene with methane by various metals on ZSM-5 was investigated, and the results showed that toluene can be converted through two different pathways: methylation by methane and disproportionation (Adebajo et al., 2001). It was proposed that catalysts with more acid sites will mainly lead to the disproportionation pathway (M. O. Adebajo, et al., 2001). Furthermore, He and his co-workers studied the effect of the framework, the Si/Al ratio and pore size structure. The presence of aluminium in the framework of the catalyst is important for the generation of the Bronsted acid sites that are necessary for the reaction, the pore structure also affects the product selectivity, the 12-membered ring pore size (Hbeta and HY) favors the secondary reaction to formation of more bulky product, while 10-membered ring ZSM-5 showed higher selectivity to xylenes (Adebajo et al., 2005).

The non-oxidative methylation of benzene with methane was studied in order to prevent the formation of undesirable products such as  $\text{CO}_2$ , CO and  $\text{H}_2\text{O}$ . Prior to discussing on the methylation of benzene with methane, the non-oxidative activation of methane in the presence of other nucleophiles is described.

Choudhary and co-workers reported that non-oxidative activation of methane can occur by hydrogen transfer reactions between methane and alkenes over galloaluminosilicate ZSM-5 zeolite. The proposed mechanism is the activation of methane occurring over the non-framework Ga-oxide species, in which carbonium ion is an intermediate (Choudhary et al., 1997). However, Naccache and co-workers in 2002 repeated the experiment with  $^{13}\text{C}$ -labelled methane and showed that there was no significant incorporation of  $^{13}\text{C}$  into the products under that condition, contrary to the results of Choudhary (Naccache et al., 2002). However, Choudhary's experiment was supported by the research of Baba and Sawada in the same year (Baba et al., 2002). HZSM-5 loaded with silver cation was used as a catalyst and the results indicated that  $^{13}\text{C}$ -labelled propylene was produced from the reaction of methane in the presence of ethylene, conditions in which methane conversion can reach 13.2 mol%. In addition, the reaction of benzene with  $^{13}\text{CH}_4$  was done in a gas circulation system, and Ag/HZSM-5 produced toluene in a 5.8 mol% yield in 2 minutes and the conversion of benzene was 6.1 mol%, while in a flow reactor system, the conversion of methane and benzene were much lower 2.2 and 1.6 mol%, respectively. The proposed mechanism is presented in Figure 2.7 (Baba et al., 2002).



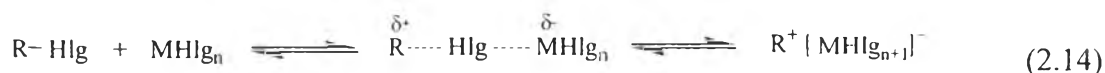
**Figure 2.7** The mechanism of methylation of benzene with methane on Ag/H-ZSM-5. (T. Baba, et al., 2002)



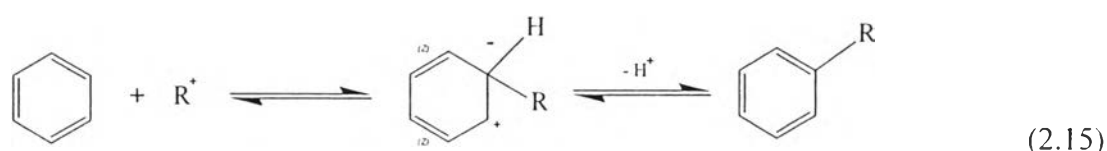
Conversion of methane was examined over various metal cation-loaded HZSM-5 catalysts in the presence of ethylene. The results showed that methane provides high reactivity on HZSM-5 loaded with silver, molybdenum, and indium with the conversion of 13.2, 9.5 and 8.1 mol%, respectively, while non-metal loaded HZSM-5 cannot activate methane (Baba et al., 2003). Moreover, the conversion of methane in the presence of ethylene was performed over silver-exchanged zeolite with various structures (A, Y, and ZSM-5) and silver salt ( $\text{Ag}_3\text{PW}_{12}\text{O}_4$ ), the results showed that propylene was produced over all of the Ag-exchanged zeolites with Ag/ZSM-5 providing the highest selectivity, while silver salt containing silver cations cannot catalyze the reaction (Baba et al., 2007). In addition, conducting the reaction between benzene and methane in a flow reactor, the conversion of methane and benzene were 8.5 and 8.3 mol%, respectively, with selectivity to toluene and xylene of 89 mol% and 11 mol%, respectively (Baba, 2005; Baba et al., 2005). Lukyanov and Vazhnova in 2009 investigated the alkylation of benzene with methane into toluene over Pt/HMFI bifunctional catalyst. The reaction was carried out in a 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 a 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 (Lukyanov et al., 2009).

#### 2.2.4.2 Indirect Methylation of Benzene with Methane Derivative (Methyl Halide and Methyl Alcohol)

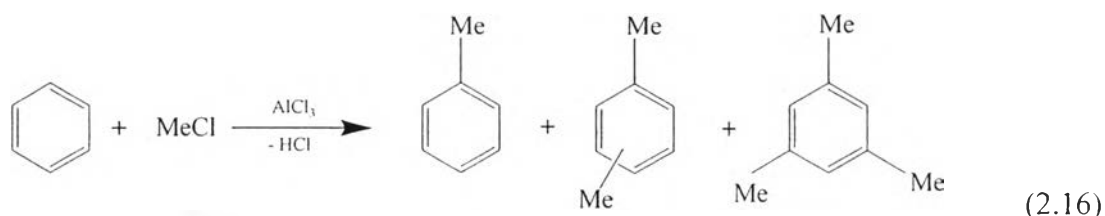
Olah and Molnar in 2003 reported that the methylation of benzene by methyl halide is usually achieved by using Friedel-Crafts catalysts (Olah et al., 2003), the most effective and most frequently used catalysts are  $\text{AlCl}_3$ ,  $\text{GaCl}_3$ ,  $\text{FeCl}_3$ , and  $\text{BF}_3$ . Since the reaction is catalyzed by metal halides, this reaction is the so-called Friedel-Crafts alkylation. The mechanism of Friedel-Crafts alkylation with alkyl halides involves initial formation of the active alkylating agent ( $\text{R}^+$ ), which then reacts with the aromatic ring. The reaction depends on the catalyst ( $\text{MHlg}_n$ ), the solvent, the reaction conditions, and the alkyl halide ( $\text{R-Hlg}$ ). The formation of a polarized donor-acceptor complex or real carbocations ( $\text{R}^+$ ) can be illustrated by the reaction below:



It is usually considered that the carbocation formed ( $\text{R}^+$ ) attacks the aromatic ring and forms the product through a  $\sigma$ -complex or arenium ion in the typical aromatic electrophilic substitution as shown in equation Eq. 2.15.



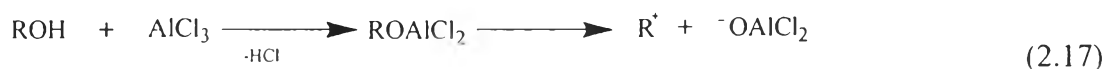
For example, the alkylation of benzene with methyl chloride can be achieved by passing methyl chloride through moderately heated benzene containing aluminum chloride, resulting in the evolution of hydrogen chloride and the formation of toluene with smaller amounts of xylenes, mesitylene, and higher-boiling polymethylbenzene as shown below:



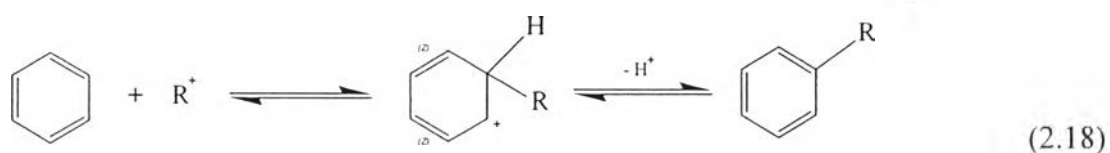
The advantages of this process are that the reaction has high reactivity and requires moderate energy. However, several disadvantages are also presented; for instance, the reaction is complicated by other side reactions, and these include formation of saturated hydrocarbons, dealkylation, and disproportionation (transalkylation). Moreover, it requires solvents, which can cause a problem in the final purification step and the aluminum chloride (catalyst) can be slightly dissolved in the benzene

The methylation with methyl alcohol, Olah and Molnar reported that alkylation of aromatic hydrocarbons with alcohols in the presence of protic catalysts yields products expected from typical electrophilic alkylation. When using Friedel-

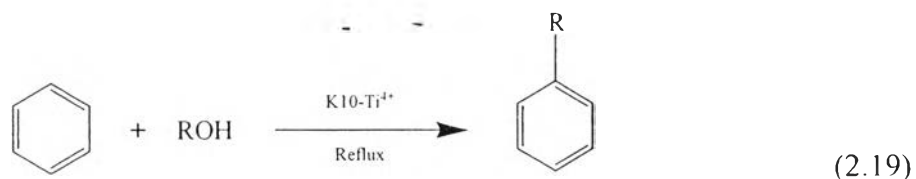
Crafts halides (usually  $\text{AlCl}_3$  and  $\text{BF}_3$ ) as catalysts, the carbocation ( $\text{R}^+$ ) will be formed according to the following equation:



Then, this generated carbocation will be directly attached to the aromatics ring by means of electrophilic substitution as shown below:

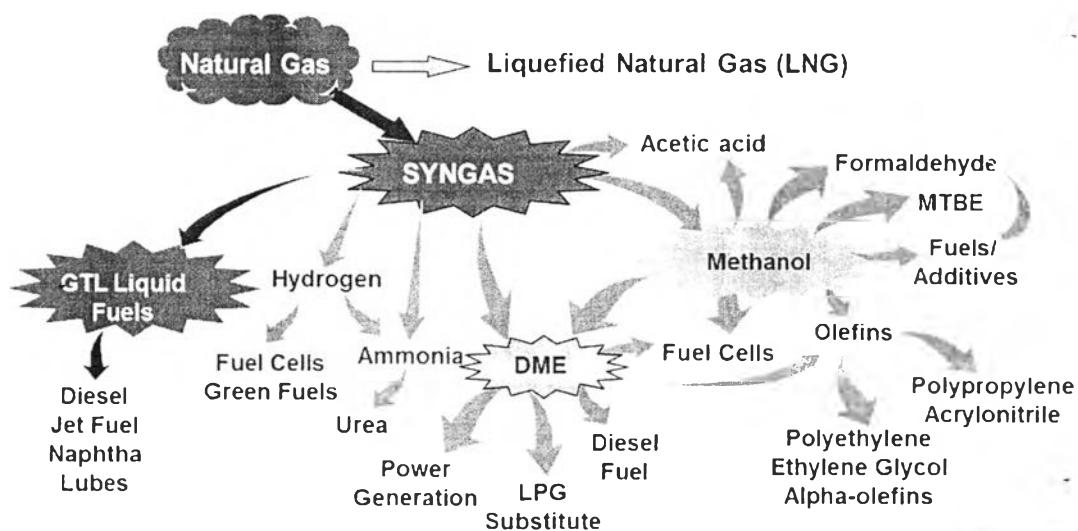


The advantages and disadvantages are the same as for methylation with methyl halides, if Friedel-Crafts halides catalysts were applied. Moreover, in case of aluminum chloride, it would lose its activity when dissolved in excess methanol used as an alkylating agent. In addition, acidic clay catalyst can also be used in alkylation with alcohols. The main advantages of these catalysts are that a reduced catalyst amount can be used to carry out alkylation compared with conventional Friedel-Crafts halide catalysts. Furthermore, it can be possibly regenerated and provide satisfactory yields. Natural montmorillonite (K10 clay) doped with transition metal cations was suggested to be an effective catalyst (Olah et al., 2003).



### 2.3 Gas-to-liquids (GTL) Technology

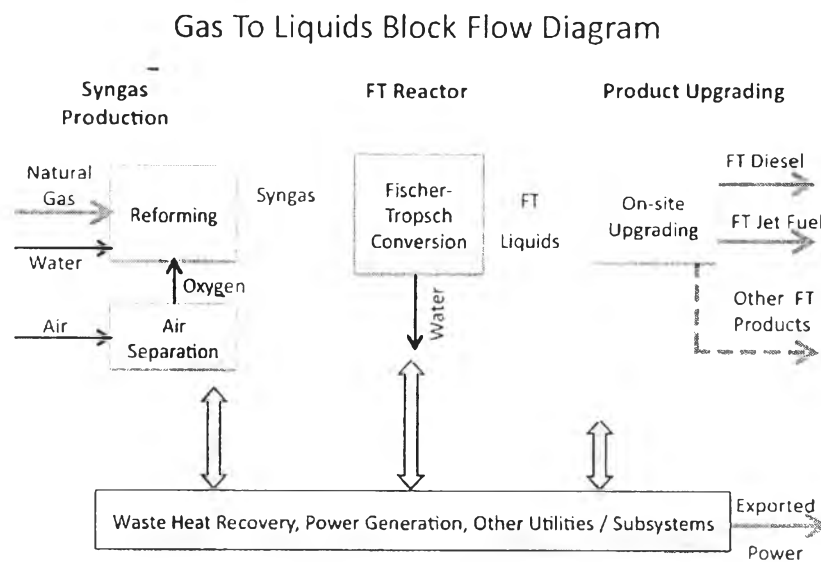
Several gas-to-liquids (GTL) technologies have emerged for the past three decades as a credible alternative for natural gas utilization. While pipeline and liquefied natural gas (LNG) options focus on the natural gas markets, GTL presents an attractive alternative for gas monetisation for gas-producing countries to expand and diversify into the transportation fuel markets and chemicals feedstock markets (Wood, 2005; Wood et al., 2012). An overview of natural gas utilization is illustrated in Figure 2.8. It is obvious that any products derived from natural gas are all achieved via synthesis gas (syngas) intermediate. Thus, conversion of natural gas into synthesis gas is necessary and is typically produced using either steam reforming or partial oxidation process.



**Figure 2.8** An overview of natural gas utilization.

The present thesis focused on one of the gas-to-liquids (GTL) technologies, which is a process to transform natural gas, predominantly by methane, into a variety of high-quality fuel, including diesel (without sulfur and having high cetane number), jet fuel, and high-quality paraffinic wax. The heart of the technology is the Fischer Tropsch synthesis (FT) process, developed originally in the 1920s, and deployed at the commercial scale during the Second World War to convert coal into liquid fuels,

and then perfected at large commercial scale in South Africa beginning in the 1950s (ESP, 2014). A general GTL process is comprised of 3 major sub-processes: (1) synthesis gas production, (2) Fischer-Tropsch synthesis, and (3) product upgrading, as depicted in Figure 2.9.



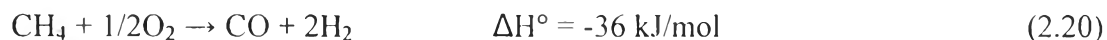
**Figure 2.9** A block flow diagram of the gas-to-liquids (GTL) process.

### 2.3.1 Synthesis Gas Production from Natural Gas

Natural gas-derived synthesis gas, a gas mixture of carbon monoxide and hydrogen, contains high  $H_2:CO$  ratio ( $\sim 2$ ), which can be used in the FT process without the need for water gas shift (WGS); note that WGS is used to boost the  $H_2/CO$  ratio for cases where low  $H_2/CO$  ratio is being used (e.g., certain cases of coal and/or biomass gasification). It is initially produced from the methane molecule by several technologies as following:

#### 2.3.1.1 *Partial Oxidation of Methane*

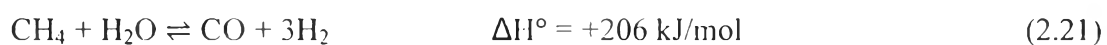
The chemical reaction involved in this approach requires air separation units to remove the nitrogen from air to yield an oxygen-based atmosphere for the reaction:



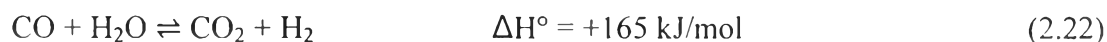
Rahmim in 2003 noted that the key components required for this approach include (1) a combustion chamber operated at high temperatures (1200-1500 °C) without catalysts; (2) process designs to impede a competing reaction to syngas formation which involves the decomposition of methane to carbon black (due to high temperature, non-catalytic nature of the chemistry). Three process sections are typically involved (1) a burner section where combustion occurs (with oxygen only and excluding nitrogen); (2) a heat recovery section; and (3) a carbon black removal section: first by water scrubbing, then extraction by naphtha from the sludge (Rahmim, 2003; Wood et al., 2012). In addition to bare partial oxidation of methane, catalytic partial oxidation of methane was also suggested. It was discovered in 1929 by Liander (Liander, 1929). Ni and Co-based catalysts are typically used as the catalysts. Moreover, other non-noble catalysts (e.g., Cu, Fe, Re, La<sub>2</sub>O<sub>3</sub>, Mo<sub>2</sub>C, Mayenite, WC, Y<sub>2</sub>O<sub>3</sub>, YSZ, and ZrO<sub>2</sub>) and noble catalysts (e.g., Ir, Pt, Pd, Rh, Ru) are applicable (Enger et al., 2008).

### 2.3.1.2 Steam Reforming

Steam reforming of natural gas or sometimes referred to as steam methane reforming (SMR) is the most widely used for producing synthesis gas for feedstock of petrochemical processes and for the production of hydrogen used in refinery hydro-crackers. This reaction is reversible in nature and highly endothermic:



The steaming reforming reaction is typically carried out at high temperatures (i.e., 700 – 1100 °C) and in the presence of a metal-based catalyst (nickel), steam reacts with methane to yield carbon monoxide and hydrogen. The process is typically conducted in tubular, packed reactors with heat recovery from flue gases used to pre-heat the feed gas or to raise steam in waste heat boilers (Wood et al., 2012). If desired, additional hydrogen can be recovered by a lower-temperature water gas-shift reaction with the carbon monoxide produced, and this reaction is described below:



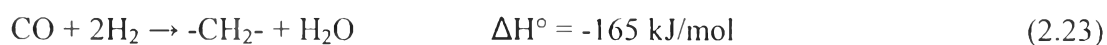
### 2.3.1.3 Autothermal Reforming (ATR)

In Auto Thermal Reformers (ATRs), the synthesis gas production process combines steam reforming with partial oxidation. It uses the heat produced from partial oxidation to provide heat for steam reforming. Gases from the partial oxidation burner are mixed with steam and sent to the steam reformer, rendering the process autothermal. In autothermal processes the temperature level at which the reaction proceeds is maintained by the heat of reaction alone (Wood et al., 2012).

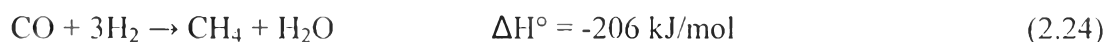
## 2.3.2 Fischer-Tropsch Process

### 2.3.2.1 Process Description

Fischer-Tropsch synthesis is one of several technologies to polymerise the carbon and hydrogen components into long-chain molecules:



The process involves some carbon dioxide emission and water/steam production along with the hydrocarbon liquid production. The typical FT reactions compete with the methanation reaction, which is also highly exothermic (Wood et al., 2012):



In general, the Fischer-Tropsch synthesis (FTS) process is operated in the temperature range of 150–300 °C. Higher temperatures lead to faster reactions and higher conversion rates but also tend to favor methane production. Accordingly, the temperature is usually maintained at the low to middle part of the range, and depends on catalyst type. Higher pressure is important as it enhances conversion rates to long-

chained products. Typical pressures range from one to several tens of atmospheres. Even higher pressures would be favorable, but the benefits may not justify the additional costs of high-pressure equipment, and, moreover higher pressures can lead to catalyst deactivation via coke formation (Wikipedia, 2014a). One exception to this is supercritical FTS, where the supercritical fluid (e.g., hexane/pentane mixture) can extract carbonaceous deposits in-situ (Jacobs et al., 2003).

### 2.3.2.1 *Gas-based Fischer-Tropsch Synthesis Technologies*

Based on operating conditions, natural gas-based FT process technology can be categorized into 2 major types: (1) high-temperature and (2) low-temperature. In High-Temperature Fischer Tropsch (HTFT), with severe conditions and catalysts involved, the synthetic crude produced includes a high percentage of short chain (i.e., <10 carbon atoms) with significant amounts of propane and butane mixed with olefins (e.g., propylene and butylene). These short-chain hydrocarbon gases are typically extracted from the tail gas stream by cryogenic separation. The resultant lean tail gas is recycled and mixed with additional lean feed gas for further synthesis gas production (Minnie, 2005). Typical temperature and pressure for operating HTFT in the presence of iron-based catalyst are approximately 320 °C and pressures 2.5 MPa, respectively. HTFT processes are normally conducted in either circulating fluidized bed reactors or fluidized bed reactors (Velasco et al., 2010). Low-Temperature Fischer Tropsch (LTFT) involves the use of low-temperature (LT), cobalt-based catalyst processes, either in slurry-phase bubble-column reactors (e.g., Sasol) or in multi-tubular fixed-bed reactors (e.g., Shell). LTFT produces a synthetic fraction of diesel (GTL diesel) that is virtually free of sulphur and aromatics. Typical process operation conditions for LTFT are temperatures of approximately 220-240 °C and pressures of approximately 2.0-2.5 MPa. Conversion in LTFT is typically only about 60% with recycle or the reactors operating in series to limit catalyst deactivation (De Klerk, 2012). The primary focus of most large-scale FT technologies in current market conditions is to produce high-quality low-emissions GTL diesel, jet fuel, and naphtha (for petrochemical feedstock or gasoline blending) (Wood et al., 2012). Note that microchannel and small channel reactors are



also being developed. They are more portable and could be used in remote locations for monetizing stranded gas.

#### 2.3.2.1 Fischer-Tropsch Catalysts

A variety of catalysts can be used for the Fischer-Tropsch process, but the most common are the transition metals (i.e., cobalt (Co), iron (Fe), and ruthenium (Ru)). Nickel (Ni) can also be used, but it tends to favor methane formation (methanation).

Cobalt catalysts are more active for Fischer-Tropsch synthesis from synthesis gas derived from natural gas having high H<sub>2</sub>/CO ratio (1.8-2.1). Iron catalysts are often but not exclusively preferred for lower quality feedstock such as coal or biomass. Synthesis gas derived from these hydrogen-poor feedstocks has a low-hydrogen-content and requires the water-gas-shift reaction to adjust the H<sub>2</sub>/CO ratio upward to achieve a desirable stoichiometry. Unlike the other metals used for this process (Co, Ni, Ru), where the metallic state is active for the reaction, iron carbides play an important role as active sites for the reaction (Wikipedia, 2014a). To improve metal dispersion and catalyst activity, all active metals are normally supported on high-surface-area binders/supports such as silica, alumina, titania, or zeolites (Jacobs et al., 2002; Khodakov et al., 2007). This is not necessarily the case for iron catalysts, although Si is often incorporated as a structural promoter, whereas K is added to facilitate CO dissociation (and carbide formation), and Cu facilitates reduction.

In addition to the active metal, the catalysts typically contain a number of promoters, including in the case of cobalt-based catalysts noble metals, in the case of iron catalysts alkali metals, or in either case Group 11 transition metals (Balonek et al., 2010; Jacobs et al., 2002; Jacobs et al., 2009). For example, cobalt supported alumina (Co/Al<sub>2</sub>O<sub>3</sub>) is an effective Fischer-Tropsch synthesis catalyst. There is general agreement that reduced Co metal surface sites serve as active sites for Fischer-Tropsch synthesis over this catalyst. Unlike other metals typically employed in catalysis, cobalt on alumina for FTS is often loaded in high amounts, often at or exceeding 20% by weight. Due to a strong interaction between alumina support and cobalt (Espinoza, 1998; Van Berge et al., 2001), high Co loadings is

necessary to facilitate the reduction of cobalt oxide species during activation and make the catalyst more resistant to deactivation (e.g., by oxidation at high conversion) (Espinoza, 1998; Van Berge et al., 2001). Despite high Co metal loadings, the support still hinders the ability of cobalt oxide to be reduced during thermal activation in H<sub>2</sub> at moderate temperatures (e.g., 350 °C for 10 h in H<sub>2</sub>). Noble metals are primarily used as metal promoters since they are resistant to corrosion and oxidation reactions. Moreover, they can be reduced into the metallic phase at lower temperatures compared to Co, thus providing a metal surface to chemisorb and dissociate H<sub>2</sub>, with spill over to facilitate the reduction of cobalt oxides. Metal promoter such as Pt, Ru, and Re (Arnoldy et al., 1985; Das et al., 2003; Jacobs et al., 2004; Jacobs et al., 2002; Jacobs et al., 2007; Kogelbauer et al., 1996; Rygh et al., 2000; Schanke et al., 1995) are commonly employed to facilitate the reduction of Co oxides in Co/alumina catalysts. An improvement in reducibility by adding these promoters also translates to an increase in Co metal site densities and, respectively, an increase in activity/selectivity of the Co/alumina catalyst. Note that residual CoO in the catalyst tends to produce CO<sub>2</sub> by WGS. Palladium (Pd) as a promoter was also studied by our group (Jacobs et al., 2012). Unlike Pt, Ru, and Re addition, Pd addition deleteriously affects to the FT product selectivity. Ir oxide (Cronauer et al., 2011) and Re oxide (Jacobs et al., 2002) reduce at higher temperature than Pt, Ru, and Pd and close to the Co<sub>3</sub>O<sub>4</sub> to CoO reduction step. However, once reduced, they efficiently catalyze the second reduction step (CoO to Co<sup>0</sup>). Moreover, using Group 11 (Cu, Ag, Au) as metal promoters was also reported (Jacobs et al., 2009). Cu facilitates Co oxide reduction, but the increased fraction of reduced Co does not translate to improved active site densities; moreover, it also results in a decrease in CO conversion and an increase in light product selectivity (Jacobs et al., 2009). Small quantities of gold (Au) are known to increase the reducibility of cobalt oxides (Jacobs et al., 2009; Jalama et al., 2007; Leite et al., 2002); moreover, improved CO conversion, slight decreases in light product selectivity with slight increases in C<sub>3</sub>+ selectivity are obtained (Jacobs et al., 2009). Ag promoter provides not only a significant gain in Co active site densities, but also a remarkably improved CO conversion together with slightly improved FT product selectivity (Jacobs et al., 2009). These results of Ag promotion still holds true even at

high Ag loading (Jermwongratanachai et al., 2013). On the other hand, alkali oxides on cobalt catalysts generally cause activity to drop severely even with very low alkali loadings. Note that Ag is two orders of magnitude lower in price than typically used promoters (e.g., Pt).

Iron as a Fischer Tropsch synthesis catalyst needs alkali promoter to attain high activity and stability. Generally, iron is also supported on high-surface-area  $\text{SiO}_2$  or  $\text{Al}_2\text{O}_3$  for structural promotion or these oxides are incorporated into the structure by other means (unsupported case). Following activation, several iron carbide phases and elemental carbon are formed whereas iron oxides are still present in addition to some metallic iron forms. With iron catalysts, two directions of selectivity have been pursued. One direction has aimed at a low molecular weight olefinic hydrocarbon mixture to be produced in an entrained phase or fluid bed process (i.e., Sasol Synthol process). Due to the relatively high reaction temperature (e.g.,  $340^\circ\text{C}$ ), the average molecular weight of the product is so low that no liquid product phase occurs under reaction conditions. The catalyst particles moving around in the reactor are small (i.e., particle diameter is approximately 100  $\mu\text{m}$ ) and carbon deposition on the catalyst does not disturb reactor operation. Thus a low catalyst porosity with small pore diameters as obtained from fused magnetite (plus promoters) after reduction with hydrogen is appropriate. For maximizing the overall gasoline yield, the olefins,  $\text{C}_3$ ,  $\text{C}_4$  have been oligomerized. However, recovering the olefins for use as chemicals in e.g. polymerization processes is advantageous today. For carbided alkali iron catalyst, olefin selectivity is likely correlated to the basicity of the promoter in the order  $\text{Cs} > \text{Rb} > \text{K} > \text{Na} > \text{Li} > \text{unpromoted}$  (Ribeiro et al., 2011). The second direction of iron catalyst development has aimed at high catalyst activity to be used at low reaction temperature where most of the hydrocarbon product is in the liquid phase under reaction conditions. Typically, such catalysts are obtained through precipitation from nitrate solutions. A high content of a carrier provides mechanical strength and wide pores for easy mass transfer of the reactants in the liquid product filling the pores. The main product fraction then is a paraffin wax, which is refined to marketable wax materials; however, it can also be very selectively hydrocracked to a high quality premium diesel fuel. Thus, iron catalysts are very flexible (Wikipedia, 2014a).

Ruthenium is the most active Fischer Tropsch synthesis catalyst working at the lowest reaction temperature. It acts as a Fischer Tropsch catalyst as the pure metal, without any promoters, thus providing the simplest catalytic system of Fischer Tropsch synthesis. Like with nickel, the selectivity changes to mainly methane at elevated temperature. Like Co, Ru is almost always supported, where its dispersion and, subsequently, activity on a per gram catalyst basis (i.e., not TOF) can be improved. Compared with Ru/SiO<sub>2</sub>, the Ru/SNT (silica nanotubes) catalyst exhibits higher activity in FTS because of the higher dispersion of ruthenium particles in SNTs (Tang et al., 2011). Although Ru shows high catalytic activity and selectivity to liquid hydrocarbons, its high price and limited world resources may preclude industrial application. Systematic Fischer Tropsch studies with ruthenium catalysts should contribute substantially to further exploring of the fundamentals of Fischer Tropsch synthesis (Wikipedia, 2014a).

### 2.3.3 Product Upgrading

The synthetic crude can be refined by using conventional refinery cracking processes to produce diesel, naphtha and lube oils for commercial markets (Agee, 2005). By starting with very long chain molecules the cracking processes can be adjusted to an extent in order to produce more of the products in demand by the market at any given time. In most applications it is the middle distillate diesel fuels and jet fuels that represent the highest-value bulk products with lubricants and premium waxes offering high-margin products for more limited volume markets. In modern plants, GTL unit designs and operations tend to be modulated to achieve a desired product distribution and range of product slates (Wood et al., 2012).