

CHAPTER II

LITERATURE REVIEW

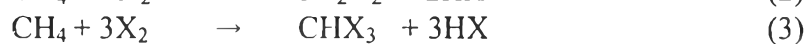
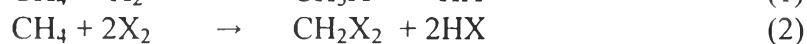
2.1 Methane Activation

Utilization of natural gas as an alternative chemical feedstock is becoming more important due to the reduction of reserves and the enhancing consumption of crude oil. However, more than one-third of the natural reserves are classified as stranded because the location far from industrial centers and transportation costs obstruct its efficient utilization. It has been estimated that approximately 150 billion m³ of natural gas has been flared or vented annually worldwide, which is equivalent to about 5% of global annual natural gas consumption (BP, 2006, WorldBank, 2006). Therefore, a low-energy, high-yield process using a small facility that can be located close to the stranded natural gas source is desirable.

However, the high stability of the C–H bonds in methane (C–H = 410 kJ/mol) which is supposed to be the first step for methane activation makes the conversion limited. In the current industrial technologies, the production of chemicals from methane is typically divided into two groups; one-step reaction process (direct routes) and multi-step reaction process (indirect routes). For the indirect route via synthesis gas, natural gas is firstly converted to synthesis gas by steam reforming, and then synthesis gas is converted to higher hydrocarbons by F-T process or to methanol over the Cu/ZnO/Al₂O₃ catalyst (Hutchings *et al.*, 1990). Methanol could also be converted to hydrocarbons over doped zeolite catalysts (Chang, 1983, Stocker, 1999). However, the synthesis gas process is known to be a highly energy consuming and greenhouse gas-releasing process. Up to 25% of natural gas must be burnt to generate energy for the natural gas steam reformation. More energy-saving and less greenhouse gases emission is expected in natural gas industries. On the other hand, direct routes for methane conversion have shown more potential advantages, partial oxidation of methane to methanol and formaldehyde on MoO₃/SiO₂ (Crabtree, 1995) and V₂O₅/SiO₂ (Otsuka *et al.*, 1987) has been extensively studied for many years but low conversion, low yield, and poor catalyst stability renders it less competitive and un-commercialized.

2.2 Halogenation of Methane

Methane activation by free radical reaction is one of the most extensively studied methane utilization pathways. Among the radicals commonly used to initiate such reactions, halogens stand out as being the best understood (Lorkovic *et al.*, 2006). Methane halogenation is a chain reaction initialized by the formation of halogen radicals ($X\bullet$) through the dissociation of halogen (X_2) as following;



The enthalpy and free energy of formation of methane–halogen reactions are shown in Table 2.1. Fluorination seems to have relatively high reaction enthalpy which means the reaction itself provides enough energy to initiate the reaction. However, highly exothermic reaction is difficult to be controlled and may cause an explosion. Chlorine is not favorable owing to corrosive problem and the products of chlorination are quite low selectivity. For iodine reactions, the low reactivity of iodine results in low conversion even at high reaction temperature. Therefore, among the halogens, bromine has been found to be the best choice for methane activation. The slightly exothermic reaction between bromine and methane possesses the advantage of halogenation can be easily controlled. Moreover, the high methane conversion, high methyl bromide selectivity and easier regeneration from HBr make it more attractive. Typically, at a temperature of 525 °C and CH_4/Br_2 ratio of 1, the selective conversion of methane to methyl bromide is 70–80% with the byproducts, primarily dibromomethanes and small amount of tribromomethanes (Degirmenci *et al.*, 2005).

Table 2.1 Enthalpy and free energy of formation of methane–halogen reactions (Reid *et al.*, 1977)

$\text{CH}_4 + \text{X}_2 \rightarrow \text{CH}_3\text{X} + \text{HX}$		
X	$\Delta H_0(\text{kJ/mol})$	$\Delta G_0(\text{kJ/mol})$
F	-427.0	~-430.0
Cl	-99.8	-107.9
Br	-28.3	-32.3
I	53.2	49.1

If the bromination products are used as feedstock for a catalytic carbon-coupling reaction to produce higher hydrocarbons, the formation of polybromomethanes (CH_2Br_2 and CHBr_3) during reaction is a serious problem because the polybromomethanes can deactivate the catalyst. Separation of these polybromomethanes before introducing into the coupling unit makes the process more expensive. Thus, many publications have been focused on the ability to produce highest selectivity bromomethane against polybromomethanes (Ding *et al.*, 2013).

George A. Olah (1985) proposed halogen radicals ($\text{Br}\cdot$ and $\text{Cl}\cdot$) for the activation of methane by extracting hydrogen from methane and producing methyl halides under relatively mild conditions, then the catalytic hydrolysis of methyl halides to achieve the production of dimethyl ether and methanol. In these reactions, different supported solid super-acids were used. They found out that 98% CH_3Cl could be obtained with SbF_5 -graphite catalyst while both $\text{SbOF}_3/\text{Al}_2\text{O}_3$ and $\text{TaOF}_3/\text{Al}_2\text{O}_3$ gave 99% CH_3Br selectivity. Hydrolysis of methyl halides over γ -alumina supported metal oxide/metal hydroxide catalysts with 25% conversion offers an alternative way to produce higher hydrocarbon instead of the synthesis gas route.

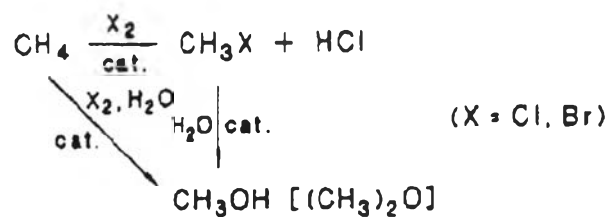


Figure 2.1 Halogenation of methane followed by hydrolysis to obtain methyl alcohol and dimethyl ether (Olah, 1987)-

Zhou *et al.* (2003) also described an integrated multi-step process for the partial oxidation of alkanes to produce dimethyl ether via halogenation. In this route, alkanes reacted with bromine in the first part of a reactor to produce alkyl bromides and HBr, and then followed by a reaction with a solid metal oxide (MO), generating dimethyl ether and metal bromide (MBr₂) in the second part. Finally, the metal bromide reacted with oxygen by the oxygenation to quantitatively regenerate metal oxide and bromine. However, the obstacle of this process is solid transferring problem and giving the poor selectivity to monosubstituted alkyl bromide.

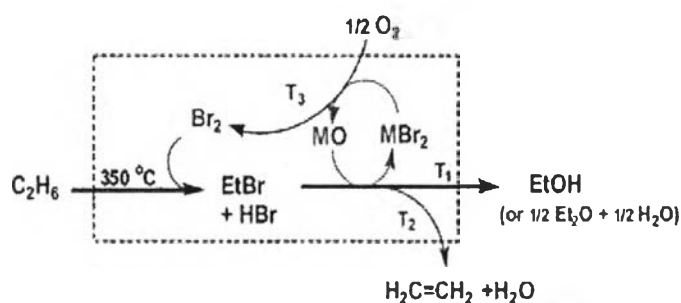
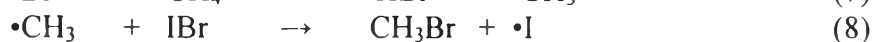
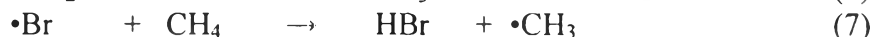


Figure 2.2 Partial oxidation of alkanes via bromination followed by the reaction with solid metal oxide mixtures (Zhou *et al.*, 2003).

Ding *et al.* (2013) showed that a small amount addition of iodine (I₂/Br₂ = 1/9) improves the conversion of methane to CH₃Br and the selectivity against formation of CH₂Br₂ within a short reaction time. Iodine radical could readily abstract

Br from CH_2Br_2 . After a series of reaction (Eq.5-9), CH_4 and CH_2Br_2 are converted to CH_3Br leading to higher CH_4 conversion and higher selectivity to CH_3Br . This can be the beneficial when selective methyl bromide is desired.



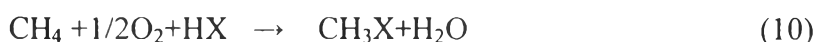
The sum of these reactions is



Although the methane activation by halogenation approach is dominated in the industrial technologies, the drawbacks of this route are; 1) the poor selectivity to monosubstituted alkyl bromide from the free radical reaction mechanism. 2) bromine in large quantity is a hazardous oxidant. 3) regeneration of bromine is not easy (Wang *et al.*, 2006).

2.3 Oxidative Bromination of Methane (OBM)

In recent years, many researchers have proposed the concept of oxidative halogenation of methane. They used $\text{HX}/\text{H}_2\text{O}$ (solution) and O_2 as mediator instead of X_2 for the methane activation. (X = halogen)

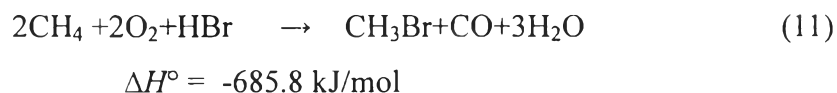


Most common halogens are chlorine and bromine. Nevertheless, comparing between the methane chlorination and methane bromination, the process of methane chlorination is not commercialized owing to the low selectivity of CH_3Cl . Chlorine atom is much smaller than bromine, it will be easy to form polychloromethane (CH_2Cl_2 , CHCl_3) as by-products.

Oxidative bromination of methane is preferable. Because of the space limit around carbon and the big atomic size of Br results in one carbon atom cannot hold too many bromine atoms around it. On the other hand, bromine is a better leaving group. Hence, high CH_3Br selectivity can be gained (Xu *et al.*, 2005).

Methane activation by oxidative bromination (OBM) has several advantages;

1. The OBM reaction is a highly exothermic reaction (Eq.11). Thus, it is an energy-saving process.

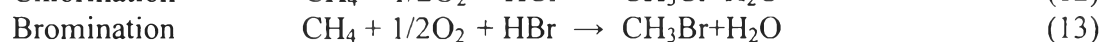


2. Methyl bromide, the main product of the OBM reaction, could be converted to many useful chemicals, such as methanol, dimethyl ether and higher hydrocarbon and the HBr in the effluent could be easily recycled.

3. It does not require only a high selectivity of methyl bromide. If the final product is acetic acid, it can provide both CH_3Br and CO in an equimolar (Lin *et al.*, 2010).

2.4 Related Articles of Oxidative Bromination of Methane

Albert E. Schweizer (2002) suggested in the patent that the methane could be activated by reacting with chlorine or bromine to produce chloromethane or bromomethane (Eq.12-13), and then convert halomethane to higher hydrocarbon via the hydrolysis reaction. However, there is no detail of the catalyst and reaction data.



Xu *et al.* (2005) and Wang *et al.* (2005) used Ru/SiO_2 catalyst, prepared by impregnation method, in the oxidative bromination of methane to produce CH_3Br and CO , which in turn converted to dimethyl ether (CH_3Br only) or (CH_3Br with CO) to acetic acid. Table 2.2 shows the different product distribution of OBM reaction. Up to 78.8% CH_3Br selectivity was achieved, a good feedstock for dimethyl ether production, whereas, 72.4% CH_3Br selectivity and 25.5 % CO selectivity could be attained by controlling the conditions in order to synthesize acetic acid.

Table 2.2 Product distribution of OBM reaction with different desired product

Desired product	T (°C)	CH ₄ (mL/min)	O ₂ (mL/min)	CH ₄ conversion (%)	Selectivity (%)		
					CH ₃ Br	CH ₂ Br ₂	CO
DME	560	5.0	20.0	31.8	78.8	2.3	18.9
Acetic acid	560	5.0	15.0	30.1	72.4	2.1	25.5

In the later, Wang *et al.* (2006) tried to develop the new catalyst for the oxidative bromination of methane by adding some metals on Ru/SiO₂, e.g. Mg Ca Y La Sm Bi Ba Ni. They found that 2.5% Ba 2.5% La 0.5% Ni 0.1% Ru/SiO₂ showed the best performance, giving a high methane conversion, as well as high CH₃Br and CO selectivity : 62.9% of methane conversion with CH₃Br, CH₂Br₂, CO, and CO₂ selectivity of 54.5%, 5.3%, 34.6%, and 5.6%, respectively. From the Table 2.3 indicated that using suitable catalyst and adjustment the reaction temperature is a practicable ways to reach the target.

Table 2.3 Catalyst performance for OBM reaction (Wang *et al.*, 2006)

Entry	T (°C)	Catalyst	X (%)	Selectivity (%)			
				CH ₃ Br	CH ₂ Br ₂	CO	CO ₂
1	580	0.1% Ru/SiO ₂	38.4	52.9	0	47.1	0
2	580	0.1% Rh/SiO ₂	35.9	37.9	0	62.1	0
3	580	5% Mg 0.1% Ru/SiO ₂	32.1	53.1	4.5	42.4	0
4	580	5% Ca 0.1% Ru/SiO ₂	20.9	33.1	3.3	63.6	0
5	580	5% Ba 0.1% Ru/SiO ₂	25.9	76.8	6.6	16.6	0
6	580	5% Y 0.1% Ru/SiO ₂	69.9	15.4	1.8	77.7	5.1
7	580	5% La 0.1% Ru/SiO ₂	72.2	30.7	5.6	61.0	2.7
8	580	5% Sm 0.1% Ru/SiO ₂	81.4	7.6	2.1	86.9	3.4
9	600	5% Sm 0.1% Ru/SiO ₂	86.6	6.8	1.2	88.0	4.0
10	580	2.5% Ba 2.5% La 0.1% Ru/SiO ₂	42.9	55.9	6.1	38.0	0
11	580	2.5% Ba 2.5% La/SiO ₂	15.7	52.2	14.6	33.2	0
12	600	2.5% Ba 2.5% La 0.1% Ru/SiO ₂	58.8	53.4	4.9	41.7	0
13	580	2.5% Ba 2.5% Sm 0.1% Ru/SiO ₂	34.5	61.8	9.1	29.1	0
14	600	2.5% Ba 2.5% Sm 0.1% Ru/SiO ₂	41.5	57.2	5.0	37.8	0
15	580	2.5% Ba 2.5% Bi 0.1% Ru/SiO ₂	18.2	60.2	16.2	23.6	0
16	600	2.5% Ba 2.5% Bi 0.1% Ru/SiO ₂	37.1	49.9	5.8	44.3	0
17	600	2.5% Ba 2.5% La 0.5% Bi 0.1% Ru/SiO ₂	50.0	54.4	7.0	38.6	0
18	600	2.5% Ba 2.5% La 0.5% Fe 0.1% Ru/SiO ₂	59.3	51.7	3.1	40.4	4.8
19	600	2.5% Ba 2.5% La 0.5% Co 0.1% Ru/SiO ₂	52.1	52.2	3.4	38.2	6.2
20	600	2.5% Ba 2.5% La 0.5% Ni 0.1% Ru/SiO ₂	62.9	54.5	5.3	34.6	5.6
21	600	2.5% Ba 2.5% La 0.5% Cu 0.1% Ru/SiO ₂	41.3	51.4	2.8	39.4	6.4
22	600	2.5% Ba 2.5% La 0.5% V 0.1% Ru/SiO ₂	57.6	50.5	3.0	38.0	8.5
23	600	2.5% Ba 2.5% La 0.5% Mo 0.1% Ru/SiO ₂	53.6	52.1	2.4	36.0	9.5

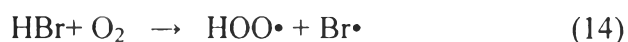
Note: Methane flow 5.0 mL/min, oxygen flow 5.0 mL/min, 40 wt.% HBr/H₂O flow 4.0 mL (liquid)/L catalyst 1.0000 g. X denotes the conversion of methane.

Liu *et al.* (2007) designed a two-stage system for synthesizing higher hydrocarbon. First, methane is converted to methyl bromide, and methyl bromide is converted to higher hydrocarbon in the second reactor. They presented the new catalyst for oxidative bromination of methane, Rh/SiO₂ catalyst prepared by sol-gel method. Methane single-pass conversion of 36% and an overall selectivity for methyl bromide and methylene dibromide of 87% was achieved in this paper. Thus, the Rh/SiO₂ was proved to be better than the Ru/SiO₂ reported previously. Additionally, Liu also deduced that the presence of HBr inhibits the deep oxidation and steam reforming of methane.

The previous investigation demonstrated that the role of catalyst has influenced to the product distribution. Therefore, Yang *et al.* (2008) became focused in the reaction pathway for OBM reaction over Rh/SiO₂. From their result experiment, it can be deduced that the reaction took place both in the gas phase and over the surface of the catalyst. But the surface reactions contributed the major part in the formation of CH₃Br and CH₂Br₂.

The reaction pathway might be;

Step 1 HBr reacts with O₂ to form water and active bromine species, such as the bromine radicals (Br•) in the gas phase and the adsorbed species (Br*) over the surface of the catalyst.



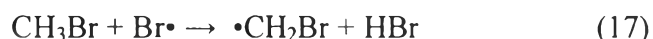
Step 2 Active bromine species react with CH₄ to form HBr and methyl species (CH₃•radicals and the adsorbed surface species CH₃*)



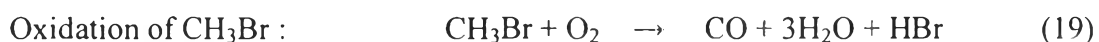
Step 3 The methyl species react with active bromine species to form CH₃Br



Step 4 If CH₃Br reacted with active bromine species again, CH₂Br₂ could be formed as by product as well as the CHBr₃ formation.



Step 5 The generation of CO and CO₂ are mostly due to the oxidation or water reforming of CH₃Br.



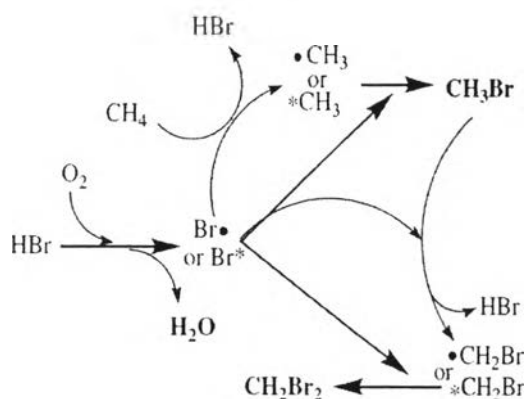
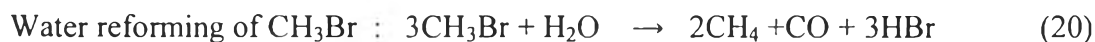


Figure 2.3 Possible reaction pathways for the OBM reaction : gas phase and the surface of the catalyst reaction (Yang *et al.*, 2008).

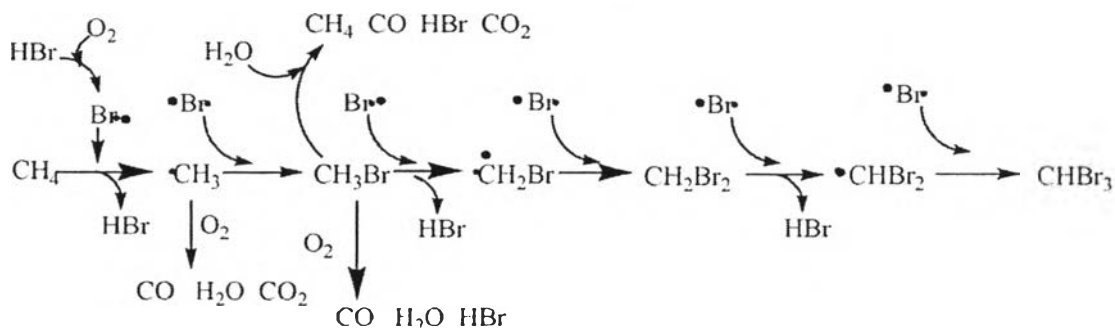


Figure 2.4 Possible reaction pathways for the OBM reaction : monobromomethane (main product), polybromomethanes, and another byproducts (Wang *et al.*, 2006).

In the meantime, Lin *et al.* (2009) successfully developed a series of supported non-noble metal oxide catalysts for the production of equimolar CH_3Br and CO . This investigation emphasized on replacing noble metal catalysts with cheaper oxides and various silica-supported oxide catalysts were surveyed. It was found that the redox ability of different metals had a strong impact on the product distribution. Among the surveyed catalysts, BaO/SiO_2 displayed the best total selectivity of CH_3Br , CH_3OH and CO , which can provide a perfect feedstock for the synthesis of

acetic acid ($\text{CH}_3\text{Br} + \text{CH}_3\text{OH}$): $\text{CO} = 1$ (mol/mol). Consequently, it was chosen for further experiments.

Table 2.4 OBM reaction on different supported metal oxide catalysts (Lin *et al.*, 2009)

Oxidative bromination of methane on different supported metal oxide catalysts.

Catalysts	Conversion (%)	Selectivity (C%)						
		CH_4	CH_3OH	CH_3Br	CH_2Br_2	CHBr_3	CO	CO_2
Blank	20.0		13.6	55.4	21.4	1.9	7.6	0
5 V	25.8		3.5	9.2	0.5	0	86.7	0
10 Ce	28.1		0	3.2	0.2	0	93.6	3.0
5 Mo	29.6		18.0	34.3	3.4	0	43.0	1.3
10 Ba	30.6		11.2	47.6	1.9	0	38.3	2.0
5 W	31.4		14.7	26.5	0.4	0	58.4	0

Reaction variables: T 650 °C; 40 wt.% $\text{HBr}/\text{H}_2\text{O}$ flow 8.0 ml/h; gas flow 25 ml/min ($\text{CH}_4:\text{O}_2 = 4.0$).

Up to now, noble metal catalysts still be the superb catalyst for the oxidative bromination of methane with high methyl bromide selectivity. Liu *et al.* (2010) indicated that that using suitable catalyst preparation conditions, catalyst with desired specific surface area could be prepared in the OBM reaction over Rh/SiO_2 catalysts. Adjustment the calcinations conditions, we could obtain either high yield of CH_3Br or CH_3Br and CO from the reaction as the following;

If only CH_3Br is preferred which could be converted to high hydrocarbons, methanol, or dimethyl ether through other catalytic reactions, the Rh/SiO_2 catalyst should be calcined at a temperature as high as 900 °C for a longer time.

If equal yields of CH_3Br and CO are preferred which the final product is acetic acid, the Rh/SiO_2 catalyst should be calcined at a relatively low temperature within a shorter time.

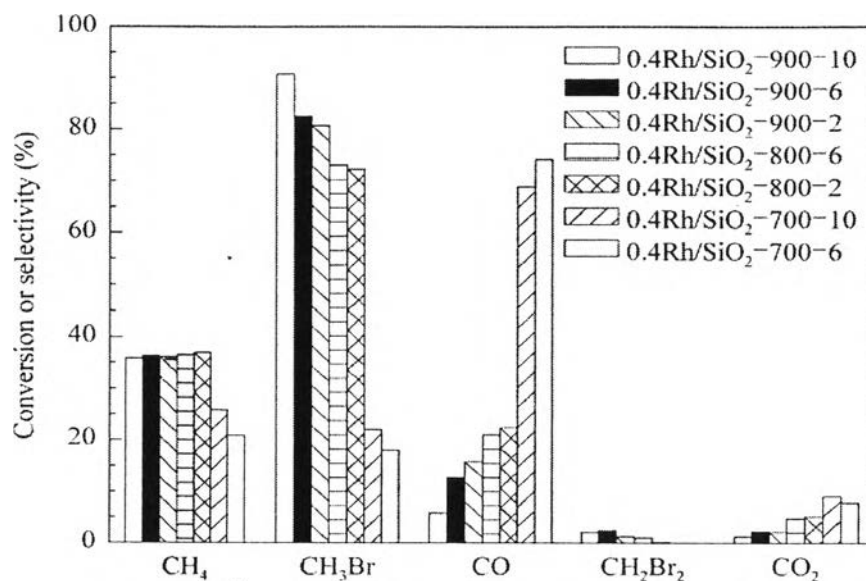


Figure 2.5 The product distribution of the OBM reaction with different calcination conditions.

Note : 0.4Rh/SiO₂-900-10 was denoted as, 0.4 was the Rh loading in weight percentage, and 900 and 10 were the calcinations temperature (°C) and time (h), respectively (Liu *et al.*, 2010).

2.5 Related Articles of Methylation with Alkylating Agent

Aboul-Gheit *et al.* (2011) studied the reaction of toluene methylation with methanol over Pd/H-ZSM-5 catalyst. They found that Pd can act as a promoter to activate this reaction by the presence of a vacant d-orbital in the Pd atom. As a result, the *para*-xylene selectivity was found to increase significantly with the 0.2%Pd/H-ZSM-5 catalyst. They also proposed a mechanism (Fig 2.6): firstly, methanol or methyl ether (formed by methanol dehydration over Pd/H-ZSM-5 catalyst) adsorbed on the acid sites of catalyst and formed the corresponding oxonium ion. Then the methyl group transferred to the aromatic ring and a proton transferred back to the catalyst site. The role of Pd is apparently concerned in second step where the carbocation formed requires stabilization such that the reaction passes safely to the right hand side and enhancing the xylene yield.

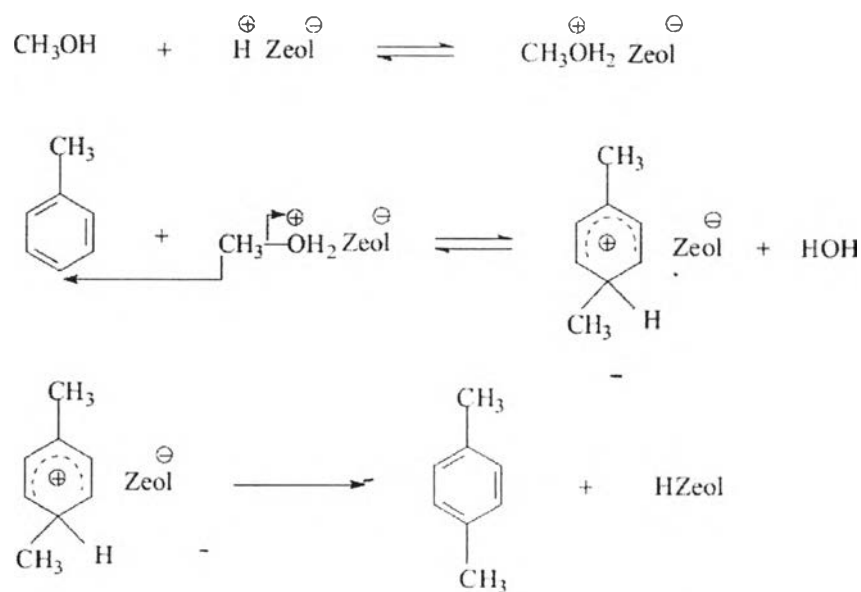


Figure 2.6 Mechanism of toluene alkylation with methanol using H-zeolite (Aboul-Gheit *et al.*, 2011).

In the latest research; Zhou *et al.* (2013) proposed a new catalytic process for *para*-xylene synthesis from the methylation of toluene with CH_3Br . CH_3Br was prepared from the oxidative bromination of natural gas (CH_4), by using $\text{HBr}/\text{H}_2\text{O}$, O_2 as mediator over supported Rh catalyst (Liu *et al.*, 2010). The methylation reaction was investigated using HZSM-5 or modified HZSM-5 catalyst hereinafter.

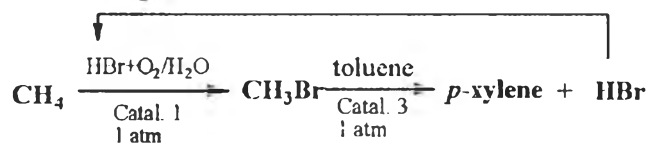


Figure 2.7 Process for preparation of *para*-xylene from the alkylation of toluene with CH_3Br (Zhou *et al.*, 2013).

It was observed in Figure 2.8 that Si-P/HZSM-5 performed an excellent catalyst for selective formation of *para*-xylene in 5ntoluene methylation with 27.7% toluene conversion, 93.1% *para*-xylene selectivity, and up to 21% *para*-xylene yield. The toluene conversion depends on the concentration of total acid sites, whereas the

para-selectivity depends on the relative ratio of strong to weak acid sites: decline in strong acid sites means higher *para*-xylene selectivity.

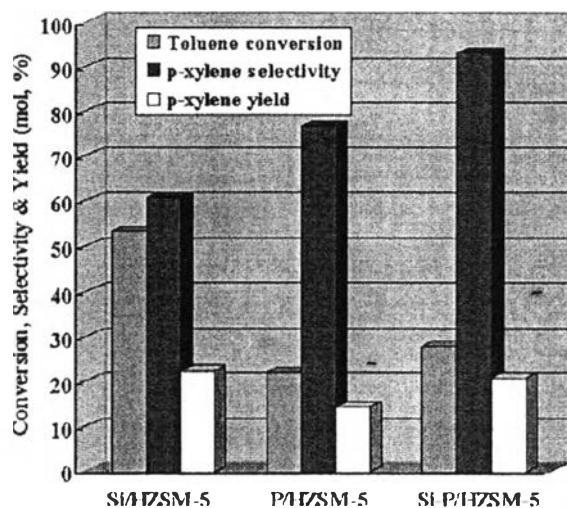


Figure 2.8 Catalytic performance comparison of P/HZSM-5, Si/HZSM-5 and Si-P/HZSM-5 (Zhou *et al.*, 2013).

Xiao-Ping Zhou also proposed a possible mechanism of toluene methylation with CH_3Br over Si-P/HZSM-5 (Fig.2.9). First, CH_3Br chemisorbed on the strong acid sites and yields methyl cations. Then, the electrophilic agents attack toluene to form *para*-xylene on the weak acid sites. Then, the isomerization of *para*-xylene occur on the strong acid sites and a mixture of all xylene (*p*-xylene, *m*-xylene and *o*-xylene) are produced.

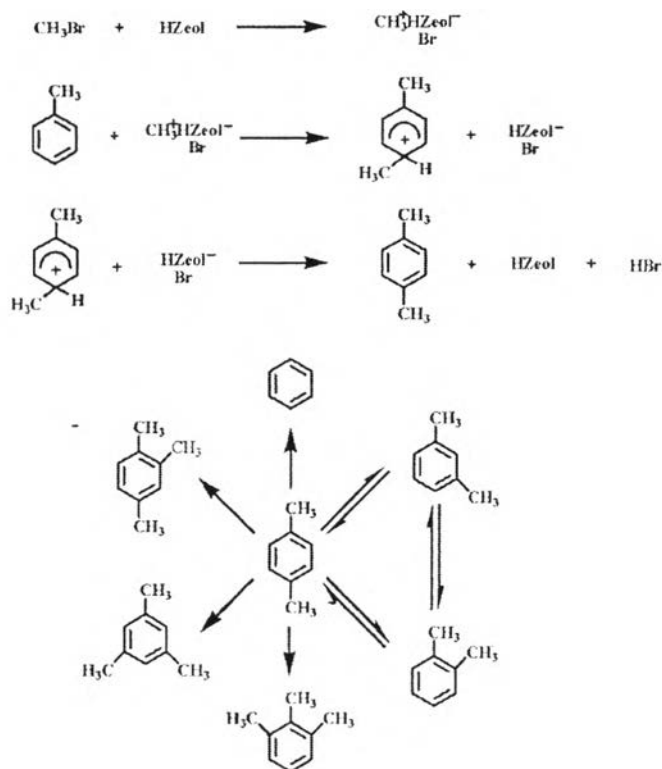


Figure 2.9 Possible reaction mechanism over Si-P/HZSM-5 catalyst (Zhou *et al.*, 2013).

Over a decade ago, many researchers have been successful in developing a chemical process to convert natural gas into various petrochemical feedstocks. Xiao-Ping Zhou was one of those researchers. He has studied the oxidative bromination of methane to synthesize high selectivity of methyl bromide (CH_3Br), the good precursor for acetic acid, dimethyl ether, and higher hydrocarbon production. Especially, in the latest publication, Zhou aimed at *para*-xylene synthesis via the methylation of toluene with methyl bromide. Oxidative bromination of methane involving a heterogeneous catalyst was the recommended route to provide methyl bromide. Accordingly, his researches were extremely beneficial to those interested in this field.

I have collected and applied the useful knowledge from Zhou's researches to my thesis work focused on the high yield and selectivity of methyl bromide. Rh/SiO₂ was chosen since the previous studies done by Zhou have shown the most effective catalyst. Methyl bromide will be further conducted to react with benzene in order to

generate toluene or *para*-xylene, the important raw materials for the manufacturing of textile, automotive, and food packaging industries.