CHAPTER II
LITERATURE REVIEW

2.1 Utilization of Methane

Due to the diminishing proven reserves and the increasing consumption of crude oil, utilization of methane as an alternative chemical feedstock is becoming more urgent. So far, the main use of methane is limited to energy production because of its highly symmetrical tetrahedral geometry and strong C–H bonds (439 kJ/mol), and the selective activation of methane presents a formidable challenge to catalysis (Crabtree *et al.*, 1995).

Industrial technologies for the production of chemicals from methane are dominated by an indirect route via syngas, i.e., methane is firstly transformed to syngas before further converting into other useful products. However, the production of syngas from methane is known to be an energy- and capital-intensive process (Lunsford *et al.*, 2000). On the other hand, direct routes for methane conversion, e.g., selective oxidation of methane to C_1-oxygenates (Conley *et al.*, 2006) and oxidative coupling of methane to ethene (Lunsford *et al.*, 1995) , have shown potential advantages, but these processes remain un-commercialized because of their low methane conversions and poor product selectivities.

The concurrent production of commodity and intermediate chemicals in large gas conversion plants can influence economic incentives by increasing margins and it can lead to earlier profitable implementations of emerging technologies. The synthesis of chemicals will continue even after the gas conversion to fuels window and it will provide the cleanest and most economical routes to many of the chemicals currently produced from oil. 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.

2.2 Halogenation of Methane

Methane is an unreactive molecule and methane activation is not easy. Halogenation of alkane is one of the way to activate methane by extracting hydrogen from methane and producing methyl halides under relatively mild conditions, then the catalytic reaction of methyl halides to achieve the higher hydrocarbon.

Among the radicals commonly used to initiate such reactions, halogens stand out as being the best understood (Lorkovic *et al*, 2006).

$CH_4 + X_2 \rightarrow CH_3X + HX$ (2.1)
$CH_4 + 2X_2 \rightarrow CH_2X_2 + 2HX$ (2.2)
$CH_4 + 3X \rightarrow CHX_3 + 3HX$ (2.3)
$CH_4 + 4X_2 \rightarrow CX_4 + 4HX$ (2.4)

In order to better understand the mechanism, the accepted mechanism of free radical halogenations reactions of alkane, which are shown below:

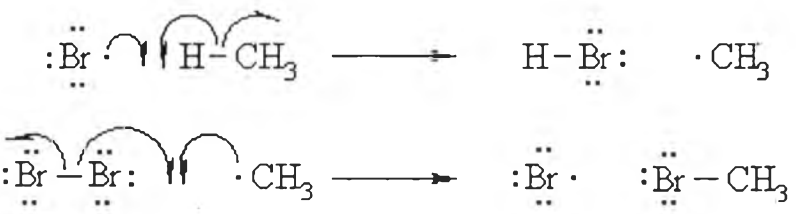
Radical Chain Mechanism for Reaction of Methane with Br_2
(http://www.mhhe.com/physsci/chemistry/carey/student/olc/ch04radical.html)

Step 1 (Initiation)

Heat or UV light causes the weak halogen bond to undergo homolytic cleavage to generate two bromine radicals and starting the chain process.

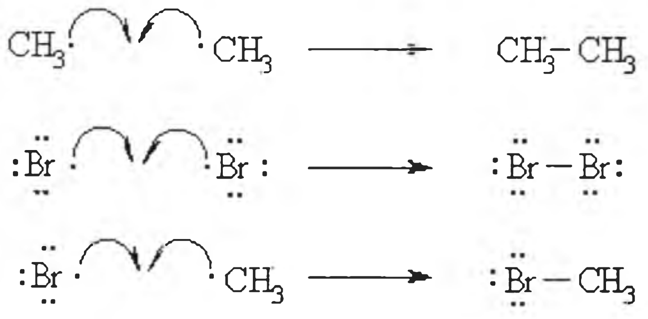
Step2 (Propagation)

A bromine radical abstracts a hydrogen to form HBr and a methyl radical, then the methyl radical abstracts a bromine atom from another molecule of Br_2 to form the methyl bromide product and another bromine radical, which can then itself undergo reaction creating a cycle that can repeat.

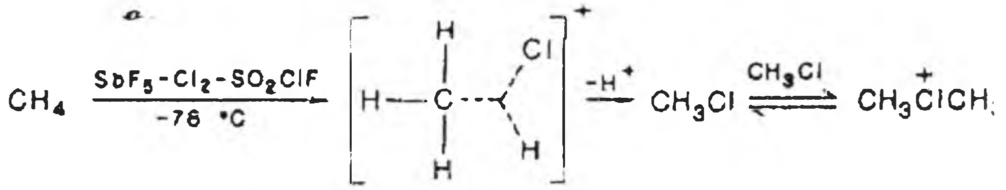


Step 3 (Termination)

Various reactions between the possible pairs of radicals allow for the formation of ethane, Br_2 or the product, methyl bromide. These reactions remove radicals and do not perpetuate the cycle.



In 1972, Olah and coworker (1972) first observed that chlorination of methane in low-nucleophilicity, superacidic solutions at low temperature gives methyl chloride in high selectivity.No methylene chloride or chloroform was observed in the reaction. Under the used stable ion conditions dimethylchloronium ion formation also occurs. This is, however, a reversible process and helps to minimize competing alkylation of methane to ethane (and higher homologues) which is becoming more predominant when methyl fluoride is formed via halogen exchange.



(2.5)

In extending the electrophilic halogenation (chlorination and bromination) of methane to catalytic heterogeneous gas-phase reactions, we have recently found that methane can be chlorinated or brominated over various solid acid or supported platinum group metal catalysts (the latter is the heterogeneous analogue of Shilov's solution chemistry) to methyl halides with high selectivity under relatively mild conditions. In the halogenation of methane hydrogen halides are the equimolar byproducts. Hydrogen halides are similarly byproducts in subsequent condensation or substitution reactions. Their recycling by oxyhalogation is essential to be able to utilize halogen only as catalytic agent in the overall conversion of methane into methyl alcohol, ethylene, or higher hydrocarbon products.

Olah *et al* (1985) also studied on methane halogenation. In their process, methane was first converted to methyl halides by reacting methane with elemental chlorine or bromine as a reactant. HCl or HBr was formed as by-product.And also in Olah group's work, they focused the work on methane chlorination and chloromethane hydrolysis reaction. However, because chlorine atom is much smaller than bromine, it will be easy to form methane dichloride, methane trichloride, and methane tetrachloride as by-products. The selectivity to CH_3Cl was low. Because of the space limit around carbon and the big atomic size of Br, one carbon atom cannot hold too many bromine atoms around it. Hence, high CH_3Br selectivity can be obtained. On the other hand, bromine is a better leaving group than chlorine. The hydrolysis reaction of bromomethane will be much more faster than the hydrolysis reaction of chloromethane.

Other halogenation approaches for methane conversion are by means of the oxidative halogenation of methane using hydrogen halide as the halogen source, such as methane chlorination in Reaction (Lersch, 1991) . The methane chlorination process is not commercialized due to the following reasons: (i) low methane conversion, (ii) high CO and CO2 emissions, (iii) low methyl chloride selectivity, and (iv) poor reactivity in the dehydrochlorolation of methyl chlorides.

$$CH_4 + Cl_2 \longrightarrow CH_3Cl + HCl \qquad (2.6)$$

$$CH_4 + 1/2O_2 + HCl \longrightarrow CH_3Cl + H_2O \qquad (2.7)$$

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 are difficult to controlled and cause an explosion. Chlorine is not favourable owing to corrosive problem and the products of chlorination are low selectivity. For Iodine reactions, the low reactivity of iodine results in low conversion even at high temperature reaction. Therefore, among the halogens, bromine has been found to be the best choice for methane activation. The slightly exothermic reaction between bromine and methane posses the advantage of halogenation can be easily controlled. Moreover, the high equilibrium conversion, high methyl bromide selectivity and easier regeneration from HBr make it more attractive. Typically, at a temperature of 525 °C and a CH_4/Br_2 ratio of 1, the selective conversion of methane to methyl bromide is 70–80% with the byproducts being primarily dibromomethane and small amounts of tribromomethane (Degirmenci *et al.*, 2005).

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

$CH_4 + X_2 \rightarrow CH_3X + HX$

X	ΔH^0 (kJ/mol)	ΔG^0 (kJ/mol)
F	−427.0	~ −430.0
Cl	−99.8	−107.9
Br	−28.3	−32.3
I	53.2	49.1

Hence, Bromine is the most suitable halogen for methane activation because of higher equilibrium conversion and methyl bromide selectivity and easier regeneration from HBr.

2.3 Oxidative Bromination of Methane (OBM)

The oxidative bromination of halogenation as an alternative approach for light alkane conversion, mediated by HBr looks attractive. Compared with the energy-consuming syngas route, the OBM reaction is a strongly exothermic reaction (reaction 2.8).

$$CH_4 + 1/2O_2 + HBr \rightarrow CH_3Br + H_2O \qquad (2.8)$$

$$\Delta H^\circ = -166.3 \text{ kl/mol}$$

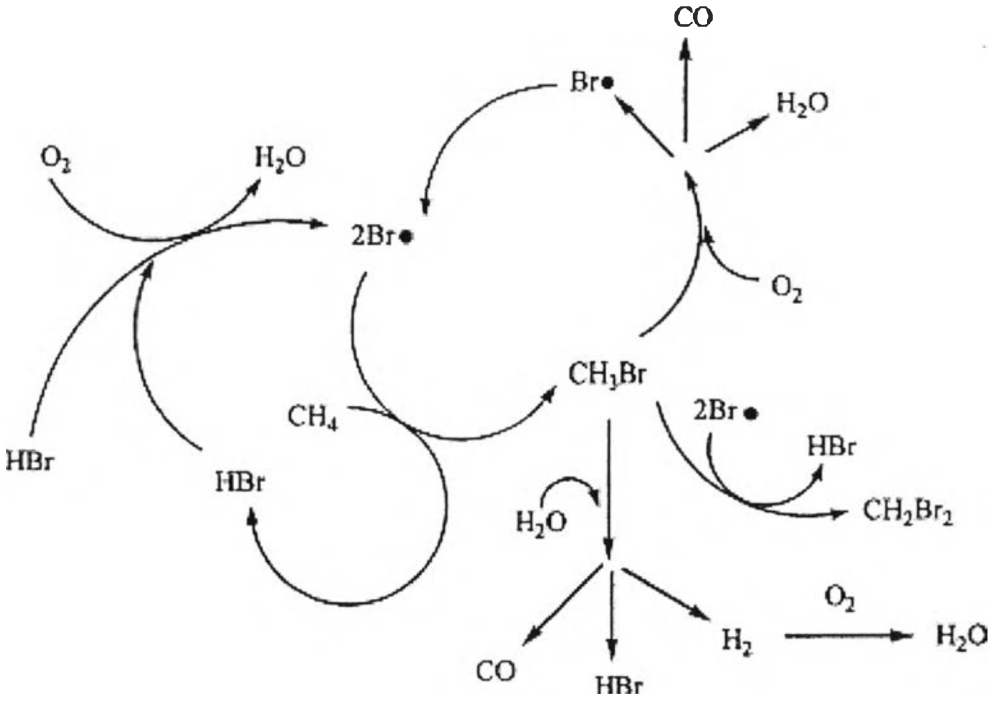


Figure 2.1 Possible pathway for CH3Br and CO formation.

A literature survey on the topic confirms that the OBM reaction could offer routes to convert methane to dimethyl ether (Xu *et al.*, 2005) and acetic acid (Wang *et al.*, 2005). To synthesize all the above value-added compounds, CH_3Br is the platform compound,which could be obtained from the oxidative bromination of methane.

In recent years, many researchers have proposed the concept of oxidative halogenation of methane. They used HBr/H_2O (solution) and O_2 as mediator instead of Br_2 for the methane activation.

Zhou *et al.* (2003) also described an integrated multi-step process for the partial oxidation of alkane to produce dimethyl ether via halogenation. In this route, alkane was react 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(MBr_2) in the second part. Finally, the metal bromide was reacted with oxygen by the oxygenation to quantitatively regenerate metal oxide and bromine. However, the drawback of this process is solid transferring problem and giving the poor selectivity to monosubstitued alkyl bromide.

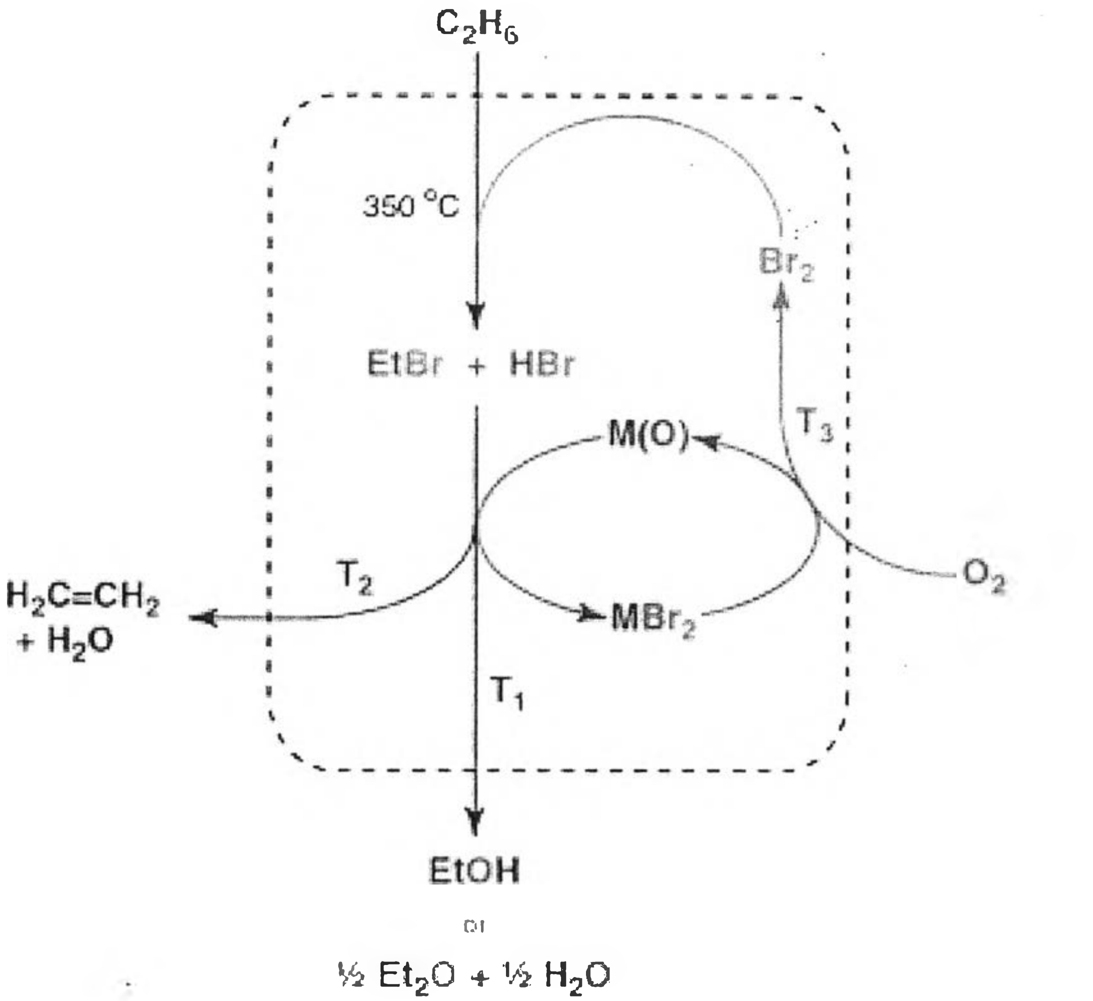


Figure 2.2 Partial oxidation of alkanes *via* bromination followed by the reaction with solid metal oxide mixtures (Zhou *et al.*, 2003).

Lorkovic *et al.* (2004) studied oxidative bromination of methane. In their process, alkane is brominated in the first part of a reactor followed by a reaction with solid metal oxide to generate oxygenated products in the second part. The reaction of 50/50 CuO/ZrO2 catalyst at 8.1% methane conversion produce the products of CH_3OH (37%), CO_2 (35%) and unconverted CH_3Br (29%). Application of another catalyst, 43/7/50 $Co_3O_4/Sm_2O_3/ZrO_2$, results in the products of CH_3OH(20%), $(CH_3)_2O$(20%), CO_2 (5%) and unconverted CH3Br (40%) and CH2Br2 (15%).

The success of halogen-assisted methane activation hinges on the ability to produce CH_3Br with highest selectivity (against CH_2Br_2). In this article we show that the addition of a small amount of I_2 catalyzes the reaction of Br_2 with CH_4 and accelerates the reaction kinetics as equilibrium is approached. Higher methane conversion and methyl bromide selectivity can be achieved at a comparatively short reaction time. Gas-phase I_2 in these experiments satisfies the traditional definition of a catalyst: it participates in the reaction but it is not consumed by it.

Ding *et al.* (2013) showed that a small amount addition of iodine (I_2/Br_2 = 1/9) improves the conversion of methane to CH_3Br and the selectivity against formation of CH_2Br_2 within a short reaction time. Iodine radical could readily abstract Br from CH_2Br_2.After a series of reaction(2.9-2.13), 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 methylbromide is desired.

$$\cdot I + CH_2Br_2 \rightarrow IBr + \cdot CH_2Br \tag{2.9}$$
$$\cdot CH_2Br + HBr \rightarrow CH_3Br + \cdot Br \tag{2.10}$$
$$\cdot Br + CH_4 \rightarrow HBr + \cdot CH_3 \tag{2.11}$$
$$\cdot CH_3 + IBr \rightarrow CH_3Br + \cdot I \tag{2.13}$$

The sum of these reactions is

$$CH_2Br_2 + CH_4 \rightarrow 2CH_3Br \tag{2.14}$$

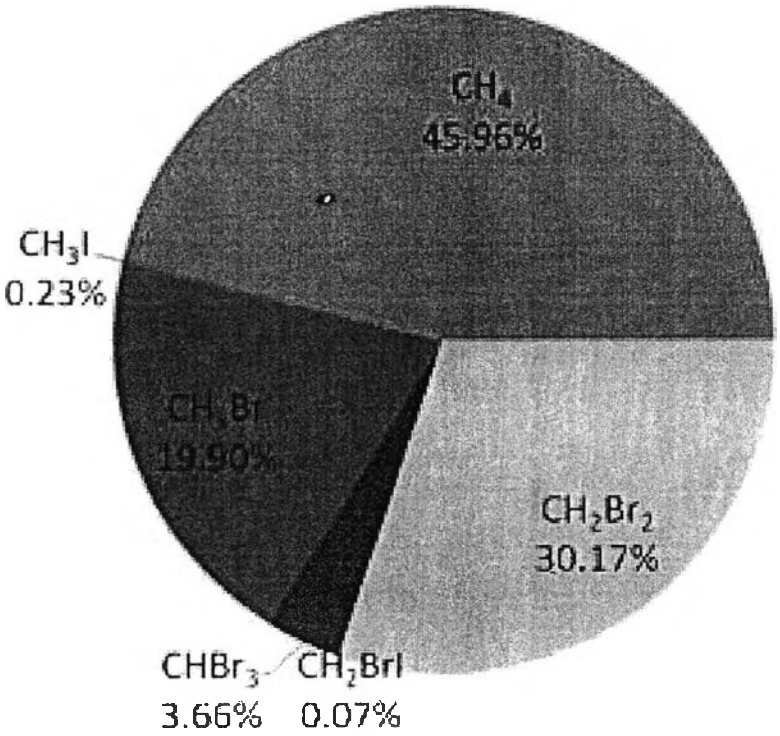


Figure 2.3 Product distribution in the reaction of CH_4 with CH_2Br_2in the presence of I_2 (Ding *et al.*, 2013).

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

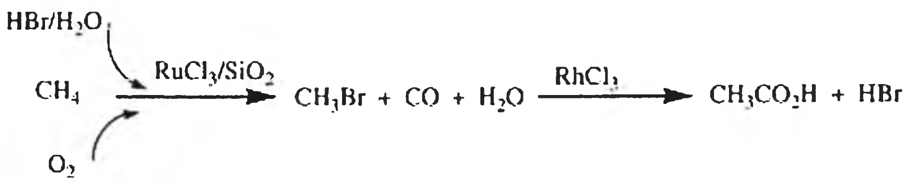
1. The OBM reaction is a highly exothermic reaction (reaction 2.15). Thus, it is an energy-saving process.

$$2CH_4 + 2O_2 + HBr \rightarrow CH_3Br + CO + 3H_2O \qquad (2.15)$$
$$\Delta H^{\circ} = -685.8 \text{ kJ/mol}$$

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

Wang *et al.* (2005) tried to synthesis acetic acid via oxidative bromination of methane with hydrogen bromide (40 wt.% HBr/H_2O) and oxygen to give CH_3Br and CO over a Ru/SiO_2catalyst, prepared by impregnation method. The as-generated CO and CH_3Br reacted with water under the catalysis of $RhCl_3$ to produce acetic acid (reaction 2.16), methanol, and methyl acetate.



$$CH_4 \xrightarrow[O_2]{HBr/H_2O,\ RuCl_3/SiO_2} CH_3Br + CO + H_2O \xrightarrow{RhCl_3} CH_3CO_2H + HBr \qquad (2.16)$$

In the step of oxidative bromination reaction, 30.1% of methane single pass conversion with 72.4% of CH_3Br selectivity and 25.5% of CO selectivity was attained and shown in table 2.2. This study also indicated that in the oxidative bromination of methane, bromomethane and CO were produced simultaneously, and the selectivities to bromomethane and carbon monoxide can be adjusted by changing reaction conditions or/and using different.

Table 2.2 Methane oxidative bromination results over Ru/SiO_2 (Wang *et al.* , 2005)

T (°C)	CH_4 (ml/min)	O_2 (ml/min)	CH_4 conversion (%)	Selectivity (%)		
				CH_3Br	CH_2Br_2	CO
530	5.0	10.0	19.1	90.0	1.7	8.4
560	5.0	15.0	30.1	72.4	2.1	25.5

In the same time, Xu *et al.* (2005) synthesized dimethyl ether from methane via oxidative ~~bromination~~ with 40 wt.% HBr/H_2O and oxygen over 0.10 wt% Ru/SiO2 catalyst. The result are shown in table 2.3, up to 31.8% methane conversion with 78.8% CH_3Br selectivity was reached in a single pass. CH_3Br, CH_2Br_2, and CO were detected as major carbon containing product.

Table 2.3 Methane oxidative bromination results over Ru/SiO2 catalyst (Xu *et al.*, 2005)

T (°C)	CH_4 (ml/min)	O_2 (ml/min)	CH_4 conversion (%)	Selectivity (%)		
				CH_3Br	CH_2Br_2	CO
530	5.0	15.0	27.6	80.0	1.9	18.2
530	5.0	20.0	24.4	89.4	1.7	8.8
560	5.0	20.0	31.8	78.8	2.3	18.9

Hence, Wang *et al.* (2005) and Xu *et al.* (2005) could achieve their goal by using methane as a feedstock to produce the dimethyl ether and acetic acid, respectively. The OBM can be an alternative route to convert methane to higher hydrocarbon. Then, Wang *et al.* (2006) also synthesized acetic acid from methane by reacting methane with oxygen in the presence of HBr and H_2O over total of 19 catalysts and the related catalytic activities are depicted in Table 2.3, Silica was chosen as support material because it does not react with HBr. First, they tested Ru and Rh as active components and found that 0.1%Ru/SiO_2 is better than 0.1% Rh/SiO_2; the former exhibited higher methane conversion and better CH3Br and CO selectivity (entries 1 and 2). Hence, we focused on the improvement of the Ru/SiO_2 catalyst. The addition of Mg, Ca or Ba to Ru/SiO_2 led to a decrease in methane conversion (entries 3–5). One can see that Mg caused a very slight increase, while Ca caused a large decrease in CH_3Br selectivity; as for Ba addition, there was a significant increase in CH_3Br selectivity (from 52.9 to 76.8%). As a matter of fact, if high CH_3Br selectivity is desired, the 5% Ba 0.1% Ru/SiO2 catalyst is the best choice among the catalysts recorded in Table 2.3. The addition of Y, La or Sm would lead to significant increase in methane conversion but large decrease in CH_3Br selectivity (entries 6–8). Hence, if high catalytic activity is desired, the addition of Y, La or Sm would be a good decision, but La should be the best option because it showed the highest CH_3Br selectivity among the three. As directed by the results above, we examined multicomponent catalysts such as BaLaRu/SiO_2, BaSmRu/SiO_2, and BaBiRu/SiO_2 (entries 10, 12–16). Among the three, BaLaRu/SiO_2 showed high performance: 42.9% methane conversion with 55.9% CH_3Br selectivity at 580 8C (entry 10), and methane conversion and CH3Br selectivity of 58.8 and 53.4%, respectively, at 600 8C (entry 12). In order to confirm the role of Ru, we tested a BaLa/SiO_2 catalyst (entry 11). It was found that without Ru, catalytic activity was low (methane conversion 15.7%) and there was high CH_2Br_2 formation (selectivity 14.6%). Hence, it is clear that Ru is an essential element for CH_3Br formation. For the search of even better catalysts, we added Bi, Fe, Co, Ni, Cu, V or Mo to BaLaRu/SiO_2. Comparing the results (entries 17–23), we found that only the Fe and Ni ones (entries 18 and 20) showed positive effects. From entries 8 to 16, one can see that over equal catalysts, methane conversion increased while CH_3Br selectivity decreased when reaction temperature was raised from 580 to 600 °C. It is clear that both CH_3Br and CO were the major products. In most cases, CH_2Br_2 selectivity was low and CO_2 was not formed below 600 °C. For the purpose of synthesizing acetyl bromide, we hope to achieve high methane conversion as well as, good CH3Br and CO selectivities. It seems that adjustment of reaction temperature is a good way of reaching such a goal. From the results in Table 2.3, catalyst 2.5% Ba 2.5% La 0.5% Ni 0.1% Ru/SiO_2 is the best: 62.9% of methane conversion with CH_3Br, CH_2Br_2, CO, and CO_2 selectivity of 54.5%, 5.3%, 34.6%, and 5.6%, respectively, was obtained.

Table 2.4 Catalyst performance for OBM reaction (Wang *et al.*, 2006)

Entry	*T* (°C)	Catalyst	*X* (%)	Selectivity (%)			
				CH_3Br	CH_2Br_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

The catalyst 2.5%Ba 2.5% La 0.5% Ni 0.1% Ru/SiO2 was tested at different 40 (wt.%) HBr/H_2O flow rates, and the results collected at 620 °C are shown in Fig. 2.4. One can see that with the increase of flow rate from 4 to 8 mL/h, methane conversion decreased from 63.2 to 57.0%, the CH_3Br selectivity increased from 32.0 to 72.0%, the selectivity of CO decreased from 46.0 to 18.6%, whereas the CO_2 selectivity decreased from 19.8 to 2.7%. The increase in CH_3Br and CH_2Br_2 selectivity and the decrease in CO and CO_2 selectivity with the reduction of contact time indicated that CH_3Br and CH_2Br_2 are primary products, whereas CO and CO_2 are secondary products.

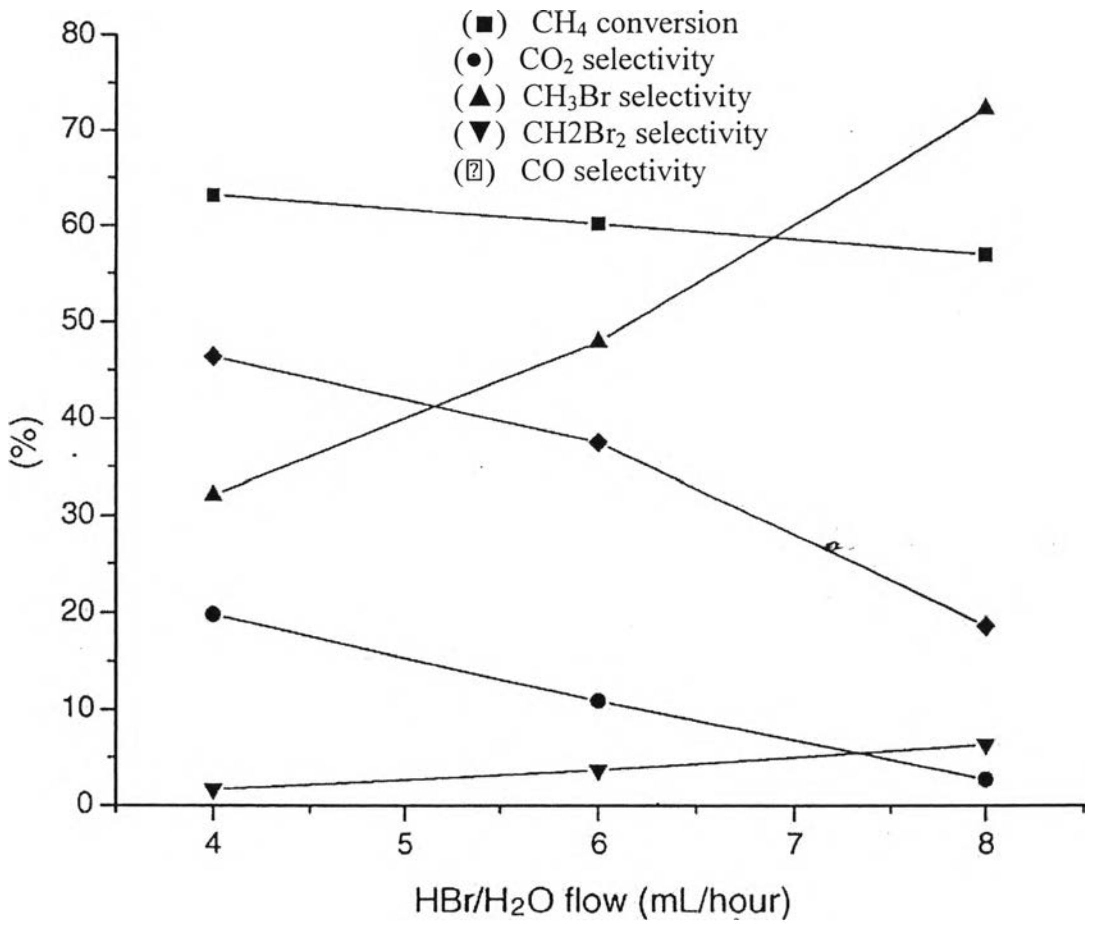


Figure 2.4 The influence of 40 (wt.%)HBr/H2O flow rates on OBM reaction. Condition: 620 °C, methane flow of 5.0 mL/min, and oxygen flow of 5.0 mL/min over 2.5% Ba 2.5% La 0.5% Ni 0.1% Ru/SiO_2.

For the reaction temperature, Keeping the HBr/H_2O flow rate at 8.0 mL/h, we varied the reaction temperature (Fig. 3). With the reaction temperature being raised from 560 to 660 °C, methane conversion over the 2.5% Ba 2.5% La 0.5% Ni 0.1% Ru/SiO_2 catalyst increased from 26.2 to 70.0% and changed little when the temperature was further raised to 680 °C. Within the 560–680 °C range, CO and CO_2 selectivity increased, whereas CH_3Br and CH_2Br_2 selectivity decreased, and at 660 ^{O}C CH_3Br and CO were similar in selectivity. At this temperature, the selectivity of CO_2 and CH_2Br_2 were 5.4 and 4.6%, respectively. The results demonstrated that by adjusting the reaction temperature, high methane conversion could be achieved with low CO_2 and CH_2Br_2 yields, and also, the CH_3Br to CO ratio could be adjusted according to actual requirements.

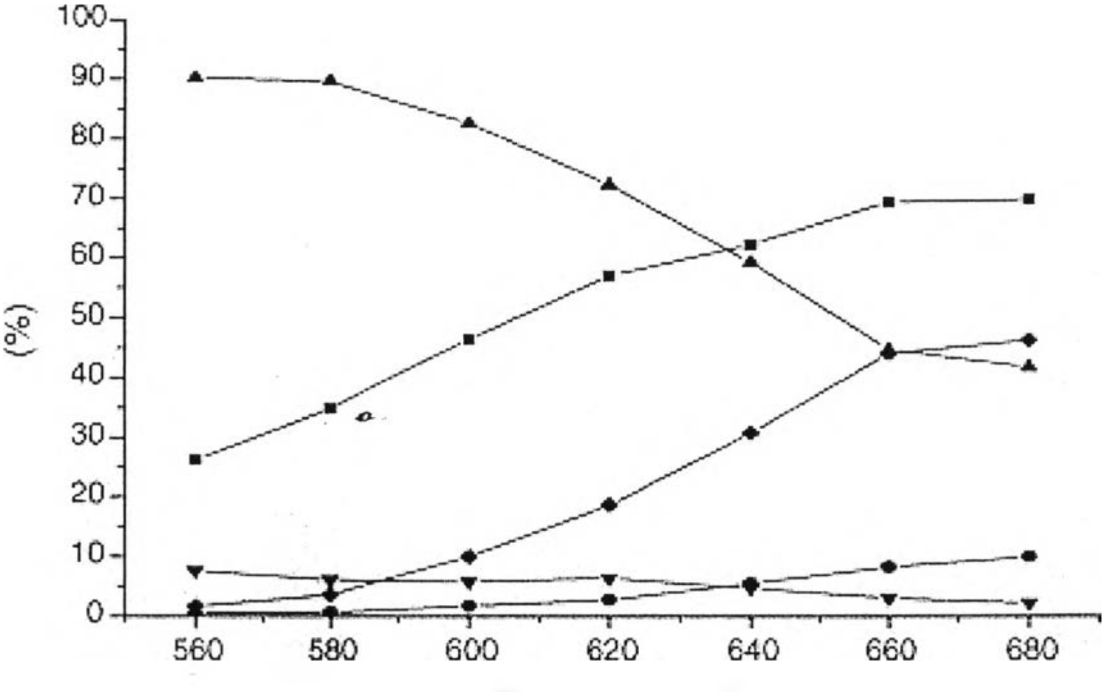
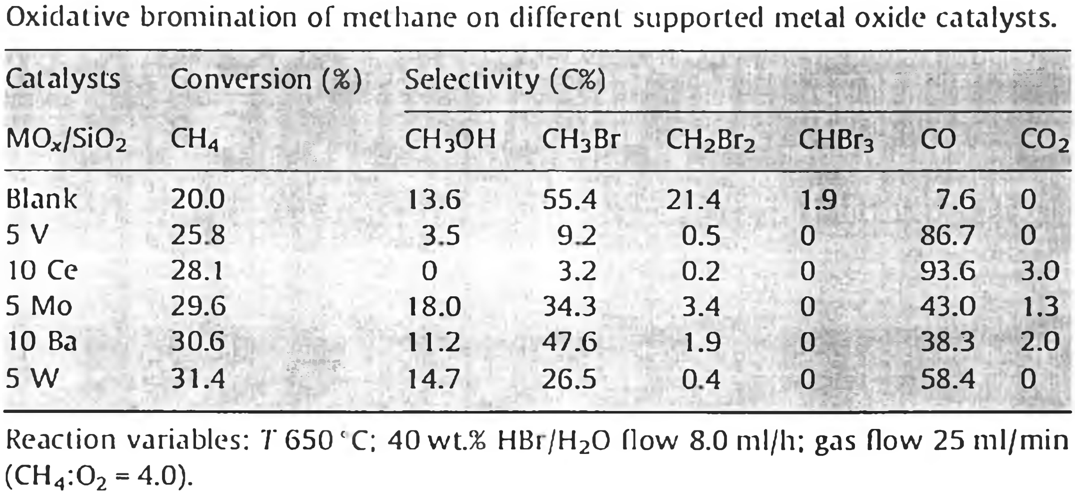


Figure 2.5 Methane oxidative bromination as a function of temperature at CH_4, O_2, and 40.0 (wt.%) HBr/H_2O (liquid) flow rates of 5.0, 5.0, 8.0 mL/h, respectively: (■) CH_4 conversion; (●) CO_2 selectivity; (▲) CH_3Br selectivity; (▼) CH_2Br_2 selectivity; and (♦) CO selectivity.

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 (CH_3Br + CH_3OH): CO = 1 (mol/mol). Consequently, it was chosen for further experiments.

Table 2.5 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%)					
MO_x/SiO_2	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.% HBr/H_2O flow 8.0 ml/h; gas flow 25 ml/min (CH_4:O_2 = 4.0).

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.

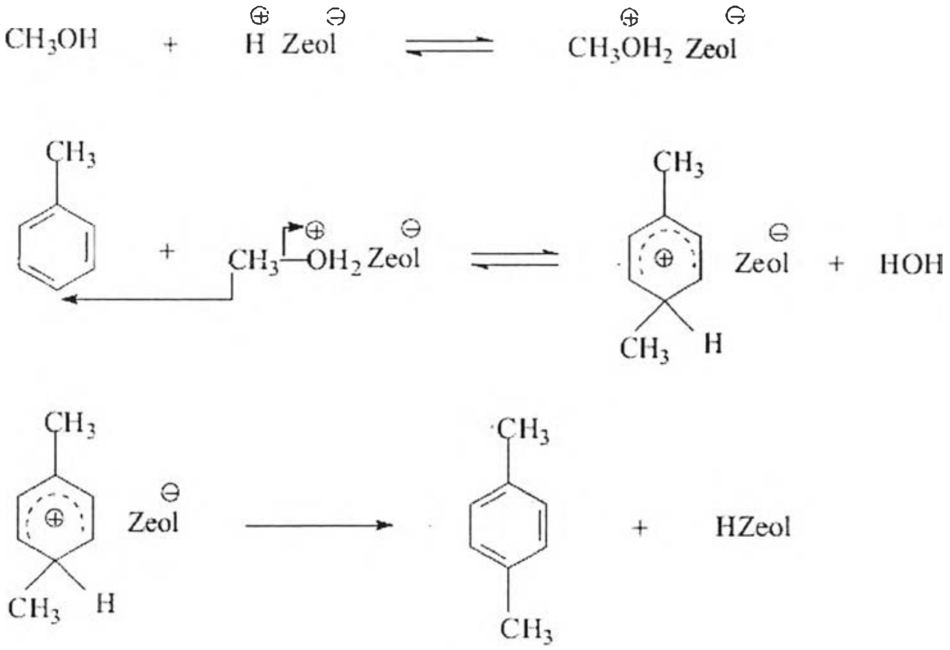


Figure 2.6 Mechanism of toluene alkylation with methanol using H-zeolite (Aboul-Gheit *et al.*, 2011).

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 HBr/H_2O, 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.

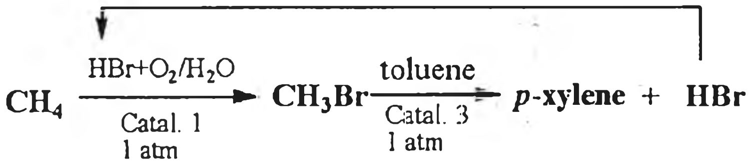


Figure 2.7 Process for preparation of *para*-xylene from the alkylation of toluene with CH_3Br (Zhou *et al.*, 2013).

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.

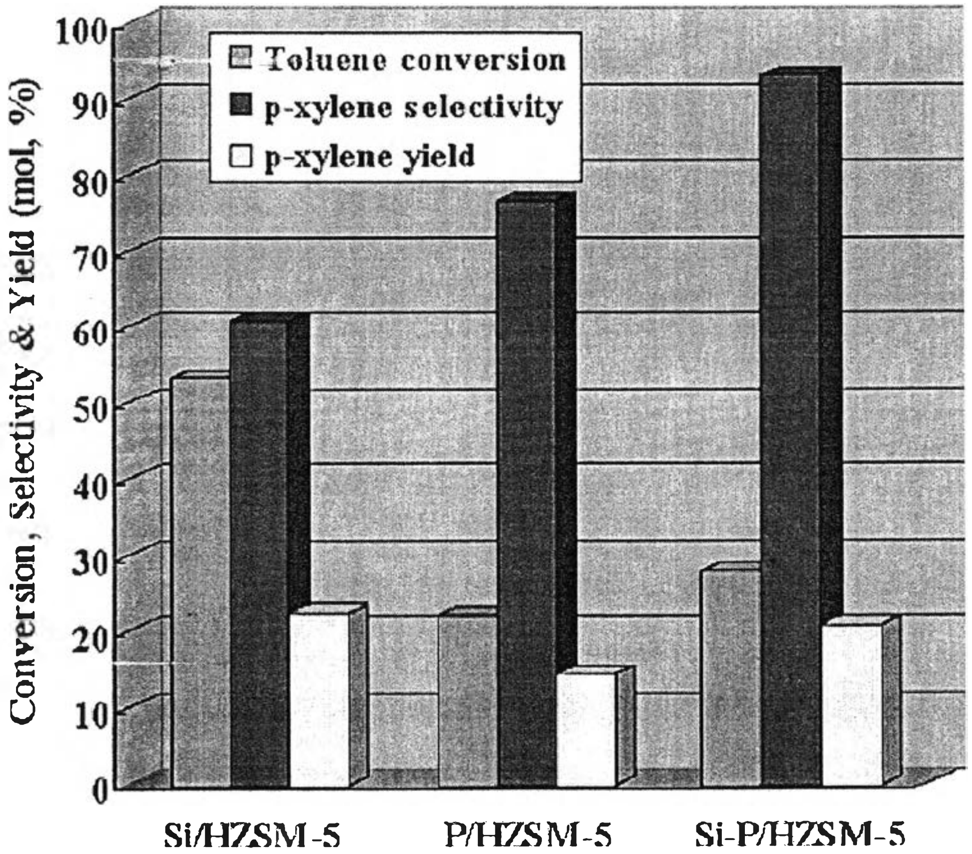


Figure 2.8 Catalytic performance comparison of P/HZSM-5, Si/HZSM-5 and Si-P/HZSM-5 (Zhou *et al.*, 2013).

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 *p*ara-xylene occur on the strong acid sites and a mixture of all xylene (*p*-xylene, *m*-xylene and *o*-xylene) are produced.

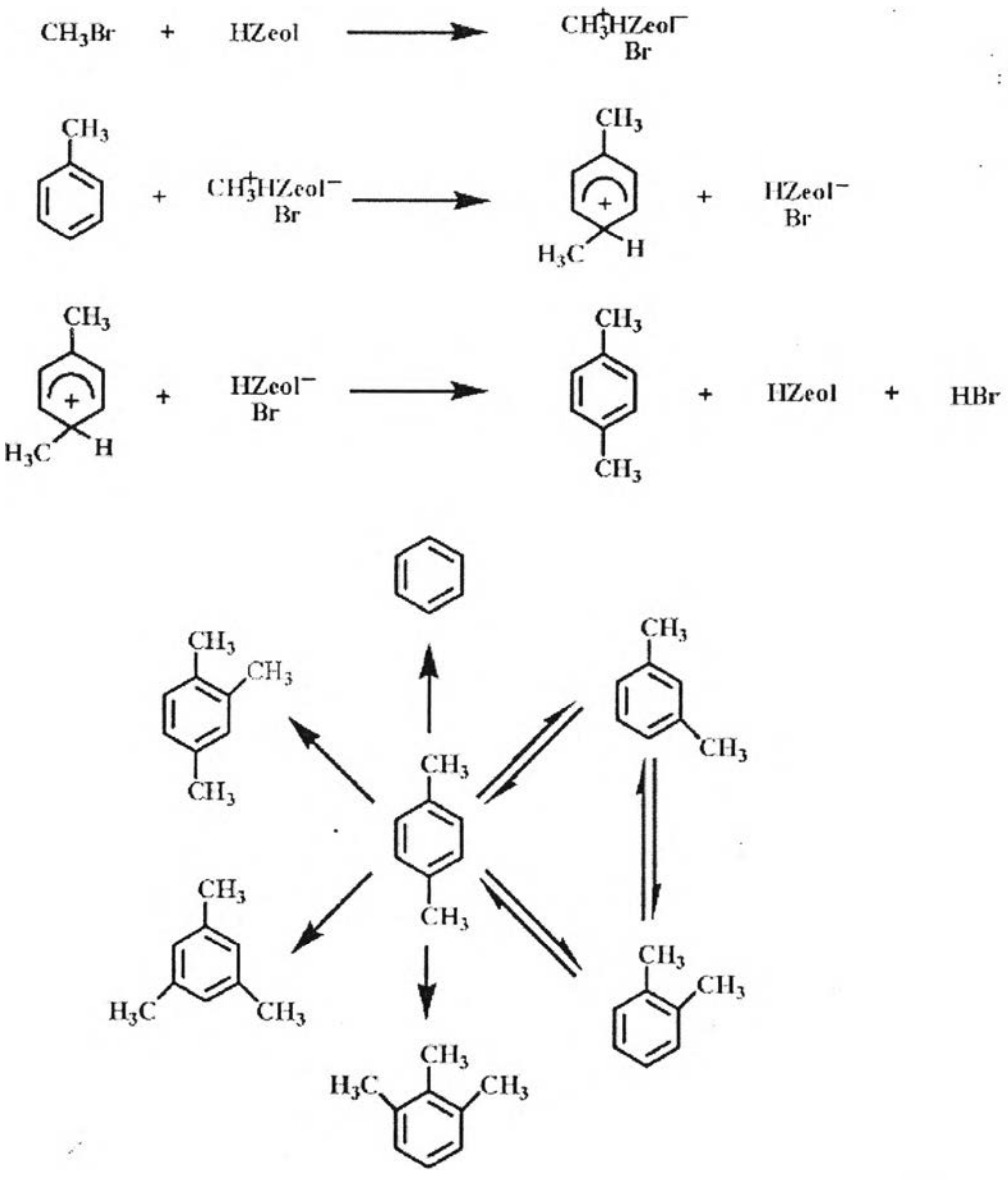


Figure 2.9 Possible reaction mechanism over Si-P/HZSM-5 catalyst (Zhou *et al.*, 2013).

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/SiO_2 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.