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Methane to higher hydrocarbons via halogenation

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Abstract

Activation of methane with a halogen followed by the metathesis of methyl halide is a novel route from methane to higher hydrocarbons or oxygenates. Thermodynamic analysis revealed that bromine is the most suitable halogen for this goal. Analysis of the published data on the reaction kinetics in a CSTR enabled us to judge on the effects of temperature, reactor residence time and the feed concentrations of bromine and methane to the conversion of methane and the selectivity towards mono or dibromomethane. The analysis indicated that high dibromomethane selectivity is attainable (over 90%) accompanied by high methane conversions. The metathesis of dibromomethane can provide an alternative route to the conversion of methane (natural gas) economically with smaller installations than the current syn-gas route.

Keywords: Methane; Dibromomethane; Syn-gas

1. Introduction

In 1956, M King Hubert proposed a life cycle model for petroleum widely known as “Hubbert’s Model” [1]. His prediction that oil production in U.S. would peak around 1969, actually happened in 1970, which was only off by 1 year. The extension of this model predicts that the rate of world oil production starts to decrease after 2010 and petroleum will be exhausted by about 2060 [2]. The decline in the crude oil reserves increases the importance of alternative hydrocarbon sources. Natural gas is the World’s second largest hydrocarbon reserve, which could be a substitute for crude oil. The typical composition of natural gas consists of 70–90% methane and the rest is higher volatile hydrocarbons. However, the end use of natural gas is almost completely methane, above 99% after some purification.

The direct conversion of methane to liquid fuels has been the subject of catalysis community in the past couple of decades. Direct oxidative coupling of methane drew great attention in the previous decade. Although several catalysts were investigated, low yield and low selectivity problems could not be overcome. Any catalyst that could reach yields higher than 25% and selectivity over 80% could not be put into practice for economical reasons [3]. Studies focusing on one-step partial oxidation of methane to methanol or formaldehyde confronted with the problems of low selectivity accompanied by long residence times [4]. The utilization of HZSM-5 and metal supported HZSM-5 zeolites in the direct conversion of methane to liquid hydrocarbons have not achieved high selectivity values [5]. Pulsed discharge plasma processes also applied to methane conversion with the advantage of low gas phase temperature. But, low energy efficiencies revealed a drawback for this approach [6]. Besides, the photo catalytic reactions managed to activate methane, however, they do not result in high yields [7,8].

High stability of the methane molecule is the biggest obstacle against the way from the smallest hydrocarbon to fuels or petrochemicals. As far as the activation of methane is concerned, breaking the carbon–hydrogen bond in the molecule under either oxidative or non-oxidative condition is revealed to be the necessary step. Halogenation of methane towards higher hydrocarbons has been intensively studied in the past by Weissman and Benson [9,10]. The Benson process required the use of chlorine as a catalyst. But, the corrosive nature of the reactants and the products,

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primarily HCl, was the major drawback in front of the commercialization. Olah [11,12] proposed halogen radicals for the activation of methane by extracting hydrogen from methane molecule and producing methyl halides under relatively mild conditions, then the catalytic hydrolysis of methyl halides to achieve the production of higher hydrocarbons or oxygenates. He studied supported Lewis acid halide-oxyhalide catalysts, FeOCl/A1$_2$0$_3$, TaOF$_3$/A1$_2$0$_3$, NbOF$_3$/Al$_2$O$_3$, ZrOF$_2$/A1$_2$0$_3$, SbF$_5$-graphite and TaF$_5$-Nafion-H and Nafion-H as catalysts for mono chlorination and SbOF$_3$/A1$_2$0$_3$ and TaOF$_3$/A1$_2$0$_3$ for mono bromination of methane. In addition, Pd/BaSO$_4$ and Pt/Al$_2$O$_3$ catalyzed chlorination reactions were investigated. They found out that the 98% CH$_3$Cl selectivity could be obtained accompanied by a 7% conversion at 180 °C with SbF$_5$-graphite type catalyst. In bromination reactions, both catalysts gave 99% selectivity of CH$_3$Br. Supported platinum and palladium metal catalyzed halogenation of methane gave similar results. Hydrolysis of methyl halides to methyl alcohol and dimethyl ether, over γ-alumina and γ-alumina-supported metal oxide/hydroxide catalysts such as ZnO/A1(OH$_3$)/γ-Al$_2$0$_3$ with 25% conversion revealed an alternative way to produce methyl alcohol and dimethyl ether instead of the synthesis gas route used in industry presently.

Lorkovic et al. [13] studied partial oxidation of alkanes to alcohols, ethers or olefins via halogenation. In this route, 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/ZrO$_2$ catalyst at 8.1% methane conversion produce the products of CH$_3$OH (37%), CO$_2$ (35%) and unconverted CH$_3$Br (29%). Application of another catalyst, 43/7/50 Co$_3$O$_4$/Sm$_2$O$_3$/ZrO$_2$, results in the products of CH$_3$OH (20%), (CH$_3$)$_2$O (20%), CO$_2$ (5%) and unconverted CH$_3$Br (40%) and CH$_2$Br$_2$ (15%).

In this study, the gas phase homogenous halogenation reactions are compared thermodynamically and a reaction model was thoroughly studied to determine the optimum reactor conditions for bromination reactions.

2. Results and discussion

The enthalpy and free energy of formation of all halogenation reactions are presented in Table 1. The low activation energy for the chain propagating steps and the large overall heat of reaction makes fluorine highly reactive towards methane. Highly exothermic fluorine–methane reactions are not easy to control and even cause explosions. The use of chlorine is not preferable due to its corrosive effects. In addition, the reaction of methane with chlorine results in polychlorinated products easily, which makes it difficult to stop the reaction from further chlorination when one or two substituted methane halides are desired. Methane–iodine reactions are thermodynamically limited to the equilibrium conversions of 10% even at 650 °C. Finally, the low reactivity of iodine leaves bromine as the most suitable halogen for methane activation. Slightly exothermic reaction of bromine and methane has the advantage to control the degree of halogenation.

Table 1
Enthalpy and free energy of formation of methane–halogen reactions [14]

$CH_4 + X_2 \rightarrow CH_3X + HX$

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

Table 2
Enthalpy and free energy of formation of methane–bromine reactions at standard states [14]

	Reaction	ΔH^0 (kJ/mol)	ΔG^0 (kJ/mol)
1	$CH_4 + Br_2 \rightarrow CH_3Br + HBr$	−28.3	−32.3
2	$CH_3Br + Br_2 \rightarrow CH_2Br_2 + HBr$	−70.6	−40.8
3	$CH_2Br_2 + Br_2 \rightarrow CHBr_3 + HBr$	−11.3	−37.91
4	$CHBr_3 + Br_2 \rightarrow CBr_4 + HBr$	−5.2	−2.5

The enthalpy and free energy of formation of bromination reactions at standard states are presented in Table 2. It is seen that the formation of CH$_2$Br$_2$ is most exothermic reaction and are all spontaneous and the formation of CBr$_4$ is less favorable. The Gibbs' free energies of reactions presented in Table 2 were calculated and plotted in Fig. 1. It was observed that formation of CH$_2$Br$_2$ becomes non-spontaneous at 450 °C.

In the literature, bromination reaction rates have been studied by either direct bromination reaction method [15], i.e. the reaction system composed of single reactant CH$_4$ and Br$_2$ or a competitive bromination reaction method [16], i.e. a reference compound is brominated simultaneously with CH$_4$, which results in similar reaction rates. Kistiakowski and Van Artsdalen [15] studied the thermal bromination of methane at 570 K and Amphlett and Whittle [16] resulted in the similar reaction rate results by competitive reaction analysis.

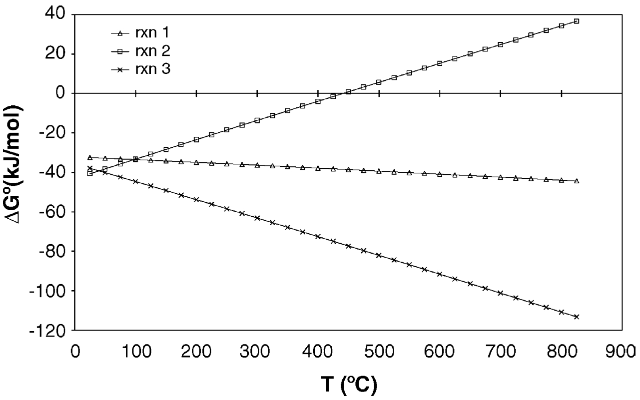

Fig. 1. Free energy of formation of methane–bromine reactions as a function of temperature.

The rate of formation of methyl bromide and rate of consumption of methane was obtained [15] for the accepted mechanism of free radical halogenation reactions of alkanes, which are shown below:

Reaction mechanism:
1. $Br_2 \overset{K_{eq}}{\longleftrightarrow} Br^\bullet + Br^\bullet$ Initiation
2. $CH_4 + Br^\bullet \xrightarrow{k_2} CH_3{}^\bullet + HBr$ Propagation
3. $CH_3{}^\bullet + Br_2 \xrightarrow{k_3} CH_3Br + Br$
4. $CH_3{}^\bullet + HBr \xrightarrow{k_4} CH_4 + Br^\bullet$ Inhibition
5. $CH_3Br + Br^\bullet \xrightarrow{k_5} CH_2Br^\bullet + HBr$
6. $CH_2Br^\bullet + Br_2 \xrightarrow{k_6} CH_2Br_2 + Br^\bullet$ Poly bromination

Rate equations:

$$\frac{d}{dt}[CH_3Br] = \frac{k[CH_4][Br_2]^{1/2}}{1 + \frac{k_4[HBr]}{k_3[Br_2]}} - k'[CH_3Br][Br_2]^{1/2} \qquad (1)$$

$$-\frac{d}{dt}[CH_4] = \frac{k[CH_4][Br_2]^{1/2}}{1 + \frac{k_4[HBr]}{k_3[Br_2]}} \qquad (2)$$

where $k = k_2 K_{eq}^{1/2}$ and $k' = k_5 K_{eq}^{1/2}$, k_2 [15,17] and k_5 [15,18] are:

$$k_2 = 6 \times 10^{13} \exp\left[\frac{-76,060\,(\text{j/mol})}{RT}\right]$$

$$k_5 = 1.67 \times 10^{13} \exp\left[\frac{-66,320\,(\text{j/mol})}{RT}\right]$$

Kistiakowski and Van Artsdalen [15] calculated the equilibrium constant for dissociation of bromine from the thermodynamic data of Gordon and Barnes [19]. The effect of inhibition step of radical reactions is involved in relations in terms of rate constant (k_4). The assumption of $k_4/k_3 = 0.1$ does not bring about significant error [20]. Radical reactions may continue until all the hydrogen atoms in the methane molecule are replaced by a halogen, which is commonly encountered in chlorine reactions. However, low reactivity of bromine towards alkenes prevents the formation of three or four substituted carbon molecules [17].

It is assumed that the bromination reaction takes place in a well mixed reactor (CSTR). The reaction rates mentioned above are used with the reactor model. Methane conversion and the product selectivity were obtained at different temperatures (Fig. 2). In Fig. 2, it is seen that the reactor temperature increases the methane conversion and dibromomethane selectivity.

The methane conversion and product selectivity can also be manipulated by changing the reactor feed conditions. If the amount of bromine is decreased in the feed both the conversion of methane and the selectivity of CH_2Br_2 decrease. Conversely, both conversion and selectivity increases with excess amount of bromine in the feed.

In the reaction model, it was observed that monobromination reaction is difficult to control. However, dibromination reaction can run with high methane conversions and with high dibromomethane selectivity. For instance, it is possible to obtain methane conversions above 90% accompanied by high CH_2Br_2 selectivity above 90% at 330 °C at a residence time of 3 s (Fig. 3; $T = 330$ °C, $\tau = 3$ s, $\theta = 3$).

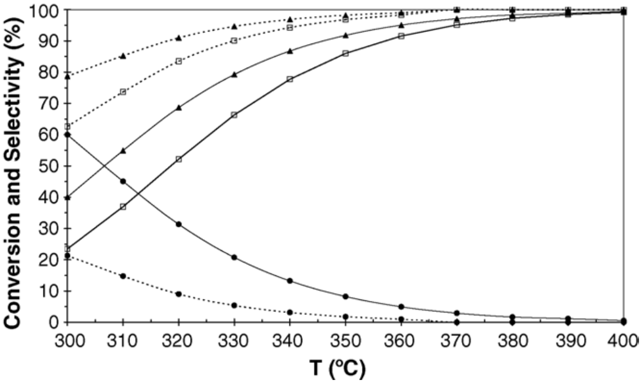

Fig. 2. Conversion of CH_4 (□) and selectivity of CH_3Br (●) and CH_2Br_2 (▲) at different temperatures for two different residence times: 0.5 s: (—) and 3 s: (- - -) for $C_{Br_2}/C_{CH_4} = 3$.

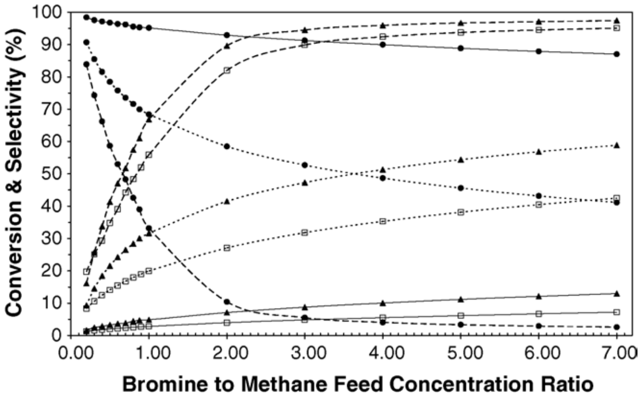

Fig. 3. Conversion of CH_4 (□) and selectivity of CH_3Br (●) and CH_2Br_2 (▲) at 330 °C at three different residence times: 0.01 s: (—), 0.1 s: (· · ·) and 3 s: (- - -).

3. Conclusions

In this study, it was observed that dibromomethane synthesis route can be favorable in terms of methane conversions and dibromomethane selectivity. The analysis briefly presented above indicated that it is possible to activate methane at relatively low temperatures and pressures than that required by the syn-gas requiring routes. The activated halo-methane compounds can further react over appropriate catalysts to produce higher hydrocarbons and/or oxygenates. This feature, in addition to the low separation requirements due to the high selectivity of dibromomethane will significantly decrease the operating costs.

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