A THERMODYNAMIC EQUILIBRIUM ANALYSIS ON OXIDATION OF METHANE TO HIGHER HYDROCARBONS

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ABSTRACT

Thermodynamic chemical equilibrium analysis using total Gibbs energy minimization method was carried out for methane oxidation to higher hydrocarbons. For a large methane conversion and also a high selectivity to higher hydrocarbons, the system temperature and oxygen concentration played a vital role whereas, the system pressure only slightly influenced the two variables. Numerical results showed that the conversion of methane increased with oxygen concentration and reaction temperature, but decreased with pressure. Nevertheless, the presence of oxygen suppressed the formation of higher hydrocarbons that mostly consisted of aromatics, but enhanced the formation of hydrogen. As the system pressure increased, the aromatics, olefins and hydrogen yields diminished, but the paraffin yield improved. Carbon monoxide seemed to be the major oxygen-containing equilibrium product from methane oxidation whilst almost no H_2O, CH_3OH and $HCOH$ were detected although traces amount of carbon dioxide were formed at relatively lower temperature and higher pressure. The total Gibbs energy minimization method is useful to theoretically analyze the feasibility of methane conversion to higher hydrocarbons and syngas at the selected temperature and pressure.

Keywords: Thermodynamic chemical equilibrium, Gibbs energy minimization, Methane conversion, Higher hydrocarbons

1. Introduction

The study on thermodynamic equilibrium composition has been used in investigating the feasibility of many types of reaction e.g. simultaneous partial oxidation and steam reforming of natural gas [Chan and Wang, 2000; Lutz et al., 2003; Lutz et al., 2004; Zhu et al., 2000]. Meanwhile, the minimization of Gibbs free energy using Lagrange's multiplier was applied by Lwin et al. (2000); Douvartzides et al. (2003); Chan and Wang (2000;2004), and Liu et al. (2003) for solving thermodynamic equilibrium analysis of autothermal methanol reformer, solid oxide fuel cells, natural-gas fuel processing for fuel cell applications, and catalytic combustion of methane, respectively.

Following the oil crisis in the 1970s, there seems to be many efforts focusing on synfuel production [Hutching and Scurrel, 1998]. Hence, the development of a simple and commercially advantageous process for converting methane, the major constituent of natural gas, to more valuable and easily transportable chemicals and fuels becomes a great challenge to the science of catalysis. However, methane is the most stable and symmetric organic molecule consisting of four C-H covalence bonds with bond energy of 440 kJ/mol [Banares, 1999]. Thus, effective methods to activate methane are desired.

Thermodynamic constraints on the reactions in which all four C–H bonds of CH_4 are totally destroyed, such as CH_4 reforming into synthesis gas is much easier to overcome than the reactions in which only one or two of the C–H bonds are broken under either oxidative or non-oxidative conditions. For this reason, only indirect conversions of CH_4 via synthesis gas into higher hydrocarbons or chemicals are currently available for commercialization [Xu et al., 2003]. Nonetheless, heat management issues are common to CH_4 reforming. With steam reforming, large quantities of heat must be supplied, whereas, with catalytic partial oxidation, a large amount of heat is released at the front end of the catalyst bed as CH_4 undergoes total oxidation ($CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$) [Lunsford, 2000].

As an alternative approach, transformation of methane to aromatics has also attracted great interests from many researchers [Shepeley and Ione, 1983; Anderson and Tsai, 1985; Han et al., 1994]. They reported that only trace amount of aromatics could be detected if CH_4 reacted with O_2 or NO over HZSM-5 zeolite, and the main products would be CO_x and H_2O. In an attempt to avoid the use of

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oxygen, several researches tried to transform methane into higher hydrocarbon in the absence of oxygen. Mo supported on HZSM-5 zeolite has been reported as the most active catalyst for non-oxidative aromatization of methane [Xu et al., 2003; Xu and Lin, 1999; Li et al., 1999] but its activity and stability are still inadequate for the aromatization process to be commercialized. Previous work have also shown that the conversion of methane to liquid fuels is promising by using metal modified ZSM-5 (or with MFI structure) zeolite as catalysts [Amin and Anggoro, 2002 ; 2003].

The main objective of this paper is to perform a thermodynamic chemical equilibrium analysis of possible equilibrium products formed in a methane reaction under oxidative and non-oxidative conditions. In this analysis, the effect of various conditions, i.e. temperature, CH_4/O_2 feed ratio and system pressure, on chemical equilibrium are discussed. The thermodynamics analysis is important to study the feasibility of reactions in a reacting system, and also to determine the reaction conditions and the range of possible products that can be formed.

2. Methodology

The total Gibbs energy of a single-phase system with specified temperature T and pressure P, $(G^t)_{T,P}$ is a function of the composition of all gases in the system and can be represented as,

$$(G^t)_{T,P} = g(n_1, n_2, n_3, ..., n_N) \tag{1}$$

At equilibrium condition the total Gibbs energy of the system has its minimum value. The set of n_i's which minimizes $(G^t)_{T,P}$ is found using the standard procedure of the calculation for gas-phase reactions and is subject to the constraints of the material balances. The procedure, based on the method of Lagrange's undetermined multipliers, is described in detail by Smith et al. [Smith et al., 1996].

In this paper, the gas equilibrium compositions of a system which contains CH_4, C_2H_6, C_2H_4, C_3H_8, C_3H_6, C_4H_{10}, C_4H_8, C_5H_{12}, C_5H_{10}, C_6H_6, C_7H_8, C_8H_{10}, CO, CO_2, H_2, H_2O, CH_3OH and HCOH species at 900-1100K, various oxygen/methane mole ratio and 1-10 bar are calculated. These products are chosen as they are likely to be produced from the reaction between CH_4 and O_2. The oxygen/methane mole ratio is set to be 0.04, 0.05, 0.1 and 0.2. The condition without oxygen is also simulated. In the preliminary calculations, the compositions of O_2 and C_{6+} aliphatic hydrocarbons are always less than 1E-10 mol% and for that reason the subsequent calculations only involved the C_1-C_5 aliphatic hydrocarbons.

3. Results and Discussion

3.1 Methane Conversion

The methane conversion, based on carbon number basis, and the equilibrium compositions, shown in Tables 1 and 2 increase with system temperature at all conditions. The results are in agreement with the equilibrium conversion of methane calculated by Zhang et al. (1998) based on reaction (5):

$$6CH_4 \rightarrow C_6H_6 + 9H_2 \tag{5}$$

The equilibrium methane conversions at temperatures 973K, 1023K, 1073K, 1123K and 1173K are reported as 11.3%, 16%, 21%, 27% and 33% respectively but lower than the result calculated in this work for non-oxidative conditions since they considered only benzene as the hydrocarbon product.

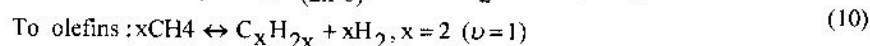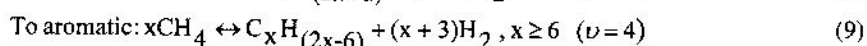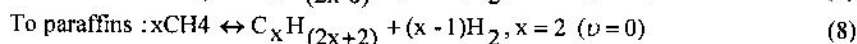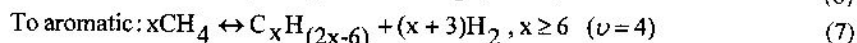Table 1: The effect of oxygen/methane mole ratio on methane equilibrium conversions at 900K – 1100K and 1 bar.

Temperature (K)	CH4 Conversion (%)				
	0.00*	0.04*	0.05*	0.10*	0.20*
900	6.64	8.21	10.02	19.08	33.74
1000	14.07	13.65	13.82	20.22	39.41
1100	25.07	25.29	25.28	26.29	40.24

* : O2/CH4 ratio

Table 2: The effect of system pressure on methane equilibrium conversions at 900K - 1100K and oxygen/methane mole ratio = 0.1.

| Temperature (K)	CH4 Conversion (%)				
	1 bar	2 bar	3 bar	5 bar	10 bar
900	19.08	17.61	16.35	14.54	12.41
1000	20.22	19.86	19.72	19.04	17.40
1100	26.29	22.07	20.83	20.23	19.89

The effect of oxygen/methane ratio on methane conversion is tabulated in Table 1. The conversion of methane is enhanced by increasing the oxygen/methane ratio as methane can be easily oxidized to carbon oxides in the presence of oxygen. Nevertheless, the methane conversion decreases as the system pressure increased. By examining the calculated equilibrium compositions, it is apparent that the conversions of methane involve the following reactions:

$$\text{Partial Oxidation} : CH_4 + \tfrac{1}{2}O_2 \rightarrow CO + 2H_2 \quad (\upsilon = 1\tfrac{1}{2}) \tag{6}$$

$$\text{To aromatic} : xCH_4 \leftrightarrow C_xH_{(2x-6)} + (x+3)H_2, x \geq 6 \quad (\upsilon = 4) \tag{7}$$

$$\text{To paraffins} : xCH4 \leftrightarrow C_xH_{(2x+2)} + (x-1)H_2, x = 2 \quad (\upsilon = 0) \tag{8}$$

$$\text{To aromatic} : xCH_4 \leftrightarrow C_xH_{(2x-6)} + (x+3)H_2, x \geq 6 \quad (\upsilon = 4) \tag{9}$$

$$\text{To olefins} : xCH4 \leftrightarrow C_xH_{2x} + xH_2, x = 2 \quad (\upsilon = 1) \tag{10}$$
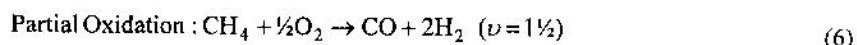
Except for equations (7) and (9), Equations (6), (8) and (10) have positive υ value. The increase in the system pressure shifts the reaction with the positive υ to the left [Smith et al., 1996], resulting in the decrease of methane equilibrium conversion in consistent with the results reported in the literature [Liu et al., 2003; Istadi and Amin, 2005].

3.2 Aromatics, Paraffin and Olefin Yields

Table 3 shows the distribution of products with concentrations > 0.01mol% as a function of system temperature and oxygen/methane mole ratio. It is interesting to note that no aromatics are formed when the levels of CO_2 and H_2O yields became noticeable. The observation is consistent with the literature report on methane oxidation over Mo/HZSM-5 [Tan et al., 2002; Yuan et al., 1999] and La_2O_3 + Mo_3/HZSM-5 [Liu et al., 1998] catalysts. The existence of CO_2 and H_2O not only suppressed the active carbon surface species on the catalysts, but the aromatics are converted to CO and H_2 via steam and carbon dioxide reforming, as shown in the following equations:

$$C_xH_{(2x-6)} + xH_2O \rightarrow xCO + (2x-3)H_2 \tag{11}$$

$$C_xH_{(2x-6)} + xCO_2 \rightarrow 2xCO + (x-3)H_2 \tag{12}$$
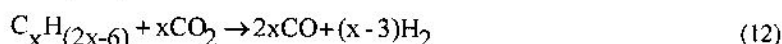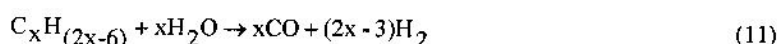
Table 3: Distribution of product concentration > 0.01 mole% as a function of system temperature and oxygen/methane mole ratio.

Temperature	O_2/CH_4	Concentration > 0.01 mole%						
900K	0	-	-	H_2	-	C_2H_4	C_2H_6	Aromatics
	0.04	CO	CO_2	H_2	H_2O	-	C_2H_6	-
	0.05	CO	CO_2	H_2	H_2O	-	C_2H_6	-
	0.1	CO	CO_2	H_2	H_2O	-	-	-
	0.2	CO	CO_2	H_2	H_2O	-	-	-
1000K	0	-	-	H_2	-	C_2H_4	C_2H_6	Aromatics
	0.04	CO	-	H_2	-	C_2H_4	C_2H_6	Aromatics
	0.05	CO	-	H_2	-	C_2H_4	C_2H_6	Aromatics
	0.1	CO	CO_2	H_2	H_2O	C_2H_4	C_2H_6	-
	0.2	CO	CO_2	H_2	H_2O	-	-	-
1100K	0	-	-	H_2	-	C_2H_4	C_2H_6	Aromatics
	0.04	CO	-	H_2	-	C_2H_4	C_2H_6	Aromatics
	0.05	CO	-	H_2	-	C_2H_4	C_2H_6	Aromatics
	0.1	CO	-	H_2	-	C_2H_4	C_2H_6	Aromatics
	0.2	CO	-	H_2	H_2O	C_2H_4	-	-

The results in Table 3 clearly reveal that reactions (11) and (12) are thermodynamically favorable at the given conditions and are only retarded when CO_2 and H_2O concentrations are low.

The effects of system pressure on the equilibrium aromatics yield in Table 4 shows that the aromatic yield decreases with increasing system pressure. According to Equation (8) the increment of the system pressure shifts the reaction to the left, and suppresses the formation of aromatics due to the positive υ in the stoichiometric reaction.

Table 4: The effect of system pressure on aromatic equilibrium yield at equilibrium at 900K - 1100K and oxygen/methane mole ratio = 0.1.

Temperature (K)	Aromatics yield				
	1 bar	2 bar	3 bar	5 bar	10 bar
900	≈0	≈0	≈0	≈0	≈0
1000	0.0643	0.00456	0.00104	≈0	≈0
1100	5.61	1.55	0.478	0.0776	0.00604

The equilibrium yields of paraffin and olefin are also affected by the system pressure. The paraffin yield increases with pressure, but the olefin yields decreases as the system pressure increases as shown in Table 5. The results may be attributed to the positive υ as shown in Eqn (10). Similar trends have also been observed in the literature [22].

Table 5: The effect of system pressure on (a) paraffin and (b) olefin equilibrium yields at equilibrium at 900K - 1100K and oxygen/methane mole ratio = 0.1.

(a)

Temperature (K)	Paraffin yield				
	1 bar	2 bar	3 bar	5 bar	10 bar
900	0.0245	0.0283	0.0322	0.0392	0.0531
1000	0.0615	0.0627	0.064	0.0677	0.0792
1100	0.100	0.129	0.139	0.143	0.148

(b)

Temperature (K)	Olefin yield				
	1 bar	2 bar	3 bar	5 bar	10 bar
900	0.00516	0.00325	0.00267	0.0022	0.00187
1000	0.0785	0.0405	0.0279	0.0183	0.0118
1100	0.513	0.381	0.284	0.175	0.00929

Table 6 show the dependency of hydrogen equilibrium yield, based on hydrogen number basis, on the system pressure. The yield decreases with the system pressure. Meanwhile, the reacted oxygen is converted to mostly CO with trace amounts of CO_2. Yields of CH_3OH and HCOH can be neglected for the fact that the yields are below 3.0×10^{-5} % at the given conditions.

Table 6: The effect of system pressure on hydrogen equilibrium yields at equilibrium at 900K - 1100K and oxygen/methane mole ratio = 0.1.

Temperature (K)	Hydrogen yield				
	1 bar	2 bar	3 bar	5 bar	10 bar
900	18.78	16.88	15.31	13.10	10.22
1000	20.02	19.75	19.48	18.69	16.64
1100	24.47	21.39	20.50	20.08	19.57

Figures 1 and 2 illustrate the effect of oxygen/methane ratio at T, P constant and the effect of system pressure on carbon oxide (CO_x) yield at fixed T and oxygen/methane ratio respectively. Overall, the total CO_x yield increase with increasing oxygen content in the system as oxygen conversion is 100% in all cases. As shown in Figure 2, at methane to oxygen ratio equal to 0.2, some of the oxygen is converted to CO_2 at 900K causing a slight reduction in the total CO_x equilibrium yield. The CO_x yield does not seem to be greatly affected by the reaction temperature, except for the conditions where the oxygen concentration and the pressure are high. When the system pressure increases, lowering the system temperature would increase the CO_2 yield, but the CO and overall CO_x yields would be reduced.
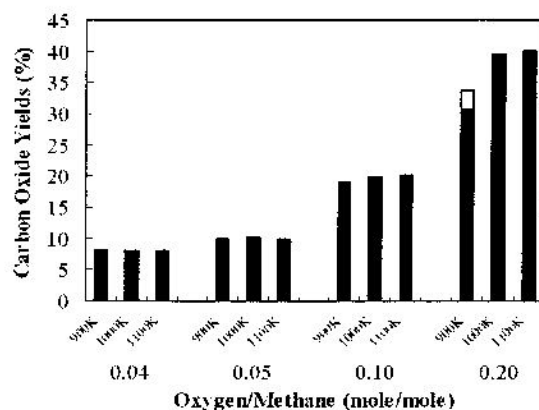
Fig. 1: The effect of oxygen/methane mole ratio at initial unreacted state and system temperature on carbon monoxide. (■) and carbon dioxide (□) yields.
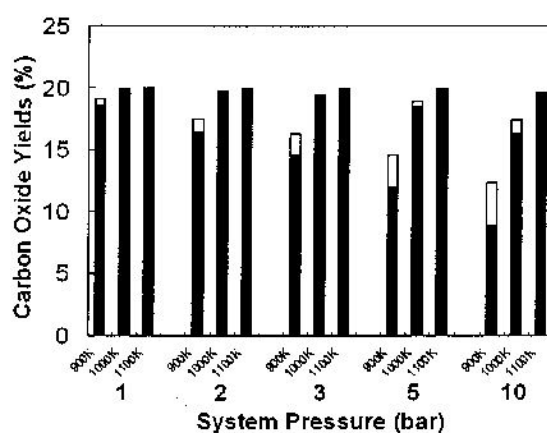

Fig. 2: The effect of system pressure and system temperature on carbon monoxide (■) and carbon dioxide (□) yields. Oygen/methane mole ratio =0.2

4.0 Conclusions

The effects of system pressure, temperature and oxygen/methane mole ratio on the methane conversion and product distribution at equilibrium have been studied. The formations of CH_3OH, HCOH, CO_2, H_2O, paraffins and olefins are unfavorable at the selected temperature, pressure and oxygen/methane mole ratio. Meanwhile, CO, H_2 and aromatics are the major equilibrium products. In order to achieve high conversion and high aromatics yield, the system temperature should be kept as high as possible whilst the system pressure and oxygen/methane mole ratio should be low. The conversion of methane to aromatics and syngas is theoretically feasible at the selected temperature, pressure, and oxygen/methane ratio.

Notation
Greek symbols

λ_k Lagrange multiplier of element k.

υ the total stoichiometric number.

Φ_i *fugacity coefficient of species i in solution. The* Φ_i *are all unity if the assumption of ideal gases is justified in all cases.*

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