Kinetic Investigation of Oxidative Methane Pyrolysis at High CH$_4$/O$_2$ Ratio in a Quartz Flow Microreactor below 1073 K

Young-Gil Cho, Kyong-Hoon Choi,[†] Yong-Rok Kim,[†] and Sung-Han Lee[*]

Department of Chemistry, Yonsei University, Wonju 220-710, Korea. [*]E-mail: shl2238@yonsei.ac.kr
[†]Department of Chemistry, Yonsei University, Seoul 120-749, Korea

Oxidative coupling of methane in the presence of metal oxide catalyst generally takes place in the temperature range of 873-1173 K and methyl radical is generated on the catalyst surface and coupled into C$_2$ compounds in the gas phase.[1,2] In CH$_4$/O$_2$ reaction, the reaction pathway is generally determined by the CH$_4$/O$_2$ ratio.[3] A decrease in the CH$_4$/O$_2$ ratio drives the production of C$_n$(n≥2) hydrocarbons, but it favors transfer of the reaction from the reaction on catalyst surface to the gas phase.[4] Nersesyan *et al.*[5] found the presence of methyl- and hydro-peroxy radicals in the gas phase for methane oxidation over SiO$_2$ in the 843-903 K temperature range using the kinetic radical freezing method, which enables us to consider that methyl radical can be formed on the surface of quartz reactor itself even at the given low temperature although the nature of active site on silica surface is not fully understood. For these reasons, to understand the reaction mechanism and optimize the performances for oxidative coupling of methane using a quartz flow reactor, kinetic investigation of oxidative methane pyrolysis in the absence of catalyst is required. Oxidative methane pyrolysis is known to be composed of many elementary reactions[6,7] and influenced by temperature, space velocity, mixture composition, and additives.[8] Until now, various flow reactors have been designed and examined for the reaction above 1473 K.[9-12] However, few results have been reported for the reaction in the temperature range of 873-1173 K where oxidative coupling of methane occurs. In this work, oxidative methane pyrolysis was carried out in an empty quartz reactor at various flow rates of CH$_4$/O$_2$ reaction mixture in the temperature range of 873-1073 K and a catalytic effect of quartz reactor itself on the reaction was investigated.

Experimental

Oxidative methane pyrolysis was performed in a quartz flow microreactor which was made of quartz tubing with a smaller inner diameter of 3.81 mm in order to minimize a thermal gradient in the reactor. The quartz tube was coiled itself round with five turns so as to give a larger capacity of the reactor as far as possible. The reaction volume located in the constant temperature zone of a muffle furnace was 4.23 cm^3. Inlet and outlet tubes in the reactor were filled with silica wool in order to reduce the dead volume. The reaction

mixture with CH$_4$/O$_2$ ratio of 5 without diluent gas was used for oxidative methane pyrolysis. The purity of CH$_4$ and O$_2$ gases was greater than 99.99% and the gases were dehydrated and purified with suitable filters. The reactor effluent gases were analyzed using on-line gas chromatography system and H$_2$ product was separately analyzed with a TCD in another gas chromatography. The residence time of reaction mixture was calculated by the gas phase volume (4.23 cm^3)/the total flow rate (cm^3/s). The details of kinetic experiments were described in the previous papers.[13,14] In this work, there was no coke deposition in the reactor. H$_2$, CO, C$_2$ hydrocarbons, and H$_2$O were produced as major products. CO$_2$, C$_2$H$_2$, and C$_3$ hydrocarbons were produced as minor products and CH$_2$O as a trace.

Results and Discussion

Figure 1 presents kinetic curves for accumulation of reaction products and methane for the oxidative methane pyrolysis in the quartz flow reactor, where the methane conversion and the fraction of each product are significantly varied with the residence time. The methane conversion was increased with increasing the residence time and the temperature, but the values obtained at the reaction conditions did not exceed 25%. Figure 2 presents the H$_2$ yields as a function of temperature at various residence times. At each residence time, the H$_2$ yield remained nearly constant up to 923 K, rapidly increased with temperature above 923 K, and its maximum yield was 16.5% at 21.2 s residence time and 1073 K. Figure 3 exhibits variations of the C$_2$ yield and the C$_2$H$_4$/C$_2$H$_6$ ratio with temperature at various residence times, where both the C$_2$ yield and the C$_2$H$_4$/C$_2$H$_6$ ratio increase with increasing the residence time and the temperature. The maximum yield of C$_2$ hydrocarbons was 12.4% at 998 K and 21.2 s residence time. Figure 4 reveals relationships among the H$_2$ fraction, the C$_2$ fraction, the C$_2$H$_4$/C$_2$H$_6$ ratio, and the CH$_4$ conversion for the oxidative methane pyrolysis. With an increase in the CH$_4$ conversion, the C$_2$ selectivity decreased while the C$_2$H$_4$/C$_2$H$_6$ ratio increased. Disappearance rate of CH$_4$ and appearance rate of each product were plotted as a function of reciprocal temperature according to Arrhenius-type equation, rate $\propto \exp(-E_a/RT)$, which are presented in Figure 5. Apparent activation energies for the CH$_4$ consumption and the formation of each product were
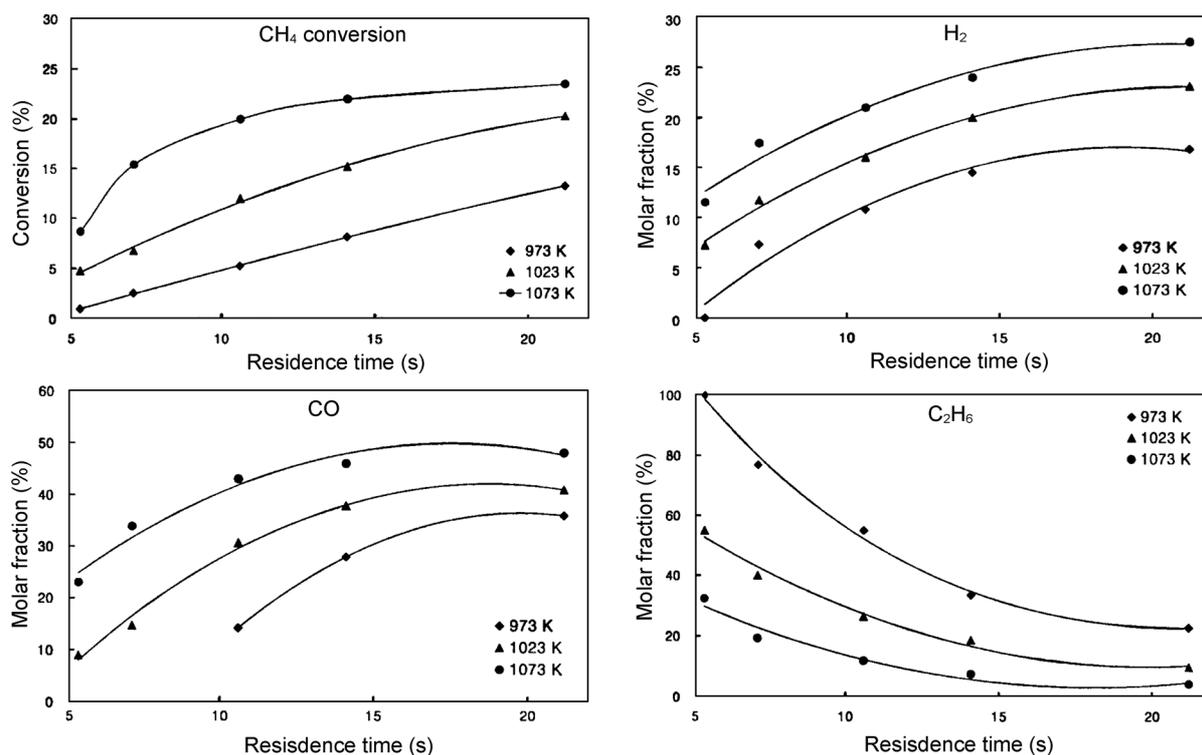
Figure 1. Methane conversion and fractions of products as a function of residence time for the oxidative methane pyrolysis at 973, 1023, and 1073 K.
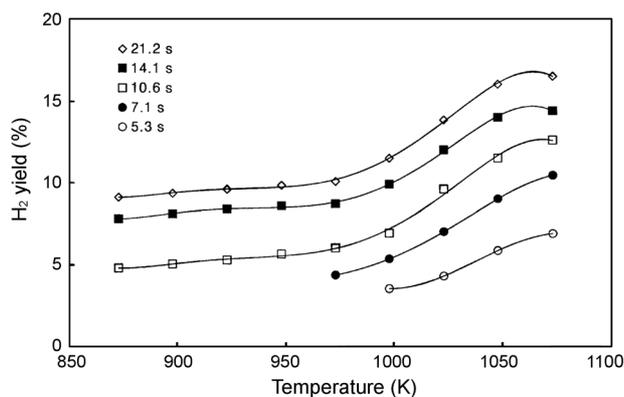

Figure 2. Variation of H_2 yield with temperature at various residence times for the oxidative methane pyrolysis.

estimated in the temperature range showing a linearity in the curve and the values are listed in Table 1.

CO was produced to a larger extent as compared to other products and its selectivity increased with increasing the temperature and the residence time, as shown in Figure 1. The result enables us to consider that the partial oxidation of methane to CO is favorable under the reaction conditions. It is known that the formation of carbon solids is minimized in the partial oxidation of methane.[9] No carbon formation in this work suggests that the partial oxidation of methane to CO may be favorable in the methane pyrolysis. CO can be produced by following partial oxidations,

$$CH_4 + 1/2\ O_2 \rightleftharpoons 2H_2 + CO\ (\Delta H^o = -8.5\ kcal/mol) \quad (1)$$

$$CH_4 + 3/2\ O_2 \rightleftharpoons CO + 2H_2O\ (\Delta H^o = -124\ kcal/mol) \quad (2)$$
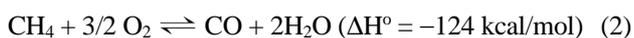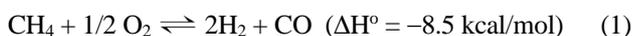
If reaction (1) is favorable in the process, the fraction of H_2 product would be higher than the fraction of CO product. However, Figure 1 shows that the CO fraction is much higher than the H_2 fraction at the same condition. In this reaction, reaction (2) is considered to be more favorable rather than reaction (1). Because reaction (2) produces water and CO, the water-gas shift reaction may occur under the reaction conditions.

$$CO + H_2O \rightleftharpoons CO_2 + H_2\ (\Delta H^o = -9.8\ kcal/mol) \quad (3)$$

From the viewpoint of thermochemistry, the water-gas shift reaction in the absence of catalyst occurs above 1090 K. In this work, CO_2 was negligibly produced below 1023 K and in small amounts ($< 5\%$) at 1073 K, suggesting that reaction (3) is negligible. According to Fleys *et al.*,[3] CO_2 is essentially produced *via* surface reactions at temperatures below 1073 K in partial oxidation of methane, which is agreeable to the present result.

On the other hand, for the direct conversion of methane to ethane, the process for the generation of methyl radical should be involved in the reaction mechanism. Methyl radical can be generated by thermal cracking of methane, reaction (4), in the gas phase.

$$2CH_4 \rightleftharpoons C_2H_6 + H_2\ (\Delta H^o = +16\ kcal/mol) \quad (4)$$
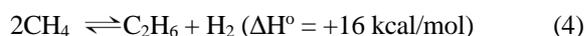
The process seems to be improbable to occur under the present conditions because the methane cracking is a highly endothermic process occurring above 1473 K. Therefore, another process must be considered for the formation of methyl radical. As listed in Table 1, the apparent activation

Notes

Bull. Korean Chem. Soc. **2008**, Vol. 29, No. 8   1611
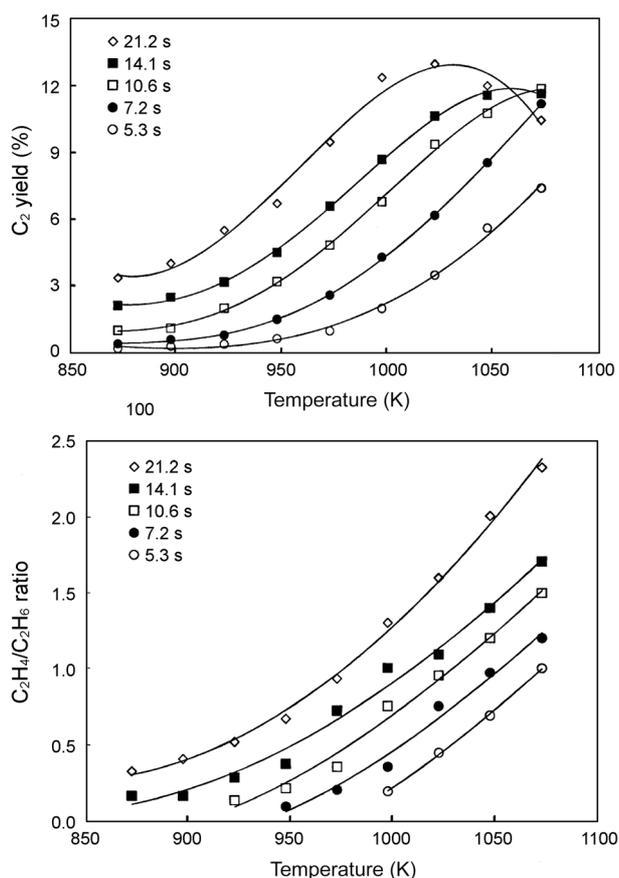
Figure 3. Variations of C_2 yield and C_2H_4/C_2H_6 ratio with temperature at various residence times for the oxidative methane pyrolysis.

Figure 4. Relationships between C_2 fraction, H_2 fraction, $C_2H_4/$ C_2H_6 ratio, and CH_4 conversion in the oxidative methane pyrolysis.

silica consisting of quartz reactor is considered to act as activate site for methane, where methyl radical is formed by the surface reaction, $CH_4 + O(ads) \rightarrow CH_3 \cdot + OH(ads)$, as suggested by other investigators for methane oxidation over silica.[4,5] Although the feasibility of methane cracking owing to thermal energy emitted by reaction (2) cannot be excluded, it is believed from the activation energy of C_2H_6 formation that methyl radical is preferably produced by the surface reaction rather than the gas phase reaction.

In Figure 3, the C_2H_4/C_2H_6 ratio increases with increasing the residence time and the temperature. Figure 4 reveals that with an increase in the methane conversion, the C_2 selectivity decreases while the ethylene/ethane ratio increases, indicating a tendency that the H_2 fraction slightly increases with an increase in the C_2H_4/C_2H_6 ratio. The results implies that ethylene is produced from ethane by reaction (5).

$$C_2H_6 \rightleftharpoons C_2H_4 + H_2 \ (\Delta H^o = +33 \text{ kcal/mol}) \qquad (5)$$
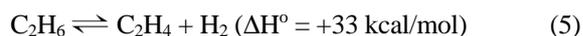
In Table 1, the apparent activation energies for the C_2H_6 and C_2H_4 formations are significantly varied with the residence time. At lower temperatures, the rate of C_2H_6 or C_2H_4 formation increased with increasing the residence time, but at higher temperatures decreased with increasing the residence time. It seems that a reverse reaction like C_2H_6 $+ H_2 \rightarrow 2CH_4$ or $C_2H_4 + 2H_2 \rightarrow 2CH_4$ becomes significant at longer residence times or higher temperatures. When such a reverse reaction occurs at longer residence times or higher

energy for the formation of C_2H_6 varied with the residence time and the values were less than 26.9 kcal/mol. Available kinetic data of the methyl radical or C_2H_6 formation for the oxidative coupling of methane over catalyst are limited at present. According to Lunsford *et al.*,[15] the activation energy for the $CH_3 \cdot$ formation over Li/MgO catalyst is 26 kcal/mol. Otsuka *et al.*[16] determined the activation energy for the C_2H_6 formation over Sm_2O_3 catalyst to be 32 kcal/mol in the temperature range of 823-1023 K. Their values are close to 26.9 kcal/mol obtained at 5.3 and 7.1 sec residence times in this work, suggesting that methyl radical is generated by a catalytic process. Active oxygen formed on the surface of

Table 1. Apparent activation energies for the CH_4 consumption and the formation of each product in the oxidative pyrolysis of methane at various residence times

Residence time (s)	Apparent activation energy (kcal/mol)			
	CH_4 consumption (923-1073 K)	H_2 formation (923-1073 K)	C_2H_4 formation (873-998 K)	C2H6 formation (873-973 K)
5.3	43.1	59.5	–	26.9
7.1	38.8	54.3	63.3	26.9
10.6	31.2	42.7	54.6	21.3
14.1	23.6	31.3	35.4	11.6
21.2	15.4	23.5	28.0	–

Reactio conditions: p_{tot} = 1 atm, CH_4:O_2 = 5:1 molar ratio.
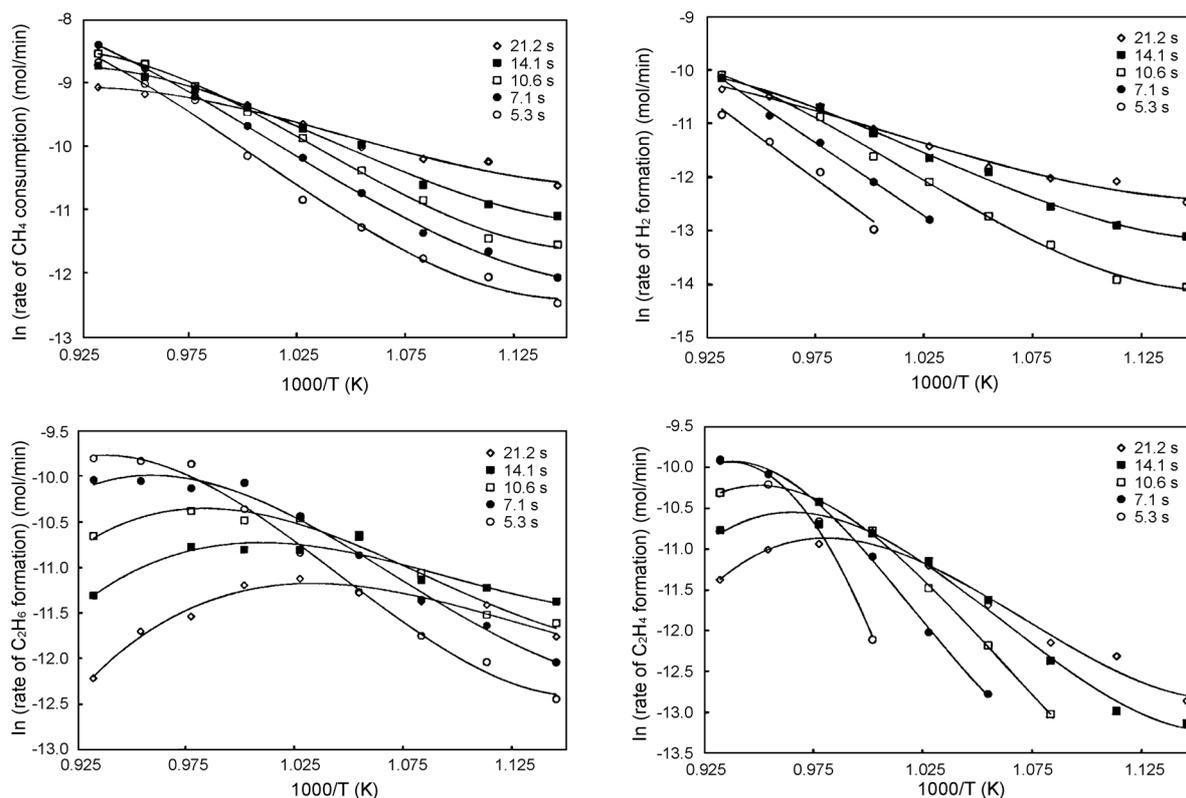
Figure 5. Rates for CH_4 consumption, H_2 formation, C_2H_6 formation, and C_2H_4 formation as a function of reciprocal temperature for the oxidative methane pyrolysis.

temperatures, the net formation of ethane or ethylene and the net conversion of methane will be reduced, resulting in lowering the apparent activation energy as obtained in this work. The apparent activation energy for C_2H_4 formation is much higher than that for C_2H_6 formation. According to Otsuka *et al.*,[16] the activation energy for the oxidative dehydrogenation of C_2H_6 to C_2H_4 is 41.8 kcal/mol in the temperature range of 850-1023 K. The summed value of the 41.8 kcal/mol for the dehydrogenation of C_2H_6 and the 26.9 kcal/mol for the C_2H_6 formation at 7.1 sec residence time is 68.7 kcal/mol which is close to 63.3 kcal/mol for the C_2H_4 formation. Figure 5 shows that the rate of C_2H_4 formation is slower than that of C_2H_6 formation at the same condition. The results suggests that ethylene is formed stepwise. Namely, ethylene is formed from ethane in the gas phase according to reaction (5) and not directly formed from methane on the surface.

Consequently, the product distribution for the oxidative methane pyrolysis in the quartz flow reactor is strongly influenced by the residence time in the temperature range of 873-1073 K. Silica consisting of the quartz reactor is believed to play an important role on the generation of methyl radical for the oxidative methane pyrolysis and the nature of active sites on the silica surface remains to be further studied. The resulting methyl radicals are coupled to ethane and ethylene is subsequently formed from ethane in the gas phase. At the reaction conditions, the partial oxidation of methane to CO is considered to occur preferentially, but CO_2 formation is unfavorable.

References

1. Keller, G. E.; Bhasin, M. M. *J. Catal.* **1982**, *73*, 9.
2. Lunsford, J. H. *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 970.
3. Fleys, M.; Simon, Y.; Marquaire, P. M. *J. Anal. Appl. Pyrolysis* **2007**, *79*, 259.
4. Garibyan, T. A.; Margolis, L. Ya. *Catal. Rev.-Sci. Eng.* **1989**, *31*, 355.
5. Nersesyan, L. A.; Vardanyan, I. A.; Margolis, L. Ya.; Nalbandyan, A. B. *Dokl. Akad. Nauk. SSSR* **1975**, *220*, 605.
6. Benson, S. W. *Int. J. Chem. Kin.* **1996**, *28*, 665.
7. Tsang, W.; Hampson, R. F. *J. Phys. Chem. Ref. Data* **1986**, *15*, 1087.
8. Choudhary, V. R.; Chaudhari, S. T.; Rajput, A. M. *AIChE J.* **1991**, *37*, 915.
9. Huff, G. A.; Vasalos, L. A. *Catalysis Today* **1998**, *46*, 223.
10. Muradov, N.; Smith, F.; Huang, C.; T-Raissi, A. *Catalsis Today* **2006**, *116*, 281.
11. Gao, Z.; Kobayashi, M.; Wang, H.; Onoe, K.; Yamaguchi, T. *Fuel Processing Technology* **2007**, *88*, 996.
12. Abanades, S.; Flamant, G. *Chem. Eng. Proc.* **2008**, *47*, 490.
13. Lee, J.-K.; An, B.-I.; Kim, D.; Min, S.-H.; Jung, J.-S.; Lee, S.-H. *Bull. Korean Chem. Soc.* **2007**, *28*, 121.
14. An, B.-I.; Ryu, K.-H.; Kim, Y.-R.; Lee, S.-H. *Bull. Korean Chem. Soc.* **2007**, *28*, 1049.
15. Xu, M.; Yang, S. X.; Rosynek, M. P.; Lunsford, J. H. *J. Phys. Chem.* **1992**, *96*, 6395.
16. Otsuka, K.; Jinno, K.; Morikawa, A. *J. Catal.* **1986**, *100*, 353.