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Simultaneous production of syngas and ethylene from methane by combining its catalytic oxidative coupling over $Mn/Na_2WO_4/SiO_2$ with gas phase partial oxidation

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A new route of methane utilization is presented, in which methane is converted to H_2, CO and C_2H_4 simultaneously with equal mole ratio, in order that the produced mixture could be used in the synthesis of propanal via hydroformylation. Kinetically controlled free radical gas phase methane oxidation was combined with its catalytic oxidative coupling over $Mn/Na_2WO_4/SiO_2$ to concomitantly acquire ethylene and syngas with close concentration. Under the optimal reaction condition, a mole ratio of $CO:H_2:C_2H_4 = 1.0:1:0.9$ was obtained with a yield of 11.6% and a selectivity of 68% to the target products based on C, while the selectivity to CO_2 is as low as 18.1%.

KEY WORDS: methane; OCM; $Mn/Na_2WO_4/SiO_2$; syngas; ethylene; kinetical control.

1. Introduction

In the past decade, the conversion of methane, the major constituent of natural gas, into value-added chemicals received great attention. In addition to the important route of methane oxidative coupling into C_2 hydrocarbons [1–5], the majority of recent work focuses on converting methane into synthesis gas [6–8], which can then be converted to higher hydrocarbons through the Fischer–Tropsch chemistry [9]. Extensive research has been conducted on direct conversion of methane by OCM. However, per-pass C_2 yield on all catalysts reported was limited to about 25% [10]. In order for the direct conversion of CH_4 to C_2H_4 to become economically feasible, the C_2H_4 yield should be greater than 40% in single-pass mode [11].

A new strategy of methane activation to produce more valuable substances was proposed previously, that is, methane was partially oxidized with oxygen, or oxygen and carbon dioxide to produce syngas and ethylene simultaneously, and the produced mixture with a ratio of $CO:H_2:C_2H_4 = 1:1:1$ could be used into the synthesis of propanal: $CO + H_2 + C_2H_4 \rightarrow CH_3CH_2COH$, thus the commercial value of natural gas could be elevated [12,13]. This way of methane utilization makes CO, a by-product in OCM, a useful one, and favors the successive process. Most of the active and selective catalysts for the OCM reaction are composed of two or three irreducible oxides, e.g., alkali metal oxides, alkali earth metal oxides, or rare earth metal oxides [14–17]. $Mn/Na_2WO_4/SiO_2$ catalyst firstly reported by Fang [18,19] et al, has got great attention for its good performance. On this catalyst, Lunsford and co-workers achieved a methane conversion of 20% at a C_2 selectivity of ≥80% at 800 °C and 1 atm, using a CH_4/O_2 ratio of 8/1, with no diluent in the reagents [20]. This catalyst was found stable for a period of up to 97 h [21]. The mechanism of OCM over $Mn/Na_2WO_4/SiO_2$ was demonstrated to be the same as that over other OCM catalysts. Namely, methyl radicals, formed on the surface, couple in the gas phase to produce C_2H_6; ethylene is mainly a secondary product, although a very small amount occurs as an initial product [22]. Somorjai proposed that short contact time, high-temperature catalytic processes (catalytic combustion and pyrolysis) were frontier areas of catalysis science in the 21st century [23]. Such processes permit kinetic control of the formation of products by isolation and trapping of reaction intermediates that are thermodynamically less stable [24]. Schmidt and co-workers studied the catalytic oxidative dehydrogenation of alkanes under short contact time (10^{-5}–10^{-3} s), and prospective results were achieved [25–28]. In the present work, kinetically controlled free radical gas phase partial oxidation of methane was performed in combination with the catalytic partial oxidation of it over $Mn/Na_2WO_4/SiO_2$ to acquire ethylene and syngas simultaneously with close concentration of CO, H_2 and C_2H_4.

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2. Experimental

The catalyst was prepared by two-step incipient wetness impregnation of a silica gel support (20–40 mesh, 300 m^2/g) with aqueous solution having appropriate concentrations of $Mn(NO_3)_2$ and Na_2WO_4. The catalyst was dried firstly at 80 °C in water bath, and then at 120 °C in air for 4 h, and finally calcined in air at 750–800 °C for 5 h.

Activity measurements were carried out using a single-pass, plug flow micro-reactor, equipped with on-line gas chromatographic (Agilent1790) sampling analysis using a plot-C2000 capillary column. The oven employed in this research has good heat preservation performance, and the length of the constant temperature segment is 120 mm. Reactant gases including CH_4 (99.995%) and O_2 (99.95%) were used without dilution at a total velocity of 120 mL/min. The velocities of reactant gases were controlled by two mass flow controllers, and that of the effluent gas mixture was measured by a mass flow meter (Seven Star D07).

The gas phase partial oxidation of methane was carried out in two quartz tubular reactors with different inner diameters (12 and 8 mm). The reactor was first heated to 600 °C in Ar, and then the reactant gases with CH_4/O_2 = 3:1 were introduced into the reactor. The effluent mixture was monitored after 30 min online. The reaction temperature was then increased to 650, 700, 720, 750, 770, 800 °C at a ramp of 5 °C /min and kept at the every temperature for about 1h to examine the influence of temperature on the reaction.

The combination of methane catalytic oxidation and gas phase oxidation was carried out in the reactor with 12 mm inner diameter. The catalyst was diluted with 1.7 mL silica sand to decrease the temperature grade in the catalyst bed, and at each end of the catalyst bed another 1 mL silica sand was added. The reactor was first heated to 800 °C in Ar, and then the reactants were introduced into the reactor. The effluent mixture was sampled after 30 min on line.

3. Results and discussion

3.1. Gas phase methane oxidation

Two quartz tubular reactors of different inner diameters (12, 8 mm) were employed in the experiments of gas phase methane oxidation. The results are shown in Table 1.

Ethane, ethylene, carbon monoxide and carbon dioxide are formed by gas phase methane oxidation, and this point is consistent with the results of Côme et al. [29,30]. In the bulkier tubular reactor (12 mm), methane shows visible conversion at about 700 °C, and the effect of reaction temperature on the gas phase methane oxidation was studied between 700 and 800 °C. Methane conversion increases with the rise of reaction temperature; while C_2 hydrocarbon selectivity shows a maximum of 39.0% at 720 °C, and then decreases with farther temperature rise. The yield of C_2 hydrocarbon augments from 2.4% to 6.4% when the reaction temperature going from 700 to 800 °C, whereas CO selectivity shows a monotonous ascending trend in this procedure. The CO_2 selectivity changes slightly. These tendencies of composition variation are all similar to what reported by Côme et al. using a continuous flow stirred tank reactor between 700 and 900 °C at CH_4:O_2:He = 13.9:2.8:83.3 (mol ratio) [29]. The higher methane conversions, higher C_2 hydrocarbon yields and lower C_2 hydrocarbon selectivity comparing to [29] in the present work may be originated from the different reaction conditions employed, such as reactor figure, the reactant CH_4/O_2 ratio and gas space time $t_g = V/F$ (V volume of reactor in constant temperature segment of oven, F volumetric flow rate at the inlet of the reactor).

At F = 120 mL/min, t_g is 6.6 s for 12 mm tubular reactor, and t_g is 3 s for 8 mm tubular reactor. With t_g

Table 1
Gas phase methane oxidation

I.d. of reactor (mm)	Temperature (°C)	CH_4 Conversion (%)	Selectivity (%)			C_2 Yield (%)	Mole ratio	
			CO_2	CO	C_2		CO:H_2:C_2H_4	C_2H_4:C_2H_6
12	700	6.2	13.2	48.6	38.2	2.4	1.3:1:0.2	0.8
	720	8.9	11.1	50.0	39.0	3.4	1.4:1:0.3	1.2
	750	14.3	11.2	50.8	37.9	5.4	1.4:1:0.4	1.9
	770	17.5	12.2	52.2	35.5	6.2	1.3:1:0.3	2.4
	800	19.5	13.2	54.1	32.7	6.4	1.0:1:0.2	3.6
8	<750	No activity						
	770	1.8	39.1	4.9	56.0	1.0	0.1:1:0.3	—[a]
	800	8.6	10.2	42.3	47.5	4.1	1.1:1:0.4	1.6

Reaction conditions: CH_4:O_2 = 3:1; F = 120 ml/min.
[a] no ethane detected.

decreasing from 6.6 to 3 s, the lowest temperature of methane conversion increases from 700 to 770 °C. At 800 °C, with t_g shortening, methane conversion dropped from19.5% to 8.6%. It is interesting to note that a linear relationship between methane conversion and the corresponding t_g is observed assuming zero methane conversion at $t_g = 0$, that is to say, methane oxidation is at a non-equilibrium state under both of the two reaction conditions. The selectivity of C_2 hydrocarbons became higher, but that of CO_x and the C_2H_4/C_2H_6 ratio in the produced mixture decreased with decreasing t_g. The possible reason is that C_2 hydrocarbons are the intermediates in the total process, and could be deeply oxidated into CO_x. It is well known that ethylene comes from ethane oxidative dehydrogenation in OCM [22], and t_g shortening obstructs this process.

As shown in Table 1, the mole ratio of CO/H_2 in the products is about 1, but the C_2H_4 concentration is only about half of that of CO or H_2. In order to contact with the process of propanal synthesis, C_2H_4 selectivity should be improved.

3.2. Combination of catalytic and uncatalytic reactions

Homogeneous reaction often goes with heterogeneous reaction at high temperature, especially on the monolithic catalysts, and the combination of them can influence the product distribution [32,33].

In previous papers on the oxidative coupling of methane, the target product is C_2 hydrocarbons even only ethylene, and COx are by-products. Some measures were adopted to decrease the selectivity of COx, for example, decreasing the reactor dead volume to constrain gas phase reaction. CO concentration in the OCM producing mixture over $Mn/Na_2WO_4/SiO_2$ was much lower than ethylene. In order to obtain the gas mixture having the same mole ratio of CO, H_2 and C_2H_4, the quartz tubular reactor used in this paper has bigger inner diameter than that of previous papers (ID about 6 mm mostly), the aim is to have obvious gas phase methane conversion and raise the concentration of CO, H_2. We combined the gas phase reaction and the surface reaction over $Mn/Na_2WO_4/SiO_2$ catalyst.

3.2.1. Catalyst dose (m)

In the 12 mm reactor, a series of methane oxidative reaction were performed with various dose of catalyst. The results are shown in Table 2. When the catalyst doses are 0.05 and 0.1 g, methane conversion is lower than that in the gas phase methane oxidation. The possible reason is that the addition of catalyst and silica (3 mL) into the reactor decreased t_g to 5.4 s, and constrained gas phase methane conversion. On the other hand, methane catalytic conversion is very small for the little dose of catalyst, so the total methane conversion became lower than that in gas phase experiment; such an influence to gas phase reaction by the addition of catalyst and silica also existed at catalyst dose above 0.1 g. The mole ratio of ethylene to ethane shows its maximum of 6.08 at $m = 0.05$ g, which is much bigger than in gas phase reaction and at other catalyst dose. It is observed that methane conversion go up continuously with increasing catalyst dose. It is reasonable that the selectivity and yield of C_2 hydrocarbons also rise. The total selectivity of deeply oxidative products CO_x increased with m, but CO_2 selectivity went up firstly, and reached its maximum at $m = 0.2$ g, and then went down slightly.

CO, H_2 and C_2H_4 are all our target products in this paper, and their relative mole ratio in the producing mixture were calculated, according to:$\frac{[CO]}{[H_2]} : 1 : \frac{[C_2H_4]}{[H_2]}$. With increasing m, this tri-ratio changed, and the mole ratio between ethylene and hydrogen increased continuously. At $m = 0.2$ g, the tri-ratio of three aim products is 1.2:1:1.1, which is very close to the needed value for the synthesis of propanal.

When m is 0.2 g, the selectivity of by-product of carbon dioxide is 25.02%, so, in the following experiment, we changed the CH_4/O_2 ratio of reactants to decrease it.

3.2.2. Influence of CH_4/O_2 ratio on the composition of the effluent

On the condition of $m = 0.15$ g, $F = 120$ mL/min, a serious of experiments were carried out through changing the CH_4/O_2 ratio as 2, 3, 4.5, 5 to tune the producing mixture composition. As shown in figure 1a,

Table 2
influence of the catalyst dose on the product composition

Weight (g)	Conversion (%)		Selectivity (%)			C_2 Yield (%)	Mole ratio	
	CH_4	O_2	CO_2	CO	C_2		$CO:H_2:C_2H_4$	$C_2H_4:C_2H_6$
0.05	17.9	84.4	15.7	46.8	37.5	6.7	1.3:1:0.4	6.1
0.1	18.8	83.1	18.3	35.7	46.1	8.7	1.6:1:0.7	2.6
0.15	21.4	93.2	19.8	36.8	43.4	9.3	1.7:1:0.8	3.3
0.2	21.4	93.5	25.0	22.1	52.9	11.3	1.2:1:1.1	3.1
0.25	22.9	94.7	23.2	18.6	58.2	13.3	1.3:1:1.5	2.6

Reaction conditions: T = 800 °C; $CH_4:O_2 = 3:1$; $F = 120$ ml/min.

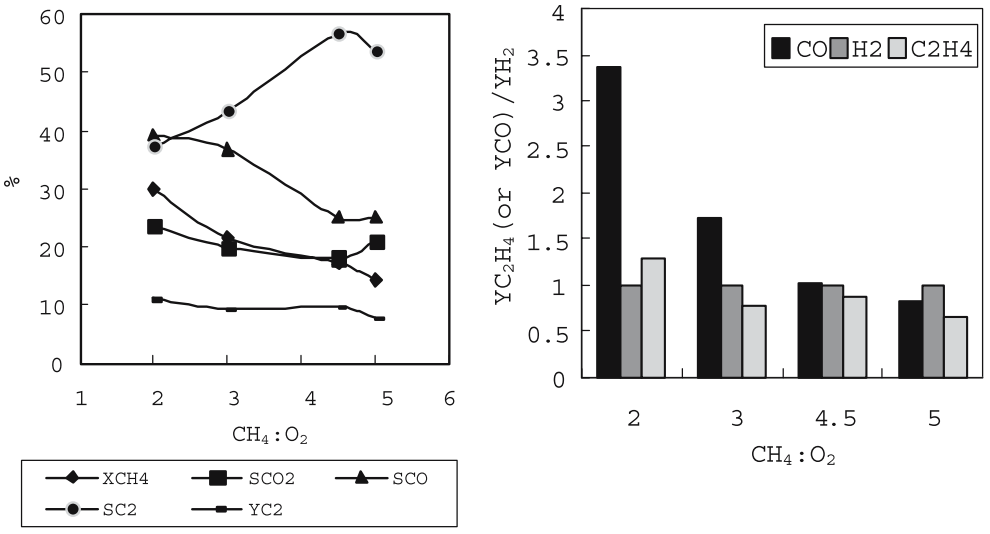

Figure 1. The effect of CH_4:O_2 on the product composition. Reaction conditions: $T = 800$ °C, $F = 120$ mL/min, $m = 0.15$ g.

methane conversion decreased continuously with the ratio of methane to oxygen, but C_2 hydrocarbons selectivity increased firstly and reached the maximum at $CH_4/O_2 = 4.5$, and now the selectivity of CO_x get its minimum.

When the CH_4/O_2 ratio increased from 4.5 to 5, the selectivity of C_2 became lower. This phenomenon is due to the shortage of oxygen in the reactant mixture, and a large part of oxygen was expended before catalyst bed, so the amount of oxygen which took part in the catalytic reaction was very small. At $CH_4/O_2 = 4.5$, the relative mole ratio of three target products got the best value of this series experiments as 1.0:1:0.9. Comparing with that best value in 3.2.1, ethylene concentration is lower, but under this condition, the carbon dioxide selectivity of 18.1% is obviously lower than the value (25%) obtained when $m = 0.2$ g and $CH_4/O_2 = 3$.

3.2.3. Stability test of the catalyst

The stability test was carried out at $m = 0.15$ g and $CH_4/O_2 = 4.5$ (figure 2) within 600 min. This reaction system became stable within 100 min. In the 600 min test, the catalyst did not lose its activity obviously. The mole ratio of three target products did not change either.

3.3. The simultaneous production of syngas and ethylene

$Mn/Na_2WO_4/SiO_2$ is an excellent OCM catalyst, on which C_2 selectivity of 80% had been achieved. In previous literatures on OCM, reactors were all filled with quartz chips above and below the catalyst bed to minimize the contribution from any gas-phase reactions, and the blank methane conversion was usually below 1% [20]. Somorjai and Schmidt carried out alkanes' pyrolysis and dehydrogenation at short contact time, so that the reaction rates were under kinetic rather than thermodynamic control, and reaction intermediates were captured [24–28]. In this work, a bulky silica tubular reactor was employed with 12 mm inner diameter and 70 cm long, in which kinetically controlled gas phase methane oxidation under appropriate contact time is combined with OCM over $Mn/Na_2WO_4/SiO_2$ to control the product distribution. Through the modulation of catalyst dose (m) and the ratio of CH_4/O_2, a

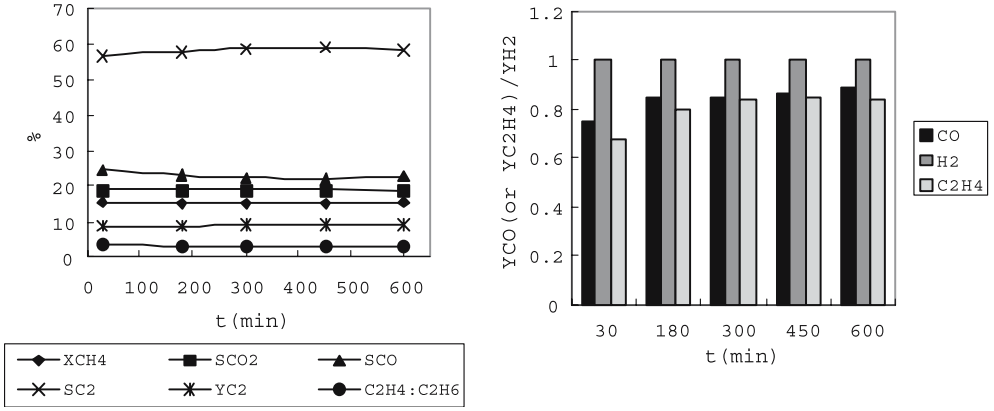

Figure 2. The stability of this reaction system. Reaction conditions: $T = 800$ °C, $F = 120$ mL/min, $m = 0.15$ g, CH_4:$O_2 = 4.5$:1.

mixture with close concentration of H_2, CO and C_2H_4 was achieved. It is revealed that short contact time, high-temperature catalytic process could be employed in the activation and utilization of natural gas.

4. Conclusions

The present work shows that the combined partial oxidation of methane via gas phase reaction and catalytic reaction over $Mn/Na_2WO_4/SiO_2$ is an effective way to adjust the mole ratio of $CO:H_2:C_2H_4$ in the producing mixture. With 0.2 g catalyst dose and $CH_4/O_2 = 3/1$, the best result was achieved as $CO:H_2:C_2H_4 = 1.2:1:1.1$ with an ethylene yield of 8.5% and a methane conversion of 21.4%, and the selectivity of CO_2 is 25.0%. When the CH_4/O_2 ratio was 4.5, the value of $CO:H_2:C_2H_4$ in product was1.0:1:0.9 with an ethylene yield of 7.3%, a methane conversion of 17.1% and a CO_2 selectivity of 18.1%. The catalytic performance and the composition of the effluent are stable during the 600 min experiment.

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References

[1] G.E. Keller and M.M. Bhasin, J. Catal. 73 (1982) 9.
[2] V.R. Choudhary, S.A.R. Mulla and B.S. Uphade, Ind. Eng. Chem. Res. 37 (1998) 2142.
[3] V.R. Choudhary, S.A.R. Mulla and V.H. Rane, J. Chem. Technol. Biotechnol. 71 (1998) 167.
[4] G. Gayko, D. Wolf, E.V. Kondratenko and M. Baerns, J. Catal. 174 (1998) 441.
[5] Y. Wang, Y. Takahashi and Y. Ohtsuka, Appl. Catal. A-Gen. 172 (1998) L203.
[6] Y.H. Hu and E. Ruckenstem, Catal. Rev. 44 (2002) 423.
[7] G. Veser, J. Frauhammer and U. Friedle, Catal. Today. 61 (2000) 55.
[8] V.R. Choudhary, S.D. Sansare and A.S. Mamman, Appl. Catal. A-Gen. 90 (1992) L1.
[9] M.K. Dry, Catal. Today. 71 (2002) 227.
[10] J.H. Lunsford, Catal. Today. 63 (2000) 165.
[11] Y. Jiang, I.V. Yentekakis and C.G. Vatenas, Science 264 (1994) 1563.
[12] C.W. Hu, H.L. Zhang and J.J. Wu, 227th ACS National Meeting, Anaheim, ACS, 2004, Fuel, No. 51.
[13] H.L. Zhang, J.J. Wu and C.W. Hu et al., Petrochem. Technol. 33 (2004) 263(China).
[14] T. Ito and J.H. Lunsford, Nature 314 (1985) 721(London).
[15] E. Iwamatsu, T. Moriyama, N. Takasaki and K. Aika, J. Catal. 113 (1988) 25.
[16] K. Aika, T. Moriyama, N. Takasaki and E. Iwamatsu, J. Chem. Soc. Chem. Commun. (1986) 1210.
[17] K. Otsuka, K. Jinno and A. Moriwaka, Chem. Lett. (1985) 499.
[18] X.P. Fang, S.B. Li and J.Z. Lin et al., J. Mol. Catal. 6(4) (1992) 255(China).
[19] X.P. Fang, S.B. Li and J.Z. Lin et al., J. Mol. Catal. 6(6) (1992) 427(China).
[20] D.J. Wang, M.P. Rosynek and J.K. Lunsford, J. Catal. 155 (1995) 390.
[21] S. Pak and J.H. Lunsford, Appl. Catal. A: Gen. 168 (1998) 131.
[22] S. Pak, P. Qiu and J.H. Lunsford, J. Catal. 179 (1998) 222.
[23] G.A. Somorjai and K. Mccrea, Appl. Catal. A: Gen. 222 (2001) 3.
[24] L. Romm and G.A. Somorjai, Catal. Lett. 64 (2000) 85.
[25] M. Huff and L.D. Schmidt, J. Phys. Chem. 97 (1993) 11815.
[26] D.A. Goetsch and L.D. Schmidt, Science 271 (1996) 1560.
[27] A.S. Bodke, D.A. Olschki, L.D. Schmidt and E. Ranzi, Science 285 (1999) 712.
[28] A.S. Bodke, D. Henning, L.D. Schmidt, S.S. Bharadwaj, J.J. Maj and J. Siddall, J. Catal. 191 (2000) 62.
[29] G.M. Côme, Y.D. Li and P. Barbé et al., Cata. Today 30 (1996) 215.
[30] P. Barbé, Y.D. Li, P.M. Marquaire, G.M. Côme and F. Baronnet, Cata. Today 21 (1994) 409.
[31] S.L. Liebmann and L.D. Schmidt, Appl. Catal. A: Gen. 179 (1999) 93.
[32] A.S. Bodke, D. Henning and L.D. Schmidt et al., J. Catal. 191 (2000) 62.
[33] L. Romm and G.A. Somorjai, Catal. Lett. 64 (2000) 85.