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$Na_2WO_4/Co–Mn/SiO_2$ Catalyst for the Simultaneous Production of Ethylene and Syngas from CH_4

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Abstract $Na_2WO_4/Co–Mn/SiO_2$ catalyst was prepared and used for the simultaneous production of ethylene and syngas from CH_4. A CH_4 conversion of 38% and a yield of 21% for (C_2H_4 + CO), with a $C_2H_4/CO/H_2$ ratio of 1/0.7/0.7 were obtained under the optimized conditions.

Keywords Methane · Ethylene · Syngas · $Na_2WO_4/Co–Mn/SiO_2$ catalyst

1 Introduction

A wide variety of catalysts, mainly metal oxide based catalysts, have been studied for the conversion of methane into value-added organic compounds, which is of significant scientific and industrial relevance. For instance, syngas could be achieved from the partial oxidation or the steam and/or dry reforming of methane [1–10], and could be used to produce methanol, oxygenated derivatives and gasoline, while C_2 hydrocarbons could be produced by the oxidative coupling of methane [11–18].

In our previous work, a strategy of methane utilization to convert methane to more valuable substances has been proposed [19, 20]. That is, in a combination system of methane gas phase oxidation and catalytic oxidative coupling, converting methane simultaneously to syngas and ethylene with similar mole concentration by controlling the gas phase uncatalytic reaction. And the products were suitable for the direct use in hydroformylation to propanal. The relative mole ratio of the target products got the most promising value of $CO/H_2/C_2H_4$ = 1/1/0.9 with a yield of about 12% to the target products based on carbon, under the optimized reaction conditions. In the most recent work [21], ethylene and carbon monoxide with a C_2H_4/CO ratio of 1/1 were produced simultaneously over the La-promoted $Na_2WO_4/Mn/SiO_2$ catalysts, and the total yield of C_2H_4 and CO was about 25%. The mixed products could be used for the further utilization in the hydroformylation to propanal by adding suitable amount of hydrogen. As ethylene and syngas/carbon monoxide were both the aim products of the methane partial oxidation, no separation was needed, and the utilization factor of methane could be enhanced in a way.

In this paper, we investigated a dual-functional catalyst for the conversion of methane simultaneously to ethylene and syngas with suitable ratios.

2 Experimental

2.1 Preparation of the Catalysts

The Na_2WO_4/Co(x wt.%)–Mn/SiO_2 catalysts, noted as Co(x), where x donated the percentage of Co in the catalyst, were prepared by incipient wetness impregnation of SiO_2 support (20–40 mesh, 338 m^2/g) with aqueous solutions containing appropriate concentrations of $Mn(NO_3)_3$ and $Co(NO_3)_3$ for 24 h, followed by drying at 120 °C for 4 h and calcining at 750–800 °C for 5 h. The obtained materials were impregnated with aqueous Na_2WO_4 for 24 h, and then dried at 120 °C for 4 h and calcined at 750–800 °C for 5 h.

2.2 Activity Test

The catalytic reaction was carried out in a tubular fixed-bed flow micro-reactor made of quartz (70 cm length, 8 mm

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i.d.) under atmospheric pressure. The catalyst was heated from room temperature to reaction temperature (800 °C) at the rate of 10 K min^{-1} in a flow of Ar (99.999 %, 20 mL min^{-1}) before the introduction of reactant gases composed of CH_4 (99.995%) and O_2 (99.95%) with suitable CH_4/O_2 ratios. The velocity of the reactant gases was controlled by mass flow controllers (D07-11A/ZM made by Beijing Sevenstar Huachuang Electronic Co. Ltd), and the effluent was also measured by a mass flow meter (Severnstar D07-12AM/ZM) at the end of the reaction system. At the reactor outlet, the effluent gas after removal of H_2O was analyzed by an on-line gas chromatograph (Agilent 1790 GC) with a plot-C2000 capillary column to separate different components of the effluent gas.

All the activity results discussed in this paper were obtained after the reaction got its stabilization state in about three hours, and the deviation of the activity was ±0.2%.

3 Results and Discussions

3.1 The Dual-catalytic Performances of Na_2WO_4/Co–Mn/SiO_2

The performances of Na_2WO_4/Co(x wt.%)–Mn/SiO_2 catalysts with different Co contents were listed in Table 1. Over all of these catalysts, ethylene and syngas could be produced simultaneously. The conversion of methane was about 37% over the Co(0.1) catalyst, and decreased slightly with the increase of Co content, except for Co(2) and Co(4). The conversions of methane were only about 17% and 21% over Co(2) and Co(4), respectively, much lower than over other catalysts. A comparison of the selectivity to the main products showed that, Co(2) and Co(4) catalysts were still exceptions: the selectivity of syngas (carbon monoxide and hydrogen) was much higher than other catalysts, while the selectivities of C_2 hydrocarbons and carbon dioxide were relatively lower. The above data indicated that, the oxidative coupling and the partial oxidation of methane occurred simultaneously over the Na_2WO_4/Co(x wt.%)–Mn/SiO_2 catalysts. It could also be deduced that, the partial oxidation of methane could be promoted effectively over Co(2) and Co(4) catalysts, while the Co(0.1), Co(0.25), Co(0.5), Co(1) and Co(10) catalysts displayed a better catalytic performance for the oxidative coupling of methane (OCM).

Figure 1 showed the relative ratios of target products (ethylene, carbon monoxide and hydrogen) from the conversion of methane over the Na_2WO_4/Co(x wt.%)–Mn/SiO_2 catalysts. The partial oxidation of methane (POM) could be promoted more obviously than the OCM reaction, over the Co(2) and Co(4) catalysts, and the mole ratios of $C_2H_4/CO/H_2$ were about 1/3.4/4.2, and 1/2.9/3.6, respectively, which were quite different from that over the other catalysts tested. The values were not suitable for our targets. When the Co contents were 0.1, 0.25, 0.5, 1 and 10, OCM and POM reaction obtained appropriate promotions, and the ratios of the target products ($C_2H_4/CO/H_2$) reached the most promising value of about 1/0.6/0.9 in this series over the Co(10) catalyst.

In the Na_2WO_4/SiO_2 system, the reconstruction of surface WO_4 tetrahedral units into a structure containing a W=O and three W–O–Si surface bonds was responsible for the OCM reaction via a redox mechanism [22, 23], and molecular oxygen is activated by an F-center to produce lattice oxygen O^{2-} [24]. Cobalt catalysts supported on alumina can catalyze methane partial oxidation [25], as well as CO_2 reforming of methane [26]. Slagtern et al. [27] proposed that, the Co catalyst displayed a moderate CO selectivity in its presumably unreduced state, and this may be caused by reforming of the primarily formed total oxidation products, or by Co giving a reasonably high primary selectivity to CO. Thus, the Na_2WO_4/Co(x wt.%)–Mn/SiO_2 catalysts displayed a dual-function: converting methane to C_2 hydrocarbons, primarily ethylene, via oxidative coupling reaction, and to the syngas via partial oxidation reaction. The composition of product gas, mainly the ratios of each component, might be due to the relative amount of

Table 1 The influence of Co content on the catalyst performance

Co content (wt.%)	Conversion of CH_4 (%)	Selectivity (%)				C_2H_4/C_2H_6 mole ratio	Yield (%)		
		CO	C_2	CO_2	H_2		CO	C_2H_4	H_2
0.1	36.6	12.0	64.0	24.0	8.2	2.7	4.4	17.1	3.0
0.25	35.4	12.4	62.7	24.9	5.7	2.5	4.4	15.8	2.0
0.5	34.9	12.6	62.9	24.5	6.7	2.6	4.4	15.8	2.3
1	35.0	12.5	61.5	26.0	5.9	2.5	4.4	15.4	2.1
2	17.2	49.8	42.5	7.7	30.8	2.2	8.6	5.0	5.3
4	20.8	45.0	43.4	11.6	27.9	2.5	9.4	6.5	5.8
10	34.3	12.8	59.8	27.4	9.3	2.4	4.4	14.5	3.2

Reaction conditions: 800 °C, catalyst: 0.3 g, total flow rate = 120 mL/min, CH_4/O_2 = 3

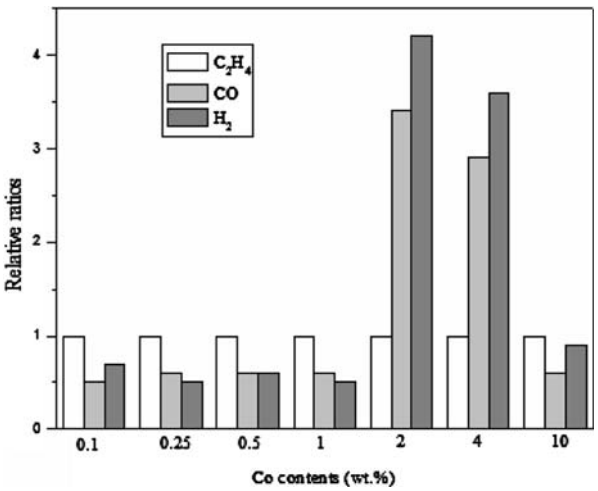

Fig. 1 The influence of Co content on the relative ratios of the products. Reaction conditions: 800 °C, catalyst: 0.3 g, total flow rate = 120 mL/min, $CH_4/O_2 = 3$

active centers for each reaction, and the reaction conditions.

3.2 Optimization of Operation Conditions

As the ratio of $C_2H_4/CO/H_2$ reached the most promising value of about 1/0.6/0.9 over the Co(10) catalyst, the influences of CH_4/O_2 mole ratio and the total flow rate of reactants were investigated over this catalyst.

3.2.1 The Effect of CH_4/O_2 Ratio on the Reaction

The effect of CH_4/O_2 ratio on the reaction was investigated by keeping the reactants total flow rate a constant at 120 mL/min, and varying the CH_4/O_2 mole ratio as 2.0, 2.5, 3.0, 3.5, 4.0. The results were shown in Table 2 and Fig. 2.

The conversion of methane and the selectivity to CO and CO_2 decreased with the increase of CH_4/O_2 mole ratio in reactants, while the selectivity to C_2 and hydrogen displayed the opposite tendency. Similar variations were observed in our previous work [19]. When the CH_4/O_2 mole ratio increased from 2.0 to 4.0, the yield of CO and C_2H_4 decreased from 6.8 % to 3.4 % and from 15.5 % to 12.7 %, respectively, while the yield of H_2 increased. As a result, the ratio of CO/C_2H_4 in products decreased along with the increasing CH_4/O_2 ratio, while the H_2/C_2H_4 increased. It was obvious that the ratio of CO/C_2H_4 reached the most promising value of about 0.9 when $CH_4/O_2 = 2.0$, and the ratio of H_2/C_2H_4 reached its best value of about 1.1 when $CH_4/O_2 = 3.5$ or 4.0, as shown in Fig. 2. When $CH_4/O_2 = 2.5$, the ratio of $CO/H_2 = 1$, and the C_2H_4/syngas was about 0.7.

3.2.2 The Effect of Space Velocity on the Reaction

The influences of the total flow rate (F) on the catalytic performance and the composition of products over the dual-functional Co(10) catalyst were summarized in Table 3 and Fig. 3.

As shown in Table 3, when F increased from 60 to 180 mL/min, the conversion of methane varied slightly around 35%. The selectivity to H_2 and CO_2 decreased along with increasing F, while that of CO increased. Nagai [29] and Dalai [30] had investigated the Water-Gas-Shift reaction (WGS, $CO + H_2O \rightarrow CO_2 + H_2$) over the Co-containing and Mn-containing catalysts, respectively, and found that the yield of CO_2 decreased with increasing F. Thus, the decrease of H_2 and CO_2 yields might be caused by the decrease of WGS with increasing F, that is to say, the increase of F resulted in a decrease of feed contact time, and this decreased the CO conversion in WGS reaction and the production of CO_2 and H_2. In general, it could be considered that, the selectivity to H_2 and CO_2 decreased along with increasing F, while CO increased. Moreover, the reduction of H_2 selectivity at high F might be also due to the mass transfer processes [31, 32]. Figure 3 gave the relative mole ratios of target products with varying F. When F = 60 mL/min, the ratio of H_2/C_2H_4 was around 1.0, and then decreased with the increase of F. While the ratio of CO/C_2H_4 obtained its minimum of about 0.6 at F = 60 mL/min, and increased slightly with increasing F to

Table 2 The influence of CH_4/O_2 mole ratio on catalytic performance

CH_4/O_2	Conversion of CH_4 (%)	Selectivity (%)				C_2H_4/C_2H_6 mole ratio	Yield (%)		
		CO	C_2	CO_2	H_2		CO	C_2H_4	H_2
2.0	41.6	16.4	51.3	32.3	5.0	2.6	6.8	15.5	2.1
2.5	37.7	14.2	56.8	29.0	7.0	2.5	5.4	15.4	2.6
3.0	34.3	12.8	59.8	27.4	9.3	2.4	4.4	14.5	3.2
3.5	30.8	12.4	60.2	27.4	11.5	2.6	3.8	13.3	3.5
4.0	28.7	12.0	62.4	25.6	12.3	2.4	3.4	12.7	3.5

Reaction conditions: 800 °C, Co(10) catalyst: 0.3 g, total flow rate = 120 mL/min

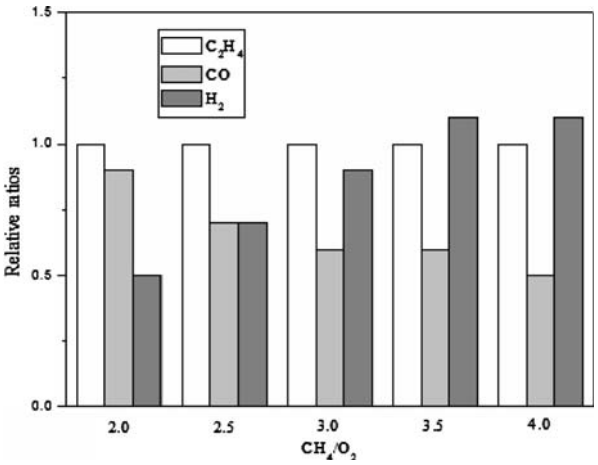

Fig. 2 The influence of CH_4/O_2 mole ratio on the relative ratios of the products. Reaction conditions: 800 °C, catalyst: 0.3 g, total flow rate = 120 mL/min

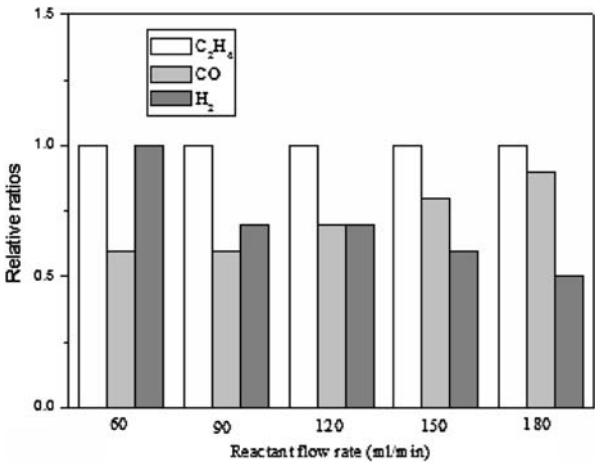

Fig. 3 Influence of reactant total flow rate on the relative ratios of the products. Reaction conditions: 800 °C, catalyst: 0.3 g, CH_4/O_2 = 2.5

Table 3 The influence of reactant total flow rate on the catalytic performance

F (mL/min)	Conversion of CH_4 (%)	Selectivity (%)				C_2H_4/C_2H_6 mole ratio	Yield (%)		
		CO	C_2	CO_2	H_2		CO	C_2H_4	H_2
60	34.8	13.4	54.2	32.4	10.8	3.6	4.7	14.8	3.8
90	37.3	12.5	57.6	29.9	7.9	2.9	4.7	15.9	2.9
120	37.7	14.2	56.8	29.0	7.0	2.5	5.4	15.4	2.6
150	37.4	14.8	56.0	29.2	5.6	2.3	5.5	14.6	2.1
180	36.0	18.0	55.4	26.5	4.4	2.3	6.5	13.9	1.6

Reaction conditions: 800 °C, catalyst: 0.3 g, CH_4/O_2 = 2.5

about 0.9, when F = 180 mL/min. When F = 120 mL/min, the ratio of CO/H_2 = 1, and the C_2H_4/syngas was about 0.7, with a yield of about 21% to the target products based on carbon.

The feedstock for hydroformylation to propanal ($C_2H_4/CO/H_2$ = 1/1/1) could also be obtained by adding suitable amount of syngas to the products obtained over the Na_2WO_4/Co–Mn/SiO_2 catalysts [21]. As the ratio of CO/H_2 in syngas produced by methane conversion was 1 or <1, the total flow rate of reactants should be controlled more than 120 mL/min.

4 Conclusions

The OCM and POM reactions could be carried out simultaneously over the Na_2WO_4/Co(x wt.%)–Mn/SiO_2 catalysts, and the target products composed of ethylene and syngas could be obtained simultaneously in this catalytic system. The catalytic performance and the relative ratios of target products could be varied by the contents of Co in catalysts as well as the reaction conditions. Over the Na_2WO_4/Co(10 wt.%)–Mn/SiO_2 catalyst, the mole ratio of $C_2H_4/CO/H_2$ = 1/0.7/0.7, with a yield of about 21% to the target products based on carbon could be obtained, under the conditions of F = 120 mL/min with a CH_4/O_2 ratio of 2.5.

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