Dual Catalyst Bed for the Oxidation of CH_4 Simultaneously to C_2H_4 and Syngas

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Dual catalyst bed system was introduced into the conversion of methane in one reactor simultaneously to ethylene and syngas with appropriate concentrations, which could be used for further production of propanal via hydroformylation. To avoid the over consumption of O_2 on the first catalyst bed, the moderately active catalyst Co/γ-Al_2O_3 for methane partial oxidation was employed, followed by Na_2WO_4/Mn/SiO_2 catalyst, which was one of the most effective catalysts for the oxidative coupling of methane. The distribution of products could be tuned by controlling the relative dosages of the two catalysts and the reaction conditions. A mixture with the desired composition of $CO/H_2/C_2H_4 = 1.1/1/1.2$ was achieved, with the total yield of CO and C_2H_4 of about 18.5%, under the following optimized conditions: $F = 150$ *cm^3/min, $CH_4/O_2 = 3$,* $M_1:M_2 = 0.01$ *g:0.16 g (1: Co/γ-Al_2O_3; 2: Na_2WO_4/Mn/SiO_2).* © 2007 American Institute of Chemical Engineers *AIChE J,* 53: 2925–2931, 2007

Keywords: dual catalyst bed, Co/γ-Al_2O_3, Na_2WO_4/Mn/SiO_2 catalyst, methane partial oxidation, oxidative coupling of methane

Introduction

The conversion of methane to value-added products has long been a goal in catalysis studies in the past two decades. Currently, the most economically available operating process for the utilization of methane is the steam reforming[1–4] to produce syngas with a high H_2/CO ratio (≥ 3), which is not suitable for the downstream processes to liquid fuel or chemicals. The dry reforming of methane with carbon dioxide[5–8] has attracted increasing interest, as it yields syngas with H_2/CO ratio around 1, which is suitable for the production of oxygenated derivatives. However, this process is highly endothermic and, highly energy intensive and is easily interrupted due to the carbon deposition and the shattering of catalyst. Partial oxidation of methane (POM)[9–12] is moderately exothermic and can produce syngas of a molar ratio of H_2/CO of 2/1, which can be directly used as feed for methanol synthesis or the Fischer-Tropsch reaction. Much of the researches have also been devoted to the oxidative coupling of methane (OCM) to ethane and ethylene, since the early work of Keller and Bhasin.[13] And the Na–Mn–W catalyst system was proposed to be one of the most effective catalysts for the OCM reaction.[14–19] Although this reaction appears to be more promising, the cost of separation and transportation should be considered as ethylene is a gas at standard temperature and pressure.

The combination of process control and catalytic reaction permitted the more effective catalytic processes. Somorjai proposed that short contact time, high-temperature catalytic processes were frontier areas of catalysis science in the 21st century, and such processes permit kinetic control of the formation of products by isolation and trapping of reaction intermediates that are thermodynamically less stable.[20,21] For instance, the C_2 yields could be enhanced to more than 50% over Sm_2O_3 catalyst in a simulated countercurrent moving-bed chromatographic reactor.[22] Moreover, it can be increased up to 88% in a gas recycle high-temperature electrocatalytic

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reactor, in which the recycled gas passes continuously through a molecular sieve trap in the recycle loop.[23]

In our previous investigations, a new strategy of methane activation to convert it to more valuable substances has been proposed.[24,25] 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.

In this work, dual catalyst bed technique was employed for the simultaneous formation of syngas and ethylene from methane to enhance the yield of target products. The first bed layer was composed of a methane partial oxidation catalyst, and the second layer was effective for the OCM.

Experimental

Preparation of the catalysts

$Na_2WO_4/Mn/SiO_2$ catalyst was prepared by two-step incipient wetness impregnation of silica support (20–40 m, 338 m^2/g) with aqueous solutions containing appropriate concentrations of $Mn(NO_3)_3$ and Na_2WO_4, according to Ref. 24.

$Co/\gamma\text{-}Al_2O_3$ catalyst was prepared by impregnation of γ-Al_2O_3 support with aqueous solution having appropriate concentration of $Co(NO_3)_2$ for 24 h, then dried at 393 K for 4 h, followed by calcination at 773 K for 3 h to decompose the nitrate, and finally calcined at 1073 K for 5 h to formulate the catalyst.

Activity test

The catalytic reaction was carried out in a tubular fixed-bed flow microreactor made of quartz (70 cm length, 8 mm i.d.) under atmospheric pressure. A thermocouple binding to the out wall of the reactor was used to control the reaction temperature (T_c), and another thermocouple was placed at the bottom of the catalyst bed to measure the actual temperature of effluent gas that left the catalyst bed (T_a). In the dual catalyst bed system, $Co/\gamma\text{-}Al_2O_3$ catalyst was used as the first catalyst layer due to its moderate activity for methane partial oxidation, and followed by the $Na_2WO_4/Mn/SiO_2$ catalyst. These two catalyst beds were separated by 0.5-cm^3 silica sand. The catalyst beds were first heated to 1073 K (T_c = T_a) at the rate of 10 K/min in a flow of Ar (99.999%, 20 cm^3/min), and then the reactants (CH_4 and O_2) were introduced into the reactor without any dilute gas. The velocity of reactant gases was dominated by mass flow controllers (D07-11A/ZM made by Beijing Sevenstar Huachuang Electronic). At the reactor outlet, the effluent gas after removal of H_2O was analyzed by 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 article were obtained after the reaction got its stabilization state in about 3 h, and the deviation of the activity was about ±0.2%, obtained by at least three parallel tests.

Calculations

The conversion of CH_4, the selectivity of the products, the yield, and the mole ratio of main products for all experiments were defined, respectively, as follows:

$$X_{CH_4} = \frac{2F_{C_2H_4} + 2F_{C_2H_6} + F_{CO} + F_{CO_2}}{F_{CH_4\ \text{inlet}}}$$

$$S_{C_2H_4} = \frac{2F_{C_2H_4}}{2F_{C_2H_4} + 2F_{C_2H_6} + F_{CO} + F_{CO_2}}$$

$$S_{C_2} = \frac{2F_{C_2H_4} + 2F_{C_2H_6}}{2F_{C_2H_4} + 2F_{C_2H_6} + F_{CO} + F_{CO_2}}$$

$$S_{CO} = \frac{F_{CO}}{2F_{C_2H_4} + 2F_{C_2H_6} + F_{CO} + F_{CO_2}}$$

$$S_{CO_2} = \frac{F_{CO_2}}{2F_{C_2H_4} + 2F_{C_2H_6} + F_{CO} + F_{CO_2}}$$

$$S_{H_2} = \frac{2F_{H_2}}{4F_{C_2H_4} + 6F_{C_2H_6} + 2F_{H_2}}$$

$$Y_{C_2H_4+CO} = X_{CH_4} \bullet (S_{C_2H_4} + S_{CO})$$

$$CO/H_2/C_2H_4 = S_{CO}/2S_{H_2}/\frac{1}{2}S_{C_2H_4}$$

where Fi is the flow rate of species i (cm3/min).

A carbon balance was calculated around each experiment by comparing the carbon outlet in gas phase against the carbon inlet, which is expressed as follows:

$$\text{C balance} = \frac{2F_{C_2H_4} + 2F_{C_2H_6} + F_{CO} + F_{CO_2} + F_{CH_4\ \text{outlet}}}{F_{CH_4\ \text{inlet}}}$$

The C balance results of all experiments were above 90%, as shown in Tables 1 and 3. The activity results were all calculated according to C balance.

Results and Discussion

Effect of dual catalyst bed

The catalytic performances of the dual catalyst bed, and $Co/\gamma\text{-}Al_2O_3$ and $Na_2WO_4/Mn/SiO_2$ catalysts were investigated comparatively. The results are shown in Table 1.

Over $Co/\gamma\text{-}Al_2O_3$ catalyst, the main products were hydrogen, carbon monoxide, and carbon dioxide, and very little amount of C_2 hydrocarbons could also be obtained. The ratio of $CO/H_2/C_2H_4$ over 0.02 g $Co/\gamma\text{-}Al_2O_3$ catalyst was about 0.7/1/0.1, with about 35% methane conversion and 50% CO selectivity. Slagtern et al.[26] investigated the POM over $Co/La/Al_2O_3$ and found a moderate CO selectivity over the presumably unreduced catalyst, whereas CoO showed a moderate activity for total oxidation of methane. The investigation of methane partial oxidation over $Co/C/\gamma\text{-}Al_2O_3$ catalyst[27] revealed that the disappearance of cobalt metal and the increased amount of $CoAl_2O_4$ resulted in the decrease of catalytic activity and selectivity, as the $CoAl_2O_4$ was a less active and less selective component of the catalysts. The XRD results in the present investigation confirmed the existence of $CoAl_2O_4$, as shown in Figure 1. Thus, the $Co/\gamma\text{-}Al_2O_3$ catalyst was considered to be a moderate active catalyst for POM, attributed to the formation of cobalt aluminate

Table 1. Comparison of the Performance of $Na_2WO_4/Mn/SiO_2$ and Co/γ-Al_2O_3 Catalysts As Well As the Dual Catalyst Bed

		Conversion, %		Selectivity, %						Mole Ratio	
Catalyst Bed	T_a, K	CH_4	O_2	CO_2	H_2	CO	C_2	C_2H_4	$Y_{CO+C_2H_4}$, %	$CO/H_2/C_2H_4$	C Balance, %
Co/γ-Al_2O_3	1105	24.9	18.6	32.2	36.6	51.3	16.5	12.2	15.8	0.7/1/0.1	95
$Mn/Na_2WO_4/SiO_2$	1080	34.7	100	23.3	7.1	15.6	61.1	43.1	20.4	1.1/1/1.5	98
Dual catalyst bed	1057	29.0	100	39.3	9.7	19.4	41.3	22.5	12.1	1.0/1/0.6	98

Reaction conditions: T_c = 1073 K; CH_4/O_2 = 3/1; F = 120 cm^3/min; M_1:M_2 = 0.02 g:0.15 g (1: Co/γ-Al_2O_3; 2: $Na_2WO_4/Mn/SiO_2$).

$CoAl_2O_4$ on the catalyst. The selectivity and yield to C_2 hydrocarbons over 0.15 g $Na_2WO_4/Mn/SiO_2$ catalyst could reach about 61% and 21%, respectively, under the following conditions: T = 1073 K, F = 120 cm^3/min, CH_4/O_2 = 3/1. Although the selectivities of CO and H_2 over the $Na_2WO_4/Mn/SiO_2$ catalyst were much lower than those over Co/γ-Al_2O_3 catalyst, that is, only about 15.6% and 7.1% were obtained, respectively, and the ratio of $CO/H_2/C_2H_4$ was about 1.1/1/1.5. The resulting mixtures obtained over these two single catalysts were both unsuitable for the hydroformylation of ethylene to propanal.

In the dual catalyst bed system, Co/γ-Al_2O_3 catalyst was placed in the upstream of the reactor followed by $Na_2WO_4/Mn/SiO_2$ catalyst; otherwise, the much more active C_2 hydrocarbons formed over $Na_2WO_4/Mn/SiO_2$ might be further oxidized over Co/γ-Al_2O_3 catalyst. The dosage of each catalyst was similar to that in the single catalyst system, that is, 0.02 g Co/γ-Al_2O_3 and 0.15 g $Na_2WO_4/Mn/SiO_2$. As it is well known, in $Na_2WO_4/Mn/SiO_2$ system, the presence of gas phase O_2 is essential for obtaining an active catalyst.[15,17] According to Yu et al.'s pulse reaction experiments,[28] bulk lattice oxygen species do not participate directly in the OCM reaction, and the active oxygen species involved in the activation of methane exist only in the presence of gas phase oxygen. Thus, very little amount of moderate catalyst for POM was used to avoid the complete consumption of gas phase oxygen in the first catalyst layer, so as to make sure the presence of gas phase oxygen over $Na_2WO_4/Mn/SiO_2$ catalyst. The temperature of the mixed gas encountering the second catalyst layer would be higher because of the exothermic partial oxidation and combustion reactions over the first catalyst layer. This was confirmed by the measured T_a as shown in Table 1. The T_a of single catalyst bed of Co/γ-Al_2O_3 was about 1105 K, much higher than T_c (1073 K). The higher temperature could also influence the reactions over the second layer.

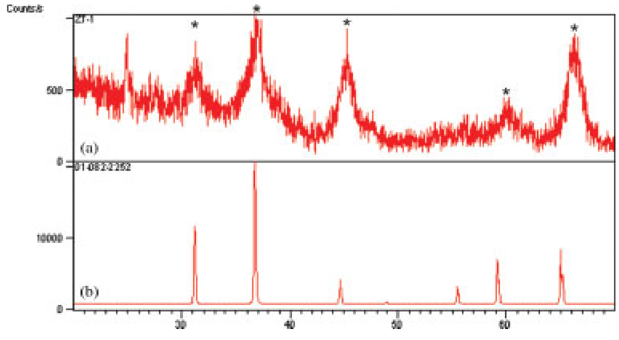

Figure 1. (a) Results of XRD characterization for Co/γ-Al_2O_3 catalysts (*: $CoAl_2O_4$); (b) The standard pattern of $CoAl_2O_4$.

[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

It was observed that the conversion of methane in dual bed system increased only about 4%, compared to the Co/γ-Al_2O_3 system, while the oxygen was completely consumed, and the selectivity to C_2 hydrocarbons was about 2.5 times as that over the single bed of Co/γ-Al_2O_3 catalyst. The distribution of the effluent from dual bed system and single Co/γ-Al_2O_3 system are listed in Table 2. Comparing the concentrations of H_2 and CO in dual catalyst bed system (5.6% and 5.6%, respectively) with those in the single Co/γ-Al_2O_3 catalyst system (12.5% and 8.9%, respectively), significant reductions in both H_2 and CO in the dual catalyst bed system were observed, while the concentrations of C_2H_4 and C_2H_6 increased from 1.8 to 3.3% and from 0.7 to 2.7%, respectively, because of the OCM reaction over the second layer. There were two possible reasons. First, the gas phase reactions in dual bed system were different from those in the single catalyst system, and this difference could also influence the product distribution. Considering the homogeneous uncatalytic gas phase reactions discussed earlier,[25,29] the effluent from the single bed of Co/γ-Al_2O_3 catalyst might be an integrated result of catalytic effect and gas phase uncatalytic reaction. The addition of a second bed of $Na_2WO_4/Mn/SiO_2$ catalyst could not only enhance the OCM reaction but also inhibit the gas phase homogeneous reactions, as the conversion of oxygen over this catalyst was 100%. As a result, the amount of CO and H_2 in dual bed system was reduced, for the gas phase reaction might produce hydrocarbons, carbon monoxide, and carbon dioxide.[30,31] Second, reactions between CO and H_2 might occur along with the oxidation of methane in this dual bed system to consume H_2 and CO. A control experiment to test the possible reaction between CO and H_2 over the $Na_2WO_4/Mn/SiO_2$ catalyst has been carried out, and a little amount of CH_4 was found to form, indicating that the formation of CH_4 from CO and H_2 was possible. It

Table 2. Comparing the Constitutions of Effluence Between the Dual Catalyst Bed and Single Co/γ-Al_2O_3 Catalyst System

	Concentration, mol %						
Catalyst Bed	H_2	O_2	CO	CH_4	CO_2	C_2H_4	C_2H_6
Co/γ-Al_2O_3	12.5	17.8	8.9	50.2	8.1	1.8	0.7
Dual catalyst bed	5.6	0	5.6	71.3	11.4	3.3	2.7

Reaction conditions: T_c = 1073 K; CH_4/O_2 = 3/1; F = 120 cm^3/min; M_1:M_2 = 0.02 g:0.15 g (1: Co/γ-Al_2O_3; 2: $Na_2WO_4/Mn/SiO_2$).

Table 3. Optimization of Reaction Conditions

Optimized Conditions		X_{CH_4}, %	Selectivity, %					$Y_{CO+C_2H_4}$, %	Mole Ratio CO/H_2/C_2H_4	C Balance, %
			CO_2	H_2	CO	C_2	C_2H_4			
Catalyst dosage* (M_1:M_2/g)	0.01:0.16	33.8	29.1	5.7	14.9	56.0	36.0	17.2	1.3/1/1.6	101
	0.02:0.15	29.0	39.3	9.7	19.4	41.3	22.5	12.2	1.0/1/0.6	98
	0.03:0.14	25.7	46.6	17.8	28.4	25.0	13.6	10.8	0.8/1/0.2	97
	0.07:0.10	25.7	46.7	31.6	44.2	9.2	5.4	12.7	0.7/1/0.04	93
Total flow rate of reagents† (F), cm^3/min	60	30.2	34.4	13.7	16.4	49.2	35.5	15.7	0.6/1/0.7	101
	90	30.8	30.2	12.9	15.5	54.3	40.0	17.1	0.6/1/0.8	99
	100	32.1	29.0	9.6	15.4	55.7	38.3	17.2	0.8/1/1.0	98
	150	33.2	25.6	7.6	16.8	57.6	39.0	18.5	1.1/1/1.2	98
Ratio of CH_4/O_2 in reagents‡	2	40.6	29.1	6.4	21.7	49.2	36.3	23.5	1.7/1/1.4	97
	2.5	37.0	26.7	6.5	18.3	55.0	37.8	20.8	1.4/1/1.4	97
	3.5	31.4	24.6	7.1	14.1	61.4	40.2	17.1	1.0/1/1.4	98
	4	28.6	23.3	8.4	13.4	62.2	40.0	15.3	0.8/1/1.2	97

Other condition parameters: *T_c = 1073 K, CH_4/O_2 = 3/1, F = 120 cm^3/min.
†T_c = 1073 K, CH_4/O_2 = 3/1, M_1:M_2 = 0.01 g:0.16 g.
‡T_c = 1073 K, F = 150 cm^3/min, M_1:M_2 = 0.01 g:0.16 g (1: Co/γ-Al_2O_3; 2: Na_2WO_4/Mn/SiO_2).

should be noted that the exact reaction conditions over the Na_2WO_4/Mn/SiO_2 catalyst in the dual catalyst bed system, such as the compositions of mixed gas (because of safety consideration), temperatures, and so on, were difficult to simulate. Thus, the certainty and details of the reaction $3H_2$ + CO → CH_4 + H_2O in this dual bed system could not be clarified. Because no C_2H_4 was detected in the control experiment, the increase of C_2H_4 in the dual bed system was hardly assigned to the existence of the reaction $4H_2$ + 2CO → CH_2CH_2 + $2H_2O$. Thus, the reduction of H_2 and CO might be caused by the reduced importance of gas ghase reactions, and/or the methanation of CO over Na_2WO_4/Mn/SiO_2 catalyst followed by OCM. This deserved further investigations.

The temperature profiles have also been investigated. In single catalyst system, the T_a was 1105 and 1080 K, respectively, over Co/γ-Al_2O_3 and Na_2WO_4/Mn/SiO_2 catalysts. Both of them were higher than T_c, as the POM and OCM as well as the combustion of methane were all exothermic reactions. The much higher temperature over Co/γ-Al_2O_3 catalyst might be caused by the combustion of methane. This could be confirmed by the higher CO_2 selectivity over Co/γ-Al_2O_3 than Na_2WO_4/Mn/SiO_2, as shown in Table 1. Whereas in dual bed system, T_a was 1057 K, much lower than T_c. This indicated that over the second bed, the products formed over the first catalyst layer may undergo some acute endothermic reactions leading to the decrease of T_a, these reactions might be the following:

$$H_2O + CH_4 \longrightarrow CO + 3H_2 \qquad \Delta H_{298} = 260\ \mathrm{kJ/mol}$$

$$CO_2 + CH_4 \longrightarrow 2CO + 2H_2 \qquad \Delta H_{298} = 247\ \mathrm{kJ/mol}$$

$$CO_2 + 2CH_4 \longrightarrow C_2H_6 + CO + H_2O \qquad \Delta H_{298} = 62\ \mathrm{kJ/mol}$$

$$2CO_2 + 2CH_4 \longrightarrow C_2H_4 + 2CO + 2H_2O \quad \Delta H_{298} = 196\ \mathrm{kJ/mol}$$

Optimization of reaction conditions in dual bed system

The influence of reaction conditions in the dual catalyst bed system, such as the relative dosages of catalysts, the total flow rate (F), and the ratio of CH_4/O_2 in the feed, was investigated. The results are listed in Table 3.

Influence of the Relative Dosages of Catalysts. The total amount of the two catalysts was kept constant at 0.17 g, while the relative dosages of each catalyst were varied. The amounts of Co/γ-Al_2O_3 catalyst used were 0.01, 0.02, 0.03, 0.07 g, and the amounts of Na_2WO_4/Mn/SiO_2 catalyst were 0.16, 0.15, 0.14, and 0.10 g, correspondingly.

In the dual catalyst bed system, oxygen could be completely consumed in all experiments, while methane was not. From Table 3, it could be found that the increase of catalyst dosage in the first bed resulted in the decrease of total methane conversion. More amounts of oxygen would be consumed over the first bed of Co/γ-Al_2O_3 catalyst when the dosage of this catalyst increased. Then the concentrations of oxygen in the mixed gas that encountered the second bed of Na_2WO_4/Mn/SiO_2 catalyst decreased, and this resulted in the decrease of CH_4 conversion over the second catalyst layer. Combining with the results shown in Table 1, it is clear that the catalytic activity of Na_2WO_4/Mn/SiO_2 catalyst for the conversion of methane is higher than that of Co/γ-Al_2O_3 catalyst. Therefore, the increase of the dosage in first bed resulted in the decrease of total methane conversion. However, when the dosage of Co/γ-Al_2O_3 catalyst increased from 0.03 to 0.07 g, no significant variation in the conversion of methane occurred. When the dosage of Co/γ-Al_2O_3 catalyst was 0.07 g, the oxygen could be completely consumed over the first layer, as the selectivity of C_2 was very low (much lower than that over single Co/γ-Al_2O_3 catalyst). Also, the reactions occurred over the second layer were mainly the slow reactions of the products that formed over the first layer. More amount of Co/γ-Al_2O_3 catalyst resulted in more CO_2 that formed over the first layer, and then the endothermic reactions involving CH_4 and CO_2 mentioned earlier could be enhanced. This could be cleared by the similar selectivity of CO_2 between the systems of M_1:M_2 = 0.03:0.14 and 0.07:0.10 (1: Co/γ-Al_2O_3; 2: Na_2WO_4/Mn/SiO_2), as well as the reduction of increasing extent of T_a when M_1 increased from 0.03 to 0.07 g. As a result, although there might be no OCM reaction occurred over the second layer, there still existed methane consumption over this catalyst bed. Also the contribution of all possible reactions, including

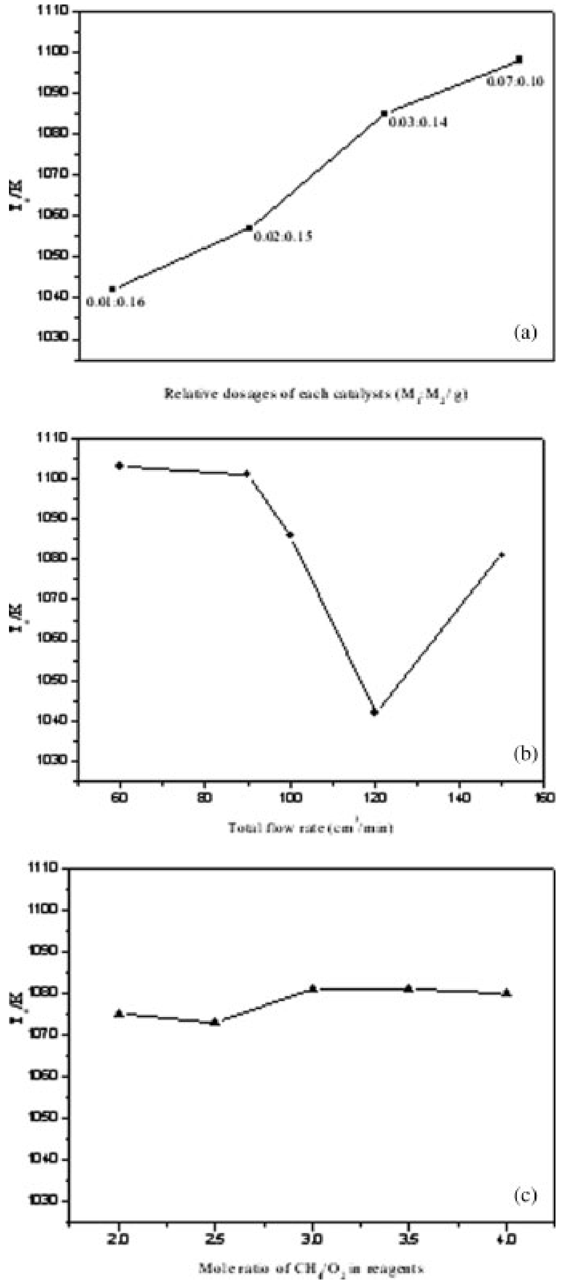

Figure 2. The variation of T_a.

(a) Influence of catalyst dosage, other reaction conditions: T_c = 1073 K, CH_4/O_2 = 3/1, F = 150 cm^3/min. (b) Influence of total flow rate, other reaction conditions: T_c = 1073 K, CH_4/O_2 = 3/1, M_1:M_2 = 0.01 g:0.16 g. (c) Influence of the mole ratio of CH_4/O_2, other reaction conditions: T_c = 1073 K, F = 150 cm^3/min, M_1:M_2 = 0.01 g:0.16 g (1: Co/γ-Al_2O_3; 2: Na_2WO_4/Mn/SiO_2).

the catalytic reactions, gas phase reactions, and some slow reactions of the products that formed over the first layer, resulted in the similar methane conversion when M_1 increased from 0.03 to 0.07 g.

The selectivity of H_2 and CO increased with the increase in the relative dosage of Co/γ-Al_2O_3 catalyst, while the selectivity of C_2 and the ratios of CO/H_2 and C_2H_4/H_2 decreased. This indicated that in dual catalyst bed system, the primary contribution of the first bed of Co/γ-Al_2O_3 catalyst was to produce the syngas, while the second bed of Na_2WO_4/Mn/SiO_2 catalyst was mainly used to produce ethylene. When the amount of Co/γ-Al_2O_3 catalyst was 0.01 g, and the amount of Na_2WO_4/Mn/SiO_2 catalyst was 0.16 g, the total yield of CO + C_2H_4 reached the maximum of about 17.2%, and the ratio of target products was about CO/H_2/C_2H_4 = 1.3/1/1.6. It could be concluded that the application of dual catalyst bed could obviously influence the products distribution as well as the conversion of methane. Because the conversion of oxygen in the presence of the second catalyst layer was 100%, the gas phase reaction occurred in the void space between catalyst particles could be neglected.[29] As a result, the gas phase reaction in the dual bed systems tested were similar to each other. The increase of H_2 and CO formation, with the increase of dosage in the first layer would be mainly due to the enhancement of POM reaction over the first catalyst layer. The increase of Co/γ-Al_2O_3 catalyst dosage enhanced the POM and methane combustion over the first layer and inhibited the endothermic reaction over the second catalyst layer, and the cooperation of them resulted in the continuous increase of T_a (as shown in Figure 2a).

Figure 2a shows the variation of T_a with the relative dosages of catalysts. It was obvious that the increase of dosage in the first bed resulted in a continuous increase in T_a. This might be caused by the following: the increase of Co/γ-Al_2O_3 catalyst dosage enhanced the POM reaction as well as the acute exothermic reaction of methane combustion over the first layer. This could be understood easily from the increase of CO, H_2, and CO_2 selectivity with the increase of Co/γ-Al_2O_3 catalyst dosage. On the other hand, when the dosage of Co/γ-Al_2O_3 catalyst increased from 0.03 to 0.07 g, methane was mainly oxidized over the first layer, and this still resulted in the increase of T_a. Although, little or even no OCM reaction occurred over the second layer and the main reactions over this layer were the endothermic reactions involving CH_4 and CO_2. As a result, the increased extent of T_a could be inhibited when M_1 increased from 0.03 to 0.07 g.

In the dual catalyst bed system, the different reaction conditions (such as gas space time and CH_4/O_2 ratio in the feed) resulted in different conversion of methane and oxygen over each catalyst layer as well as the product distribution. The target of this work, that is, producing ethylene, CO, and H_2 simultaneously with the CO/H_2/C_2H_4 ratio of about 1/1/1, could be achieved by adjusting the above operation conditions to appropriate values.

Influence of the Total Flow Rate of the Feed. Based on the results obtained earlier, the dual bed system composed of 0.01-g Co/γ-Al_2O_3 catalyst and 0.16-g Na_2WO_4/Mn/SiO_2 catalyst was chosen for further investigations. Adjusting F could alter the contact time of reactants over these two catalysts and tune the activity and selectivity of the dual bed system. The conversion of methane increased along with the increase of F, when $F \leq 120$ cm^3/min. The increase of F resulted in the decrease of methane conversion over the first layer as well as the oxygen conversion. As a result, the concentrations of methane and oxygen in the mixed gas that encountered the second layer increased, and this resulted in a higher conversion of methane over the second layer. For the catalytic activity of Na_2WO_4/Mn/SiO_2 catalyst for methane conversion is higher than that of the Co/γ-Al_2O_3 catalyst, the decreased amount of methane conversion over the first layer was less than the increased amount over the second layer, and then, an increased total conversion of methane could be obtained. When F increased from 120 to 150 cm^3/min, the contact time of reactants decreased, and the endothermic reactions involving methane and the products formed over the first layer could be inhibited significantly. Moreover, the decrease of contact time decreased the formation of CO_2 over the first layer (as shown in Table 3, the selectivity of CO_2 decreased continuously with the increase of F), and this could also result in the inhibition on the endothermic reactions. This inhibition could be confirmed by the T_a increase, which will be discussed later. When F was higher than 120 cm^3/min, the decreased amount of methane conversion via the above endothermic reactions was equivalent to the increased amount via OCM. As a result, there was no significant variation in methane conversion, when F was increased from 120 to 150 cm^3/min.

The selectivities of H_2 and CO decreased with the increase of F when $F \leq 120$ cm^3/min, then increased with further increase of F. The increase of F decreased the conversion of methane and oxygen over the first catalyst bed and resulted in the decrease of the selectivities of H_2 and CO, as the syngas was mainly produced over the first bed catalyst. Moreover, with the increase of F, T_a decreased, as shown in Figure 2b, and this could also reduce the formation of CO and H_2. However, when F increased to more than 120 cm^3/min, the inhibition of F on the slow reactions of the products that formed over the first layer, such as further oxidation and the methanation of CO, would be more effective than on the decrease of H_2 and CO production. And this resulted in the increase of selectivities to CO and H_2 when F increased from 120 to 150 cm^3/min. Furthermore, the selectivity of CO_2 decreased continuously with the increase of F, for the shortness of contact time could prevent the occurrence of the further oxidation of products. As the conversion of methane and oxygen decreased over the first catalyst bed with the increase of F, the oxygen concentration in the mixed gas encountering the second catalyst bed would be increased. Therefore, on account of the increase of methane conversion over the second catalyst bed, and the inhibition on the further oxidation of ethane and ethylene, the selectivity of C_2 hydrocarbons in dual bed system increased continuously with the increase of F.

The T_a decreased with the increase of F when $F \leq 120$ cm^3/min, and then increased significantly when F increased from 120 to 150 cm^3/min, as shown in Figure 2b. When F increased from 120 to 150 cm^3/min, the inhibition of F on some slow reactions, especially the endothermic ones, would be much more effective and this might be the main reason for T_a re-raising.

Overall, the increase of F influenced the T_a and the slow reactions of the products that formed over the first layer, and the co-operation of them resulted in the variation of the methane conversion and the product distributions.

As shown in Table 3, the ratios of target products CO/H_2/C_2H_4 were about 0.8/1/1.0 and 1.1/1/1.2, respectively, when F = 100 and 150 cm^3/min, and these were close to the expected value (CO/H_2/C_2H_4 = 1/1/1) for the hydroformylation process. At the same time, the total yield of CO + C_2H_4 reached the maximum of about 18.5%, when F = 150 cm^3/min.

Influence of the Ratio of CH_4/O_2 in Reagents. Under the conditions of F = 150 cm^3/min, M_1:M_2 = 0.01 g:0.16 g (1: Co/γ-Al_2O_3; 2: Na_2WO_4/Mn/SiO_2), a series of experiments were carried out by changing the CH_4/O_2 ratio as 2.0, 2.5, 3.0, 3.5, 4.0 to tune the composition of the mixture produced.

Both Zanthoff and Baerns[32] and Chen et al.[33] investigated the influence of CH_4/O_2 initial ratio on the methane conversion in the absence of catalyst and found that higher CH_4/O_2 inlet ratios result in lower methane conversion, with the increase of selectivity to C_2 hydrocarbons. As shown in Table 3, the conversion of methane decreased continuously with the increase of CH_4/O_2 ratio, and so did the selectivity of CO_2. These were in agreement with the results obtained over Mn-Na_2WO_4/SiO_2,[14] $BaCO_3$/LaOBr,[34] and the Rh catalysts prepared on zirconia-containing and alumina-containing supports.[35] The increase of CH_4/O_2 ratio resulted in the shortage of oxygen in reagents and inhibited the combustion of methane and the deep oxidation of the products. The selectivity of H_2 and C_2 hydrocarbons increased continuously with the increase of CH_4/O_2 ratio, while the selectivity of CO and CO_2 decreased. As shown in Figure 2c, the variation of T_a was not significant among these tests (all around 1080 K).

In our previous work,[24] similar variations were observed in the system combining the gas phase POM with its catalytic oxidative coupling over Na_2WO_4/Mn/SiO_2 catalyst. As shown in Table 2, at CH_4/O_2 = 3, the relative mole ratio of the target products got the most promising value of CO/H_2/C_2H_4 = 1.1/1/1.2, and the total yield of CO + C_2H_4 was about 18.5%, which was much higher than that obtained in our previous investigation.[24,25]

Thus, the dual catalyst bed could give the expected composition of mixed products, that is, the ratio of CO/H_2/C_2H_4 could be regulated to about 1/1/1, by utilizing the system with two catalyst beds and varying the catalysts dosage and controlling the reaction conditions.

Conclusions

Over Co/γ-Al_2O_3 catalyst, the main products are hydrogen, carbon monoxide, and carbon dioxide, and very little amount of C_2 hydrocarbons could also be produced. The selectivity and yield of C_2 hydrocarbons over 0.15 g Na_2WO_4/Mn/SiO_2 catalyst could reach to about 61% and 21%, respectively, under the present reaction conditions: T_c = 1073 K (T_a = 1080 K), CH_4/O_2 = 3/1, F = 120 cm^3/min. In the dual catalyst bed system composed of Co/γ-Al_2O_3 and Na_2WO_4/Mn/SiO_2 catalyst, under the optimized reaction conditions: T_c = 1073 K (T_a = 1081 K), F = 150 cm^3/min, CH_4/O_2 = 3, and M_1:M_2 = 0.01 g:0.16 g (1: Co/γ-Al_2O_3; 2: Na_2WO_4/Mn/SiO_2), the mole ratio of target products CO/H_2/C_2H_4 was 1.1/1/1.2 with a total yield of about 18.5% for CO + C_2H_4, and this effluent was suitable for the process of the hydroformylation to propanal.

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Notation

POM = partial oxidation of methane
OCM = oxidative coupling of methane
T_c = the controlled temperature
T_a = the actual temperature of effluent gas left the catalyst bed
F_i = flow rate of species i, cm^3/min
$F_{i\ \mathrm{inlet}}$ = flow rate of species i at the inlet of reactor, cm^3/min
$F_{i\ \mathrm{outlet}}$ = flow rate of species i at the outlet of reactor, cm^3/min
X_{CH_4} = conversion of CH_4, %
S_{C_2} = selectivity of C_2 hydrocarbons, %
$S_{C_2H_4}$ = selectivity of C_2H_4, %
S_{CO} = selectivity of CO, %
S_{CO_2} = selectivity of CO_2, %
S_{H_2} = selectivity of H_2, %
$Y_{C_2H_4+CO}$ = total yield of C_2H_4 and CO, %
$CO/H_2/C_2H_4$ = molar ratio of products CO, H_2, and C_2H_4
C balance = carbon mass balance, %

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