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Critical Influence of $BaCO_3$ on Low Temperature Catalytic Activity of $BaCO_3/ZrO_2$ Catalysts for Oxidative Coupling of Methane

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Abstract During low temperature oxidative coupling of methane reaction, the content of $BaCO_3$ has an important influence on the catalytic performance. The CH_4 conversion and C_2 selectivity improved with the increase of the $BaCO_3$ content. Under ignition conditions, the 7.5% $BaCO_3/ZrO_2$ catalyst had the best catalytic activity in which the 35.4% CH_4 conversion and 29.5% C_2 selectivity could be obtained at 250 °C. The temperature profiles of reactor have been described and found that the distribution of hot spots on catalyst bed is related to the low temperature activity of catalyst.

Keywords Oxidative coupling of methane · $BaCO_3/ZrO_2$ catalyst · Hot spot · Low temperature

1 Introduction

Oxidative coupling of methane (OCM) is one of the promising routes for direct conversion of methane to higher hydrocarbons (especially ethane and ethylene), and the worldwide efforts have been made in this direction for the past 20 years [1–4]. Most of the research on this reaction has been directed to developing suitable catalysts which give high yield of higher hydrocarbon, and numerous kinds of catalysts have been tested for their oxidative coupling activity. Generally, these materials are reducible metals, alkali metals, alkaline earth metals and rare earth metals. ZrO_2 has acidic, basic, oxidizing and reducing properties. Utilizing these properties, ZrO_2 catalyst has been applied to reactions such as the synthesis of methanol from synthesis gas and dehydration of alcohols [5, 6]. The alkali-metal compound promoted ZrO_2 catalysts ever exhibit noticeable C_2 selectivity in the OCM reaction.

The temperature of OCM reaction is very high which has been reported at the range of 750–900 °C. However, Cameron et al. [7] noted that the reaction temperature reported for most of the studies on OCM was not the actual reaction temperature. Baerns et al. [8] reported that hot spots of 250 °C were present during the OCM reaction over La_2O_3/CaO catalyst. Pak and Lunsford [9] described the thermal effects and magnitude of the hot spots for Na–W–Mn catalysts and found the temperature on catalyst bed was as high as 150 °C. Generally speaking, hot spots can obviously cause detrimental consequences on the operation of the reactor, such as temperature runaway, catalyst deactivation, undesired side reactions, and deep oxidation of products.

More recently, some work had been done successfully to apply the thermal effects as an energy source for low temperature OCM reaction which can run under 600 °C. Wang et al. [10] prepared $BaCO_3/La_2O_3$ catalysts by urea combustion method and achieved the well low temperature OCM performance. Dalai [11] had succeeded to apply the thermal effects as an energy source for the low temperature OCM reaction over $Mn/Na_2WO_4/SiO_2$ catalyst. Under the $CH_4/O_2 = 2.0$ and 370 °C reaction condition, 14% C_{2+} yield could be achieved. In this work, the application of thermal effect on low temperature OCM reaction over $BaCO_3/ZrO_2$ catalysts with different $BaCO_3$ content was carried out and the result revealed that the thermal effect was responsible for the OCM catalytic activity at low temperature conditions and the content of $BaCO_3$ had an important influence for the low temperature OCM reaction.

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2 Experimental

2.1 Catalyst Preparation

The catalysts were prepared as follows: a mixture of zirconium oxide (ZrO_2), barium carbonate ($BaCO_3$) and deionizer water, in an appropriate molar ratio, was stirred at room temperature to form suspension solution. Then the resultant solution was dried 120 °C for 24 h and calcined in air at 800 °C for 4 h. Because the decomposing temperature of barium carbonates is above 1,400 °C. So, in these catalysts, the element of barium exists in barium carbonate. The content of barium carbonate is in the range of 2.5–15 wt%. All the catalyst samples were crushed and sieved to 80–120 mesh size.

2.2 Catalyst Characterization

The phase structure of the catalyst was characterized by X-ray powder diffraction (XRD) on Bruker D8 diffractometer using Cu Kα radiation at 40 kV and 40 mA. The specific surface area of the catalysts was measured by nitrogen adsorption at liquid nitrogen temperature, with a Thermo Electron Corporation Sorptomatic instrument. X-ray photoelectron spectroscopy (XPS) experiment was detected on an ESCALAB250 (Thermo Electron Co.) using Al Kα as the exciting radiation at a constant pass energy of 50 eV. The binding energy values were corrected using the C 1s peak at 285.0 eV. Near-surface compositions were calculated from peak areas using the sensitivity factors, which were provided in the software of the instrument. Temperature-programmed desorption of carbon dioxide (CO_2-TPD) experiments were carried out using a Thermo Electron Corporation TPD/R/O 1100 series catalytic surfaces analyzer equipped with a TCD detector. The catalyst sample (0.1 g) was treated at 800 °C in helium flow for 1 h and then saturated with pure CO_2 flow after cooling to 100 °C. After purging with helium at 100 °C for 1 h to remove weakly physisorbed CO_2, the sample was heated to 450 °C at a rate of 10 °C/min in a helium flow (20 ml/min).

2.3 Catalytic Activity Measurement

The catalytic activity test was carried out in a tubular fixed-bed flow micro-reactor made of quartz (i.d., 6 mm; length, 350 mm) under atmospheric pressure. Fresh catalyst (0.5 g, 80–120 mesh) was loaded in the reactor and the length of the catalyst bed was ca. 10 mm. Before reaction, the catalysts were pretreated with O_2 at 700 °C for 30 min, and decreased reactor temperature to 500 °C. Then, reactant gasses, methane and oxygen without any diluents, at the gas hourly space velocity (GHSV) of 18,000 ml/g h were co-fed into the reactor. The temperature of reactor was controlled using a thermocouple attached to the outer wall of the reactor at a position corresponding to the center of the catalyst bed length. Additionally, a small diameter quartz capillary tube was used as a thermocouple well, in which a thermocouple could be moved easily to measure the axial temperature along the length of the catalyst bed. The outlet products were detected by two on line gas chromatography (Beijing East & West Electronics Institute, GC-4000A) equipped with a TCD detector with a TDX column which can separate O_2, CO, CH_4, and a Poropak Q column which can separate CH_4, CO_2, C_2H_4 and C_2H_6. The calculations of methane conversion and C_2 selectivity were based on total carbon balance.

3 Results and Discussion

3.1 Characterization Results of Catalysts

The XRD patterns of the fresh catalysts are shown in Fig. 1. The ZrO_2 sample shows the crystalline bulk structures of pure ZrO_2 to be dominated by monoclinic zirconium oxide (m-ZrO_2, Fig. 1a). For $BaCO_3/ZrO_2$ catalysts, besides $BaCO_3$ and monoclinic ZrO_2, some trace amounts of tetragonal ZrO_2 (t-ZrO_2) and/or face-centered cubic ZrO_2 (c-ZrO_2) are also detectable. Generally, ZrO_2 has acidic, basic, oxidizing and reducing properties [12]. The basic of the ZrO_2 favors adsorption of CO_2 to form carbonate in air. However, no carbonate phases of the zirconium species are observed from XRD results. Based on the XPS analyses, some CO_3^{2-} are detected on the surface of ZrO_2 sample. Hence it is reasonable to believe that the carbonates, which are formed during preparation,

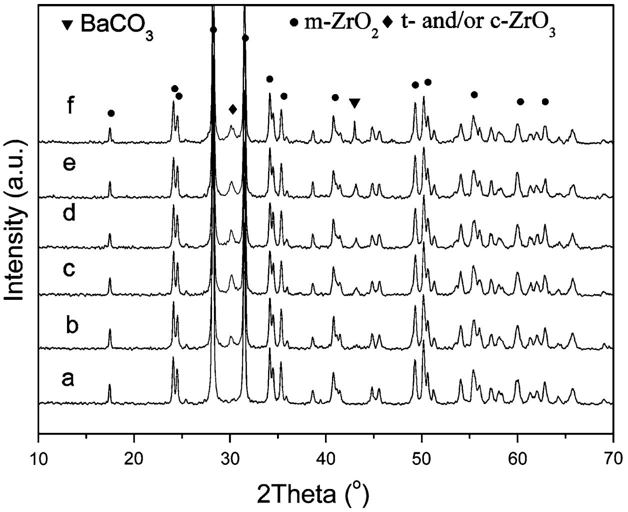

Fig. 1 The XRD pattern of fresh catalysts (*a*) ZrO_2; (*b*) 2.5% $BaCO_3/ZrO_2$; (*c*) 5.0% $BaCO_3/ZrO_2$; (*d*) 7.5% $BaCO_3/ZrO_2$; (*e*) 10% $BaCO_3/ZrO_2$; (*f*) 15% $BaCO_3/ZrO_2$

Table 1 Characterization results of the fresh and used catalysts

Catalysts	Zr $3d_{5/2}$		Ba $3d_{5/2}$		O 1s		C 1s		XRD results			Surface area (m^2/g)
	BE (eV)	at.%	BE (eV)	at.%	BE (eV)	at.%	BE (eV)	at.%	ZrO_2^b	$BaCO_3$	Crystal size (nm)[c]	
ZrO_2	181.7	69.4	–	–	531.4	27.9	289.6	2.7	m	–	44.1	3.9
ZrO_2 (used)[a]	181.6	69.3	–	–	531.2	27.9	289.7	2.8	m	–	44.5	3.4
2.5% $BaCO_3/ZrO_2$	181.8	71.8	780.5	0.7	531.4	25.0	289.6	2.5	m, t, c	No	42.2	3.5
2.5% $BaCO_3/ZrO_2$ (used)[a]	181.7	71.5	780.4	0.9	531.3	25.2	289.7	2.4	m, t, c	No	43.1	3.1
5.0% $BaCO_3/ZrO_2$	181.8	71.1	780.5	0.9	531.2	25.1	289.7	2.9	m, t, c	Yes	42.7	3.3
5.0% $BaCO_3/ZrO_2$ (used)[a]	181.6	70.5	780.5	1.2	531.3	25.3	289.6	3.0	m, t, c	Yes	43.3	3.0
7.5% $BaCO_3/ZrO_2$	181.7	69.2	780.3	1.4	531.3	26.3	289.6	3.1	m, t, c	Yes	42.5	3.2
7.5% $BaCO_3/ZrO_2$ (used)[a]	181.8	68.7	780.4	1.6	531.2	26.4	289.7	3.3	m, t, c	Yes	43.6	2.8
10% $BaCO_3/ZrO_2$	181.8	68.2	780.5	3.1	531.3	25.9	289.6	3.5	m, t, c	Yes	42.3	3.0
10% $BaCO_3/ZrO_2$ (used)[a]	181.8	66.4	780.3	3.6	531.4	26.3	289.7	3.7	m, t, c	Yes	43.7	2.7
15% $BaCO_3/ZrO_2$	181.7	57.3	780.4	4.0	531.3	33.8	289.6	4.9	m, t, c	Yes	41.3	2.7
15% $BaCO_3/ZrO_2$ (used)[a]	181.8	55.7	780.5	4.7	531.2	34.4	289.6	5.2	m, t, c	Yes	42.8	2.5

[a] The used catalysts were drawn after auto-extinct of OCM reaction at the holding temperature

[b] *m* monoclinic ZrO_2; *t* tetragonal ZrO_2; *c* face-centered cubic ZrO_2

[c] Crystal size of ZrO_2 was determined from X-ray diffraction data using Scherrer's equation

Table 2 Catalytic performance of the $BaCO_3/ZrO_2$ catalyst at 350 °C

Catalysts	Starting T (°C)	Holding T (°C)	Conv. CH_4 (%)	Sel. (%)				Yield C_2 (%)	Holding Time (h)
				C_2	C_2H_4	CO_2	CO		
ZrO_2	630	600	23.6[a]	26.8[a]	15.1[a]	40.8[a]	32.2[a]	6.33[a]	1.2
2.5% $BaCO_3/ZrO_2$	570	175	38.2	27.6	17.8	58.6	13.8	10.5	13.1
5.0% $BaCO_3/ZrO_2$	570	250	38.5	29.7	18.9	57.2	13.1	11.4	10.7
7.5% $BaCO_3/ZrO_2$	580	250	39.2	30.1	19.8	55.6	14.3	11.8	7.4
10.0% $BaCO_3/ZrO_2$	590	250	36.1	31.5	20.2	54.8	13.7	11.4	5.3
15.0% $BaCO_3/ZrO_2$	590	300	32.7	32.2	20.9	54.4	13.4	10.5	0.6
$BaCO_3$	750	750	4.9	51.1[b]	13.7[b]	31.1[b]	17.8[b]	2.5[b]	–

Reaction conditions: GHSV = 18,000 ml/g h, $CH_4/O_2 = 2.0$

[a] The data were recorded at reactor temperature = 600 °C

[b] The data were recorded at reactor temperature = 750 °C

are highly dispersed in ZrO_2 catalysts. For 2.5% $BaCO_3/ZrO_2$ sample, only the ZrO_2 phases are detected. With the increase of $BaCO_3$ content, $BaCO_3$ phases are also detected at 5.0% and above 5.0% $BaCO_3$ content. The XRD patters of the used catalysts are also tested (no shown) and phase structures are similar with that of the fresh catalysts. However, the ZrO_2 crystal size of the used catalysts is bigger than that of the fresh catalysts (Table 1).

The XPS results and surface areas of the fresh and used catalysts are shown in Table 1. It can be seen that the binding energy (BE) values of Zr $3d_{5/2}$ peak and Ba $3d_{5/2}$ peak are ca. 181.7 eV and ca. 780.5 eV, respectively. The C 1s spectra shows two peaks at 285.0 and 289.6 eV, which can be assigned to surface contaminants and CO_3^{2-}, respectively. Based on the XPS peak areas and the atomic sensitivity factors of elements, the elemental compositions on the surface of $BaCO_3/ZrO_2$ catalysts are calculated. For the fresh catalyst, with increasing $BaCO_3$ content from 2.5 to 15%, the surface composition of barium increases from 0.7 to 4.0%, while the surface composition of zirconium decreases from 71.8 to 57.3%. This suggests that Ba accumulated on the surface of catalysts with increasing $BaCO_3$ content. At the same time, the specific surface areas of the fresh catalysts slightly decrease from 3.5 to 2.7 m^2/g.

From Table 1, it can be seen that the Zr.$3d_{5/2}$ and Ba $3d_{5/2}$ BE values of the used catalysts (after stability test at holding temperature, see Table 2) were essentially identical to those of the fresh catalysts, but significant changes in the composition of Zr and Ba were seen after the reaction. For the $BaCO_3/ZrO_2$ catalysts, the amount of Zr decreased

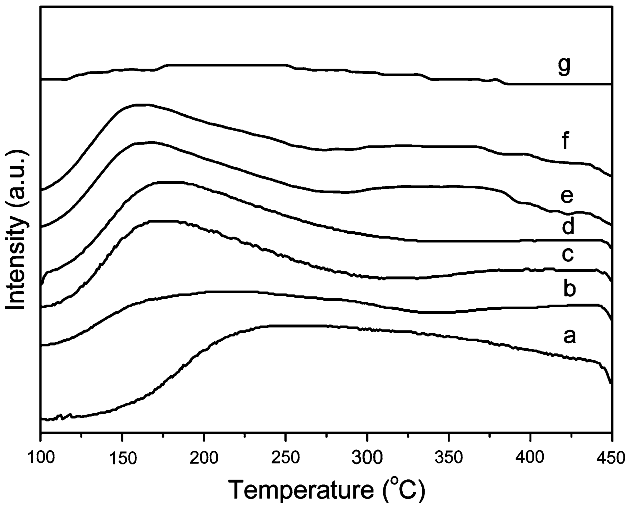

Fig. 2 CO_2-TPD profiles of catalysts (*a*) ZrO_2; (*b*) 2.5% $BaCO_3/ZrO_2$; (*c*) 5.0% $BaCO_3/ZrO_2$; (*d*) 7.5% $BaCO_3/ZrO_2$; (*e*) 10% $BaCO_3/ZrO_2$; (*f*) 15%$BaCO_3/ZrO_2$; (*g*) $BaCO_3$

on the used catalysts, whereas the amount of Ba increased markedly. The above results indicate that the accumulation of Ba occurred on the surface of the catalyst in the OCM reaction. In addition, as compared with the fresh catalysts, the surface area of the used catalysts also has a slight decrease (Table 1).

Based on CO_2 desorption peaks, the weak base sites, moderate based sites and strong base sites can be identified [13]. From the CO_2-TPD profiles of the catalysts, it can be seen that the profile of ZrO_2 revealed a very board peak which indicated that three type based sites were presented in ZrO_2 catalyst (Fig. 2a). Whereas only slightly moderate based sites was observed on the $BaCO_3$ catalysts (Fig. 2g). For the $BaCO_3/ZrO_2$ catalyst, the CO_2-TPD profiles have an obvious difference with that of ZrO_2. With higher $BaCO_3$ loading, the CO_2 desorption peak shifts to lower temperature and the desorption amount of CO_2 also decreases gradually. The result indicates that the addition of $BaCO_3$ changed the base sites and amount of base.

3.2 Catalytic Activity

In the activity test, the detailed process is following: once the OCM reaction is started at starting temperature (the start temperature of OCM reaction), the reactor temperature was first increased to 700 °C and hold for 30 min, then decreased to lower temperature every 50 °C. At every temperature point, after 30 min holding time, the outlet products were detected by two on line gas chromatography. The catalytic performance of the catalysts is shown in Table 2. For the OCM reaction, it can be observed that the holding temperature (the lowest reaction temperature at which OCM reaction can run) varies with the content of the $BaCO_3$ in the catalysts. For the pure ZrO_2 catalyst, the OCM reaction can start at 630 °C and hold at 600 °C. Suzuki and Moffat [14] reported the similar results in which the OCM reaction can run at 530 °C over the pure ZrO_2 catalyst. However, when adding some $BaCO_3$ to the ZrO_2 catalysts, the starting and holding temperature have remarkable decrease. For example, for the 2.5% $BaCO_3/ZrO_2$ catalyst, the OCM reaction can start at 570 °C, whereas hold at 175 °C. Nevertheless, with higher $BaCO_3$ loading, the starting and holding temperature are elevated correspondingly. For example, 5.0–15% $BaCO_3/ZrO_2$ catalysts can begin OCM reaction at 570, 580 and 590 °C, while hold at 250 and 300 °C, respectively (Table 2). Once the beginning of OCM reaction, the reaction can be operated at the lower temperature. For 5.0–10% $BaCO_3/ZrO_2$ catalysts, the OCM reaction can run at the holding temperature of 250 °C about 2 h (Table 2). However, for 15% $BaCO_3/ZrO_2$ catalyst, the reaction will be extinct soon after the control temperature is below 300 °C (Table 2).

To some extent, the difference of the holding temperature represents the catalytic activity of the catalysts. It should be noted that the CO_2 selectivity is very high over all the catalysts. Especially on the $BaCO_3$ promoted ZrO_2 catalysts, the CO_2 selectivity is above 54.4%. This result suggests that, in the OCM reaction, the highly exothermic methane combustion (Eq. 1) occurs in a notable extent. As a result, the large heat can be given in the reaction.

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \quad \Delta H_{298} = -802\,\mathrm{kJ/mol} \qquad (1.)$$

For the pure ZrO_2 catalyst, with the addition of 2.5% $BaCO_3$, the CO_2 selectivity has an obvious enhancement (from 40.8 to 58.6%). Therefore, more heat releases in the OCM reaction on the 2.5% $BaCO_3/ZrO_2$ catalyst. This indicates the $BaCO_3$ can increase methane combustion catalytic activity of the ZrO_2 catalyst. Moreover, the releasing heat can help to ignite or hold OCM reaction in some condition. As a result, the starting and holding temperature of the $BaCO_3/ZrO_2$ catalysts have an obvious decrease comparing with that of the pure ZrO_2 catalyst. The CO_2 selectivity gradually decreases with the increase of $BaCO_3$ content, while the C_2 selectivity increases concomitantly. This result indicates that the high content of $BaCO_3$ can restrain the methane combustion activity and increase the OCM activity of the $BaCO_3/ZrO_2$ catalysts. For the used catalyst, the average crystal size of ZrO_2 has slight increase and the surface areas of the catalysts also has some decrease, which might be a reason for the catalyst deactivation. In addition, the changes in surface composition could be another reason for changes in the catalytic activity of ZrO_2-based catalyst. The above XPS results indicate the amount of Ba increased obviously, which can restrain the OCM catalytic activity and methane combustion activity.

For the $BaCO_3$ catalyst, the CH_4 conversion is 4.9% at 750 °C. The pure ZrO_2 catalyst has poor OCM catalytic activity at 600 °C. With the addition of $BaCO_3$, the catalytic activity has an obvious enhancement. The CH_4 conversion improves and reaches maximum (39.2%) over the 7.5% $BaCO_3/ZrO_2$ catalyst. With higher $BaCO_3$ loading (above 7.5%), the CH_4 conversion decreases gradually. Although C_2 selectivity increases gradually with higher $BaCO_3$ content from 2.5 to 15%, the maximum C_2 yield can be drawn on the 7.5% $BaCO_3/ZrO_2$ catalyst. At the same time, with increasing C_2 selectivity, CO_x selectivity decreases gradually, particularly CO_2 selectivity decreases from 58.6 to 54.4%. Au and co-workers [15] claimed that with addition of $BaCO_3$, the dioxygen species of catalyst could be deprived. As a result, the CH_4 oxidative dehydrogenation process is enhanced, while deep oxidation process is suppressed. Therefore, $BaCO_3$ is a good promoter for ZrO_2 catalysts to product C_2 hydrocarbons by OCM reaction. In comparison with OCM catalytic activity of catalysts one another, 7.5% $BaCO_3/ZrO_2$ catalyst is selected as a representation for further study.

The influence of temperature on OCM reaction over 7.5% $BaCO_3/ZrO_2$ catalyst is shown in Fig. 3. The CH_4 conversion and CO_2 selectivity decrease from 38.2 and 60.0 to 35.4 and 53.5%, respectively, with the decrease of reactor temperature from 700 to 250 °C, whereas the C_2 selectivity increases from 22.6 to 29.5%. This result suggests, at least in the range of reactor temperature (700–250 °C), that low temperature does not favor the conversion of CH_4, but benefits the manufacture of C_2 hydrocarbons. For the 7.5% $BaCO_3/ZrO_2$ catalysts, OCM reaction can hold at as low reactor temperature as 250 °C. This mainly caused by the methane combustion which can supply large heat for the OCM reaction. From Fig. 3, it can be seen that the maximum peak temperature is as high as 555.1 °C on the 7.5% $BaCO_3/ZrO_2$ catalysts. This is the reason why the OCM reaction can run at as low reactor temperature as 250 °C.

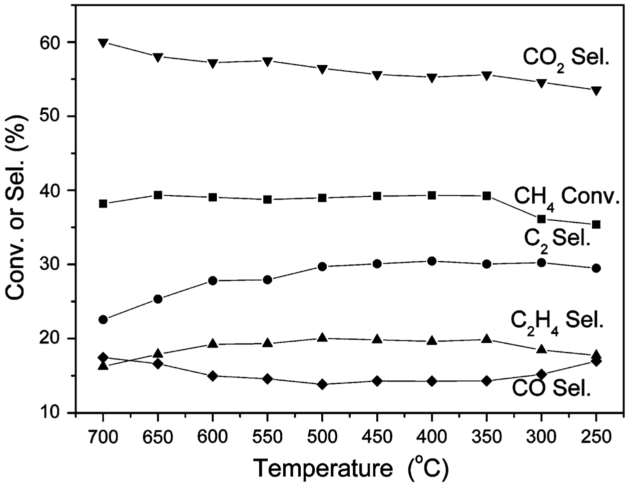

Fig. 3 Effect of reactor temperature on the performance of 7.5% $BaCO_3/ZrO_2$ catalyst GHSV = 18,000 ml/g h, CH_4/O_2 = 2.0

Table 3 lists the catalytic performance of OCM reaction under different CH_4/O_2 ratio over 7.5% $BaCO_3/ZrO_2$ catalyst. It can be seen that the CH_4/O_2 ratio has an obvious effect on catalytic activity of the OCM reaction. With increasing CH_4/O_2 ratio from 2.0 to 3.0, the CH_4 conversion decreases from 39.2 to 28.7% and the C_2 selectivity increases from 30.1 to 36.1%, respectively. In addition, the starting temperature elevates from 580 to 590 °C and the holding temperature increases from 250 to 410 °C, respectively. Correspondingly, the CO_2 selectivity decreases from 55.6 to 44.8%. That means, with the increase of CH_4/O_2 ratio, the CH_4 oxidative dehydrogenation process is enhanced, while the methane combustion process is suppressed. As a result, the holding temperature increases because of the less exothermic reactions.

3.3 Temperature Profiles

Although the OCM reaction is known to be highly exothermic, relatively little research has addressed the magnitude of the temperature profiles (hot spots) that may exist in catalyst bed during the reaction. Along the axis of the catalyst bed, the temperature profiles were measured during reaction by sliding the internal thermocouple 15 mm upstream and downstream from the center of the catalyst bed. It is estimated that the position of the inner thermocouple is accurate to ±1 mm. The axial temperature profiles of $BaCO_3/ZrO_2$ catalyst bed are shown in Fig. 4. The temperature of the thermocouple on the outside of the reactor is 350 °C. When the CH_4/O_2 mixtures are

Table 3 Catalytic activity under different CH_4/O_2 over 7.5% $BaCO_3/ZrO_2$ catalyst

CH_4/O_2 ratio	Starting T (°C)	Holding T (°C)	Conv. CH_4 (%)	Sel.				Yield C_2 (%)
				C_2 (%)	C_2H_4 (%)	CO_2 (%)	CO (%)	
2.0:1	580	250	39.2	30.1	19.8	55.6	14.3	11.8
2.5:1	580	315	33.4	32.7	19.4	50.3	17.0	10.9
3.0:1	590	410	28.7	36.1	18.9	44.8	19.1	10.4

Reaction conditions: GHSV = 18,000 ml/g h, reactor temperature = 450 °C

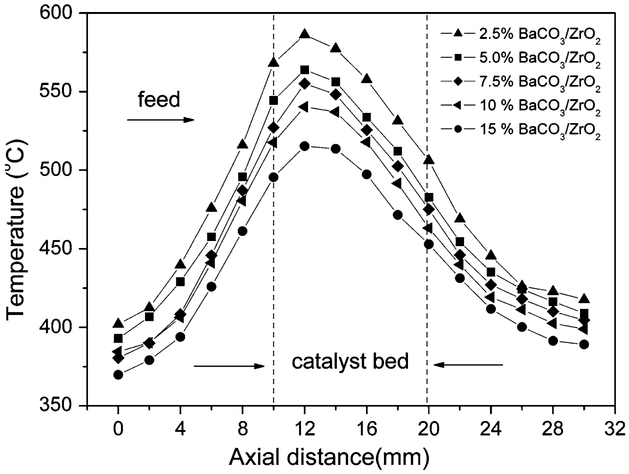

Fig. 4 Axial temperature profile in the reactor on $BaCO_3/ZrO_2$ catalyst at $CH_4/O_2 = 2.0$, GHSV = 18,000 ml/g h, Reactor temperature = 350 °C

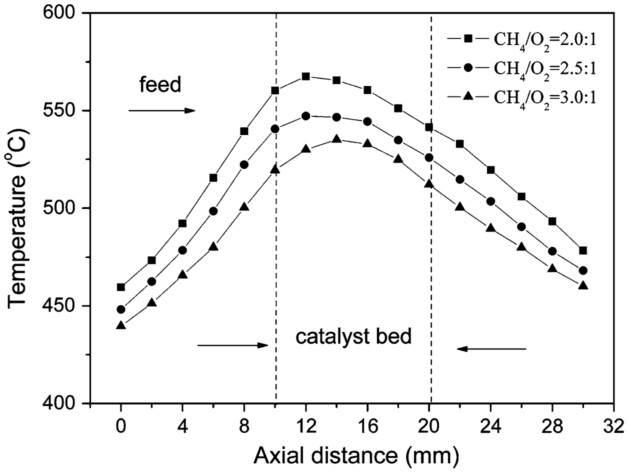

Fig. 5 Axial temperature profile in the reactor on 7.5% $BaCO_3/ZrO_2$ catalyst at GHSV = 18,000 ml/g h, Reactor temperature = 450 °C

introduced to the reactor, a rapid increase in temperature is detected near the entrance of the catalyst bed. The position of the maximum peak temperature is detected near 2 mm upstream from the entrance of the catalyst bed. This is mainly a result of thermal conductivity along the thermocouple and the wall. This phenomenon is also responsible, in part, for the broadening of the temperature profile in the catalyst bed. Similar results were obtained by Lunsford over the $Mn/Na_2WO_4/SiO_2$ and $Mn/Na_2WO_4/MgO$ catalysts [9]. The temperature of upstream is lower than that of the downstream along the direction of feed flow. This may be caused by the thermal conductivity and thermal radiation along the thermocouple and the wall. For 2.5% $BaCO_3/ZrO_2$ catalyst, the maximum peak temperature of catalyst bed is higher than those of other catalysts, which is agree with the lowest holding temperature (175 °C). At the same time, the highest peak temperature (586.2 °C) at the entrance of the catalyst bed corresponds to the highest CO_2 selectivity (Table 2). Therefore, with higher $BaCO_3$ content, the methane combustion activity of the catalysts and the maximum of temperature profile decreases gradually. Correlated with the catalytic performance, this phenomenon is agree with the change of the C_2 and CO_x selectivity over the $BaCO_3/ZrO_2$ catalysts.

Figure 5 shows the temperature profiles of 7.5% $BaCO_3/ZrO_2$ catalyst bed under different CH_4/O_2 ratio and reactor temperature = 450 °C. When the CH_4/O_2 ratio increases from 2.0 to 3.0, the position of the maximum peak temperature on the catalyst bed moves to downstream about 2 mm (Fig. 5). This may be mainly caused by the thermal conductivity along the thermocouple and the wall. The maximum peak temperature at $CH_4/O_2 = 2.0$ ratio is 117.5 °C higher than the outer reactor temperature. And even at the $CH_4/O_2 = 3.0$ ratio, the temperature increases by 85.1 °C. The decrease of the maximum peak temperature indicates that there has less methane combustion reaction with high CH_4/O_2 ratio. Correspondingly, an obvious decrease in the CH_4 conversion and CO_2 selectivity are observed (Table 3), which are correspond with the small shift decrease of the hot spot temperature.

Clearly, the exothermic oxidation reaction occurs mainly in a small volume near the entrance of the catalyst bed, producing hot spots that further accelerate the rate of reaction until the depleted. It should be noted that in all cases the O_2 is almost completely (>90%) consumed. For low-temperature OCM reaction, because of the limit of activation energy, the existence of hot spots are firstly due to the highly exothermic formation of CO_x, which consequently provides heat for the ignition of OCM reaction to produce C_2H_4 and C_2H_6. It is the thermal effect which is believed to be responsible for the OCM reaction taking place as low as 175 °C over 2.5% $BaCO_3/ZrO_2$ catalyst. So the thermal effect is a positive factor to keep the reactive activity for low-temperature OCM reaction.

4 Conclusions

The low-temperature catalytic performance of ZrO_2 for OCM reaction is observably enhanced by the addition of $BaCO_3$. The content of $BaCO_3$ has an important influence on the catalytic activity of the OCM and the holding temperature of the catalysts. The 7.5% $BaCO_3/ZrO_2$ catalyst shows excellent catalytic activity, the 35.4% CH_4 conversion and 29.5% C_2 selectivity can be achieved at 250 °C. Below 700 °C, lower temperature is benefit to suppress the deep oxidation and enhance C_2 selectivity. The magnitude of the hot spots has been characterized. The results reveal that hot spots which are due to the thermal effects of OCM reaction are responsible for the catalyst activity at low temperature. The thermal effects of OCM reaction could be properly applied as a positive factor to make the reaction in progress at low temperature.

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