Critical influence of Mn on low-temperature catalytic activity of $Mn/Na_2WO_4/SiO_2$ catalyst for oxidative coupling of methane

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Oxidative coupling of methane (OCM) was investigated in the temperature range 370–775 °C over $Mn/Na_2WO_4/SiO_2$ catalysts with different loadings of manganese in integral-mode conditions. Na_2WO_4/SiO_2 shows no activity at low temperature (370 °C), whereas Mn-doped catalyst exhibits 14% C_{2+} yield under similar reaction conditions, indicating that manganese plays a critical role in low-temperature methane coupling reaction. Partial pressure of oxygen in the feed also influences the low-temperature OCM activity of the catalysts.

KEY WORDS: oxidative coupling of methane; low-temperature activity; hot-spot and manganese.

1. Introduction

Natural gas deposits are being continually discovered at a significant rate around the world. The main constituent, methane (CH_4), is a valuable component by virtue of its heating value. However, the use of methane as a chemical feedstock has been limited because of its inherently high chemical stability. Nevertheless, with suitable chemical processes, methane directly or indirectly can be converted to active and value-added chemicals. Oxidative coupling of methane is one of the most promising routes for the direct conversion of methane to higher hydrocarbons (especially ethane and ethylene), and worldwide efforts have been made in this direction for the past 20 years [1–5].

In 1992, 1.9%Mn/5%Na_2WO_4/SiO_2 catalyst was first identified as one of the promising catalysts for the OCM reaction [6] in which tetrahedral WO_4 surface species was proposed as the OCM active site. It was suggested that manganese oxide makes the electron-transfer process easier from methane to the oxygen [7] and enhances the exchanges between gaseous and lattice oxygen [8,9], thereby increasing the catalyst activity. The catalyst was found active for periods in excess of 97 h [10,11]. Under integral conditions ethane was the primary product that readily undergoes homogeneous oxidative dehydrogenation to ethylene [11].

Although the dehydrogenation of methane was known to be thermodynamically unfavorable (equation (1)), oxidative coupling of methane and the accompanying side reactions are highly exothermic (equation (2)).

$$\Delta G^\circ_{298.15\,\mathrm{K}}\ (\mathrm{kJ/mol})$$

$$2CH_4 \rightarrow C_2H_6 + H_2 \qquad 69 \qquad (1)$$

$$6CH_4 + 5O_2 \rightarrow C_2H_6 + C_2H_4 + CO + CO_2 + 7H_2O \qquad -1792.4 \qquad (2)$$

Cameron *et al.* [12] noted that the reaction temperatures reported for most of the studies on OCM are not the actual reaction temperatures. In many cases, this is not a problem since the reactions are generally carried out in an integral mode with the oxygen consumption being almost 100%. Lunsford and Pak [10] studied the thermal effects and the temperature profile in a catalyst bed during the oxidative coupling of methane over the $Mn/Na_2WO_4/SiO_2$ catalyst. They also described the magnitude of the hot spots and their effects on catalyst performance. It was expected, because of modest activity, that the heat would be more uniform throughout the length of the catalyst bed and hence significant hot spots would not occur. However, they observed significant temperature differences at a different part of the catalyst bed. Based on the observation, they proposed that the exothermic nature of the OCM gives hot spots over the $Mn/Na_2WO_4/SiO_2$ catalyst, increasing bed temperature as large as 150 °C [10]. They also observed that the thermal effects of the catalyst were related to the $CH_4 : O_2$ ratios as well as the catalyst activity [10].

The reported studies were done at 800 °C, and to the best of our knowledge, no report has ever employed in any application of the OCM studies the "thermal effect" as an energy source for the OCM reaction at low temperature. This paper deals with the application

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of thermal effects on the low-temperature OCM activity of $Mn/Na_2WO_4/SiO_2$ catalysts with different loadings of the manganese. Results reveal that hot spots, which are due to the thermal effects of the OCM reaction, seem to consist of the highly active intermediates as well as heat and are responsible for the catalyst activity at low temperatures. The nature of these spots, however, depends on the $CH_4:O_2$ ratio as well as the catalyst activity. Manganese has a critical effect on the low-temperature catalyst activity and is found to promote the Na_2WO_4/SiO_2 catalyst. Also, the low-temperature catalytic activity over $Mn/Na_2WO_4/SiO_2$ depends on the partial pressure of oxygen.

2. Experimental

2.1. Catalyst preparation

n% $Mn/5\%Na_2WO_4/SiO_2$ catalysts ($n = 0.5$, 1, 2 and 4) were prepared using a sequential impregnation method as described by Malekzadeh *et al.* [7]. An aqueous solution of manganese nitrate salt of appropriate concentration was impregnated into the 60–100 mesh size silica gel (Davisil, grade 645 from Aldrich). The impregnated catalyst was dried at 120 °C overnight. A dried sample was impregnated with an aqueous solution of an appropriate concentration of sodium tungstate and was dried at 120 °C overnight, followed by calcination at 800 °C for 8 h. 5% Na_2WO_4/SiO_2 catalyst was prepared following a similar procedure as above, using an aqueous solution of an appropriate concentration of sodium tungstate.

2.2. Temperature-programmed reduction (TPR) studies

Temperature-programmed reduction studies were performed in a conventional temperature program reduction–oxidation apparatus (Chembet-3000) using 2.7% H_2 in N_2. The gas stream (30 mL/min) was used through a quartz reactor containing 60 mg of the fresh catalyst. Each run was conducted between the ambient temperature and 1000 °C at a heating rate of 10 °C/min.

2.3. Catalyst activity

Catalytic oxidative coupling of methane over the $Mn/Na_2WO_4/SiO_2$ catalysts was carried out in the integral-mode conditions using a fixed-bed quartz reactor at ambient pressure. The reactor was filled with a small amount of ceramic wool below the catalyst bed, where the diameter of the reactor decreased (figure 1(a) and (b)) in order to minimize any reaction that might occur in the post-catalytic volume. 500 mg of each fresh catalyst was used in each experiment at a feed ($CH_4 + O_2$) flow rate of 135 mL/min (STP) (*i.e.*, at a gas hourly space velocity (GHSV) of 16 200 cm^3/hg_{cat}) without any diluents. The volume of the catalyst bed was approximately 1.1 mL and its length was almost 10 mm. The reaction temperature was measured using a thermocouple attached to the outer wall of the reactor, centered along the catalyst bed. First, catalysts were heated to 800 °C in an oxygen flow rate of 5 mL/min. Temperature was decreased to 600 °C and the performance test was carried out after adjusting the flow rate of gases followed by steady-state operation. Blank runs with ceramic wool and with an empty reactor showed conversion less than 1% at the reaction conditions. The products were detected using a TC detector for detecting carbon dioxide, carbon monoxide and unreacted oxygen, and an FI detector was used for detecting the C_{2+} hydrocarbons and unreacted methane. The hot spot was characterized inserting a thermocouple (movable within a quartz thermo-well, od = 0.5 mm) inside the reactor tube.

3. Results and discussion

The BET surface area, pore volume and pore size of the SiO_2 support were measured as 310 m^2 g, 0.114 cm^3 g and 147 Å, respectively. After impregnation of manganese nitrate and sodium tungstate followed by calcination at 800 °C, these values were reduced to 1–2.4 m^2 g, 0.005–0.004 cm^3 g and 13–69 Å, indicating a drastic change in the structure of the support material.

3.1. Temperature-programmed reduction (TPR)

Temperature-programmed reduction (TPR) patterns for the fresh Na_2WO_4/SiO_2 and Mn-doped Na_2WO_4/SiO_2 catalysts calcined at 800 °C are presented in figure 2. Trace (a) shows a broad peak due to hydrogen consumption starting at about 700 °C and the peak which is associated with tungstate reduction attains its maximum at high temperature (about 980 °C). This profile is almost similar to that reported previously by Jiang *et al.* [9] and Lambert *et al.* [13]. The broad TPR peaks reveal that reduction of the tungstate component may go through some transition states with the temperature. However, the interaction of tungsten ion, in different oxidation states, with the silica support or manganese cannot be ruled out.

On the basis of O_2 TPD, Liu *et al.* [14] reported that desorption of surface oxygen takes place at about 800 °C. Also, the oxygen desorption peak at higher temperature (850 °C) was attributed to the bulk oxygen, which is accountable for both methane activation and deep oxidation [14]. In the present study, observation of high-temperature broad reduction peaks could be due to the elimination (reduction) of the oxygen from different parts of the catalyst. Similarly, broad features of traces (b), (c), (d) and (e) in figure 2 at elevated temperature ($\geq$800 °C) are the tungstate-reduction features

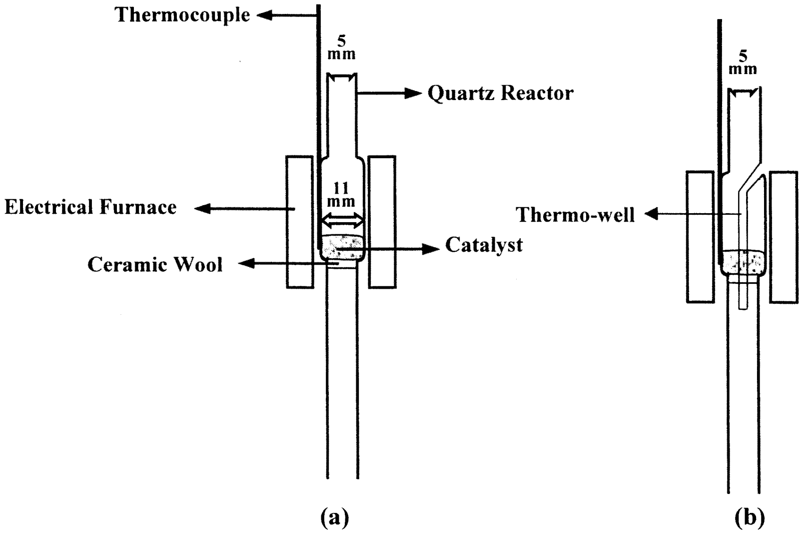

Figure 1. Reactor and furnace system. (a) Unmodified and (b) modified or new reactor.

in the $Mn/Na_2WO_4/SiO_2$ catalysts. It is observed that the characteristic reduction temperature of the tungstate shifts to higher values in the $Mn/Na_2WO_4/SiO_2$ catalyst. Similar observations were reported earlier [9,13]. Traces (b), (c), (d) and (e) show that the tungstate reduction starts at about 800 °C. An increase in the manganese loading shifts the tungstate-reduction characteristic peak slightly to lower temperature and also favors tungstate reduction in a narrower temperature range. These results suggest that increase in manganese loading increases the interaction between tungstate and silica support. At least manganese equimolar with tungstate ($Mn:WO_4^{2-} = 1$) is critical for it (trace (c)).

3.2. Oxidative coupling of methane

Table 1 shows the effect of methane to oxygen ratio on threshold temperatures over catalysts with different manganese loading. It may be noted here that the temperature at which OCM activity begins is defined as the

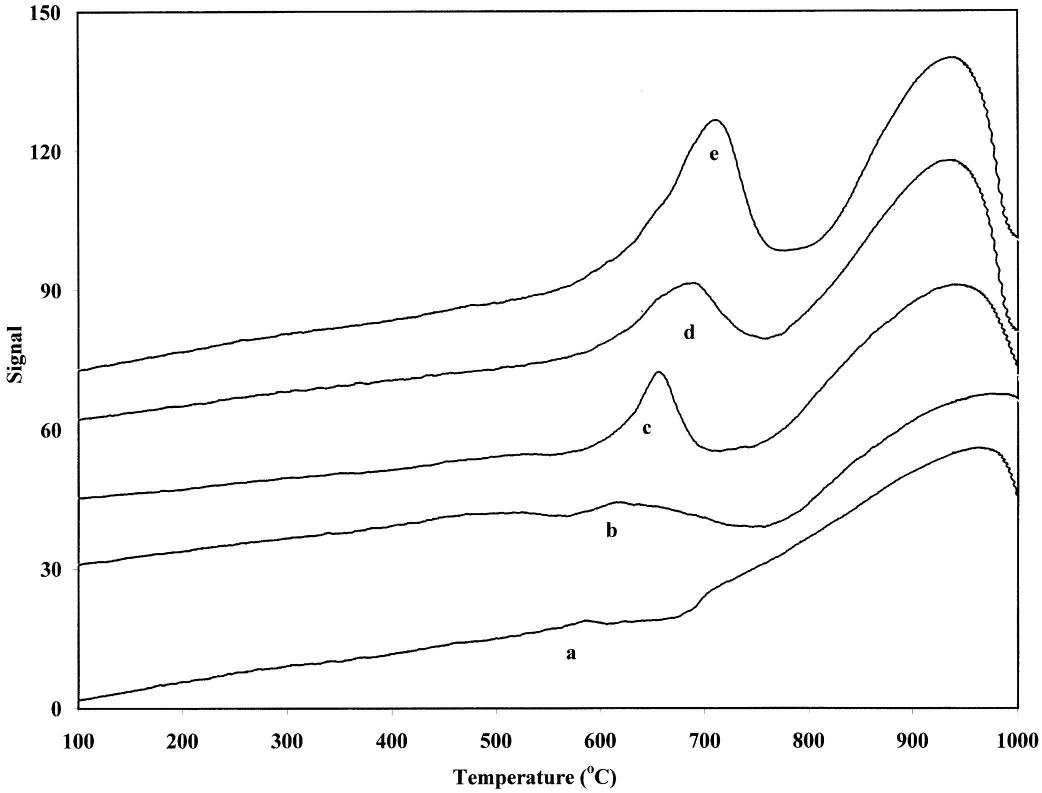

Figure 2. TPR results of n% $Mn/Na_2WO_4/SiO_2$ catalysts. n is (a) 0, (b) 0.5%, (c) 1%, (d) 2% and (e) 4%.

Table 1
Threshold temperatures for OCM over various Mn-promoted Na_2WO_4/SiO_2 catalysts at $CH_4:O_2$ ratios of 2–7.5.

Catalyst	$CH_4:O_2$ ratio		
	2	4	7.5
Na_2WO_4/SiO_2	775 °C	775 °C	775 °C
0.5% $Mn/Na_2WO_4/SiO_2$	720 °C	740 °C	775 °C
1% $Mn/Na_2WO_4/SiO_2$	720 °C	740 °C	775 °C
2% $Mn/Na_2WO_4/SiO_2$	720 °C	740 °C	775 °C
4% $Mn/Na_2WO_4/SiO_2$	720 °C	740 °C	775 °C

Table 2
Catalyst performance over $Mn/Na_2WO_4/SiO_2$ catalysts at $CH_4:O_2$ ratio of 7.5 at 775 °C and GHSV of 16 200 cm^3/hg_{cat}.

Catalyst	CH_4 conversion (mol%)	C_{2+} selectivity	C_{2+} yield (mol%)	$C_2H_4:C_2H_6$ ratio
Na_2WO_4/SiO_2	7	40	3	0.4
0.5% $Mn/Na_2WO_4/SiO_2$	23	75	17	1.4
1% $Mn/Na_2WO_4/SiO_2$	22	81	18	1.3
2% $Mn/Na_2WO_4/SiO_2$	24	77	18	1.4
4% $Mn/Na_2WO_4/SiO_2$	20	76	15	1.4

threshold temperature. It is seen that the sample loaded with manganese required significantly lower temperature than that without manganese to begin the OCM activity, of course at low methane to oxygen ratio. However, at high ratio ($CH_4:O_2 = 7.5$) the threshold temperatures were the same for all the catalyst samples. These results suggest that threshold temperature depends both on methane to oxygen ratio and on manganese loading. In an earlier study, it was reported that manganese loading on Na_2WO_4/SiO_2 drastically increases the electrical conductivity during OCM activity as well as increases methane conversion and C_2 product selectivity [7]. It is known that nucleophilic oxy-species such as O_2^-, O_2^{2-} and O^- are highly reactive and can abstract hydrogen from methane [15]. Impregnation of manganese probably helps in forming these species at lower temperature than that of the catalyst without manganese, thereby increasing methane conversion and product selectivity. The data in table 1 also indicate that a low quantity of manganese loading (only 0.5 wt%) is enough to bring the threshold temperature down to 720 °C from 775 °C. Higher amounts of manganese loadings (>0.5 wt%) did not change the threshold temperature; however, they affect product selectivity (*cf* table 2), probably due to the formation of multilayers of manganese oxide that affect generation of nucleophilic oxy species.

Different threshold temperatures at various $CH_4:O_2$ ratios over an active catalyst like $Mn/Na_2WO_4/SiO_2$ indicate that the activation energy depends on the oxygen partial pressure in the feed. Reaction initiation was always accompanied by a temperature rise (measured by the external thermocouple attached to the reactor), and the extent of temperature rise was found to depend on the $CH_4:O_2$ ratio. For example, with $CH_4:O_2 = 7.5$, the temperature was increased by about 20 °C after the reaction began at 775 °C, and a CH_4 conversion of 24 mol% was observed. In the case of the $CH_4:O_2 = 4$, the temperature increased by 25 °C, and when the $CH_4:O_2 = 2$ the increase in temperature was about 50 °C higher than the threshold temperature (*cf* table 1). The temperature rise after reaction genesis is due to the exothermicity (equation (2)), which gives rise to the hot spot in the catalyst bed. While trying to investigate the nature of the hot spot and catalyst activity below its threshold temperature (which was 720 °C) it was observed that the reaction could be kept alive at 370 °C with a methane to oxygen ratio of 2, and with an increase in this ratio from 2 to 7 the threshold temperature and the temperature to which the activity can be kept alive increased significantly (*cf* table 1 and figure 3, note that the conversion at 370 °C for a $CH_4:O_2$ ratio of 2 is not shown in figure 3). To characterize the hot spot in the catalyst bed a new reactor was designed, the details of which are described in the following section.

3.3. Characterization of the hot spot

The existence of the hot spot inside the catalyst bed, during the OCM reaction, was observed by previous researchers [2,4]. As described above, in our experiments, we also noticed a significant rise in the reactor temperature (measured by the thermocouple attached to the outer surface of the reactor). Assuming that this rise in temperature was due to formation of the hot spot, a new reactor was designed of dimensions the same as the one used above (*cf* figure 1(a)), except that in the new reactor a thermo-well of outer diameter 0.5 mm was built (*cf* figure 1(b)). A type 'K' thermocouple, which was movable inside the thermo-well, was used to measure the catalyst-bed temperature. It may be noted here that the catalyst-bed height was increased by 2 mm compared to the one in the unmodified reactor. As observed, the catalyst-bed temperature at the hottest spot was 135–140 °C higher than the furnace temperature (*cf* figure 4). This observation is in agreement with the earlier report by Pak and Lunsford [10], who also observed a similar rise in the catalyst-bed temperature over the manganese-loaded Na_2WO_4/SiO_2 catalyst. To investigate catalyst activity below the threshold value and to study the movement of the hot spot down the catalyst bed, a time-on-stream OCM reaction was carried out at a furnace temperature of 720 °C for about 23 h. The catalyst-bed temperatures at various bed depths were recorded (*cf* figure 4). The data indicate that a hot spot is formed at around 4 mm down the catalyst bed. Also, the hot spot did not move down the catalyst bed in 22.5 h of time-on-stream study. It may be noted here that the catalyst-bed temperature was measured over a

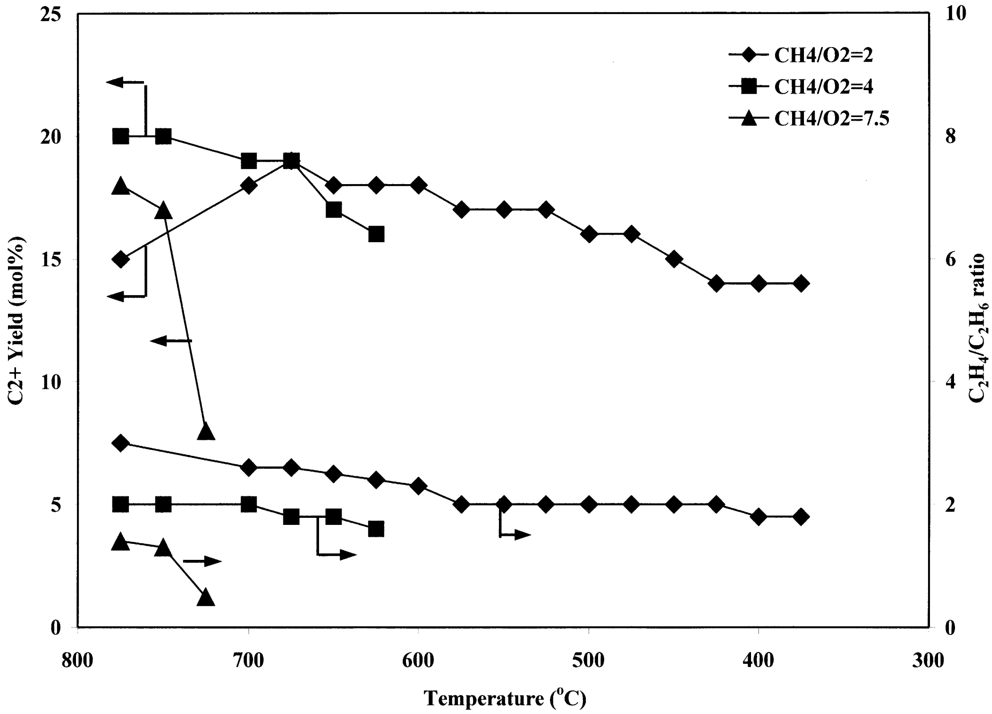

Figure 3. Catalyst performance and $C_2H_4:C_2H_6$ ratio in product gas over 2% Mn/Na$_2$WO$_4$/SiO$_2$ catalyst as a function of reactor temperature. Reaction conditions: $CH_4/O_2 = 2$, GHSV = 16 200 cm^3/hg$_{cat}$.

catalyst-bed depth of 12 mm, *i.e.*, from top to bottom (*cf* figure 1(b)). Pak and Lunsford [10] in their experiment observed movement of the hot spot in the catalyst bed. However, they did not report any result on the activity of the catalyst below its threshold temperature, which was 800 °C. To investigate catalyst activity below the threshold temperature a time-on-stream reaction was performed at 370 °C. The C_2^+ yield in this case was maintained at ~14 mol% (*cf* figure 5). It may be noted here that a C_2^+ yield of 18 mol% was obtained for a period of 170 h at 775 °C, indicating that the catalyst was quite active for a long period of time (data not presented). On the other hand, the reaction failed after about 2 h of time-on-stream at 370 °C (*cf* figure 5). The original activity in this case could be recovered again by simply increasing the temperature to 720 °C.

The activity failure during the time-on-stream study could be due to catalyst deactivation by the deposition

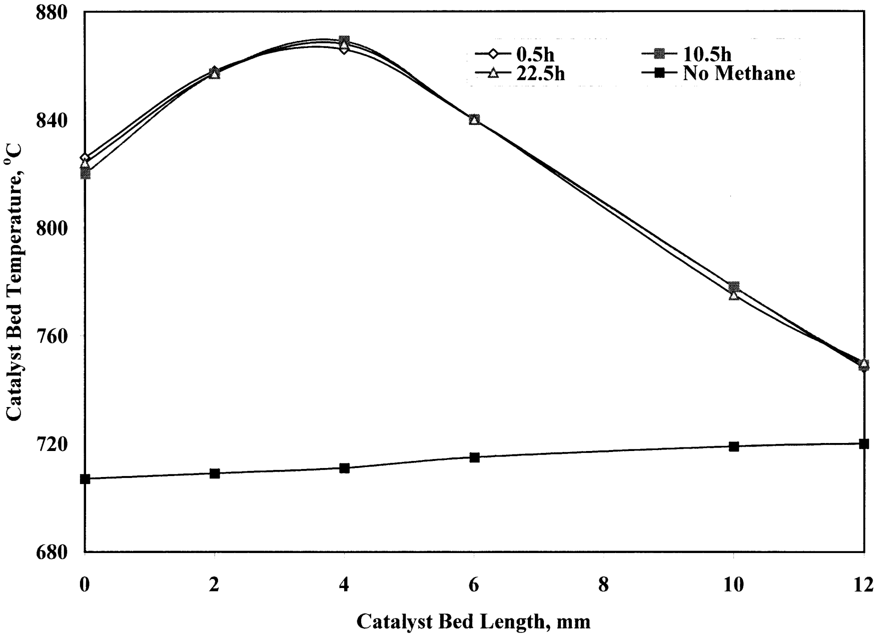

Figure 4. Effect of time-on-stream on the movement of the hot spot down the catalyst bed. Reaction conditions: $CH_4/O_2 = 2$, GHSV = 16 200 cm^3/hg$_{cat}$.

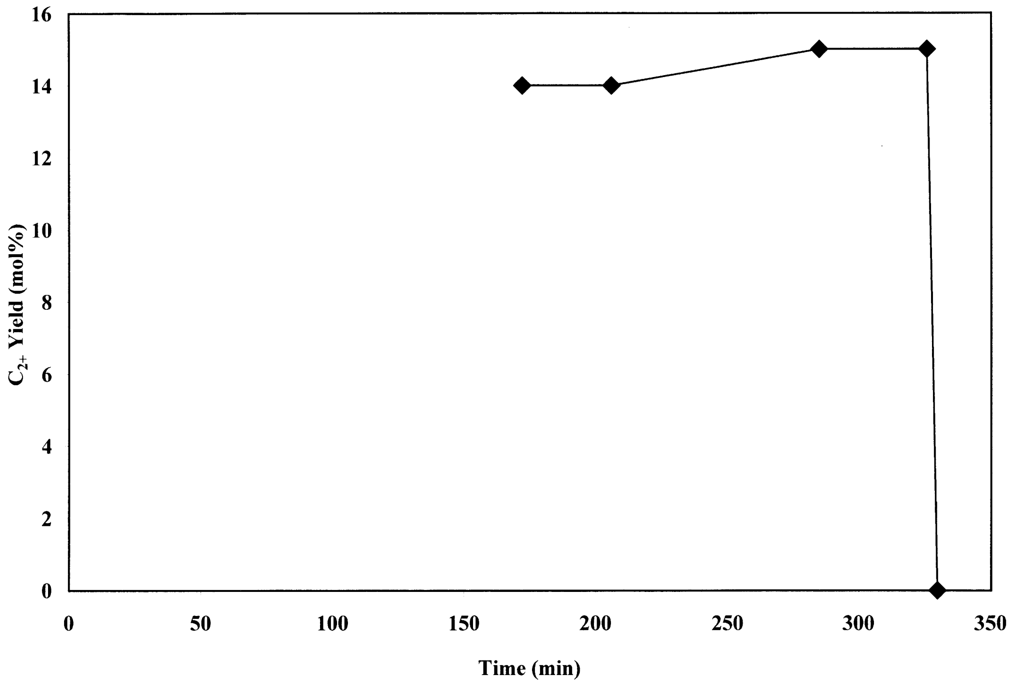

Figure 5. Catalyst performance over 2% $Mn/Na_2WO_4/SiO_2$ catalyst on stream at 370 °C.

of carbonaceous material. To verify this, catalysts used at 720 °C and 370 °C (used for time-on-stream as in the case of table 1 and figure 5, respectively) were analyzed for carbon. However, they showed no carbon, indicating that the sudden failure of the reaction at 370 °C is not due to the carbon deposition on the catalyst surface. Initially, it was speculated that the reaction failure at 370 °C could be due to movement of the hot spot in the catalyst bed as a function of reaction time. Pak and Lunsford [10] showed that after 16 h of TOS over the $Mn/Na_2WO_4/SiO_2$ catalyst the hot spot is moved by 4 mm. However, contrary to their observation we did not see any movement of the hot spot (*cf* figure 4) even after 22.5 h of TOS. In another experiment (*cf* figure 6), it was observed that with a decrease in furnace temperature (measured by the external thermocouple), below its threshold value,

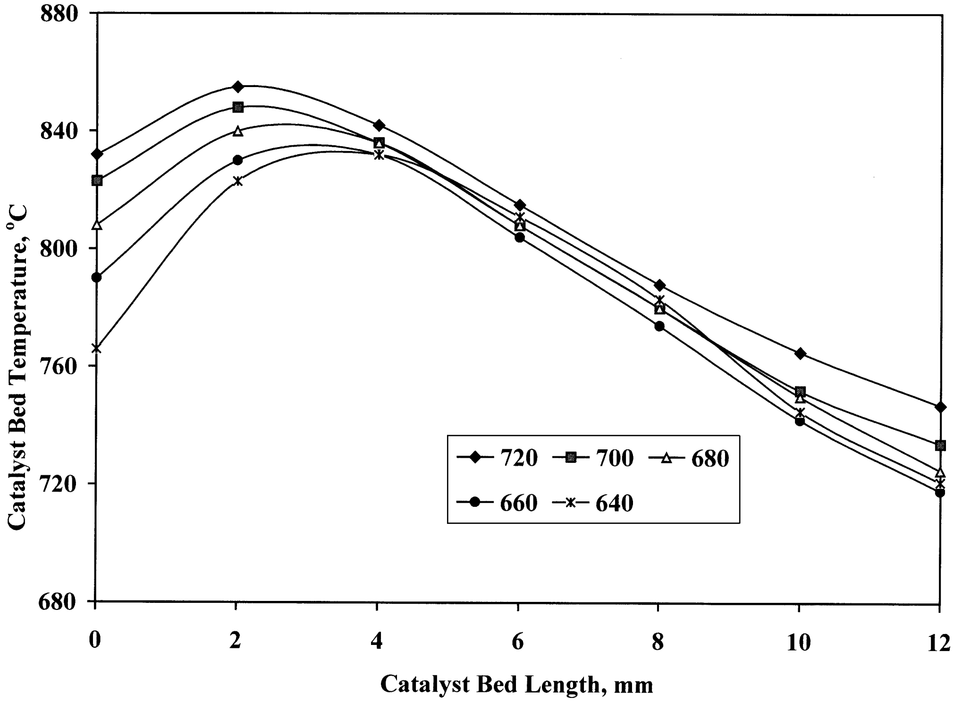

Figure 6. Effect of variation in furnace temperature on the movement of the hot spot down the catalyst bed. Reaction conditions: $CH_4/O_2 = 2$, GHSV = 16 200 cm^3/hg_{cat}.

the location of the hottest spot gradually moved down the catalyst bed. The details of the observation at steady-state conditions at different furnace temperatures reveal that the location of the hottest spot is shifted by 2 mm with a decrease in furnace temperature by about 80 °C (from 720 to 640 °C). It may be noted here that the reaction was traced back to 640 °C. The reaction failure below 640 °C in the case of a modified reactor may be due to the relative flattening of the temperature-distribution curve across the catalyst bed, indicating a more uniform distribution of temperature that ultimately destroys the hot spot. This probably suggests that due to the more uniform temperature profile in the catalyst bed the OCM activity failed at 370 °C (*cf* figure 5).

Formation of the C_{2+} hydrocarbons below the threshold temperature suggests that hot spots, which emerge during the oxidative coupling of methane reactions, seem to contain highly reactive intermediates as well as heat energy. These energy sources containing highly reactive intermediates are capable of activating methane and oxygen and protecting the reaction, particularly at low temperatures. Utilization of hot spots as an energy source of the endothermic OCM reactions, which are methane C–H and oxygen activation on the catalyst surface, is limited to the quantity and distribution of the OCM thermal effects. In the $Mn/Na_2WO_4/SiO_2$ catalyst, manganese is responsible for the high catalytic activity.

4. Conclusions

It can be concluded that the hot spots, which are the effects of the OCM exothermicity, are a suitable source for protecting catalytic activity at low temperature over $Mn/Na_2WO_4/SiO_2$ catalysts with different loading of the manganese. Manganese is critical for the low-temperature catalytic activity. However, the activity is independent of the manganese loading. High activity and reasonable C_2H_4/C_2H_6 fraction in the product gas (about 2) at low temperature (370 °C) suggest that the hot spots contain highly reactive intermediates and are contained in the catalyst matrix. Low-temperature catalytic activity depends on both the amount and the distribution of the hot spots. The thermal effects of the OCM reaction depend on the $CH_4:O_2$ ratio as well as on the catalyst activity. The threshold temperature of the catalyst activity also depends on the $CH_4:O_2$ ratio.

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