JOURNAL OF CATALYSIS **179,** 222–230 (1998)
ARTICLE NO. CA982228

Elementary Reactions in the Oxidative Coupling of Methane over $Mn/Na_2WO_4/SiO_2$ and $Mn/Na_2WO_4/MgO$ Catalysts

Sergei Pak, Ping Qiu, and Jack H. Lunsford[1]

Department of Chemistry, Texas A&M University, College Station, Texas 77843

Received January 21, 1998; revised July 7, 1998; accepted July 10, 1998

Although it is possible to achieve 20% CH_4 conversion and 80% C_{2+} selectivity during the oxidative coupling of CH_4 (OCM) over $Mn/Na_2WO_4/SiO_2$ and $Mn/Na_2WO_4/MgO$ catalysts at 800°C, these materials are considerably less active than a Sr/La_2O_3 catalyst. Similarly, the SiO_2- and MgO-based catalysts are less active in the formation of $CH_3\cdot$ radicals that emanate into the gas phase and in the secondary reaction of these radicals with the catalysts. During the OCM reaction, ethane is the primary product; ethylene is produced only in small amounts at short contact times. As a secondary product, however, ethylene competes with methane in the formation of carbon dioxide. The conversion of C_2H_4 to CO_2 at 800°C is largely a result of a heterogeneous reaction, due to the inhibiting effect of CH_4 on the gas phase oxidation reaction. Pulse experiments demonstrated that the presence of gas phase O_2 is essential for obtaining an active catalyst. Presumably, an endothermic equilibrium reaction involving O_2 results in a form of surface oxygen that is capable of abstracting a hydrogen atom from CH_4. The unusually large activation energy of ca. 63 kcal/mol for both catalysts may result, in part, from this oxygen equilibrium. © 1998 Academic Press

INTRODUCTION

One of the most effective catalysts for the oxidative coupling of methane (OCM) is $Mn/Na_2WO_4/SiO_2$, which was first reported by Fang *et al.* (1). With this catalyst, it is possible to obtain in the single-pass mode, a C_{2+} selectivity of 80% at a CH_4 conversion of 20% for periods in excess of 97 h (2,3). In a recycle mode with continuous removal of alkenes, yields of *ethylene* in excess of 70% have been achieved (4). Similar single-pass selectivities and conversions have been obtained with the related $Mn/Na_2WO_4/MgO$ catalyst, although this material deactivates with time on stream (2,3).

Fundamental studies have been carried out to determine the active components on the surface. Jiang *et al.* (5) concluded that a surface W species containing a W=O and three W-O-Si bonds is responsible for the OCM reaction; whereas, manganese oxide, present as Mn_2O_3 promotes lattice oxygen transport. By contrast, Wang *et al.* (2) suggested that a Na-O-Mn species is responsible for the activation of methane. The loss of activity in the $Mn/Na_2WO_4/MgO$ catalyst is attributed to the decrease in the Mn concentration at the surface (3). The active species is not stable unless gas phase O_2 is present.

The goal of this study was to obtain reliable kinetic data under controlled conditions so that questions concerning the reaction mechanism could be addressed. Since the OCM reaction is exothermic, one must be concerned with thermal effects in the catalyst. It has been demonstrated that under integral conditions, narrow zones may exist in the catalyst bed which are 150°C greater in temperature than the walls of the reactor (3). Obviously, such hot spots make it difficult to obtain accurate kinetic data. Other significant issues center on the role of $CH_3\cdot$ radicals in the coupling reaction (6). One might speculate that the high selectivities obtained at modest conversions indicate a different mechanism which involves only surface chemistry. Carbene intermediates, for example, might give ethylene as a primary product. A related question concerns the origin of CO_2. Is it formed from CH_4 via the reaction of $CH_3\cdot$ radicals, or is C_2H_4 an important source of CO_2, as is observed over other OCM catalysts (7,8)? Control over the CO_2-forming reactions clearly is important for obtaining high C_2 selectivities and yields.

EXPERIMENTAL

Catalysts

The method for catalyst preparation was similar to that described previously (2); however, additional details are given here. A catalyst containing 2 wt% Mn and 5 wt% Na_2WO_4 on SiO_2 ($Mn/Na_2WO_4/SiO_2$) was prepared by incipient wetness, using 20–40 mesh size Davison grade 57 silica gel. Ten ml of aqueous solution containing 0.70 g of $Mn(NO_3)$ were added to 5 g of silica gel at 85°C. This material was then dried in air at 130°C for 5 h. After cooling to 25°C, 10 ml of solution containing 0.27 g of Na_2WO_4 was added to the solid. The catalyst was dried at 130°C for 8 h and was calcined in air at 800°C for 8 h. A catalyst containing 2 wt% Mn and 5 wt% Na_2WO_4 on MgO

0021-9517/98 $25.00

($Mn/Na_2WO_4/MgO$) was prepared by slurrying MgO (Fisher "light," M-349-4) with H_2O at boiling conditions in a 500-ml, 3-neck, round-bottomed flask, equipped with a funnel and a water-cooled condenser. Appropriate amounts of $Mn(NO_3)_2$ and Na_2WO_4 were added to the boiling slurry over a 15 min period. After maintaining these conditions for 30 min, the flask was opened to the atmosphere (no condenser), and the slurry was converted to a thick paste, which was dried at 130°C for 5 h. The resulting material was then calcined at 800°C for 8 h. For most experiments, 20–45 mesh size catalyst particles were used; however, for the pulse experiments, 45–80 mesh size particles were used to provide better contact between catalyst granules and the thermocouple well. The 1 wt% Sr/La_2O_3 catalyst was provided by Amoco.

Reactor Systems

Reactions were carried out at a total pressure of 760 torr in the differential mode using three different reactors that were constructed of fused-quartz tubing. In one reactor, depicted in Fig. 1a, the internal diameter decreased from 7 mm to 2 mm. The catalyst bed was located above and in the volume where the diameter decreased in order to minimize any reactions that might occur in the postcatalytic volume. Quartz chips were placed above and below the catalyst bed to preheat the reagents and to decrease the free volume. A similar microreactor, depicted in Fig. 1b, had a heated zone only 15 mm in length in order to minimize noncatalytic reactions. The third reactor, used in the pulse experiments, consisted of a 4-mm ID fused-quartz tube.

For more accurate measurement of the catalyst temperature during the exothermic reactions, a small diameter, thin-walled quartz capillary (ca 1.5-mm OD) was used as a thermocouple well. This well was placed in the center, along the axis of the catalyst bed. The thermocouple, which was 0.5-mm OD, could be moved easily in the well, allowing the measurement of the temperature along the length of the catalyst bed.

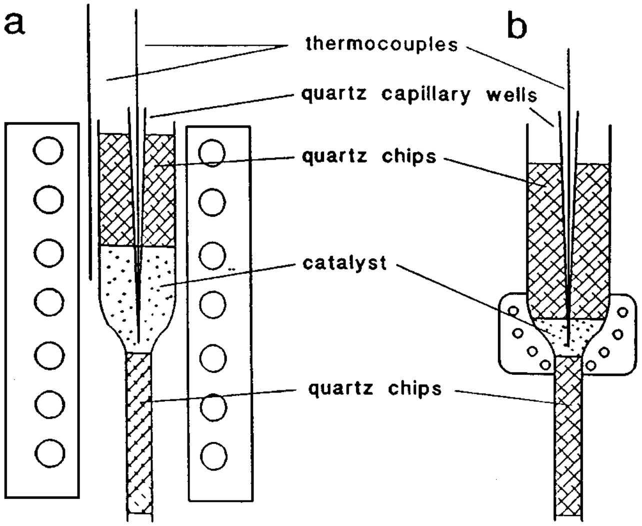

FIG. 1. Fused-quartz reactors: (a) reactor used under integral and differential conditions; (b) reactor with a minimum heated volume.

A recycle system, described in detail previously (7), was used to investigate the origin of CO_x. In the recycle system a certain amount of isotopically labeled material could be added to the reagent gases (CH_4, O_2, and He). After mixing the gases in a circulation loop, they were diverted over the catalyst which had been at a predetermined temperature. A GC/MS system that consisted of a Hewlett-Packard Model 5890 gas chromatograph with a Model 5971 mass selective detector was used to analyze the gases and determine their isotopic composition.

The formation and reactions of methyl radicals were studied using the matrix isolation electron spin resonance (MIESR) system that has been described previously (9). The formation of $CH_3\cdot$ radicals was determined both in the low pressure mode ($P(\text{total}) \simeq 1$ torr) and in the high pressure mode ($P(\text{total}) = 760$ torr).

Secondary reactions of $CH_3\cdot$ radicals with the catalysts were determined using the method of Tong *et al.* (10), in which $CH_3\cdot$ radicals are generated over one catalyst (Sm_2O_3) and reacted over a second catalyst. The second catalyst is generally at a sufficiently low temperature so that its rate of radical production is small. The distance between the radical generator and the scavenger was ca. 12 cm, and the pressure in this region was ca. 1 torr. Reaction efficiencies (RE) of the oxides are reported relative to quartz chips by using the equation

$$\%\mathrm{RE} = \frac{[\mathrm{CH_3}\cdot]_Q - [\mathrm{CH_3}\cdot]_S}{[\mathrm{CH_3}\cdot]_Q} \times 100, \qquad [1]$$

where $[CH_3\cdot]_Q$ and $[CH_3\cdot]_S$ are the radical amounts determined by ESR using quartz chips and the oxide of interest, respectively, as the scavenger.

RESULTS AND DISCUSSION

Kinetic Parameters

As noted above, it has been observed that "hot spots," or large axial temperature gradients, are present in the catalyst bed when the reaction is carried out under integral conditions (3). To minimize these large temperature gradients and to achieve differential conditions, small amounts of catalyst (20–40 mg or 4–6 mm of bed thickness) were used for the kinetic studies. But even under these conditions the temperature in the catalyst bed increased dramatically when the reaction was initiated. At the beginning of the reaction over the MgO-based catalyst, the temperature in the bed was 882°C while the temperature measure at the wall was 800°C. With time on stream the CH_4

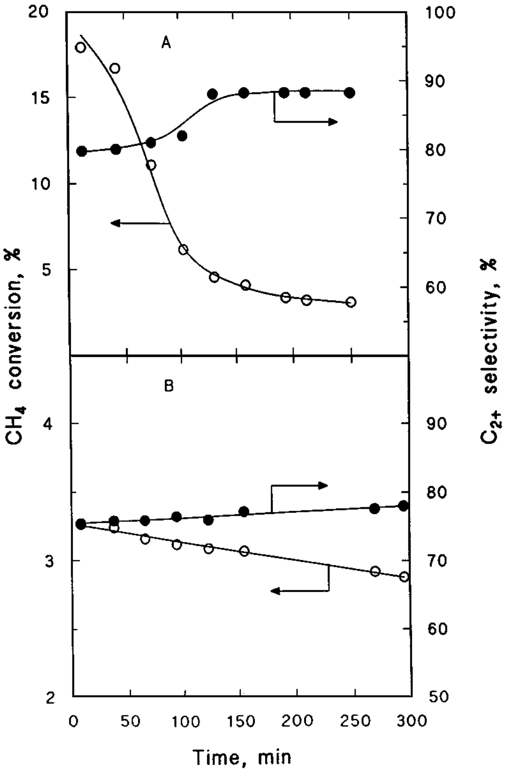

FIG. 2. Variation in conversion (○) and selectivity (●) with time on stream over a (A) $Mn/Na_2WO_4/MgO$ and (B) $Mn/Na_2WO_4/SiO_2$: 40-mg catalyst, T(reactor) = 800°C, $CH_4/O_2 = 7.4$, 110 ml/min (STP) flow rate.

conversion decreased and the C_{2+} selectivity increased, as shown in Fig. 2a. Correspondingly, after steady state was reached (ca. 200 min) the temperature of the catalyst decreased to 807°C. Similar effects were noted for the SiO_2-based catalyst as shown in Fig. 2b, although the initial activity and the decline in activity were not as large. The temperature of the SiO_2-based catalyst was comparable to that of the steady state MgO-based catalyst. It is surprising that the SiO_2-based catalyst declined at all because in the integral mode, the motion of the hot spot along the length of the catalyst bed was small over a 97 h period (3). Apparently the thermal effect (i.e., the hot spot) masks the deactivation in a larger catalyst bed since it was found that with partially deactivated catalysts, the original 20% CH_4 conversion and 80% C_{2+} selectivity could be recovered by simply increasing the temperature.

The specific activities for CH_4 conversion over the $Mn/Na_2WO_4/SiO_2$ and $Mn/Na_2WO_4/MgO$ catalysts were obtained under nearly steady state conditions and the results are compared in Table 1. The Sr/La_2O_3 catalyst is included for reference purposes since it is known to be very active (11). Because of the high activity and the problem of hot spots, the rate for this catalyst was obtained over the temperature range 694°C–722°C and was extrapolated to 800°C. The SiO_2- and MgO-based catalysts have comparable activities per unit of mass, but the activity based on surface area is much greater over the $Mn/Na_2WO_4/SiO_2$ catalyst. Both of these catalysts are considerably less active than the Sr/La_2O_3 catalyst.

Activation energies were determined for the steady state SiO_2- and MgO-based catalysts, using a loading of 40 mg, 110 ml/min flow rate, and a CH_4/O_2 ratio of 7.4 with no diluent. The values of the activation energies were 63 and 64 kcal/mol for the $Mn/Na_2WO_4/MgO$ and $Mn/Na_2WO_4/SiO_2$ catalysts, respectively, which supports the earlier conclusion that the same active component exists on both materials. Wu and Li (12) reported a value of 58.1 kcal/mol for the reaction over a $Mn/Na_2WO_4/SiO_2$ catalyst. These activation energies are unusually large for the OCM reaction, particularly since there was only a small CO_2 poisoning effect with these catalysts (2,13).

There was concern that the unusually large E_a's may have resulted from temperature gradients within the catalyst particles; therefore, additional experiments were carried out with a diluent added to the reagent gases. Helium was chosen as the diluent because of its relatively large thermal conductivity. At the same reaction conditions, but with $CH_4/O_2/He = 7.4/1/25$, activation energies of 64 and 67 kcal/mol were obtained for the $Mn/Na_2WO_4/MgO$ and $Mn/Na_2WO_4/SiO_2$ catalysts, respectively. The value for the MgO-based catalyst was essentially the same as that obtained with the undiluted stream and the value for the SiO_2-based catalyst was somewhat larger. Thus, it appears that the large activation energies are an intrinsic property of these catalysts and are not an artifact of the exothermic reaction.

Orders of reaction with respect to CH_4 and O_2 also were determined at 800°C over 40 mg of catalyst at a flow rate of 105 ml/min. In one set of experiments, the O_2 pressure was kept at 36 torr while the CH_4 pressure was varied from 181 to 724 torr; whereas, in another set of experiments the CH_4 pressure was kept at 608 torr while the O_2 pressure was varied from 30 to 122 torr. Again, the effect of CO_2 was not a concern. Over the $Mn/Na_2WO_4/SiO_2$ catalyst, the orders of reaction with respect to O_2 and CH_4 were 0.53 and 1.05; over

TABLE 1

Comparison of Rates for Methane Conversion

Catalyst	Surface area[a] m^2/g	Rate of conversion $\mu mol/g \cdot s$	$\mu mol/m^2 \cdot s$
$Mn/Na_2WO_4/MgO$[b]	4.5	30	7
$Mn/Na_2WO_4/SiO_2$[b]	0.7	30	42
Sr/La_2O_3[c]	7.6	1900	250

[a] For used catalysts.

[b] 40 mg of catalyst; $CH_4/O_2 = 7.4$; flow rate = 110 ml/min; $T = 800°C$.

[c] 10 mg of catalyst; $CH_4/O_2 = 7.4$; flow rate = 267 ml/min; reaction rates were obtained in the temperature range 694–772°C, and the results were extrapolated to 800°C.

the $Mn/Na_2WO_4/MgO$ catalyst, the corresponding orders were 0.48 and 0.98. These orders of reaction are consistent with a general mechanism of the type

$$O_2 \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} 2O_s, \qquad \text{fast}, \qquad [2]$$

$$CH_4 + O_s \xrightarrow{k_3} CH_3\cdot + OH_s, \qquad \text{slow}, \qquad [3]$$

where O_s and OH_s are believed to exist as surface ions. The fact that reaction [3] is rate limiting does not negate the role of temperature on the equilibrium for reaction [2], which may give rise to the large E_a's that were observed. That is, if reaction [2] were endothermic (contrary to what might be expected for simple dissociative adsorption of O_2), then E_a could be considerably larger than E_3 since $E_a = E_3 + \Delta H/2$. Here, ΔH is the heat of reaction [2].

Primary Products

Although it is generally accepted that C_2H_4 is formed via the reaction sequence

$$CH_4 \rightarrow C_2H_6 \rightarrow C_2H_4, \qquad [4]$$

it was of interest to determine whether C_2H_4 might be formed directly from CH_4. Hutchings and co-workers (14) have examined this direct pathway over a Li/MgO catalyst and concluded that a very small amount of C_2H_4 might occur by a direct route. In the present study, small loadings of catalysts (20 mg) were used, along with high flow rates of the methane and oxygen mixtures. The results of Fig. 3 show that at low conversions and short residence times the main product was C_2H_6. Nevertheless, the selectivity of C_2H_4 did not extrapolate zero at zero residence time, even when the results were corrected for the partial conversion of C_2H_4 to CO_2. At the highest flow rates used, the ethylene selectivities were from 5–8%. Similar results were obtained when the flow rate was kept constant but the amount of catalyst was decreased to 10 mg.

To confirm these results, similar experiments were carried out in the reactor depicted in Fig. 1b, which was designed to minimize the homogeneous oxidative dehydrogenation of C_2H_6 to C_2H_4, and the results were essentially the same as those obtained in the other differential reactor. Moreover, experiments were carried out in the reactor with the short heating zone with only C_2H_6 and O_2 as reagents. No dehydrogenation of ethane occurred at conditions corresponding to those used in the OCM reaction. Therefore, at small methane conversion levels (<5%), part of the C_2H_4 may be formed by a direct pathway, but under integral conditions most of the C_2H_4 is formed via C_2H_6.

Pulse Experiments

Previous pulse experiments had demonstrated that O_2 must be present with CH_4 in order to achieve a high level of conversion (2). In view of the more recent information on hot spots and the large activation energies that have been observed, it was of interest to repeat the pulse experiments under conditions that minimize thermal effects. Here, we describe pulse reactions that were carried out using either undiluted or progressively diluted reagent mixtures, while measuring the temperature in the catalyst bed.

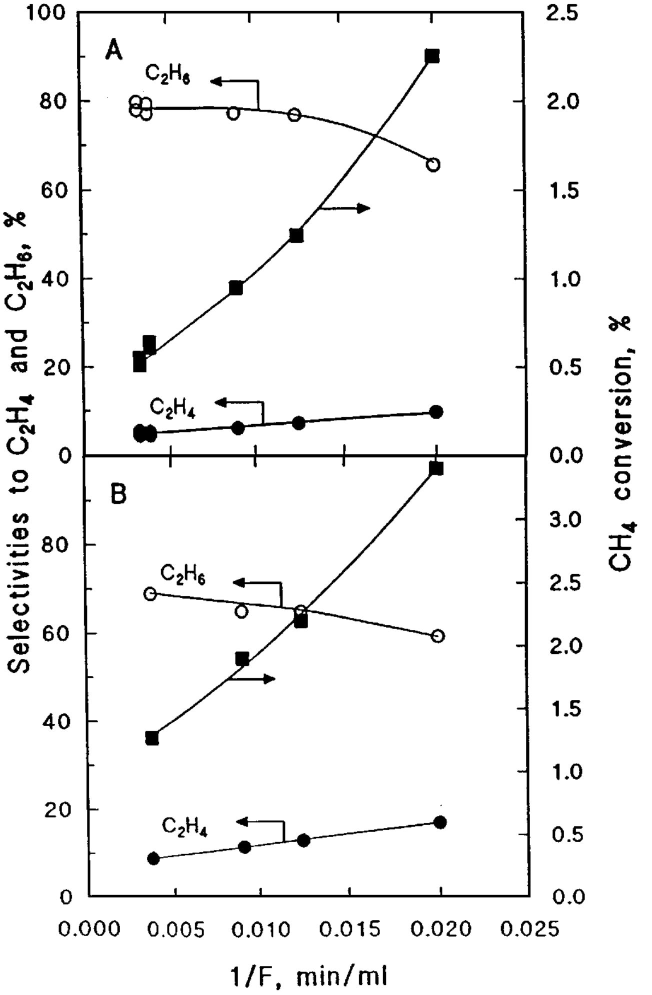

FIG. 3. Effect of residence time (1/*F*) on the methane conversion and hydrocarbon selectivities over (A) $Mn/Na_2WO_4/SiO_2$ and (B) $Mn/Na_2WO_4/MgO$: 20-mg catalyst, *T*(reactor) = 800°C, $CH_4/O_2 = 7.4$.

In the first set of experiments, pure CH_4 pulses were interspersed with co-fed pulses of CH_4/O_2 in a 5 : 1 ratio. The time between pulses was ca. 20 min and the volume of the pulses was 1 ml. The results of Fig. 4 show that over the $Mn/Na_2WO_4/MgO$ catalyst the methane conversion decreased from 20% in the presence of oxygen to a constant level of 2% in the absence of oxygen. Similar results were obtained over the SiO_2-based catalyst, but with a lower conversion in the absence of O_2. The C_{2+} selectivity was somewhat greater in the absence of O_2. It was observed that during reaction in the co-feed mode there was a temperature increase of about 5°C in the catalyst bed, even with the

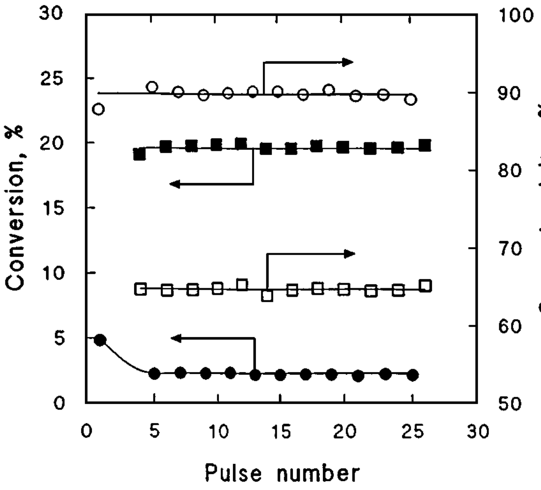

FIG. 4. Pulse experiments over $Mn/Na_2WO_4/MgO$; ○, ●, with CH_4 pulses; □, ■, with $CH_4/O_2 = 5$ pulses. 40-mg catalyst, T(Reactor) = 800°C, He flow rate = 43 ml/min, pulse size = 1 ml.

small loading and small amount of reagent per pulse. The surface temperature of the catalyst could have been even larger than that registered by the thermocouple, which may have caused, in part, the larger conversions observed in the co-feed mode.

To minimize the effect of hot spots, pulse experiments were carried out with progressively diluted CH_4/O_2 mixtures, and the results are given in Table 2. At approximately 90% dilution of the reaction mixture, no measurable temperature rise was detected at the center of the catalyst bed; yet, there remained a much greater CH_4 conversion with oxygen present in the pulses. This difference was even larger with the $Mn/Na_2WO_4/SiO_2$ catalyst than with the $Mn/Na_2WO_4/MgO$ catalyst, which indicates that the latter material has a greater storage capacity for oxygen, perhaps in the Mg_6MnO_8 phase (2). The results obtained with the diluted pulses confirm that rapid equilibration of the surface with gas phase O_2 (reaction [2]) results in the formation of sites that activate CH_4 (reaction [3]).

TABLE 2

The Result of Dilution of the CH_4/O_2 and CH_4 Pulses with He[a]

		CH_4/O_2 pulses			CH_4 pulses	
Catalyst	CH_4 (%)[b]	C (%)[c]	S (%)[c]	ΔT, °C[d]	C (%)	S (%)
$Mn/Na_2WO_4/SiO_2$	83	21	68	3	0.5	62
	42	20	69	2		
	21	18	69	1		
	10	13	69	0	0.6	78
	5	9	71	0	0.5	68
$Mn/Na_2WO_4/MgO$	83	20	65	5	2	89
	21	17	65	1	3	74
	10	12	63	0	4	75
	6	7	56	0	4	63

[a] Helium flow rate = 43 ml/min; T of the reactor = 800°C.
[b] Percentage CH_4 in the gas stream.
[c] C = percentage conversion; S = percentage C_2 selectivity.
[d] Increase of the bed temperature relative to the wall temperature.

Origin of CO_x

A previous investigation on the origin of CO_x during the OCM reaction revealed that over several catalysts the rate constant for CO_x formation from C_2H_4 oxidation is up to six times greater than that from the *direct* oxidation of CH_4 (7). The experiment involves the addition of $^{13}C_2H_4$ to a recirculating mixture of gases during the OCM reaction. A quantity R has been defined as the ratio of the percentage of ^{13}C in the CO_x products to that in the feed gas. The value of R equals the ratio of the rate constant for CO_x formation relative to that from CH_4, provided the following assumptions are valid: (i) the formation of CO_x is first order with respect to the hydrocarbon concentration; (ii) $[CH_4] \gg [C_2H_4]$; (iii) $[^{12}CO_x] \gg [^{13}CO_x]$; (iv) the conversion is small; and (v) the major pathway for ethylene formation is via ethane. The assumptions are either generally true for the OCM reaction or they can be accommodated by establishing the proper experimental conditions. One of the checks on the validity of the analysis is that the value of R remains constant when the amount of $^{13}C_2H_4$ or the CH_4 conversion is varied. The results of Tables 3 and 4 confirm that value of R remained nearly constant when the amount of $^{13}C_2H_4$ added to the system was approximately doubled or the CH_4 conversion was varied. The CH_4 conversion could be increased by simply increasing the time that the gases remained in the recirculation reactor.

Two of the variables that might affect the value of R are reaction temperature and the CH_4/O_2 ratio. From the results of Table 5, it is evident that the values of R remained nearly constant at 750°C and 800°C, but increased somewhat at 850°C. This may result from the increased homogeneous oxidation of C_2H_4 at higher temperatures (see below). It also is interesting to note from these results that at each temperature the value of R was greater for the MgO-based catalyst than for the SiO_2-based catalyst. The

TABLE 3

Effect of the Amount of $^{13}C_2H_4$ on the Value of R over $Mn/Na_2WO_4/SiO_2$[a]

$^{13}C_2H_4$ added (torr)	CH_4 conversion (%)	C_{2+} selectivity (%)	R
1.6	8.8	71.2	8.2
	12.1	72.0	8.3
3.4	9.4	73.3	8.1
	12.1	73.4	7.8

[a] 40 mg $Mn/Na_2WO_4/SiO_2$, T = 800°C, $P(CH_4)$ = 200 torr, $P(O_2)$ = 100 torr, He = balance.

TABLE 4

Effect of Methane Conversion on the Value of *R* over $Mn/Na_2WO_4/MgO$[a]

Circulation time (min)	CH_4 conversion (%)	C_{2+} selectivity (%)	*R*
3	2.0	84.7	7.2
6	2.8	81.5	6.7
12	5.1	83.4	7.4
15	6.0	83.0	6.7
35	11.2	79.5	7.0
55	15.9	78.1	7.0
75	20.3	77.4	7.1

[a] 40 mg $Mn/Na_2WO_4/MgO$, $T = 800°C$, $P(CH_4) = 200$ torr, $P(O_2) = 27$ torr, $P(^{13}C_2H_4) = 3.4$ torr, He = balance.

TABLE 6

Effect of CH_4/O_2 Ratio on Origin of CO_2[a]

CH_4/O_2	CH_4 conversion (%)	C_{2+} selectivity (%)	*R*
$Mn/Na_2WO_4/SiO_2$[b]			
2.0	9.4	73.3	8.1
7.4	9.0	79.3	5.4
$Mn/Na_2WO_4/MgO$[c]			
2.0	8.0	78.9	7.3
7.4	6.0	83.0	6.7

[a] $P(CH_4) = 200$ torr.

[b] 40 mg $Mn/Na_2WO_4/SiO_2$.

[c] 40 mg $Mn/Na_2WO_4/MgO$, $P(^{13}C_2H_4) = 3.3–4.6$ torr, He = balance.

effects of the CH_4/O_2 ratio are shown in Table 6, where it is evident that larger ratios result in smaller values of *R*. The conversions and selectivities obtained in the recycle reactor (Table 6) are consistent with those obtained in the single-pass reactor (Tables 3 and 4).

In general, the results show that the rate constant for C_2H_4 oxidation is six to eight times as great as that for CH_4 oxidation during the OCM reaction. The consequence of this observation, however, must be considered in view of the partial pressures of the reagents and products. For example, at 20% CH_4 conversion and 80% C_{2+} selectivity (approximately half of which would be C_2H_4) less than half of the CO_2 would be derived from C_2H_4 because the concentration of C_2H_4 is much less than that of CH_4. Nevertheless, the continuous removal of C_2H_4 by a contact membrane allows one to achieve high ethylene yields (>70%) in a recycle reactor (4).

The ethylene may be converted to CO_2 both by heterogeneous and homogeneous oxidation reactions. Experiments to estimate the contribution from each were carried out in the recycle reactor. The results shown in Fig. 5 reveal an unexpected, but very significant phenomenon. In particular, they demonstrate that CH_4 has a strong inhibiting effect on the rate of C_2H_4 conversion during a homogeneous reaction. With He as the diluent, only 6-min circulation time was required to react all of the ethylene, but with methane present, only 15% of the $^{13}C_2H_4$ was converted in 75 min. As expected, the corresponding CH_4 conversion was even less. In the latter case, the maximum oxygen conversion was ca. 25%. Although the mechanism for the inhibition by CH_4 is not clear, its role is essential for obtaining the yields of C_2H_4 that are achieved during the OCM reaction at 800°C. A comparison is made in Fig. 6 between the oxidation of ethylene via the purely homogeneous reaction and during the OCM reaction which would include both a homogeneous and a heterogeneous component. It is evident that the rate of ethylene reaction is ca. four times as great over the $Mn/Na_2WO_4/SiO_2$ catalyst as over the quartz chips. The homogeneous component will depend on the residence

TABLE 5

Dependence of *R* on Reaction Temperature[a]

T (°C)	CH_4 conversion (%)	C_{2+} selectivity (%)	*R*
$Mn/Na_2WO_4/SiO_2$[b]			
750	11.5	77.8	5.4
800	9.0	79.3	5.4
850	13.5	79.4	6.8
$Mn/Na_2WO_4/MgO$[c]			
750	8.8	73.0	6.1
800	6.0	83.0	6.7
850	10.2	86.4	8.7

[a] $P(CH_4) = 200$ torr.

[b] 40 mg $Mn/Na_2WO_4/SiO_2$.

[c] 40 mg $Mn/Na_2WO_4/MgO$, $P(O_2) = 27$ torr, $P(^{13}C_2H_4) = 3.3–4.6$ torr, He = balance.

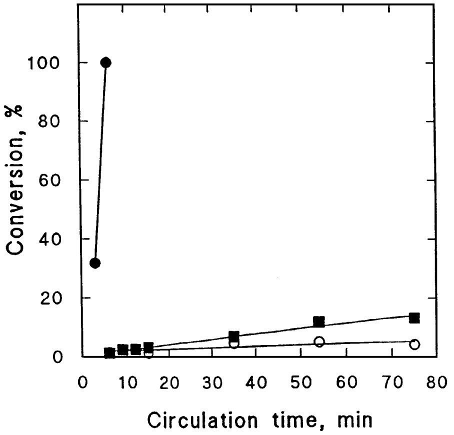

FIG. 5. Ethylene and methane conversion in the recycle reactor with only quartz chips (i.e., no catalyst); ●, ethylene conversion with 4 torr C_2H_4 initially; ■, $^{13}C_2H_4$ and, ○, CH_4 conversion with 3.6 torr $^{13}C_2H_4$ and 200 torr CH_4. $P(O_2) = 100$ torr, balance He, *T*(reactor) = 800°C.

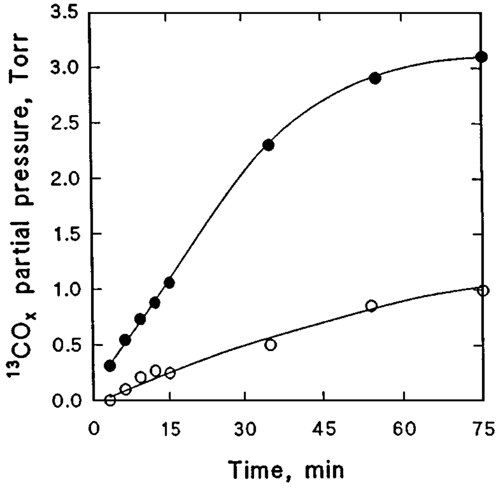

FIG. 6. Formation of $^{13}CO_x$ as a function of time in the recirculation reactor (●) with 40-mg $Mn/Na_2WO_4/SiO_2$ as the catalyst and (○) with only quartz chips in the reactor: $P(CH_4) = 200$ torr, $P(^{13}C_2H_4) = 3.5$ torr, $P(O_2) = 100$ torr, balance He, $T(\text{reactor}) = 800$°C.

time in the heated zone after the catalyst bed; however, one may conclude that, in general, the oxidation of C_2H_4 to CO_2 is largely a heterogeneous process.

Formation and Reactions of Methyl Radicals

A considerable body of experimental evidence supports the view that $CH_3\cdot$ radicals, formed via reaction [3], couple in the gas phase to produce ethane (6). This mechanism is applicable for the OCM reaction even over catalysts containing transition metal ions; however, the efficient formation of $CH_3\cdot$ radicals over these materials may require operation at a higher pressure than that normally used in the MIESR system (15). The positive effect of the higher pressure is mainly due to an increase in the partial pressure of O_2. For surface-generated gas-phase $CH_3\cdot$ radicals to be important in C_2H_6 formation, it is not only essential that they be produced at a reasonable rate, but also that they couple before they are consumed through secondary reactions on the surface. Typically, good OCM catalysts are effective in $CH_3\cdot$ radical production and are poor radical scavengers (10).

The relative rates for $CH_3\cdot$ radical formation and secondary reaction were determined for $Mn/Na_2WO_4/SiO_2$, $Mn/Na_2WO_4/MgO$, and Sr/La_2O_3. The Sr/La_2O_3 catalyst was used for purposes of comparison because it is known to be active for $CH_3\cdot$ radical formation and relatively inactive for secondary reactions (16,17). A comparison of the relative rates of radical formation with the relative activity for CH_4 conversion, as determined from Table 1, provides additional insight into the mechanism over the three catalysts.

The methyl radical spectra over the three catalysts of interest, obtained in the low pressure mode, are depicted in Fig. 7. Since the line widths are essentially the same, one can estimate the radical concentration, which is proportional to the rate of radical formation, from the peak-to-peak amplitudes of the derivative spectra. Qualitatively, it is obvious that the rate of radical formation was much greater over the Sr/La_2O_3 catalyst, which is consistent with the results of Table 1. From a comparison of the spectra, the ratio of the rates of formation on a per gram basis at 800°C is $Sr/La_2O_3 : Mn/Na_2WO_4/MgO : Mn/Na_2WO_4/SiO_2 = 84 : 1.2 : 1$. Because of the pretreatment conditions, the catalysts were similar to fresh materials.

The results for the CH_4 reaction rate and those for $CH_3\cdot$ radical formation as reported in Tables 1 and 7, respectively, were obtained under similar conditions. The MIESR results were obtained in the high pressure mode over catalysts that had been on stream for 2 h; thus, they had nearly reached steady-state activity. In order to operate under conditions such that the O_2 was not completely consumed, it was necessary to obtain data over the very active Sr/La_2O_3 catalyst at shorter contact times than those used over the other two catalysts. After correcting for this effect, it is evident that the ratios for radical formation are in the order $Sr/La_2O_3 : Mn/Na_2WO_4/MgO : Mn/Na_2WO_4/SiO_2 = 13 : 1.6 : 1$. The observation that the activity for radical formation parallels that for the OCM reaction indicates that

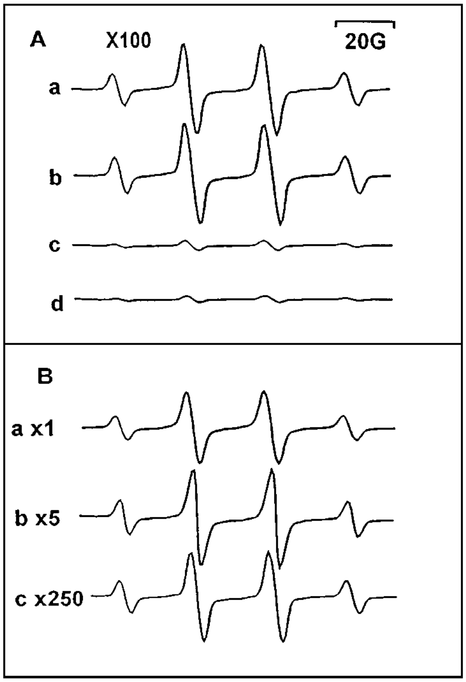

FIG. 7. ESR spectra of $CH_3\cdot$ radicals formed over catalysts in the low pressure mode: A, (a) over $Mn/Na_2WO_4/SiO_2$ at 800°C; (b) over $Mn/Na_2WO_4/MgO$ at 800°C; (c) over $Mn/Na_2WO_4/SiO_2$ at 600°C; (d) over $Mn/Na_2WO_4/MgO$ at 600°C. B, over Sr/La_2O_3 at (a) 800°C; (b) 600°C; (c) 400°C. $P(\text{total}) = 1$ torr; $CH_4 : O_2 : Ar = 1 : 0.016 : 3.9$; 150 mg of catalyst.

TABLE 7

Comparison of Methyl Radical Formation[a]

	Flow rates, ml/min			
Catalyst (mass)	CH_4	O_2	Ar	Relative radical conc.[b]
$Mn/Na_2WO_4/SiO_2$ (150 mg)	75.0	10.5	80.0	1
$Mn/Na_2WO_4/MgO$ (150 mg)	75.0	10.5	80.0	1.6
Sr/La_2O_3 (50 mg)	216	30.2	242	13

[a] $P(\text{total}) = 760$ torr; $T = 800°C$.

[b] Relative radical concentrations were normalized to the same mass of catalyst and flow rates.

the mechanism over all three catalysts involves the coupling of gas-phase methyl radicals. In these experiments it should be noted that the spectra were largely those of $CH_3O_2\cdot$ because unreacted O_2 combined with $CH_3\cdot$ as the matrix was formed at ca. 15 K. Nevertheless, in the catalytic reactor, at elevated temperatures, the equilibrium strongly favors $CH_3\cdot$ and O_2, rather than $CH_3O_2\cdot$ (18).

Secondary reactions of $CH_3\cdot$ radicals with several materials are reported in Table 8. Cerium oxide was included in the study because it is known to be relatively active with respect to $CH_3\cdot$ radicals. But even with this oxide the reactive sticking coefficient was only 10^{-5} at 650°C (17). Since the rates of radical formation over the MgO-based and SiO_2-based catalysts were relatively small, it was possible to study these materials as scavengers at temperatures up to 790°C. Considering an experimental error of about ±5% for the two terms in Eq. [1], one may conclude that over the temperature range studied, the $Mn/Na_2WO_4/MgO$ and $Mn/Na_2WO_4/SiO_2$ catalysts are unreactive with respect to $CH_3\cdot$ radicals. This could explain, in part, the high C_2 selectivities attained over these catalysts at low conversion levels. The Sr/La_2O_3 is somewhat more active with respect to $CH_3\cdot$ radicals, and, in agreement with previous results, CeO_2 is even more active.

TABLE 8

Secondary Reactions of Methyl Radicals with Metal Oxides

Catalyst[a]	T (°C)	RE (%)[b]
$Mn/Na_2WO_4/SiO_2$	400	11
	600	0
	790	0
$Mn/Na_2WO_4/MgO$	400	0
	600	0
	790	8.3
Sr/La_2O_3	400	26
CeO_2	400	62

[a] 150 mg of catalyst.

[b] Reaction efficiency (see Eq. [1]).

CONCLUSIONS

In comparison to Sr/La_2O_3, $Mn/Na_2WO_4/SiO_2$, and $Mn/Na_2WO_4/MgO$ are not particularly active catalysts for the OCM reaction. The more modest activity is not a technological limitation, however, since heat removal and the control of hot spots would be a major problem, even with the SiO_2- and MgO-based materials.

The activation energy for CH_4 conversion over these two catalysts is unusually large. This may reflect an equilibrium between gas phase O_2 and the catalyst, through which active oxygen is formed on the surface. The presence of gas phase oxygen is essential for favorable activity, and the order of reaction with respect to oxygen (0.48–0.53) suggests that the equilibrium dissociation of O_2 is involved.

The mechanism appears to be the same as that for other OCM catalysts. Namely, methyl radicals, formed on the surface, couple in the gas phase to produce C_2H_6. Ethylene is mainly a secondary product, although a very small amount occurs as an initial product. The rate constant for the formation of CO_2 from C_2H_4 is about six times as great as that from CH_4, but under reasonable operating conditions, both hydrocarbons would contribute to the formation of CO_2. The oxidation of C_2H_4 to CO_2 occurs mainly on the catalyst because CH_4 inhibits the homogeneous oxidation reaction. The $Mn/Na_2WO_4/SiO_2$ and $Mn/Na_2WO_4/MgO$ catalysts are relatively unreactive with respect to $CH_3\cdot$ radicals, even at temperatures up to 790°C. It is unlikely, therefore, that the conversion of CH_4 to CO_2 involves the surface reaction of $CH_3\cdot$ radicals. The small activity of these two materials with $CH_3\cdot$ radicals may be responsible for their favorable performance as OCM catalysts.

ACKNOWLEDGMENT

This research was funded, in part, by the National Science Foundation under Grant CHE-9520806.

REFERENCES

1. Fang, X., Li, S., Lin, J., Gu, J., and Yang, D., *J. Mol Catal. (China)* **6**, 427 (1992).
2. Wang, D., Rosynek, M. P., and Lunsford, J. H., *J. Catal.* **155**, 390 (1995).
3. Pak, S., and Lunsford, J. H., *Appl. Catal. A* **168**, 131 (1998).
4. Cordi, E., Pak, S., Rosynek, M. P., and Lunsford, J. H., *Appl. Catal. A* **155**, L1 (1997).
5. Jiang, Z., Yu, C., Fang, X., Li, S., and Wang, H., *J. Phys. Chem.* **97**, 12870 (1993).
6. Campbell, K. D., Morales, E., and Lunsford, J. H., *J. Am. Chem. Soc.* **109**, 7900 (1987); Campbell, K. D., and Lunsford, J. H., *J. Phys. Chem.* **92**, 5792 (1988); Lunsford, J. H., *Angew. Chem. Intl. Ed. Engl.* **34**, 970 (1995).

7. Shi, C., Rosynek, M. P., and Lunsford, J. H., *J. Phys. Chem.* **98**, 8371 (1994).
8. Nelson, P. F., and Cant, N. W., *J. Phys. Chem.* **94**, 3756 (1990).
9. Martir, W., and Lunsford, J. H., *J. Am. Chem. Soc.* **103**, 3728 (1981).
10. Tong, Y., Rosynek, M. P., and Lunsford, J. H., *J. Phys. Chem.* **93**, 2896 (1989); Tong, Y., and Lunsford, J. H., *J. Am. Chem. Soc.* **113**, 4741 (1991).
11. Mimoun, H., Robine, A., Bonnaudet, S., and Cameron, C. J., *Chem. Lett.*, 2185 (1989).
12. Wu, J.-G., and Li, S.-B., *J. Natural Gas Chem.*, 219 (1995).
13. Xu, M., Shi, C., Yang, X., Rosynek, M. P., and Lunsford, J. H., *J. Phys. Chem.* **96**, 6395 (1992).
14. Hutchings, G. J., and Scurrell, M. S., *in* "Methane Conversion by Oxidative Processes" (E. E. Wolf, Ed.), p. 201. Van Nostrand Reinhold, New York, 1992.
15. Tong, Y., and Lunsford, J. H., *J. Chem. Soc., Chem. Commun.*, 792 (1990).
16. Xu, M., and Lunsford, J. H., *Catal. Lett.* **11**, 295 (1991).
17. Xu, M., and Lunsford, J. H., *J. Phys. Chem.* **99**, 14494 (1995).
18. Lin, C.-H., Wang, J.-X., and Lunsford, J. H., *J. Catal.* **111**, 302 (1988).