Oxidative Coupling of Methane over Perovskite-Type Oxides and Correlation of

T_{max} for Oxygen Desorption with C_2 Selectivity

by

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ABSTRACT:

Oxidative coupling of methane co-fed with oxygen to C_2+ hydrocarbons has been investigated both in the absence and in the presence of $La_{0.9}Na_{0.1}MnO_3$ at 1 and 3.6 atm pressures. It was found that residence time, temperature, methane-to-oxygen ratio, and pressure are the major factors affecting the conversion and selectivity both in the empty reactor and in the presence of the catalyst. Significant gas-phase reactions were observed at higher pressure, O_2:CH_4 ratio, and contact time. The results suggest that the activation of methane occurs both in the gas phase and on the surface of the catalyst, and the surface reactions appeared to be important in oxidizing the intermediates $CH_3\cdot$, C_2H_4, C_2H_6, and CO to carbon dioxide. Temperature-Programmed desorption studies on a series of perovskite-type catalysts showed that T_{max}, the temperature at which maximum O_2 desorbs, correlates very well with the C_2 selectivity for oxidative coupling of Methane; and these results suggest that a strong binding of oxygen to the surface site is essential to selectively produce C_2+ hydrocarbons from methane as opposed to complete oxidation leading to carbon dioxide.

BACKGROUND:

Methane is the principal component of natural gas, which is found in porous reservoirs generally associated with crude oil. Some of these abundant reserves of natural gas exist in locations too remote from market areas to be recovered on a commercial basis by present methods. A promising new methane conversion technology uses catalytic oxidative coupling as the first step in the process.[1-3] The oxidative coupling step converts natural gas to olefins, which could be subsequently converted to higher hydrocarbons.[4] A key to developing this technology is optimization of the oxidative-coupling step, such as using novel catalysts. We have shown that by proper cation substitution in perovskite-type oxides, superior catalysts for the oxidative coupling of methane to higher hydrocarbons can be obtained.[5,6] Recent studies showed that gas-phase reactions, especially at higher pressures, play a significant role in the partial oxidation of methane.[7-9] Furthermore, there appers to be a discrepancy between the results obtained by Ito et al.[10] and the results obtained by Yates and Zlotin[7] for empty reactors. Therefore, in order to gain further insight into this catalytic and noncatalytic system, the oxidative coupling of methane was investigated at several reaction conditions, both in the presence and absence of the perovskite-type oxide $La_{0.9}Na_{0.1}MnO_3$.

One of the most important factors which govern the catalytic oxidation process is the metal-oxygen bond strength.[11] For metal oxide catalysts, usually three different types of oxygen may be detected, namely, lattice oxygen, adsorbed

oxygen and absorbed oxygen.[12] These activated oxygen species have widely different properties in catalytic oxidation and can affect the activity of a particular catalyst. In the case of metal oxide catalysts, reactivity of these oxygen species depends largely upon the kind of component metal cation present.

Temperature-Programmed Desorption (TPD) is one of the techniques that can be used to obtain useful information on the existence of oxygen species in discrete states and/or over a broad distribution of energies.[12-14] Such information when combined with the results of catalytic reaction studies, carried out under identical conditions, can provide an insight into the catalytic-oxidative conversion of methane to hydrocarbons. In this paper, we report the oxygen-sorptive properties of perovskite-type catalysts in relation to their catalytic activity and selectivity.

EXPERIMENTAL:

The details of preparing the perovskite-type oxides have been reported elsewhere.[5] A 0.235m long downflow alumina reactor tube (9.53mm o.d., 6.35mm i.d., calculated heated volume = 2.0 cm^3) with a quartz thermowell was used as a fixed-bed reactor with 0.5 g of catalyst (-28/+48 mesh) held in place by quartz wool. Electronic mass flow controllers were used to feed methane (99.99%), oxygen (99.8%), and helium (99.999%). The reactor was electrically heated to reaction temperatures under a flow of helium. All transfer lines and valves were 316 stainless steel and held at 150 °C. Product analyses were performed by online gas chromatography (GC) and mass spectrometry (MS). The products were sampled but not analyzed until performance stabilized and this

never exceeded 30 minutes. Samples were analyzed for ethane, ethylene, propane, propylene, hydrogen, carbon oxides, formaldehyde, and water. A thermal conductivity detector was used with a 1m x 3.2mm o.d. stainless steel molecular sieve 5A column and a 3.7m x 3.2mm o.d. stainless steel Porapak Q (80/100 mesh) column at isothermal oven temperatures of 100 and 120 °C, respectively. Results are reported on a carbon-mol % basis (Table 1).

Temperature-programmed studies were performed by passing oxygen (99.8%) over the catalyst and raising the temperature from room temperature to 820 °C with a heating rate of 5 °C/min, and cooling the catalyst to room temperature under oxygen atmosphere. Any excess oxygen not consumed by the catalyst was then flushed out by using high purity He (99.999%). Oxygen desorption was performed by raising the temperature linearly (heating rate = 60 °C/min) with time and using high purity He (30 cm^3/min) as carrier gas. Products were analyzed by online gas chromatography (GC) and mass spectrometry (MS). For the blank experiment, where no catalyst was present in the reactor, no appreciable traces of oxygen were detected.

RESULTS:

The oxidative coupling of methane co-fed with oxygen was studied in an empty alumina reactor with and without dead volume (Table 1). The results showed that extensive conversion of methane and oxygen occurred in the empty reactor, especially at higher pressures and contact times. The heated volume of the reactor was calculated to be 2.0 cm^3 with a contact time of 2.4 seconds at maximum dead volume. However, as the contact time was reduced (< 1 second), by

minimizing the dead volume in the reactor, the contribution from the gas-phase reaction was significantly reduced. Since we were not able to measure the exact volume of the reactor with the minimized dead volume, the contact time is reported as "< 1 second".

Pressure also appears to be an important factor affecting conversion and selectivity both in the gas phase and on the surface of the catalyst. For example, at 1.0 atm pressure and 740 °C (not shown in Table 1), about 1.5 % of the methane and about 1.7 % of the oxygen were converted to products (9% C_2H_4, 38% C_2H_6, 3% CO_2, and 49% CO) in the empty reactor (contact time =2.4 seconds and $CH_4:O_2$ = 2:1). When the pressure was raised to 3.6 atm, the methane and oxygen conversions increased to 35.7 and 96.8 %, respectively. The product distribution in this case was 11.2% C_2H_4, 4.6% C_2H_6, 15.8% CO_2, and 68.4% CO.

The effects of temperature and pressure on conversions and selectivity to C_2+ hydrocarbons, over $La_{0.9}Na_{0.1}MnO_3$ catalyst, are shown in Figure 1. At 3.6 atm pressure and temperatures below 780 °C, higher methane and oxygen conversions and higher selectivity to C_2+ hydrocarbons were observed compared to those at 1 atm. However, when the temperature increased the C_2+ selectivity at low pressure (1 atm) increased to a maximum value, while at the higher pressure the C_2+ selectivity slightly decreased. Furthermore, a higher molar ratio of $C_2H_4:C_2H_6$ was observed at higher pressure. In the presence of the catalyst, the major portion of the carbon oxides was carbon dioxide, indicating that the catalyst played a significant role in the reaction sequences and altered the product distribution.

The dependence of conversion and selectivity on the methane-to-oxygen ratio over $La_{0.9}Na_{0.1}MnO_3$ was also studied (Figure 2.). Lower conversion of methane and higher selectivity to C_{2+} hydrocarbons were obtained when the methane-to-oxygen ratio was increased. This result indicates that methane and higher hydrocarbon products, at higher oxygen partial pressures and in the presence of the catalyst, were increasingly converted to carbon dioxide.

Temperature-Programmed Desorption:

Temperature-Programmed desorption studies on a series of perovskite-type catalysts with general formula $A_{1-x}B_xMnO_3$ (where A is Gd, Sm, La, or Ho, B is either Na or K and x= 0 or 0.1) were carried out and the temperature at which maximum oxygen desorbed (T_{max}) was correlated with the C_2 selectivity. The TPD chromatograms for oxygen desorption are shown in Figure 3 as plots of mass spectrometer signal (desorption rate) for oxygen (m/e = 32) versus temperature. All chromatograms are characterized by the appearance of two types of oxygen. The first type, (α) oxygen, desorbs at a lower temperature compared to the second type, (β) oxygen, which desorbs at higher temperature. The values for T_{max}, corresponding to the maxima for (α) oxygen desorption, are plotted in Figure 4 along with the C_2 selectivities obtained in the earlier studies.[6] The values for T_{max} ranges from 860 °C for $Gd_{0.9}Na_{0.1}MnO_3$ to 695 °C for $LaMnO_3$ and is sensitive to the presence of alkali metal ion B as well as to substitution at site A.

The results presented in Figure 4 show that T_{max} for (α) oxygen desorption correlates very well with the C_2 selectivity. The catalyst $Gd_{0.9}Na_{0.1}MnO_3$ with

(α) oxygen desorbing at the highest temperature (865 °C) showed the highest selectivity for C_2 products whereas $LaMnO_3$ which desorbs at the lowest temperature (695 °C) is the least selective for the conversion of methane to C_2 products.[5] It is interesting to note that optimum conditions (higher C_2 selectivity) for conversion of methane over $La_{0.9}Na_{0.1}MnO_3$ catalyst correspond to the temperature (820 °C) which matches very nicely with the T_{max} for that catalyst. For the perovskite-type catalysts examined, it has been speculated earlier that the oxygen binding energy decreases in this order $(La,Na)MnO_3 >$ $(La,K)MnO_3 > (La,[ ])MnO_3$.[15] Present TPD studies provide an experimental basis for that trend in oxygen binding energies for these compounds and also similar information on other catalysts. For example, when comparing $LaMnO_3$ with $La_{0.9}K_{0.1}MnO_3$ and $La_{0.9}Na_{0.1}MnO_3$, it becomes apparent that it is the nature of metal-oxygen bond that controls the catalytic activity of oxide catalysts. Therefore we suggest that in catalytic oxidation of methane to higher hydrocarbons, the most important factor may very well be the binding energy of oxygen to a surface site of the catalyst. This observation also agrees well with the earlier claim that some of the common selective oxidation catalysts (e.g. V_2O_3, MoO_3 and Bi_2MoO_6) did not contain weakly adsorbed oxygen.[13]

CONCLUSIONS:

We have shown that by proper cation substitution in perovskite-type oxides, superior catalysts for the oxidative coupling of methane to higher hydrocarbons can be obtained. The results show that surface reactions are important in oxidizing the intermediates $CH_3\cdot$, C_2H_4, C_2H_6, and CO to carbon dioxide. It was found that contact time, temperature, methane-to-oxygen ratio

and pressure were the major factors affecting the conversion and selectivity in the presence and absence of the catalyst. Furthermore, the high activity observed by Yates and Zlotin[7] for the empty reactor could be a result of the higher contact time and possible back pressure (caused by the capillary tube) when compared with the results reported by Ito et al.[10] The activation of methane appeared to be occurring both in the gas phase and on the surface of the catalyst. In the gas phase, methane was possibly activated by diatomic oxygen. The oxidation of methane in the gas phase by diatomic oxygen has been discussed in other reports.[16,17]

The types of oxygen species on the surfaces of the catalyst responsible for the activation of methane are not well defined. However, the activation of methane by surface oxygen species has been proposed by several researchers. Liu et al.[18] have shown O^- ions; Driscoll et al.[19] have proposed $[Li^+O^-]$ centers; and Otsuka and Jinno[20] have proposed adsorbed diatomic oxygen, as being responsible for the activation of methane.

From the TPD studies, we can conclude that for the perovskite-type catalysts examined, a strong binding of oxygen to the surface site is essential to selectively produce C_2+ hydrocarbons from methane as opposed to complete oxidation leading to undesirable carbon dioxide. Present results suggest a possibility that TPD technique can be utilized to find more effective catalysts by selecting a proper combination of A and B site substitution in perovskite-type catalysts.

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Table 1. Comparison of Activity and Selectivity of Oxidative Coupling of Methane in the Presence and Absence of Catalyst at 845 °C, Alumina Reactor, $CH_4/He/O_2=20/20/10 \ cm^3/min$ NPT flow rates.

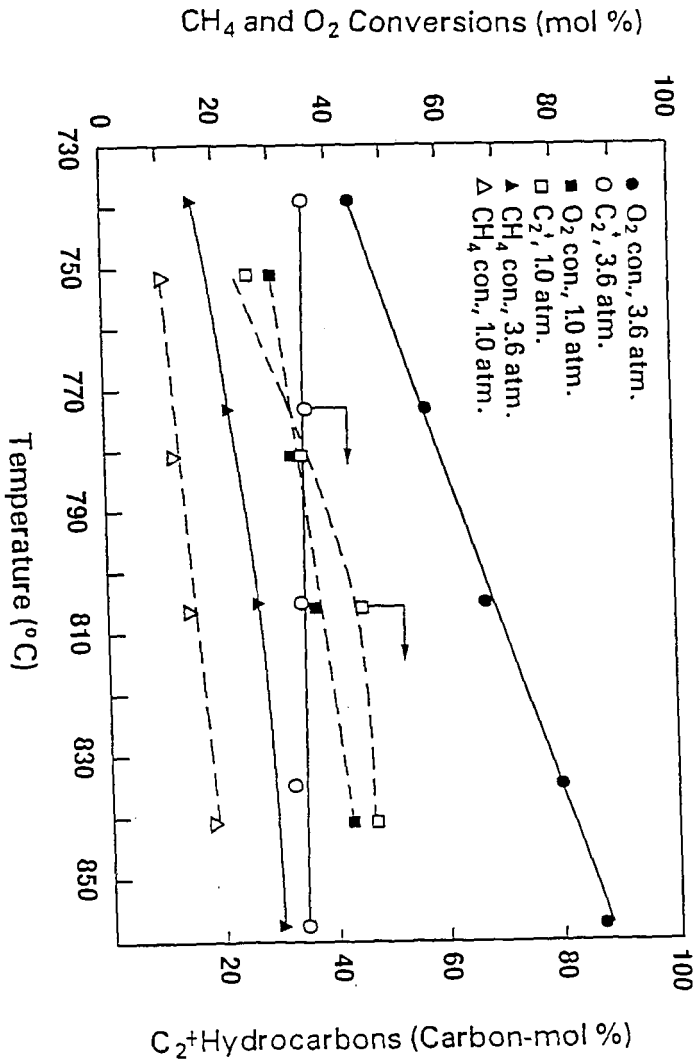| Catalyst/ Conditions	Conversion (mol%)		Selectivity (carbon-mol%)			
	Methane	Oxygen	C_2H_4	C_2H_6	CO_2	CO
Empty, Contact time 2.4 seconds, 1 atm.	29.9	62.9	19.0	5.7	8.8	66.5
Empty, Contact time < 1 second, 1 atm.	1.0	0.5	34.8	51.5	1.2	12.5
Empty, Contact time < 1 second, 3.6 atm.	18.5	37.7	21.8	12.4	8.9	56.9
$La_{0.9}Na_{0.1}MnO_3$, 0.5 g, Contact time 0.4 second, 1 atm.	19.8	44.5	30.0	17.4	41.5	11.1
$La_{0.9}Na_{0.1}MnO_3$, 0.5 g, Contact time 2.4 seconds, 1 atm.	37.2	85.1	36.6	13.7	43.2	6.5

Figure captions:

Figure 1. Dependence of conversion and selectivity on temperature and pressure over $La_{0.9}Na_{0.1}MnO_3$ Catalyst: $CH_4/He/O_2$ = 20/20/10 NPT flow rates; contact time = 0.4 seconds; 0.5 g catalyst.
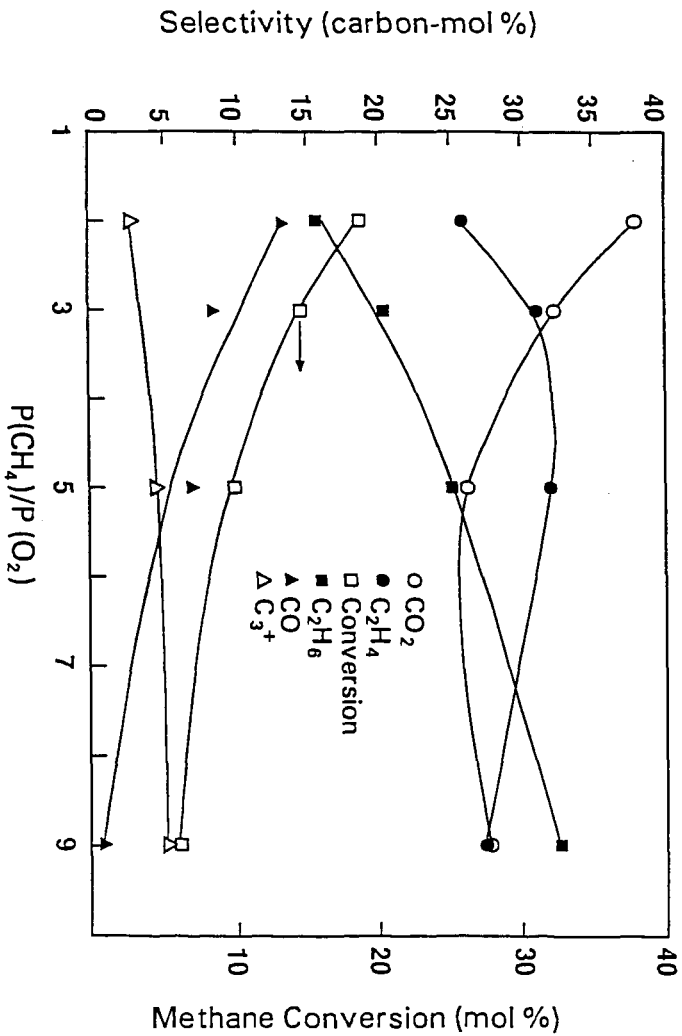
Figure 2. The effect of methane-to-oxygen ratio on conversion and selectivity over $La_{0.9}Na_{0.1}MnO_3$ in an alumina reactor: 1.0 atm pressure; 830 °C; $CH_4/He/O_2$ = 20/20/10 NPT flow rates; contact time = 0.4 second; 0.50 g catalyst.

Figure 3. Temperature-programmed desorption of oxygen (m/e = 32): Heating rate = 1 °C/sec., He flow rate = 0.5 cm^3/sec., 0.25 g catalyst.

Figure 4. Correlation of C_2 Selectivity with the temperature at which maximum O_2 desorbs (T_{max}): 0.25 g catalysts tested at 820 °C, CH_4/O_2 ratio = 5.

CH$_4$ and O$_2$ Conversions (mol %)

- ● O$_2$ con., 3.6 atm.
- ○ C$_2^+$, 3.6 atm.
- ■ O$_2$ con., 10 atm.
- □ C$_2^+$, 10 atm.
- ▲ CH$_4$ con., 3.6 atm.
- △ CH$_4$ con., 10 atm.

Temperature (°C)

C$_2^+$Hydrocarbons (Carbon-mol %)

C89-467-E AA3

1398

Desorption Rate ⟶

$La_{0.9}Na_{0.1}\,MnO_3$ — (a)
LaMnO$_3$ — (b)
$Sm_{0.9}Na_{0.1}\,MnO_3$ — (c)
$Ho_{0.9}Na_{0.1}\,MnO_3$ — (d)
$Gd_{0.9}Na_{0.1}\,MnO_3$ — (e)
$La_{0.9}K_{0.1}\,MnO_3$ — (f)

Temperature (°C)

250 450 650 850 1050

a
b
c
f
ex4
dx8

C₂ Selectivity (carbon-mol %) vs T_max (°C)