

Partial Oxidation of Ethane and Ethylene in the
Presence and Absence of ^{13}C Labeled Methane
on Reducible and Non-Reducible Oxide Catalysts

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INTRODUCTION

In recent years, there has been considerable progress in the development of catalysts for the conversion of natural gas to more useful chemicals and fuels. Oxidative coupling of methane to ethane and ethylene, and subsequent conversion of these chemicals to liquid fuel, is one approach that has attracted great interest in recent years (Liu et al., 1984; Yates and Zlotin, 1988; Otsuka et al., 1986). We have shown that by proper cation substitution in pervoskite-type oxides, active and selective catalysts for the oxidative coupling of methane to higher hydrocarbons can be obtained (France et al., 1988 (a and b); Shamsi and Zahir, 1989; Siriwardane and Shamsi, 1990). Recent studies have shown that gas-phase reactions, especially at higher pressures, play a significant role in the partial oxidation of methane (Labinger and Ott, 1987; Lane and Wolf, 1988; Shamsi and Zahir, 1989).

Despite intensive research on oxidative coupling of methane, no one has yet achieved a single pass yield large enough for a process to be economical. McCarty (1992) has evaluated several approaches for achieving higher yield in methane conversion processes. He has concluded that oxidative coupling of methane into desirable products is limited by two types of side reactions: "1) direct oxidation of reactive intermediates, and 2) the parallel conversion of desired metastable products into deep oxidation by-products."

Mazanec et al. (1992) studied methane conversion to higher hydrocarbons using electrocatalytic cells. They have concluded that "there is a fundamental mechanistic limitation to the conversion of methane to higher hydrocarbons." Olsbye et al. (1992) studied the effects of adding ethane and ethylene to an oxidative coupling reaction and found that methane is formed from the C_2 products. They suggested that the C_2 products are more reactive to form methane than the reverse methane coupling reaction. Mazanec et al. (1992) and Labinger (1992) have proposed a simple two-step "ABC" model. In this model, A is the reactants, B is the desired products, and C is the by-products. In this simplified model where

$$\text{A} \xrightarrow{k_1} \text{B} \xrightarrow{k_2} \text{C}, \text{ the } k_2/k_1 \text{ ratio is used to estimate the desired } \text{C}_2 \text{ yield.}$$

The challenging problem in converting methane to ethane and ethylene is the reactivity of methane relative to its products. There are at least three vital points in converting methane to ethane and ethylene using oxidative coupling. First, at high temperature and pressure, both homogeneous and heterogeneous reactions occur during oxidative coupling of methane, and the major precursors are produced in the gas phase (Shamsi and Zahir, 1989; Liu et al., 1984). Consequently, under these conditions it is difficult to change the product distribution entirely by tailoring the catalyst. Second, methane is much less reactive than its products, ethane and ethylene. Therefore, high conversion with high selectivity is very difficult to obtain. Third, complete oxidation of intermediates to carbon dioxide becomes increasingly important at higher pressure, which is required for a commercial process. The first and third problems could be overcome by developing a catalyst to activate methane at temperatures below 600°C and by designing a process that operates at 1 atm pressure. However, neither the catalyst nor the process design can solve the second problem. Ethane and ethylene, depending on their partial pressures, will compete for active species in the gas phase and for active centers on the catalyst surfaces as will be discussed later.

EXPERIMENTAL

See publication by Shamsi, A. and Zahir, K., (1989) for details.

RESULTS AND DISCUSSION

Earlier studies on oxidative coupling of methane indicated that the activation of methane occurs both in the gas phase and on the surfaces of the catalyst (Shamsi and Zahir, 1989). The results also showed that contact time, temperature, pressure, and methane-to-oxygen ratio are the major factors affecting conversion and selectivity in the presence and absence of the catalyst. Before investigating the catalytic oxidation, the effects of pressure, temperature, and contact time on partial oxidation of ethane and ethylene in an empty reactor were studied. This will determine the extent of gas-phase contribution to the overall reactions at various experimental conditions.

Ethane was partially oxidized by co-feeding ethane, helium, and oxygen into the reactor. The dependence of conversion and selectivity on temperature, pressure, and contact time is shown in Tables 1, 2, and 3. Ethane oxidation commenced at temperatures higher than 550°C. Higher ethane and oxygen conversions were obtained at higher temperatures, pressures, and contact times. Ethylene is the major product at low ethane conversion, and its concentration decreased with increasing temperature, pressure, and contact time. The amounts of CO and CO₂, carbon monoxide being predominant, also increased with increasing conversion. Methane, higher hydrocarbons, and formaldehyde were also detected at higher temperatures, pressures, and contact times, indicating that ethylene further reacts with oxygen to form formaldehyde and carbon oxides.

Ethylene was mixed with helium and oxygen and co-feed into the reactor. The dependence of conversion and selectivity on temperature, pressure, and contact time is shown in Tables 4, 5, and 6. Ethylene oxidation commences at temperatures higher than 500°C, about 50°C lower than required for ethane activation. Higher ethylene and oxygen conver-

sions were observed at higher temperatures, pressures, and contact times. Furthermore, at low ethylene conversion, ethylene oxide and formaldehyde are the major products, and their concentrations decreased with increasing conversion. The amount of CO increased with increasing conversion. This indicates that formaldehyde and ethylene oxide underwent further reactions to form carbon monoxide. Methane and higher hydrocarbons were also detected at higher temperatures, pressures, and contact times. Comparison with ethane shows that ethylene in an empty reactor, mainly gas-phase reactions, is oxidized more easily than ethane. These results are in good agreement with those reported by Burch and Tsang (1990). However, they have reported neither formaldehyde nor ethylene oxide.

Temperature-programmed partial oxidation of ethane, ethylene, and ^{13}C labeled methane was studied separately. Results are shown in Figures 1. The temperature was raised from 400 to 700°C at 40°C/min. Abundance of $^{12}\text{CO}_2$, $^{13}\text{CO}_2$, and oxygen were monitored using a GC with an MSD. The temperature at which 50% of the oxygen converted during oxidation of ethane and ethylene is significantly less than the temperature at which 50% of the oxygen converted during oxidation of methane. The rates of activation of these hydrocarbons on sodium promoted Sm_2O_3 decrease in the order of ethane > ethylene >> methane. Using these results and those in the literature to compare the reactivity of ethane and ethylene with methane would be misleading. According to the results shown in this graph, ethane and ethylene are activated at significantly lower temperatures than that required for methane activation. Therefore, any ethane or ethylene formed during oxidative coupling of methane would be consumed before any methane could be activated. The earlier results in this laboratory and elsewhere showed that this is not correct. Therefore, the relative reactivity of ethane and ethylene are different in the presence of methane and the catalyst as will be discussed later.

A mixture of ethylene in ^{13}C labeled methane were co-fed with oxygen and helium into the reactor (total flow rate of 17.5 cm³/min; hydrocarbon:oxygen ratio=2:1) containing 0.5 grams of 1.4 wt% sodium promoted Sm_2O_3 . The temperature of the catalyst bed was raised from 400 to 700°C at 40°C/min and held for 7.5 min at 720°C. The abundance (concentration, a.u.) of $^{12}\text{CO}_2$ and $^{13}\text{CO}_2$ was monitored using GC with an MSD. The concentrations of ethylene varied from 5 to 50 vol%. When the ethylene concentration was about 5 vol%, $^{13}\text{CO}_2$ was slightly more abundant than $^{12}\text{CO}_2$. However, increasing the concentrations of ethylene to 10 and 50 vol% formed more CO_2 from ethylene than from methane. No significant amount of carbon dioxide was detected at temperatures of less than 400°C and ethylene concentration of less than 10 vol%. However, when the concentration increased to more than 10 vol%, ethylene was activated at temperatures less than 400°C.

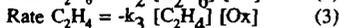
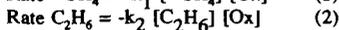
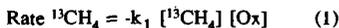
A plot of $^{12}\text{CO}_2$ to $^{13}\text{CO}_2$ ratios versus ethylene concentrations is shown in Figure 2. These data were obtained at steady state conditions of 720°C and 1 atm pressure. At a lower ethylene concentration of 5 vol%, ethylene was 7.8 times more reactive than methane. However, as the concentrations of ethylene increased to 10 and 50 vol%, the reactivity of ethylene decreased to 7.5 and 3.6, respectively. The relative reactivity was calculated based on the assumption that at equal reactivity and replacing 5, 10, and 50 vol% of ^{13}C labeled methane by ^{12}C ethylene, the $^{12}\text{CO}_2$ to $^{13}\text{CO}_2$ ratios will increase to 0.105, 0.222, and 2.0,

respectively. In all cases, when a mixture of methane and ethylene partially oxidized over quartz or the catalyst, higher ratios of $^{12}\text{CO}_2$ to $^{13}\text{CO}_2$ were obtained.

Temperature-programmed partial oxidation of mixtures of ethane in ^{13}C labeled methane over 1.4 wt% sodium promoted Sm_2O_3 were also studied. The temperature of the catalyst bed was raised from 400 to 700°C at 40°C/min and held for 7.5 min at 730°C. The abundance of $^{12}\text{CO}_2$ and $^{13}\text{CO}_2$ was monitored using GC with an MSD. The concentrations of ethane varied from 5 to 50 vol%. When the ethane concentration was about 5 vol%, the $^{13}\text{CO}_2$ was slightly more abundant than the $^{12}\text{CO}_2$, indicating that more than two moles of methane were converted to carbon dioxide per one mole of ethane. Increasing the concentrations of ethane to 10 and 50 vol% formed more carbon dioxide from ethane than from methane.

A plot of $^{12}\text{CO}_2$ to $^{13}\text{CO}_2$ ratios versus ethane concentrations is shown in Figure 3. These data were obtained at steady state conditions of 730°C and 1 atm pressure. At a lower ethane concentration of 5 vol%, ethane was about 5.5 times more reactive than methane. However, as the concentrations of ethane increased to 10 and 50 vol%, the relative reactivity of ethane decreased to 4.7 and 3.5, respectively. Comparing with ethylene mixtures, ethane at concentrations less than 10 vol% is about 1.5 times less reactive than ethylene. However, at concentrations of more than 10 vol%, ethane and ethylene show a similar reactivity and were about 3.5 times more reactive than methane.

Mazanec et al.(1992) have proposed that at the relative rates of methane and ethylene activation, k_2/k_1 , in equations (1) and (2) determine the upper limit of C_2 yield, considering ethane can be converted to ethylene readily by "non-oxidative pyrolysis".



They have also reported that "ethylene is more stable than ethane and the rate of ethylene activation is considered to be the limiting feature." However, the results obtained by passing a mixture of methane (34.7%), ethane (19.4%), ethylene (13.1%), and oxygen (32.8%) over a catalyst containing reducible oxides of transition metals (Ca/Ni/K= 2:1:0.1) show that almost all the ethylene was consumed while the concentration of ethane was reduced to 13.3% at 600°C and 1 atm pressure. When this similar mixture was passed over quartz chips at the same conditions, the concentrations of methane and ethylene increased to 42.7 and 19.1%, respectively. Therefore, rate equation (3) was added to explain the relative reactivity of methane and ethylene as the ratio of k_3/k_1 .

CONCLUSION

This study was conducted to understand the relative reactivity of ethane and ethylene compared to methane and to determine whether a catalyst could be designed to overcome the limitation in yield required for an economical process to convert natural gas to liquid fuels.

The most widely acceptable mechanism for activation of methane appears to be the reaction of methane from the gas phase with surface oxygen, which abstracts hydrogen from methane to form methyl radicals (Ahmed and Moffat, 1990). The methyl radicals are released into the gas phase and form ethane. However, the reaction pathways for activation of ethane and ethylene are not well established. The relative H-abstraction rates for hydroxyl radicals in the gas phase for C_2H_6/CH_4 and C_2H_4/CH_4 are reported by McCarty (1992). From these data and suggestion from Lunsford that the C-H bond strength in ethylene is greater than methane, the relative gas-phase reactivity can be estimated to be in the order of $C_2H_6 > CH_4 > C_2H_4$. However, this order was not observed in this study, and it has been reported only for $LiCl/MnO_x$ catalyst (Burch and Tsang, 1990), indicating that the H-abstraction is not the only pathway for ethane and ethylene activation. Likewise, depending on the catalyst and the experimental conditions, C-C and C=C bonds are also attacked by the active centers on the catalyst and by the active species in the gas phase. Therefore, the relative reactivity of ethane and ethylene compared to methane appears to strongly depend on the partial pressures of reactants and the type of catalysts used.

The relative reactivities are in the order of ethylene > ethane >> methane for reactions in the gas phase and on the catalysts containing reducible oxides of transition metals such as Ca/Ni/K. However, this order changed to ethane > ethylene >> methane for a non-reducible catalyst such as sodium promoted Sm_2O_3 . Oxidation of ethane and ethylene in the presence of methane and catalyst show that methane and ethylene, depending on their partial pressures, compete for active centers, and neither formaldehyde nor ethylene oxide were detected in the presence of methane and the catalyst.

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Table 1. Effect of Temperature on Ethane Conversion and Selectivity in an Empty Alumina Reactor at 1 atm Pressure, $C_2H_6/He/O_2=20/20/10$ cm³/min NPT Flow Rates, Contact Time = 2.4 s

	Temperature (°C)		
	550	580	610
Conversion, Mol%			
Ethane	2.1	23.1	58.6
Oxygen	1.4	26.4	99.3
Product Distribution, Carbon Mol%			
C ₂ H ₄	100	84.9	54.2
CH ₄	0.0	2.1	8.3
CO	0.0	7.3	26.3
CO ₂	0.0	0.6	1.2
C ₃ ⁺	0.0	2.9	7.4
HCHO	0.0	2.3	2.6

Table 2. Effect of Pressure on Ethane Conversion and Selectivity in an Empty Alumina Reactor at 550°C, $C_2H_6/He/O_2=20/20/10$ cm³/min NPT Flow Rates, Contact Time = 2.4 s

	Pressure (atm)		
	1.0	1.7	2.4
Conversion, Mol%			
Ethane	2.1	8.1	57.4
Oxygen	1.4	7.5	99.4
Product Distribution, Carbon Mol%			
C ₂ H ₄	100	92.5	49.8
CH ₄	0.0	1.2	10.2
CO	0.0	1.9	27.2
CO ₂	0.0	0.9	1.4
C ₃ ⁺	0.0	2.1	7.2
HCHO	0.0	1.5	4.3

Table 3. Effect of Contact Time on Ethane Conversion and Selectivity in an Empty Alumina Reactor at 550°C, 1 atm Pressure, $C_2H_6/He/O_2=20/20/10$ cm³/min NPT Flow Rates

	Contact Time (s)		
	2.4	4.8	9.6
Conversion, Mol%			
Ethane	2.1	10.9	47.8
Oxygen	1.4	11.5	99.3
Product Distribution, Carbon Mol%			
C_2H_4	100	92.2	55.5
CH_4	0.0	1.4	6.6
CO	0.0	3.3	23.9
CO_2	0.0	0.3	1.3
C_3^+	0.0	0.0	8.3
HCHO	0.0	2.7	4.4

Table 4. Effect of Temperature on Ethylene Conversion and Selectivity in an Empty Alumina Reactor at 1 atm Pressure, $C_2H_4/He/O_2=20/20/10$ cm³/min NPT Flow Rates, Contact Time = 2.4 s

	Temperature (°C)			
	500	538	546	560
Conversion, Mol%				
Ethylene	2.1	10.0	14.0	46.9
Oxygen	3.0	19.7	30.2	96.4
Product Distribution, Carbon Mol%				
C_2H_6	0.0	0.7	0.0	2.4
CH_4	0.2	0.7	1.0	14.3
CO	15.8	39.4	46.2	70.5
CO_2	3.8	2.2	2.3	4.4
C_3^+	2.2	5.9	5.8	2.6
HCHO	26.0	19.4	14.8	2.4
C_2H_4O	52.0	31.7	29.9	3.4

Table 5. Effect of Pressure on Ethylene Conversion and Selectivity in an Empty Alumina Reactor at 500°C, C₂H₄/He/O₂=20/20/10 cm³/min NPT Flow Rates, Contact Time = 2.4 s

	Pressure (atm)			
	1.0	1.7	2.4	3.0
Conversion, Mol%				
Ethylene	0.9	5.7	18.1	44.4
Oxygen	1.3	6.1	37.6	90.2
Product Distribution, Carbon Mol%				
C ₂ H ₆	0.0	0.0	0.3	2.7
CH ₄	0.2	0.0	0.5	16.4
CO	15.8	23.7	37.9	66.3
CO ₂	3.8	3.1	4.4	5.0
C ₃ ⁺	2.2	3.1	6.1	2.2
HCHO	26.0	22.3	14.6	3.6
C ₂ H ₄ O	52.0	47.8	36.1	3.6

Table 6. Effect of Contact Time on Ethylene Conversion and Selectivity in an Empty Alumina Reactor at 500°C, 1 atm Pressure, C₂H₄/He/O₂=20/20/10 cm³/min NPT Flow Rates

	Contact Time (s)			
	2.4	3.2	4.8	9.6
Conversion, Mol%				
Ethylene	4.2	5.3	7.8	21.1
Oxygen	2.7	4.7	10.6	51.0
Product Distribution, Carbon Mol%				
C ₂ H ₆	0.0	0.0	0.0	0.6
CH ₄	0.2	0.3	0.5	1.0
CO	15.8	24.6	31.2	46.0
CO ₂	3.8	2.4	2.5	3.3
C ₃ ⁺	2.2	2.8	4.1	5.7
HCHO	26.0	21.5	18.1	10.3
C ₂ H ₄ O	52.0	48.4	43.6	33.2

Figure 1. Temperature-Programmed Oxidation of Ethane, Ethylene and ^{13}C Labeled Methane Over Sodium Promoted Sm_2O_3

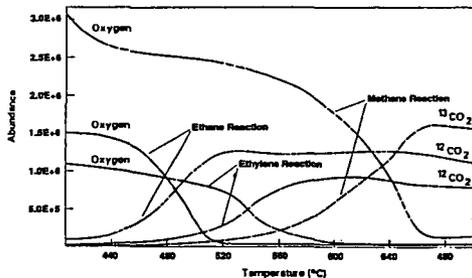


Figure 2. Effect of Ethylene Concentration in ^{13}C Labeled Methane on CO_2 Formation Over Sodium (1.4wt%) Promoted Sm_2O_3 at 725°C and 1 Atm Pressure

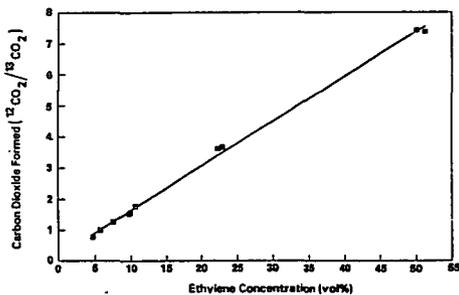


Figure 3. Effect of Ethane Concentration in ^{13}C Labeled Methane on CO_2 Formation Over Sodium (1.4wt%) Promoted Sm_2O_3 at 725°C and 1 Atm Pressure

