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**Enhancement of Methane Conversion
Using Electric Fields**

**Quarterly Report
July - September 1995**

Richard G. Mallinson
Lance L. Lobban

November 1995

Work Performed Under Contract No.: DE-FG21-94MC31170

For
U.S. Department of Energy
Office of Fossil Energy
Morgantown Energy Technology Center
Morgantown, West Virginia

By
The University of Oklahoma
Norman, Oklahoma

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PROJECT ABSTRACT

The goal of this project is the development of novel, economical, processes for the conversion of natural gas to more valuable projects such as methanol, ethylene and other organic oxygenates or higher hydrocarbons. The methodologies of the project are to investigate and develop low temperature electric discharges and electric field-enhanced catalysis for carrying out these conversions. In the case of low temperature discharges, the conversion is carried out at ambient temperature which in effect trades high temperature thermal energy for electric energy as the driving force for conversion. The low operating temperatures relax the thermodynamic constraints on the product distribution found at high temperature and also removes the requirements of large thermal masses required for current technologies. With the electric field-enhanced conversion, the operating temperatures are expected to be below those currently required for such processes as oxidative coupling, thereby allowing for a higher degree of catalytic selectivity while maintaining high activity.

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QUARTERLY OVERVIEW

Good progress is continuing with two reactors in operation. The DC catalytic reactor, in which we continue to examine different catalysts and compare with non-catalytic discharge and thermal catalytic experiments. It appears that some of the synergistic effects may be explained by induced heating causing an apparent temperature shift of the catalyst and we are working to elucidate the magnitude of this effect. A tubular AC reactor with axial electrodes has shown some promising results for oxidative coupling with non-thermal selectivity patterns operating with the bulk gas at room temperature. We also have some interesting results with a Na-zeolite in this reactor. A draft paper which summarizes recent results is included as an appendix to this report.

APPENDIX

An Experimental Study on the Oxidative Coupling of Methane in a Corona Discharge Reactor over Sr/La₂O₃ Catalyst

An Experimental Study on the Oxidative Coupling of Methane in a Corona Discharge Reactor over Sr/La₂O₃ Catalyst

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ABSTRACT

The homogeneous and catalytic oxidative coupling of methane (OCM) for converting methane directly into higher hydrocarbons has been the subject of a large body of research. The present study on conversion of methane in DC corona discharge packed bed reactors may significantly improve the process economics. Experimental investigations have been conducted in which all the reactive gases pass through a catalyst bed which is situated within the Corona-induced plasma zone. In this study, a typical OCM catalyst, Sr/La₂O₃, was used to investigate experimentally the corona discharge OCM reactions. Experiments were conducted over a wide range of temperatures (823 K to 1023 K) and input powers (0 to 6 w) with both positive and negative corona processes. Compared to the catalytic process in the absence of corona discharge, the corona discharge results in higher methane conversion and larger yield for C₂ products even at temperatures at which there is no C₂ activity for the catalyst alone. The methane conversion and C₂ yield increase with O₂ partial pressure during the corona-enhanced catalytic reactions, while the selectivity decreases slightly with increasing O₂ partial pressure. Compared to results obtained in the absence of corona discharges, methane conversion in the presence of the DC corona was nearly five times larger and the selectivity for C₂ over eight times higher at 853K. A great enhancement in catalytic activity has also been achieved at a temperature, at which the catalyst alone shows no C₂ activity. The conversion at higher temperature (more than 953K) is limited by the poor corona performance and the availability of active oxygen species.

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INTRODUCTION

Natural gas, of which about 90% is methane, is a relatively inexpensive and abundant energy resource. The oxidative coupling of methane (OCM) has been extensively studied for some time as a possible effective and economic way to convert methane to C_2 or higher hydrocarbons since the creative works of Keller and Bhasin.^[1] The primary catalysts for the OCM reaction may be classified as either reducible or irreducible metal oxides.^[2] Over reducible oxides, reactants (methane and oxygen) may be fed alternately. A redox mechanism of the reaction has been suggested^[2] for the production of C_2 products, and the metal oxide acts as both the reducing and oxidizing agent rather than as a true catalyst. Irreducible metal oxides, such as catalysts with rare-earth oxides, Sr/La_2O_3 ,^[3] Sm_2O_3/Al_2O_3 ,^[4] Ba/CeO_2 ,^[5] Ba/La_2O_3 ,^[6] Na_2O/Pr_2O_3 ,^[7] and $LaAlO_3$,^[8] act as catalysts which are favorable for the oxidative coupling of methane. However, over both reducible and irreducible catalysts oxides, OCM requires sufficiently high reaction temperatures that the reaction probably proceeds both heterogeneously and homogeneously. Sufficiently high selectivity for C_2 hydrocarbons has not been achieved because of the nonselective heterogeneous and gas phase reactions to CO_x . The need for higher C_2^+ selectivity has led to research on electro-catalytic conversion of methane. Most such studies have utilized membrane reactor systems as an advanced reaction method in which the membranes are also solid electrolytes. Eng and Stoukides^[9] have reviewed applications of these electrolyte materials in catalysis in detail. The three most common applications of solid electrolytes are for solid electrolyte potentiometry (SEP), solid oxide fuel cells (SOFC) and electrochemical oxygen pumping (EOP). Experiments have shown that higher C_2^+ selectivity may be achieved using these electrocatalytic methods,^[9-15] although selectivity remains limited because oxygen supplied through the membrane also forms CO_x . The activity is also relatively low because the performance of membrane catalysts is restricted by the oxygen ion transfer rate.

The previous catalytic research has generally concluded that lattice oxygen (O^{2-}) is the active site for methane activation on the reducible catalysts, and O^- -type species are the active site on the irreducible catalysts. We hypothesize that negatively charged gaseous oxygen species could also activate the methane molecule. If this is true, gas discharges, such as a corona discharge, can provide us with a source of these negative oxygen ions, O^- or O_2^- , formed via electron attachment to oxygen molecules in the gas phase.^[17] Because the corona is relatively easy to establish, it has had wide applications in a variety of processes, including synthesis of chemicals.^[18] In fact, some plasma techniques have been applied to the ionization of methane. Two important applications of methane plasmas are the use of ionized methane as the ion source of a mass spectrometer and the production of diamond coatings. Progress in understanding methane plasmas and the chain reactions involving ionized methane can be found in the literature.^[19-21] Plasma techniques for the conversion of methane were investigated as early as the 1920's. Alexander^[22] reported the complete oxidation of methane by gas discharge. Mach and Drost^[23] published results of methane conversion directly to C_2 hydrocarbons in a low pressure glow discharge reactor; in their work, methane radicals were excited by high energy electrons, and a steady state methane conversion of 98% was reported. Fujii and Syouji^[24,25] used mass spectrometry to analyze products from a methane/oxygen plasma in order to determine the effects of oxygen on a low pressure methane plasma. In fact, most of the previous homogeneous research was conducted at low pressure. Only conversion of CH_4 to C_2H_2 was reported to be conducted at atmospheric pressure^[26,27]. Because of the low pressure and the resulting low mass flow rate, as well as the poor understanding of plasma chemistry, applications of methane plasma for the industrial production of chemicals have not been developed. Regarding this, Changlin Chen et al^[36] and Suib and Zenger^[37] have published their results on OCM over proton conductive catalysts^[36] and the regular catalysts, Li/MgO , La_2O_3 , and Sm_2O_3 ^[37], using microwave plasmas. Compared to the catalysis run in the absence of plasma, there is a change in both the product selectivity and yield with a lower reaction (gas) temperature over proton conductive catalysts when plasma was used. For the regular catalysts,

however, there is no proven improvement on the product selectivity and yield by microwave plasmas.^[37] We have previously studied OCM in a corona discharge reactor without heterogeneous catalysts and found the gas ionization to be effective for obtaining high selectivity to C₂ products. Here we report the results of our investigation of OCM during a combination of the corona discharge and catalysis in a packed bed reactor using Sr/La₂O₃. The results suggest that the combination of Corona discharge and heterogeneous catalysis may lead to an improvement in C₂ selectivity and yield.

EXPERIMENTAL

The experimental apparatus flow diagram is shown in figure 1. The reactor is a quartz tube with an I.D. of 7 mm. The reactor was heated by a cylindrical furnace placed around the reactor. The flow rates of feed gases helium, methane and oxygen were regulated by three Porter Instrument Co. model 201 mass flow controllers. Methane and oxygen were mixed with the dilution gas, helium, and then introduced downward through the reactor for all experiments. The feed was analyzed by on-line gas chromatography (HP 5890 equipped with a molecular sieve packed column and a thermal conductivity detector). The exhaust gas from the reactor was introduced into a condenser in which a mixture of dry ice and acetone was used to remove the residual water. The effluent gas from the condenser was also analyzed by the gas chromatograph. The condensate was analyzed by a GCD system (HP GCD G1800A) using Electronic Ionization Detector. The reaction products are mainly ethylene, ethane, carbon dioxide, carbon monoxide and trace formaldehyde. All experiments were carried out at atmospheric pressure.

The ionized gases are formed in a gap between two stainless steel electrodes. For DC corona reactions, the top wire electrode is a 1/16" stainless steel rod concentric with the reactor tube, while the lower electrode is circular and positioned perpendicular to the reactor axis and 10 mm below the tip of the top electrode. The lower plate electrode is held at a

potential of 0 volts (i.e., grounded). The catalyst bed is supported by the lower electrode. The catalyst bed of 0.1g Sr/La₂O₃ is about 8 mm deep, thus the wire electrode is situated about 2 mm above the catalyst bed, as shown in Figure 2. The DC discharge is created using a high voltage power supply (Model 210-50R, Bertan Associates Inc.). The reactor configuration, including electrodes, is identical to that used for the study of corona-induced OCM in the absence of catalysts.^[32] In the discharge volume between electrodes, the interaction between accelerated charged particles (i.e., electrons and ions) and other chemical species (i.e. molecules and radicals) takes place. This interaction leads to the synthesis of new chemical species including ethane and ethylene. In our experiments, a low input power (0~6w) was applied for all conditions. In present reactor design, we choose the stable wire high electric field characteristics and stable hydrodynamics of DC direct Corona (as shown in Figure 2) to make the catalyst powders charged and further get the stable charge accumulation on catalysts to enhance the catalysis process. And this is different from the design of Suib and Zerger^[37] who put the catalyst at the post plasma zone. The catalyst used in the DC corona experiment was Sr/La₂O₃ with a size of 40~60 mesh, prepared using the Pechini method^[20] as described in detail by Ajmera.^[16] An XRD characterization of the fresh catalyst phase indicated the catalyst composition to be approximately 30% La(OH)₃, 68% La₂O₃ and around 1% SrCO₃.

The non-thermal plasma characterizes itself intrinsically low gas temperature and high electronic temperature, and the electronic temperature, which corresponds to electron energy, has been restricted by corona discharge, as discussed in next discussion. Gas temperature would be an important parameter for corona discharge OCM. However, there is a difficulty in measuring gas temperature if thermocouple is situated at the inside of the reactor. The difficulty occurs when a high voltage is applied. A silent discharge will be easy to be initiated between the tip of wire electrode and the insulator and move the plasma to a small volume around the tip, as shown in figure 3. A temperature calibration conducted by comparing the measured temperature outside and inside the reactor with and without plasma reactions was

carried out first to ensure the accuracy of temperature measurements (within $\pm 5\%$). The calibration was performed carefully to control the plasma to be situated between two electrodes. The calibrated outside temperature will be referred as gas temperature with plasma reaction.

(FIGURE 1)

(FIGURE 2)

(FIGURE 3)

RESULTS and DISCUSSION

Studies of discharge reactions in the absence of catalyst were previously conducted and reported^[33]. Discharge reactions during corona processes depend on the polarity of the discharge and the characteristics of the gas mixture, specifically on the electron attaching species, such as oxygen. For the wire-plate electrode geometrical configuration (Figure 2), the term 'positive corona' is applied when the wire electrode potential is positive compared to the plate electrode potential. Both positive and negative DC corona processes in the absence of catalyst showed selectivity for C_2 products while no C_2 products formed in the blank reactor in the absence of corona discharge under the same reaction conditions. As the voltage was increased, the current increased and with it the conversion in the reactor, until a "saturation discharge current" was found. Beyond this point, increases in voltage caused only small increases in either current or methane conversion. The saturation current was obtained at a supply voltage of about 1.6kV for DC corona discharge at the reactor temperatures and gas compositions used in that study. The saturation phenomena was also observed at the same supply voltage in the present study.

1. DC Corona Discharge Reactions

(1) Effect of discharge on methane conversion

Figure 4 shows the effect of the positive corona on methane conversion at varying temperatures and at methane:oxygen feed ratios of 4:1. Particularly at lower temperatures there appears to be a synergistic effect in which methane conversion in the corona with catalyst bed is greater than the sum of the conversions in the corona only and catalyst run only individually. Compared with results of the packed bed only, the methane conversion in the corona with catalyst is almost five times higher while the selectivity for C_2 is over eight times larger at a temperature of 853K. The yield of C_2 products is increased by a factor of over 40 at such a temperature. Figure 5 shows a very similar result at a methane:oxygen feed ratio of 2:1. Over the entire range of conditions studied, the presence of the corona increases both the selectivity and yield achieved over the packed bed alone. Especially at 823K, corona discharge show us a great promotion of C_2 yield; with the catalyst alone, there is no C_2 catalytic activity at 823K. At higher temperature (i.e., above 973 K) the enhanced catalytic performance is limited by the availability of oxygen which, even in the absence of the corona, is completely consumed. The other reason for the limited enhancement is thought to be that, as temperature increases, the corona active volume will be reduced, as discussed in much more detail in our another paper^[33].

(Figure 4)

(Figure 5)

(2) Effect of oxygen partial pressure in the feed

Figure 6 shows the methane conversion and C_2 selectivity as a function of oxygen partial pressure with 100 sccm flowrate at 823 K, at which there is no C_2 catalytic activity for this catalyst (catalytic C_2 selectivity is zero as shown in Figure 6). For the corona discharge only, the oxygen partial pressure has only a slight influence on methane conversion and C_2

yield. For both positive and negative corona catalytic processes, however, methane conversion increases quickly with increasing oxygen partial pressure in the feed, although C_2 yield increases only slightly because C_2 selectivity decreases slowly with increasing oxygen partial pressure. Compared to results with catalyst alone and corona discharge alone, the catalyst plus corona discharge (both positive and negative) promotes significantly the catalytic conversion of methane to C_2 products. Plasma and catalyst characterizations are necessary to understand the type and extent of the catalyst surface modification leading to the enhancement.

(Figure 6)

(3) Polarity effect

Figure 6 already shows a significant polarity effect, and it is clear that the catalyst plus positive corona is more productive than the catalyst plus negative corona. Tables 1 and 2 demonstrates also the effects of polarity at two different gas temperatures. In all cases the plate electrode is grounded; for positive corona the wire electrode is held at +5 kV while for negative corona the wire electrode is held at -5 kV. The highest C_2 yields were obtained with positive corona packed bed processes. With either positive or negative corona, methane conversion decreases and oxygen conversion increases as the methane/oxygen ratio is increased. The ethylene/ethane ratio decreases with increasing methane/oxygen ratio, which suggests oxygen plays an important role in ethylene formation, i.e., via oxidative dehydrogenation of ethane during corona discharge OCM. A similar result was observed with corona discharge only.^[33]

We have reported the effect of polarity in homogeneous corona discharge OCM^[33]. In general, the reactivity of corona catalytic processes is related to the electronic performance of the corona. The positive corona typically exhibits streamer or glow characteristics, while the negative corona exhibits Trichel pulse or pulseless characteristics^[33]. The streamer corona possesses a much greater active volume than the other corona discharge forms, which are

limited by their generation mechanisms to the near-electrode regions, so that the positive corona catalytic process is more favorable for OCM.

Table 1: Comparison of Corona processes with catalyst (100ml/min, 953K)

CH ₄ /O ₂	Wire electrode potential, kV	Selectivity for C ₂ products, %	Yield of C ₂ Products, %	Conversion of methane, %	Conversion of Oxygen, %	C ₂ H ₄ /C ₂ H ₆
10:1	0	42	4.2	9.8	93	0.19
	+5	55	6.7	12.2	100	0.28
	-5	54	5.9	11.0	100	0.26
2.5:1	0	25	5.8	23.7	99	0.50
	+5	34	9.4	28.0	100	0.69
	-5	33	8.9	27.2	100	0.68
2:1	0	23	6.7	29.6	88	0.61
	+5	27	9.6	36.0	100	0.78
	-5	31	8.3	26.5	90	0.54

Table 2: Comparison of Corona processes with catalyst (100ml/min, 823K)

CH ₄ /O ₂	Wire electrode potential, kV	Selectivity for C ₂ products, %	Yield of C ₂ Products, %	Conversion of methane, %	Conversion of Oxygen, %	C ₂ H ₄ /C ₂ H ₆
10:1	0	0	0	1.8	44.1	
	+5	51	5.1	10.0	88.2	0.24
	-5	40	2.9	7.3	85.6	0.25
2.5:1	0	0	0	8.4	19.4	
	+5	43	8.7	20.2	85.0	0.59
	-5	33	5.3	16.0	72.6	0.61
2:1	0	0	0	8.8	12.3	
	+5	40	11.0	27.4	88.0	0.73
	-5	31	6.5	20.9	83.3	0.67

2. Discussion

It is generally accepted that OCM includes heterogeneous and homogeneous reactions. Basically, the activation of methane by the catalyst active sites to form reactive methyl radicals

will be followed by homogeneous radical reactions. In the presence of gas phase oxygen, it is difficult to prevent the formation of the thermodynamically favorable products CO_2 and CO . A gas discharge will be very helpful for both heterogeneous and homogeneous reactions towards the selective products by electron impact and/or electron attachment reactions with gaseous species. These reactions will change the chemical state of reactants which may react further on the catalyst surface and in the gas phase. In the Corona packed bed process electrons may collide with gas phase molecules and the catalyst surface. The interaction of excited species of a plasma with catalyst surface will change adsorption potentials and energetics of desorption of catalyst^[38]. This change will be favorable for the selective products of OCM and has been conformed experimentally. In addition, gas discharges will change the state of active species and CO_2 amount will be reduced by electron energy control of plasma. In our experiments, the DC Corona induces electrons with electron energy of about $5\text{eV}^{[29,30]}$. These relatively low energy electrons have insufficient energy to ionize methane, which has an ionization potential greater than $12\text{eV}^{[31]}$, but their energy is sufficient to initiate dissociative attachment reactions of oxygen leading to negatively charged oxygen ions.^[17,30] Due to its electronegative nature, oxygen easily forms negative ions either by direct attachment or by dissociative attachment. This will vary the gaseous oxygen state and reduce the formation rate of carbon dioxide. The increasing probability of a collision in the catalyst layer should also lead to the electron energy decrease and electron attachment. Similar to O^- species on solid catalysts, the oxygen ions in the plasma extract a hydrogen from methane molecules to activate the methane. Additionally, if the microelectric field between the charged particles is sufficiently strong, surface adsorption performance could be modified which could also enhance the conversion of methane by increasing the amount of chemisorbed oxygen or methane on the charged catalyst surface. Further research is being conducted to understand the mechanism of electron excitation heterogeneous reactions.

CONCLUSIONS

The present results demonstrate that:

1. The combination of catalyst and DC corona discharge shows a selectivity and activity enhancement beyond that achieved by either process alone for the oxidative coupling of methane. The lower the temperature the greater the enhancement.
2. DC corona processes exhibit a saturation discharge effect.
3. Increasing oxygen partial pressure in the feed will increase conversion of methane and yield of C₂ products.
4. The positive DC corona shows slightly better enhancement than does the negative corona.

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FIGURE 1 The Corona Reactor System

Figure 2 Corona Discharge Catalyst Bed

FIGURE 3 TEMPERATURE CALIBRATION

(a)

(b)

FIGURE 4 EFFECT OF TEMPERATURE ON POSITIVE CORONA DISCHARGE REACTIONS

FLOWRATE: 100sccm INPUT POWER: 5.6w CH₄/O₂: 4

(a)

(b)

FIGURE 5 EFFECT OF TEMPERATURE ON POSITIVE CORONA DISCHARGE REACTIONS

FLOWRATE: 100sccm, INPUT POWER: 5.6w CH₄/O₂: 2

(a)

(b)

FIGURE 6 EFFECT OF OXYGEN PARTIAL PRESSURE ON C2 SELECTIVITY AND METHANE CONVERSION

FLOWRATE: 100sccm INPUT POWER: 5.6w CH₄/O₂: 4
TEMPERATURE: 823K