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# An Experimental Study on the Oxidative Coupling of Methane in a Direct Current Corona Discharge Reactor over Sr/La<sub>2</sub>O<sub>3</sub> Catalyst

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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/La<sub>2</sub>O<sub>3</sub>, was used to investigate experimentally the corona discharge OCM reactions. Experiments were conducted over a wide range of temperatures (823–1023 K) and input powers (0–6 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 of C<sub>2</sub> products even at temperatures at which there is no C<sub>2</sub> activity for the catalyst alone. The methane conversion and C<sub>2</sub> yield increase with O<sub>2</sub> partial pressure during the corona-enhanced catalytic reactions, while the selectivity decreases slightly with increasing O<sub>2</sub> 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 C<sub>2</sub> over eight times higher at 853 K. A great enhancement in catalytic activity has also been achieved at a temperature at which the catalyst alone shows no C<sub>2</sub> activity. The conversion at higher temperature (more than 953 K) is limited by the poor corona performance and the availability of active oxygen species.

## 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 as a possible effective and economic way to convert methane to C<sub>2</sub> or higher hydrocarbons since the creative work of Keller and Bhasin (1982). The primary catalysts for the OCM reaction may be classified as either reducible or irreducible metal oxides (Lee and Oyama, 1988). Over reducible oxides, reactants (methane and oxygen) may be fed alternately. A redox mechanism of the reaction has been suggested (Lee and Oyama, 1988) for the production of C<sub>2</sub> products, and the metal oxide acts as both the reducing and oxidizing agents. Irreducible metal oxides, such as catalysts with rare-earth oxides (e.g., Sr/La<sub>2</sub>O<sub>3</sub> (DeBoy and Hicks, 1988), Sm<sub>2</sub>O<sub>3</sub> (Ekstrom, 1992), Ba/CeO<sub>2</sub> (Otsuka, et al., 1987), Ba/La<sub>2</sub>O<sub>3</sub> (Yamagata et al., 1993), Na<sub>2</sub>O/Pr<sub>2</sub>O<sub>3</sub> (Gaffney et al., 1988), and LaAlO<sub>3</sub> (Imai and Tagawa, 1986)), act as catalysts which are favorable for the oxidative coupling of methane. Over both reducible and irreducible oxide catalysts, OCM still requires such high reaction temperatures that the reaction probably proceeds both heterogeneously and homogeneously. Sufficiently high selectivity for C<sub>2</sub> hydrocarbons has not been achieved because of the nonselective heterogeneous and gas phase reactions to CO<sub>x</sub>. The need for higher C<sub>2</sub><sup>+</sup> selectivity has led to research on electrocatalytic 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 (1991) have reviewed catalytic

applications of these electrolyte materials. 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<sub>2</sub><sup>+</sup> selectivity may be achieved using these electrocatalytic methods (Eng and Stoukides, 1991; Nagamoto et al., 1990; Otsuka et al., 1985; Fujimoto et al., 1991; Seimanides, 1986), although selectivity remains limited because oxygen supplied through the membrane can also lead to CO<sub>x</sub>. 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<sup>2-</sup>) is the active site for methane activation on the reducible catalysts, and O<sup>-</sup>-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<sup>-</sup> or O<sup>2-</sup>, formed via electron attachment to oxygen molecules in the gas phase (Grill, 1994). Because the corona is relatively easy to establish, it has been applied in a variety of processes, including synthesis of chemicals (Flamant, 1994). In fact, some plasma techniques have been applied for 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 (Tachibana et al., 1984; Fraser et al., 1985; Ohl, 1994). Plasma techniques for the conversion of methane were investigated as early as the 1920s. Alexander (1929) reported the complete oxidation of methane by gas discharge. Mach and Drost

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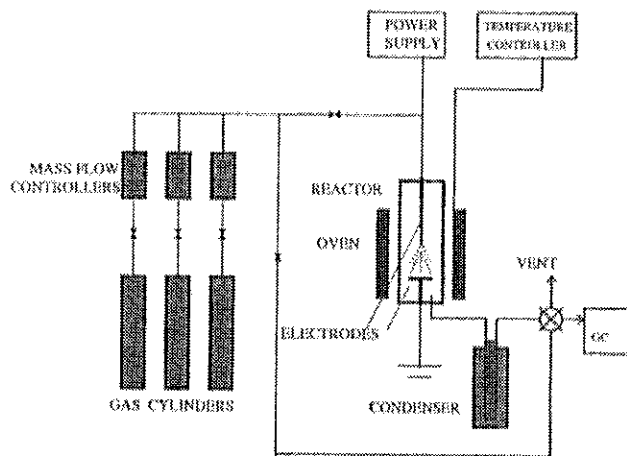


Figure 1. Outline of the corona reactor system.

(1983) 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 (1993, 1994) 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 (Amouroux and Talbot, 1968; Nester et al., 1988). Because of the low pressure and the resulting low mass flow rate, as well as the poor understanding of plasma chemistry, applications of methane plasmas for the industrial production of chemicals have not been developed. Chen et al. (1995) and Suib and Zenger (1993) have published their results on OCM over proton conductive catalysts (Chen et al., 1995) and catalysts  $Li/MgO$ ,  $La_2O_3$ , and  $Sm_2O_3$  (Suib and Zenger, 1993) using microwave plasmas. Compared to the results in the absence of plasma, a change in both the product selectivity and yield with a lower reaction (gas) temperature was observed over proton conductive catalysts when plasma was used. However, there was no proven improvement on the product selectivity and yield by microwave plasmas over the other catalysts (Suib and Zenger, 1993). 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  $C_2$  products (Liu et al., 1996). 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  $Sr/La_2O_3$ . The results suggest that the combination of corona discharge and heterogeneous catalysis may lead to an improvement in  $C_2$  selectivity and yield.

## Experimental Section

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, to maintain a total flow rate of 100 sccm and then introduced downward through the reactor for all experiments. The feed was analyzed by on-line gas

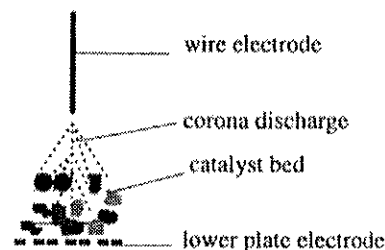


Figure 2. Wire-plate electrode configuration.

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 cooled by a mixture of dry ice and acetone that 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 an 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  $1/16$  in. stainless steel rod concentric with the center of the reactor tube, while the lower electrode is a circular disk 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 V (i.e., grounded). The catalyst bed is supported by the lower electrode. The catalyst bed of 0.1 g of  $Sr/La_2O_3$  is about 8 mm deep; thus, the wire electrode is situated about 2 cm 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. 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 (0–6 W) was applied for all conditions. We use one wire electrode and one plate electrode. This configuration has been found to yield stable dc coronas, in part because of its strong electric field present at the tip of the wire electrode. The catalyst is placed between the two electrodes (in the corona), which we speculate results in charge accumulation on the catalyst, potentially altering catalyst activity. This differs from the design of Suib and Zenger (1993), who put the catalyst in the post-plasma zone. The catalyst used in the dc corona experiment was  $Sr/La_2O_3$  with a size of 40–60 mesh, prepared using the Pechini method as described in detail by Ajmera (1995). An XRD characterization of the fresh catalyst indicated the catalyst composition to be approximately 30%  $La(OH)_3$  and 68%  $La_2O_3$ .

The nonthermal plasma is characterized by low gas temperature and high electron temperature. The electronic energy, which corresponds to electron temperature, has been restricted to be less than 6 eV (Eliasson and Kogelschatz, 1991) by the corona discharge, as discussed next. Gas temperature is an important parameter for corona discharge OCM. Measurement of gas temperature within the corona is complicated by the discharge which can occur between the wire tip and the

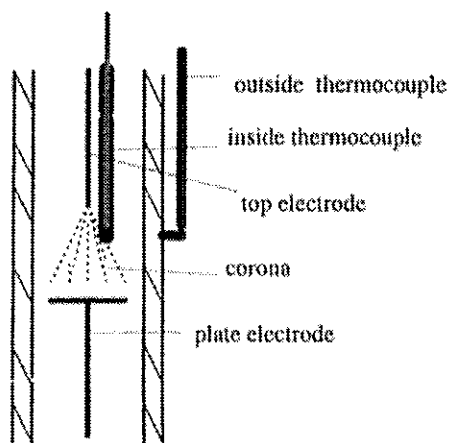


Figure 3. Temperature calibration.

insulated inner thermocouple. Such discharge would move the plasma to a small volume around the thermocouple tip, as shown in Figure 3. During the corona experiments, therefore, the inner thermocouple was removed, and the outer thermocouple was used to monitor gas temperature. A temperature calibration conducted by comparing the measured temperature outside (outer wall temperature) and inside the reactor with and without plasma reactions was carried out first to ensure the accuracy of temperature measurements. The calibration was performed under controlled conditions to ensure that discharge occurred only between the two electrodes and not between electrode and thermocouple. The temperature measured by the thermocouple placed against the reactor outer wall was found to be lower than the inside temperature by 10–60 °C, depending on the reaction and discharges.

## Results and Discussion

Studies of discharge reactions in the absence of catalyst were previously conducted and have been reported (Liu et al., 1996). 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<sub>2</sub> products, while no C<sub>2</sub> products formed in the blank reactor (with electrodes in place) 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 1.6 kV for the dc corona discharge and was almost constant for all reactor temperatures and gas compositions used in this study. The saturation phenomena was also observed at the same supply voltage in the present study, i.e., over Sr/La<sub>2</sub>O<sub>3</sub> catalyst.

### 1. Results of dc Corona Discharge Reactions.

**1.1. 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 is a synergistic effect in which methane conversion in the corona with catalyst bed is

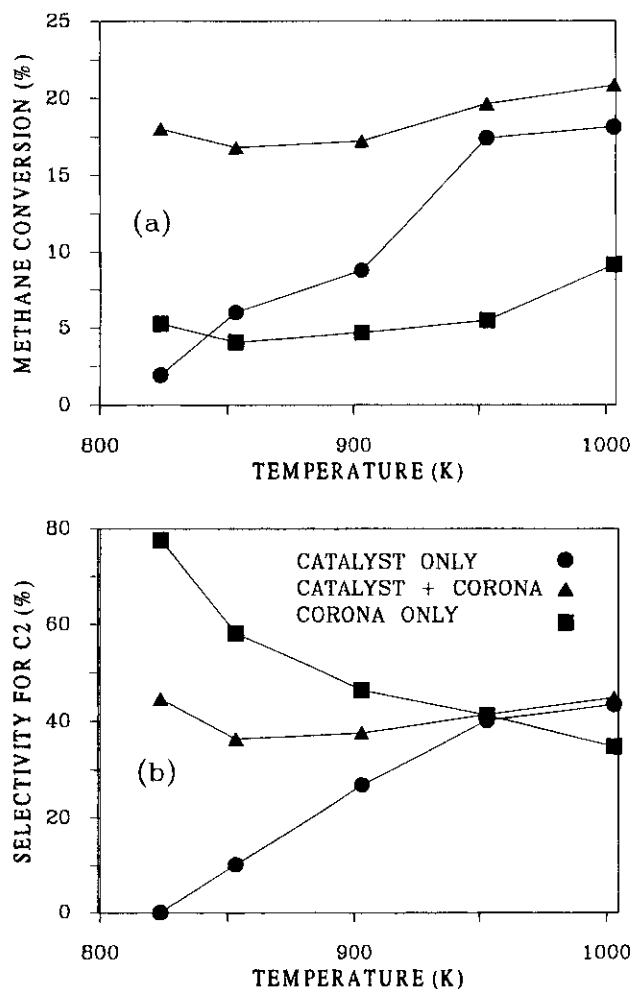
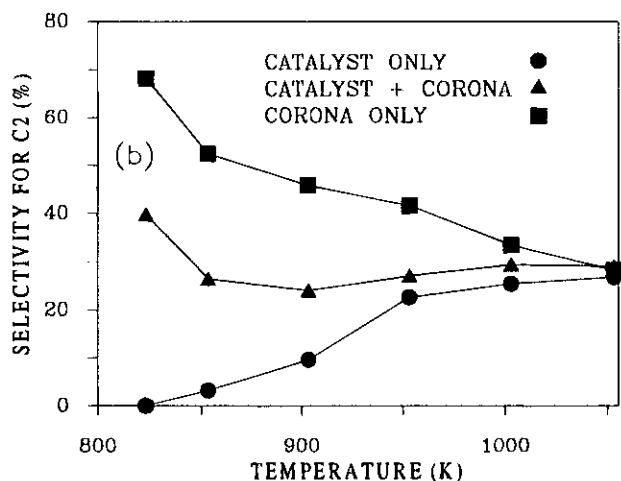
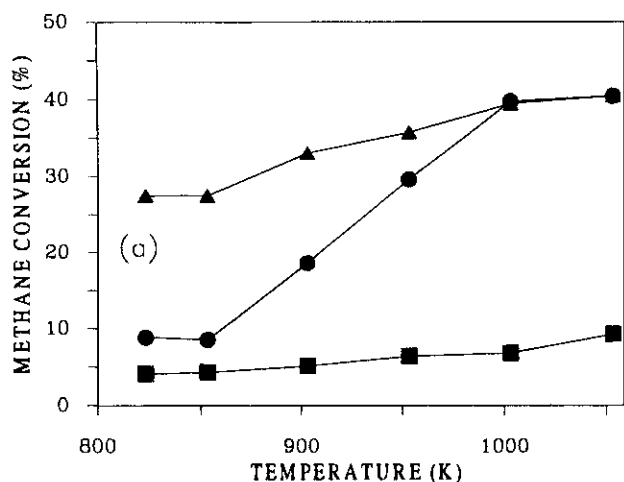


Figure 4. Effect of temperature on positive corona discharge reactions: flow rate, 100 sccm; input power, 5.6 W; CH<sub>4</sub>/O<sub>2</sub>, 4.

greater than the sum of the conversions obtained with the corona only and with the catalyst only under identical feed and temperature conditions. 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<sub>2</sub> is over eight times larger at a temperature of 853 K. The yield of C<sub>2</sub> products is increased by a factor of over 40 at this 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 823 K, the corona discharge shows a great promotion of C<sub>2</sub> yield. With the catalyst alone, there is no C<sub>2</sub> catalytic activity at 823 K. Above 973 K the corona-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 at elevated temperature is thought to be that, as temperature increases, the corona active volume will be reduced, as discussed in greater detail elsewhere (Liu et al., 1996).

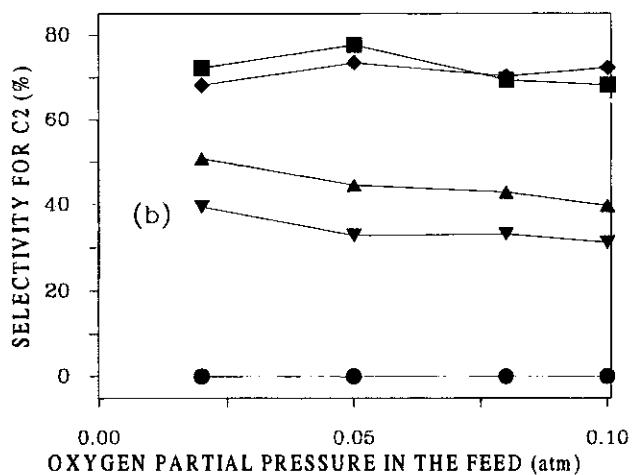
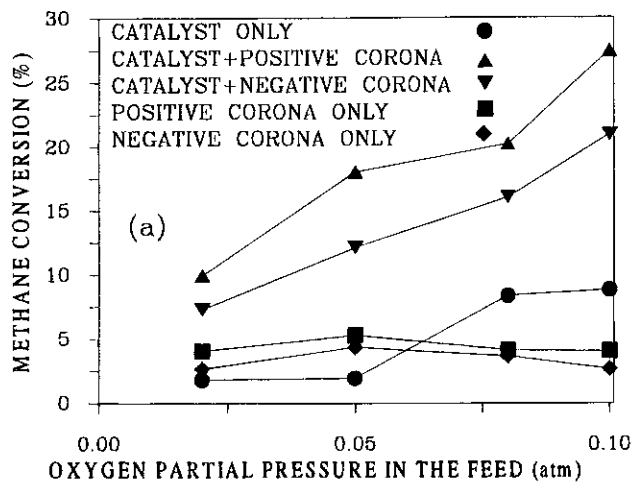
**1.2. Effect of Oxygen Partial Pressure in the Feed.** Figure 6 shows the methane conversion and C<sub>2</sub> selectivity as a function of oxygen partial pressure with 100 sccm flow rate at 823 K, under which conditions there is no C<sub>2</sub> catalytic activity for this catalyst (catalytic C<sub>2</sub> 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<sub>2</sub>



**Figure 5.** Effect of temperature on positive corona discharge reactions: flow rate, 100 sccm; input power, 5.6 W; CH<sub>4</sub>/O<sub>2</sub>, 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<sub>2</sub> yield increases only slightly because C<sub>2</sub> 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<sub>2</sub> products. Plasma and catalyst characterizations are necessary to understand the type and extent of the catalyst surface modification leading to the enhancement.

**1.3. 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 also demonstrate 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<sub>2</sub> 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.



**Figure 6.** Effect of oxygen partial pressure on C<sub>2</sub> selectivity and methane conversion: flow rate, 100 sccm; input power, 5.6 W; CH<sub>4</sub>/O<sub>2</sub>, 4; temperature, 823 K.

We have reported the effect of polarity in homogeneous corona discharge OCM (Liu et al., 1996). 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. 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 high conversion of methane. It should be noted that the positive corona is also more effective for ozone formation (Eliasson and Kogelschatz, 1991); however, the presence of ozone is not expected to improve C<sub>2</sub> selectivity.

**2. Discussion.** It is generally accepted that catalytic 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<sub>2</sub> and CO.

The gas discharge enhances both homogeneous and heterogeneous reactions through electron impact and/or electron attachment with gaseous species. Interaction with discharge electrons changes the chemical state of gaseous species leading to further reactions in the gas phase or on the catalyst surface. While it is difficult

**Table 1. Results of Corona Discharge Processes with a Sr/La<sub>2</sub>O<sub>3</sub> Catalyst<sup>a</sup>**

CH <sub>4</sub> /O <sub>2</sub>	wire electrode potential, kV	selectivity for C <sub>2</sub> product, %	yield of C <sub>2</sub> products, %	conversion of methane, %	conversion of oxygen, %	C <sub>2</sub> H <sub>4</sub> /C <sub>2</sub> H <sub>6</sub>
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

<sup>a</sup>Total gas flow rate = 100 mL/min, *T* = 953 K.

**Table 2. Results of Corona Discharge Processes with a Sr/La<sub>2</sub>O<sub>3</sub> Catalyst<sup>a</sup>**

CH <sub>4</sub> /O <sub>2</sub>	wire electrode potential, kV	selectivity for C <sub>2</sub> product, %	yield of C <sub>2</sub> products, %	conversion of methane, %	conversion of oxygen, %	C <sub>2</sub> H <sub>4</sub> /C <sub>2</sub> H <sub>6</sub>
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

<sup>a</sup> Total gas flow rate = 100 mL/min, *T* = 823 K.

to ascertain the exact nature of the relevant excited species, some information is available. In our experiments, the dc corona induces electrons with electron energies of about 6 eV (Eliasson and Kogelschatz, 1991). These relatively low-energy electrons have insufficient energy to ionize methane, which has an ionization potential greater than 12 eV (Sorensen et al, 1995), but their energy is sufficient to initiate dissociative attachment reactions of oxygen leading to negatively charged oxygen ions (Grill, 1994; Eliasson and Kogelschatz, 1991). Due to its electronegativity, oxygen easily forms negative ions either by direct attachment or by dissociative attachment. We believe that, similar to O<sup>-</sup> species on solid catalysts, the plasma oxygen ions activate methane by extraction of a hydrogen. Homogeneous reaction then results in C<sub>2</sub> products (i.e., reaction between two methyl radicals) or in carbon oxides (i.e., reaction between methyl radicals and oxygen).

In addition, in the corona packed bed process electrons may collide with and excite adsorbed species on the catalyst surface, or excited species in the gas phase may collide with the catalyst surface. The adsorption potentials and desorption energetics of excited species are significantly different from those of stable species (Rapakoulis, 1993), which may be favorable for increased conversion or selectivity for OCM as suggested by our results.

Finally, electrons may collide with the catalyst itself, charging the catalyst particles. 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, e.g., 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 of heterogeneous reactions.

## Conclusions

The present results demonstrate the following:

(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 C<sub>2</sub> products.

(4) The positive dc corona shows slightly better enhancement than does the negative corona.

The dc corona discharge modified catalytic conversion of methane over Sr/La<sub>2</sub>O<sub>3</sub> has shown us that a much lower operating temperature is needed (200 °C less), compared to the catalytic operation in the absence of discharges. This suggests the corona heterogeneous technique has potential for improving the process economics.

## Acknowledgment

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