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Enhancement of Methane Conversion Using Electric Fields

**Quarterly Report
December 1994 - March 1995**

Richard G. Mallinson
Lance L. Lobban

April 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
University of Oklahoma
Norman, Oklahoma

MASTER

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**By
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Office of Research Administration
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April 1995

PROJECT ABSTRACT

The goal of this project is the development of novel, economical, processes for the conversion of natural gas to more valuable products 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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Introduction

This report summarizes the second quarter of the project. With funding from several research projects, The BET system (partially funded by this project) is on order as is a new gas analysis GC and a GC with a mass detector (partially funded by this project). Amongst these, our analytical capability will be sufficient to properly support the project.

Task 2: Electric Field Conversion

Material balance experiments have been initiated and we expect to be in a position to initiate experiments to achieve project objectives during May, with the completion of courses the students are presently diverted with.

Construction of the new reaction system is complete except for the new power supply which is being ordered (we can temporarily use the existing components in this system). This system is a flat plate geometry, approximately 12 cm wide and 90 cm long, giving an electrode area similar to the present system, as was discussed in the last report. This system should also become operational during May.

Task 3. Electric Field Enhanced Conversion

The focus here has shifted towards a new system configuration in which we are initiating a DC discharge in proximity to a catalytic substance. In experiments so far, a number of interesting enhancements to thermal rates and selectivity patterns have been observed which go beyond the probable localized catalyst heating, as is discussed in the draft paper appended to this report.

APPENDIX

An Experimental Study of DC Electric Field Effects on the Oxidative

Coupling of Methane by Gas Discharge

INTRODUCTION

Natural gas, of which about 90% is methane, is an inexpensive, abundant natural resource in the world. A great effort has been made to study catalysts which are active and selective for the oxidative coupling of methane, which is considered as the most effective and economic way to convert methane to C_2 or higher hydrocarbons since the creative works of Keller and Bhasin^[1]. It has been shown that metal oxides mixed with rare-earth oxides, such as Sr/La_2O_3 ^[2], Sm_2O_3/Al_2O_3 ^[3], Ba/CeO_2 ^[4], $BaLa_2O_3$ ^[5], Na_2O/Pr_2O_3 ^[6] and $LaAlO_3$ ^[7] are favorable for the oxidative coupling of methane. However, the high enough selectivity for C_2 hydrocarbons has not been met because of the nonselective gas phase reactions for CO_x induced by catalyst surface. The effort for higher C_2^+ selectivity has resulted in researches on electrocatalytic conversion of methane, and almost all these studies claimed membrane reactor systems as an advanced reaction method, with which most of these membrane are solid electrolytes. Eng and Stoukides^[8] have reviewed applications of these electrolyte materials in catalysis in detail, of which three principle applications of solid electrolytes, solid electrolyte potentiometry (SEP), solid oxide fuel cells (SOFC) and electrochemical oxygen pumping (EOP) have been discussed. Experiments have also shown that by-products of OCM reaction is decreased and higher C_2^+ selectivity is achieved by using these

electrocatalytic methods.^[9-16] In these system, oxygen ion was supplied from air side to methane side through a solid electrolyte in which oxygen ion transport was controlled by electromotive force, the difference between potentials of both sides. The activity, however, is still low, because the performance of membrane catalysts was found to be determined by the composition of metal oxides,^[15,17] while the selectivity was not still high enough, because gaseous oxygen supplied through the membrane caused CO_x formation too. A improvement has been done by Tokao Nozaki and Kaoru Fujimoto.^[18] Instead of oxygen supplied through the membrane, methane is selectively converted to C₂ hydrocarbons by the lattice oxygen of Lead oxide that was considered to transport through the membrane by the concentration gradient of lattice oxygen. The high selectivity (~90%) has been achieved; but, unfortunately, the high activity still has not been met.

In this paper, we present a comparative research of another potential improvement, which external electric field will be applied to enhance the catalytic conversion of methane.

Experimental Details

The experimental setup for investigation of the electric field enhanced catalytic conversion of methane is shown in Figure 1. The design of the reactor itself is of interest and

(Figure 1)

simple. The catalyst disk of about 1.5mm thick, made by pressing the catalyst powder under pressure of about 200 atm. The catalyst placed on one of the two stainless steel electrodes, the gap between the two electrodes is 12.5 mm. The inner diameter of the quartz tube reactor is 10 mm.

(Figure 2)

A high voltage power supply (Model 210-50R, Bertan Associates Inc.) was used to supply

the upper electrode with single polarity high potential. A DC electric field between catalyst disk established like this way.

Catalysts used in this experiment were Li/MgO, prepared based on the method of Wen-Yuan Tung and Lance Lobban^[19], $\text{La}_{0.9}\text{Sr}_{0.1}\text{O}_{1.45}$ and $\text{La}_{0.8}\text{Sr}_{0.2}\text{YO}_{2.9}$ prepared using the Pechini method.^[20]

Methane and oxygen ($\text{CH}_4/\text{O}_2=4$) were mixed with helium and then introduced to the reactor with flowrate of 100 ml/min. The exhaust gas 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 analyzed by a HP5890 gas chromatograph with a thermal conductivity detector and a molecular sieve packed column, made by Alltech Associates Inc.

RESULTS and DISCUSSIONS

1. Blank test:

A blank test was conducted first. Both positive and negative polarities of upper electrode showed a electrocatalytic effect for C_2 products without catalyst, while no C_2 products formed without electric field. The electric field enhancement occurred only with a gas discharge current, which was produced when the hot gas passed through the upper electrode. A saturation discharge current was found. In order to get this current, 1.6kV was needed for positive polarity and 2.4kV for negative at 600 °C. As shown in figure 3, the DC electric field inhibited CO_2 reaction and no CH_4 and O_2 conversion with +2KV potential, with temperature less than 650°C. An increase in C_2 selectivity and CH_4 and O_2 conversions observed when temperature reached 650°C.

(Figure 3)

With a potential up to 3KV, the C_2 selectivity reached its highest value (83.5%) at 550°C

and then decreased with increase in temperature. For negative polarity with 2.4~3.0KV potential of upper electrode, the similar trend were found but less electrocatalytic active for C_2 products, compared to positive polarity. All the tests was conducted at saturation current.

2. Catalyst Run:

As mentioned in blank test, the electric field enhancement with catalyst run only also occurs with gas discharge current for both positive and negative polarities. Only the saturation discharge current accompanies the stable electric field enhancement effect. The current, for all catalysts and all reaction conditions tested, was 1.02 mA. A relaxation time has been found to reach this saturation current, and this suggested there was a relaxation reaction rate to reach the saturation electric field enhanced effect. The potential and relaxation time to get the saturation discharge current were different and depended on temperature, catalyst, residence time, oxygen partial pressure and polarity of electrodes. Figure 4 shows the potential effect on the oxidative coupling reaction for the catalyst of $La_{0.8}Sr_{0.2}YO_{2.9}$. It was evident that the saturation effect happened at 2.4KV. Figures 5 and 6,7 show the effects of residence time and oxygen partial pressure, respectively. The control step of reactions is different with the different residence time. As this residence time less than 0.4s, figure 5 suggested the reaction a surface reaction control mechanism, but as the residence larger than 0.4s, a transfer control mechanism was suggested. On the other hand, from figures 6 and 7, the most favorable oxygen partial pressure was 0.05 in order to reach the optimum production. Although the oxygen partial pressure have a important effect on the catalyst conductivity, a small change of electric field enhanced catalytic performance with the oxygen partial pressure was found.

This means the nature of gas discharge have much more important role for this research.

(FIGURE 4,5,6,7)

For all three catalysts tested, Li/MgO, $\text{La}_{0.9}\text{Sr}_{0.1}\text{O}_{1.45}$ and $\text{La}_{0.8}\text{Sr}_{0.2}\text{YO}_{2.9}$, different electric field enhanced effects were found. For Li/MgO, both the positive and negative polarities of upside electrode made a lot of increase in C_2 selectivity (the largest increase in S_{C_2} was 78.9% with negative polarity at 550°C), but the negative polarity showed a larger enhancement in C_2 yield, CH_4 and O_2 conversions than positive polarity at temperature of $600\sim 800^\circ\text{C}$. A similar phenomenon was found for the $\text{La}_{0.8}\text{Sr}_{0.2}\text{YO}_{2.9}$ catalyst, but the positive polarity showed more favorable C_2 selectivity. A very different result was presented for the catalyst of $\text{La}_{0.9}\text{Sr}_{0.1}\text{O}_{1.45}$, which the negative polarity inhibited the C_2 yield with a lower C_2 selectivity and a lower CH_4 conversion, compared with results without electric field, as was shown in figure 8.

(FIGURE 8)

The catalyst run has suggested different oxidative coupling mechanisms, specially probably different active oxygen species, with and without electric field. Further research should be conducted to understand these reactions.

CONCLUSIONS

The present results demonstrate that:

1. DC electric field shows a selectivity and activity enhancement in the oxidative coupling of methane, and this enhancement only occurs with gas discharge. A much larger enhancement was found at the temperature less than 650°C .
2. There is a saturation discharge current for both positive and negative polarities.

3. There is a relaxation time to reach the saturation current. Further to understand the relaxation phenomena, the dynamic performance of the reaction system could be understood.

4. Possible surface reaction control mechanism and charge transfer control mechanism have been suggested by the effect of residence time. Further research towards these mechanisms may explain some unstable phenomena and important electrocatalytic performance.

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EFEC EX.SETUP

Figure.1

FIGURE 2. CLOSEUP REACTOR

Figure 2

FIGURE COMPARISON OF RESULTS WITH AND WITHOUT ELECTRIC FIELD

Fig 3a

NO CATALYST; FLOWRATE:100 ml/min; CH₄/O₂:20/5

DATA WITH ELECTRIC FIELD ▲
DATA WITHOUT ELECTRIC FIELD ●

NEGATIVE POLARITY UPSIDE ELECTRODE

FIGURE 3: COMPARISON OF RESULTS WITH AND WITHOUT ELECTRIC FIELD

CATALYST: $\text{La}_{0.8}\text{Sr}_{0.2}\text{YO}_{2.9}$; TEMP.: 600°C CH₄/O₂: 20/5 FLOWRATE: 100ml/min

FIGURE EFFECT OF VOLTAGE ON SC₂,XCH₄,XO₂,YC₂

Fig 41

CATALYST: LaSrYO TEMP.: 600°C CH₄/O₂=4
 DATA WITHOUT ELECTRIC FIELD ●
 DATA WITH ELECTRIC FIELD WITH 2.4-3.0KV POSITIVE POTENTIAL UPSIDE ELECTRODE ▲
 DATA WITH ELECTRIC FIELD WITH 2.4-3.0KV NEGATIVE POTENTIAL UPSIDE ELECTRODE □

FIGURE Effect of residence time

CATALYST: LaSrYO TEMP.: 600°C CH₄/O₂=4

DATA WITHOUT ELECTRIC FIELD ●

DATA WITH ELECTRIC FIELD WITH 2.4-3.0KV POSITIVE POTENTIAL UPSIDE ELECTRODE ▲

DATA WITH ELECTRIC FIELD WITH 2.4-3.0KV NEGATIVE POTENTIAL UPSIDE ELECTRODE □

FIGURE EFFECT OF OXYGEN PARTIAL PRESSURE

Fig 7

CATALYST: LaSrO FLOWRATE: 100ml/min CH₄/O₂=20/5

DATA WITHOUT ELECTRIC FIELD ●

DATA WITH ELECTRIC FIELD WITH 2KV POSITIVE POTENTIAL UPSIDE ELECTRODE ▲

DATA WITH ELECTRIC FIELD WITH 2.7-3KV NEGATIVE POTENTIAL UPSIDE ELECTRODE □

FIGURE: COMPARISON OF RESULTS WITH AND WITHOUT ELECTRIC FIELD

Fig 8