Profiles of Methane Dimerization with a Glow Discharge Plasma System

By

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The dimerization of methane in the absence of oxygen has been investigated in order to evaluate a newly-developed glow-discharge plasma reactor operated at atmospheric pressure. A homogeneous circular plasma zone is observed between two electrodes of a rotor and a stator, the former of which is rotating at a high speed to make a larger reaction zone. It was recognized that in a stream of flowing helium that methane is converted to C 2 hydrocarbons at high selectivities which decreased with the residence time in the plasma zone. The ratio of ethane : ethylene : acetylene (2 : 2 : 5) produced was, however, independent of the methane conversion.

1. Introduction

During the recent years various gaseous reactions in plasma reactors have been the subject of numerous research groups. Most plasma reactions in the gas phase have been performed in a microwave region[1-4] under considerably low pressure to maintain a longer life of excited plasma species. Microwave-induced reactions in the gas phase have primarily been pursued by Wan et al.[1] Pulsed microwave catalysis of methane coupling,[2] hydrocarbon oxidation,[2] destruction of environmental pollutants,[2] decomposition of organic halides,[3] decomposition of olefins,[4] production of acetylene,[5] and other reactions have been reported. Other groups such as Rossy et al.[6] have used similar approaches to study hydrocarbon rearrangements.

Our work in this area has focused on the study of microwave plasmas to make catalysts[7,8] and in combination with catalysts to enhance selectivity of methane origomerization[10,11] and oxidation of methane to oxygenates such as methanol and formaldehyde.[12] Many of the principles of microwave plasmas are similar to microwave heating as well as the potential use of glow-discharges in catalytic reactions.

The present paper reports a qualitative examination of a newly-designed reactor with a glow-discharge plasma used at atmospheric pressure. The reactor consists of two electrodes, a rotor and a stator. The former electrode is rotating at a high speed during operation in order to produce a large plasma zone, i. e., to compensate shorter lives of the plasma species under atmospheric pressure. Another advantage of this reactor is that the high-speed rotation of the electrode also makes a gradientless condition of the reactant mixture in the plasma zone. There are, at present, few articles concerning glow-discharge plasma reactions at atmospheric pressure.

Methane coupling has been carried out for evaluation of the reactor. The conversion of methane which is an abundant resource of natural gas into variable C2 hydrocarbons has recently been of considerable interest. Methane coupling has widely been studied in the presence of appropriate amounts of oxygen over various catalysts. The reaction has been performed in the absence of oxygen in the present system, i. e., the reaction product will be free from oxygenated contaminants such as water and carbon oxides.

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2. Experimental

The configuration of the plasma reactor used in the present work is demonstrated in Fig. 1. The flow diagram of the experimental apparatus is shown in Fig. 2. The glow-discharge plasma occurs between two electrodes, a rotor with 12 thin blades (A) and a stator in the shape of a circular wall (B), made of iron and copper, respectively. The distance between the two electrodes is 0.3 mm. The reactor is tightly covered by quartz funnels (D) with rubber O rings. Under operating conditions, the rotor (A) driven by a motor (C) is rotating at a high speed (3,000 rpm) in a stream of continuous flowing reactant gases. The input AC power is 3 kV in the frequency of 60 kHz for the discharge in this experiment. As the result, a homogeneous circular light of discharge with a diameter of 6 cm was observed under the operating condition. The condition of discharge (wave forms of current and potential) is monitored during operation with a digital oscilloscope with a high voltage probe.

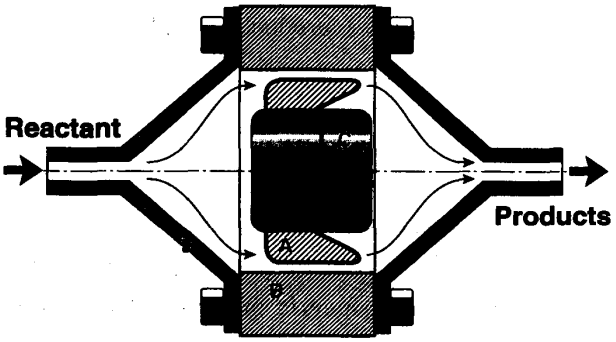

Fig. 1 Configuration of the glow-discharge plasma reactor : A, blade of rotor electrode (Fe); B, stator electrode (Cu); C, high-speed motor ; D, quartz wall.

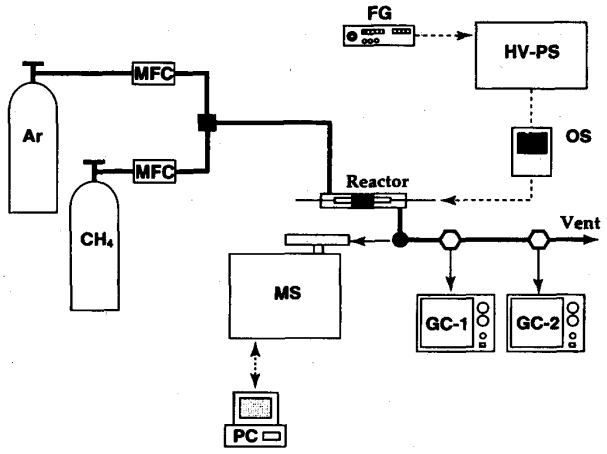

Fig. 2 Schematic diagram of the flow system : MFC, mass flow controllers ; MS, mass spectrometer ; GC-1 and GC-2, gas chromatograph ; PC, multi channel programmer operated by a computer ; FG, function generator ; HV-PS, high-voltage power supply system ; OS, digital oscilloscope.

Prior to each reaction, the electrodes were treated with plasma generated with pure helium for 30 min to clean the surface of the electrodes. A reactant gas of 20% methane in helium is premixed from flow rates with mass flow controllers and then introduced into the reactor at a total flow rate of 25–96 mL min^{-1} under atmospheric pressure. Analyses of reactant/product gas mixture were carried out continuously with a mass spectrometer (Ulvac, MSQ-150) with a multichannel programmer through an orifice sampling system and periodically with a gas chromatographs through a six-port valve with sampling loop.

3. Results

The appearance of the reactor under operation changes as follows. When the power (AC 3 kV and 60 kHz) was supplied to the reactor in a stream of pure helium, 46 mA of the current was passed and a circular homogeneous light was observed between the two electrodes of the rotor and stator. The breakdown and normal glow voltages measured with the digital oscilloscope were 2,350 and 650 V, respectively, under the operating condition. Upon the introduction of 20% methane in helium into the reactor, no substantial changes in these voltages were observed, although the blue light in pure helium turned to a bright white. At the same time the wave form of voltage for the typical glow-discharge in the oscilloscope became more noisy, in the form of a "showering arc" which is probably due to excitations of methane molecule. A comparatively small emission of heat was observed during the methane reaction, i.e., the maximum temperature of the reactor wall remained unchanged at about 360 K during the discharge for 3 hours.

A large amount of hydrogen formation was observed right after the introduction of the reactant gas into the reactor. The hydrocarbon products in this reaction system consisted of mainly C 2 hydrocarbons, ethane, ethylene and acetylene, and negligible amounts of C 3 and C 4 hydrocarbons. A steady state

of methane conversion was attained within 10 min after the reaction started and no appreciable decrease in the conversion was observed during two hours of continuous operation. In addition to the hydrogen and light hydrocarbon products, a substantial amount of carbon formation was observed on the surface of the electrodes after a long period of the reaction. This surface carbon was oxidized into carbon monoxide and carbon dioxide by the discharge in a stream of 20%oxygen in helium. A gradual decrease in the methane conversion (probably due to coke formation) was observed with time on stream after about two hours of operation.

The product distribution obtained in the reaction of methane under steady-state conditions is given in Table 1, where the experiments were carried out at flow rate of 25–96 mL min^{-1} with 20% methane in helium. The steady-state conversion of methane decreased appreciably with increase in the flow rate of the reactant gas.

In the presence of appropriate amounts of oxygen (as is widely performed in conventional catalysis[13,14]) methane converts exclusively into carbon monoxide and hydrogen in the present plasma reactor under similar condition used here. The presence of oxygen in the system, however, almost completely prevents the formation of carbon on the electrode surface. No substantial decrease of methane conversion in this partial oxidation was observed with increasing time on stream. This observation suggests another advantage of the present glow-discharge plasma reactor.

Table 1. Results of methane reactions in the glow-discharge plasma reactor at atmospheric pressure.

Flow rate (mL min^{-1})	CH_4 Conv.	C_2H_2	C_2H_4 (%)	C_2H_6
25	22.5	8.0	3.8	3.4
50	14.8	6.2	2.6	2.5
50	14.2	5.7	2.5	2.6
75	9.6	4.4	1.8	1.7
75	9.4	4.6	1.7	1.8
96	8.5	4.1	1.6	1.7
96	7.7	3.7	1.5	1.6

Electrode; rotor-Fe, stator-Cu.
Reactant; 20% CH_4 in HE.
Input power; 3kV, 60kHz.

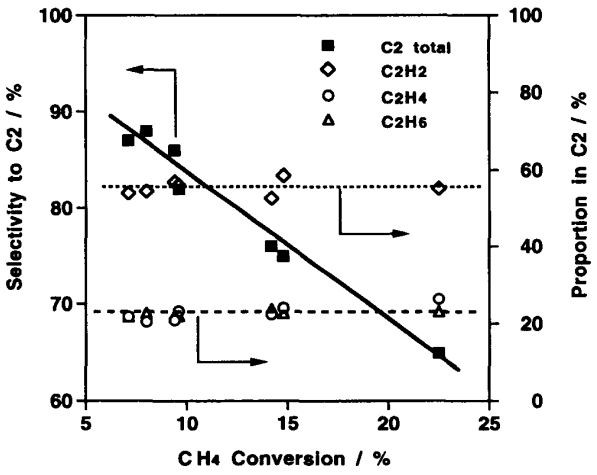

Fig. 3 Product distribution of methane dimerization with the plasma reactor.

4. Discussion

A profile of the formation of C 2 hydrocarbons is illustrated in Fig. 3. At flow rates higher than 75 mL min^{-1} the gaseous product of the reaction consisted of mostly C 2 hydrocarbons. The selectivity to these compounds decreased with increase in methane conversion. This presumably indicates that the primary products in this reaction system are C 2 hydrocarbons and that with increasing the residence time in the plasma zone (with decreasing flow rate) the C 2 hydrocarbons further convert into coke. The noise in the wave shape of the voltage-time trace due to showering arcs became stronger with the accumulation of carbonaceous material on the electrode surface.

The proportion of each C 2 hydrocarbon formed is also shown in Fig. 3. Under steady-state conditions, methane converts into ethane, ethylene and acetylene in a ratio of 2 : 2 : 5, respectively. This ratio, which is consistent with those obtained in a microwave plasma by Platzner and Marcus,[15] remained unchanged with change of the methane conversion. From this point of view, the reaction mechanism for the formation of each C 2 hydrocarbon is considered to be completely different (the simultaneous reactions). For example, the excited species for these C2 products are independent each other.

The excited species in plasma zones responsible for the formation of each hydrocarbon are still under considerable debate. Oumghar et al[16,17] stated that the methane reaction in plasma zones involved many

kinds of free-radical processes and that energetic electrons allow the formation of C, CH and CH_2 radicals which primarily produce acetylene. Hiraoka et al.[18] found in a glow-discharge plasma under a low pressure, on the other hand, that these radicals react with methane to produce mainly acetylene, ethylene and ethane, respectively.

In conventional catalytic reactions, methane coupling have been performed with appropriate amounts of oxygen in order to make favorable thermodynamic conditions which involve formation of water. The temperature (probably the electron temperature) is considered to be extremely high (probably above 2000 K) in the plasma zone of this reactor under operating condition tested. Free from oxide contaminants, such as water and carbon dioxide, might be another advantage of this system.

Traditional techniques of the discharge plasma have widely been investigated in the field of "plasma processing." For the most part, discharges in the corona and the arc regions have been employed with these techniques. One of the objectives of the present study is to take advantage of the application of "gentle" glow-discharge plasmas for a chemical reaction in the gas phase. Although further detailed investigations are required for the evaluation of this system, we believe that overall capabilities of the plasma reactor operated at atmospheric pressure have been demonstrated in this preliminary work.

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