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Oligomerization and Carbon Dioxide Reforming of Methane in a Dielectric-barrier Discharge-plasma System

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At room temperature and under atmospheric pressure, direct oligomerization of CH₄ to C₂ and C₃ hydrocarbons and CO₂ reforming of CH₄ to CO and H₂ in the Ar stream have been investigated by a nonthermal dielectric-barrier discharge-plasma reactor. Conversion and selectivity of the reactions strongly depended on input voltage, on concentration and on the ratio of the reactant. It was confirmed that the reactions in the Ar stream occurred where the input voltage was above *ca.* 1, which was considered as the break-down voltage of Ar. The intensity of emission spectra due to Ar excitation decreased with increasing reactant concentration. From these points of view, the reactions in the plasma zone were, therefore, found to proceed *via* energy transfer from excited species of Ar atoms to the reactant molecules in the plasma zone. The energy efficiency of the reforming reaction of the present plasma system increased with decreasing input voltage.

1. Introduction

During the past decade, the use of natural gas (mainly methane) and carbon dioxide as new energy sources has become most important and urgent. And with it, pollution and environmental problems have come to the fore. These molecules are, however, thermodynamically stable to be activated by conventional thermal and catalytic processes. In the two recent years, we have been investigating performances of cold discharge plasma systems to activate stable small molecules under atmospheric pressure, *i.e.*, decompositions of NO¹⁾, H₂O²⁾, and CO₂^{3),4)}.

Various types of energy and radiation such as microwave^{5),6)}, radio frequency^{7),8)} and electricity can be used^{9),10)}. However, only limited number of studies in these plasmas are available due to the low yields resulting from factors as due to the use of low pressure, mass transfer limitations, and high operational costs. Many researchers have been devoting their studies for practical applications¹¹⁾ of packed-bed corona-discharge plasma reactors used under atmospheric pressure; for example, in the decomposition especially of freons^{12),13)}. Moreover, Futamura *et al.* are investigating the mechanism involved in the decomposition of volatile organic compounds^{14),15)}.

One of the authors has already studied oligomeriza-

tion^{16)~18)} and partial oxidation^{19)~21)} of CH₄ using a microwave induced plasma reactor in the presence of a catalyst. These new processes were, however, investigated under considerably low pressures, since the life times of excited species were too short to perform such chemical reactions under atmospheric pressure. In the present study, a system of cold discharge plasma²²⁾ with low power consumption in the ac glow discharge region²³⁾ has been examined under atmospheric pressure.

2. Experimental

2.1. Plasma Reactor

The dielectric-barrier discharge (silent-discharge) plasma reactor used in the present work is illustrated in Fig. 1. By tube fittings (Swagelok made of perfluoroalkoxide), an inner electrode (Cu in most experiments) 8 mm outside diameter and 70 mm long was supported at the center of a quartz tube of 10 mm inside diameter. The quartz tube is tightly surrounded with a copper tape 70 mm long as an external electrode. The distance between the inner electrode and the reactor wall was 1 mm in the present experiments. When ac current of high voltage from 1 to 7 kV was supplied to the system in the stream of pure Ar, and reactant mixtures of CH₄/Ar, or (CH₄ + CO₂)/Ar, a homogeneous cylindrical discharge occurred between the inner electrode and the quartz wall of the reactor tube.

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Fig. 1 Profile of the Dielectric-barrier Discharge-plasma Reactor

MFC, mass flow controllers; MS, mass spectrometer; PC, programming computer; GC, gas chromatograph; FG, function generator; HV-PS, high voltage power supply system; OS, digital oscilloscope.

Fig. 2 Schematic Diagram of the Plasma Reaction Apparatus

2. 2. Apparatus and Procedure

Oligomerization of CH_4 to C_2 and C_3 hydrocarbons in the absence of such oxidant as O_2 , and CO_2 reforming of CH_4 to CO and H_2 in Ar plasma were carried out under atmospheric pressure by using a conventional flow system with a high voltage power supply^{1),2)}, as shown in Fig. 2. Using mass flow controllers (MFCs), the reactant gas mixtures from high pressure cylinders were prepared in advance and they were then introduced into the reactor at a flow rate of $50 \text{ cm}^3 \text{ min}^{-1}$. The reaction products were monitored continuously by a mass spectrometer (MS, Ulvac MM-100) with a multi-channel programmer (PC), through an orifice sampling system, and analyzed periodically by gas chromatographies (GC-1 and 2) with three different types of columns, i.e., Porapak Q, active carbon, and Unipak S, through the six-port valves with sampling

Fig. 3 Effect of the Input Voltage on Power in Pure Ar Stream

loops of 1 cm^3 .

The electric system is schematically shown also in Fig. 2. In the present study Trek-20/20 an ac power supply system (HV-PS) was used with a function generator (FG, Wavetek FG-2A), which was capable of changing such electrical parameters as voltage, current, frequency, and ac wave shape. Basically ac sine-wave of 1 kHz of power was supplied in most of the reactions in the present work. Electrical parameters were continuously monitored during operation, with multi-channel digital oscilloscope (OS, Yokogawa DL-1200). Although most of the electrical parameters could be controlled independently by this apparatus, the current increased slightly by increasing the input voltage as shown in Fig. 3, indicating that the increase in power was not proportional to the input voltage.

2.3. Plasma Diagnostic

Emission spectra from the plasma zone in the region of wave length between 200 and 900 nm were measured by a visible-ultra violet spectrometer (SPEX 270-M) attached with a back-thinned illuminated CCD array matrix detection system (ISA)^{1),2)}. The emission lights from eight small windows (1.5 mm diameter), which were located at the center of the external electrode, were collected into the instrument through eight fiber optics (outside diameter of 1 mm). Short periods of integration from 0.01 to 1 sec, and large numbers of accumulation from 20 to 200 times were applied to prevent saturation of the CCD matrix detector.

3. Results and Discussion

3.1. Direct Oligomerization of Methane

In the application of discharge plasmas for chemical reactions under atmospheric pressure, an important problem concerned is the small reaction zone of discharging plasmas since the discharge commonly occurs at points ends between two electrodes. One of the smart resolutions is the application of a silent-discharge plasma system by interpositioning of the dielectric materials (quartz reactor tube in the present study-**Fig. 1**) between two electrodes to produce a homogeneous cylindrical discharge zone.

The most important electric parameter in the present plasma reaction system was recognized to be the input discharge voltage. When high voltage was supplied to the reactor in a pure argon stream, an appreciable amount of current immediately started to flow, and a homogeneous reddish light was observed between the inner electrode and the quartz wall of the reactor tube. A relatively small emission of heat was observed during the discharge, *i.e.*, the temperature of the reactor wall gradually increased and remained unchanged at *ca.* 330 K for 20 min after discharging started. During the Ar discharge several emission spectra were observed in a lower energy region between 650 and 850 nm as shown in **Fig. 4**.

Figure 5 shows that intensities of typical emission spectra for Ar atom excitations²⁴⁾, *i.e.*, 696, 705, 750 and 811 nm, increased proportionally by increasing the input voltage above *ca.* 1 kV. All of the intensities for these spectra, furthermore, could be extrapolated into one point of the input voltage, suggesting that the break-down voltage for Ar discharge was 1 kV in the present system. The break-down voltage of Ar gas was almost independent of such metals as Au, Pt, Cu, Ni and Fe coated on the internal electrode. The minimum voltage for the Ar excitation, however, rapidly increased by increasing the distance between two electrodes.

By introduction of CH₄ into the Ar stream, a reddish purple light from the Ar plasma turned into bright pink.

Fig. 4 Emission Spectra from Ar Discharge in the Region of Wave Length from 650 to 850 nm

Fig. 5 Effect of the Input Voltage on the Intensity of Typical Ar Emission Spectra

The shape of sine wave in the voltage and the current observed with a oscilloscope became noisy. The CH₄ conversion in the Ar stream was recognized above *ca.* 1 kV; it then increased with increasing the input voltage, as represented in **Fig. 6**. The major hydrocarbon products of CH₄ oligomerization were C₂H₆, C₂H₄ and C₃H₈. The similar dependence of conversion on the input voltage was observed by Shepelev *et al.* in the partial oxidation of CH₄ using a silent discharge reactor¹⁶⁾.

The minimum input voltage for the CH₄ conversion coincided well with the break-down voltage of the Ar discharge. In the case of pure CH₄ as the reactant (in the absence of Ar), on the other hand, the reaction started at input voltage of *ca.* 3 kV, as also shown in **Fig. 6**. In the case of pure CH₄, an appreciable amount of car-

Fig. 6 The CH₄ Conversion in the Absence and Presence of 90% Ar

bon deposit was observed on the surface of the inner electrode. The CH₄ conversion in the absence of Ar was much lower than that in the presence of Ar. From these observations, it might be conceivable that CH₄ oligomerization was promoted dramatically by Ar excitation in the absence of oxidants, that is, energy transfer occurs from the excited Ar atoms to CH₄ molecules in the ground state as a dominant pathway in the CH₄ oligomerization.

This speculation about the energy transfer from excited Ar species to CH₄ molecules could be confirmed by the observation of emission spectra during the reaction. Intensities of the spectra due to Ar excitation were greatly reduced by the introduction of a small amount of CH₄ into the Ar stream. At the same time, only two distinct spectra due to CH· radicals and C₂-SWAN system (an index for the excitation of carbon species) were observed at *ca.* 432 and 517 nm, respectively, as shown in Fig. 7. Figure 8 shows the effect on the emission intensity of CH₄ concentration in the reactant gas mixture. The intensities of the excited Ar species sharply decreased with the increase in CH₄ concentration. On the other hand, the intensity of the C₂-SWAN system increased correspondingly, suggesting that this type of energy transfer occurred quite effectively in the present system.

Major hydrocarbon products in the CH₄ oligomerization with the silent discharge reactor were C₂H₄, C₂H₆, and C₃H₈. In addition considerable amounts of carbonaceous materials deposited on the electrode surface, and H₂ in the gas phase were observed. These major products were produced approximately in C₂H₄ : C₂H₆ : C₃H₈ = 1 : 3 : 2. In the CH₄ conversion brought about by use of a microwave induced plasma reactor with bimetallic catalysts, on the other hand, Anpo and co-

Fig. 7 Emission Spectra for CH Radicals and C₂-Swan System

Fig. 8 Effect of CH₄ Concentration on the Intensity of Spectra for Ar and C₂-Swan System

worker²⁵⁾, found, under similar chemical conditions, C₂H₂, C₂H₄, and C₂H₆ as major products; and their molar ratios of these products *ca.* 2 : 5 : 3, respectively. We also observed almost identical results from a glow discharge plasma reactor²⁶⁾.

Effects of the residence time in the plasma zone on

Fig. 9 Effects of Residence Time in Plasma Zone on the Yield and Selectivity with 10% CH₄ in Ar

Fig. 10 Effect of Residence Time in Plasma Zone on the Intensities of Emission Spectra with the Reactant of 10% CH₄ in Ar

Fig. 11 Effect of Electrode Metal and the Input Voltage on the CH₄ Conversion with 10% CH₄ in Ar

the CH₄ oligomerization were examined by changing the flow rate of the reactant gas mixture. Yields of major products increased with increasing the residence time (Fig. 9), as was expected. However, by increasing the residence time selectivities of C₂H₄, C₂H₆ and C₃H₈, decreased instead, and the amount of carbon formation increased to attain 65% of selectivity at residence time of 4.7 sec. Intensities of the emission spectra for both of the Ar species and the C₂-SWAN system gradually increased with increasing residence time (Fig. 10). One of the most important problem to be considered concerning direct decomposition of CH₄ is, therefore, how to prevent the formation of carbonaceous species on the electrode surface.

In order to examine the catalytic effect of the electrode surface, oligomerization of CH₄ was carried out in a plasma reactor where inner electrode was coated with various kinds of catalytically active metal, such as Au, Pt, Pd, Rh, Ni, and Fe. No substantial difference was observed in the CH₄ conversion by these metals

performed under various input voltages as shown in Fig. 11. Furthermore, selectivities of such major hydrocarbon products as C₂H₄, C₂H₆ and C₃H₈ were also independent of these coated metals within the limits of experimental errors as shown in Fig. 12. Catalytic effects in thermal processes require appropriate temperatures and large surface area of the active metal components. The plasma-catalytic system examined in the present study was, however, carried out at room temperature. The surface area plated with a metal component was very small in the present system. As a result, the CH₄ oligomerization in the present system was found not to be "plasmocatalysis"^{1)~4)} but a gas phase reaction in the plasma zone.

3. 2. Carbon Dioxide Reforming of Methane

The CO₂ reforming of CH₄ was investigated in the plasma reactor in order to examine the effective use of

Fig. 12 Effect of Electrode Metal on the Selectivities to Each Major Product with 10% CH₄ in Ar under the Input Voltage of 5.0 kV

CO₂. By introducing a reactant mixture consisting of 10% CH₄ and 10% CO₂ in Ar or N₂ into the reactor under high input voltages, CO and H₂ were immediately formed as major products. When the molar ratio of reactant mixture (CH₄/CO₂) was unity, the molar ratio of product mixture (H₂/CO) was almost unity as shown in Table 1. A small amount of C₂H₆ was observed as a by-product in the gas phase; however, no substantial formation of carbon was observed on the inner electrode in this reaction system, indicating that CO₂ played an important role in reducing the carbon deposition on the electrode surface.

It was also observed that the minimum input voltage for the reaction was *ca.* 1 kV in the stream of Ar. Such minimum voltage suggests the role of a carrier

gas, *i.e.*, the reactant molecules are presumably excited *via* the energy transfer from the excited Ar species with the break-down voltage of 1 kV. Thus, the presence of CO₂ in the reaction system dramatically changes the reaction scheme in the plasma zone.

Both CH₄ and CO₂ conversion decreased gradually with the increase of the CH₄ and CO₂ concentrations (with the decrease in the Ar concentration). Yields of CO and H₂ were almost independent of reactant concentration. The product ratio, H₂/CO, also remained unchanged, *i.e.*, it was found to be unity in all cases examined. As represented in Fig. 13, CH₄ and CO₂ conversions increased by increasing not only the input voltages but also by increasing the Ar concentration.

From these points of view, Ar gas plays a very important role in plasma reactions²⁴⁾, especially under atmospheric pressure. It plays the role not only as a diluent or a balance gas but also as an energy carrier. The life-time of the excited plasma species with higher energy is too short to perform chemical reactions, since it easily loses its energy by collision with other atoms or molecules under high pressure. Thus, only low conversions were observed in the direct oligomerization by pure CH₄ as the reactant (Fig. 6). Most of the excited Ar species probably is in the meta-stable state, where direct transition of the excited species to ground state is forbidden. The excited Ar species in the meta-stable state gives the energy to the reactant molecules to be stabilized in the ground state. Such energy transfer was considered to occur effectively in the present plasma zone as shown in Figs. 4, 5 and 7.

Rates of H₂ and CO formations were, on the other hand, strongly depended on the reactant ratio, CH₄/CO₂. Experiments were carried out under the input voltages of 5.0 and 6.4 kV in order to better understand the effect of reactant ratio on the rate of

Table 1 Effect of Ar Concentration on CO₂ Reforming of CH₄

Reactant composition [%]			Conversion [%]		Consumption [$\mu\text{mol} \cdot \text{min}^{-1}$]		Formation [$\mu\text{mol} \cdot \text{min}^{-1}$]			Ratio
Ar	CO ₂	CH ₄	CO ₂	CH ₄	CO ₂	CH ₄	CO	H ₂	C ₂ H ₆	H ₂ /CO
<i>V</i> = 3.5 kV										
80	10	10	6.6	5.9	25.8	17.3	26.2	25.0	4.2	0.95
60	20	20	3.2	4.4	23.0	24.6	24.8	24.0	4.4	0.97
40	30	30	3.2	2.9	31.0	24.3	21.9	21.3	4.0	0.97
20	40	40	1.9	2.3	23.6	25.1	20.3	18.5	3.5	0.91
<i>V</i> = 5.0 kV										
80	10	10	8.4	10.5	33.2	30.8	41.8	39.5	6.6	1.0
60	20	20	5.2	7.7	36.7	42.9	43.0	41.0	7.4	1.0
40	30	30	4.0	5.2	39.1	42.9	42.4	40.9	7.6	1.0
20	40	40	3.8	4.8	46.9	52.9	44.9	40.3	7.4	0.9
<i>V</i> = 6.4 kV										
80	10	10	10.1	14.9	39.6	43.5	54.4	52.3	8.2	0.96
60	20	20	6.6	10.7	46.9	60.0	59.2	56.2	9.9	0.95
40	30	30	5.6	7.9	55.5	65.3	61.9	58.1	10.7	0.94
20	40	40	5.5	7.3	67.3	79.7	55.5	58.4	10.7	0.88

Total flow rate = 50 cm³ · min⁻¹. Supplied power = 1 kHz, sine wave.

Fig. 13 Effects of Ar Concentration and the Input Voltage on the CH₄ and CO₂ Conversion with 10% CH₄ and 10% CO₂ in Ar

Fig. 14 Effects of Reactant Ratio, CH₄/CO₂, on the Rates of CO and H₂ Formation in Ar under the Input Voltage of 5.0 and 6.4 kV

product formation. The results are shown in **Fig. 14**. With increasing reactant ratio, CH₄/CO₂, the rate of H₂ formation increased whereas that of CO formations decreased below CH₄/CO₂ = 1 at which the same rates of H₂ and CO formation was observed.

The product ratio was completely independent of input voltage, although the rates of H₂ and CO formations increased with increasing voltage. The product ratio, H₂/CO, increased proportionally with increasing

Fig. 15 Effect of the Input Voltage on the Energy Efficiency with 10% CH₄ and 10% CO₂ in Ar

Table 2 Energy Yield vs. CH₄ Concentration in CO₂ Reforming of CH₄

CH ₄ conc. [%]	CH ₄ /CO ₂ ratio	E_y [g·(kWh) ⁻¹]	
		CO ₂	CH ₄
V = 4.86 kV			
5	0.25	32.8	11.7
10	0.50	25.1	11.5
15	0.75	21.9	21.4
20	1.00	19.7	24.3
V = 6.24 kV			
5	0.25	22.1	8.9
10	0.50	19.1	11.1
15	0.75	16.9	18.2
20	1.00	15.5	19.3

Reactor = tube. CO₂ concentration = 20%. Total flow rate = 50 cm³·min⁻¹. Supplied power = 1 kHz, sine wave.

Energy yield was calculated as follows:

$$E_y [\text{g} \cdot (\text{kWh})^{-1}] = \frac{\text{Amount of reacted CO}_2 \text{ or CH}_4 [\text{g}]}{\text{Supplied power} [\text{kWh}]}$$

reactant ratio, CH₄/CO₂. It should be noted that the stoichiometric reaction of $\text{CH}_4 + \text{CO}_2 = 2\text{CO} + 2\text{H}_2$ proceeded exclusively only at the reactant ratio CH₄/CO₂ = 1. More CO than H₂ produced in a CO₂-rich reactant mixture. The direct decomposition of CO₂ to CO and O₂, therefore, proceeded simultaneously in this region of reactant ratio. In a CH₄-rich region, on the other hand, direct dimerization of CH₄ to produce C₂H₆ seemed to occur independently along with the main reaction.

In the application of plasmas for chemical reactions, the most important factors to consider is high energy consumption. One of the useful factors for evaluating energy balance is the energy yield (E_y) defined by Jogan, Mizuno, Yamamoto and Chang²⁷. Energy yield is estimated as the amount of consumed reactants in grams by one kilowatt-hour of energy supplied to the reactor. The effect of input voltage and that of ratio, CH₄/CO₂, on E_y values are shown in **Fig. 15** and **Table**

2, respectively.

The E_y values calculated both for the CH_4 and CO_2 consumptions decreased by increasing the input voltage. These E_y values are almost of the same magnitude to that obtained in a packed-bed corona-discharge plasma reactor²⁷⁾. In the plasma zone of the reactor, CO_2 was more reactive than CH_4 . One of the specific features of the silent-discharge reactor is that thermodynamically stable CO_2 molecules are readily excited in the plasma zone. Man-made sources of CO_2 production, which is greatly responsible for global warming are difficult to reduce at present. Additionally, further detailed investigations on higher reactant concentration in the N_2 or air stream are required to use the processes and systems here studied practically.

4. Conclusions

Results obtained in the present study for CH_4 reforming by use of a dielectric-barrier silent discharge-plasma reactor are summarized, as follows:

- (1) The direct oligomerization of CH_4 to C_2 and C_3 hydrocarbons proceeded with notably high rates in the stream of Ar without oxidants, such as O_2 .
- (2) Reactant molecules were effectively excited *via* the energy transfer from the excited Ar species.
- (3) No appreciable catalytic effects of the electrode surface were observed in this reaction system.
- (4) The CO_2 reforming of CH_4 to CO and H_2 proceeded selectively with the reactant molar ratio $\text{CH}_4/\text{CO}_2 = 1$.
- (5) The energy efficiency of the reaction decreased by increasing the input voltage. By increasing the ratio, CH_4/CO_2 , the energy yield for CH_4 increased but that for CO_2 decreased.

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要 旨

誘電体バリアー放電プラズマ反応器によるメタンの低重合および二酸化炭素改質

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室温大気圧の条件下, アルゴンおよび窒素気流中, 誘電体バリアー放電低温プラズマ反応器によるメタンの C₂, C₃ 炭化水素への低重合反応と水素への二酸化炭素改質反応について検討した。これらの反応における転化率および選択率は反応物の濃度と混合比に著しく依存した。また, アルゴンおよび窒素気流中のこれらの反応は, 印加電圧がそれぞれの破壊電圧である約

1 および 2 kV 以上で進行した。さらに, アルゴン励起に起因する発光スペクトル強度は反応物濃度の増加とともに急激に減少した。これらの事実から, アルゴン励起種から反応分子へのエネルギー遷移により反応が進行することが解明された。また, 本プラズマ反応器のこの改質反応におけるエネルギー効率は印加電圧の低下とともに上昇した。

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Keywords

Methane oligomerization, Carbon dioxide, Plasma reactor, Selective reaction, Reforming