Selective Oxidation of Methane to Methanol and Formaldehyde with Nitrous Oxide in a Dielectric-Barrier Discharge−Plasma Reactor

Hiroshige Matsumoto,*,† Shuji Tanabe,† Kenji Okitsu,† Yuji Hayashi,† and Steven L. Suib‡

Department of Materials Science and Engineering, Faculty of Engineering, Nagasaki University, Bunkyoumachi 1-14, Nagasaki, Japan, and U-60 Department of Chemistry, University of Connecticut, 55 North Eagleville Road, Storrs, Connecticut 06269-3060

Received: March 23, 2000; In Final Form: March 6, 2001

The partial oxidation of CH_4 with N_2O in Ar has been investigated at atmospheric pressure in a dielectric-barrier (silent) discharge plasma induced by low input power in a range from 0.27 to 7.71 $Wh(Ncm^3)^{-1}$. In an Ar stream, about 10% of the combined yield of CH_3OH and HCHO and 40% of the selectivity to these products were achieved, with CO being the other major product. Low power favored selectivities to unstable partial oxidized products and supressed further decomposition to carbon oxides and carbonaceous deposits on the electrode surface. Kinetic and spectroscopic observations indicated that Ar carrier gas played an important role in the highly selective oxidation of CH_4 to CH_3OH and HCHO via energy transfer from excited-state Ar species to the reactant molecules under the mild conditions examined.

I. Introduction

Nonthermal plasmas have been used during the past decade to excite stable small molecules using energetic electrons without gas heating. A limited number of practical studies of plasma reactions are, however, available due to problems associated with low yields from use of low pressure, mass transfer limitations, and high operational costs. Recently, we have been investigating performances in ac discharge−plasma systems in decompositions of such stable small compounds as NO,[1−3] H_2O,[2−4] and CO_2,[2,5−8] in addition to reforming reactions of CH_4 with CO[29,10] and N_2O[11] at atmospheric pressure.

Very little work about plasma synthesis of organic compounds has been reported, although the literature contains numerous references to various decompositions reactions in plasma systems. In various organic synthesis from CH_4, oligomerization and partial oxidation of CH_4 to C2−C4 hydrocarbons and CH_3OH,[12,13] occur respectively by using silent[9,10] and microwave[14−16]-induced plasmas at low pressures in the presence of catalysts. Ihara et al.,[17,18] on the other hand, studied in detail the reduction of CO_2 with H_2O to produce oxalic acid, H_2O_2, and CH_3OH in microwave-induced plasma systems at atmospheric pressure. Zhou et al.[19] have investigated experimentally and theoretically the partial oxidation of CH_4 with O_2 and air to CH_3OH in a silent-discharge−plasma system.

Although numerous investigations in conventional catalytic system have been reported on this subject from 1967, few fundamental studies have been reported. Lunsford and co-workers[20,21] first demonstrated that molybdenum supported on silica was an excellent catalyst for selective partial oxidation of CH_4 with N_2O. However, since CH_3OH and HCHO formation in the oxidation of CH_4 is limited by the equilibrium concentration, which is relatively low at temperatures required in conventional catalysis, catalytic processes are not very attractive for practical applications. The CH_3OH yield in most catalytic experiments has been reported to be below 2%, which is far removed from economical needs.[20−23] The application of dielectric-barrier discharge−plasmas (silent-discharge−plasmas) has been proposed as a new technology for CH_3OH synthesis.[19,24] In the present study, the partial oxidation of CH_4 with N_2O to CH_3OH and HCHO was explored in a nonthermal dielectric-barrier discharge systems under mild conditions. The partial oxidation of CH_4 with N_2O, at present, has been considered to be one of the most selective processes in CH_3OH synthesis.

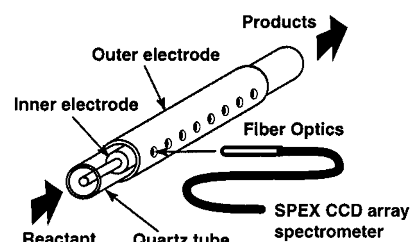

Figure 1. Dielectric-barrier discharge reactor for the partial oxidation of CH_4 and plasma diagnostics.

II. Experimental Section

The dielectric-barrier discharge (silent-discharge) plasma reactor used in this work is illustrated in Figure 1. In this simple reactor, the inner electrode of copper rod with an outside diameter of 8 mm and a length of 70 mm was rigidly supported at the center of the quartz tube with an inside diameter of 10 mm by tube fittings (perfluoroalkoxide Swagelok). The outer electrode quartz was tightly surrounded with a cylindrical jacket made of metallic aluminum with a length of 70 mm. The distance between inner electrode and reactor wall was 1 mm. The space between the outer electrode jacket and the inner electrode is defined as the plasma volume, which is estimated to be about 2.0 cm^3. The void volume of the reactor and lin is ca. 5 mL. A fluid of gas passes through it like a piston flow, quickly reaching a steady state ($<$0.2 min at a flow rate of 50 mL min^{-1}). This permits rapid and prompt monitoring of the changes in concentration. When ac current at a voltage above

* E-mail: h-matsu@net.nagasaki-u.ac.jp. Fax; 81-95-843-7251.
† Nagasaki University.
‡ University of Connecticut.

10.1021/jp001099z CCC: $20.00 © 2001 American Chemical Society
Published on Web 05/03/2001

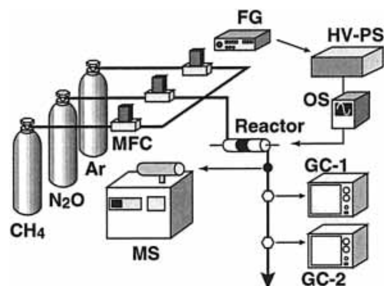

Figure 2. Schematic diagram of the experimental setup for plasma reactions.

1 kV was supplied to the reactor, where pure Ar gas was flowing, a homogeneous cylindrical discharge was observed between the inner electrode and the quartz wall of the reactor tube.

The partial oxidation of CH_4 with N_2O was carried out at atmospheric pressure by using a conventional flow reaction system, as shown in Figure 2.[1,2] The purity of Ar, CH_4, and N_2O used in the present experiment were 99.999% (Nihon Airliquid), 99.99% (Sumitomo Seika), and 99.9% (Seitetsuka-gaku), respectively. In most cases, the reactant gas mixture consisting of 5% CH_4 and 5% N_2O in Ar was introduced into the reactor from high-pressure cylinders through a Molecular Sieves 5A column and regulated with mass-flow controllers (MFC). The reaction products were monitored continuously with a mass spectrometer (MS, Ulvac MM-100) with a multichannel programmer through an orifice sampling system and analyzed periodically by gas chromatographies (GC-1 and GC-2) with Porapak Q, active carbon, and Unipak S columns with a six-port valve with a sampling loop of 1 cm^3. The reaction was performed with various mixtures of CH_4 and N_2O in the presence or absence of Ar at atmospheric pressure.

The electric power was supplied to the reactor by an ac high-voltage power supply (HV-PS, Trek-20/20) with a function generator (FG, Wavetec FG-2A). During the operation, such electric parameters as ac wave form, input voltage, current, and frequency were continuously monitored with a multichannel digital oscilloscope (OS, Yokogawa DL-1200). The present data were taken using ac current with a sine wave from 1 to 7 kV and a constant frequency of 1 kHz. The input power was calculated from the mean square voltage and current measured with a digital oscilloscope.[25]

The diagnostics of the plasma zone were performed by an ultraviolet–visible spectrometer (SPEX 270-M) with a back-thinned illuminated CCD array matrix detection system (ISA).[1,3] The emission from eight small windows with diameters of 1.5 mm were located along the outer electrode jacket (Figure 1) as collected and directed into the spectrometer through eight fiberglass optic cables with an outside diameter of 1 mm. Short periods of integration from 0.01 to 1 s and large numbers (20–200) of accumulation were applied to prevent saturation of the CCD matrix detector. Experiments were performed in the wavelength range 200 to 900 nm, and the emission lines in the spectra from Ar gas were accurate to ±0.1 nm.

Conversions of CH_4 (X_{CH_4}) and N_2O (X_{N_2O}) are calculated from the concentrations of CH_4 and N_2O before reaction ($[CH_4]_s$ or $[N_2O]_s$) and the amount of CH_4 or N_2O consumed ($[CH_4]_c$ or $[N_2O]_c$) reaction, respectively, as given by eqs 1 and 2

$$X_{CH_4} = 100\% \ ([CH_4]_c/[CH_4]_s) \quad (1)$$

$$X_{N_2O} = 100\% \ ([N_2O]_c/[N_2O]_s) \quad (2)$$

Yields of such major products as CH_3OH (Y_{CH_3OH}) and HCHO (Y_{HCHO}) are estimated from concentrations of CH_4 supplied ($[CH_4]_s$) and CH_3OH ($[CH_3OH]_f$) and HCHO ($[HCHO]_f$) formed, respectively, as given in eqs 3 and 4

$$Y_{CH_3OH} = 100\% \ ([CH_3OH]_f/[CH_4]_s) \quad (3)$$

$$Y_{HCHO} = 100\% \ ([HCHO]_f/[[CH4]_s]) \quad (4)$$

Selectivities to CH_3OH (S_{CH_3OH}), HCHO (S_{HCHO}), CO (S_{CO}), and C_2H_6 ($S_{C_2H_6}$) are calculated from concentrations of CH_4 consumed ($[CH_4]_c$) and concentrations of CH_3OH, HCHO, CO, and C_2H_6 after reaction, respectively, as given in eqs 5–8

$$S_{CH_3OH} = 100\% \ ([CH_3OH]_f/[CH_4]_c) \quad (5)$$

$$S_{HCHO} = 100\% \ ([HCHO]_f/[CH_4]_c) \quad (6)$$

$$S_{CO} = 100\% \ ([CO]_f/[CH_4]_c) \quad (7)$$

$$S_{C_2H_6} = 200\% \ ([C_2H_6]_f/[CH_4]_c) \quad (8)$$

Rates of CH_4 (R_{CH_4}) and N_2O (R_{N_2O}) consumption are, on the other hand, calculated from conversions of CH_4 and N_2O, initial concentrations of CH_4 and N_2O, and total flow rates of reactant gas (F), respectively, as given eqs 9 and 10

$$R_{CH_4} = X_{CH_4}[CH_4]F \ \mu\text{mol s}^{-1} \quad (9)$$

$$R_{N_2O} = X_{N_2O}[N_2O]F \ \mu\text{mol s}^{-1} \quad (10)$$

III. Result and Discussion

A. Conversion of CH_4 and N_2O. The plasma reactions depend on a large number of electrical and chemical variables. The input voltage was recognized to play the most important role among the electrical parameters in the selective partial oxidation of CH_4. When a power with higher voltage above 1 kV was supplied to the reactor in the pure Ar flowing, a homogeneous emission was observed, and an appreciable current passed between the inner electrode and the quartz wall of the reactor tube. During the Ar discharge, several sharp and strong lines of the emission spectra were observed at wavelengths of 696, 706, 750, and 811 nm, all of which correspond to energy emissions of 13.08–13.33 eV. Figure 3a shows intensities of these emission spectra, which are identified to be due to excitation of electrons from the 3p to the 4s orbital in Ar atoms.[27] The intensities increased rapidly with an increase in input voltage.[26] Other Ar excited species[4,28] such as Ar_2, Ar^+, and Ar_2^+ were not observed in the present experiments. All of these spectra for the Ar atom excitations, furthermore, could be extrapolated to one point at about 1 kV on the input voltage axis, suggesting that the breakdown voltage of the Ar discharge was 1 kV in the present system.

Upon the introduction of a reactant mixture of CH_4 and N_2O into the Ar stream, the reddish purple emission turns bright pink, although no appreciable changes in the voltage and current were observed. The sine wave shape of voltage on the oscilloscope became noisy at the same time, showing a "showering arc" due to excitation of reactant molecules. A comparatively small emission of heat was observed during the discharge, as also observed by Zhou et al.[19] The temperature of reactor wall gradually increased with time on stream and became constant at 330 K in 20 min after the discharge started. The rates of CH_4 and N_2O consumption were observable above 1 kV and

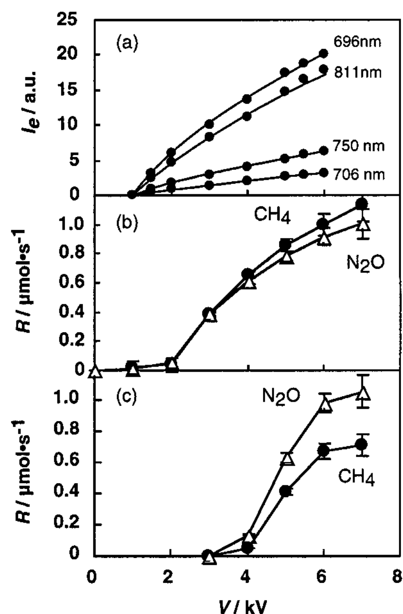

Figure 3. Effects of input voltage on Ar emission spectra and (a) steady-state rates of CH_4 and N_2O consumption in the presence of Ar (b) and in the absence of Ar (c). Gas composition: (a) pure Ar, (b) 5% CH_4 and 5% N_2O in Ar, and (c) 50% CH_4 and 50% N_2O. Total gas flow rate, 50 cm^3 min^{-1}.

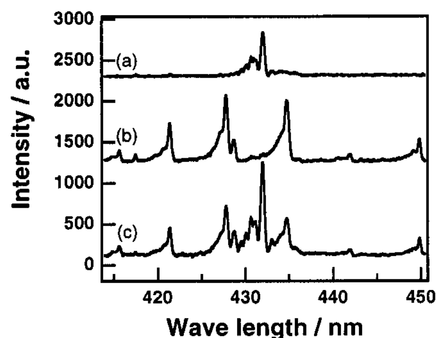

Figure 4. Emission spectra of (a) 2% CH_4, (b) 5% N_2O, and (c) 5% CH_4 and 5% N_2O in Ar stream during the discharge. Input voltage, 5 kV. Total gas flow rate, 50 cm^3 min^{-1}.

then increased with increasing input voltage, as shown in Figure 3b. No substantial differences between CH_4 and N_2O conversion were observed in Ar at all input voltages examined. From the point of view that the minimum voltage for the reactions of CH_4 and N_2O coincided with the breakdown voltage for Ar discharge, the reaction was considered to be promoted by Ar excitation. Energy transfer probably occurred from excited Ar species to reactant molecules.

In the absence of Ar, on the other hand, the conversions of CH_4 and N_2O were observed at input voltages above 3 kV, as shown in Figure 3c, indicating that the conversion of N_2O was higher than that of CH_4 in the whole range of input voltages examined. The plasma reaction between CH_4 and N_2O without Ar gas proceeds via direct excitation of reactant molecules involving electron impact.[28] The difference of the minimum voltage for the reaction in the presence and in the absence of Ar carrier is considered to be other evidence that the energy transfer from excited Ar species to reactant molecules effectively promotes reactions in the present reaction system.

B. Excitations in Plasma Zone. Optical emission studies of plasmas were done to understand the mechanism of interaction between CH_4 and N_2O in Ar. Figure 4 shows emission spectra from 415 to 450 nm for discharges in mixtures of (a) CH_4 in

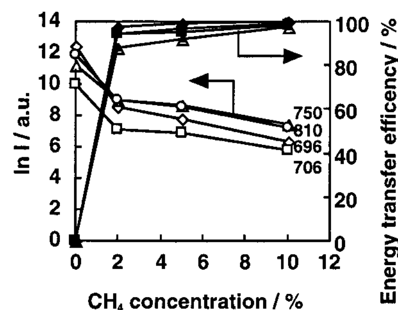

Figure 5. Effect of CH_4 concentration in Ar on spectral intensities of Ar and energy-transfer efficiency. Input voltage, 5 kV. Total gas flow rate, 50 cm^3 min^{-1}.

Ar, (b) N_2O in Ar, and (c) $CH_4 + N_2O$ in Ar mixtures. No emission due to Ar was observed in this region. For spectra of 2% CH_4 in Ar, as shown in Figure 4a, a sharp peak was observed at the wavelength of 432 nm, which is due to CH radicals ($A^2\Delta - X^2\Pi$).[26] A broad emission peak due to CH_4 excitation was observed in the region of 513 to 518 nm (not shown), corresponding to the C_2−Swan system ($A^3\Pi_g - X^3\Pi_u$).[26] No appreciable spectra due to other radicals, such as CH_3 and CH_2, were observed in this experiment.

Spectra for 5% N_2O in Ar, as shown in Figure 4b, show intense broad emission at 425−435 nm. Distinct signals of the N_2 second positive system of the transition from C $^3\Pi u$ to B $^3\Pi g$ were observed at 425−435 nm.[26,29,30] No distinct peaks corresponding to NOx excited species were recognized, however, in the region from 250 to 900 nm. When a mixture of 5% CH_4 and 5% N_2O was introduced into Ar, both emission spectra due to CH_4 and N_2O excitation overlapped one another, as shown in Figure 4c. This indicated that both CH_4 and N_2O molecules were simultaneously excited in the present plasma reaction system. Zhou et al. suggests that excited oxygen atoms O (1D) act an important role in providing initial free radicals in the CH_4 oxidation.[19] The bonding energy between nitrogen and oxygen atoms in N_2O molecules is weak enough (167 kJ mol^{-1}) to supply excited oxygen species to such excited hydrocarbon species as CH_3, CH_2, and/or CH radicals.[19,31]

Optical emission spectroscopy was also used to understand the important role of Ar gas in the reaction. The concentration of excited species of Ar atoms was strongly affected in the presence of reactant gases. Effects of CH_4 concentration in Ar on the logarithmic intensities of Ar emission spectra are shown in Figure 5. The intensities for Ar excitation dramatically decreased upon introduction of only a small concentration of CH_4 (2%) into the Ar stream. All of the important lines for the Ar excitations at 696, 706, 750, and 810 nm decreased similarly with increasing CH_4 concentration. These data further suggest that energy transfer from excited Ar species to reactant CH_4 molecules occurs in this dielectric-barrier discharge system. Efficiency of the energy transfer[3] from the excited Ar species to CH_4 molecules can be estimated from the intensity ratio of Ar emission by using CH_4/Ar mixtures and pure Ar gas. These results are also shown in Figure 5. A high-energy transfer efficiency of greater than 80% was observed at all CH_4 concentrations examined. The supplied electrical energy is consumed during excitation of Ar atoms, which transfers energy efficiently to reactant molecules in this system. As shown in Figure 3c, appreciable reactions of CH_4 and N_2O were observed also in the absence of Ar, indicating direct formations of CH_3-OH and HCHO by the electron impact dissociation of the reactant molecules. Therefore, it is important to consider another possibility that CH_4 and N_2O affect the discharge region and

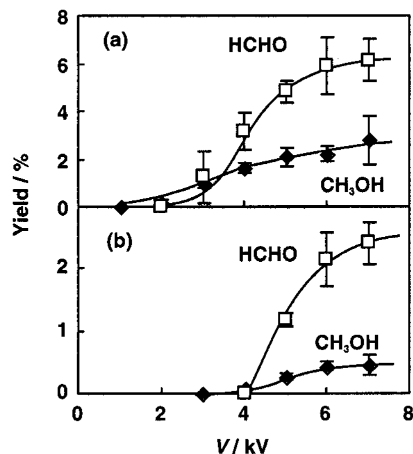

Figure 6. Yields of CH_3OH and HCHO (a) in the presence of Ar and (b) in the absence of Ar. Gas composition: (a) 5% CH_4 and 5% N_2O in Ar and (b) 50% CH_4 and 50% N_2O. Total gas flow rate, 50 cm^3 min^{-1}.

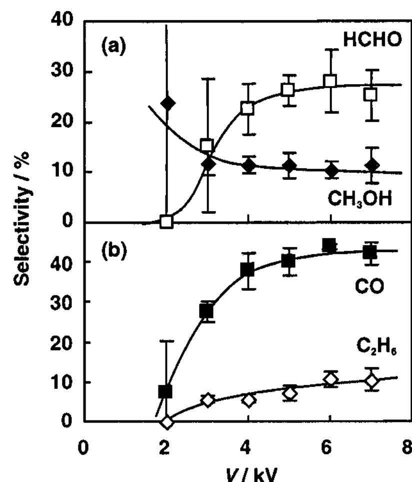

Figure 7. Effect of input voltage on selectivities to major products. Gas composition: 5% CH_4 and 5% N_2O in Ar. Total gas flow rate, 50 cm^3 min^{-1}.

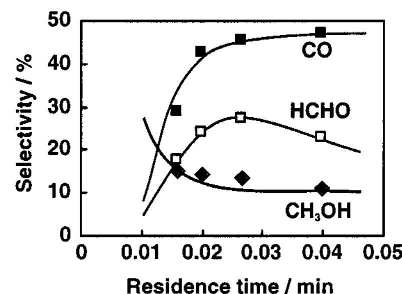

Figure 8. Effect of residence time in the plasma zone on selectivities to major products. Gas composition: 5% CH_4 and 5% N_2O in Ar. Input voltage. 5 kV.

abundance and energy of electrons, which are considered to be precursors of the excited Ar species.

C. Yield and Selectivity of Products. Major products containing carbon were CH_3OH, HCHO, and CO. In addition to these main products, formation of small amount of C_2H_6 and carbonaceous materials was observed at higher input voltages in the gas phase and on the surface of the internal electrode, respectively. Yields of these products depended strongly on input voltage. Panels a and b of Figure 6 show the CH_3OH and HCHO yield in the presence and in the absence of Ar carrier gas,[10,19] respectively. In the Ar stream, CH_3OH started to produce at an input voltage of 1 kV, which coincided well with the breakdown voltage of the Ar discharge, indicating that the initial step in CH_3OH formation was the charge and energy transfer from excited Ar species to reactant molecules. The CH_3OH yield increased almost proportionally with increasing the input voltage above 1 kV and reached 4 mol % at 7 kV. HCHO formation started at 3 kV and then rapidly increased with increase in input voltage. A maximum HCHO yield of 6 mol % was achieved at 7 kV, as shown in Figure 6a.

In the absence of Ar gas, on the other hand, the minimum voltages for the CH_3OH and HCHO formation were observed to be 3 and 4 kV, respectively, which were distinctly higher than those in Ar plasmas shown in Figure 6b. The formation of HCHO was more pronounced in the absence of Ar. The yields of CH_3OH and HCHO at 7 kV in the absence of Ar were 2.5 and 0.5 mol %, respectively, which were appreciably low in comparison to those in the presence of Ar. The results shown in Figure 6 suggest an important role of Ar in the reaction system, supporting spectroscopic evidence of energy transfer between excited species of Ar atoms and the reactant molecules, as shown in Figures 3−5.

Selectivity to each product also depended on the voltage supplied, as shown in Figure 7a,b. With increasing input voltage, the selectivity to CH_3OH decreased slowly above 1 kV, whereas the selectivity to HCHO increased rapidly above 3 kV. Both the selectivities to CO and C_2H_6, on the other hand, increased simply with input voltage. The selectivities to CH_3OH and HCHO at low voltage appear to be very uncertain. This might be attributable to small yields of these products at low input powers. The formation of carbonaceous materials increased with increasing input voltage by estimating the mass balance of carbon compounds. With the present dielectric-barrier discharge system, the maximum combined yield and selectivity of about 10% and 43% for CH_3OH and HCHO formation, respectively, could be achieved in the partial oxidation of CH_4 with N_2O at an input voltage of 7 kV and a residence time of 0.027 min.

Figure 8 shows effects of the residence time of the reactant in the plasma zone on selectivities to each product. With an increase in residence time, the selectivity to CH_3OH decreased gradually while that to HCHO increased initially and then decreased slowly. The selectivity to CO, on the other hand, simply increased with residence time. From these points of view, CH_3OH was oxidized into HCHO, which was further decomposed into CO (and/or carbonaceous materials) as the final product in the dominant reaction pathway; i.e., CH_3OH and HCHO were considered to be more unstable than CO and carbon deposits. To obtain more CH_3OH and HCHO, therefore, it is important to remove these products from the plasma zone as soon as they have been produced.

D. Energy Efficiency of Plasma System. Energy efficiency is an important measure in the practical use of plasma systems for any chemical reaction. Zhou et al.[19] reported results in similar silent discharge systems that the highest CH_3OH yield of 3% was achieved at a specific power of 6.7 kWh/Nm^3 and the highest CH_3OH selectivity of 30% was obtained at 1.1 kWh/Nm^3 in CH_4/O_2 reactant mixture. It is very difficult, however, to compare the energy consumption in plasma systems with conventional catalytic processes. The maximum combined yield of CH_3OH and HCHO (about 10%) obtained in the present system is clearly higher than those obtained in conventional catalysis, i.e., 3.4% in the reaction with CH_4/N_2O on Mo/carb−O−Sil catalyst at 870 K[20] and 7% in CH_4/O_2 reactions on Co−Mo−Al_2O_3 catalysts at 730 K.[32]

TABLE 1: Electrical Conditions, Formation Rates, and Energy Yields (E_y) of the Partial Oxidation on Methane with Nitrous Oxide over Dielectric-barrier Discharge System[a]

		$R/\mu mol\ s^{-1}$		$E_y/mol\ kW^{-1}\ h^{-1}$	
V/kV	P/Wh (N cm^3)$^{-1}$	CH_3OH	HCHO	CH_3OH	HCHO
2	0.27	0.0154	–	0.104	–
3	0.38	0.0529	–	0.256	–
4	1.58	0.0829	0.112	0.0955	0.129
5	3.87	0.115	0.206	0.0540	0.0970
6	6.40	0.121	0.151	0.0344	0.0430
7	7.71	0.190	0.293	0.0447	0.0690

[a] Electrical parameters: f = 1 kHz (sine wave), electrode = Cu (L = 7 cm), gap = 1 mm. Reaction condition: 10% CH_4, 10% N_2O, balance = Ar, F_R = 50 cm^3 (STP) min^{-1}.

A useful quantity for evaluating the energy efficiency in plasma systems is the energy yield (E_y) defined by Jogan, Mizuno, Yamamoto, and Chang[33] as the amount of formation of each product in moles per 1 kW h of power supplied by the reactor (mol kW^{-1} h^{-1}). Previous studies of CO_2 dissociation[5,6] have made clear the effects of various plasmochemical parameters, such as the voltage and frequency of input power, the flow rate and concentration of reactant mixture, the kind of carrier gas, and the metallic component of inner electrodes, on the efficiency of the reaction. Effects of such electrical and kinetic parameters as voltage, power, and rates of reaction on the estimated energy yields for CH_3OH and HCHO formation in the present system are cited in Table 1. With increasing supplied power to the system at constant flow rate of the reactant mixture, the steady-state reaction rate of CH_3OH gradually increased above 3 kV, whereas that of HCHO formation rapidly increased above 4 kV of input voltage. Both of the E_y values for CH_3OH and HCHO formation, on the other hand, decreased with power. The specific power consumption, which is defined as the input energy in MJ for the formation of 1 kg of the expected products (CH_3OH + HCHO in this study), is estimated to be 468−540 MJ kg^{-1} at 3−7 kV of input voltage. These values are very small in comparison with 2.106 MJ kg (CH_3-OH + HCHO)$^{-1}$, which was obtained by a microwave-induced plasma reactor reported in previous work.[16]

VI. Conclusions

Partial oxidation of CH_4 in Ar proceeded efficiently in a simple reactor using dielectric-barrier ac discharge−plasmas at atmospheric pressure. Major products of the reaction were CH_3-OH, HCHO, CO, and carbonaceous materials deposited on the electrode surface. CH_3OH formation was observed at an input voltage above 1 kV and increased gradually with power supplied to the reactor. HCHO formation, on the other hand, occurred above 3 kV input voltage and increased rapidly with power. A combined yield of CH3OH and HCHO of about 10 mol % was achieved for 5% CH_4 and 5% N_2O in Ar at 50 cm^3 min^{-1} total flow rate and 7 kV input voltage. Increasing residence time in the plasma zone led to a decrease in selectivity of CH_3OH and HCHO.

Kinetic and spectroscopic measurements indicated that the initial stages of CH_3OH formation involved Ar excitation and energy transfer from excited Ar species to reactant molecules in the plasma zone. The initially formed CH_3OH was oxidized to HCHO, which decomposed to CO and carbonaceous materials on the electrode surface. To obtain more CH_3OH and/or HCHO, therefore, an important problem to be addressed is how to remove unstable species from the plasma zone as soon as they are produced.

Acknowledgment. This study was partially supported by a Grant-in-Aid for Scientific Research in Priority Areas from the Ministry of Education, Science and Culture of Japan. We acknowledge Dr. Manuel Marquez of the University of Connecticut and Miss Kayo Egashira of Nagasaki University for their help with emission spectra and kinetic measurements, respectively.

References and Notes

(1) Luo, J.; Suib, S. L.; Marquez, M.; Hayashi, Y.; Matsumoto, H. *J. Phys. Chem. A* **1998**, *102*, 7954.
(2) Suib, S. L.; Brock, S. L.; Marquz, M.; Luo, J.; Matsumoto, H.; Hayashi, Y. *J. Phys. Chem. B* **1998**, *102*, 9661.
(3) Luo, J.; Suib, S. L.; Hayashi, Y.; Matsumoto, H. *J. Phys. Chem. A* **1999**, *103*, 6151.
(4) Chen, X.; Marquez, M.; Rozak, J.; Marun, C.; Luo, J.; Suib, S. L.; Hayashi, Y.; Matsumoto, H. *J. Catal.* **1998**, *178*, 372.
(5) Brock, S. L.; Marquez, M.; Suib, S. L.; Hayashi, Y.; Matsumoto, H. *J. Catal*. **1998**, *180*, 225.
(6) Brock, S. L.; Shimojo, T.; Marquz, M.; Marun, C.; Suib, S. L.; Matsumoto, H.; Hayashi, Y. *J. Catal.* **1999**, *184*, 123.
(7) Wang, J. Y.; Xia, G.-G.; Aimin, H.; Suib, S. L.; Hayashi, Y.; Matsumoto, H. *J. Catal.* **1999**, *185*, 152.
(8) Matsumoto, H.; Tanabe, S.; Okitsu, K.; Hayashi, Y.; Suib, S. L. *Bull. Chem. Soc. Jpn.* **1999**, *72*, 2567.
(9) Tanabe, S.; Matsuo, H.; Matsuguma, H.; Hayashi, Y.; Okitsu, K.; Matsumoto, H.; Suib, S. L.; Hiramatsu, M.; Kanamori, M. *J. Jpn. Petrol. Inst*. **1999**, *42*, 383.
(10) Huan, A.; Xia, G.-G.; Wang, J.; Suib, S. L.; Hayashi, Y.; Matsumoto, H. *J. Catal*. **2000**, *189*, 349.
(11) Tanabe, S.; Egashira, K.; Okitsu, K.; Matsumoto, H. *Chem. Lett.* **1999**, 871.
(12) Suib, S. L.; Zerger, R. P. *J. Catal.* **1993**, *140*, 383.
(13) Huang, J.; Badani, M. V.; Suib, S. L.; Harrison, J. B.; Kablaui, M. *J. Phys. Chem.* **1994**, *98*, 206.
(14) Suib, S. L.; Zhang, Z. U.S. Patent 5,0131,993, July 21, 1992.
(15) Suib, S. L.; Zhang, Z. U.S. Patent 5,015,349, May 14, 1991.
(16) Huang, J.; Suib, S. L. *J. Phys Chem.* **1993**, *97*, 9403.
(17) Ihara, T.; Kiboku, M.; Iriyama, Y. *Bull. Chem. Soc. Jpn*. **1994**, *67*, 312.
(18) Ihara, T.; Ouro, T.; Ochiai, T.; Kiboku, M.; Iriyama, Y. *Bull. Chem. Soc. Jpn.* **1996**, *69*, 241.
(19) Zhou, L. M.; Xue, B.; Kogelschatz, U.; Eliasson, B. *Plasma Chem. Plasma Proc*. **1998**, *18*, 375.
(20) Liu, R.-S.; Iwamoto, M.; Lunsford, J. H. *J. Chem. Soc., Chem. Commun.* **1982**, 78.
(21) Liu, H.-F.; Liu, R.-S.; Liew, K. Y.; Johnson, R. E.; Lunsford, J. H. *J. Am. Chem. Soc.* **1984**, *106*, 4117.
(22) Casey, P. S.; MacAllister, T.; Foger, K. *Ind. Eng. Che. Res*. **1994**, *33*, 1120.
(23) Lodens, R.; Lindvag, O. A.; Soraker, P.; Roterud, P. T.; Onsager, O. T. *Ind. Eng. Chem. Res.* **1995**, *34*, 1044.
(24) Yu, O. S.; Yasuda, H. K. *Plasma Chem. Plasma Proc*. **1998**, *18*, 461.
(25) Chakrabarti, A.; Mizuno, A.; Shimizu, K.; Matsuoka, T.; Furuta, S. *IEEE Trans. Ind. Appl*. **1995**, *31*, 500.
(26) Pearse, B.; Gaydon, A. G. *The Identification of Molecular Spectra*; Chapman and Hall: London, 1984; p 388.
(27) Platzner, I.; Marcus, P. Intern. *J. Mass Spec. Ion Phys*. **1983**, *46*, 333.
(28) Maezono, I.; Chang, J.-S. *IEEE Trans. Ind. Appl.* **1990**, *26*, 651.
(29) Oumghar, A.; Legrand, J. C.; Diamy, A. M.; Turillon, N. *Plasma Chem. Plasma Proc*. **1995**, *15*, 87.
(30) Piper, L. G.; Gunndel, L.; Velazco, J. E.; Setser, D. W. *J. Phys. Chem.* **1975**, *62*, 3883.
(31) Shepelev, S. S.; Gesser, H. D.; Hunter, N. R. *Plasma Chem. Plasma Proc*. **1993**, *13*, 470.
(32) Sokolobski, V. D.; Coville, N. J.; Parmaliana, A.; Eskendirov, I.; Makoa, M. *Catal. Today* **1998**, *42,* 191.
(33) Jogan, K.; Mizuno, A.; Yamamoto, T.; Chang, J.-S. *IEEE Trans. Ind. Appl.* **1993**, *29*, 876.