Partial Oxidation of Methane with Nitrous Oxide in a Dielectric-Barrier Discharge System

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The partial oxidation of CH_4 by N_2O was investigated in a dielectric-barrier discharge system at atmospheric pressure. CH_4 converted to CH_3OH, HCHO, and CO in this system. Total yield of CH_3OH and HCHO reached about 10 % in the Ar stream. It was suggested that excited Ar species and electrons might behave important role to promote the partial oxidation reaction.

CH_3OH is an important material from the point of view as a gasoline additive and as an automobile fuel. CH_3OH is also key material to produce hydrogen that will be used with fuel cells. In general, CH_3OH is manufactured from synthesis gas over Cu-based catalysts.[1] The partial oxidation of CH_4 to CH_3OH is more desirable if high selectivity to CH_3OH and reasonable conversion rate can be obtained. Active research efforts are directed to find out processes that can selectively oxidize CH_4 to CH_3OH.[2-4] It's widely recognized that nonequilibrium plasma technique is one of the solutions for this process.[5-7] In this report, partial oxidation of CH_4 has been investigated by using dielectric-barrier discharge (DBD) system. CH_4 could directly be converted to CH_3OH by N_2O as an oxidant, and high yield for CH_3OH was achieved with the system.

The DBD plasma reactor in this work was basically similar to that of Chen et al.[8] A Cu rod was used as internal electrode (8 mm od, 100 mm length) that was supported in the center of quartz tube (10 mm id, 200 mm length). The thickness of quartz barrier was 1 mm. Outer surface of the glass tube was tightly covered by Cu foil as external electrode (7 cm length). High-voltage power was supplied between two electrodes (gap = 1mm) with an amplifier and a function generator. The electric conditions such as wave shape, frequency, voltage, and current were simultaneously monitored with a digital oscilloscope. In this study, sin wave ac (frequency, f = 1 kHz) was supplied to produce a DBD plasma. The reactant gases were mixed and supplied with mass flow controllers. In most cases the reactant gas mixture consisted of 10% CH_4 and 10% N_2O in Ar was supplied at a flow rate (F_R) of 50 cm^3(STP)•min^{-1}. The reactant and product were analyzed by GC with Porapak Q and Molecular Sieve 5A columns. Plasma diagnoses were performed with an emission spectrometer.

The intensity of the emission spectra due to Ar excitations proportionally increased with increasing supplied voltage.[8,9] When reactant gas was introduced into Ar stream, new emission peaks due to the exited species of reactant were observed, and at the same time the emission intensities from Ar significantly decreased. Figure 1 shows the effect of input voltage on the yields of CH_3OH and HCHO. The other products were CO, C_2H_6, H_2, N_2, and H_2O. It is clearly demonstrated that the reaction starts at 1 kV, then the yield of CH_3OH and HCHO increases with the increase of input voltage. The overall yield of CH_3OH and HCHO exceeded 10% at an input voltage of 7 kV. This value is clearly higher than those of conventional catalysis, i. e., 3.4% with CH_4/N_2O on Mo/Carb-O-Sil at 870 K,[2] 7% with CH_4/NO on V_2O_5/SiO_2 at 883 K,[3] and 1.4% with CH_4/O_2 on CoO-MgO-Al_2O_3 at 730 K.[4]

Figure 2 shows the effect of residence time (t_R) on the selectivity of major products, such as CH_3OH, HCHO, and CO. The selectivity of CH_3OH gradually decreased with the increase of the residence time. The selectivity of HCHO increased with increasing the residence time, then decreased at a longer residence time above 0.022 s. However, the selectivity of CO monotonously increased with increasing the time. It was speculated that the initially formed CH_3OH was oxidized to HCHO, which finally converted to CO.[10] The selectivity to CH_3OH increased with the decrease of input voltage. From these points of view, it's concluded that CH_3OH is easily decomposed to HCHO and CO.[11] It is suggested for the improvement of CH_3OH selectivity, therefore, to be removed CH_3OH formed from the plasma zone as soon as possible.

Table 1 shows the energy efficiency (η_e) in the CH_3OH and HCHO formation.[12] Roughly speaking, the energy efficiency decreased with increasing the input voltage. The estimated energy efficiency of HCHO was higher than that of CH_3OH in whole range of the supplied voltage. From this result, we could estimate the specific power consumption[13] that was 468 ~ 540 MJ/kg-(CH_3OH + HCHO) at 3 ~ 7 kV of supplied voltage. This value was significantly smaller than that obtained by Suib et al.[7] in a microwave-induced plasma reactor (2106 MJ/kg-CH_3OH).

Figures 3A and 3B show the rates of formation of CH_3OH, HCHO, and CO in the presence and the absence of Ar, respectively. It should be noted that the minimum voltage to perform the reaction strongly reduced by the presence of Ar. It is considered, therefore, that excited Ar gives the charge and energy to the reactant molecules by collisions.[9] Hiraoka et al.[14]

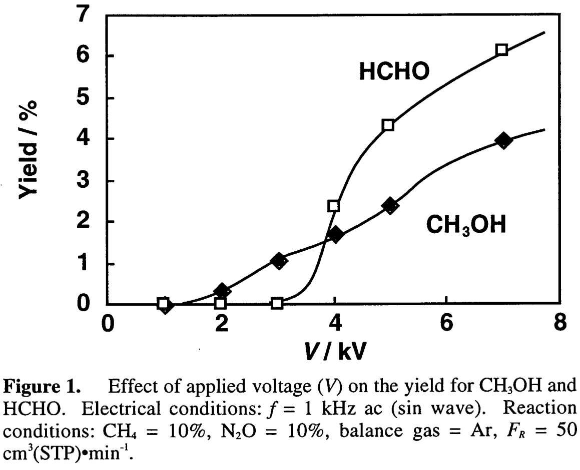

Figure 1. Effect of applied voltage (V) on the yield for CH_3OH and HCHO. Electrical conditions: f = 1 kHz ac (sin wave). Reaction conditions: CH_4 = 10%, N_2O = 10%, balance gas = Ar, F_R = 50 cm^3(STP)•min^{-1}.

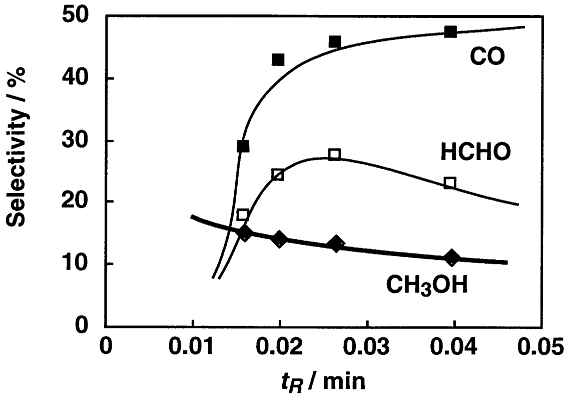

Figure 2. Effect of residence time (t_R) on the selectivity of products on partial oxidation of CH_4 with N_2O. Electrical conditions: V = 4 kV, f = 1 kHz ac (sin wave). Reaction conditions: CH_4 = 10%, N_2O = 10%, balance gas = Ar, F_R = 50 cm^3(STP)•min^{-1}.

Table 1. Electrical conditions and the energy efficiency (η_e) on partial oxidation of methane in DBD plasma

V / kV	$Power$ / W	η_e / mol • $(kWh)^{-1}$	
		CH_3OH	HCHO
2.0	0.33	0.070	-
3.0	1.73	0.097	0.168
4.0	3.06	0.092	0.176
5.0	5.77	0.063	0.147
6.0	8.48	0.047	0.131
7.0	9.98	0.040	0.115

Electrical conditions: ac sin wave, f = 1 kHz, Cu electrode, gap = 1 mm. Reaction conditions: CH_4 = 10%, N_2O = 10%, balance gas = Ar, F_R = 50 cm^3(STP)•min^{-1}.

reported that CH_4 plasma in glow discharge system had two kinds of reaction mechanisms such as radical and ionic processes. No appreciable emission peaks due to any ionic species were observed in the present reaction condition examined. It is supposed, therefore, that the partial oxidation of CH_4 with N_2O in DBD system is performed via radical reaction process. On the other hand, the reaction rate of HCHO formation in the absence of Ar (Figure 3B) was higher than that in the presence of Ar (Figure 3A). From this result, electrons behave important role at the high voltage condition, i. e., the reactant may directly be excited by electrons at an initial step of the reaction.[10] In the presence of Ar, electrons are probably spent to excite Ar. Eliasson et al.[6] has pointed out that the excited oxygen atoms $O(^1D)$ act an important role in providing initial free radicals on the CH_4 and air plasma system. It's well known that the bonding energy between nitrogen atom and oxygen atom in N_2O is weak enough (167 kJ•mol^{-1}) to supply excited oxygen species in this system. This may be reason why the present results show small specific power consumption. It is concluded, therefore, that the excited Ar may give the charge and energy to CH_4 to produce the activated species, such as CH_3, CH_2, CH radicals, react with the excited oxygen or OH radicals.[6,15] Further detailed investigations are, of course, required to gain in sight into the mechanism in this plasma reaction.

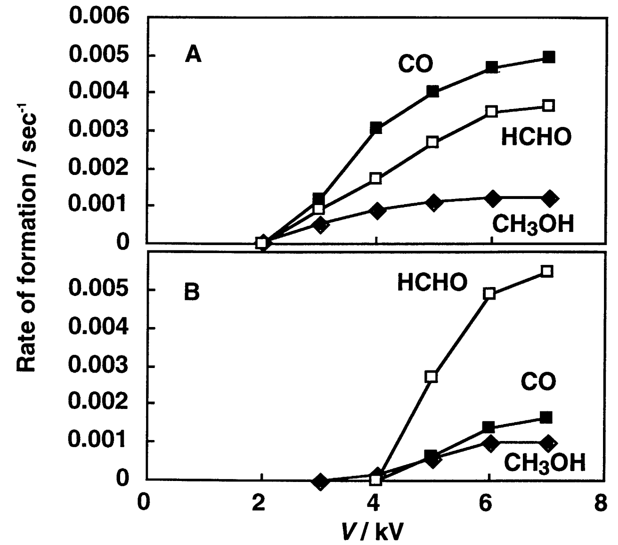

Figure 3. Effect of applied voltage (V) on the formation rate of products: **A**, Ar = 80%, CH_4 =10%, N_2O = 10%; **B**, CH_4 = 50%, N_2O = 50%; F_R = 50 cm^3(STP)•min^{-1}. Electrical conditions: f = 1 kHz ac (sin wave).

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12 The energy efficiency (η_e) was defined as the amount of formation of each product in moles per 1 kWh of power supplied to the reactor.

13 The specific power consumption was defined as the input energy in MJ per product formation of 1 kg.

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