Generation of Hydrogen from Methanol in a Dielectric-Barrier Discharge-Plasma System

Shuji Tanabe, Hiroshi Matsuguma, Kenji Okitsu, and Hiroshige Matsumoto*
Department of Materials Science and Engineering, Faculty of Engineering, Nagasaki University,
1-14 Bunkyo-machi, Nagasaki 852-8521

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The decomposition of CH_3OH was investigated in a dielectric-barrier discharge-plasma induced by low power from 0.27 to 6.40 $Wh(Ncm^3)^{-1}$. The maximum CH_3OH conversion of 80% into H_2 was achieved with CO or CO_2 being the other major product, respectively, in the absence or presence of water.

We have recently been investigating performances in ac silent-discharge-plasma systems in decompositions of such stable compounds as NO,[1] H_2O,[2] and CO_2,[3] in addition to reforming[4] of CH_4 with CO_2 and with N_2O. In the present report, the CH_3OH decomposition, which has recently been considered to be one of the attractive and practical reactions to generate hydrogen as an on-board process for vehicles with fuel cells,[5] was studied in a discharge-plasma system.[2–4] Numerical investigations in conventional catalytic system using Pd-based catalysts have been reported on this subject.[6]

The dielectric-barrier discharge-plasma reactor used in this work has been described elswhere.[2–4] Basically, the inner electrode of copper rod was supported at the center of a quartz tube, which was tightly surrounded by a cylindrical aluminum jacket as the outer electrode. The decomposition was carried out with a gas mixture of 1% CH_3OH (and/or 1% H_2O) in Ar at atmospheric pressure by using a conventional flow reaction system.[2–4] The reactant gas was fed at a flow rate of 50 mL min^{-1} into the plasma zone of 1.9 cm^3 in this work. The operating condition was 1–6 kV and 1 kHz in the present work. The reactant and products were analyzed by GC with Polapak Q and Molecular Sieves 5A. The diagnostics of the plasma zone have been also described in the previous papers.[2–4]

When a power with higher voltage above 2 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 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. Figure 1 shows intensities of these emission spectra, which increased rapidly with an increase in input voltage.[7] Input powers of 0.27, 0.38, 1.58, 3.87, and 6.40 $Wh(Ncm^3)^{-1}$ was observed at input voltages of 2, 3, 4, 5, and 6 kV, respectively. All of these spectra for the Ar atom excitation could be extrapolated to one point at about 1 kV on the input voltage axis, suggesting that the break-down voltage of the Ar discharge was 1 kV in the present system.

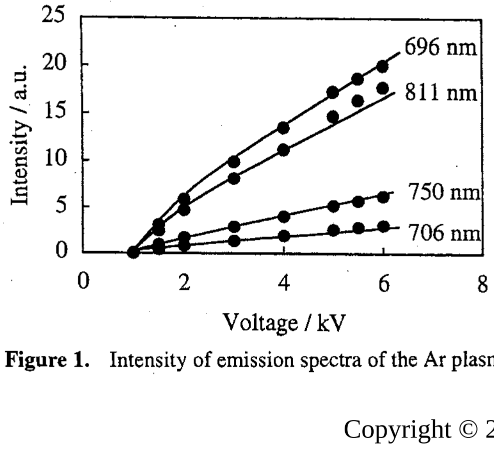

Figure 1. Intensity of emission spectra of the Ar plasma.

All of the emission spectra due to the Ar excitation almost completely disappeared upon introduction of such reactant as CH_3OH (and/or H_2O) into the Ar stream, indicating efficient energy transfers from excited Ar species to reactant molecules. Major gaseous products of the CH_3OH decomposition were H_2, CO and carbon deposit in the absence of water, and H_2 and CO_2 in the presence of water. In the absence of water, the H_2 yield increased with increasing input voltage above 1 kV and attained the maximum 80% at 6 kV, as shown by the curve (a) in Figure 2. Thus, the voltage dependence of the CH_3OH conversion well coincided with that of the emission intensity of Ar discharge (Figure 1), indicating additional evidence of the energy transfer[7] from excited Ar species to CH_3OH molecules.

With a reactant mixture containing water (curve b), on the other hand, the H_2 yield based on supplied CH_3OH ($[H_2]_{generated}/2[CH_3OH]_{supplied}$) was higher in comparison with the curve (a) and similarly increased with input voltage. At input voltages above 5 kV, the H_2 yield was observed to be more than 100%, indicating a contribution of H_2 formation from H_2O molecules. The decomposition of H_2O in the absence of CH_3OH was carried out in order to understand the reactivity of H_2O molecules, as shown by the curve (c) in Figure 2. Only small portions of H_2O below 10% were independently decomposed at above 1 kV of input voltage. The difference of the H_2 yields between the curves (a) and (b) was

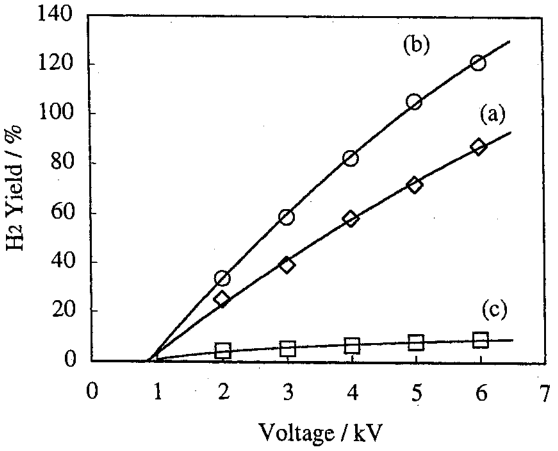

Figure 2. H_2 yield with reactants of (a) 1% CH_3OH, (b) 1% CH_3OH + 1% H_2O, and (c) 1% H_2O in Ar.

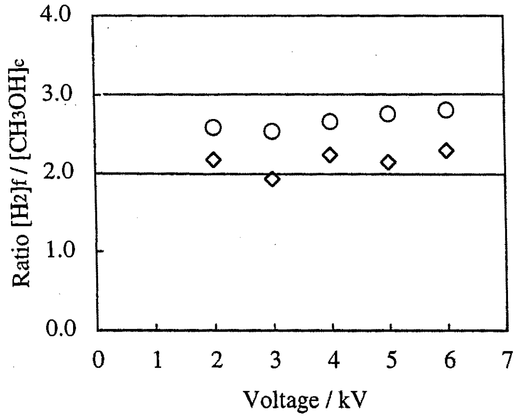

Figure 3. Ratio of the H_2 formation and CH_3OH consumption with reactants of (◇) 1% CH_3OH and (○) 1% CH_3OH + 1% H_2O in Ar.

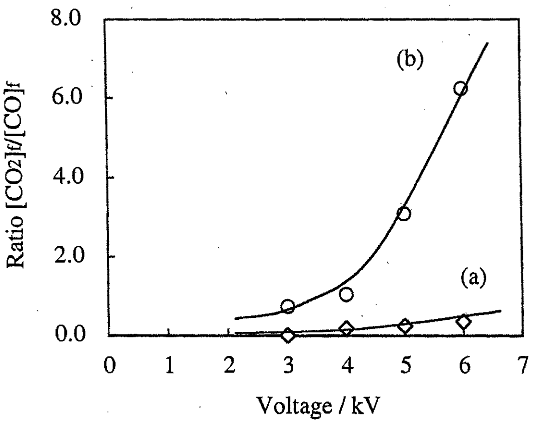

Figure 4. Ratio of the CO_2 and CO formation with reactants of (a) 1% CH_3OH and (b) 1% CH_3OH + 1% H_2O in Ar.

much larger than that in the direct H_2O decomposition (c). It is speculated, therefore, that a reaction between CH_3OH and H_2O to produce H_2 takes place in the plasma zone.

The H_2 formation in the present system can be postulated to occur by the two kinds of process (1) and (2), as follows

$$CH_3OH = 2H_2 + CO \qquad (1)$$

$$CH_3OH + H_2O = 3H_2 + CO_2 \qquad (2)$$

Figure 3 shows ratio of amount of H_2 formed ($[H_2]_f$) and that of CH_3OH consumed ($[CH_3OH]_c$). The average ratios were estimated to be 2.2 in the absence of water and 2.7 in the presence of water. It can be roughly considered from this point of view that the process (1) is the major reaction in the absence of water and that both of these processes (1) and (2) simultaneously proceed in the presence of water.

Figure 4 shows profiles in the formation of the other major products, CO_2 and CO. Ratio of the CO_2 and CO yield ($[CO_2]_f$ / $[CO]_f$) in the absence of water was very small, while that in the presence of water rapidly increased with increasing input voltage. This result in the presence of water might be attributable to water-gas shift reaction, i.e., CO formed by the decomposition of CH_3OH reacts with H_2O to form H_2 and CO_2. Further detailed investigations are, of course, required to gain insight into plasma excitation mechanism.

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