

Hydrogen Production via Steam Reforming of Methane with Nonthermal Plasma

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Introduction

Steam reforming of methane is an important process to produce hydrogen and/or synthesis gas.^{1,2} Industrially, steam reforming of methane is a process where methane reacts with excessive steam at high temperature (>1100 K) and high pressure (>20 atm) over a Ni-containing catalyst.^{1,3} In this catalytic reforming process, large thermal energy is needed to react methane at high temperature, and 20 - 40 % of the raw material is consumed by combustion owing to the supply of the excessive heat.⁴ Therefore, nonthermal plasma has been applied to methane reforming at lower temperatures with point-to-point type and dielectric barrier discharge plasma reactors for the development of cost-effective processes of hydrogen production.

Nonthermal plasma may provide a useful reaction medium for this reaction because reaction temperature can be kept as low as ambient. The recent reports have shown that reaction temperature can be decreased to 453 K in steam reforming⁵ and ambient temperature in carbon dioxide reforming.^{6,7} With the above-mentioned plasma reactors, however, formation of C₂ hydrocarbons is predominant via methane coupling. Therefore, addition of an excessive oxidizing agent such as steam and carbon dioxide is mandatory to suppress the formation of C₂ hydrocarbons.

We have already reported that a ferroelectric packed-bed reactor (FPR) has shown the higher performance compared with a silent discharge plasma reactor in the hydrogen generation from water.⁸ Nonthermal plasma has a potential for hydrogen-forming reactions such as hydrocarbon reforming and water decomposition, but its scope and limitations have not been clarified yet. It is significant to examine the reaction behavior of methane and steam in nonthermal plasma from the viewpoint of its extended application to diverse chemical processes associated with hydrogen utilization. Also, there have been no reports of the steam reforming of methane at ambient temperature.

In the present work, we have studied the steam reforming of methane for hydrogen formation at ambient temperature in nonthermal plasma, focusing on the effect of plasma-generating methods and the factors governing the reaction efficiencies. A continuous production of hydrogen from methane and steam has been also examined with FPR.

Experimental

FPR and a silent discharge reactor (SDR) used in this research were described in detail elsewhere.^{9,10} With FPR, gas flow rate ranged from 50 to 500 mL min⁻¹ (residence time 8.9 to 89 s). On the other hand, gas flow rate was fixed at 50 mL min⁻¹ (residence time 3 s) with SDR. The both reactors employed AC power supply at 50 Hz and high voltage up to 8.0 kV was applied for both the reactors. No breakdowns occurred during operations within their maximum voltages. Methane balanced with N₂ in a standard gas cylinder was introduced to the reactor through a Teflon tube by adjusting the concentrations of methane and flow rates with sets of mass flow controllers and a gas mixer. Steam was supplied to the reactors by humidifying gas (CH₄ / N₂) in a water-bubbling type device in a thermostatic bath. Steam concentrations were determined by a dew point hygrometer, and its contents were controlled within the range of 0.5 - 2.0 %. The gas streams passed through the entry tube (1/8

inch in diameter) and dispersed into plasma zone as shown in Figure 1. Steam reforming of methane was carried out at room temperature and an atmospheric pressure by using a conventional mass flow reaction system.

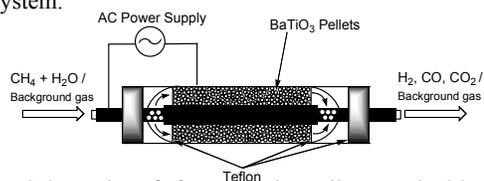


Figure 1. Schematic of ferroelectric pellets packed-bed reactor (FPR).

H₂ and methane were quantified by a TCD-GC with a packed column of Molecular Sieve 13X. CO, CO₂, ethane, ethylene, and acetylene were analyzed by TCD- and FID-GC with a packed column of Porapak Q+N and Molecular Sieve 13X.

Results and Discussion

Definitions of SED, H₂ yield, and CO yield. As a measure of the energy efficiency for FPR and SDR, specific energy density (SED) will be used later (1), where Power denotes the plug-in power.

$$\text{SED (kJ L}^{-1}\text{)} = \text{Power (kW)} / [\text{Flow rate (L/min)} / 60] \quad (1)$$

H₂ yield and CO yield are defined according to (2).

$$\text{Product yield (mol\%)} = 100 \times [\text{Product amount (mol)}] / [\text{Maximum amount of product evolved from methane (mol)}] \quad (2)$$

Effect of reactor and H₂O concentration on the steam reforming of methane. Table 1 shows the effects of reactor and H₂O concentration on steam reforming of methane in N₂ at 9 kJ L⁻¹ of SED. Gas flow rates of FPR and SDR were fixed at 100 mL min⁻¹ and 50 mL min⁻¹, respectively. With an increase in H₂O concentration, CH₄ conversion and the yield of C₂ hydrocarbons decrease while that of CO₂ increases irrespective of reactors. With FPR, H₂ yield increases with H₂O concentration and a maximum is observed for CO yield. These facts can be ascribed to the occurrence of water-gas shift reaction (CO + H₂O → CO₂ + H₂). As a result, H₂ selectivity exceeds 100 % for the H₂O concentration of 1.5 % and 2.0 %. With SDR, CH₄ conversion at the H₂O concentration of 0 % and 2.0 % were 6.5 % and 4.4 %, respectively. Also, the yields of H₂, CO, and CO₂ were much lower than with FPR under the same conditions. For methane reforming, SDR has shown the lower performance compared with FPR as in the case of H₂ generation from water.⁸

Table 1. Effects of reactor and H₂O concentration on steam reforming of methane^{a)}

Reactor	H ₂ O concentration (%)	CH ₄ conversion (mol %)	Yield (mol %) ^{c)}			
			H ₂	CO	CO ₂	C ₂ HCS ^{b)}
FPR	0	36.6	22.2	3.5	0.2	1.3
FPR	1.0	27.6	25.7	14.0	6.9	0.4
FPR	1.5	25.2	26.8	12.6	10.8	0.2
FPR	2.0	22.8	27.1	9.9	12.6	0.1
SDR	0	6.5	2.4	1.3	0.7	0.4
SDR	2.0	4.4	0.7	1.3	1.8	0.1

^{a)} Reaction conditions: methane, 1.0 %; background gas, N₂; SED, 9 kJ L⁻¹.

^{b)} C₂HCS denotes the hydrocarbons such as ethane (C₂H₆), ethylene (C₂H₄), and acetylene (C₂H₂).

^{c)} Product yield (mol%) = 100 x [Product amount (mmol)] / [Maximum amount of product evolved from methane (mmol)]

Since **FPR** and **SDR** have shown the comparable performances in the decomposition of trichloroethylene, bromomethane, and tetrafluoromethane in N_2 ,¹¹ almost the same plasma intensity should be obtained in both the reactors. These facts suggest that water activation is the common rate-determining step for the steam reforming of methane and H_2 generation from water, and that the reaction efficiency highly depends on the plasma-generating method. **SDR**, the point-to-point type of plasma reactor^{6,8} and the dielectric barrier discharge plasma⁷ belong to the same kind of barrier discharge reactor. Our findings clearly show that **FPR** works as a much better reactor for hydrogen-forming reactions than the other three ones.

Steam reforming of methane with FPR. Figure 2 shows that the CH_4 conversion and the yields of H_2 and CO_x gradually increase with an increase in SED in N_2 with **FPR**. When SED was set at 15 kJ L^{-1} , CH_4 conversion, H_2 yield, and CO_x yield were 35.4, 44.4, and 34.9 %, respectively. H_2 selectivity exceeded 100 % at SED higher than 6 kJ L^{-1} . Irrespective of the SED magnitude, almost the same CH_4 conversions and CO_x yields were obtained, i.e., carbon balances were higher than 98 %. In this reaction, no formation of carbon deposits is expected during continuous operations.

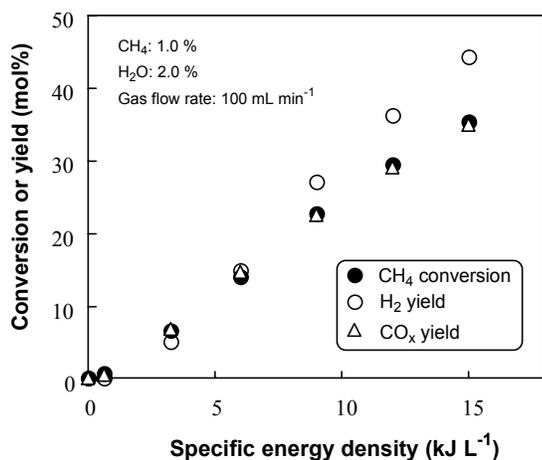


Figure 2. Effect of specific energy density on CH_4 conversion, H_2 yield, and CO_x yield in the steam reforming of methane in N_2 with **FPR**.

Effect of gas flow rate in the steam reforming of methane. The effect of gas flow rate on the yields of H_2 and CO in N_2 with **FPR** was further examined from 50 to 500 mL min^{-1} of gas flow rate under the same condition of Figure 2. With an increase in SED, the yields of H_2 and CO gradually increased at different flow rates. The highest yields of H_2 and CO were 73.4 % and 29.7 %, respectively at 30.0 kJ L^{-1} of SED at 50 mL min^{-1} of gas flow rate. An interesting trend has been observed that higher H_2 yields and CO yields are obtained at higher flow rates, i.e., shorter residence times at fixed SEDs.

Stability of reaction system in continuous synthesis gas production. Figure 3 shows the time profile of the CH_4 conversion, the yields of H_2 and CO , and the selectivities of H_2 , CO , and CO_x in the steam reforming of methane in N_2 with **FPR**. This reaction was carried out at 12 kJ L^{-1} for 10 h under the conditions as the same as for Figure 2. CH_4 conversion and the product selectivities could be kept constant for 10 h. The selectivities of H_2 and CO were 126 % and 58 % on the average, respectively. Therefore, the molar ratio of H_2 to CO was 4.3. Also, CO_x selectivity was almost 100 % for 10 h, i.e., no carbon deposits were formed during the continuous operation.

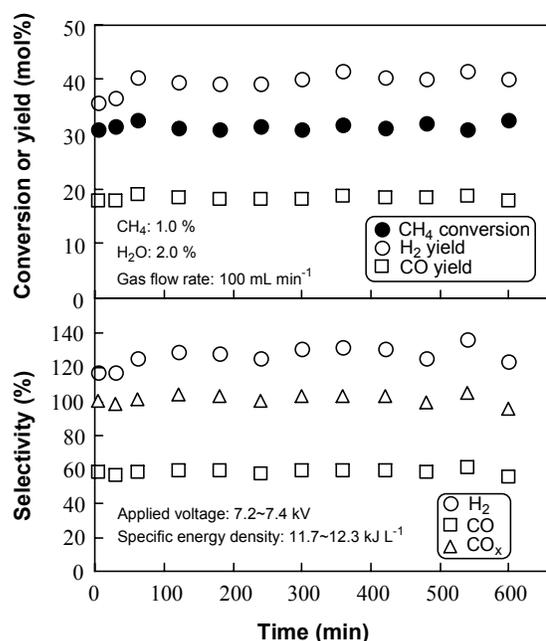


Figure 3. Time profile of the CH_4 conversion, the yields of H_2 and CO , and the selectivities of H_2 , CO , and CO_x in the steam reforming of methane in N_2 with **FPR**.

Conclusions

We have shown here the effects of plasma-generating methods and the factors governing the reaction efficiencies for steam reforming of methane. **FPR** has shown the higher performance compared with **SDR**, suggesting the different electron temperatures in both the reactors at the same input energy densities. For steam reforming of 1 %-methane in N_2 with **FPR**, the optimized water concentration is about 2.0 %. With **FPR**, CO_x selectivity as high as 98 % or higher is constantly obtained under the optimized conditions. This is why this **FPR** can be operated continuously for a long time. For steam reforming of methane at ambient temperature, **FPR** may be one of the best nonthermal plasma reactors.

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