Continuous Production of Synthesis Gas at Ambient Temperature from Steam Reforming of Methane with Nonthermal Plasma

Hajime Kabashima and Shigeru Futamura*
National Institute of Advanced Industrial Science and Technology, AIST Tsukuba West, 16-1 Onogawa, Tsukuba, Ibaraki 305-8569

(Received July 10, 2002; CL-020578)

Nonthermal plasma steam reforming of methane was carried out with two different types of reactors such as ferroelectric packed-bed (FPR) and silent discharge (SDR) in a flow reaction system. The yields of hydrogen and carbon monoxide were much higher with FPR than with SDR under the same conditions. FPR could be operated continuously for 10 h without any decrease in the yields of hydrogen and carbon monoxide.

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 temperatures (>1100 K) and high pressures (>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 synthesis gas production.

Nonthermal plasma may provide a useful reaction medium for this reaction because the reaction temperature can be kept as low as ambient. Recent reports have shown that the reaction temperature can be decreased to 453 K in steam reforming[5] and ambient temperature in carbon dioxide reforming.[6,7] With the above-mentioned plasma reactors, however, formation of C_2 hydrocarbons is predominat via methane coupling. Therefore, addition of an excessive oxidizing agent such as steam and carbon dioxide is mandatory to suppress the formation of C_2 hydrocarbons.

We have already reported that a ferroelectric packed-bed reactor (FPR) has shown the higher performance compared with a silent discharge plasma reactor (SDR) 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 hydrocarbons and steam in nonthermal plasma from the viewpoint of its extended application to diverse chemical processes associated with synthesis gas utilization. Also, there have been no reports on the steam reforming of methane at ambient temperature.

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

FPR and 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 N_2 in a standard gas cylinder was introduced to the reactor through a Teflon tube by adjusting methane concentrations and flow rates with sets of mass flow controllers and a gas mixer. Steam was supplied to the reactors by humidifying gas (CH_4/N_2) 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%. Steam reforming of methane was carried out at room temperature and an atmospheric pressure by using a conventional mass flow reaction system. H_2 and methane were quantified by a TCD-GC with a packed column of Molecular Sieve 13X. CO, CO_2, ethane, ethylene, and acetylene were analyzed by TCD- and FID-GC with a packed column of Porapak Q + N and Molecular Sieve 13X.

In this paper, each of the product yields for H_2, CO, CO_2, and C_2 hydrocarbons [eq (1)] is plotted against specific energy density (SED) given by eq (2), where ''Power'' denotes the plug-in power.

$$\text{Product yield(mol\%)} = 100 \times [\text{Product amount(mmol)}]/[\text{Maximum amount of product evolved from 1\% methane(mmol)}] \quad (1)$$

$$\text{SED(kJ L}^{-1}) = \text{Power(kW)}/[\text{Flow rate(L min}^{-1})/60] \quad (2)$$

Table 1 shows the effects of reactor and H_2O concentration on methane reforming in N_2 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 H_2O concentration, CH_4 conversion and the yield of C_2 hydrocarbons decrease, while that of CO_2 increases irrespective of reactors. With FPR, H_2 yield increases with H_2O concentration and a maximum is observed for CO yield. These facts can be ascribed to the occurrence of water-gas-shift reaction ($CO + H_2O \rightarrow CO_2 + H_2$). H_2 selectivity exceeds 100% for the H_2O concentration of 1.5% and 2.0% because H_2 is derived also from decomposition of H_2O itself[8] and water-gas-shift reaction. With SDR, CH_4 conversion at the H_2O concentration of 0% and 2.0% were 6.5% and 4.4%, respectively. Also, the yields of H_2, CO, and CO_2 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 H_2 generation from water.[8] Since FPR and SDR have shown the comparable performances in the decomposition of trichloroethylene, bromomethane, and tetrafluoromethane in N_2,[9] almost the same plasma intensity should be obtained in both the reactors. These facts suggest that water activatioin 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. FPR and SDR belong to the same kind of barrier discharge plasma reactor. On the other hand, corona discharge is produced in

Table 1. Effects of reactor and H_2O concentration on steam reforming of methane[a]

Reactor	H_2O concentration (%)	CH_4 conversion (mol%)	Yield (mol%)[c] H_2	CO	CO_2	C_2HCs[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, N_2; SED, 9 kJL^{-1}. [b]C_2 HCs denotes the hydrocarbons such as ethane, ethylene, and acetylene. [c]Product yield(mol%) = 100 × [Product amount(mmol)]/[Maximum amount of product evolved from 1% methane (mmol)].

the point-to-point type of plasma reactor.[6] Our findings clearly show that FPR works as a much better reactor for hydrogen-forming reactions than the other three ones. For example, Kado and coworkers have reproted steam reforming of methane with a point-to-point type of plasma reactor.[6] The maximun H_2 generation rate with this reactor was 210 μmol min^{-1} in 20%-CH_4/80%-H_2O at 453 K. On the other hand, the maximun H_2 generation rate with FPR was 48 μmol min^{-1} in 1%-CH_4/2%-H_2O/97%-N_2 at ambient temperature. FPR performance is 4.4-fold lower compared to that of Kado's reactor. However, the H_2 generation efficiency of FPR is estimated to be higher than that of Kado's, since the initial concentration of CH_4 is 20 times lower and the reaction temperature is lower by 150 K with FPR.

Figure 1 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 selsctivity calculated based on the CH_4 conversion 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%.

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 1. 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.

Figure 2 shows the time profiles of CH_4 conversion, the yields of H_2 and CO, and the selectivities of H_2 and 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} of SED for 10 h under the conditions as the same as for Figure 1. CH_4 conversion and 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, almost all of the carbon atoms in the reacted methane could be recovered as CO and CO_2 during the continuous operation.

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

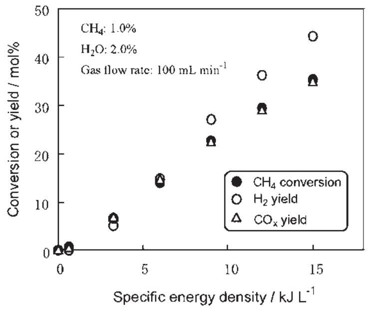

Figure 1. Effect of specific energy density on the CH_4 conversion, H_2 yield, and CO_x yield in N_2 with FPR.

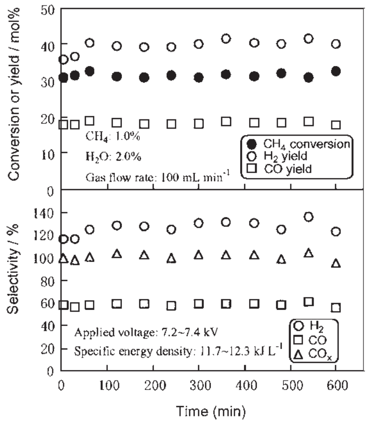

Figure 2. Time profiles of the CH_4 conversion, the yields of H_2 and CO, and the selectivities of H_2, CO, and CO_x in N_2 with FPR.

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 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.

This work was partly supported by the Grants-in-Aid from New Energy and Industrial Technology Development Organization of Japan (NEDO).

References

1 J. N. Armor, *Appl. Catal., A*, **176**, 159 (1999).
2 M. A. Pena, J. P. Gomez, and J. L. G. Fierro, *Appl. Catal., A*, **144**, 7 (1996).
3 T. E. Solh, K. Jarosch, and H. I. Lasa, *Appl. Catal., A*, **210**, 315 (2001).
4 S. Asaoka and M. Shimura, *Petrotech*, **24**, 226 (2001).
5 S. Kado, K. Urasaki, Y. Sekine, and K. Fujimoto, *Chem. Commun.*, **2001**, 415.
6 S. L. Yao, M. Okumoto, A. Nakayama, and E. Suzuki, *Energy Fuels*, **15**, 1295 (2001).
7 L. M. Zhou, B. Xue, U. Kogelschatz, and B. Eliasson, *Energy Fuels*, **12**, 1191 (1998).
8 H. Kabashima, H. Einaga, and S. Futamura, *Chem. Lett.*, **2001**, 1314.
9 S. Futamura, A. Zhang, and T. Yamamoto, *IEEE Trans. Ind. Appl.*, **36**, 1507 (2000).
10 H. Einaga, T. Ibusuki, and S. Futamura, *IEEE Trans. Ind. Appl.*, **37**, 1476 (2001).
11 S. Futamura, A. Zhang, and H. Einaga, *IEEE Trans. Ind. Appl.*, **37**, 978 (2001).