American Journal of Engineering Research (AJER)
e-ISSN: 2320-0847 p-ISSN : 2320-0936
Volume-5, Issue-12, pp-119-123
www.ajer.org
Research Paper Open Access

Enhancement of CH4 yield by a sub-atmospheric pressure pulse H2/CO2 plasma with Ni electrodes

Kyonosuke Sato[1], Fumiaki Sato[2], Satoru Iizuka[3]
[1,2,3]Departmentof Electrical Engineering, Graduate School of Engineering, Tohoku University, Sendai, Japan

ABSTRACT: *Production of CH_4 from CO_2 has been established by a pulsed H_2 plasma in sub-atmospheric pressure range with a use of pair electrodes made of Ni that acts as catalyst for generation of methane in carbon dioxide hydrogen gas system. The results are compared with those with pair electrodes made of stainless steel. Both of the CH_4 production yield and the energy efficiency for CH_4 production in the case of Ni electrodes are increased roughly by one order of magnitude higher than those with stainless steel electrodes, without a use of additional heating system for the electrodes. Synergy effect of plasma and catalyst was observed.*
Keywords - *Carbon dioxide, methane, hydrogen plasma, sub-atmospheric pulse discharge, Ni catalysis.*

I. INTRODUCTION

Carbon dioxide CO_2 has been considered as one of the causes of global warming by absorbing radiation within the infrared range. Therefore, the suppression of CO_2 emission into the environment is crucial subject that must be settled urgently. In order to suppress CO_2 emission into the environment from electrical power plants, for example, it might be desirable that CO_2 is collected and converted to methane before exhausting, if any surplus renewable electric power exists. This means that the surplus renewable energy can be stored as methane [1-2]. This method is superior to batteries, because the energy stored in methane will be conserved to energy without any loss for many years.

Production of CH_4 from CO_2 is rather easily established by hydrogen discharge plasmas [3-10]. However, a little work has been reported. In most cases, CO_2 was reduced by CH_4 to produce syngas of CO and H_2, because methane is also one of the greenhouse gases [11-17]. Eliasson et al. investigated the production of CH_4 by a dielectric barrier discharge with H_2 in detail. Mixed gas of CO_2 and H_2 was employed for CH_4 production [3]. However, for an efficient formation of methane a new innovative method has been expected.

The generation of CH_4 from CO_2 and H_2 is known as Sabatier reaction in the chemical engineering [18]. By employing catalysis such as Ni, CH_4 was generated under high pressure (several atom) and high temperature (200- 400 K) condition, where decomposition of CO_2 was carried out on the catalysis surface [19-21]. On the other hand, in a combined system of plasma and catalysis, CO_2 can be easily decomposed by plasma electrons, together with decomposition of H_2. The produced reactive species such as CO^* and H_2^* in the discharge might be available for relaxing the severer reaction condition on the catalysis surface in the plasma and catalysis reaction system.

The purpose of this study is to investigate fundamental process of the reduction of CO_2 by hydrogen radicals that were produced in CO_2/H_2 discharge [22-25]. Here, a use of Ni catalysis is examined for efficient methane production. Our method proposed here is quite unique for a production of reusable organic materials, CH_4, by using a simple sub-atmospheric pressure CO_2/H_2 discharges with Ni catalysis.

II. EXPERIMENTAL APPARATUS

Figure 1 shows a CO_2 decomposition device for a sub-atmospheric pressure discharge, consisting of a glass tube with a pair of Ni rod electrodes covered by a scrolled Ni mesh. Mixed gas of CO_2 and H_2 was supplied to the glass tube by changing flow rate ratio H_2/CO_2. The plasma discharge was generated by applying square pulse voltage to the electrodes under sub-atmospheric pressure condition. The pulse width is 5 μs. The experiment was carried out by changing the discharge parameters such as gas mixture ratio and electric input power for the discharge. The gas components before and after the discharge were analyzed by FTIR (Fourier transform infrared spectroscopy). The results were evaluated by the following quantities.

(1) CO_2 decomposition ratio α (%) = 1 - $[CO_2]_{OUT}/[CO_2]_{IN}$.
(2) CH_4 selectivity β (%) = $[CH_4]$/[all carbon species except CH_4].
(3) CH_4 production energy efficiency γ (L/kWh) = $[CH_4]$(in litter)/ electric input power for the discharge (kWh).

Electric input power was calculated from a time averaged V(t)×I(t) measured directly in the discharge circuit. Here, V(t) and I(t) are voltage and current for the discharge at time *t*, respectively.

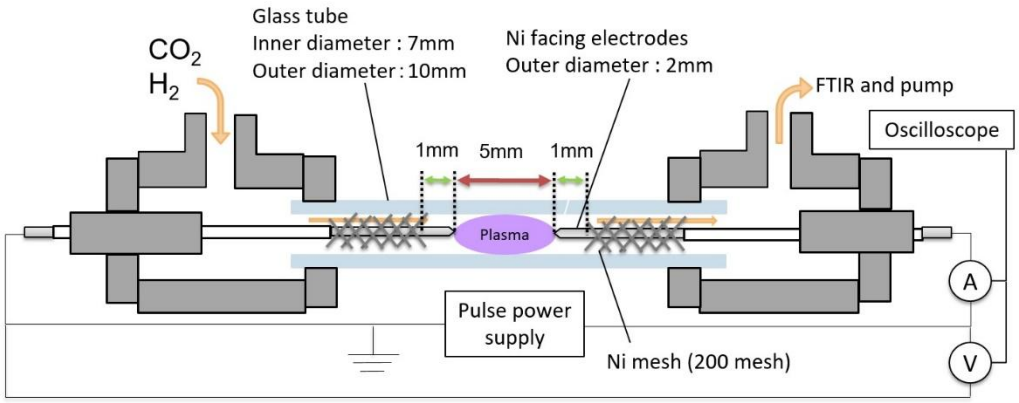

Fig. 1 Experimental apparatus

III. EXPERIMENTAL RESULTS

3.1 Gas mixture ratio and total gas pressure dependencies

Dependences of CO_2 decomposition ratio α, methane selectivity β, methane yield α×β, and energy efficiency γ on gas mixture ratio H_2/CO_2 are shown in Fig. 2 with total gas pressure as a parameter. Here, CO_2 flow rate is fixed at 2sccm (standard cubic centimeter per minute). Discharge current and pulse repetition frequency are fixed at 50 mA and 7.8 kHz, respectively.

When total pressure is 1 kPa, CO_2 decomposition ratio α becomes about 12 % in the range H_2/CO_2 = 2 - 4, then α decreases monotonically with an increase of H_2/CO_2, as shown in Fig. 2(a). On the other hand, as shown in Fig. 2(b), methane selectivity β increases first with an increase of H_2/CO_2, and finally saturated to be about 22 % in the range $H_2/CO_2 > 5$. As a result, CH_4 yield α×β has a maximum of 2.1 % at H_2/CO_2 = 4 as shown in Fig. 2(c). In this case, the methane production energy efficiency γ attains to about 0.3 L/kWh at H_2/CO_2 = 4 as shown in Fig. 2(d). Basically, similar dependencies of α and β were also obtained in the case of total pressure of 10 kPa, as shown in Figs. 2(a) and 2(b), respectively. However, as shown in Fig. 2(c), the maximum CH_4 yield is much increased to 12.2 % at H_2/CO_2 = 4, where α and β become 27.2 % and 44.9 %, respectively. In this case, the energy efficiency γ attains to the maximum of 1.62 L/kWh at H_2/CO_2 = 4. Therefore, γ at 10 kPa is increased by 5.4 times, compared to that at 1 kPa. Therefore, sub-atmospheric pressure (10 kPa) discharge is preferable for an efficient CH_4 production.

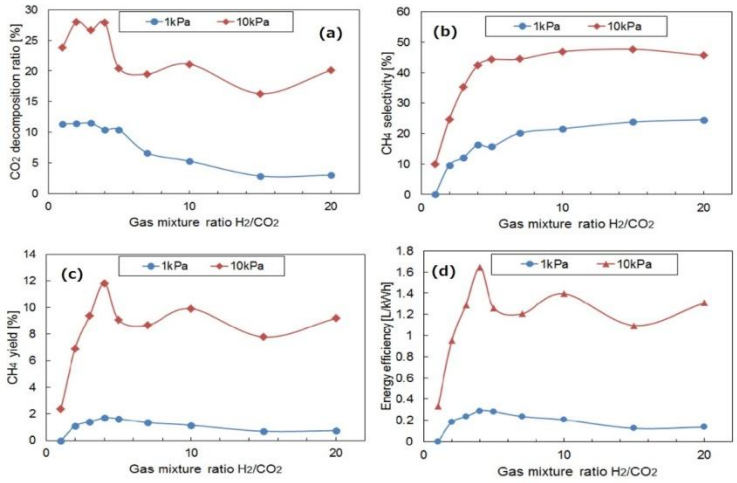

Fig. 2 Dependences of (a) CO_2 decomposition ratio α, (b) CH_4 selectivity β, (c) CH_4 yield α×β, and (d) energy efficiency γ on gas mixture ratio H_2/CO_2 with total gas pressure as a parameter.

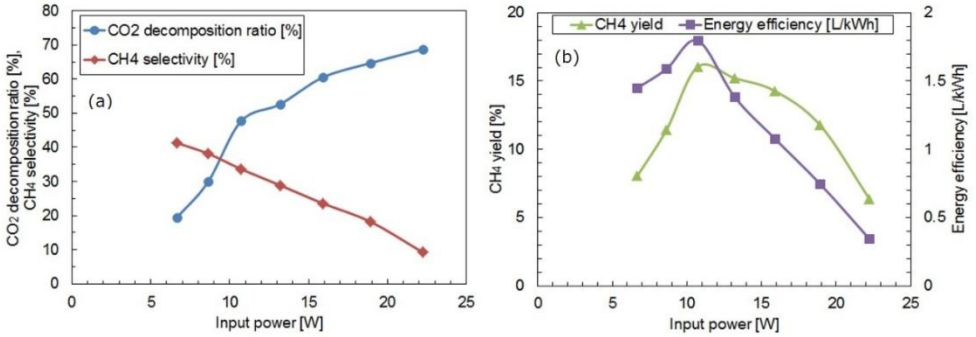

Fig.3 Dependences of CO_2 decomposition ratio α, CH_4 selectivity β, CH_4 yield α×β, and energy efficiency γ on discharge input power at total pressure 10 kPa with gas mixture ratio $H_2/CO_2 = 4$.

3.2 Discharge power dependency

Fig. 3 shows dependences of CO_2 decomposition ratio α, methane selectivity β, methane yield α×β, and energy efficiency γ on discharge input power at total pressure 10 kPa with gas mixture ratio $H_2/CO_2 = 4$. The CO_2 decomposition ratio α increases with input power, as shown in Fig. 3(a), where, on the contrary, methane selectivity β monotonically decreases with input power. Therefore, CH_4 yield α×β has a maximum of 16.5 % at input power of 10W, as shown in Fig. 3(b), where α and β become 50.2 % and 32.8 %, respectively. As a result, the energy efficiency becomes the maximum of 1.8 L/kWh at input power of 10 W, as shown in Fig. 3(b).

3.3 Effect of Ni catalyst

The results shown in Figs.2-3 were obtained with a use of a Ni electrode covered with a scrolled Ni mesh. In order to verify the catalysis effect of Ni, similar experiments are performed by using a stainless steel (SUS) electrode covered with a scrolled stainless steel (SUS) mesh. Both results are compared in Fig. 4 with metal species as a parameter. In the case of SUS, CO_2 decomposition ratio α gradually increases with input power as shown in Fig. 4(a), and α becomes 29.2 % at input power 20 W. On the other hand, methane selectivity β was not much decreased with input power as shown in Fig. 4(b), and β becomes 14.1 % at input power 20W. As a result, methane yield α×β and energy efficiency γ became maxima 4.1 % and 0.25 L/kWh at input power 20 W, as shown in Figs. 4(c) and 4(d), respectively. However, in the case of Ni, CO_2 decomposition ratio α increases largely with an increase of input power up to10 W, then gradually increases in the power range larger than 10 W, as shown in Fig. 4(a). On the other hand, methane selectivity β was much increased first to 43.2 % at 7 W. However, β was fairly decreased with input power, as shown in Fig. 4(b). As a result, methane yield α×β and energy efficiency γ became maxima 16.2 % and 1.8 L/kWh at input power 10 W, as shown in Figs. 4(c) and 4(d), respectively. From these results, it is shown that methane production yield and energy efficiency were much increased by using the Ni electrode covered with a scrolled Ni mesh, compared to those of the SUS electrode covered with a scrolled SUS mesh. In the next section, the catalysis effect of Ni is discussed.

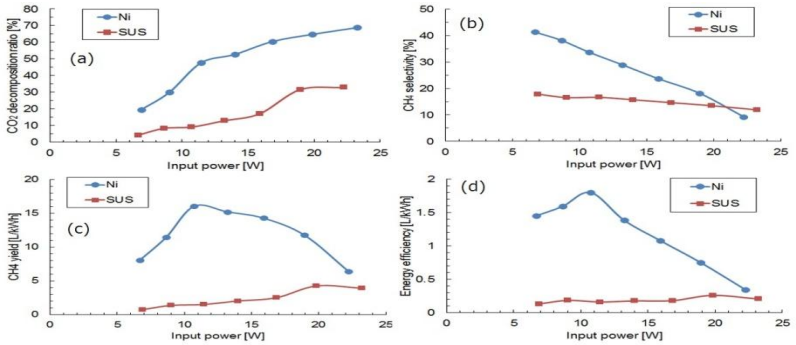

Fig. 4 Comparison of (a) CO_2 decomposition ratio α, (b) CH_4 selectivity β, (c) CH_4 yield α×β, and (d) energy efficiency γ on discharge input power between Ni and SUS electrodes covered with mesh. Total pressure is 10 kPa and gas mixture ratio is $H_2/CO_2 = 4$.

IV. DISCUSSION

First, we will discuss about optimum gas mixture ratio H_2/CO_2 for methane production shown in Fig. 2. When gas mixture ratio is $H_2/CO_2 < 4$, the amount of H_2 radical for CH_4 production is insufficient. So, β increases with H_2/CO_2, while α remains almost constant. However, when $H_2/CO_2 > 4$, relative energy for CO_2 decomposition decreases by an increase of amount of H_2, together with a decrease of residence time due to an

increase of total flow rate. So, α decreases with H_2/CO_2, while β remains almost constant. As a result, optimum condition was obtained at $H_2/CO_2 = 4$. This ratio is consistent with a stoichiometry gas mixture ratio $H_2/CO_2 = 4$ in the reaction $CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$. This property was not changed by the change of total pressure. However, methane yield α×β and energy efficiency γ became large at higher sub-atmospheric pressure because of increases of reactive radical density and their collision frequency among the radicals. So, chemical reactions for CH_4 production are promoted in the higher sub-atmospheric pressure.

Energy that CO_2 receives from plasma increases with electric input power. Therefore, CO_2 decomposition ratio α increases with input power. However, when input power further increases, CH_4 generated in plasmas is re-decomposed because of excessive energy. Therefore, CH_4 selectivity β decreases. Further, a reversal reaction described below will be important when the electrode temperature is increased in higher input power regime.

Methane production takes place basically in the space of discharge, where CO_2 is decomposed to CO + O by plasma electrons. Then, CO is reduced by H* and H_2* radicals for the generation of CH_4 and $2H_2O$ in the plasma space. On the other hand, when a catalysis is introduced in the discharge, some amount of CO_2 and CO, arriving at catalysis surface, can be decomposed to CO + O and C + O on the surface, respectively, then finally both of them are reduced by H_2 and desorbed through the reactions $C + 2H_2 \rightarrow CH_4$ and $O + H_2 \rightarrow H_2O$, respectively. Therefore, components of CO_2 and CO in the space of discharge are decreased. Conversely, CH_4 yield is increased. As a result, both of CO_2 decomposition ratio α and methane selectivity β are increased. For such a catalysis, Ni is considered, rather than Fe, because oxidization potential of Ni is lower than that of Fe. Therefore, desorption of decomposed C and O from Ni surface by hydrogen reduction would be easier than those from SUS surface. Note that stainless steel (SUS) is an alloy steel which contains Fe (iron) as a main component (50% or more) and contains Cr (chromium not less than 10.5%) that has also large oxidization potential. As a reason of such abrupt decrease of β accompanied by an increase of α, it is considered that a reversal reaction, $C + CO_2 \rightarrow 2CO$, has proceeded on Ni surface in the higher input power range with higher electrode temperature. The differences of α and β between Ni and SUS in Figs. 4(a) and 4(b), respectively, were considered as a difference of catalysis effect of Ni and SUS. Both of CH_4 production yield and energy efficiency for CH_4 production in the case of Ni electrodes are increased, being roughly by one order of magnitude higher than those with stainless steel electrodes, without a use of additional heating system for the Ni electrodes. Synergy effect of plasma and catalyst was observed.

V. CONCLUSION

In this study, CH_4 generation from CO_2 using sub-atmospheric pressure H_2 plasmas was investigated under several discharge conditions. CO_2 decomposition ratio α and CH_4 yield α×β reached the maxima at $H_2/CO_2 \approx 4$, then decreased with an increase of H_2/CO_2. Favorable results were obtained in a range of sub-atmospheric pressure. CO_2 decomposition ratio α raised monotonically with an increase of input power. On the other hand, CH_4 selectivity β simply diminished with power. CH_4 yield α×β and energy efficiency γ reached peak values at input power 10 W and gas mixture ratio $H_2/CO_2 = 4$ in the case of Ni electrode. Under optimum conditions, maxima of CH_4 yield α×β and energy efficiency γ became 16.0 % and 1.80 L/kWh, respectively, where CO_2 decomposition ratio α and CH_4 selectivity β become 41.9 % and 38.2 %, respectively, by using the Ni electrode. Catalysis effect of Ni is found to be effective for an increase of CO_2 decomposition ratio α, methane selectivity β, and energy efficiency γ for methane production.

REFERENCES

[1] L K R Struckmann, A Pesched, R H Rauschenbach, K Sundmacher, Assessment of methanol synthesis utilizing exhaust CO_2 for chemical storage of electrical energy, Ind. Eng. Chem. Res. 49, 11073-11078 (2010).

[2] S. K. Hoekman, A. Broch, C. Robbins, R. Purcell, CO_2 recycling by reaction with renewably-generated hydrogen, Int. J. Greenhouse Gas Contr. 4, 44-50 (2010).

[3] B. Eliasson, U. Kogelschatz, B. Xue, L M Zhou, Hydrogenation of carbon dioxide to methanol with a discharge-activated catalyst, Ind. Eng. Chem. Res. 37, 3350-3357 (1998).

[4] J. H. Lunsford, Catalytic conversion of methane to more useful chemicals and fuels: a challenge for the 21st century, Catal. Today, 63, 165-174 (2000).

[5] W. McDonough, M. Braungart, P. Anastas, J. Zimmerman, Peer reviewed: Applying the principles of green engineering to cradle-to-cradle design, Environ. Sci. Technol. 37, 434A-441A (2003).

[6] V. Gouyard, J Ttibouet, C B Duperyrat, Influence of the plasma power supply nature on the plasma–catalyst synergism for the carbon dioxide reforming of methane, IEEE Trans. Plasma Sci. 37, 2342-2346 (2009).

[7] D W Larkin, L LLobban, R G Mallinson, Production of organic oxygenates in the partial oxidation of methane in a silent electric discharge reactor, Ind. Eng. Chem. Res. 40, 1594-1601 (2001).

[8] D. Mei, X. Zhu, YK. He, J D. Yan, X. Tu, Plasma-assisted conversion of CO_2 in a dielectric barrier discharge reactor: understanding the effect of packing materials, Plasma Sources Sci. Technol. 24, 015011 (2015).

[9] W F L M. Hoeben, W. Boekhoven, F J C M Beckers, E J M Van Heesch, A J M Pemen, Partial oxidation of methane by pulsed corona discharges, J. Phys. D: Appl. Phys. 47, 355202 (2014).

[10] B Zhu, X S Li, J L Liu, X. Zhu, A M Zhu, Kinetics study on carbon dioxide reforming of methane in kilohertz spark-discharge plasma, Chem. Eng. J. 264, 445-452 (2015).

[11] J. R. H. Ross, Natural gas reforming and CO_2 mitigation, Catal. Today, 100, 151-158 (2005).

[12] M. Mikkelsen, M. Jorgensen, F. C. Krebs, The teraton challenge. A review of fixation and transformation of carbon dioxide, Energy Environ. Sci. 3, 43-81 (2010).
[13] R. Snoeckx, R. Aerts, X. Tu, A. Bogaerts, Plasma-based dry reforming: A computational study ranging from the nanoseconds to seconds time scale, J. Phys. Chem. C 117, 4957-4970 (2013).
[14] R. Dorai, H. Hassouni, M. J. Kushner, Interaction between soot particles and NO_x during dielectric barrier discharge plasma remediation of simulated diesel exhaust, J. Appl. Phys. 88, 6060-6071 (2000).
[15] X. Tao, M. Bai, X. Li, H. Long, S. Shaung, Y. Yin, X. Dai, CH_4–CO_2 reforming by plasma – challenges and opportunities, Prog. Energy Combust. Sci. 37, 113-124 (2011).
[16] C. Xu, X. Tu, Plasma-assisted methane conversion in an atmospheric pressure dielectric barrier discharge reactor, J. Energy Chem. 22, 420-425 (2013).
[17] R. Arts, W. Somers, A. Bogaerts, Carbon dioxide splitting in a dielectric barrier discharge plasma: A combined experimental and computational study, ChemSusChem. 8, 702-716 (2015).
[18] S. Fujita, H. Teruuma, M. Nakamura, N. Takezawa, Mechanisms of methanation of carbon monoxide and carbon dioxide over nickel, Ind. Eng. Chem. Res. 30, 1146-1151 (1991).
[19] D. E. Peebles, D. W. Goodman, J. M. White, Methanation of carbon dioxide on Ni(100) and the effects of surface modifiers, J. Phys. Chem. 87, 4378-4387 (1983).
[20] M. Araki, V. Ponec, Methanation of carbon dioxide on nickel and nickel-copper alloys, J. Catalysis 44, 439-448 (1976).
[21] D. W. Goodman, R. D. Kelley, T. E. Madey, J. T. Yates JR, Kinetics of the hydrogenation of CO over a single crystal nickel catalyst, J. Catalysys 63, 226-234 (1980).
[22] M. Kano, G. Satoh, S. Iizuka, Reforming of carbon dioxide to methane and methanol by electric impulse low-pressure discharge with hydrogen, Plasma Chem. Plasma Process, 32, 177-185 (2012).
[23] T. Tsuchiya, S Iizuka, Conversion of methane to methanol by a low-pressure steam plasma, J. Envir. Eng. Technol., 2, 35-39 (2013).
[24] K. Arita, S. Iizuka, Production of CH_4 in a low-pressure CO_2/H_2 discharge with magnetic field, J. Mater. Sci. Chem. Eng., 3, 69-77 (2015).
[25] K. Arita, S.Iizuka Conversion of CO_2 to CH_4 by a pulsed hydrogen plasma shower method, British J. Appl. Sci. Technol., 15(6), BJAST.26169, 1-8 (2016).