Low temperature reforming of methane to synthesis gas with direct current pulse discharge method

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Synthesis gas was produced by pulsed irradiation of electrons on a mixture of CH_4 and CO_2 (or H_2O) at low temperature and atmospheric pressure without catalysts; especially in the CO_2 reforming reaction, the $H_2:CO$ ratio could be controlled and depended on the concentration of CO_2 in the feed gas.

Authors have shown that when dc pulse discharge (DCPD) was applied to non-catalytic activation of methane, dehydrogenation of methane proceeded by electron collision and acetylene was produced with 95% selectivity under the conditions of ambient temperature and atmospheric pressure. Coexisting oxygen was found to be very effective in suppressing carbon deposition.[1] In this paper, carbon dioxide or steam was added, a possibility to produce synthesis gas was examined. Because carbon dioxide and steam reforming of methane are highly endothermic reactions, these reactions require temperatures > 800 K in the presence of catalysts. It has been reported that carbon dioxide reforming of methane with plasma techniques, such as dielectric-barrier discharge[2,3] and radio-frequency discharge,[4] give syngas at ambient temperature.

A flow-type tubular discharge reactor (4.0 mm i.d.) used in the present study is the same as that reported previously.[1] In the steam reforming reaction, water was fed as liquid with the micro feeder and vaporized in the preheater upstream of the reactor at 453 K. Before sampling, water was trapped in an ice trap. The temperature of the whole reactor and line to the ice trap was maintained at 453 K to prevent condensation. Carbon dioxide reforming was conducted at ambient temperature. Stainless steel rods of 1.0 mm diameter were used as the electrodes and were located 1.5 mm or 10.0 mm apart. The total flow rate was fixed at 10 cm³ min⁻¹. All experiments were conducted at atmospheric pressure and all the products were analyzed by gas chromatography. Product selectivity was defined as based on the carbon.

In the presence of CO_2 or steam, the state of discharge was stable and carbon deposition on the electrodes and the wall of the reactor was not observed. Table 1 shows the effect of supplied energy on CO_2 and steam reforming of methane. Since trace amounts of C_3 and C_4 hydrocarbons were produced, the sum of the selectivity did not reach 100%. In the reforming reaction, CO was formed as well as C_2 hydrocarbons in both

reaction systems. Also, in the presence of steam, CO_2 was produced by the water gas shift reaction. Although the formation of CO_2 is one of the serious problems in the conventional steam reforming process for making syngas, its selectivity was as low as 4% in the DCPD method in spite of the low reaction temperature of 453 K. The main component of C_2 compounds was acetylene, so the $H_2:CO$ ratio was larger than the stoichiometric ratio. With an increase of supplied energy, the conversion increased and CO selectivity increased slightly while C_2 selectivity decreased slightly. It was clarified that the DCPD method had a possibility to proceed the reforming reaction at low temperature.

Fig. 1 shows the effect of CO_2 content in the feed gas on the conversion, the selectivity and $H_2:CO$ ratio. With increasing CO_2 content, CH_4 conversion rose and reached 76% at $CH_4:CO_2 = 1:4$ while CO_2 conversion remained almost stable at *ca.* 40%. The selectivity strongly depends on the feed gas composition. With the increase of CO_2 content, C_2 selectivity decreased sharply while CO selectivity increased dramatically. Under the conditions of high CH_4 concentration, the formation
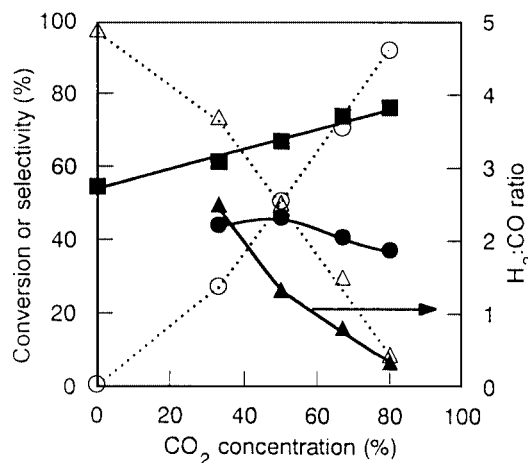

Fig. 1 Effect of carbon dioxide concentration on CO_2 reforming. Reaction conditions: 10 cm³ min⁻¹ total flow rate, ambient temperature, 0.1 MPa, 1.5 mm electrode distance, 52 W supplied energy; (■) CH_4 conv., (●) CO_2 conv., (△) C_2 sel., (○) CO sel., (▲) $H_2:CO$ ratio.

Table 1 Effect of supplied energy on reforming of methane[a]

Added gas	Supplied energy/W	Conversion(%)		Selectivity(%)			$H_2:CO$ ratio
		CH_4	CO_2 or H_2O	C_2	CO	CO_2	
CO_2	3.2	16.3	8.1	64.2	35.6	—	1.74
	10.4	30.4	17.0	62.5	37.3	—	1.56
	21.0	41.2	24.3	54.9	44.7	—	1.48
H_2O	4.4	20.2	9.4	57.0	38.0	3.2	5.44
	11.8	29.9	15.7	52.1	41.3	4.4	5.25
	24.0	39.8	22.2	48.6	45.8	3.7	4.87

[a] Reaction conditions: 10 cm³ min⁻¹ total flow rate, $CH_4:CO_2$ or $H_2O = 1$, 1.5 mm distance of electrodes, 0.1 MPa, ambient temperature in CO_2 reforming and 453 K steam reforming.

Table 2 Effect of H_2O concentration and distance of electrodes on steam reforming of methane[a]

| $CH_4:H_2O$ | Electrode distance/mm | Conversion(%) | | Selectivity(%) | | | $H_2:CO$ ratio |
		CH_4	H_2O	C_2	CO	CO_2	
5:5	1.5	39.8	22.2	48.6	45.8	3.7	4.87
2:8	1.5	49.2	11.7	19.7	64.3	15.3	4.37
2:8	10.0	82.4	19.5	11.0	83.1	5.7	3.46

[a] Reaction conditions: 10 cm³ min⁻¹ total flow rate, 453 K, 0.1 MPa, 3.0 mA.

of C_2H_2 was predominant by the coupling of CH that was produced from CH_4, whereas under conditions of high CO_2 concentration, CO became the main product because of the higher collision probability between CH and activated CO_2 species. The selectivity of C_2 and CO was equal for $CH_4:CO_2$ = 1:1. The feed gas composition also had a great influence on $H_2:CO$ molar ratio. That ratio was inversely proportional to CO_2 content and could be approximated over the whole range by the formula $R = 1.258 \times r$, where R is the $H_2:CO$ ratio and r is the mixing ratio of $CH_4:CO_2$. Synthesis gas with a $H_2:CO$ ratio of 2 was obtained at 40% CO_2 content, which is suitable for methanol synthesis *via* a catalytic process.

As shown in Table 2, increasing the steam content caused a decrease in C_2 selectivity together with an increase in CO selectivity during steam reforming. However, CO_2 selectivity increased to *ca.* 15% at $CH_4:H_2O$ = 1:4. Lengthening the distance apart of the electrodes increased CH_4 conversion and CO selectivity dramatically and decreased the C_2 and CO_2 selectivity. The results at a 10 mm distance gave 83% CO selectivity with 82% CH_4 conversion under the conditions of $CH_4:H_2O$ = 1:4.

In CO_2 reforming also, an increased distance apart of electrodes caused the same promotional effect on the conversion and selectivity (Table 3) as was observed in steam reforming. Under the conditions of $CH_4:CO_2$ = 1:1 and 10.0 mm gap, the discharge region was filled with $Ni_{0.03}Mg_{0.97}O$ prepared by the same method as Tomishige *et al.*[5] NiMgO had a great effect on the selectivity: C_2 selectivity decreased drastically to 1% and CO selectivity increased to 99%. Other hydrocarbons such as C_3 and C_4 compounds were not detected. Also, CO_2 conversion became higher than that of CH_4 probably because of the promotion of the reverse water gas shift reaction. From these results, the catalyst was found to demonstrate some effect on the DCPD reaction at low temperature. The precursor of C_2 hydrocarbons might be adsorbed onto Ni and be subjected to reforming by CO_2. As a consequence, by the combined

Table 3 Effect of distance of electrodes and catalyst on CO_2 reforming of methane[a]

| Catalyst | Electrode distance/ mm | Conversion(%) | | Selectivity(%) | | $H_2:CO$ ratio |
		CH_4	CO_2	C_2	CO	
None	1.5	41.2	24.3	54.9	44.7	1.48
None	10.0	80.9	72.7	33.6	65.4	1.00
NiMgO	10.0	69.5	79.5	1.0	99.0	0.86

[a] Reaction conditions: 10 cm³ min⁻¹ total flow rate, $CH_4:CO_2$ = 1, ambient temperature, 0.1 MPa, 3.0 mA, $Ni_{0.03}Mg_{0.97}O$ = 0.13 g.

NiMgO–DCPD system, synthesis gas was produced from methane with 70% CH_4 conversion and little C_2 hydrocarbon formation at ambient temperature.

In conclusion, the DCPD method could be applied for CO_2 and steam reforming of methane at low temperature with or without the use of catalysts. The selectivity strongly depended on the composition of the feed gas, and a desired $H_2:CO$ ratio could be obtained. NiMgO had the great effect of increasing CO selectivity to 99%. If the energy efficiency is improved in the future, the catalyst–DCPD combined system has the possibility of being developed as a brand-new reaction process.

Notes and references

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