Carbon Dioxide Reforming of Methane Using DC Corona Discharge Plasma Reaction

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Carbon dioxide reforming of methane via dc corona discharge plasma reaction at atmospheric pressure has been investigated. The effects of the CH_4/CO_2 ratio in the feed, flow rate, discharge power, and corona types have been systematically studied. The results show that the molar ratio of H_2 to CO in the products strong depends on the molar ratio of CH_4 to CO_2 in the feed. The discharge power, flow rate, and corona types have slight influence on the syngas composition. When the CH_4/CO_2 ratio is 1/2, the syngas of lower H_2/CO ratio at about 0.56 is obtained, which is a potential feedstock for synthesis of liquid hydrocarbons. The conversions of methane and carbon dioxide increase with increasing the discharge power and decrease with increasing the flow rate. The conversions of reactants via positive corona are generally higher than that via negative corona, but the ratio of H_2/CO in the products is the other way round. Besides syngas and water, other products including various hydrocarbons and oxygenates are detected by a quadrupole mass spectrometer. There is visible coke mainly depositing on the cathode when the CH_4/CO_2 ratio is higher than 2/1. We propose that the coke mainly formed via methane decomposition during the reaction.

Introduction

During the past decades, there has been increasing concern over the emission of CO_2 and CH_4 which contributes most of the human-related global warming. The chemical method of utilization of greenhouse gases, CO_2 reforming of CH_4, not only eliminates them but also yields lower H_2/CO molar ratio syngas (i.e., a mixture of H_2 and CO) which is a preferable feedstock for the Fischer−Tropsch synthesis of liquid hydrocarbons.[1,2] Thus, light gases flared in remote oil producing areas or in industry during petroleum processing can be used with CO_2 wasted in flue gas or in natural gas fields to produce valuable products.

The overall reaction stoichiometry for the production of alkanes using syngas, if there occurs the water-gas shift reaction simultaneously,[2] is

$$(n + 1)H_2 + 2nCO \rightarrow C_nH_{2n+2} + nCO_2 \qquad (1)$$

It requires that the H_2/CO ratio in the feed equals $(n + 1)/(2n)$, which is between 1/2 and 1/1. Up to now, the principal routes for the conversion of methane to syngas include steam reforming (reaction 2), partial oxidation (reaction 3), and CO_2 reforming (reaction 4).

$$CH_4 + H_2O \rightarrow 3H_2 + CO \qquad (2)$$

$$CH_4 + {}^1/_2O_2 \rightarrow 2H_2 + CO \qquad (3)$$

$$CH_4 + CO_2 \rightarrow 2H_2 + 2CO \qquad (4)$$

Stoichiometrically, CO_2 reforming produces syngas having the lowest H_2/CO ratio equaling 1/1. Moreover, the H_2/CO ratio in the products may be relatively easily controlled by adjusting the CH_4/CO_2 ratio in the feed, such as the reaction

$$CH_4 + 2CO_2 \rightarrow H_2 + 3CO + H_2O \qquad (5)$$

where the H_2/CO ratio is 1/3. Consequently, if the H_2/CO ratio less than 1/1 is desired for the production of liquid hydrocarbon, then CO_2 reforming is preferable.

CO_2 reforming using conventional catalytic methods, however, often has two serious problems. It is an intensively endothermic reaction ($\Delta H = 247$ kJ/mol) consuming much energy, and the catalysts used in CO_2 reforming are inclined to deactivate due to coke deposition on the catalysts surface.[2−7] Thermodynamic calculations suggested that the coke formation could be avoided at higher temperature (e.g., 1073 K) and with CH_4/CO_2 ratio lower than unity.[8,9] However, the higher reaction temperature and higher energy consumption is a disadvantage for the application of the process in industry. Additionally, a higher reaction temperature increases the coke deposition via CO disproportionation, which is exothermic.

Now, nonequilibrium plasma technology offers an alternative method for chemical reactions whereby electricity provides the reaction energy for endothermic process.[10,11] Nonequilibrium plasma is far from thermodynamic equilibrium; i.e., within nonequilibrium plasma free electrons have much higher energy than ions and neutral particles. Thus, nonequilibrium plasma usually has comparatively low gas temperature close to room temperature and high-energy conversion rates. Nonequilibrium plasma can be generated by different kinds of gas discharge, including glow discharge, microwave discharge, dielectric barrier discharge (DBD), corona discharge, etc. From a standpoint of industry, mainly DBD and corona discharge have chances to be applied to handle large gas volume because they could be generated at near to or higher than atmospheric pressure at lower temperature.

The characteristic of DBD is that a dielectric layer covers one or both of the electrodes, and an ac high electric field is applied to generate gas discharge. It has been reported that DBD

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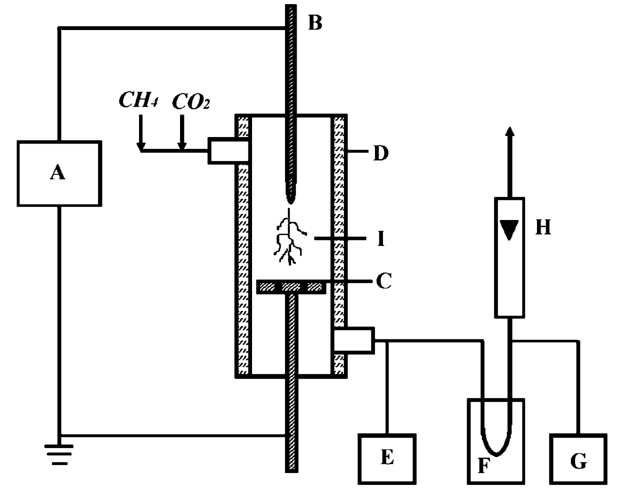

Figure 1. Schematic diagram of the process of CO_2 reforming of CH_4 via corona discharge plasma: A, high-voltage dc source; B, wire electrode; C, plate electrode; D, quartz tube; E, quadrupole mass spectrometer; F, cool trap; G, gas chromatograph; H, flow meter; I, corona discharge.

is effective in the activation of CH_4 and CO_2. In the process of CO_2 reforming via DBD, various products have been produced include not only syngas[12−17] but also higher hydrocarbons[15,16] and oxygenates,[17] implying that hydrocarbons and other organic compound may be synthesized directly from CH_4 and CO_2 at appropriate conditions via nonequilibrium plasma reaction.

Corona discharge could be initiated using a pair of inhomogeneous electrodes by a dc high electric field. In contrast with DBD, an advantage of corona discharge is that it is relatively easily to be established. Corona discharge has had many applications in industry, such as reduction of NO_x and SO_x in flue gas, destruction of toxic compounds, and generation of ozone.[18−20] It has been reported that corona discharge was used for oxidative coupling of methane[21] and decomposition of CO_2.[22]

The objective of this present study is to investigate the characteristics of corona discharge plasma reaction influencing on CO_2 reforming. The effects of reaction conditions, including the mixing ratio of CH_4/CO_2 in the feed, discharge power, flow rate, and corona types, were studied. The formation mechanisms of coke and syngas were analyzed, and the dependence of energy efficiency of the dc corona plasma reaction on experimental parameters has also been discussed.

Experimental Section

Experimental Apparatus. The schematic diagram of the experiment is shown in Figure 1. One quartz tubular reactor (with an i.d. of 13.2 mm) consisting of a wire-plate stainless steel electrode configuration was used in this investigation. The upper wire electrode was positioned with its top 10 mm above the plate electrode. The plate electrode was always grounded (i.e., its potential is 0 V), and the wire electrode was at either positive potential (called positive corona) or negative potential (called negative corona).

The reactants, CH_4 (>99.9%) and CO_2 (>99.5%) in varied ratio of CH_4/CO_2, were well mixed and then flowed through the reactor at room temperature and atmospheric pressure. A dc power supply with a high-voltage transformer was used to initiate the corona discharge. The discharge voltage and discharge current were measured with a voltage dial setting and a current dial setting, respectively, and they were calibrated by a high-voltage probe (Tektronix P6015) and a current probe (Tektronix CT-2) with a digital oscilloscope (Tektronix TDS 210) during the reaction. The discharge power is measured by electronically integrating the product of voltage and current.

The effects of the CH_4/CO_2 ratio in the feed, discharge power, flow rate of feed, and types of corona (i.e., positive corona or negative corona) on the reaction were investigated. Under each set of conditions, 30 min was allowed for stabilization before quantitative analysis.

Products Analysis and Calculations. The products were analyzed by an on-line quadrupole mass spectrometer (QMS) (Balzers MSC 200) with a Faraday cup detector. The measurement range of the QMS is between 0 and 200 amu (i.e., atomic mass unit). The chemicals in the effluent were detected by monitoring the signals of their main peaks, which are proportional to their partial pressure. The main peaks of CO_2, CH_4, H_2, and CO are at 44, 16, 2, and 28 amu, respectively.

The reactor effluent was introduced into a cool trap to remove liquid products, and then the gas products were quantitatively analyzed by an on-line gas chromatograph equipped with a carbon molecular sieve packed column and a thermal conductivity detector in argon carrier gas. The concentrations of CO_2, CH_4, H_2, and CO were determined by external standard calibrations.

The conversions (X) of CH_4 and CO_2, selectivities (S) of H_2 and CO, and balance calculation (B) of carbon are defined as

$$X(\mathrm{CH_4})\ (\%) = (\text{moles of CH}_4\text{ before reaction} - \text{moles of CH}_4\text{ after reaction})/\text{moles of CH}_4\text{ before reaction} \times 100\%$$

$$X(\mathrm{CO_2})\ (\%) = (\text{moles of CO}_2\text{ before reaction} - \text{moles of CO}_2\text{ after reaction})/\text{moles of CO}_2\text{ before reaction} \times 100\%$$

$$S(\mathrm{H_2})\ (\%) = 0.5 \times \text{moles of H}_2\text{ produced}/(\text{moles of CH}_4\text{ before reaction} - \text{moles of CH}_4\text{ after reaction}) \times 100\%$$

$$S(\mathrm{CO})\ (\%) = \text{moles of CO produced}/(\text{moles of CH}_4\text{ before reaction} - \text{moles of CH}_4\text{ after reaction} + \text{moles of CO}_2\text{ before reaction} - \text{moles of CO}_2\text{ after reaction}) \times 100\%$$

$$B(\mathrm{C})\ (\%) = [1 - (\text{moles of CH}_4\text{ after reaction} + \text{moles of CO}_2\text{ after reaction} + \text{moles of CO formed})/(\text{moles of CH}_4\text{ before reaction} + \text{moles of CO}_2\text{ before reaction})] \times 100\%$$

The energy efficiency (E) of the reaction is defined as

$$E\ (\%) = [\text{moles of CO produced} \times \Delta H_f(\mathrm{CO}) - (\text{moles of CH}_4\text{ before reaction} - \text{moles of CH}_4\text{ after reaction}) \times \Delta H_f(\mathrm{CH_4}) - (\text{moles of CO}_2\text{ before reaction} - \text{moles of CO}_2\text{ after reaction}) \times \Delta H_f(\mathrm{CO_2})]/\text{electric energy consumption} \times 100\%$$

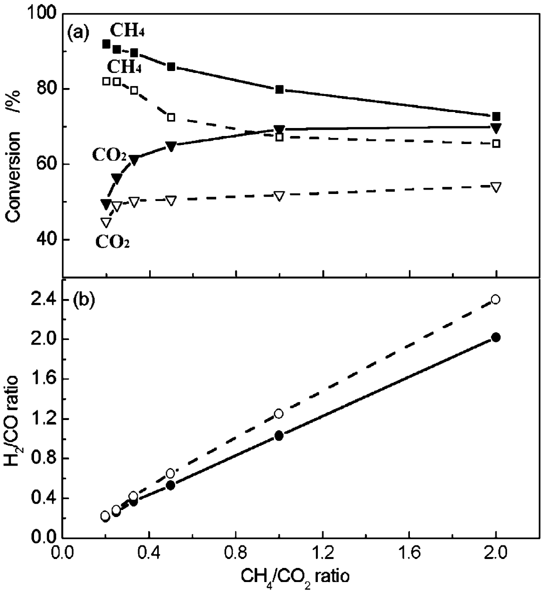

Figure 2. Effects of the mixing ratio on CO_2 reforming of CH_4 via positive corona (—) and negative corona (- - -): (a) conversions and (b) H_2/CO ratio. Flow rate, 60 mL/min; discharge power, 45 W.

TABLE 1: Effects of CH_4/CO_2 Ratio in Feeds on CO_2 Reforming of CH_4[a]

CH_4/CO_2 ratio	$S(H_2)$/%	S(CO)/%	B(C)/%
	Positive Corona		
1/5	39.4	98.9	0.66
1/4	44.1	98.5	0.95
1/3	55.3	98.2	1.21
1/2	64.8	97.1	2.10
1/1	84.0	87.6	9.27
2/1	96.7	64.5	25.4
	Negative Corona		
1/5	40.5	97.3	1.37
1/4	45.6	97.2	1.55
1/3	56.9	94.4	3.22
1/2	73.0	93.5	3.79
1/1	92.5	83.3	9.93
2/1	99.1	58.4	25.7

[a] Flow rate, 60 mL/min; discharge power, 45 W.

where ΔH_f is the heat of formation for the corresponding CO, CH_4, or CO_2. The heat of formation of hydrocarbons and coke in the reaction is excluded in the calculation. The electric energy consumption is calculated from the discharge power and the reaction time.

When the CH_4/CO_2 ratio in the feed is higher than 2/1, there is obvious coke depositing on the cathode during the reaction. The images of the coke were taken by a scanning electron microscope (SEM) (Philips XL30ESEM) and a transmission electron microscope (TEM) (JEOL JEM-100S). The C, H microanalysis of the coke is performed by an analyzer (CHN-O-Rapid) of Foss Heraeus Analysensysteme GmbH.

Results and Discussion

Effects of the CH_4/CO_2 Ratio. To better understand the influence of the feed gas composition on the reaction under corona discharge plasma, we performed experiments by varying the CH_4/CO_2 ratio from 1/5 to 2/1. A total feed flow rate of 60 mL/min and a discharge power of 45 W were applied during the reaction. Figure 2 and Table 1 reflect the experimental results.

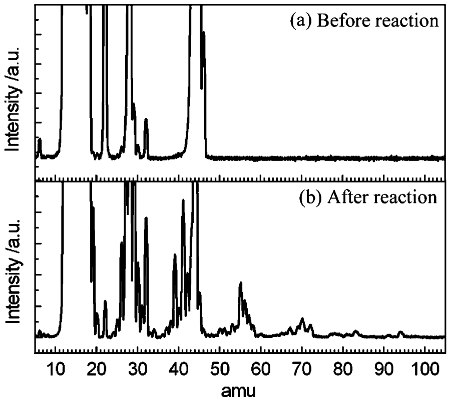

Figure 3. QMS spectra of the reactor effluents before reaction (a) and after reaction (b). Flow rate, 60 mL/min; CH_4/CO_2 ratio, 2/1; discharge power, 45 W; corona type, positive corona.

When CO_2 reforming via positive corona, as shown in Figure 2a, with increasing the CH_4/CO_2 ratio from 1/5 to 2/1, the conversion of CO_2 increases from 49.8% to 69.9%, and the conversion of CH_4 decreases from 91.9% to 72.6% simultaneously. The conversion of CH_4 is always higher than that of CO_2. Figure 2b clearly shows that increasing the CH_4/CO_2 ratio in the feed induces an increase of the H_2/CO ratio in the products. With the CH_4/CO_2 ratio increasing from 0.2 to 2.0, the H_2/CO ratio increases correspondingly from 0.21 to 2.02.

As listed in Table 1, the selectivity of H_2 increases proportionally with the increasing CH_4 concentration in the feed. It increases from 39.4% and reaches a maximum of 96.7% at $CH_4/CO_2 = 2/1$. At the same time, the selectivity of CO decreases from 98.9% to 64.5%. The balance calculation of carbon may be used to estimate the yield of byproducts except syngas. The values of B(C) indicate that the carbon-containing products except CO increase sharply when the CH_4/CO_2 ratio is higher than unity, implying that higher hydrocarbons, coke, or both of them increase as the CH_4/CO_2 ratio increasing.

Similar changes of the conversions and the H_2/CO ratio happen within negative corona. But the conversions of CH_4 and CO_2 via negative corona are obviously lower than that via positive corona. During the same tested range, the conversion of CO_2 increases from 44.9% to 54.2%, and the conversion of CH_4 decreases from 82.1% to 65.5%. However, the H_2/CO ratio via negative corona increases from 0.22 to 2.41 during the CH_4/CO_2 ratio increasing from 0.2 to 2.0, which is a little higher than that via positive corona.

The above experiments reveal that the H_2/CO ratio in the products depends strongly on the CH_4/CO_2 ratio in the feed. The ratio of H_2/CO ratio to CH_4/CO_2 ratio is a little higher than 1. The results are benefit to control the H_2/CO ratio in syngas through adjusting the CH_4/CO_2 ratio in the feed. When the CH_4/CO_2 ratio equals 1/2, the H_2/CO is approximately 0.56, which is a desirable feed for synthesis of long chain hydrocarbons.

In addition to syngas, there are some other chemicals also be found by QMS (see Figure 3). The reactor effluent not only consists of CH_4 (16 amu), CO_2 (44 amu), CO (28 amu), H_2 (2 amu), C_2H_2 (26 amu), C_2H_4 (28 amu), C_2H_6 (30 amu), and a lot of water (18 amu) but also consists of C_3-C_6 chain hydrocarbons, a little of benzene (78 amu), toluene (91 amu), etc.

Effects of the Corona Types. As discussed above, the conversions of CH_4 and CO_2 via positive corona are obviously higher than that via negative corona, but the H_2/CO ratio in the products is the other way round. Similar situation occurred when

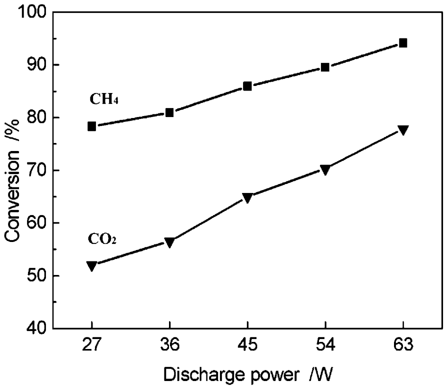

Figure 4. Effects of the discharge power on the conversions of reactants via CO_2 reforming of CH_4. Flow rate, 60 mL/min; CH_4/CO_2 ratio, 1/2; corona type, positive corona.

either the discharge power or the flow rate was changed. This is related with the different characteristics between positive corona and negative corona.

Positive corona and negative corona have different generation mechanisms.[20,23] Negative corona generally propagates by impact ionization of gas molecules, and its active volume is confined to the near-electrode region. However, positive corona depends more on photoionization for its propagation besides the impact ionization mechanism. Positive corona forms when the positive ion density is large enough to extend the region into the interelectrode gap. This process builds by photoionization, with the positive ion head moving in front of a nearly neutral column. Accordingly, positive corona has an active volume much larger than negative corona, and its electron energy is also higher than that of the negative corona. It ensures that CH_4 and CO_2 generally have higher conversions via positive corona than that via negative corona. At the same time, the selectivity of CO via positive corona is higher than that via negative corona, but the selectivity of H_2 is the other way round. As a result, the ratio of H_2/CO in the products via positive corona is lower that that via negative corona. This mechanism will be further explained later.

Following experimental results were obtained using positive corona, and the CH_4/CO_2 ratio in the feed equaling 1/2 was used to produce syngas with lower H_2/CO ratio.

Effects of the Discharge Power. In a mixture of CH_4/CO_2 ratio of 1/2 and flow rate of 60 mL/min, the effects of discharge power variation were investigated.

As depicted in Figure 4, the conversions of CH_4 and CO_2 increase from 78.3% to 94.1% and from 52.1% to 77.9% with the discharge power increasing from 27 to 63 W, respectively. The conversion of CH_4 is always higher than that of CO_2. Comparing these conversions with the equilibrium conversions,[24] we find that the conversion of CH_4 realized here equals the equilibrium conversion of CH_4 at the temperature between 900 and 1000 K, and the conversion of CO_2 equals the equilibrium conversion of CO_2 at the temperature between 900 and 1400 K. This reflects the characteristic of nonequilibrium plasma reaction.

As shown in Table 2, the main component in the products is syngas, i.e., H_2 and CO. The H_2/CO ratio is approximately 0.56 and hardly depends on the discharge power. The H_2/CO ratio indicates that the products is not according to the stoichiometry of reaction $CH_4 + 2CO_2 \rightarrow H_2 + 3CO + H_2O$, which has a H_2/CO ratio equaling 1/3, implying that there are other products formed besides syngas and water. The selectivities of H_2 and CO change within narrow ranges from 64.8% to 69.43% and from 91.7% to 98.5%, respectively.

TABLE 2: Effects of Discharge Power on CO_2 Reforming of CH_4[a]

discharge power/W	H_2/CO ratio	$S(H_2)$/%	$S(CO)$/%	$B(C)$/%
27	0.62	65.8	91.7	5.07
36	0.59	67.5	95.4	2.99
45	0.53	64.8	97.1	2.10
54	0.54	68.3	98.5	1.17
63	0.54	69.4	97.1	2.39

[a] Flow rate, 60 mL/min; CH_4/CO_2 ratio, 1/2; corona type, positive corona.

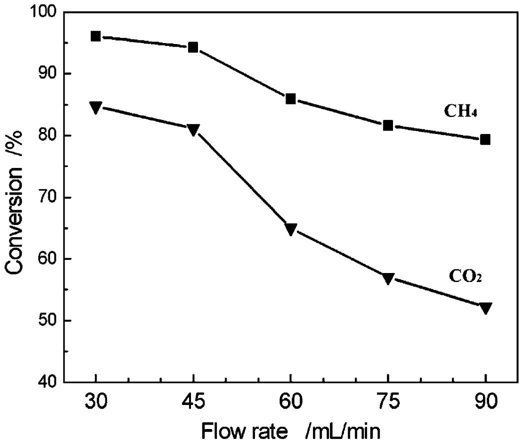

Figure 5. Effects of the flow rate on the conversions of reactants via CO_2 reforming of CH_4. CH_4/CO_2 ratio, 1/2; discharge power, 45 W; corona type, positive corona.

TABLE 3: Effects of Flow Rate on CO_2 Reforming of CH_4[a]

flow rate/mL/min	H_2/CO ratio	$S(H_2)$/%	$S(CO)$/%	$B(C)$/%
30	0.53	71.4	96.9	2.71
45	0.54	71.6	96.5	2.99
60	0.53	64.8	97.1	2.10
75	0.59	70.1	99.7	0.22
90	0.59	67.0	97.7	1.41

[a] CH_4/CO_2 ratio, 1/2; discharge power, 45 W; corona type, positive corona.

The balance calculation of carbon reflects that there is a small quantity of hydrocarbons or oxygenates forming during the reaction. There are little benzene (78 amu) and toluene (91 amu) detected by QMS. The amount of toluene decreases during the discharge power increasing, and the amount of benzene increases simultaneously. One explanation is that the dissociation energy of toluene (3.94 eV) is lower than that of benzene (4.74 eV), so toluene is easily decomposed and more stable benzene forms when discharge power increases.

Effects of the Flow Rate. The influence of the flow rate on the conversion of CH_4 and CO_2 is depicted in Figure 5. In a mixture of CH_4/CO_2 ratio of 1/2 and discharge power of 45 W, increasing flow rate decreases the conversions of CH_4 and CO_2.

Table 3 shows the effects of the flow rate on the reaction. A change in the feed flow rate does not signally affect the H_2/CO ratio. When the flow rate increases from 30 to 90 mL/min, the values of H_2/CO ratio increase from 0.53 to 0.59. Increasing flow rate results in little change for the selectivities of CO (between 96.9% and 99.7%) and H_2 (between 64.8% and 71.6%).

Coke Deposition. In CO_2 reforming, different from steam reforming, the deposited coke due to CO disproportionation (reaction 6) and CH_4 decomposition (reaction 7) cannot be volatilized by the reaction with steam (reaction 8).

$$2CO \rightarrow C + CO_2 \tag{6}$$

$$CH_4 \rightarrow C + 2H_2 \tag{7}$$

$$C + H_2O \rightarrow CO + H_2 \tag{8}$$

As a result, catalyst deactivation due to coke deposition is a serious problem for the application of catalysis method. Both thermodynamic calculations[25] and experimental observations[4,5] indicated that CO disproportionation occurred on the catalyst surface is the main contributor of the coke deposition, and there often is serious coke deposition when CH_4/CO_2 ratio is close to unity.[4−6]

During CH_4 reforming via corona plasma method, however, no coke formed evidently at low CH_4/CO_2 ratio. Interestingly, when the CH_4/CO_2 ratio is higher than 2/1, it is found that coke mainly deposited on the cathode, hardly on the anode. Figure 6 shows the SEM and TEM images of the coke depositing on the tip of wire cathode during negative corona discharge. As shown in Figure 6a, the coke has a treelike shape, which is similar to the depicted image of negative corona.[20,23] Figure 6b shows the top of the coke. There are loose structures attaching to the surface of the coke top. TEM image (Figure 6c) shows that the coke consists of many tiny granules having dimensions of approximately 50 nm.

In this corona plasma method, we suggest that coke mainly formed via CH_4 decomposition, not CO disproportionation. The dissociation energy of CO possessing of 11.1 eV is higher than that of dissociation energy of CH_x ($x = 1-4$), which is lower than 5 eV. Compare with CH_x, CO_2 is more difficult dissociated via the collision of electrons. The previous analysis of QMS indicated that there was no coke formed during CO_2 decomposing under corona discharge.[22] Moreover, our research showed that carbon nanotubes can form in low-temperature corona plasma as $H_2/CH_4 = 10/1$.[26] Therefore, CH_4 decomposition may be the main contributor of the coke deposition within nonequilibrium plasma.

There exist two possible methods for coke formation. Both of them are initiated by the decomposed of CH_4 through electron-collision dissociation

$$CH_4 + e \rightarrow CH_3 + H + e \tag{9}$$

One method is that coke mainly forms via the continue dehydrogenation of methyl radicals. The other method is that coke mainly forms via dehydrogenation of aromatics formed by polymerization of hydrocarbon such as trimerization of acetylene. For the latter situation, the coke should have a lower C/H ratio than the former. A literature reported that there was solid $(CH)_n$ deposited on the cathode during methane decomposing in glow discharge,[27] and it is generally believed that coke forms via dehydrogenation of aromatics in thermal coupling of methane.[28]

Experimentally, according to element microanalysis, the C/H ratio in coke is 85.6/4.4, indicating the coke mainly consists of carbon. Therefore, we suppose that the coke should mainly form via dehydrogenation of methyl radical. In addition, we think that some carbon-containing species are electropositive and are easily ionized within dc corona plasma. These ions moved and deposited onto the cathode under the influence of dc electric field. Then they form tiny and loose carbonaceous deposition rather than $(CH)_n$ polymer, but the accurate mechanism needs further studying.

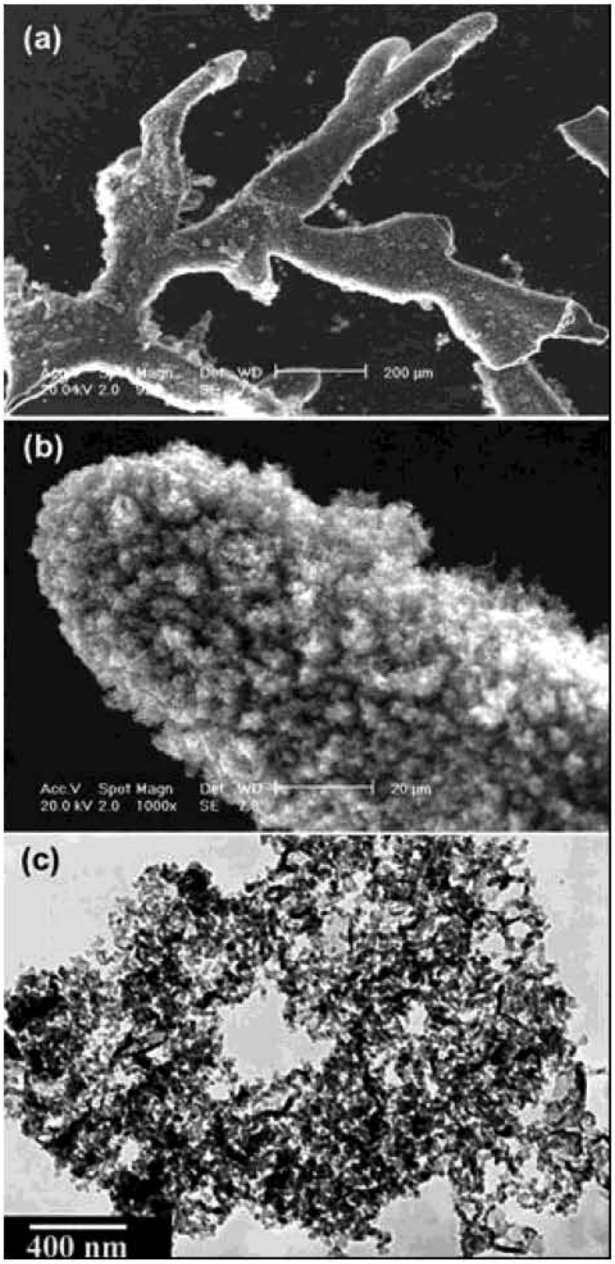

Figure 6. SEM images (a and b) and TEM image (c) of the coke deposited on the cathode (i.e., the wire electrode) during negative corona discharge. CH_4/CO_2 ratio, 4/1; flow rate, 60 mL/min; discharge power, 45 W; reaction time, 10 min.

Reaction Mechanism. It has been accepted by most researchers that free radical processes are the main mechanisms in nonequilibrium plasma reaction.[29,30] Here, the mechanism for CO_2 reforming via corona plasma reaction can simplified as follows.

For CO_2 reforming via the plasma method, the important initial step is dissociation of CH_4 and CO_2 by electron collision (reactions 9 and 10). CH_4 and CO_2 have dissociation energies of 4.5 and 5.5 eV, respectively, which lie well within the electron energy range in corona discharge.[11]

$$CO_2 + e \rightarrow CO + O + e \tag{10}$$

Expect for the dissociation of carbon dioxide, CO could form via reaction

$$C + O \rightarrow CO \tag{11}$$

Here, active oxygen atoms play an oxidant and keep coke from depositing during methane decomposition. Oxygen atoms could also react with other species and form many kinds of radical, such as OH radical forming from the reaction

$$O + H \rightarrow OH \tag{12}$$

As a result, besides molecules and ions, there exists a wide variety of active free radicals, including CH_3, CH_2, CH, H, C_2H_5, C_2H_3, C_2H, OH, O, and others.

H_2, H_2O, and hydrocarbons, such as C_2H_2, could form via the recombination of radicals

$$H + H \rightarrow H_2 \tag{13}$$

$$H + OH \rightarrow H_2O \tag{14}$$

$$CH + CH \rightarrow C_2H_2 \tag{15}$$

They could also form via the radicals reacting with each other or with molecules, for example

$$H + CH_4 \rightarrow H_2 + CH_3 \tag{16}$$

$$H + CH_3 \rightarrow H_2 + CH_2 \tag{17}$$

$$H_2 + OH \rightarrow H + H_2O \tag{18}$$

Experimentally, the H_2/CO ratio in the products mainly depends on the CH_4/CO_2 ratio in the feed. The electron energy within the tested range has a slight effect. Higher electron energy results in a lower H_2/CO ratio. It is supposed that higher electron energy enables more CO_2 molecules to be dissociated by electron collision (reaction 10) and then results in higher yield of CO and O. The active oxygen atoms readily react with hydrogen atoms (reaction 12) and reduce the concentration of hydrogen atoms. As a result, the selectivity of H_2 decreases because H_2 could form via recombination of hydrogen atoms (reaction 13). Accordingly, a lower H_2/CO ratio in the products is the result of the changes of selectivities of CO and H_2. This may be the reason why the H_2/CO ratio in the products via positive corona is lower than that via negative corona.

Theoretically, methanol has almost twice the energy content per volume in comparison to that of liquid hydrogen. The literature has reported that methanol could be synthesized through mixtures of CO_2 and H_2 using DBD.[31,32] Within the reactor of CO_2 reforming, there are large amounts of CO_2 and H_2 which might be directly converted into methanol at appropriate conditions. It has been reported that methanol formed via DBD using zeolites as catalysts.[33] However, in our plasma system, no significant methanol was detected by QMS, which is consistent with the report of Gesser et al.[12] It can be explained that the dissociation energy (4.1 eV) of $CH_3O{-}H$ is relatively low, so the newly formed methanol is in an excited stage and will be more inclined to further react with other species to produce additional hydrocarbons or oxygenates.

Energy Efficiency. The energy efficiency, *E*, reflects the efficiency of converting electric energy to chemical energy stored in the products including H_2 and CO. The energy efficiency for the reaction at different CH_4/CO_2 ratios is shown in Figure 7. *E* is in the range 7.6−12.3%. As the CH_4/CO_2 ratio increases, *E* increases initially and then decreases as the CH_4/CO_2 ratio further increases. *E* reaches a maximum at $CH_4/CO_2 = 1/3$. This is due to the formation of a maximum amount of CO at $CH_4/CO_2 = 1/3$, and CO has a higher heat of formation than hydrogen. As shown in Figure 8, when the CH_4/CO_2 ratio is 1/2 and the total flow rate is 60 mL/min, *E* decreases from 15.6% to 9.8% as the discharge power increases from 27 to 63 W. Although the total amount of reactants converted increases, *E* decreases because more electric energy was consumed. The effects of the flow rate on the energy efficiency are shown in Figure 9. Increasing the flow rate increases the energy efficiency, and the maximum energy efficiency is 13.5% in the tested range. Although the conversions of both reactants decreases, the total amount of reactants converted increases and more electric energy is converted to chemical energy stored in the products. Therefore, appropriate ratio of CH_4/CO_2 in the feed, relatively low power discharge, and relatively large flow rate are of benefit to higher energy efficiency.

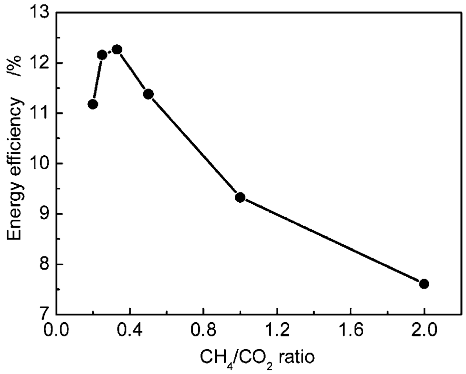

Figure 7. Effects of the CH_4/CO_2 ratio on the energy efficiency. Flow rate, 60 mL/min; discharge power, 45 W; corona type, positive corona.

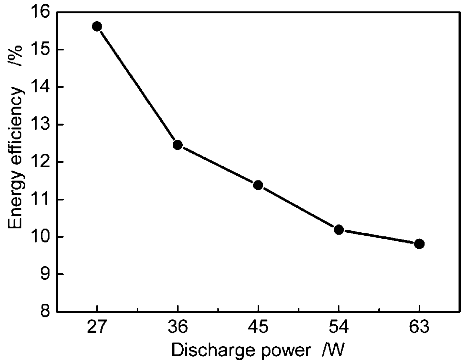

Figure 8. Effects of the discharge power on the energy efficiency. Flow rate, 60 mL/min; CH_4/CO_2 ratio, 1/2; corona type, positive corona.

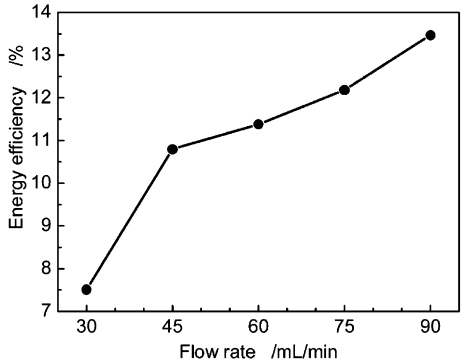

Figure 9. Effects of the flow rate on the energy efficiency. CH_4/CO_2 ratio, 1/2; discharge power, 45 W; corona type, positive corona.

As mentioned above, although the nonequilibrium plasma method operates at lower reaction temperature, which is an advantage over conventional catalytic methods, its energy efficiency is still low. Most of the electric energy is converted to heat energy, light energy, and others. Much work needs doing to fill the large energy efficiency gap for the plasma process before it becomes a competitive alternative to conventional catalytic methods.

Conclusions

This investigation offers an alternative corona plasma method for CO_2 reforming of CH_4, which is operated at atmospheric pressure. Experiments confirm that corona plasma reaction can lead to high conversions of methane and carbon dioxide, and the ratio of H_2/CO in the products strongly depends on the CH_4/CO_2 ratio in the feed. The conversions of reactants via positive corona are higher than that via negative corona. Higher electron energy within corona discharge is beneficial to higher conversions of CH_4 and CO_2 and producing syngas with lower H_2/CO ratio. Loose coke is found depositing mainly on the cathode when the CH_4/CO_2 ratio in the feed is higher than 2/1. We propose that the coke mainly forms via methane decomposition during the reaction, which is different from the mechanism of coke forming via CO disproportionation in catalytic methods received by most researchers. Except for syngas, there were various hydrocarbons and oxygenates forming simultaneously. It is estimated that more than 10% of consumed electric energy could be converted to chemical energy stored in the products during the plasma reaction.

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