Article ID : 0253-2409(2001)01-0006-06

CO-GENERATION OF SYNGAS AND HYDROCARBONS FROM METHANE AND CARBON DIOXIDE USING DIELECTRIC BARRIER DISCHARGES

JIANG Tao[1] , ZHANG Kui[1] , LIU Chang-jun[1] , LI Yang[1] , XU Gen-hui[1] ,
B. Eliasson[2] , U. Kogelschatz[2]

(1. *State Key Laboratory of C1 Chemical Technology , Tianjin University , Tianjin* 300072 , *China* ;
2. *ABB Corporate Research Ltd.* , 5405 *Baden , Switzerland*)

Abstract : Two major greenhouse gases , methane and carbon dioxide , were converted to syngas and hydrocarbons over zeolite catalyst at low temperature and atmospheric pressure in a high power dielectric barrier discharge reactor. Co-generation of syngas and hydrocarbons was demonstrated in such a reactor. Parameters investigated in this study included flow rate of the feed gas , the input power and the molar ratio of CH_4 to CO_2 in the feed.

Results indicated that low flow rate favored the conversion of CH_4 and CO_2 while high flow rate led to the production of hydrocarbons. Increasing the input power resulted in high conversion of methane and carbon dioxide and high productivity of syngas and hydrocarbons. The ratio of CH_4/CO_2 in the feed gas had the most significant effect on the ratio of H_2/CO in syngas. The highest conversion of CH_4 and CO_2 was 64 % and 39 % , respectively , at a molar ratio of CH_4/CO_2 of 1/1 , a total flow rate of 200 ml/min and an input power of 500 W. Soproduced syngas showed an arbitrary composition (H_2/CO ratio) with molar ratio of H_2/CO varied in the range from 0.7 to 3.1.

Key words : carbon dioxide ; dielectric barrier discharge ; greenhouse gases ; hydrocarbons ; methane ; syngas

CLC number : O646.9 **Document code :** A

Introduction

Both of methane and carbon dioxide are greenhouse gases. Continued excessive emissions of methane and carbon dioxide to the atmosphere may lead to the increase in the average global temperature. The emissions also result in a waste of natural carbon resources. In addition , methane is the major component of natural gas , which is suggested as an important energy resource in the coming 21 century. Converting greenhouse gases to syngas , hydrocarbons , methanol and other useful chemicals has been a subject of therefare investigation. Especially , simultaneous utilization of methane and carbon dioxide is under active study. So far , many studies for the synthesis of syngas from methane and carbon dioxide have been conducted.

The application of plasma technique in chemical synthesis has attracted much attention regarding the effective activation of methane and carbon dioxide. Syngas production from mixtures of methane and carbon dioxide has been successfully conducted in a dielectric barrier discharge (DBD) reactor[1] and a special GlidArc discharge[2] . Synthesis of methanol from carbon dioxide hydrogenation using a silent discharge was reported by Eliasson et al.[3-7] . Their results showed that the temperature range of the maximum

Received date : 2000-08-28

Author introduction : JIANG Tao (1964-) , female , Postdoctor , make a speciality chemical technology

catalytic activity was shifted from 220 ℃ to 100 ℃ in the simultaneous presence of catalyst and gas discharge. Recently, in the process of syngas production, hydrocarbons was formed in the same reactor[8]. Further investigation was performed by Eliasson et al.[9]. Co-generation of syngas and higher hydrocarbons was achieved using NaX zeolite as catalyst in a DBD reactor. In another study, conversion of methane in a corona discharge was carried out. The products contained C_2 hydrocarbons, trace C_3 hydrocarbons and syngas.

In this paper, simultaneous synthesis of syngas and hydrocarbons from methane and carbon dioxide over zeolite A promoted by DBD is investigated at low temperature and atmospheric pressure.

1　Experimental

The experimental setup is schematically illustrated in Figure 1. The reactor applied here is a cylindrical dielectric barrier discharge reactor, which is consisted of an outer steel tube of 54 mm i. d., an inserted quartz tube of 52 mm o. d. and a metallic brush. The metallic brush presses a metal foil against the inner surface of the quartz tube and serves as the HV electrode. The outer steel tube serves as the ground electrode. An annular discharge gap of 1 mm width and 310 mm length is formed, in which the discharge is maintained. A high voltage generator (Arcotec corona generator CG 20) working at about 30 kHz is applied to feed 50 W to 1 000 W into the discharge reactor. The power supplied is measured by electronically integrating the product of voltage and current. An oscilloscope (LeCroy Model LC 334A) is used to record the voltage- Lissajous diagrams. In addition, the temperature of the ground electrode can be adjusted by a closed loop of re-circulating oil from a thermostat in the range of ambient temperature to 400 ℃

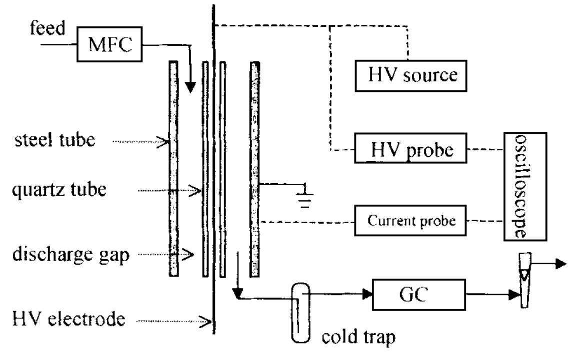

Figure 1　Configuration of DBD reactor and experimental setup

The feed gas (CH_4 and CO_2) is introduced into the reactor via mass flow controllers. The product stream is then introduced into an on-line gas chromatograph through a heated line to avoid possible condensation. The GC applied in this experiment is a MTI (Microsensor Technology Inc., M200H) dual-module micro GC. A Poraplot Q column (8 m ×0. 32 mm i. d.) and a molecular sieve 5 A Plot column (10 m ×0. 32 mm i. d.) are used to detect the exhaust gases with a thermal conductivity detector (TCD). The Poraplot Q column can separate CO_2, CH_3OH, H_2O and hydrocarbons and the molecular sieve 5 A Plot column can monitor H_2, O_2, N_2, CH_4 and CO. In order to establish a mass balance of C, H and O elements, nitrogen is chosen as a reference gas, which is added to the product stream at the exit of the reactor.

2　Results and discussion

2.1　Effect of feed flow rate　Experiments were conducted by varying the total flow rate of the feed while keeping a constant molar ratio of CH_4/CO_2 of 1/1, a pressure of 1 bar, an input power of 500 W and a constant wall temperature of 150 ℃

Figure 2a illustrates the effect of flow rate on the conversion of CH_4 and CO_2 over zeolite A using DBD. It can be seen that increasing the flow rate reduces the conversion of CH_4 and CO_2 quick-

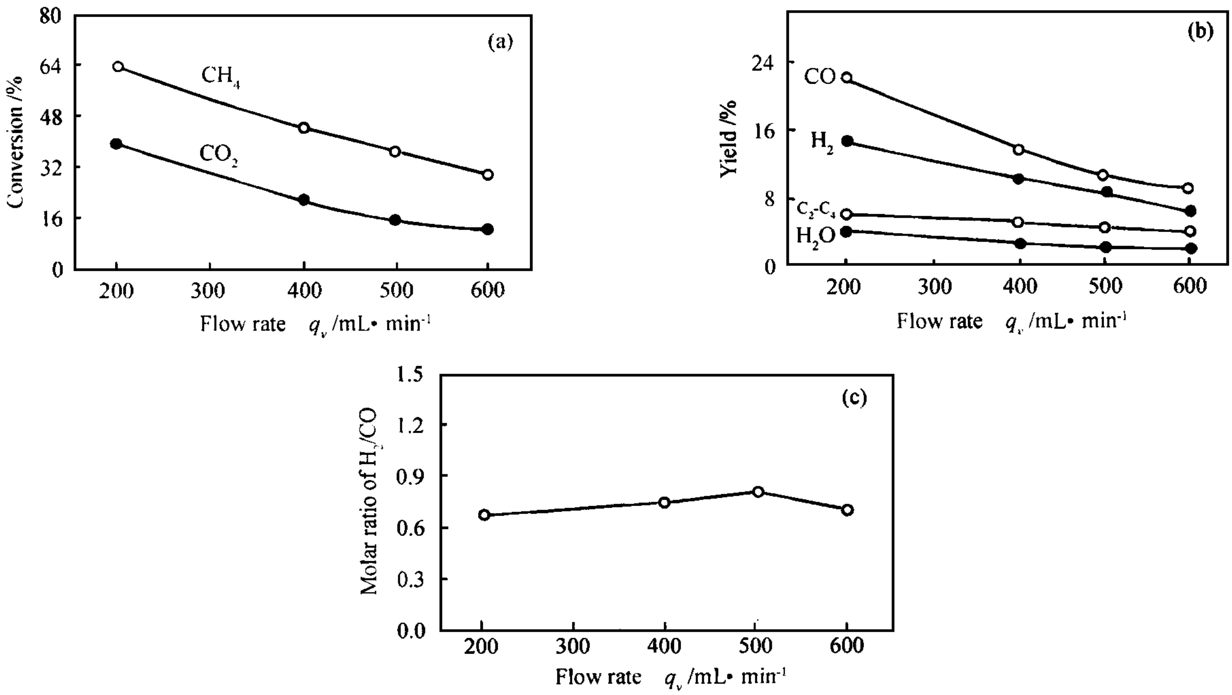

Figure 2 Effect of flow rate on experimental results

ly in the range of 200～600 ml/ min. The effect of flow rate on product yields is showed in Figure 2b. Increasing the flow rate results in a decrease in CO and H_2 yields in the beginning. The yield of C_2～C_4 hydrocarbons does not change significantly with the increasing flow rate. From results in Figure 2c one can see variation of flow rate does not affect the ratio of H_2/ CO remarkably. H_2/ CO ratio only changes from 0.67 to 0.80 in the range of flow rate 200～600 ml/ min. The effect of flow rate on selectivity is listed in Table 1. The product obtained in the catalytic DBD conversion of CH_4 and CO_2 consists of CO, H_2 and C_2～C_4 hydrocarbons. It is interesting to note that most of the product is syngas (CO and H_2). The second abundant product ethane. One can see that high flow rate favors the production of hydrocarbons.

Table 1 Effect of flow rate on selectivity

(Pressure, 1 bar; wall temperature, 150 ℃; catalyst amount, 4 g; CH_4/ CO_2 ratio in feed, 1/ 1; input power, 500 W)

Flow rate	Selectivity S_{mol}/ %							
q_v/ mL· min^{-1}	CO	H_2	C_2H_2	C_2H_6	C_3H_8	C_4	CH_3OH	H_2O
200	46.65	31.14	0.23	5.16	1.84	5.62	0.18	9.17
400	43.09	32.04	0.36	7.01	2.28	6.29	0.24	8.69
500	41.11	33.03	0.42	8.29	2.31	5.87	0.27	8.69
600	42.41	29.61	0.58	9.47	2.44	5.95	0.30	9.35

2.2 Effect of input power Input power is one of the important parameters in the DBD conversion of CH_4 and CO_2. Experiments were performed in the range of input power 100 W～500 W to get a better understanding of the effect of input power on the conversion of CH_4 and CO_2 over zeolite A in the DBD reactor. Other conditions of the experiments are a pressure of 1 bar, a total flow rate of 200 ml/ min, a molar ratio of CH_4/ CO_2 of 1/ 1 and a wall temperature of 150 ℃

Figure 3 and Table 2 show the effect of input power on the experimental results over zeolite A in the range of 100 W～500 W. Figure 3a indicates that the conversion of CH_4 and CO_2 increases with increasing input power. This can be explained that there might be more active species generated at higher input power. Therefore, the yield of CO, H_2 and hydrocarbons also increases with increasing input power (see Figure 3b). From the results in Figure 3c, molar ratio of H_2/CO in syngas quickly decreases with the increasing input power. Higher input power favors the production of syngas with low H_2/CO ratio. The H_2/CO ratio of syngas can vary in the range 0.6～1.55. Table 2 shows an increasing selectivity to C_3 and C_4 hydrocarbons and a decreasing selectivity to C_2 hydrocarbon with increasing input power. This suggests that the increased input power destroys the light hydrocarbon and then converts them to higher hydrocarbons. Higher input power is required to produce more C_3 and C_4 hydrocarbons.

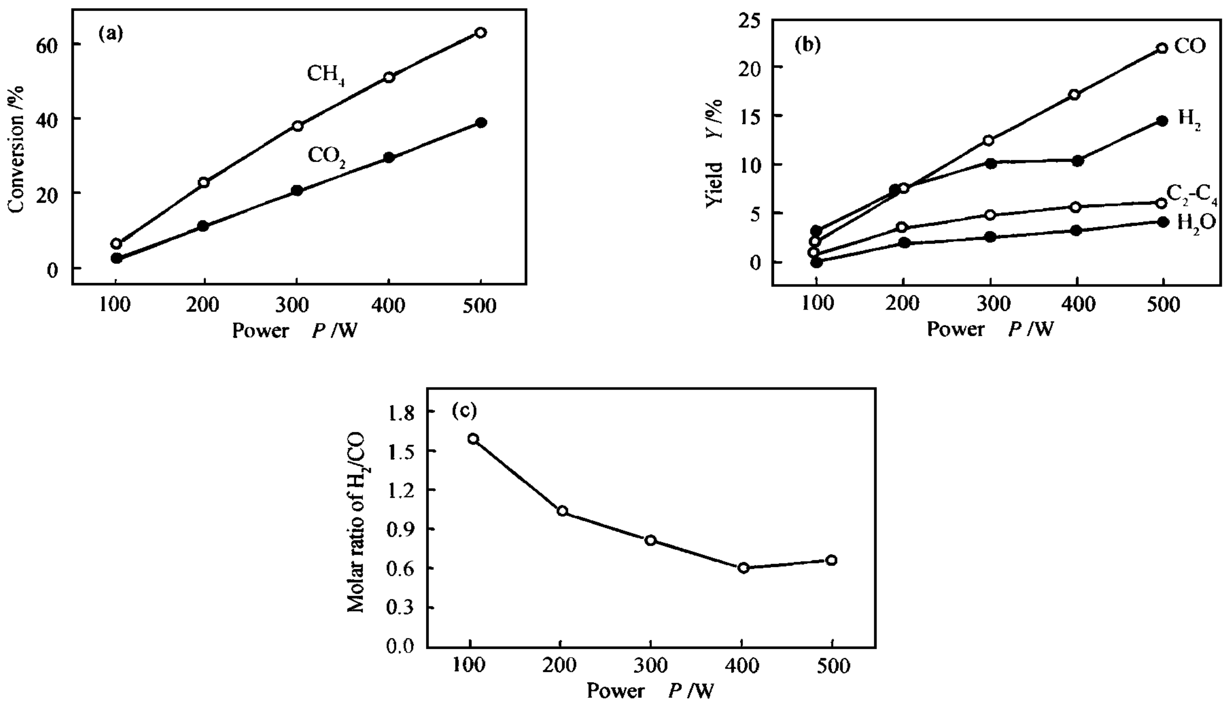

Figure 3　Effect of input power on experimental results

Table 2　Effect of input power on selectivity

(Pressure, 1 bar; wall temperature, 150 ℃; catalyst amount, 4 g; CH_4/CO_2 ratio in feed, 1/1; feed flow rate, 200 ml/min)

Power / W	Selectivity S_{mol}/ %							
	CO	H_2	C_2H_2	C_2H_6	C_3H_8	C_4	CH_3OH	H_2O
100	33.16	52.67	0.89	10.65	1.47	3.76	0.00	0.86
200	36.12	37.32	0.45	10.10	2.09	4.37	0.31	9.23
300	41.43	33.84	0.35	7.76	2.16	5.51	0.27	8.67
400	46.91	28.43	0.30	6.65	2.18	6.17	0.24	9.12
500	46.65	31.14	0.23	5.16	1.84	5.62	0.18	9.17

2.3　Effect of molar ratio of CH_4/CO_2　The effect of feed composition was studied by varying the molar ratio of CH_4/CO_2 in the range of 1/1～3/1. The total flow rate was maintained at 200 ml/min, input power at 500 W, wall temperature at 150 ℃ and pressure at 1 bar.

Figure 4 and Table 3 show the effect of CH_4/CO_2 ratio on the conversion of CH_4 and CO_2 over zeolite A in the DBD reactor. It is clear from Figure 4a that the conversion of both CH_4 and CO_2 decrease slowly with the increase of molar ratio of CH_4/CO_2. High conversion can be obtained at low molar ratio of CH_4/CO_2. The conversion of CH_4 and CO_2 is 64 % and 39 % at a molar ratio of CH_4/CO_2 of 1/1, respectively. Figure 4b indicates that the yield of H_2 and $C_2 \sim C_4$ hydrocarbons incseases with the increasing molar ratio of CH_4/CO_2. According to Figure 4c, the molar ratio of CH_4/CO_2 has a significant effect on the molar ratio of H_2/CO. The molar ratio of H_2/CO increases rapidly from 0.7 to 3.1 when the molar ratio of CH_4/CO_2 in the feed increases from1/1 to 3/1. The composition of syngas can be adjusted by changing the molar ratio of CH_4/CO_2 in the feed. From the results in Table 3, one can see that high molar ratio of CH_4/CO_2 results in high selectivity to hydrocarbons.

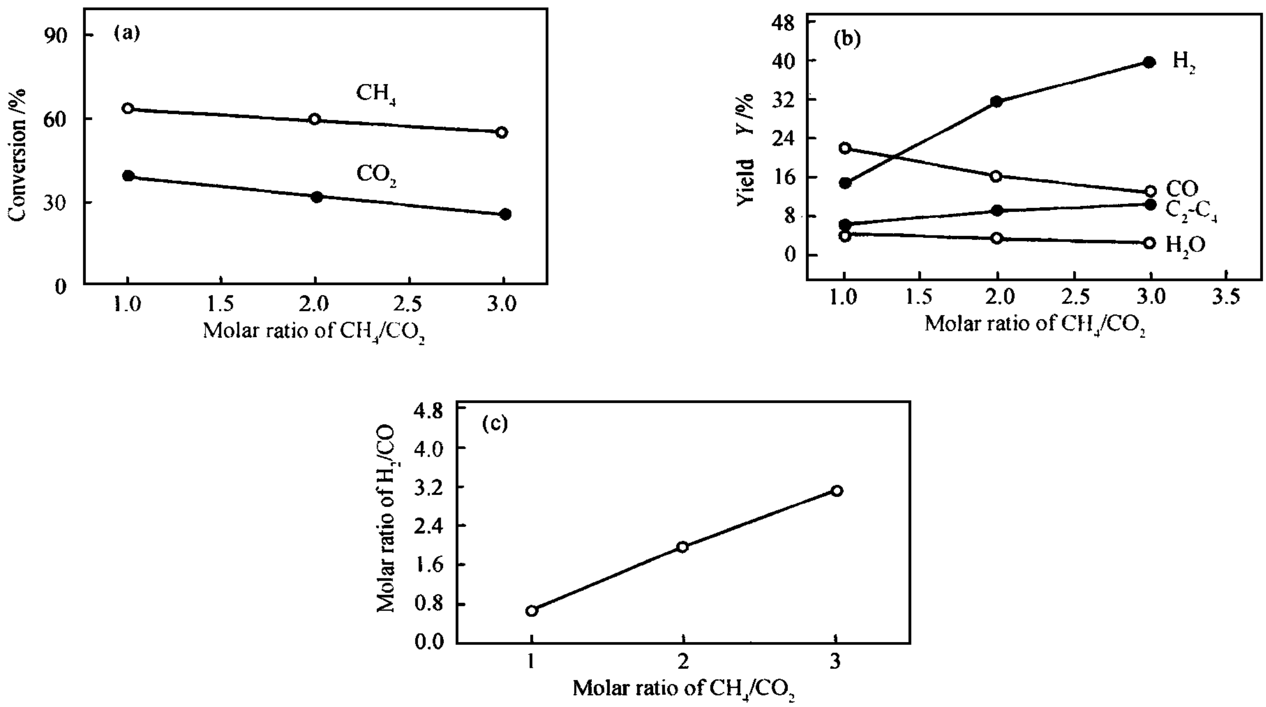

Figure 4 Effect of molar ratio of CH_4/CO_2 on experimental results

Table 3 Effect of molar ratio of CH_4/CO_2 on selectivity

(Pressure, 1 bar; wall temperature, 150 ℃; catalyst amount, 4 g; input power, 500 W; feed flow rate, 200 ml/min)

Ratio	Selectivity S_{mol}/ %							
	CO	H_2	C_2H_2	C_2H_6	C_3H_8	C_4	CH_3OH	H_2O
1/1	46.65	31.14	0.23	5.16	1.84	5.62	0.18	9.17
2/1	26.91	52.60	0.36	4.51	2.32	7.67	0.13	5.50
3/1	19.49	60.62	0.44	4.32	2.51	8.35	0.11	4.17

3 Conclusions

The conversion of CH_4 and CO_2 to syngas and hydrocarbons was experimentally investigated over zeolite A in a dielectric barrier discharge reactor at low temperature and atmospheric pressure. It is demonstrated that co-generation of syngas and hydrocarbons can be realized by using dielectric bar-

rier discharge promoted catalysis. High conversion of CH_4 and CO_2 can be achieved. Syngas composition mainly depends on the ratio of CH_4/CO_2. Flow rate of the feed, molar ratio of CH_4/CO_2 and the input power has significant effect on the plasma conversion of CH_4 and CO_2.

Rererences

[1] Hibert C, Motret O, Pellerin S, et al. Spectroscopic characterization of $CH_4 + CO_2$ plasma excited by a dielectric barrier discharge at atmospheric pressure[J]. *Plasma Chem and Plasma Process*, 1997, **17**(4): 393-407.

[2] Lesueur H, Czernichowski A, Chapelle J. Electrically assisted partial oxidation of methane [J]. *Hydrogen Energy*, 1994, **19**: 139-144.

[3] Eliasson B, Simon F G, Egli W. Hydrogenation of CO_2 in a silent discharge [A]. Penetrante B M and Schultheis S E. NATO ASI Series, V. G34, Part B, Non-thermal plasma techniques for pollution control [C]. Berlin: Springer-Verlag, 1993. 321-337.

[4] Eliasson B, Kogelschatz U, Killer E, et al. Hydrogenation of carbon dioxide and oxidation of methane in an electric discharge [A]. Proc of 11th World Hydrogen Energy Conf. (Hydrogen '96) [C]. Germany: Stuttgart, 1996, **3**: 2449-2459.

[5] Bill A, Eliasson B, Kogelschatz U, et al. Comparison of CO_2 hydrogenation in a catalytic reactor and in a dielectric-barrier discharge [J]. *Stud Surface Sci Catal*, 1998, **114**: 541-544.

[6] Bill A, Wokaun A, Eliasson B, et al. Greenhouse Gas Chemistry [J]. *Energy Convers Mgmt*, 1997, **38** (Suppl): S415-S422.

[7] Eliasson B, Kogelschatz U, Xue B, et al. Hydrogenation of carbon dioxide to methanol with discharge-activated catalyst [J]. *Ind Eng Chem Res*, 1998, **37**: 3350-3357.

[8] Zhou L M, Xue B, Kogelschatz U, et al. Non-equilibrium plasma reforming of greenhouse gases to synthesis gas [J]. *Energy & Fuels*, 1998, **12**(6): 1191-1199.

[9] Eliasson B, Liu C J, Kogelschatz U. Direct conversion of methane and carbon dioxide to higher hydrocarbons using catalytic dielectric-barrier discharges with zeolites [J]. *Ind Eng Chem Res*, 2000, **39**(5): 1221-1227.

用无声放电转化甲烷和二氧化碳同时制备合成气与烃

姜 涛[1], **张 惺**[1], **刘昌俊**[1], **李 阳**[1], **许根慧**[1], B. Eliasson[2], U. Kogelschatz[2]

(1. 天津大学 一碳化工国家重点实验室, 天津 300072; 2. ABB Corporate Research Ltd., 5405 Baden, Switzerland)

摘 要: 在低温常压条件下,研究了在无声放电反应器中以 A 型分子筛为催化剂从甲烷和二氧化碳合成烃和合成气,实现了在无声放电反应器中同时合成烃和合成气。实验在原料气流量 200～600 ml/min、原料气甲烷和二氧化碳摩尔比 1/1～3/1 及输入功率 100～500 W 的范围内进行。研究结果表明,低原料气流量有利于甲烷和二氧化碳的转化,而高原料气流量有利于烃的生成;原料气甲烷和二氧化碳摩尔比对制得合成气的 H_2/CO 摩尔比的影响最显著;甲烷和二氧化碳转化率及合成气和烃的产率均随输入功率的增加而提高。而所研究的范围内,当原料气流量为 200 ml/min、甲烷和二氧化碳摩尔比为 1/1、输入功率为 500W 时,甲烷和二氧化碳转化率达到最高值,分别为 64 %和 39 %。以此法制备的合成气的 H_2/CO 摩尔比可以在很宽的范围内变化,本研究合成气 H_2/CO 摩尔比的变化范围是 0.7～3.1。

关键词: 二氧化碳; 甲烷; 无声放电; 温室气体; 烃; 合成气

中图分类号: O646.9 **文献标识码**: A

作者简介: 姜 涛(1964-),女,黑龙江鹤岗人,天津大学博士后,化学工艺专业。