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Plasma methane conversion using dielectric-barrier discharges with zeolite A

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Abstract

Experimental investigation on plasma methane conversion in the presence of carbon dioxide using dielectric-barrier discharges (DBDs) has been conducted. Zeolite A has been applied to inhibit the formation of carbon black and plasma-polymerized film during such plasma methane conversion. A co-generation of syngas, light hydrocarbons and liquid fuels has been achieved. The conversions and selectivities are determined by the CH_4/CO_2 feed ratio, residence time and input power. Compared to the use of zeolite X within the DBDs, plasma methane conversion with zeolite A leads to a higher selectivity of light hydrocarbons (C_2–C_4). © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Dielectric-barrier discharges; Methane; Carbon dioxide; Zeolite A; Syngas; Hydrocarbons

1. Introduction

There exist abundant reserves of natural gas in the world. The direct methane conversion to more valuable products, like higher hydrocarbons and oxygenates, has been desired for several decades [1–3]. Due to the high stability of C–H bond in methane molecule, the direct methane conversion still remains as a challenge to scientists all over the world [1].

Plasma, including thermal and non-thermal plasma, has recently attracted a lot of attentions worldwide for its high effectiveness in methane conversion [4–23]. Especially, the non-thermal plasma has been demonstrated to be a promising technology in the chemical utilization of methane thanks to its high non-equilibrium characteristics, which means high energetic electrons (upto 10 eV) at the low gas temperature (even at room temperature) [5–23]. The high energetic electrons will lead to the generation of some highly active species including radicals. C_2 or C_3 hydrocarbons [7–12], syngas [10,13–15], liquid hydrocarbons [6,13], methanol [16–22], formaldehyde [16,17], formic acid [16,18] or methyl formate [16,18] can be produced from such plasma methane conversion based upon the co-feed or co-reactant applied. Oxygen [9–12,16,18–20,22], carbon dioxide [6,10,13–15], hydrogen [9], steam [14,21] or nitrous oxide [17] has been applied as a co-reactant under the conditions of corona [7,9,10,12,14,22], microwave [5,8,20], radio frequency discharge [23], spark [21] or dielectric-barrier discharge (DBD) [11,13,15–19], respectively. Various non-equilibrium plasma phenomena have been reviewed by Eliasson and Kogelschatz [24]. Most of products generated using corona, pulsed discharge and microwave discharge are some stable

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little molecules, such as ethylene, acetylene, hydrogen and carbon monoxide. Under the conditions of DBD, a series of hydrocarbons could be produced for its large volume of discharges, which makes the liquid fuel production directly from methane become true [6,13]. Such produced fuel contains a large amount of branched hydrocarbons that represents a better fuel production. However, a drawback of the direct fuel production from methane using DBDs is the formation of carbon black and plasma polymerized carbon film, even with the co-feed of oxidant like carbon dioxide [13]. To improve the selectivity of liquid fuel and to inhibit the formation of solid carbon products, 13X zeolite has been successfully applied in the previous investigation [6]. A XPS characterization of DBD used zeolite suggests some reactions within the zeolite pores [25]. In this work, the performance of plasma methane conversion using DBDs over zeolite A has been investigated. The pore diameter of zeolite A (4.2 Å) is smaller than that of zeolite X (7.4 Å). A major difference between these two zeolites is that the DBD plasma methane conversion over zeolite A leads to a more selective production of light hydrocarbons (C_2–C_4).

2. Experimental

The experimental setup is schematically illustrated in Fig. 1 and discussed previously [6,13]. The reactor applied is a cylindrical DBD reactor, which consists 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 attaches a metal foil against the inner surface of the quartz tube and serves as the high voltage electrode. The outer steel tube serves as the grounded 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 supply 50–1000 W input power 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 and current with a high voltage probe (Tektronix P6015A) and a current probe (Pearson Electronics 411). In addition, the reaction temperature can be adjusted by a closed loop of re-circulating oil from a thermostat in the range of ambient temperature to 400 °C.

The feed gases, CH_4 and CO_2, are introduced into the reactor via mass flow controllers. The product stream is then introduced into an on-line gas chromatograph (GC) through a heated line to avoid possible condensation. The GC used 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 Å 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 Å Plot column can monitor H_2, O_2, N_2, CH_4, CO and other light hydrocarbons. In order to establish a mass balance of C,

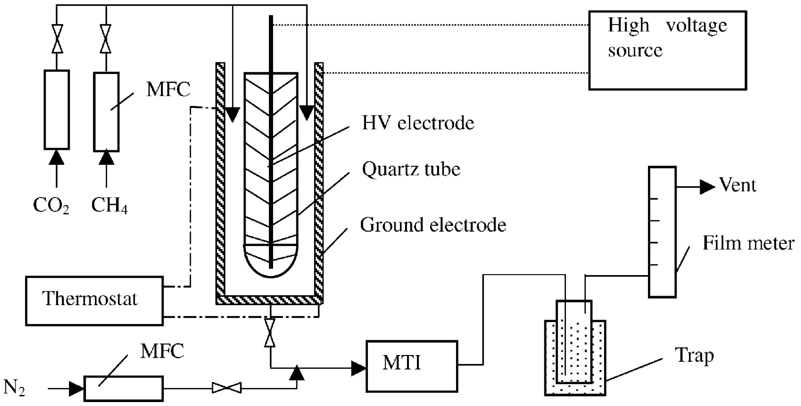

Fig. 1. Configuration of dielectric barrier discharge reactor and experimental setup.

H and O elements, nitrogen is chosen as a reference gas, which is added to the product stream at the exit of the reactor. The loading of the zeolite is the same as that reported previously [6].

3. Results and discussion

3.1. *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 at a pressure of one bar.

Table 1 illustrates the effect of flow rate on the conversion of CH_4 and CO_2 over zeolite A using DBDs. It can be seen that the increasing flow rate reduces the conversion of CH_4 and CO_2 quickly in the range of 200–600 ml min^{-1}. The conversion of CH_4 and CO_2 decreased from 63.6 and 39.52% to 29.93 and 13.02%, respectively, when the flow rate increased from 200 to 600 ml min^{-1}.

The product obtained in the catalytic DBD conversion of CH_4 and CO_2 include CO, H_2, C_2–C_4 hydrocarbons and C_5^+ components. The effect of flow rate on product yields is shown in Fig. 2a. Increasing the flow rate results in a decrease in yields of CO and H_2 at the beginning. The yield of C_2–C_4 hydrocarbons does not change significantly with the increasing flow rate. From results shown in Table 1, one can see that the 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^{-1}.

The effect of flow rate on product selectivity is shown in Fig. 2b. The selectivity of syngas (CO and H_2) is higher than other products. It is interesting to note that the selectivity of C_2 hydrocarbons increased whereas the selectivity of C_5^+ component decreased with the increased gas flow rate. One surprising result is that C_4 hydrocarbons are the second abundant product and its selectivity increased slightly with the increasing flow rate. High flow rate therefore favors the production of light hydrocarbons (C_2–C_4).

Table 1
Effect of flow rate on conversion of CH_4 and CO_2 and molar ratio of H_2/CO[a]

	Flow rate (ml min^{-1})			
	200	400	500	600
Conversion of CH_4 (%)	63.60	44.27	37.23	29.93
Conversion of CO_2 (%)	39.35	21.89	15.51	13.00
Molar ratio of H_2/CO	0.67	0.75	0.81	0.70

[a] Pressure, 1 bar; wall temperature, 150 °C; catalyst amount, 4 g; CH_4/CO_2 ratio in feed, 1/1; input power, 500 W.

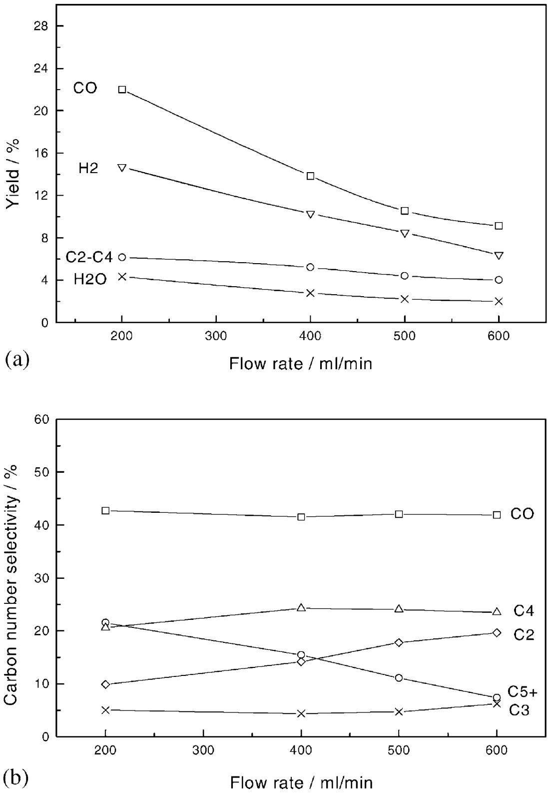

Fig. 2. Effect of flow rate on experimental results. (Pressure, 1 bar; wall temperature, 150 °C; catalyst amount, 4 g; CH_4/CO_2 ratio in feed, 1/1; input power, 500 W). C_5^+ include liquid fuel and oxygenates.

3.2. *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 100–500 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.

Fig. 3a and b and Table 2 show the effect of input power in the range of 100–500 W. Results shown in

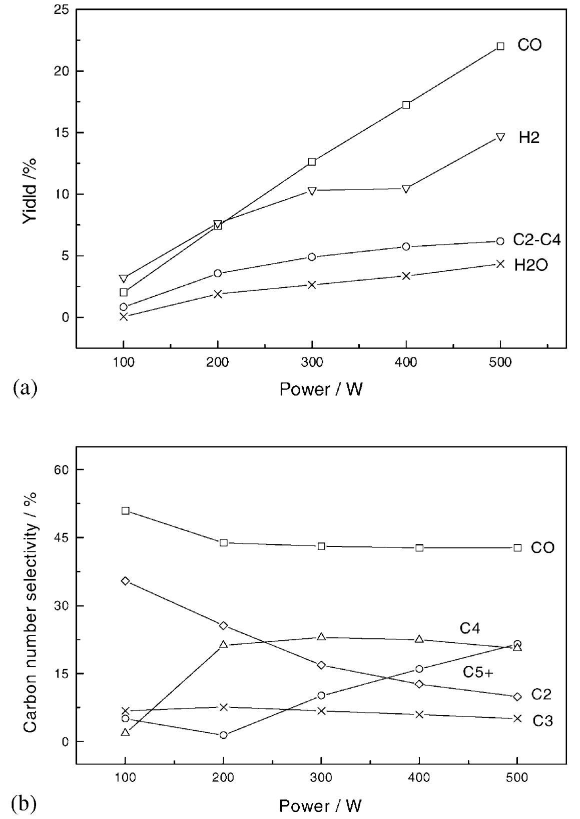

Fig. 3. Effect of input power on experimental results (pressure, 1 bar; wall temperature, 150 °C; catalyst amount, 4 g; CH_4/CO_2 ratio in feed, 1/1; feed flow rate, 200 ml min^{-1}).

Table 2 indicate that the conversion of CH_4 and CO_2 increases with the 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 the increasing input power (Fig. 3a). From the results in Table 2, 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. Although Fig. 3b shows an increasing selectivity of $C_5{}^+$ components, the selectivity of C_4 hydrocarbons remains almost constant at input power above 200 W. This figure also shows a decreasing selectivity of C_2 hydrocarbon with the increasing input power. This suggests that the increasing input power destroys the light hydrocarbon and then converts them to other higher hydrocarbons. Higher input power is required to produce more C_3 and C_4 hydrocarbons.

3.3. *Effect of feed ratio of CH_4/CO_2*

The effect of feed composition was studied by varying the feed ratio of CH_4/CO_2 in the range of 1/1–3/1. Fig. 4a and b and Table 3 illustrate the effect of CH_4/CO_2 feed ratio on the conversion of CH_4 and CO_2 over zeolite A in the DBD reactor. It is very clear from Table 3 that the conversion of both CH_4 and CO_2 decreases slowly with the increase of molar ratio of CH_4/CO_2. High conversion can be obtained at a low feed ratio of CH_4/CO_2. Fig. 4a indicates that the yield of H_2 and C_2–C_4 hydrocarbons increases with the increasing feed ratio of CH_4/CO_2. According to Table 3, the feed 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 feed ratio of CH_4/CO_2 increases from 1/1 to 3/1. The composition of syngas can be adjusted by changing the feed ratio of CH_4/CO_2. High ratio of CH_4/CO_2 favors the production of syngas with high H_2/CO ratio. From the results in Fig. 4b, one can see that the high feed ratio of CH_4/CO_2 results in high selectivity of C_4 hydrocarbon and low selectivity of $C_5{}^+$ components.

Table 2
Effect of input power on conversion of CH_4 and CO_2 and molar ratio of H_2/CO[a]

	Input power (W)				
	100	200	300	400	500
Conversion of CH_4 (%)	5.97	22.71	38.14	51.53	63.6
Conversion of CO_2 (%)	1.95	11.05	20.39	29.32	39.35
Molar ratio of H_2/CO	1.55	1.03	0.82	0.60	0.67

[a] Pressure, 1 bar; wall temperature, 150 °C; catalyst amount, 4 g; CH_4/CO_2 ratio in feed, 1/1; feed flow rate, 200 ml min^{-1}.

Table 3
Effect of molar ratio of CH_4/CO_2 on conversion of CH_4 and CO_2 and molar ratio of H_2/CO[a]

	Molar ratio of CH_4/CO_2 in feed		
	1/1	2/1	3/1
Conversion of CH_4 (%)	63.6	59.12	54.77
Conversion of CO_2 (%)	39.35	31.77	25.29
Molar ratio of H_2/CO	0.67	1.95	3.11

[a] Pressure, 1 bar; wall temperature, 150 °C; catalyst amount, 4 g; input power, 500 W; feed flow rate, 200 ml min^{-1}.

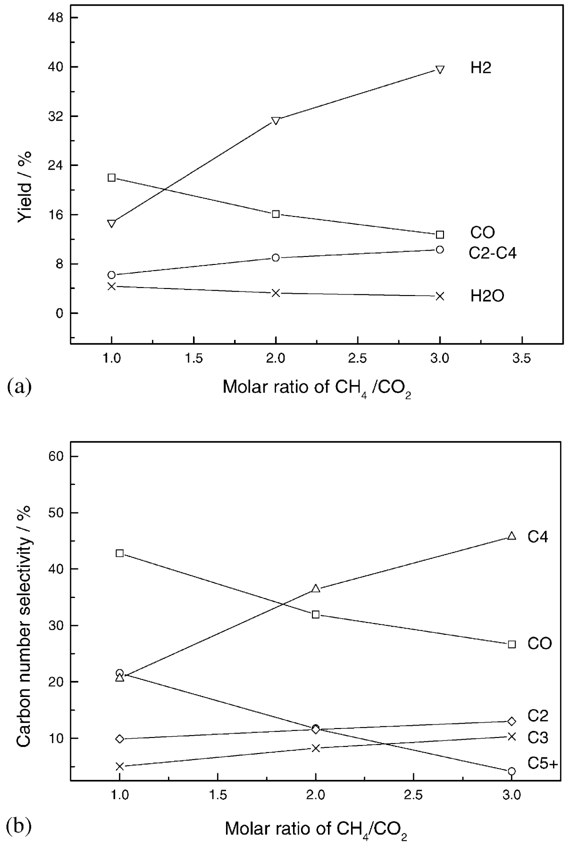

Fig. 4. Effect of molar ratio of CH_4/CO_2 on experimental results (pressure, 1 bar; wall temperature, 150 °C; catalyst amount, 4 g; input power, 500 W; feed flow rate, 200 ml min^{-1}).

3.4. Effect of wall temperature

The temperature effect was investigated in the range of 50–150 °C. The experimental results are shown in Table 4, Fig. 5a and b. Results in Table 4 shows a slight decrease in conversion of methane and carbon dioxide when reactor wall temperature is increased from 50 to 150 °C. Molar ratio of CO/H_2 remains almost constant with the increasing wall temperature. The yields of products are also constant (Fig. 5a). The selectivity of products does not change significantly within the range of wall temperatures tested, although C_4 and $C_5{}^+$ products show an increasing and decreasing selectivity, respectively.

Table 4
Effect of reactor wall temperature on conversion of CH_4 and CO_2 and molar ratio of H_2/CO^a

	Reactor wall temperature (°C)		
	50	100	150
Conversion of CH_4 (%)	68.93	66.74	63.60
Conversion of CO_2 (%)	45.72	42.42	39.35
Molar ratio of H_2/CO	0.71	0.71	0.67

[a] Pressure, 1 bar; CH_4/CO_2 ratio in feed, 1/1; catalyst amount, 4 g; input power, 500 W; feed flow rate, 200 ml min^{-1}.

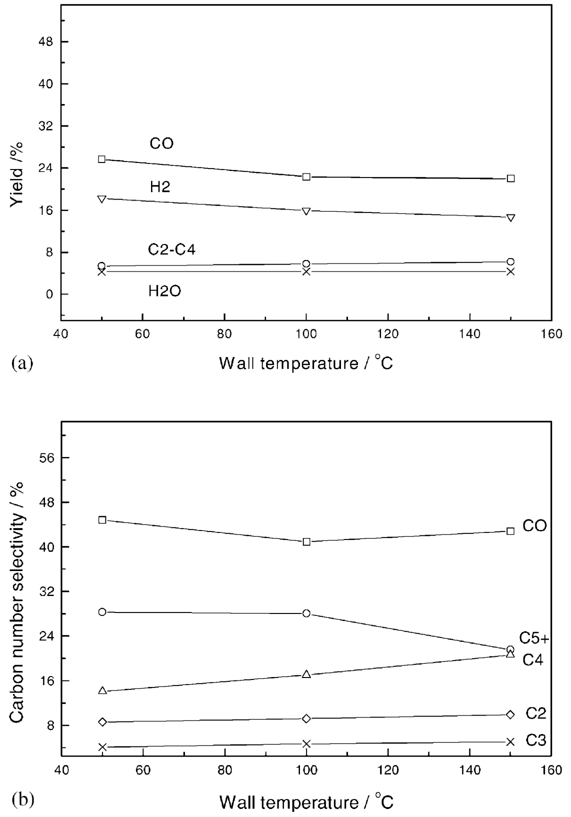

Fig. 5. Effect of wall temperature on experimental results (pressure, 1 bar; CH_4/CO_2 ratio in feed, 1/1; catalyst amount, 4 g; input power, 500 W; feed flow rate, 200 ml min^{-1}).

3.5. Effect of zeolite A

It was found that plasma methane conversion in the presence of CO_2 using DBDs produced carbon black and plasma polymerized films, which covered the surface of the quartz tube and was disfavored [13]. However, the application of zeolite A will inhibit the

Table 5
Comparison of experimental results with and without zeolite A[a]

	Conversion (%)		Carbon number selectivity (%)					Solid products
	CH_4	CO_2	CO	C_2	C_3	C_4	C_5^+	
Without zeolite	63.09	37.87	44.50	10.02	5.18	20.78	19.35	36% of C_5^+ is carbon film
With zeolite A	51.53	29.32	42.69	12.66	5.96	22.46	16.00	No carbon film

[a] Pressure, 1 bar; wall temperature, 150 °C; CH_4/CO_2 ratio in feed, 1/1; feed flow rate, 200 ml min^{-1}; input power: 400 W (500 W for zeolite X).

formation of carbon black and plasma polymerized carbon films. Table 5 is the comparative results of DBD reactions with and without zeolite A. A major difference between the results is the selectivity of C_5^+ product. In the presence of zeolite A, no plasma polymerized carbon film was produced that leads to a better production of gaseous and liquid hydrocarbons. Since the DBD plasma will induce a great change in the state of feed gases (that will be highly excited or dissociated), the mechanism for the DBD reaction with zeolites is very complex. Further investigation is being conducted.

4. Conclusions

The plasma methane conversion to higher hydrocarbons in the presence of CO_2 was experimentally investigated in a DBD reactor over zeolite A at low temperature and atmospheric pressure. Syngas, light hydrocarbons and liquid fuels can be produced this way. High conversion of CH_4 and CO_2 can be achieved. Flow rate of the feed, molar ratio of CH_4/CO_2 and the input power have significant effect on the plasma conversion of CH_4 and CO_2. The application of zeolite A inhibits the formation of carbon black and plasma polymers and leads to a higher selectivity of light hydrocarbons (C_2–C_4).

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References

[1] J.H. Lunsford, Catal. Today 63 (2000) 165.
[2] J.M. Fox, Catal. Rev.-Sci. Eng. 35 (1993) 169.
[3] N.D. Parkyns, C.I. Warburton, J.D. Wilson, Catal. Today 18 (1993) 385.
[4] L. Bromberg, D.R. Cohn, A. Rabinovich, Energy Fuels 12 (1998) 11.
[5] A. Oumghar, J.C. Legrand, A.M. Diamy, N. Turillon, Plasma Chem. Plasma Process. 15 (1995) 87.
[6] B. Eliasson, C.-J. Liu, U. Kogelschatz, Ind. Eng. Chem. Res. 39 (2000) 1221.
[7] S.L. Yao, A. Nakayama, E. Suzuki, AIChE J. 47 (2001) 413.
[8] S.L. Suib, R.P. Zerger, J. Catal. 139 (1993) 383.
[9] C.-J. Liu, R. Mallinson, L. Lobban, Appl. Catal. A 178 (1999) 17.
[10] S.L. Yao, F. Ouyang, A. Nakayama, E. Suzuki, M. Okumoto, A. Mizuno, Energy Fuels 14 (2000) 910.
[11] H.-K. Jeong, S.-C. Kim, C. Han, H. Lee, H.K. Song, B.-K. Na, Korean J. Chem. Eng. 18 (2001) 196.
[12] S. Kado, Y. Sekine, K. Fujimoto, Chem. Commun. (1999) 2485.
[13] C.-J. Liu, B. Xue, B. Eliasson, F. He, Y. Li, G.-H. Xu, Plasma Chem. Plasma Process. 21 (2001) 301.
[14] S. Kado, K. Urasaki, Y. Sekine, K. Fujimoto, Chem. Commun. (2001) 415.
[15] A. Huang, G. Xia, J. Wang, S.L. Suib, J. Catal. 189 (2000) 349.
[16] D.W. Larkin, L.L. Lobban, R.G. Mallinson, Ind. Eng. Chem. Res. 40 (2001) 1594.
[17] H. Matsumoto, S. Tanabe, K. Okitsu, Y. Hayashi, S.L. Suib, J. Phys. Chem. A 105 (2001) 5304.
[18] S.P. Bugaev, A.V. Kozyrev, V.A. Kuvshinov, N.S. Sochugov, P.A. Khryapov, Plasma Chem. Plasma Process. 18 (1998) 247.
[19] M. Okumoto, Z. Su, S. Katsura, A. Mizuno, IEEE Tran. Ind. Appl. 35 (1999) 1205.

[20] Y. Sekine, K. Fujimoto, Kinet. and Catal. 40 (1999) 294.
[21] K. Hijikata, K. Ogawa, N. Miyakawa, Heat Trans. Asian Res. 28 (1999) 404.
[22] S.L. Yao, F. Ouyang, A. Nakayama, E. Suzuki, Trans. Mater. Res. Soc. Jpn. 25 (2000) 373.
[23] S.Y. Savinov, H. Lee, H.K. Song, B.K. Na, Ind. Eng. Chem. Res. 38 (1999) 2540.
[24] B. Eliasson, U. Kogelschatz, IEEE Tran. Plasma Sci. 19 (1991) 1063.
[25] F. He, C.-J. Liu, B. Eliasson, B. Xue, Surface Interface Anal. 32 (2001) 198.