Plasma Chem Plasma Process (2008) 28:405–414
DOI 10.1007/s11090-008-9132-4

ORIGINAL PAPER

Synthesis of Ammonia Using CH_4/N_2 Plasmas Based on Micro-Gap Discharge under Environmentally Friendly Condition

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Received: 26 October 2007 / Accepted: 20 May 2008 / Published online: 20 June 2008

Abstract The synthesis of ammonia has been studied in methane-nitrogen plasmas using a micro-gap discharge under an environmentally friendly condition. The effects of some parameters such as the specific input energy, the discharge gap, the volume ratio of CH_4/N_2, the residence time, and the gas temperature on the yield of NH_3 and conversion rate of CH_4 are discussed in the paper. The results show that the highest yield of NH_3 is 8000 ppm for a residence time of 1.6 s. In addition, the yield and generating rate of H_2 are 9.1% (v/v) and 1879.8 μmol/min, respectively. Therefore, the micro-gap discharge is an efficient method for NH_3 synthesis and H_2 generation from CH_4.

Keywords Concentration of synthesized NH_3 · Conversion rate of CH_4 · Micro-gap discharge · Environmentally friendly condition

Introduction

Ammonia (NH_3), as an important chemical product, can be used to produce ammonium fertilizer, such as carbamide ammonium nitrate and ammonium bicarbonate. Hydrogen (H_2) is definitely a green energy source, and hydrogen based fuel-cell technology has been investigated extensively to develop fuel cell vehicles and cogeneration system. Methane is the major constituent of natural gas. Activation of saturated hydrocarbons and especially methane is difficult due to the high dissociation energy of C–H bonds. The direct synthesis of NH_3 using CH_4 rather than H_2 by non-equilibrium plasma at atmospheric pressure is of great importance.

Project of National Major Foundation Research from Science and Technology Ministry of China (2004CCA06300).
Support Plans of National New Century Excellent Youth of China (NCET-04-0286, -05-0398).

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A number of studies on plasma synthesis of ammonia have been carried out by radio frequency (=13.56 MHz) or microwave (=2540 MHz) discharge at low pressure. In 1994, Oumghar, Legrand et al. [1–3] investigated the conversion of CH_4 by N_2 or air microwave plasma, as well as kinetic mechanism of CH_4 conversion. C_2 hydrocarbons (C_2H_2, C_2H_4, C_2H_6) and trace amount of HCN, NH_3 were obtained, and the methane conversion rate was 80% within the power range of 350 ~ 650 W. Some studies [4, 5] reported that ammonia molecules would be formed by the reaction between NH_x radicals and hydrogen atoms. In some cases, catalysts were placed in the discharge or afterglow region, or on the cold trap wall in order to enhance the ammonia yield [5–8]. Tanaka et al. [7, 8] studied the synthesis of ammonia in N_2-H_2 plasmas by microwave or radio frequency discharge at a pressure of 650 Pa (5 Torr) with catalysts of iron and molybdenum wires of 100 pieces. The yields of NH_3 and N_2H_4 were only 1.5 mmol/g and 2.5 μmol/g, respectively, with a residence time of 2 h and power input of 180 W. The main drawback of low pressure plasmas is low energy efficiency and low yields of NH_3.

H_2 generation from water, methane, and methanol was investigated in a ferroelectric pellet packed-bed reactor (FPR) and a silent-discharge-type reactor (SDR) by Kabashima et al. [9] in 2003. The H_2-generation rate with FPR was 54 μmol/min in ambient Ar. Suid et al. [10] have reported water splitting by a dielectric barrier discharge (DBD) plasma reactor, of which the inner electrode was an Au-coated copper rod. The highest H_2-generating rate was 3.4 μmol/min in ambient Ar.

In previous studies performed by the author, the NH_3 synthesis in N_2–H_2 plasmas was carried out using the combined surface discharge and DC (direct current) discharge [11]. NH_3 yield was 5000 ppm with MgO catalyst. Subsequently, the concentration of NH_3 reached 12500 ppm by the micro-gap DBD without any catalyst [12, 13]. In this paper, the synthesis of NH_3 by N_2-CH_4 plasmas was performed. The yield of NH_3 was 8000 ppm for a residence time of 1.6 s. The whole process was carried out under atmospheric pressure without any catalyst, which is an environmentally friendly condition in line with Green Chemistry Principle [14, 15].

Plasma Processes of Micro-Gap Discharge

Comparison of Main Parameters between Several Kinds of Gas Discharges

The comparison of main parameters between several kinds of gas discharges is shown in Fig. 1. At high pressure ($\geq 10^5$ Pa), the main gas discharges are the high-voltage corona, pulse corona, general DBD, and our micro-gap discharge. Strong and weak ionization zones are separated by the line which is defined by the following parameters: the electric field intensity E_g, 100 kV/cm; the electron density in discharge path N_e, $10^{14}/cm^3$; the average electron energy T_e, 10 eV; and the fractional active volume (δ, %), 1%. The main parameters of our micro-gap discharge, which falls in the strong ionization zone, are much higher than that of other gas discharges; in particular the fractional active volume is about 2%. The fractional active volume refers to the volume ratio of the volume of all ionization discharge paths to that of micro-gap. Plasma chemistry reactions take place in the ionization discharge paths. The increase of the fractional active volume leads to more discharge paths, resulting in greater whole electron density in the micro gap. Therefore, our micro-gap discharge is an efficient method for the conversion of CH_4 into NH_3.

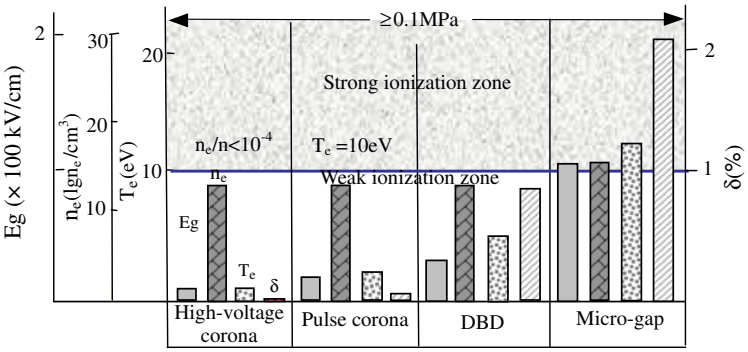

Fig. 1 Comparison of main parameter for several kinds of gas discharge

Excited Dissociation, Direct Ionization of CH_4 and Formation of H_2

The dissociative potential of C–H bond of CH_4 is less than 4.6 eV. The excited methane S_1 (9.6 and 10.4 eV) and S_2 (11.7 eV),which are formed by the electron-methane collisions, are so unstable that rapidly dissociate into radicals such as CH_3, CH_2, CH, C. The plasma reactions are as follows [1–3]:

$$e(\varepsilon > 10eV) + CH_4 \rightarrow CH_4(S_1,\ S_2) + e \tag{1}$$

$$CH_4(S_1,\ S_2) \rightarrow \begin{cases} CH_3 + H & (2) \\ CH_2 + H + H & (3) \\ CH_2 + H_2 & (4) \\ CH + H_2 + H & (5) \\ C + H_2 + H_2 & (6) \end{cases}$$

Direct Ionizations of CH_4 are as follows [12]:

$$CH_4 + e*(12.75eV) \rightarrow CH_4^+ + 2e \tag{7}$$

$$CH_4 + e*(14.3eV) \rightarrow CH_3^+ + H + 2e \tag{8}$$

$$CH_4 + e*(15.1eV) \rightarrow CH_2^+ + H_2 + 2e \tag{9}$$

$$CH_4 + e* \rightarrow H^+ + CH_3 + 2e \tag{10}$$

$$CH_4 + e*(22.2eV) \rightarrow CH^+ + H + H_2 + 2e \tag{11}$$

$$CH_4 + e* \rightarrow CH_2 + H_2^+ + 2e \tag{12}$$

$$CH_4 + e*(25eV) \rightarrow C^+ + 2H_2 + 2e \tag{13}$$

T_e in our micro-gap discharge is ≥10 eV, which means a lot of electrons have the energy ≥9.6 eV. In this study, the above plasma reactions might be dominant reactions for H_2 generation as well as the formations of CH_4, CH_3, CH_2, CH radicals and CH_4^+, CH_3^+, CH_2^+ ions.

Dissociation and Ionization of N_2 Molecule [16]

$$N_2\left(X^1\sum g^+\right) + e * (15.63eV) \rightarrow N_2^+\left(X^2\sum g^+\right) + 2e \quad (14)$$

$$N_2\left(X^1\sum g^+\right) + e * (16.84eV) \rightarrow N_2^+(A^2\Pi u) + 2e \quad (15)$$

$$N_2\left(X^1\sum g^+\right) + e * (18.76eV) \rightarrow N_2^+\left(B^2\sum u^+\right) + 2e \quad (16)$$

$$N_2\left(X^1\sum g^+\right) + e * (23.53eV) \rightarrow N_2^+\left(C^3\sum u^+\right) + 2e \quad (17)$$

$$N_2\left(X^1\sum g^+\right) + e * (24.32eV) \rightarrow N^+\left(^3P\right) + N\left(^4S\right) + 2e \quad (18)$$

$$N_2\left(X^1\sum g^+\right) + e * (26.66eV) \rightarrow N^+\left(^3P\right) + N\left(^2D\right) + 2e \quad (19)$$

Plasma Processes of NH_3 Synthesis

The CH_4, CH_3 etc. react with N_2^+, N^+, $N(^4S)$ to form the NH radicals as follows [1, 2]. Ion reactions (20) with high rate constant are the major reactions.

$$CH_4 + N_2^+ \rightarrow N_2H^+ + CH_3 \quad (20)$$

$$CH_3 + N_2^+ \rightarrow N_2H^+ + CH_2 \quad (21)$$

$$CH_4 + N^+ \rightarrow CH_3^+ + NH \quad (22)$$

$$CH_4 + N\left(^4S\right) \rightarrow CH_3 + NH \quad (23)$$

NH radicals, which are considered as the ammonia precursors, are formed by the reactions of N_2^+ with H_2, H. Also N atoms adhered to the wall react with hydrogen to form NH radicals [1, 2, 12].

$$N_2^+ + H_2 \rightarrow N_2H^+ + H \quad (24)$$

$$N_2^+ + H \rightarrow N_2H^+ \quad (25)$$

$$N_2H^+ + e \rightarrow NH + N \quad (26)$$

$$N(ads) + H \rightarrow NH(ads) \quad (27)$$

Synthesis of NH_3 molecule [12]

$$NH + H_2 \rightarrow NH_3 \quad (28)$$

$$NH + H \rightarrow NH_2 \quad (29)$$

$$NH_2 + H \rightarrow NH_3 \quad (30)$$

The N_2^+ ion is the major activated particle to form the NH radical and leads to NH_3. As for the micro-gap discharge, a lot of electrons have the energy $\geq$15.6 eV (ionization potential of N_2). Therefore, the micro-gap discharge is an efficient plasma method for the synthesis of NH_3 at atmospheric pressure.

Experiment

Experimental Setup

The experimental setup for synthesis of NH_3 using the micro-gap discharge is shown in Fig. 2. The plasma reactor 3 is rectangular, of which the dimension is 260 mm (length) × 130 mm (width) × 35 mm (thickness). The thin dielectric layers of α-AL_2O_3 are attached to both sides of discharge electrodes, of which the dimension is 175 mm (length) × 80 mm (width) × 0.3 mm (thickness). The discharge gap is 0.47 mm or 0.64 mm. The dielectric constant and the electric insulation intensity are 10 and 350 kV/cm, respectively. With this thin dielectric layer, strong streamer discharge can be obtained in the micro-gap.

Measurement System

The CH_4–N_2 gas mixture with a purity of 99.98% is fed into the reactor. The gas flow rate and mixing ratio are adjusted by the mass-flow controller 4000 Series Gas Mixing System (Environics INC in USA). The yield of ammonia is monitored on-line by GXH-105 Type Infrared Analyzer. The feed and product of gaseous hydrocarbons are analyzed with a gas chromatograph of GC-102 or HP4890 equipped with a thermal conductivity detector (TCD) and a flame ionization detector (FID). The relative standard deviation (RSD) is $<$0.5% based on the five times measurement of one sample.

The self-made power supply is applied to the discharge electrodes, leading to a continuous strong streamer discharge, of which the main parameters are as follows: the discharge power, 240 W; the applied frequency, 10 kHz; the pulse width, 40 μs. The electric parameters are measured using HV-60 High Voltage Probe (Iwatsu, Japan), SS-240 Pulse Current Probe (Iwatsu, Japan), TDS-3032B Oscilloscope (Tektronix, USA), Model HC-F1000L Frequency Meter (Hong Chong Electronic Co. Ltd) and Q3-V Electrostatic Voltage Meter (Beijing Electric Meter Factory, China).

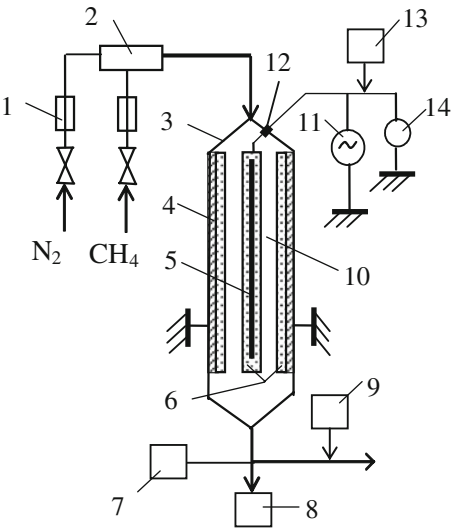

Fig. 2 Schematic diagram for the synthesis of NH_3 by CH_4–N_2 plasmas Note: 1. Gas flow meter; 2. Gas mixing system; 3. Plasma reactor; 4. Earthing electrode 5. Discharge electrode; 6. Dielectric layers; 7. NH_3 analyzer; 8. Glass for Liquid fuel; 9. Gas chromatograph; 10. Discharge gap; 11. Power supply; 12. Insulator 13. Oscillograph; 14. Electrostatic voltage meter

Evaluation of System Performance

In order to evaluate the energy efficiencies for methane conversion, the specific input energy (SIE, electrical input energy to unit volume of gas), defined in Eq. 1, is used. The discharge power is measured using the method of charge-voltage figure [17, 18], which can efficiently eliminate the measure error caused by discharge gap that was equal to a capacitor. Equations 2–3 indicate the calculation methods for generation rate and conversion rate of CH_4. The volume per mol in our experiments is 24.2 L/mol with a temperature of 22°C and an atmospheric pressure.

$$1.\ \text{Specific input energy} = \frac{\text{Discharge power}}{\text{Flow rate feed gas}} \quad (\text{J/L}) \tag{1}$$

$$2.\ \text{Generation or conversion rate} = \frac{\text{Yield (v/v)} \times \text{Flow rate}}{\text{Volume per mol}} \quad (\mu\text{mol/min}) \tag{2}$$

$$3.\ \text{Methane conversion} = \frac{\text{Consumed } CH_4}{\text{Initial } CH_4} \times 100(\text{mol}\%) \tag{3}$$

Experimental Results

Analysis of Gaseous Products for the Conversion of CH_4

The experiments were carried out at 22°C, 10^5 Pa, without any catalyst. The mixed gases of CH_4/N_2=3:1 (v/v) were fed into the reactor at a flow rate of 0.5 L/min. The specific input energy (SIE) is 29.2 kJ/L with a discharge power of 243.6 W. The discharge gap width of the plasma reactor is 0.47 mm. The yields of gaseous products in Table 1 were analyzed with a GC-102 gas chromatograph by Institute of Guang Ming Chemical Engineering. The standard gases of hydrocarbons, NH_3 and H_2 were injected into the Chromatogram to calibrate their peak values.

As shown in Table 1, hydrocarbons ($\leq C_4$) such as ethane (C_2H_6), ethylene (C_2H_4), acetylene (C_2H_2), propane (C_3H_8), propylene (C_3H_6), butane (i-C_4H_{10}, n-C_4H_{10}) are produced by electron collision reaction and recombination reaction. The yield and generation rate of hydrocarbons are of the following relationship $C_2H_6 > C_3H_8 > C_2H_2 > C_2H_4 >$ i-C_4H_{10}, n-$C_4H_{10} > C_3H_6$. 10.13% of the residual is not identified, which is possibly to be gaseous hydrocarbon ($\geq C_5$). The conversion rate of CH_4 is 4752 μmol/min.

With the electron-methane collisions, large numbers of H_2 are produced by exited dissociation and direct ionization of CH_4. The yield and generation rate of H_2 are 9.1%

Table 1 Data for the conversion of CH_4 into hydrocarbons ($\leq C_4$), NH_3 and H_2

Item	CH_4	H_2	C_2H_6	C_2H_4	C_2H_2	C_3H_8	C_3H_6	i-C_4H_{10}	n-C_4H_{10}	NH_3	Total	Products ($\geq C_5$)
Yield (v/v %)	52	9.1	1.7	0.16	0.24	0.6	0.04	0.12	0.11	0.8	64.87	10.13
Generation or conversion rate (μmol/min)	4752	1879.8	351.2	33.1	49.6	123.9	8.26	24.79	22.72	165.1		

The yields of gaseous products were tested by Institute of Guang Ming Chemical Engineering

(v/v) and 1879.8 μmol/min, respectively. These data show that the micro-gap discharge is a promising method to obtain high H_2-generating rate in the absence of catalyst.

The NH_3 is synthesized by atmospheric plasma in ambient N_2 and CH_4. The yield of synthesized NH_3 is 8000 ppm equal to 0.42 mmol/g for a residence time of 1.6 s. The yield of NH_3 would be1.89×10^3 mmol/g if the gas residence time was 2 h. However, the yield of NH_3 was only 1.5 mmol/g for a residence time of 2 h by Tanaka et al. [7, 8].

Effect of the Specific Input Energy on the Concentration of Synthesized NH_3 and Conversion Rate of CH_4

As shown in Fig. 3, the SIE has a vital effect on the concentration of synthesized NH_3 and the conversion rate of CH_4. The greater the SIE is, the more molecules of CH_4, N_2 are ionized into activated particles, thus enhancing synthesis of NH_3. When the SIE changes in the range of 5.38–29.2 kJ/L, the NH_3 concentration increases from 3600 ppm to 7000 ppm, meanwhile CH_4 conversion rate increases from 47.3% to 59.0%. The trend slows after the point where SIE is 29.2 kJ/L. When the SIE is 35 kJ/L, the highest CH_4 conversion rate of 60.0% is obtained, accordingly the highest NH_3 concentration is 7400 ppm. However SIE is not further increased due to the possibility of dielectric layer breakdown, in addition, high SIE is also unsuitable for synthesis of NH_3 from energy consumption perspective.

Effect of the Volume Ratio of CH_4 to N_2 on the Concentration of Synthesized NH_3 and Conversion Rate of CH_4

As shown in Fig. 4, the volume ratio of CH_4/N_2 has a strong effect on the concentration of NH_3, and the optimum volume ratio is 3:1, where the concentration of NH_3 and the conversion rate of CH_4 reach 7000 ppm and 59%, respectively. When the volume ratio of CH_4/N_2 is in the range of $0.25 \sim 3$, the two values increase with the volume ratio. When the ratio of CH_4/N_2 exceeds 3, the concentration of NH_3 remains constant at 7000 ppm, and the conversion rate of CH_4 decreases with the increase of the volume ratio. The optimum ratio of CH_4/N_2 3:1 is the same as that of conventional NH_3 synthesis process.

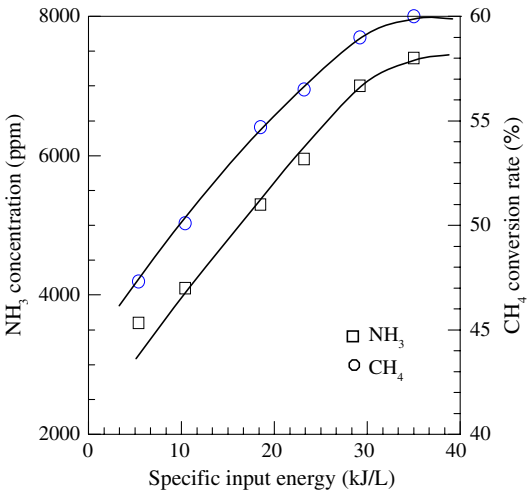

Fig. 3 SIE vs. NH_3 concentration and CH_4 conversion. Q = 0.5 L/min; CH_4/N_2 = 3:1; Gap = 0.64 mm

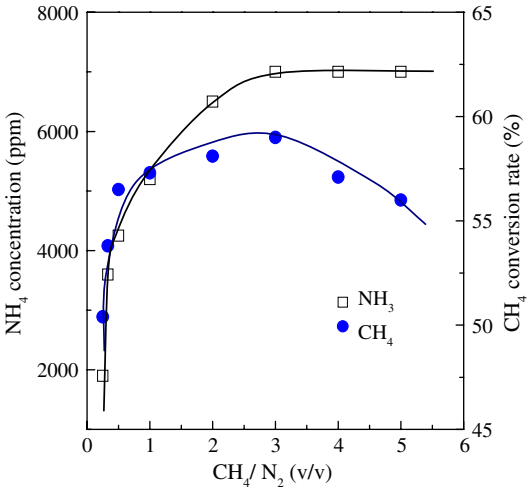

Fig. 4 Volume ratio of CH_4/N_2 vs. NH_3 concentration and CH_4 conversion rate. SIE = 30 kJ/L; Q = 0.5 L/min; Gap = 0.64 mm

Effects of the Residence Time and Discharge Gap on the Concentration of Synthesized NH_3

As shown in Fig. 5, curve 1 (0.47 mm) and curve 2 (0.64 mm) for the different discharge gaps have almost the same trend. The concentration of NH_3 increases with the residence time in the range of 0.5–2.25 s. The residence time is much shorter than that of NH_3 synthesis by Tanaka et al. [4, 5], because more CH_4 and N_2 are ionized and dissociated in our micro-gap discharge.

The discharge gap has a great effect on the concentration of NH_3. When the residence time is 1.65 s, the concentration of NH_3 is 6930 ppm for a discharge gap of 0.64 mm, 8000 ppm for a discharge gap of 0.47 mm with a 1070 ppm increase. With the same residence time, the SIE for the discharge gap of 0.47 mm is higher than that of 0.64 mm, so that higher concentration of NH_3 is obtained with the gap of 0.47 mm. In addition, when

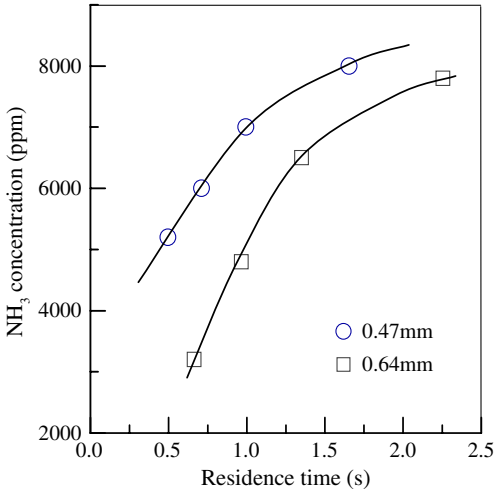

Fig. 5 Residence time vs. NH_3 concentration. Discharge power = 240 W; CH_4/N_2 = 3:1

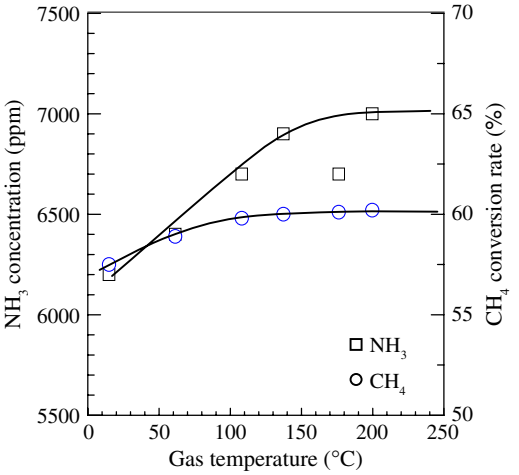

Fig. 6 Gas temperature vs. NH_3 concentration and CH_4 conversion rate. SIE = 29.2 kJ/L; CH_4/N_2 = 3:1; Q = 0.5 L/min; Gap = 0.64 mm

the discharge gap becomes narrow, the fractional active volume is correspondingly increased, resulting in the increase of high-energy electron density. As a result, more molecules of CH_4 and N_2 are ionized and dissociated to produce N_2^+, NH, CH_4, CH_3·radicals for the synthesis of NH_3.

Effect of the Gas Temperature on the Concentration of Synthesized NH_3 and Conversion Rate of CH_4

Even though the feed gas isn't heated, its temperature can go up to about 70–80 °C owing to the micro-gap discharge. As shown in Fig. 6, the concentration of NH_3 increases with the gas temperature in the range of 14.9 ~ 137.3 °C. When the gas temperature exceeds 137.3 °C, the concentration of NH_3 is almost constant at 7000 ppm. The gas temperature has light effect on the conversion rate of CH_4, which is almost constant at 60%. The activation energy of gas molecules increase with the gas temperature so that more CH_4 and N_2 are ionized and dissociated for the synthesis of NH_3. However, high temperature isn't necessary for synthesis of NH_3, and high temperature leads to electrodes breakdown and reactor destruction.

Conclusions

The conversion of CH_4 into NH_3 is investigated using the micro-gap discharge plasma. The whole reaction processes is carried out under the conditions of normal temperature and pressure without any catalyst, which is an environmentally friendly condition in accordance with Green Chemistry Principle. The results show that:

1) Analysis of gas ingredient shows that the main products of CH_4/N_2 discharge plasma are NH_3, H_2 and hydrocarbons ($\leq C_4$) such as C_2H_6, C_2H_4, C_2H_2, C_3H_8, C_3H_6, i-C_4H_{10}, n-C_4H_{10}. The yield and generation rates of hydrocarbons ($\leq C_4$) are of the following relationship $C_2H_6 > C_3H_8 > C_2H_2 > C_2H_4 >$ i-C_4H_{10}, n-$C_4H_{10} > C_3H_6$.

2) The synthesis of NH_3 is realized using CH_4/N_2 micro-gap discharge at an atmospheric pressure. The yield of NH_3 is 8000 ppm for a residence time of 1.6 s, and 1.89×10^3 mmol/g if the residence time was 2 h.
3) The micro-gap gas discharge is a promising method for high H_2 generation rate in the absence of catalyst. The yield and generation rate of H_2 are 9.1% (v/v) and 1879.8 μmol/min, respectively.

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