Extended Abstracts of the Ninth JSME-KSME Thermal and Fluids Engineering Conference
October 28-30, 2017, Okinawa, Japan

TFEC9-1449

REACTION MECHANISM OF AMMONIA DECOMPOSITION BY ATMOSPHERIC PLASMA

Y. Goto[1], Y. Hayakawa[1] and S. Kambara[1]

[1]Energy Engineering Division, Gifu University, 1-1 Yanagido, Gifu, 501-1193, Japan

ABSTRACT

Ammonia has numerous favorable characteristics that stem from its molecular structure, the primary of characteristic is high hydrogen storage capacity of 17.6 wt%. Another advantage is carbon-free at the end of use, although CO_2 emitted during the production of ammonia depends on the energy source used. Therefore, ammonia is the most promising hydrogen carrier among all of compounds hydrogen-containing. A dielectric barrier discharge (DBD) plasma is appropriate for ammonia decomposition because the electric load to the plasma reactors can be quickly controlled by adjusting the output voltage or duty cycle, which can respond well to variations in gas volume. An efficient method for using pulsed plasma to produce hydrogen from ammonia have been developed. In this study, the reaction mechanism of ammonia decomposition and hydrogen production in the plasma reactor was concerned. In the DBD pulsed plasma, electrons collide with gas molecules, wherein subsequent secondary and tertiary electron collisions convert a fraction of NH_3 into positive ions, radicals and electrons. NH_2, NH, N and H radicals are also generated by electron impact reactions. After their generation, molecular hydrogen and nitrogen are formed by recombination reactions. The overall reaction of ammonia decomposition by the pulsed DBD plasma is given by $NH_3 + e \rightarrow 0.5\ N_2 + 1.5\ H_2 + e$. Three keys reactions for ammonia decomposition by the elemental reaction simulation were found; $NH_3+H \rightarrow NH_2+H_2$, $NH_2+N \rightarrow N_2+2H$, and $N_2H_3+H \rightarrow N_2H_2+H_2$. The simulation results indicated roughly agreement with the experimental results.

KEYWORDS: Ammonia, Hydrogen, Atmospheric plasma, Reaction mechanism

1. INTRODUCTION

In order to reduce CO_2 emissions, hydrogen energy use has been expected. However, there are some issues in hydrogen use such as the large energy loss in hydrogen storage and transportation1). To solve the problems, use of hydrogen energy carrier such as ammonia is proposed2). Particularly, NH_3 is greatly expected as the hydrogen energy carrier. NH_3 has a number of favorable characteristics, the primary one being its high capacity for H_2 storage with the 17.6 wt%, based on its molecular structure. Liquefied ammonia is available for hydrogen storage and transportation, however, an effective hydrogen production from ammonia is necessary at the site of hydrogen use.

A general technique for hydrogen production from ammonia is catalytic thermal decomposition. However, a critical issue is the long start-up time for hydrogen production because the process requires heating. Non-catalytic hydrogen production using pulsed plasma may provide a solution to the critical start-up issue. In particular, a dielectric barrier discharge (DBD) plasma is appropriate for ammonia decomposition because the electric load to the plasma reactors can be quickly controlled by adjusting the output voltage or duty cycle, which can respond well to variations in gas volume3).

In this study, elementary reaction mechanism on ammonia decomposition and hydrogen production in DBD pulsed atmospheric plasma is considered to develop the high efficiency hydrogen production device. The reaction model is built on the CHEMKIN simulator, and simulation results and experimental results are compared. The key reactions of ammonia decomposition in the DBD pulsed plasma reactor is found.

*Corresponding Author: kambara@gifu-u.ac.jp

2. EXPERIMENTAL SETUP

Figure 1 shows a plasma reactor which was a coaxial configuration with quartz glass tubes and electrodes. The outer glass tube was 45 mm in diameter and 2 mm in thickness, whereas the inner glass tube was 38 mm in diameter and 2 mm in thickness. The pulsed plasma was generated in a 1.5 mm gap between the outer and inner glass tubes. The grounded electrode was made of stainless steel (SUS 304). It was 360 mm in length and 0.2 mm in thickness and covered the outside surface of the outer glass tube. The high-voltage electrode was made of stainless steel (SUS 304). It was 34 mm in diameter and 450 mm in length and was positioned inside the inner quartz tube.

100% NH_3 gas of 1.0 L/min was fed into the reactor for steady state, after that, supply of ammonia and the exhaust valve (vent.) was stopped, and the circulation pump was activated; therefore ammonia gas is circulated in the system. When atmospheric plasma is fired, ammonia gas in the system is decomposed by electron energy generated by dielectric barrier discharge. The decomposed gas was collected every few minutes by programed sampling system of gas chromatography (GC), and concentrations of hydrogen was measured.

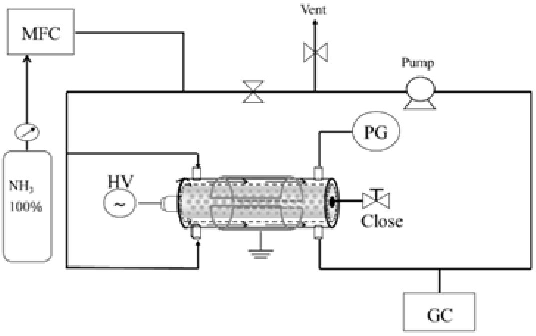

Fig.1 Experimental setup for NH_3 decomposition by PR.

3. EXPERIMENTAL RESULT

In the DBD pulsed plasma, electrons collide with ammonia gas molecules, wherein subsequent secondary and tertiary electron collisions convert a fraction of NH_3 into positive ions, radicals and electrons. NH_2, NH, N and H radicals are also generated by electron impact reactions. After their generation, molecular hydrogen and nitrogen are formed by recombination reactions. The overall reaction of ammonia decomposition by the pulsed DBD plasma is given by Eq. 1.

$$NH_3 + e \rightarrow 0.5\ N_2 + 1.5\ H_2 + e \qquad (1)$$

Figure 2 shows variation in hydrogen yield with plasma firing time (elapsed time of plasma) as a function of the total power consumption of the power supply. The hydrogen yield was calculated according to the following equation:

$$H_2\ \text{yield}, \% = [H_2]_m/[H_2]_s \times 100 \qquad (2)$$

where $[H_2]_m$ is the measured H_2 concentration by GC at the reactor exit (see Fig.1), and $[H_2]_s$ is the stoichiometric concentration of H_2 according to Eq. 1. $[H_2]_s$ is 75.0% for the 100% ammonia gas.

Hydrogen yield increased with increasing plasma firing time. The concentration of H radicals in the pulsed DBD plasma is a function of the electron mean energy, which depends on the discharge energy for plasma or the power consumption. The discharge energy and the power consumption increased proportionally with increasing the applied voltage. Therefore, an increase in the power consumption facilitates hydrogen production in the gas phase reactions. The hydrogen yield achieved was about 19% at a plasma firing time of 60 sec and the power consumption of 300 W.

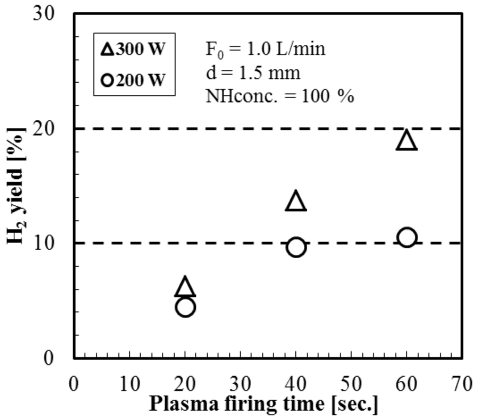

Fig.2 The effect of plasma firing time.

4. REACTION MECHANISM

CHEMKIN is available for building reaction model. As a reactor model, "Plasma-PSR-Reactor" was applied. To develop reaction model of ammonia decomposition and hydrogen production, deNOx reaction models were very helpful, because detailed elemental reaction for N and H system in gas phase is included in deNOx reaction models. Four kinds of deNOx elemental reaction model4-7) were compared in previous work as shown in Figure 38).

Among four reaction models, Skreiberg's model indicated good agreement with the experimental results. The model included reaction (3), which was not found in other models. Therefore N/H elemental reaction system of Skreiberg's model was applied to estimate ammonia decomposition and hydrogen production in the DBD pulsed plasma reactor.

$$H_2NN + NH_2 = NNH + NH_3 \qquad (3)$$

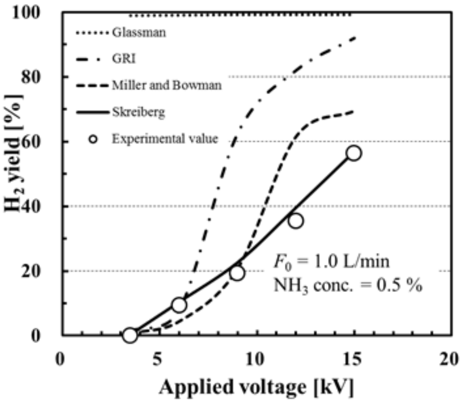

Fig.3 Comparison between four reaction models and experimental data8).

Figure 4 shows comparison between experimental results and simulation results on H_2 yield at the power consumption of 200 W. At plasma firing time of 20 sec, both data indicated completely agreement, however, greatly difference was found at 40 sec.

Fig.5 shows important reaction paths on ammonia decomposition and hydrogen production in the DBD plasma. The rate constant of hydrogen production is lower than that of ammonia decomposition; the formation rate of molecular hydrogen from H radicals generated by plasma decomposition is control step. As another possibility, molecular hydrogen generated in the plasma reactor might be decomposed, however, reaction model for H_2 decomposition by plasma is not included in the current reaction model.

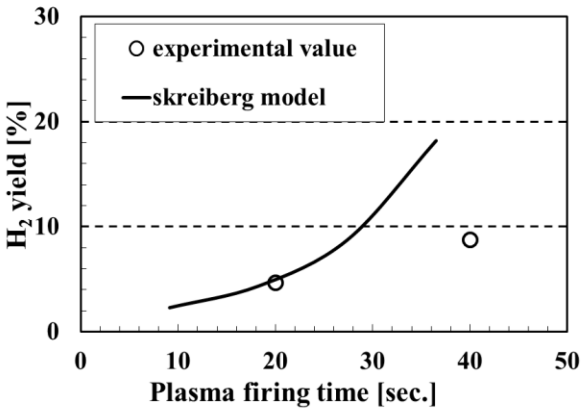

Fig.4 Comparison between simulation results and experimental values.

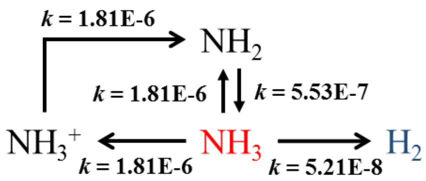

Fig.5 Reaction path of hydrogen production from ammonia by plasma.

5. CONCLUSION

Ammonia is a hydrogen storage material that may solve many problems related to hydrogen transportation and storage in a hydrogen economy. Therefore, devices that produce hydrogen from ammonia will become increasingly important. In this study, hydrogen production experiments and development of reaction model were conducted to establish an efficient method for using pulsed plasma to produce hydrogen from ammonia. In hydrogen production experiments, it found that hydrogen yield increased with increasing plasma firing time, which also depended on the power consumption.

In development of reaction model, N/H elemental reaction system of Skreiberg's model was applied to estimate ammonia decomposition and hydrogen production in the DBD pulsed plasma reactor. The developed reaction model was roughly agree with experimental data. The reaction paths for H_2 decomposition in plasma may be necessary.

REFERENCES

[1] O. Okada, Jurnal of Japan Institute Energy, 85,499-509 (2006).

[2] G. Strickland, 5th annual thermal storage meeting, 8010555-2, 10th October 1980, McLean, VA, USA.

[3] S. Kambara, Y. Hayakawa, Y. Inoue, T. Miura, J. Sustainable Development of Energy, Water and Environment Systems, 4(2), 193-202 (2016).

[4] Ø. Skreiberg, P. Kilpinen, P. Glarborg: Combust.Flame, 136, 501-518 (2004).

[5] G. P. Smith, D. M. Golden, M. Frenklach, N. W. Moriarty, B. Eiteneer, M. Goldenberg, C. T. Bowman, R. K. Hanson, S. Song, W.C. Gardiner, V. V. Lissianski, Z. Qin, http://www.me.berkeley.edu/gri_mech/

[6] J.A. Miller and C.T. Bowman: Prog. Energy Combust. Sci., 15, 287-337 (1989).

[7] I. Glassman. Combustion. Academic Press, 3rd edition, (1996).

[8] T. Kawaoka, Y. Inoue, S. Kambara, Proceedings of the 68th Gaseous Electronics Conference, No.SF1.00002, (2015).